Electronic Supplementary Material (ESI) for New Journal of Chemistry.

Supporting Information

Belonging to the manuscript

Gas-phase reactivity of Cp* Group IX metal complexes bearing aromatic *N,N*'-chelating ligands

by

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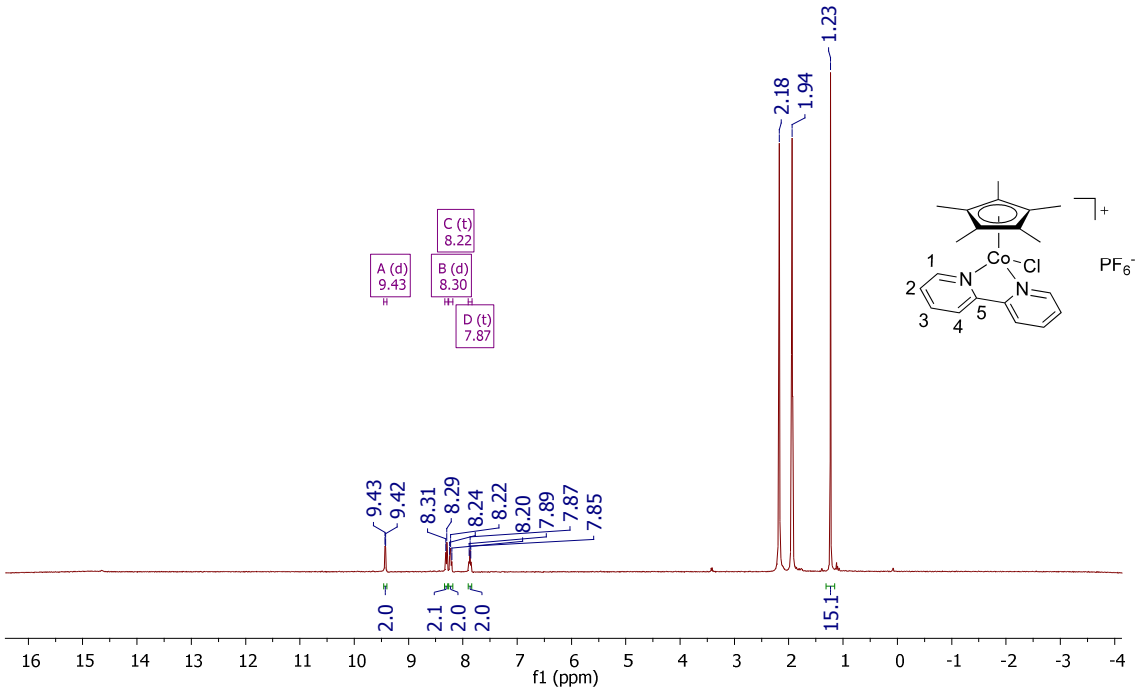
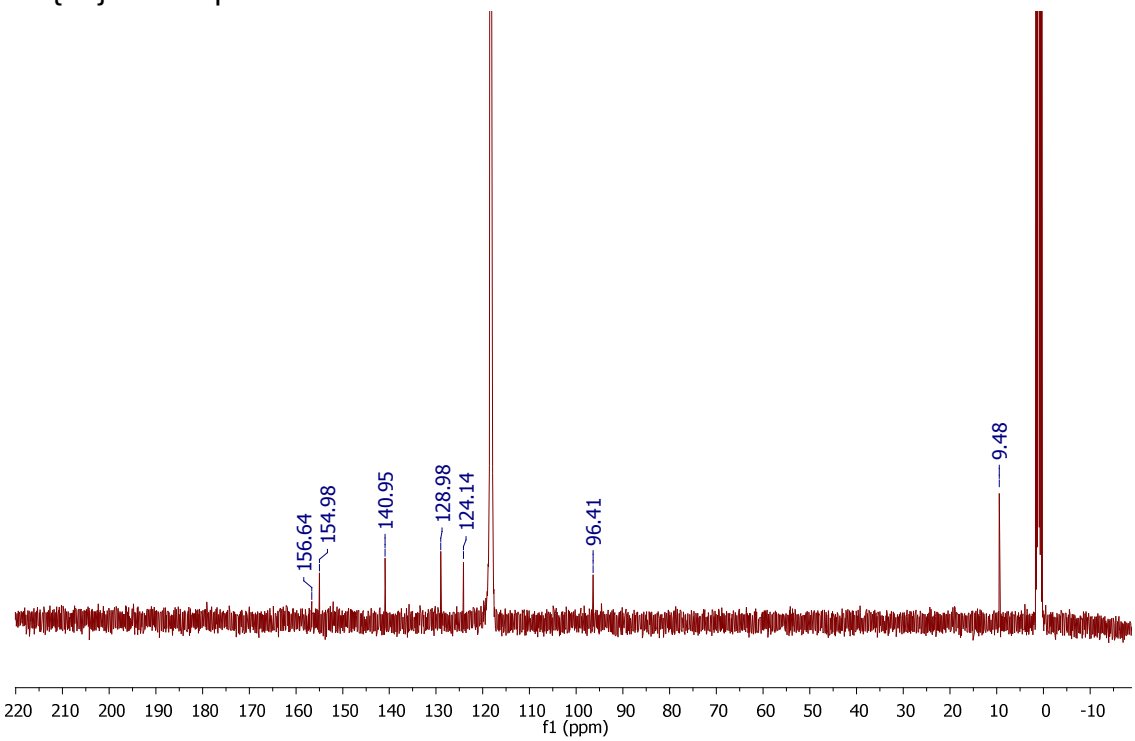
1. Spectroscopic data

2,2'-Bipyridine(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III) hexafluorophosphate (3a): see Experimental section.

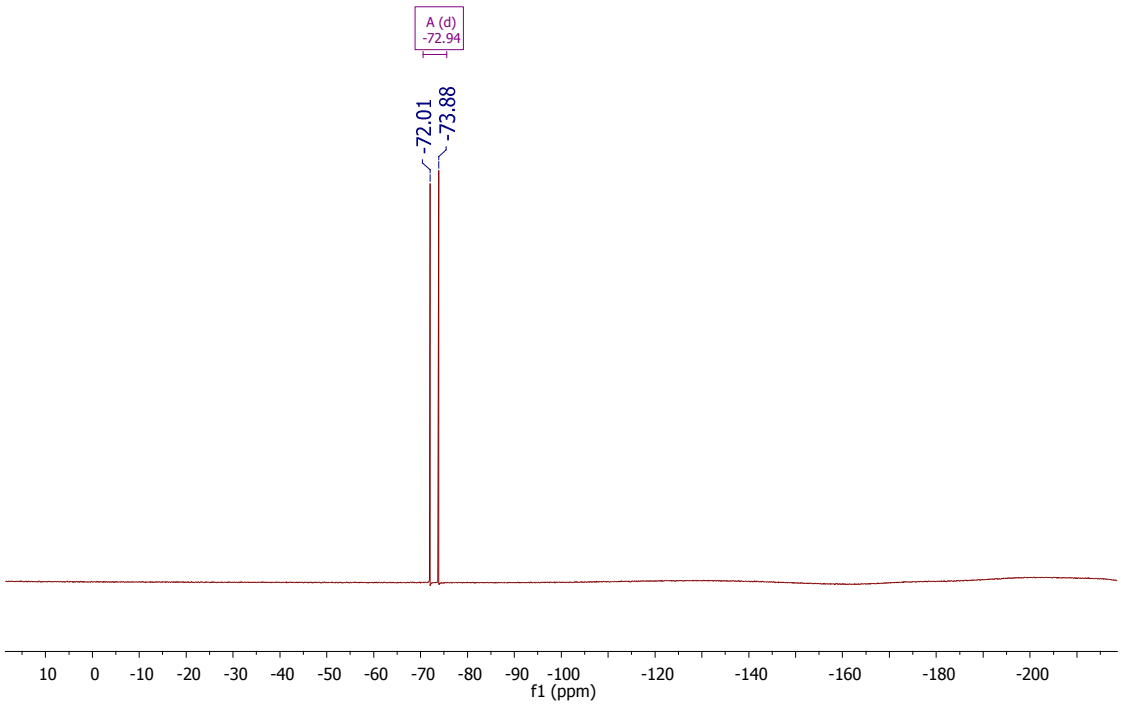
^{1}H NMR spectrum



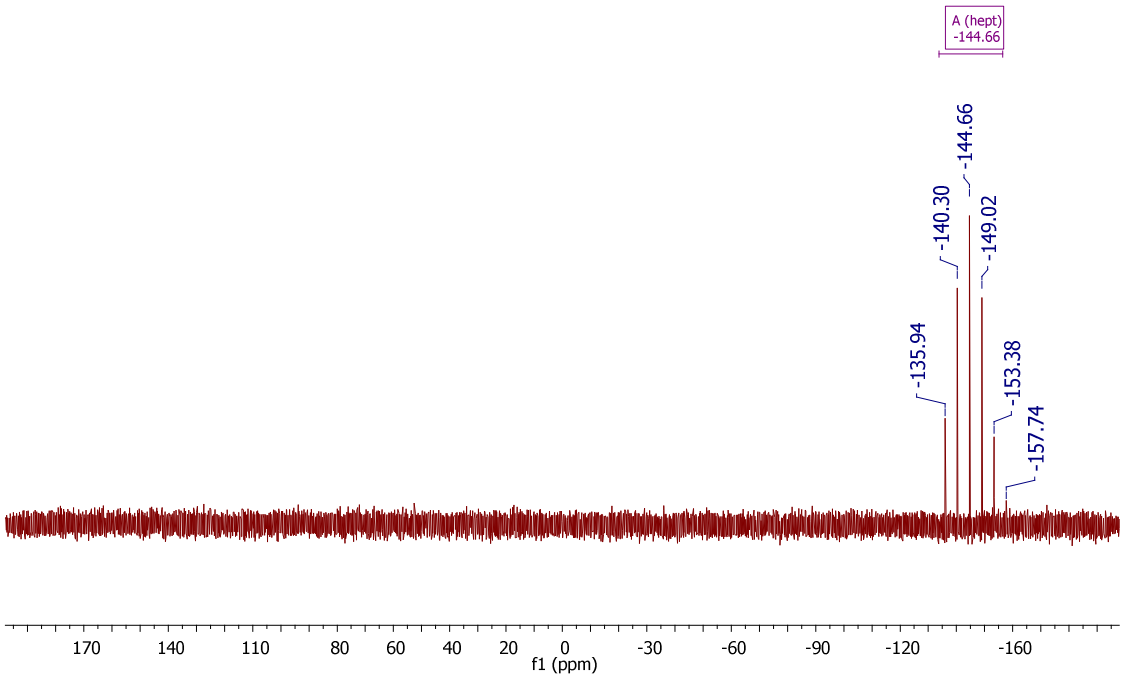
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

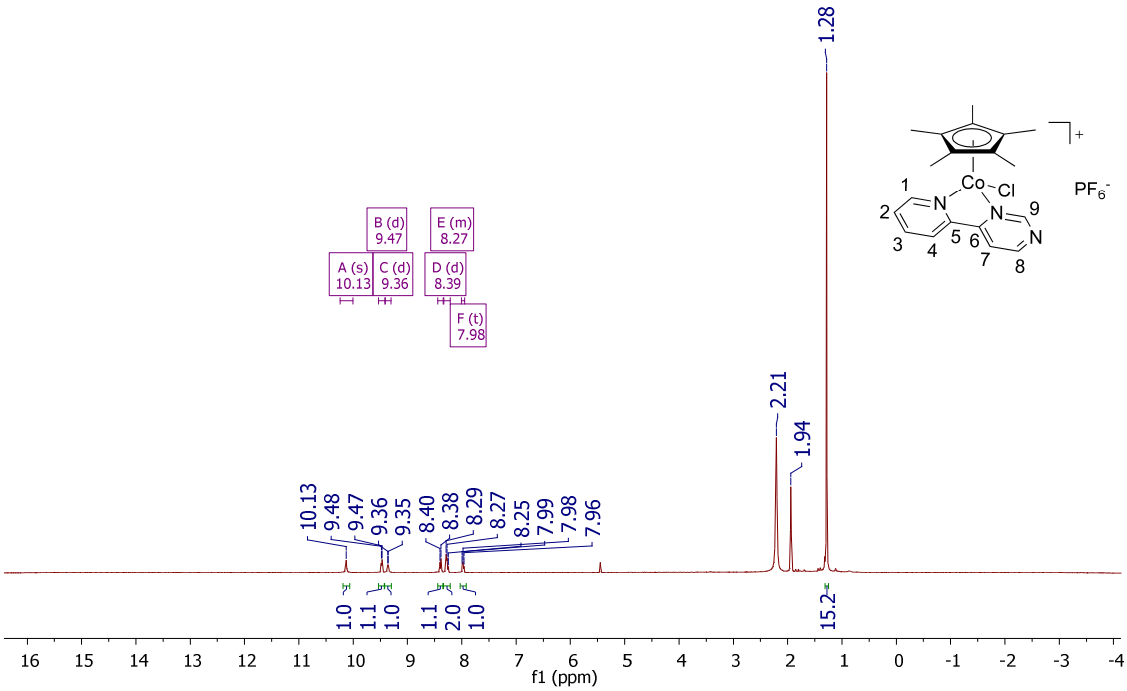


$^{31}P\{^{1}H\}$ NMR spectrum

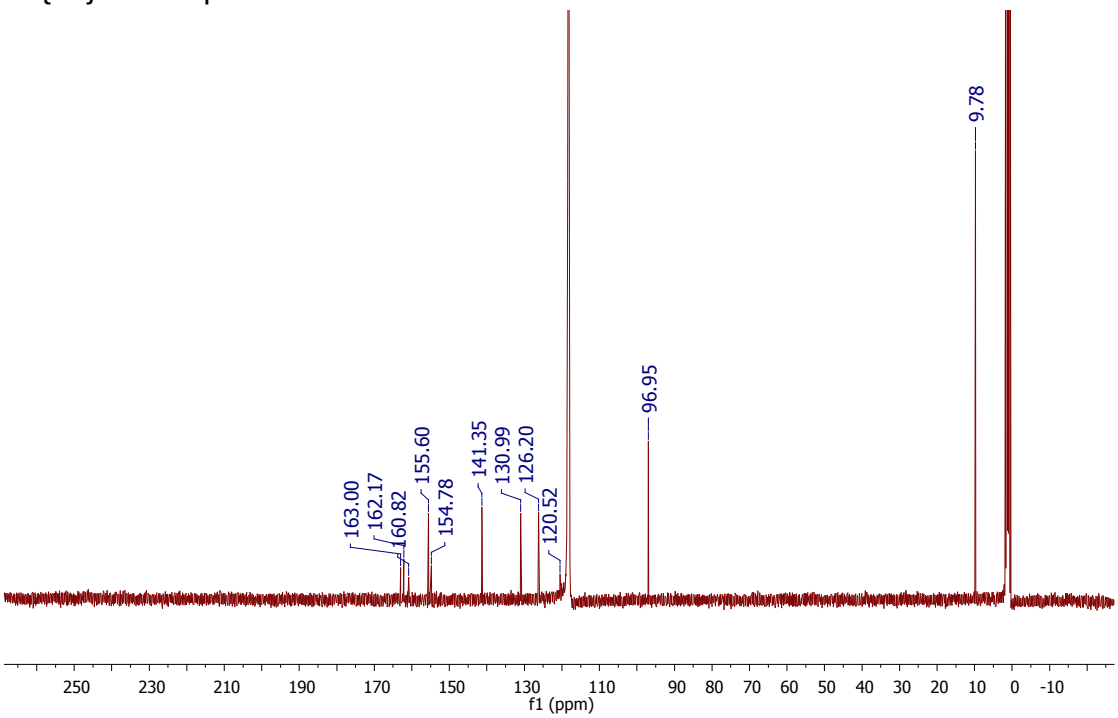


Chlorido(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)(2-pyrimidin-4-ylpyridine)cobalt(III) hexafluorophosphate (3b): see Experimental Section.

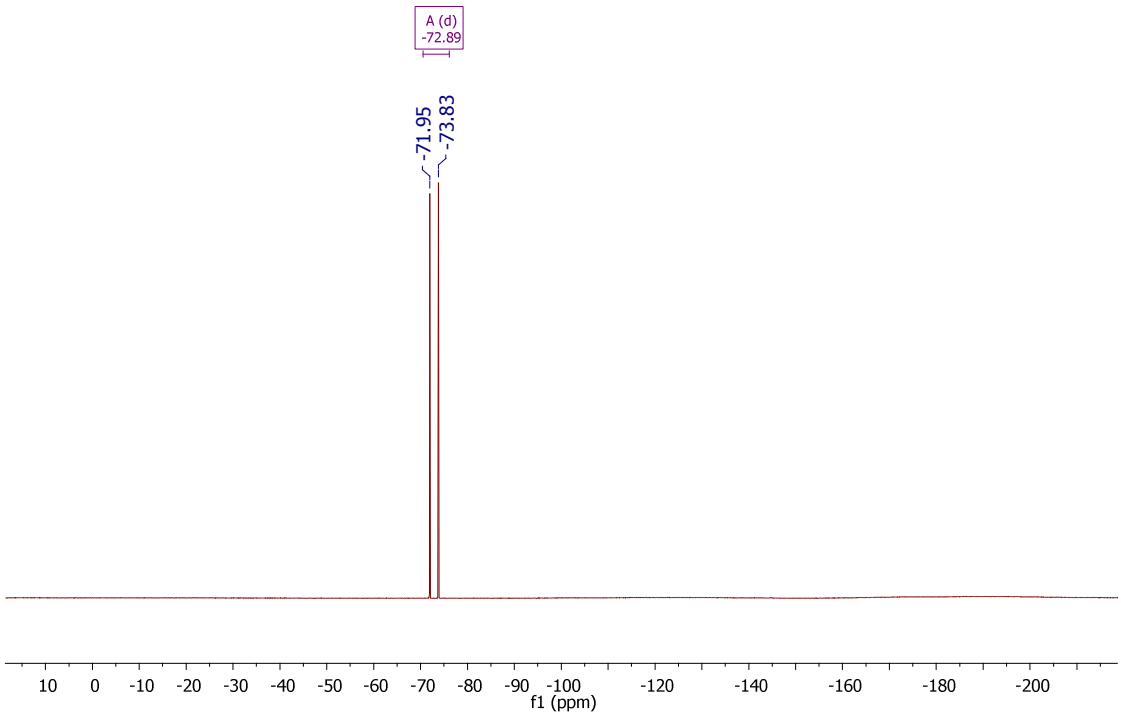
^{1}H NMR spectrum



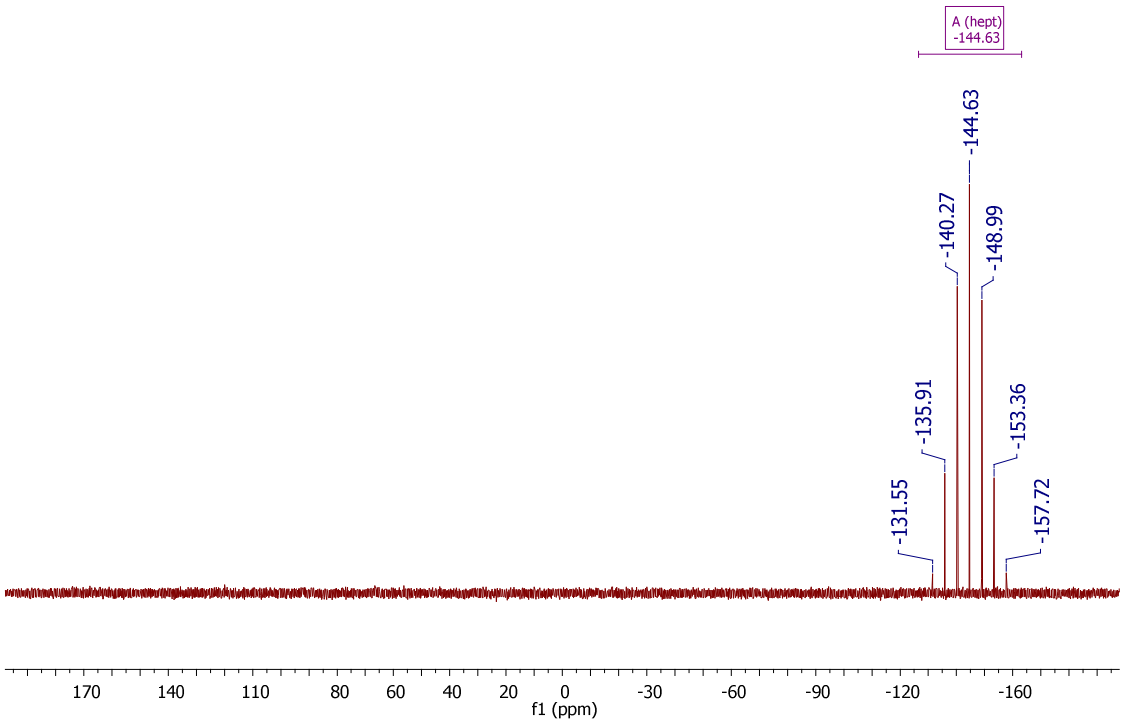
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

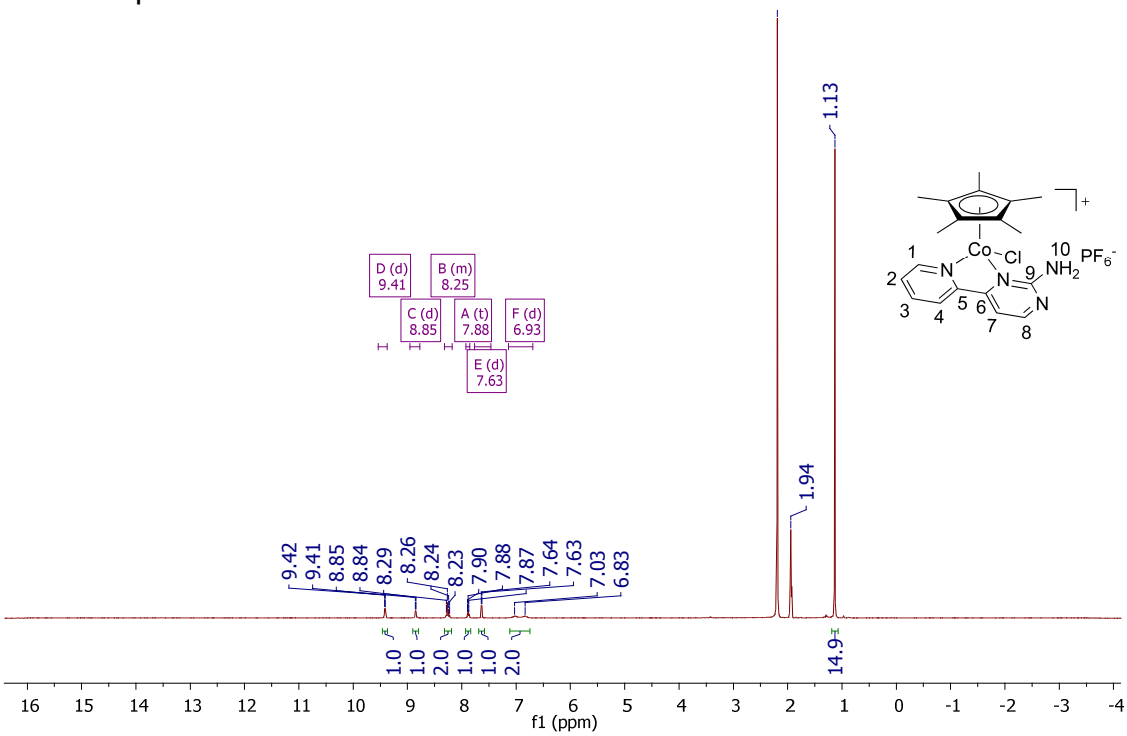


$^{31}P\{^{1}H\}$ NMR spectrum

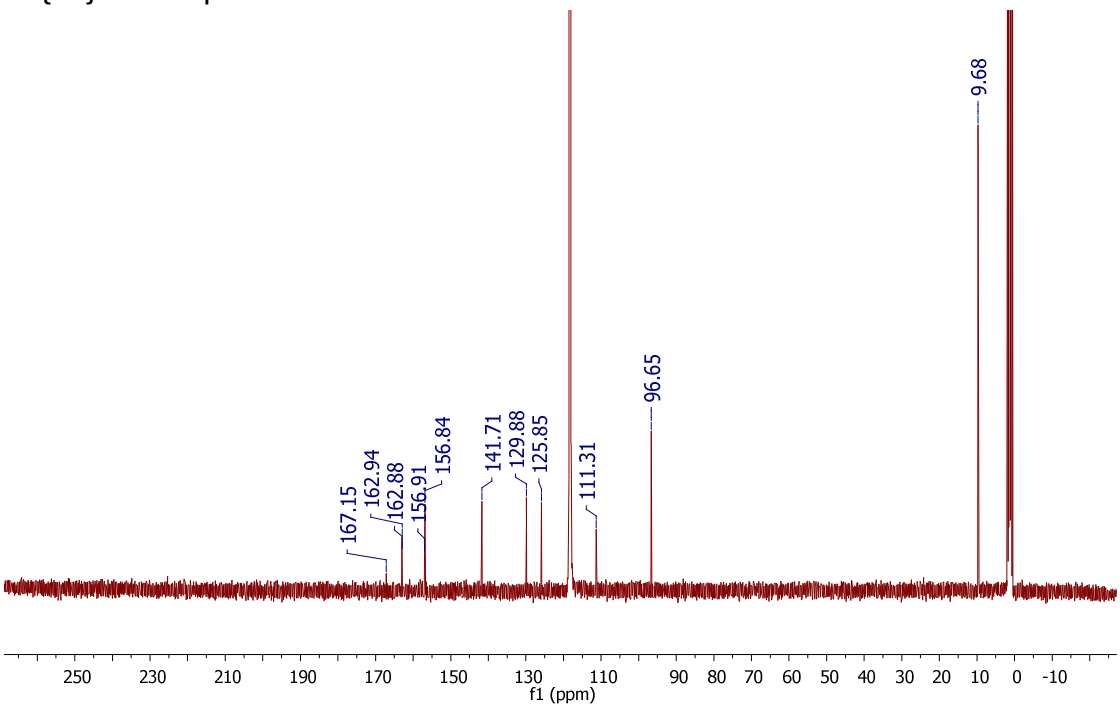


(2-(2-Aminopyrimidin-4-yl)pyridine)(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III) hexafluorophosphate (3c): see Experimental Section.

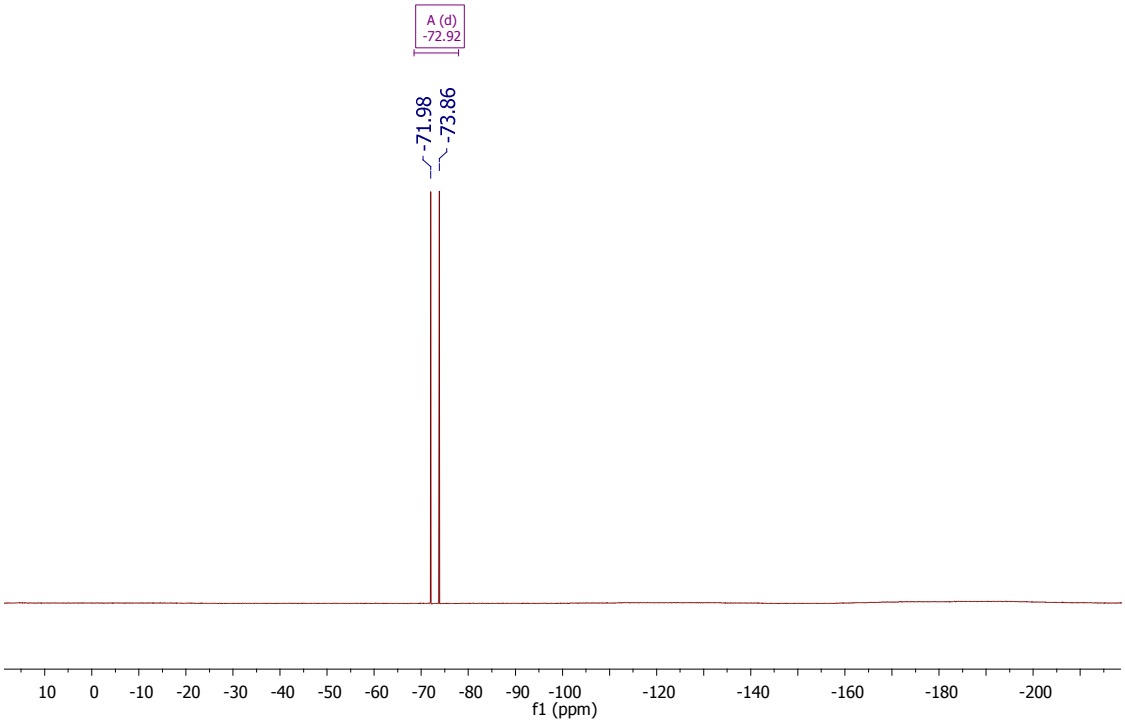
^{1}H NMR spectrum



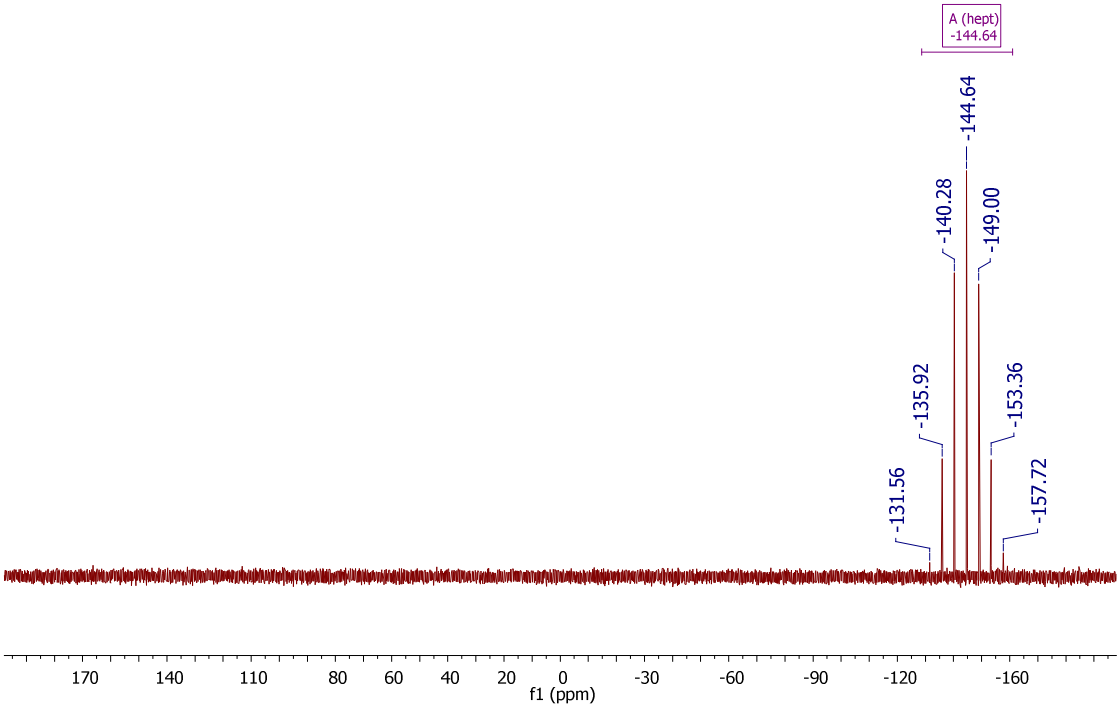
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

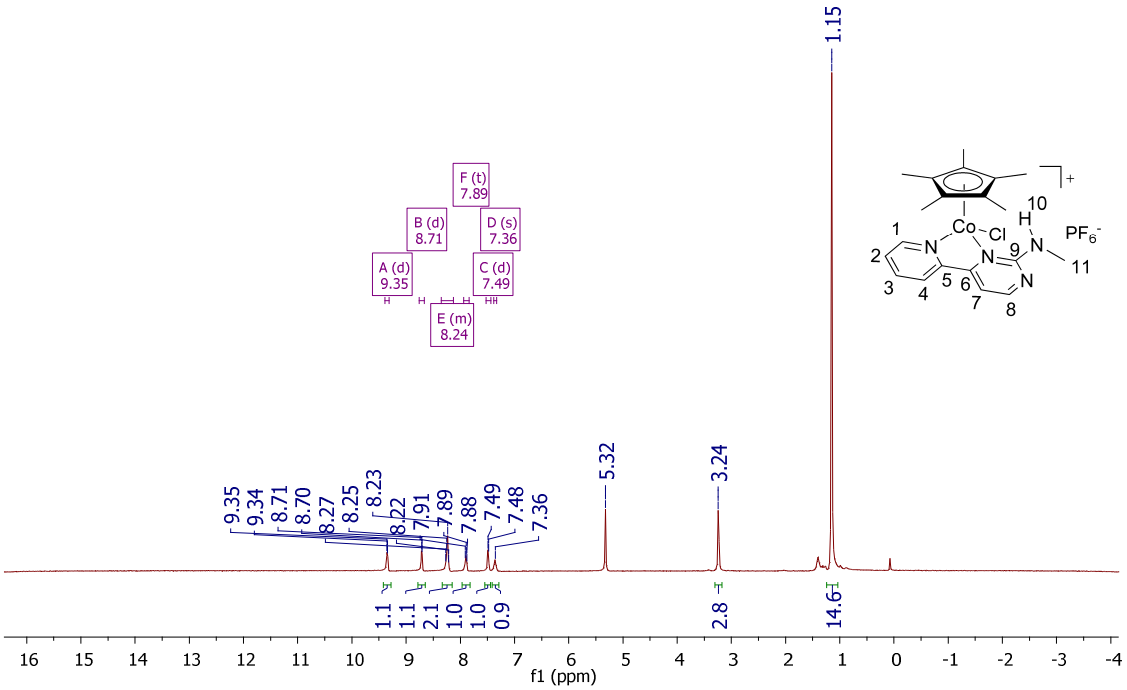


^{31}P NMR spectrum

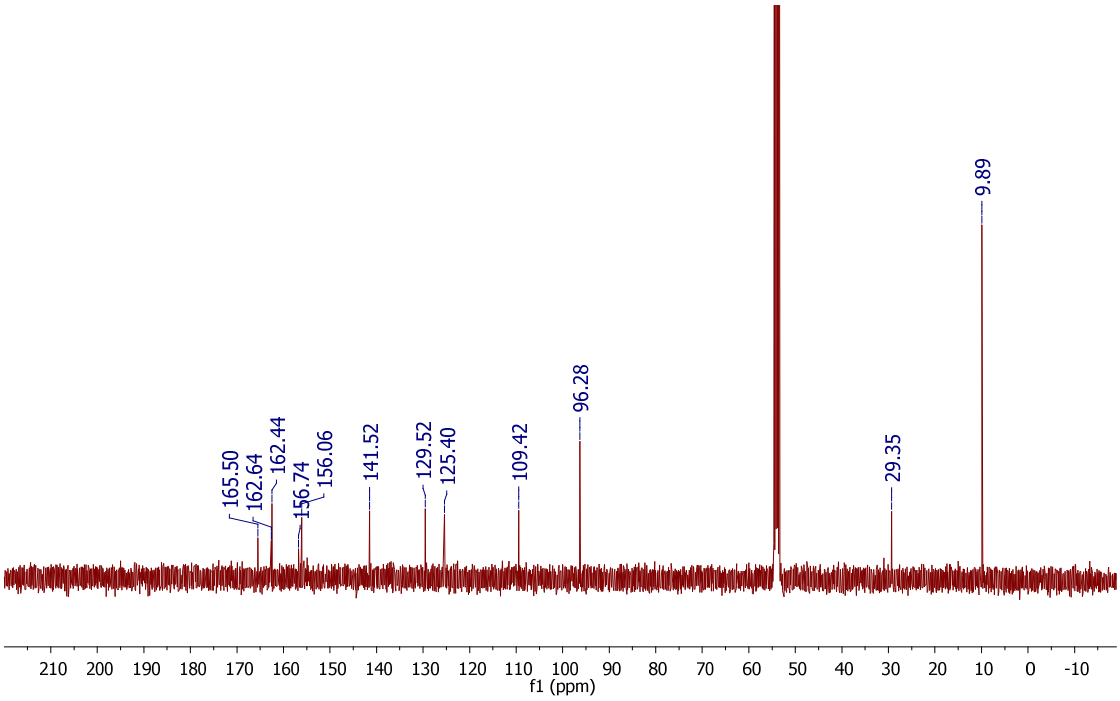


Chlorido(2-(2-methylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III) hexafluorophosphate (3d): see Experimental Section.

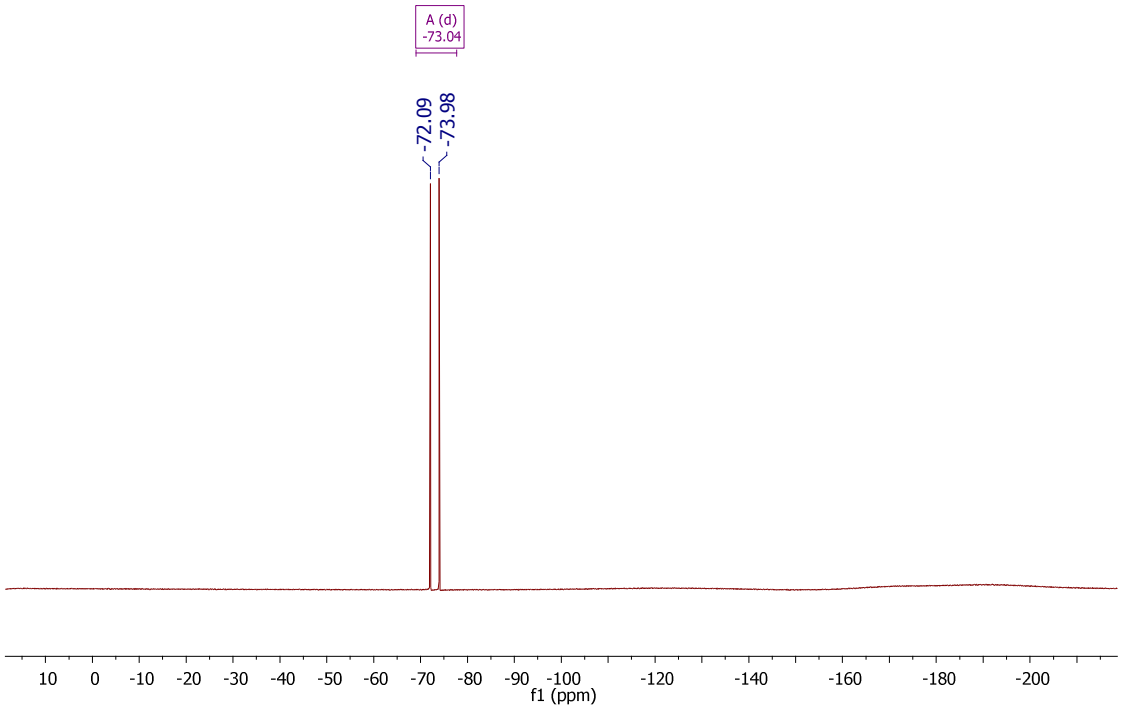
^{1}H NMR spectrum



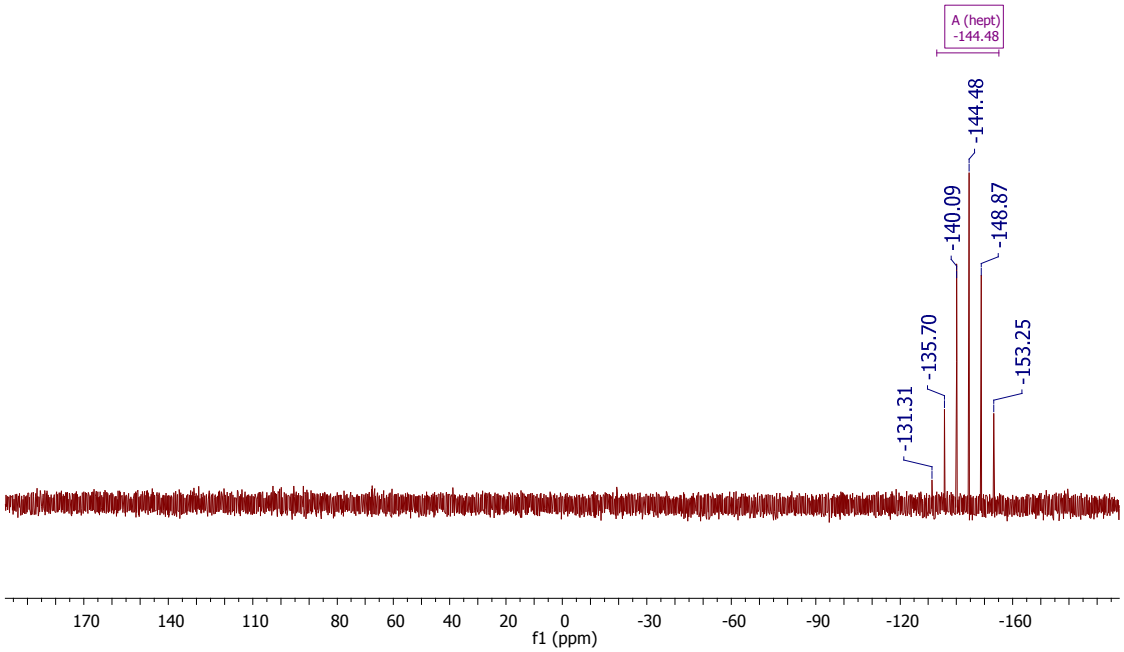
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

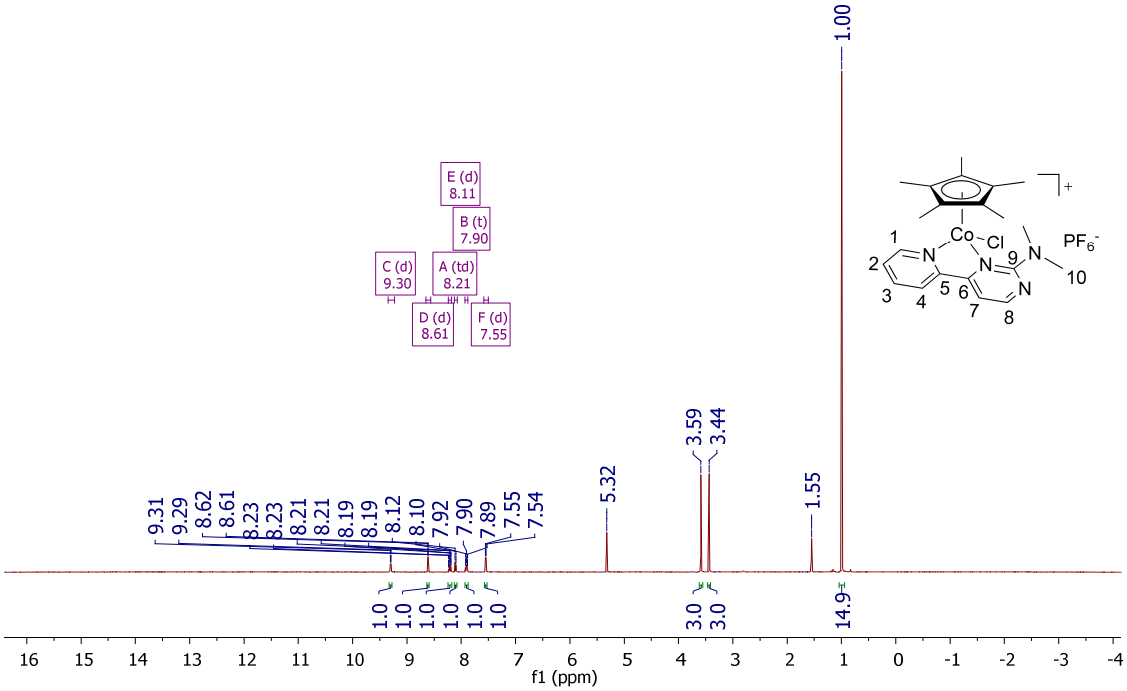


^{31}P NMR spectrum

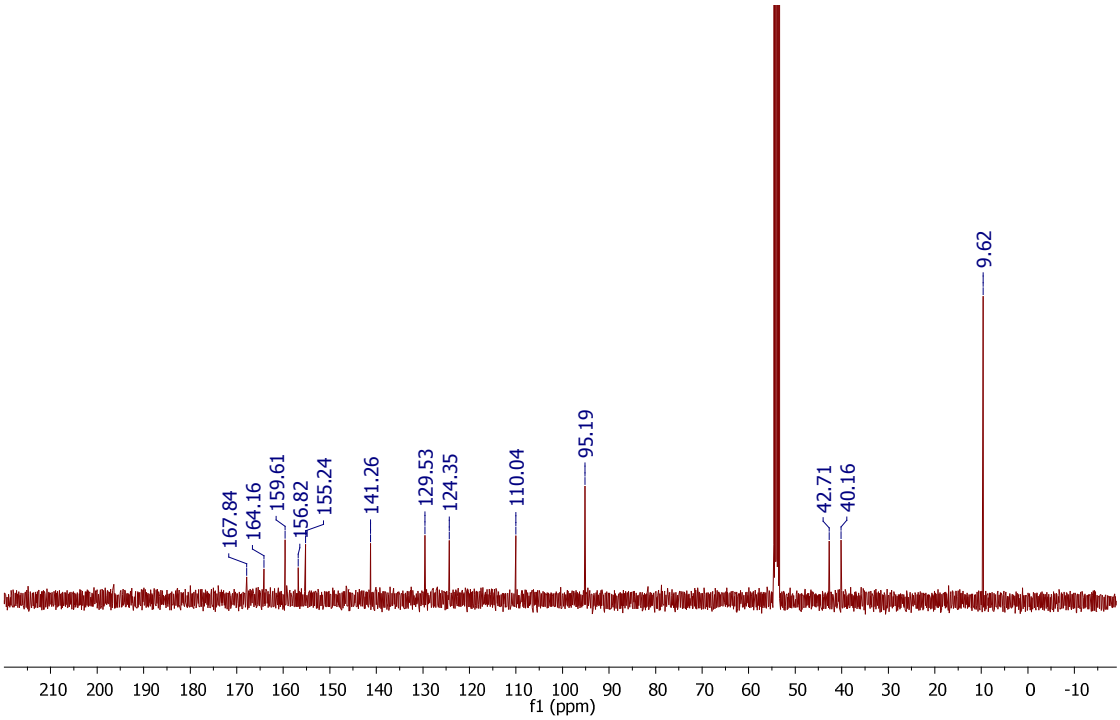


Chlorido(2-(2-dimethylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III) hexafluorophospate (3e): see Experimental Section

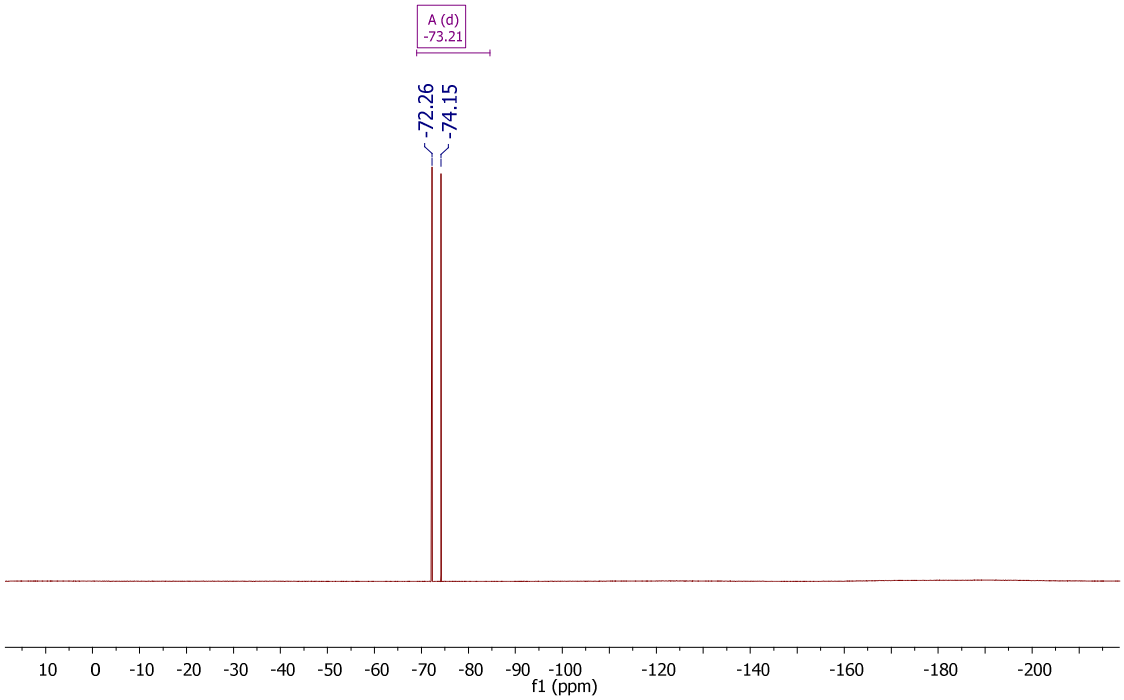
^{1}H NMR spectrum



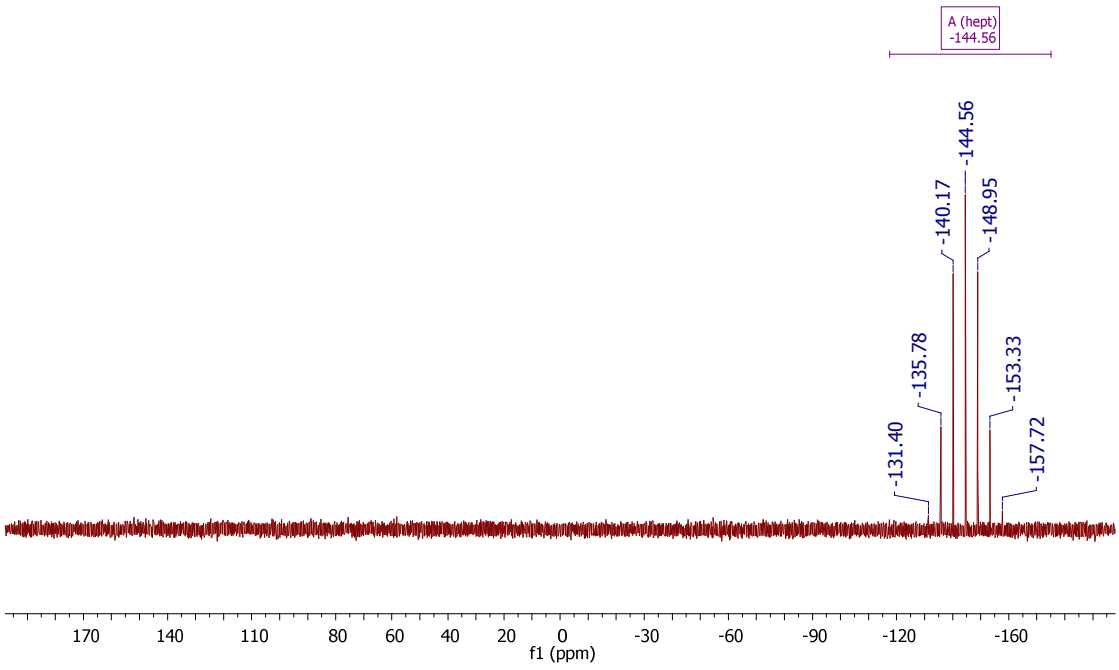
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

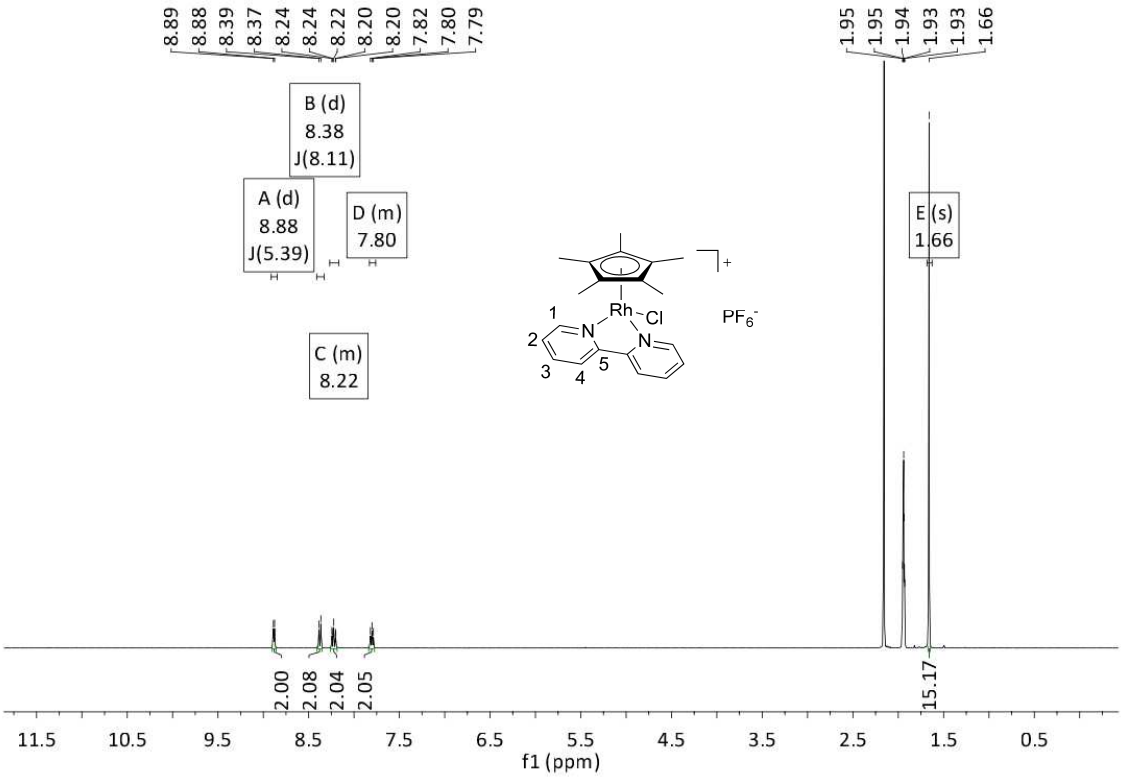


^{31}P NMR spectrum

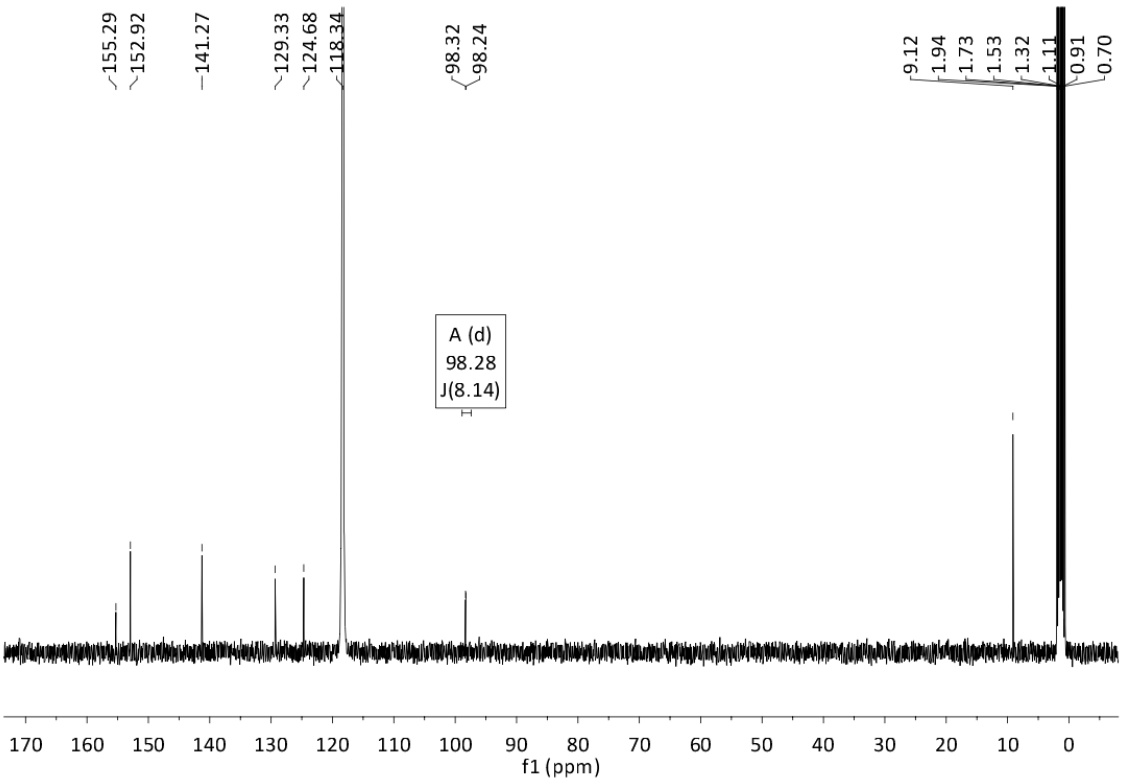


2,2'-Bipyridine(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III) hexafluorophosphate (3a): see Experimental section.

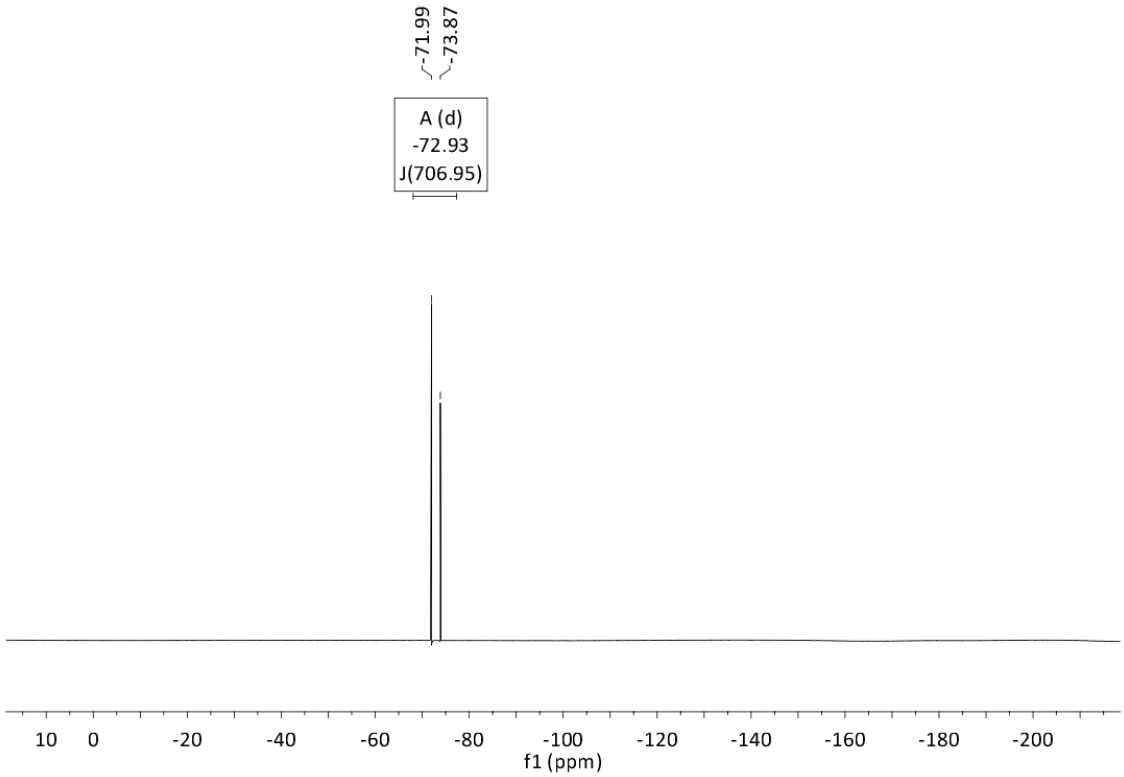
^{1}H NMR spectrum



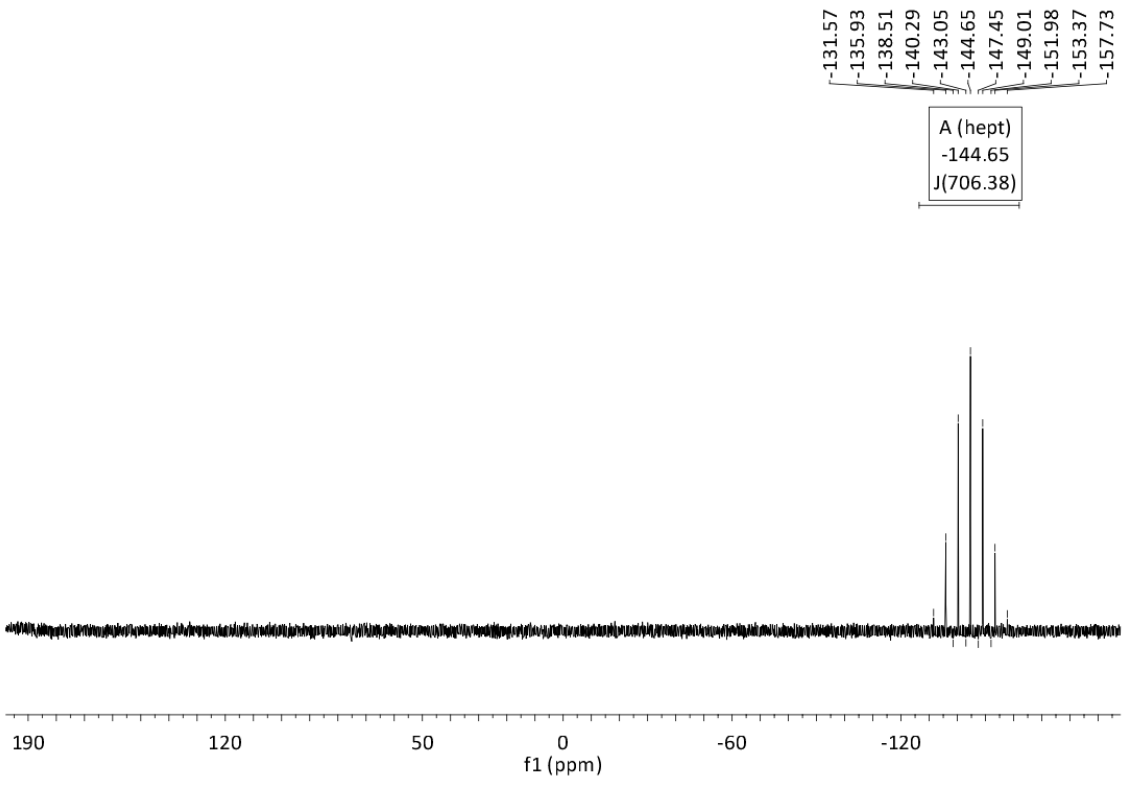
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

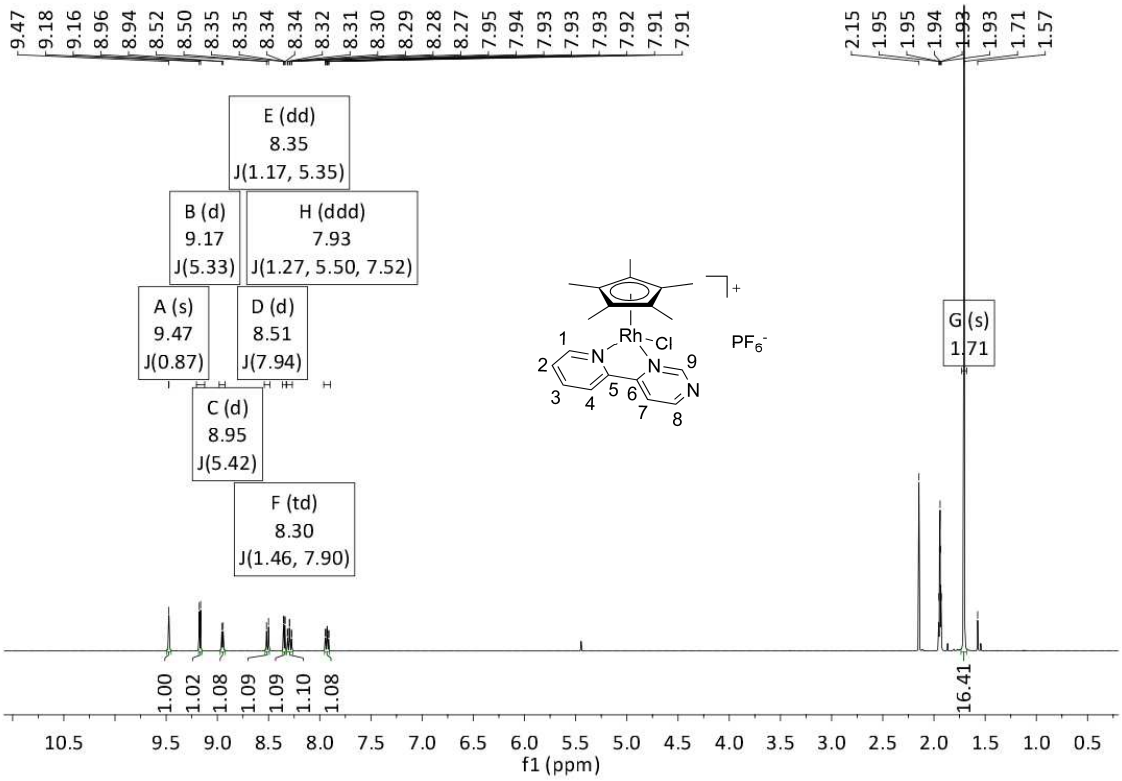


$^{31}P\{^{1}H\}$ NMR spectrum

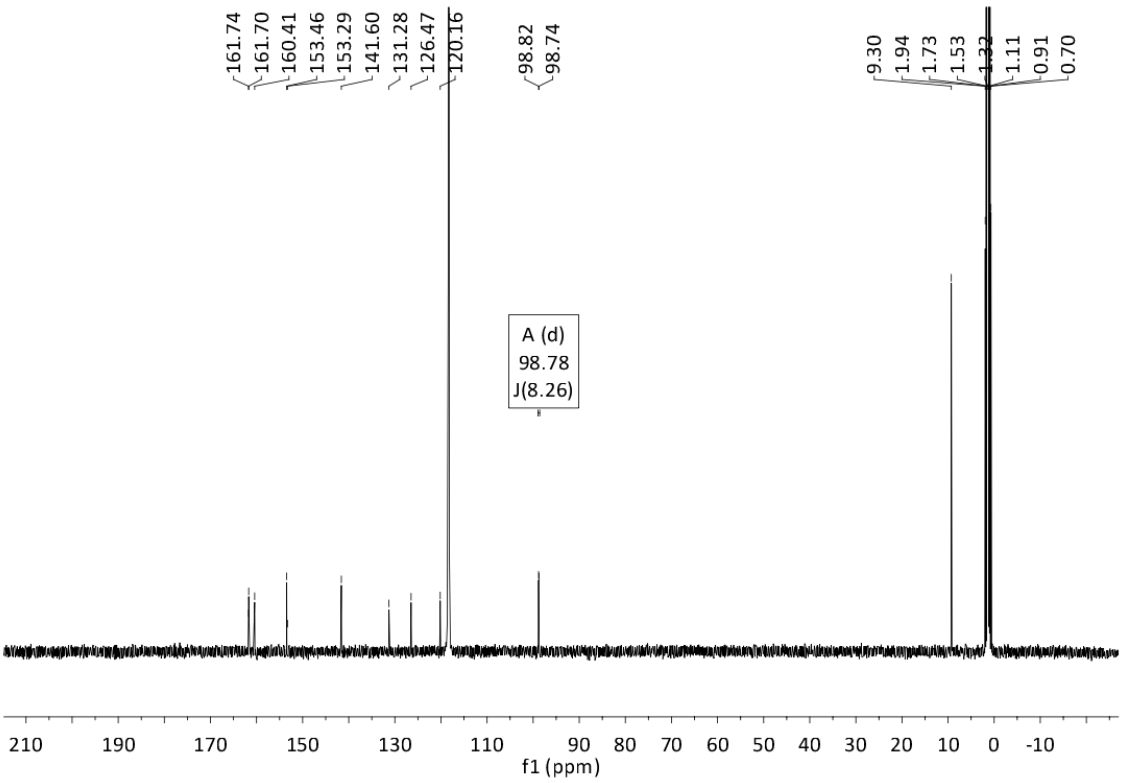


Chlorido(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)(2-pyrimidin-4-ylpyridine)-rhodium(III) hexafluorophosphate (3b): see Experimental Section.

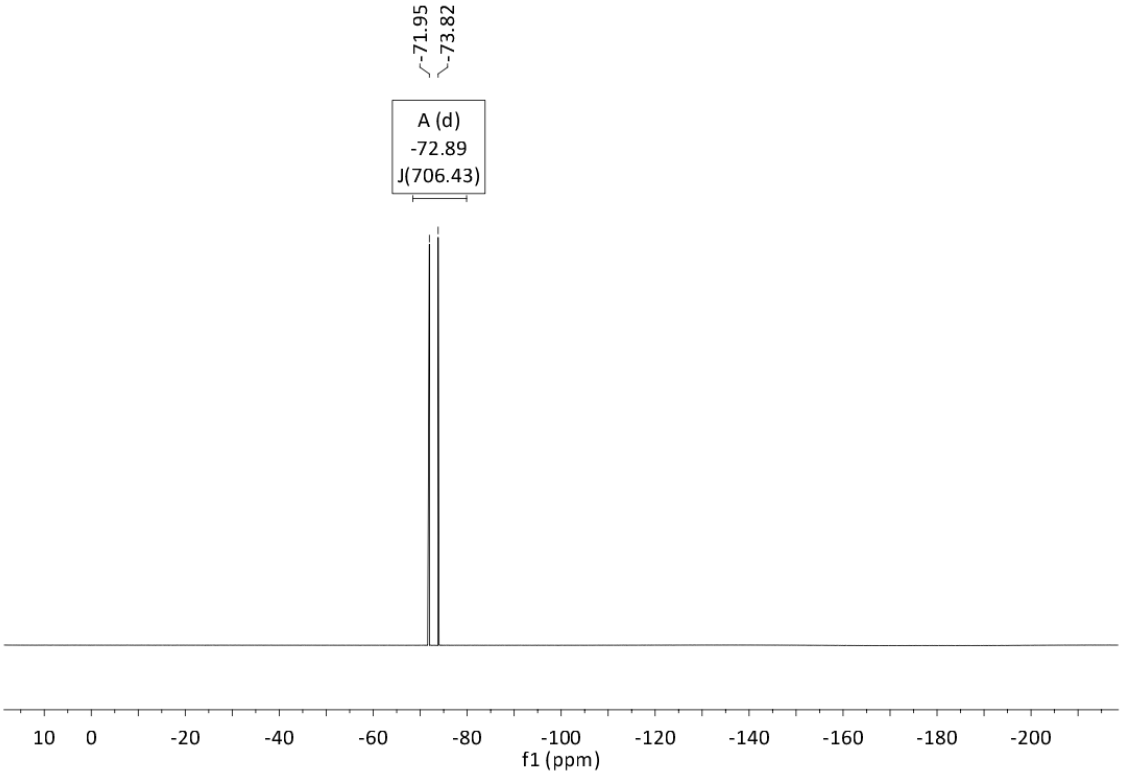
^{1}H NMR spectrum



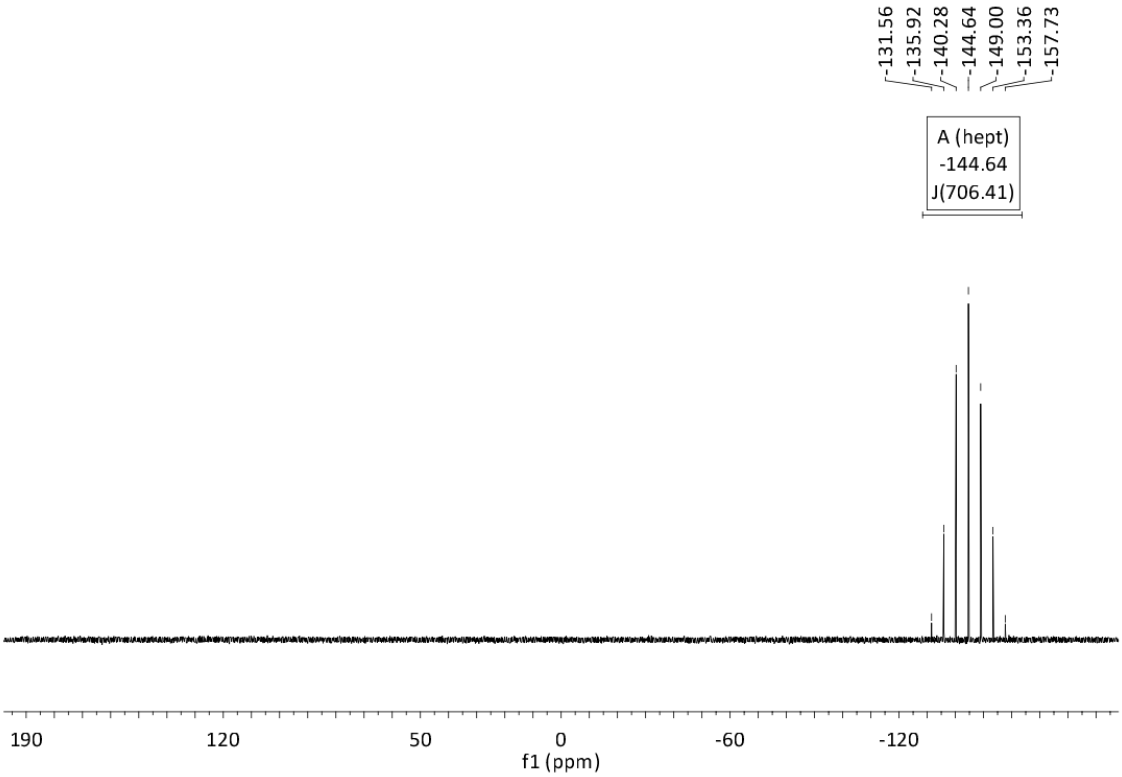
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

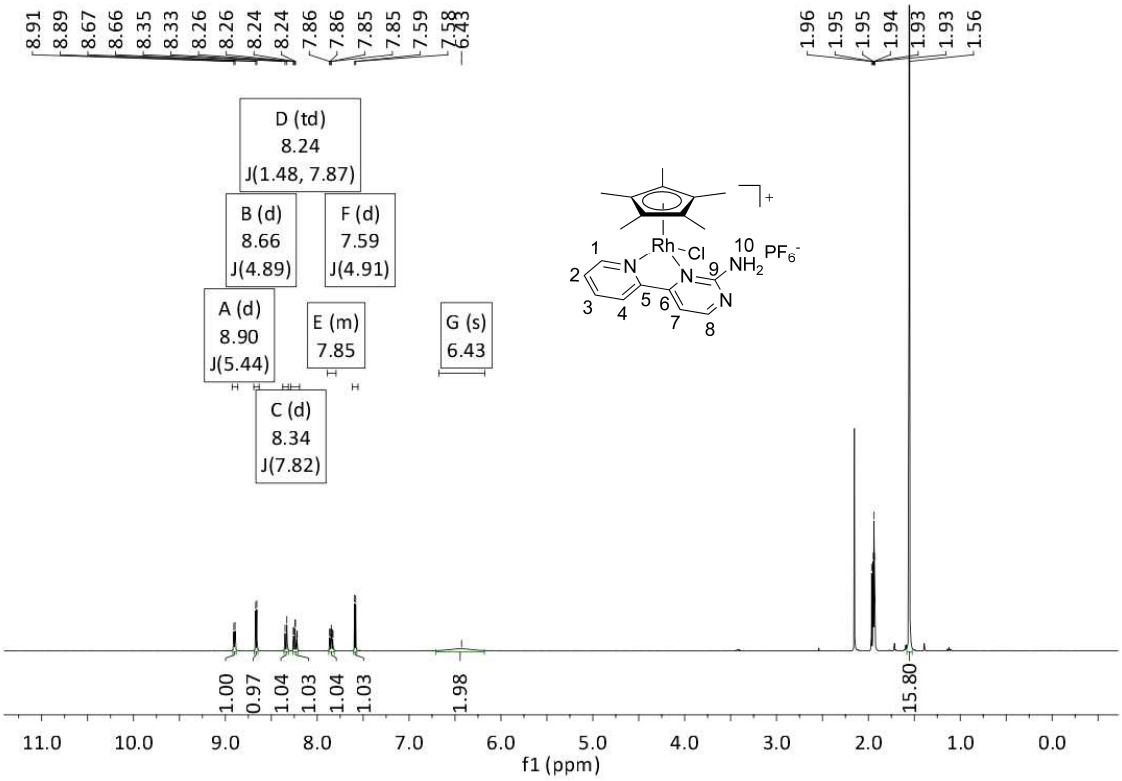


$^{31}P\{^{1}H\}$ NMR spectrum

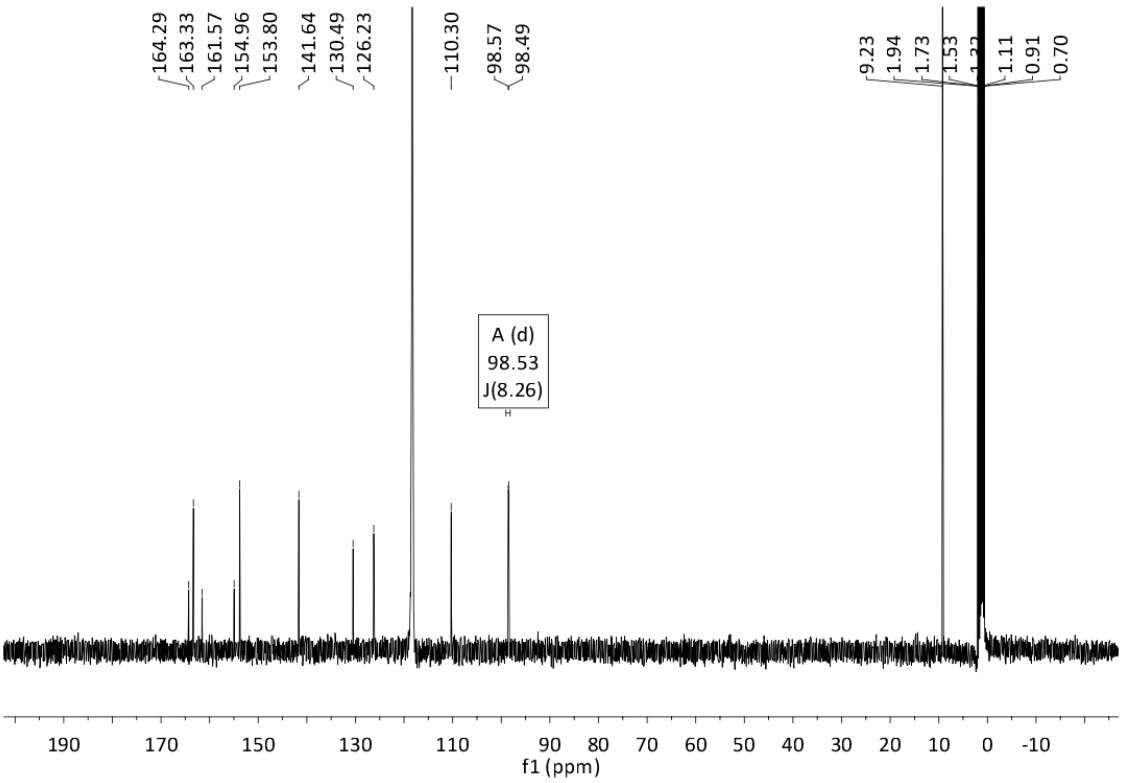


(2-(2-Aminopyrimidin-4-yl)pyridine)(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III) hexafluorophosphate (3c): see Experimental Section.

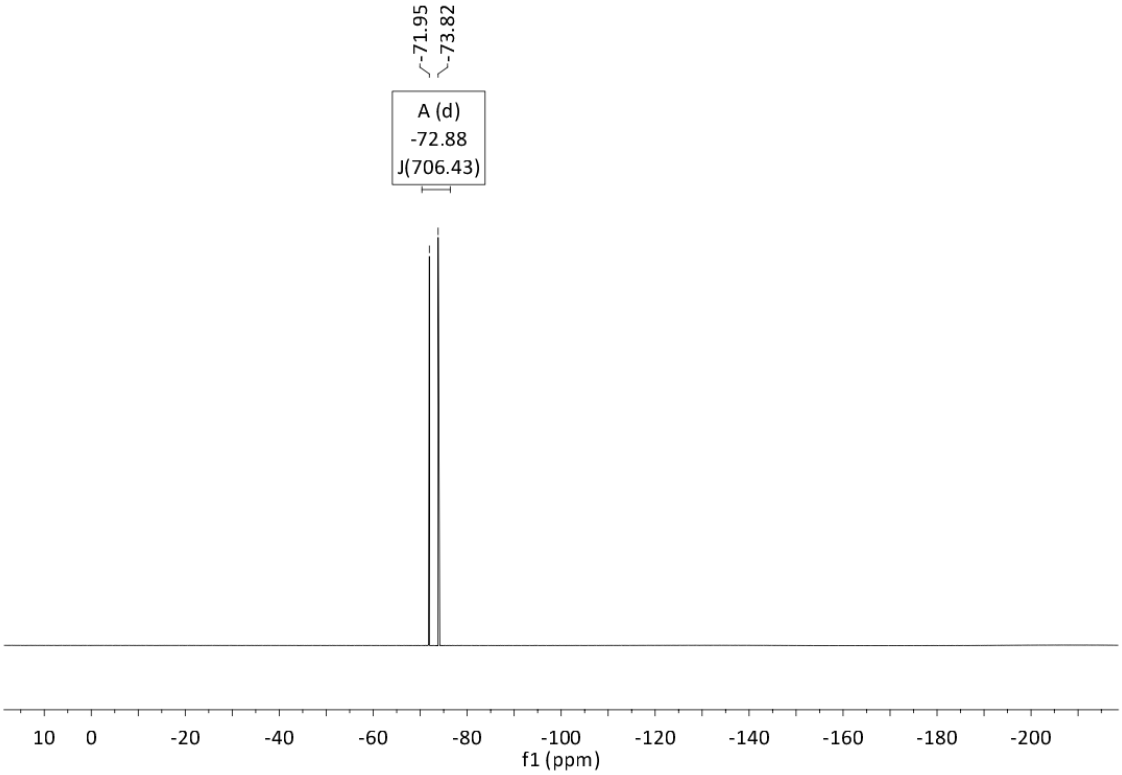
^{1}H NMR spectrum



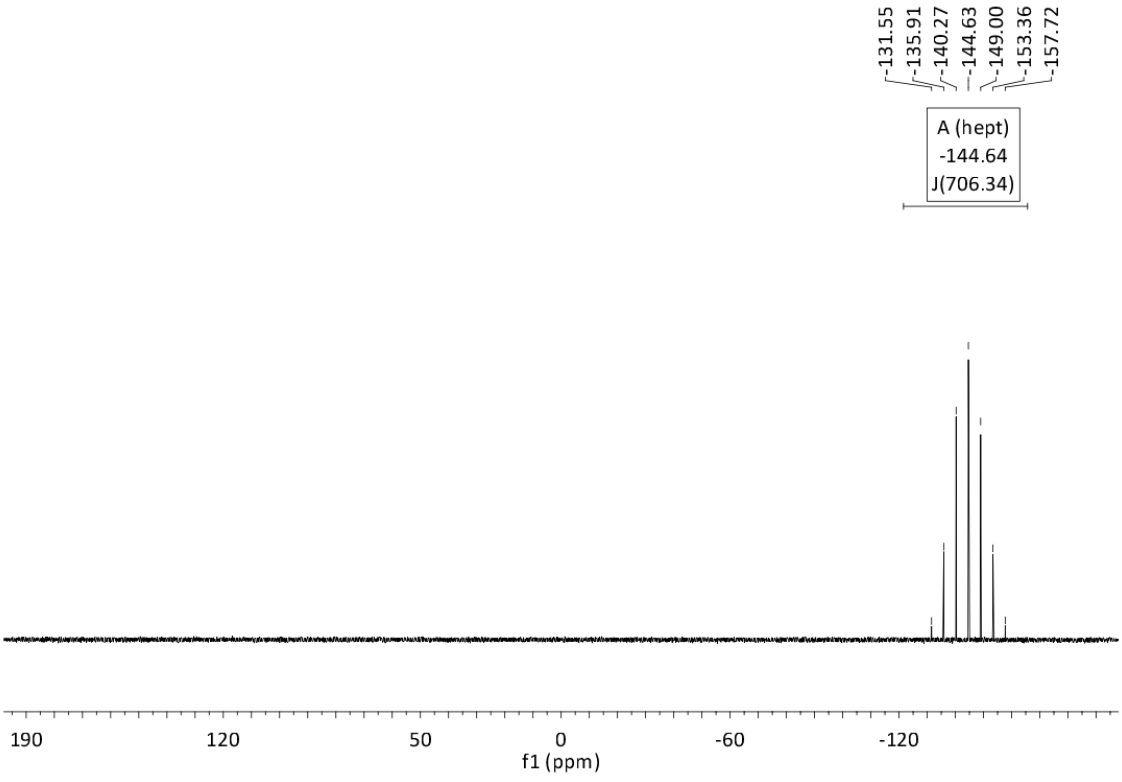
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

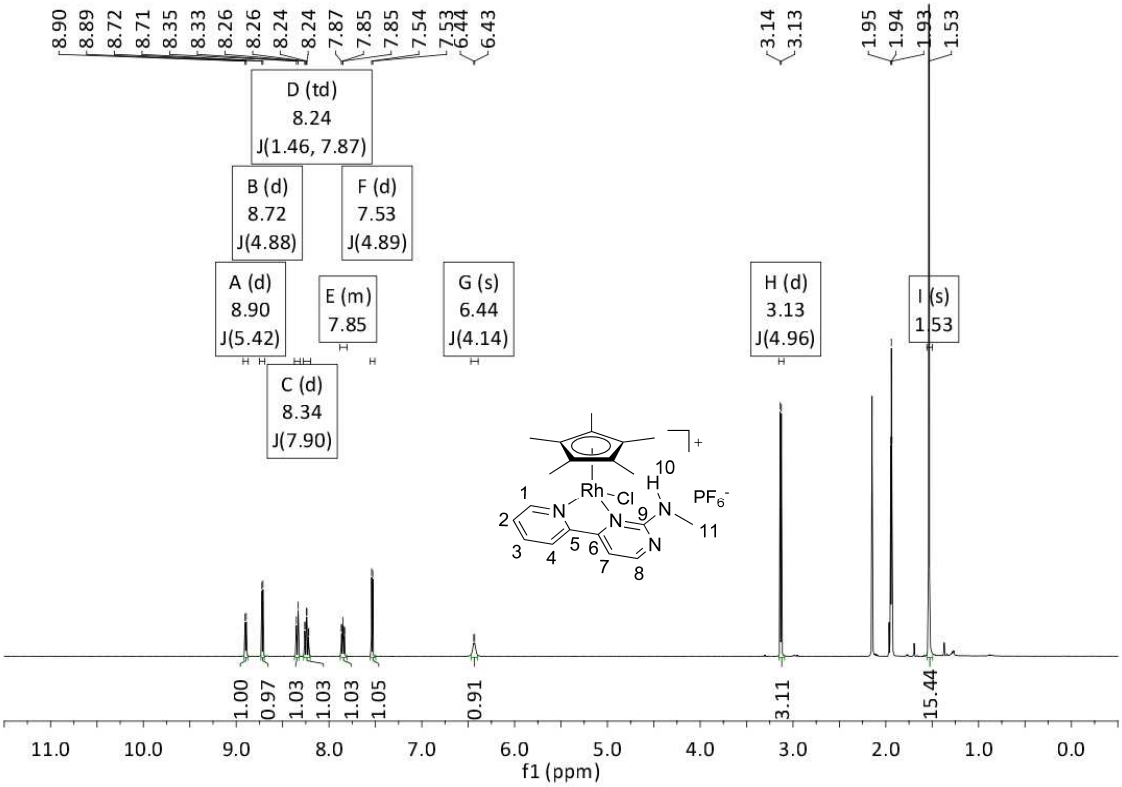


^{31}P NMR spectrum

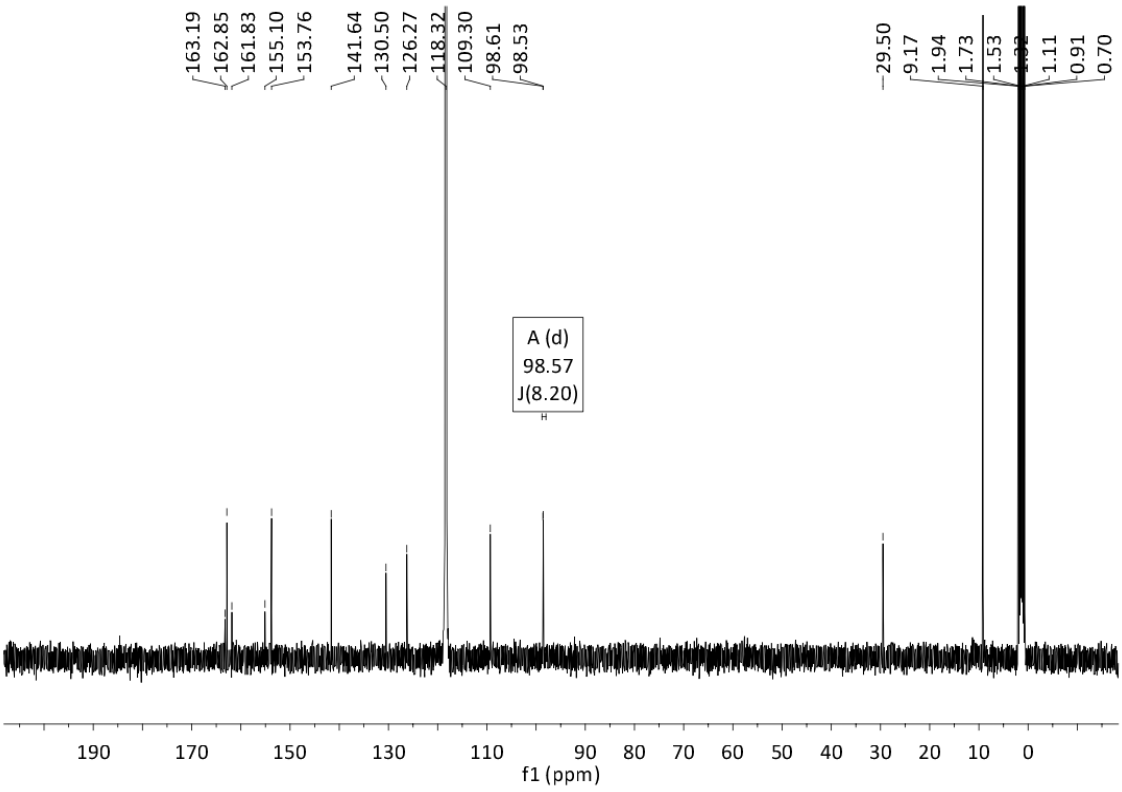


Chlorido(2-(2-methylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III) hexafluorophosphate (3d): see Experimental Section.

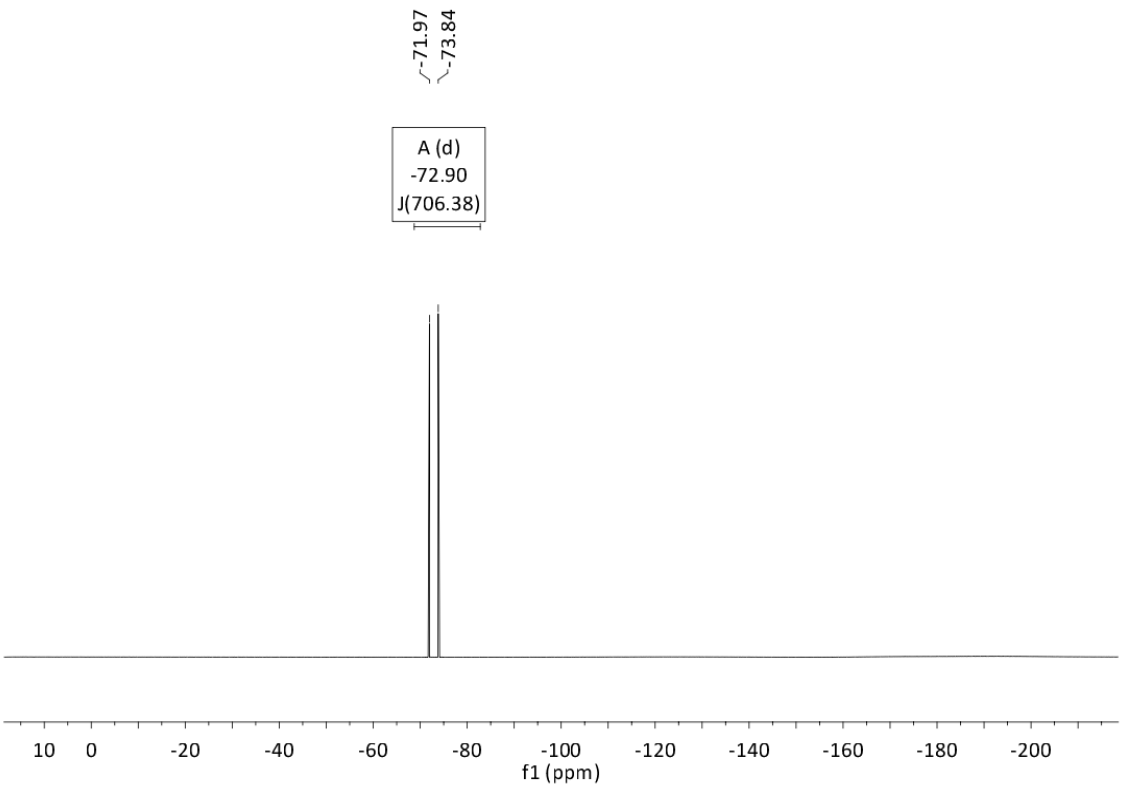
^{1}H NMR spectrum



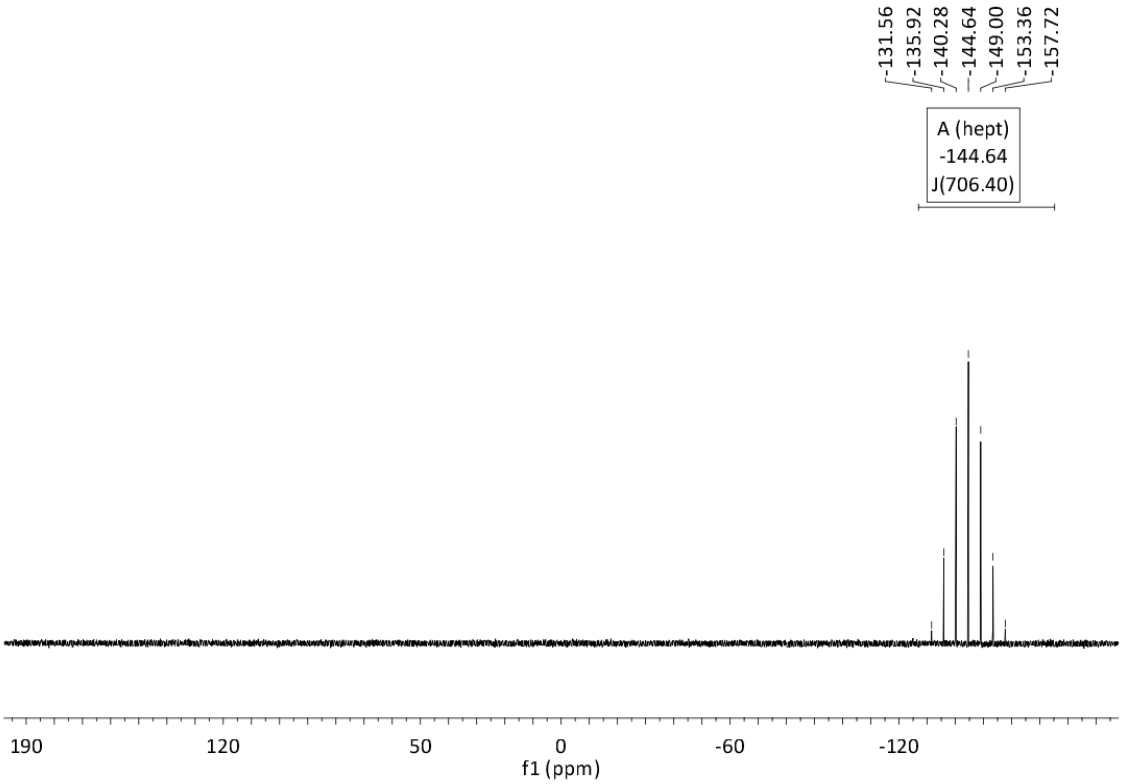
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

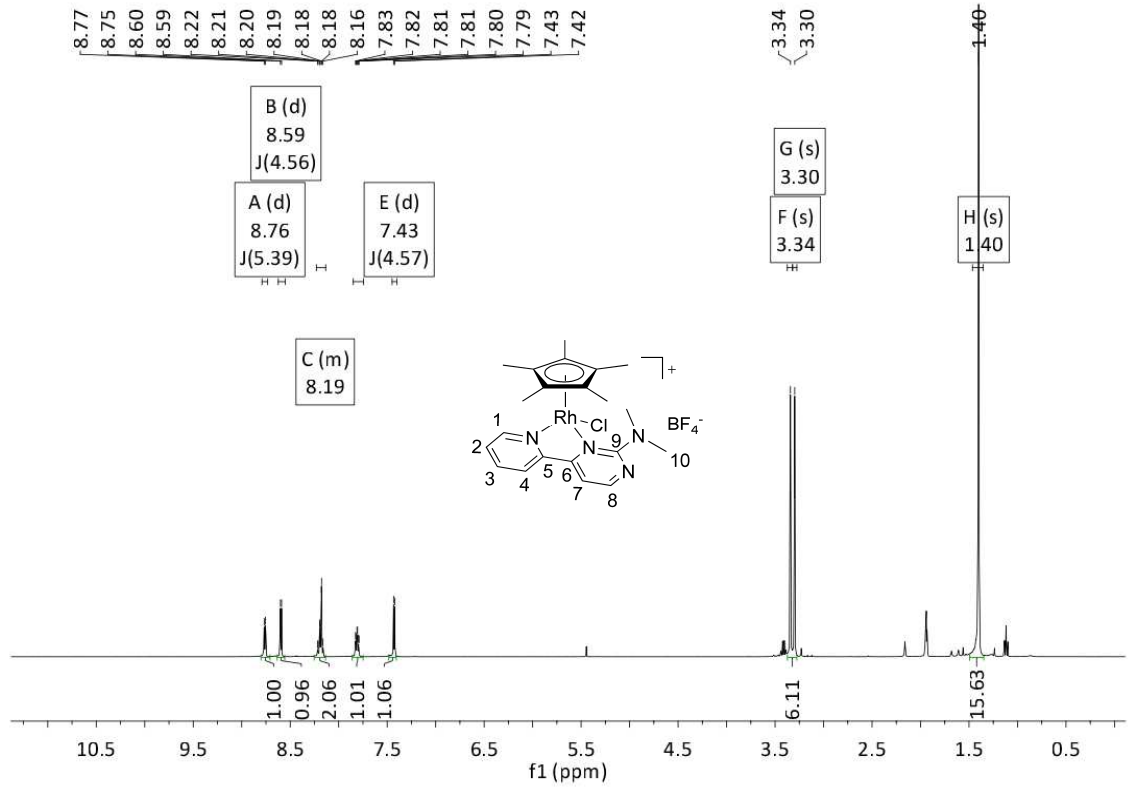


^{31}P NMR spectrum

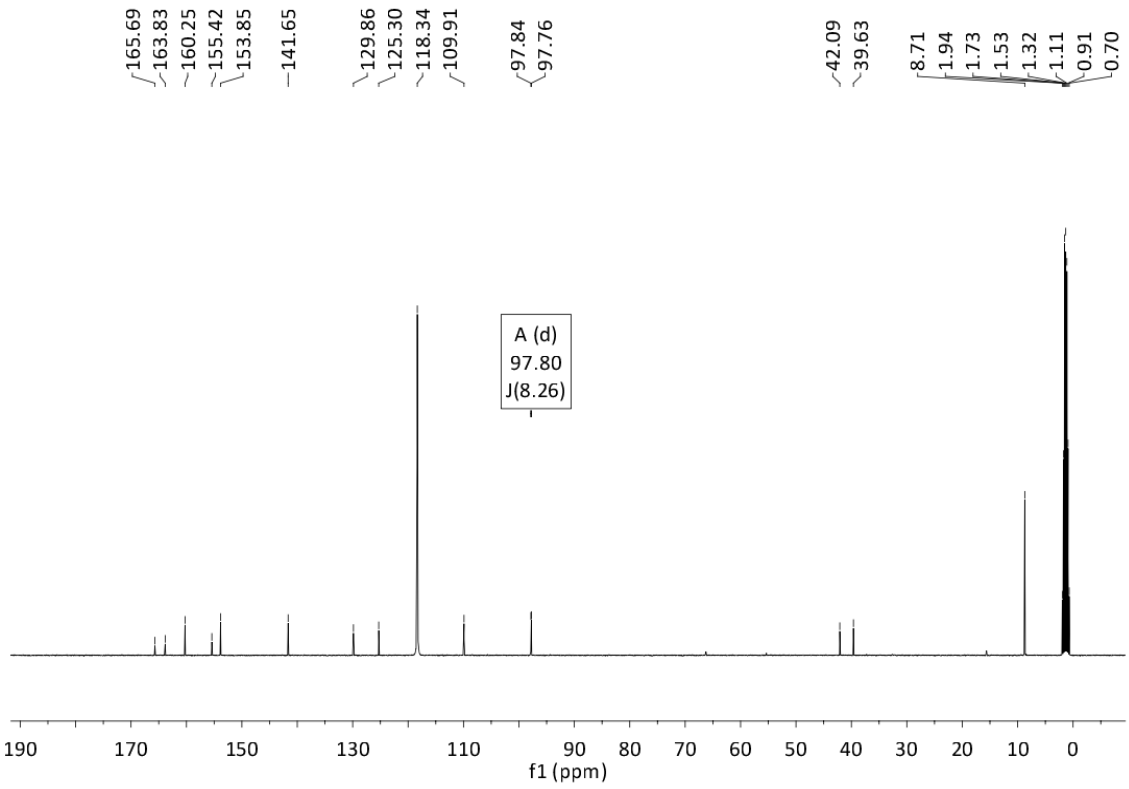


Chlorido(2-(2-dimethylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III) tetrafluoroborate (3e): see Experimental Section

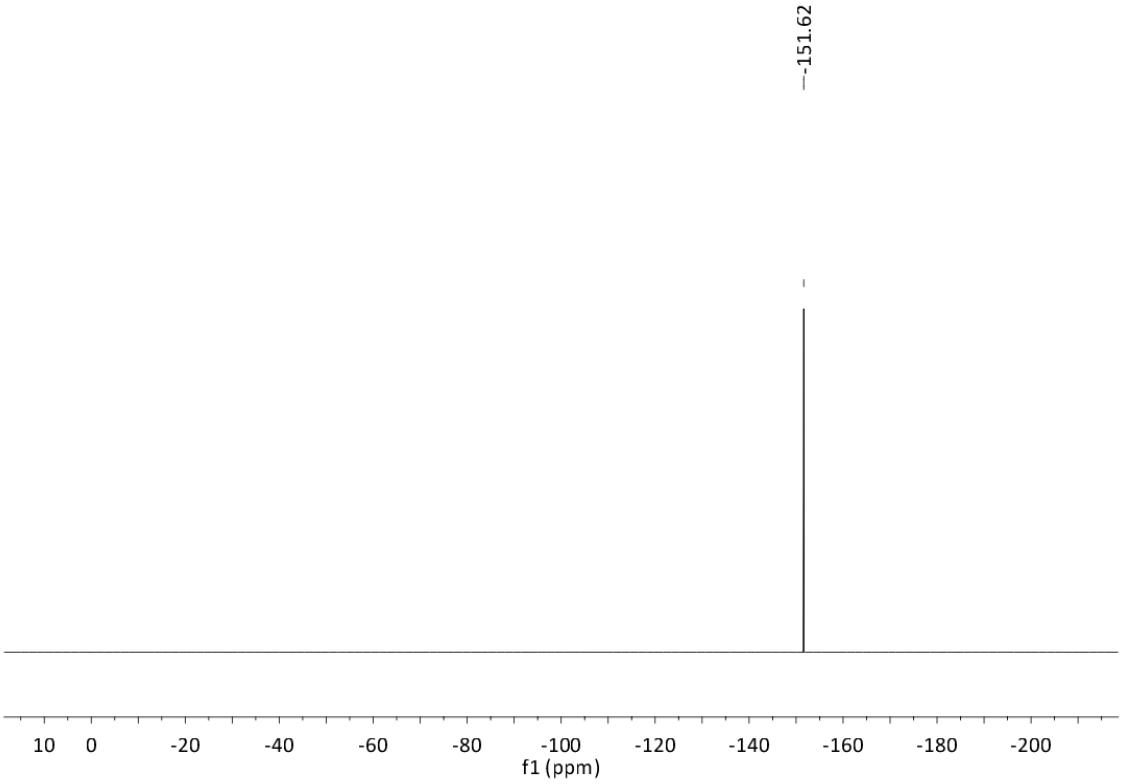
^{1}H NMR spectrum



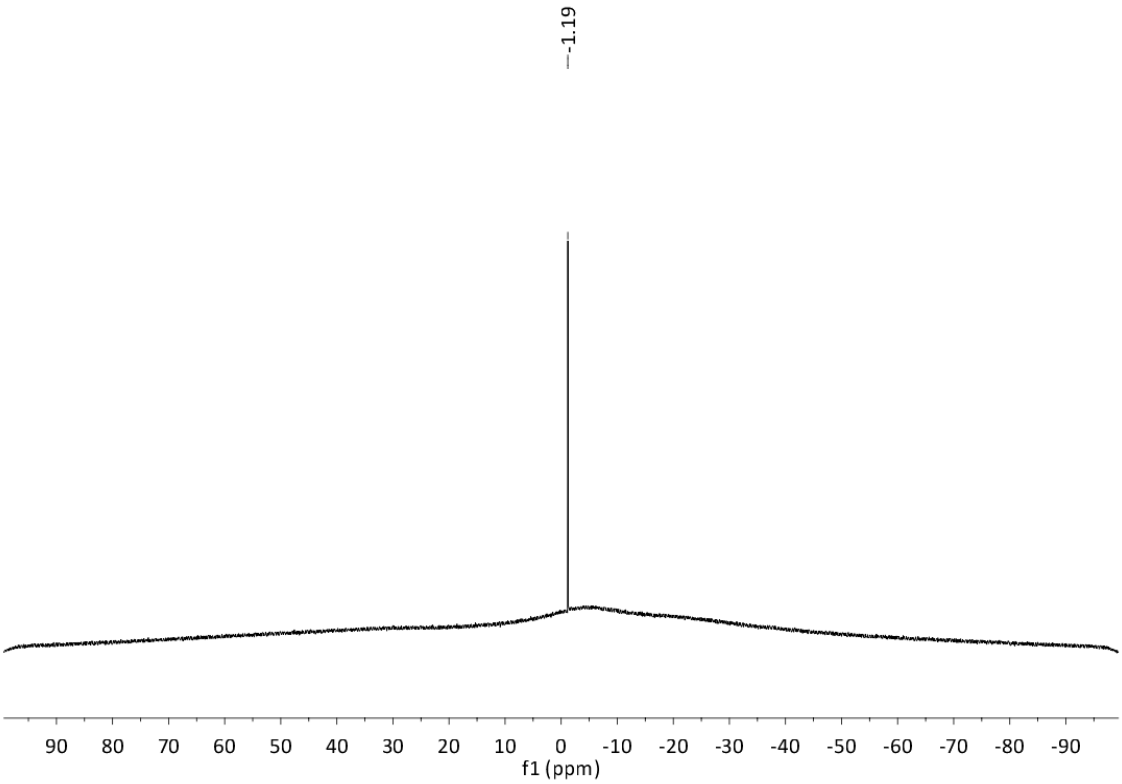
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

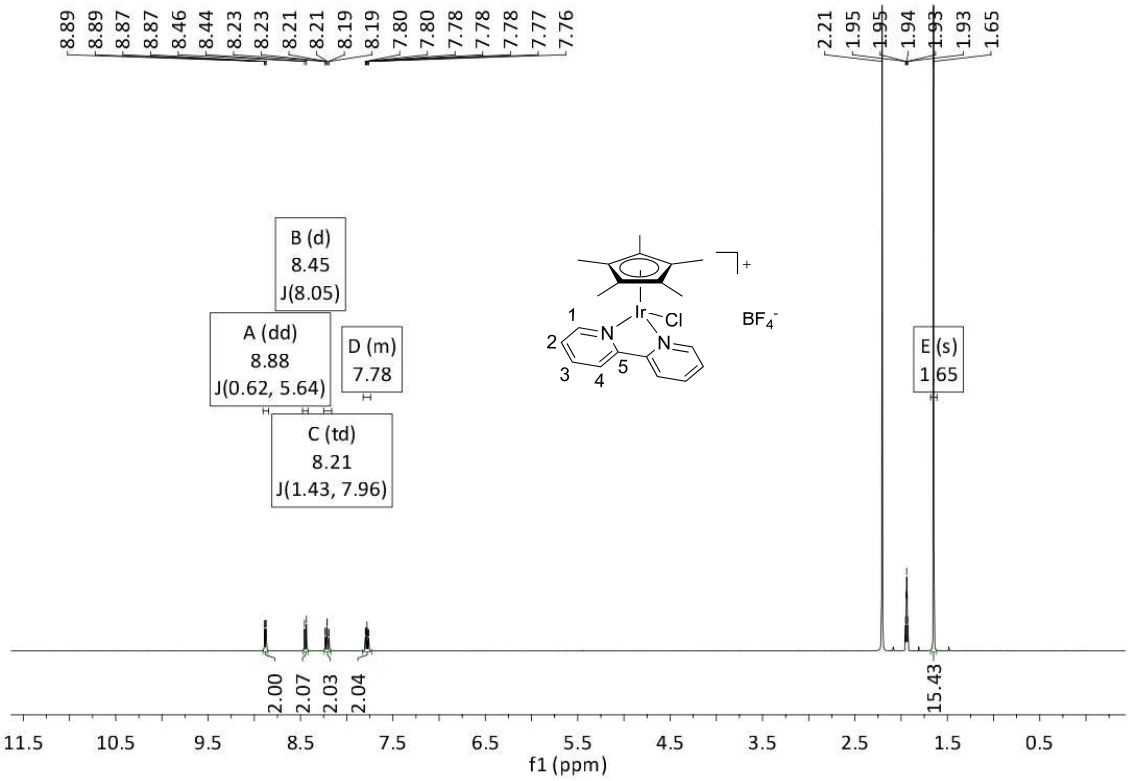


^{11}B NMR spectrum

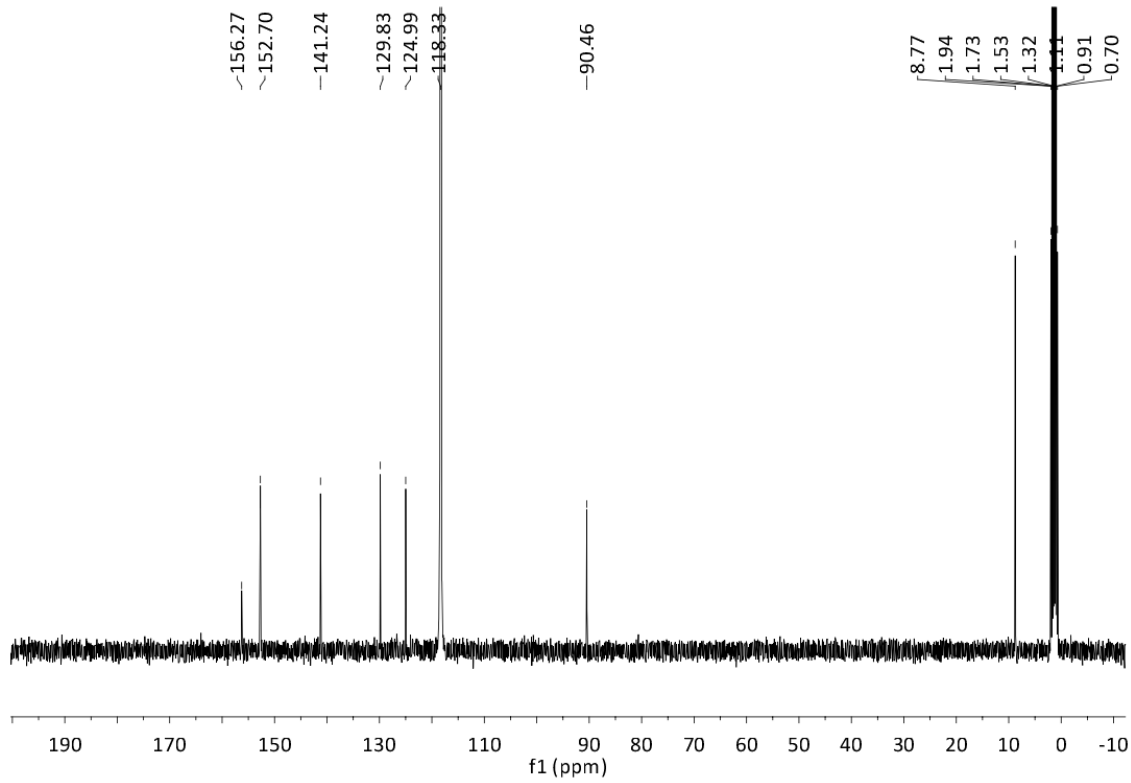


2,2'-Bipyridine(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)iridium(III) tetrafluoroborate (4a): see Experimental Section

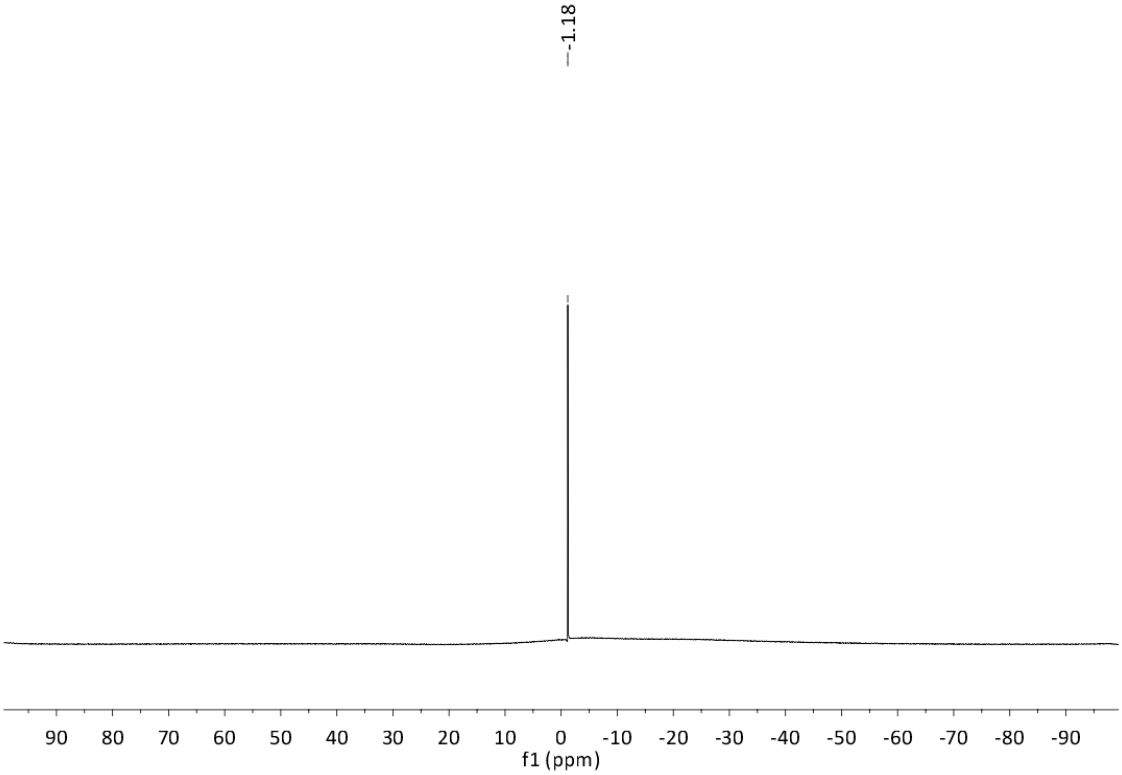
^{1}H NMR spectrum



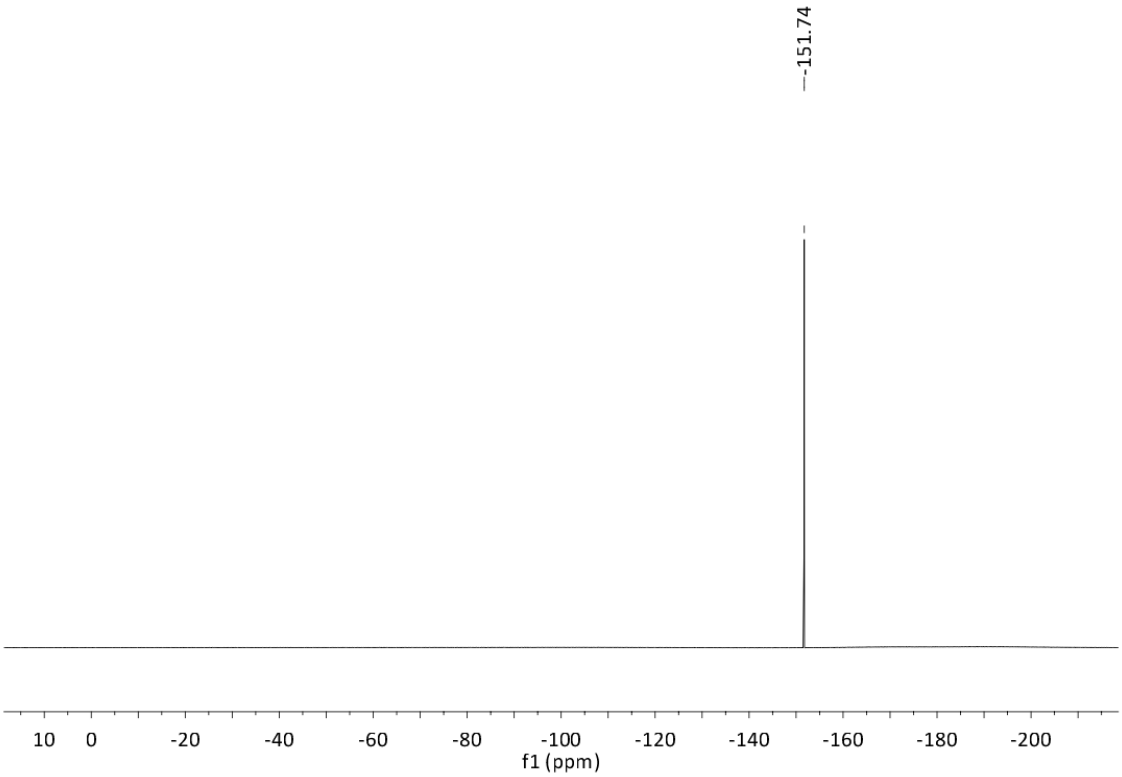
^{13}C{^{1}H} NMR spectrum



^{11}B NMR spectrum

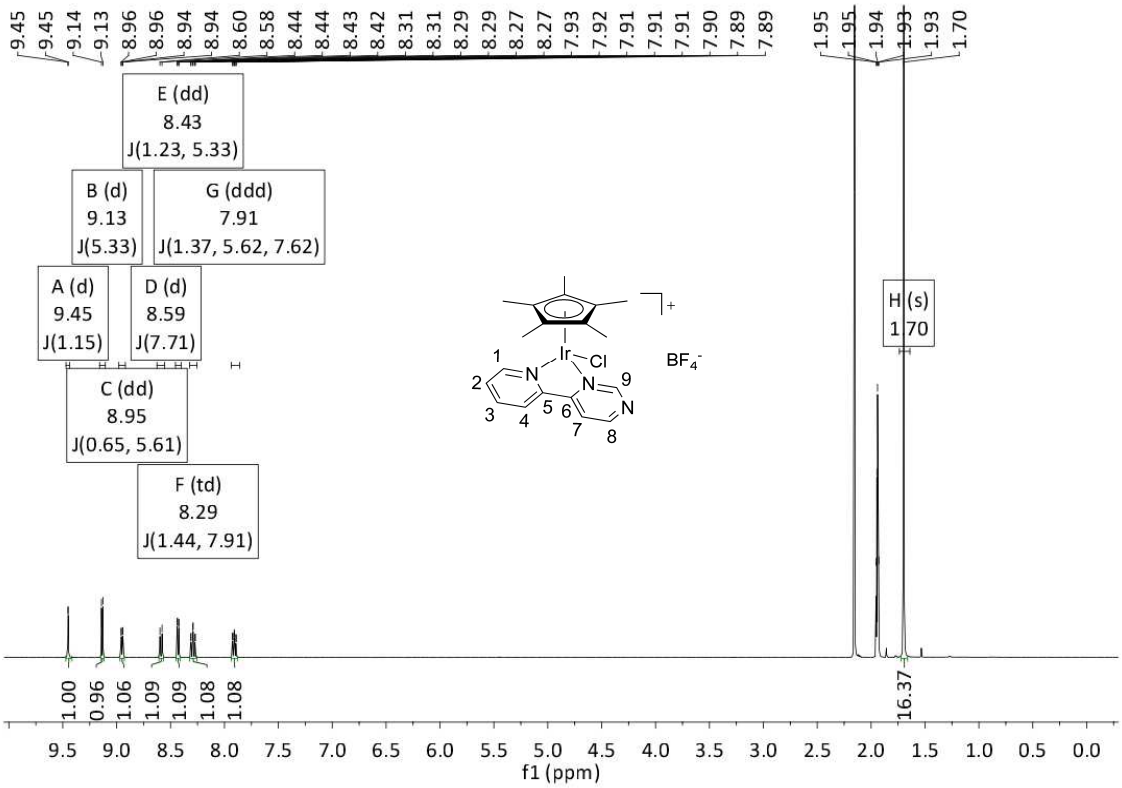


^{19}F NMR spectrum

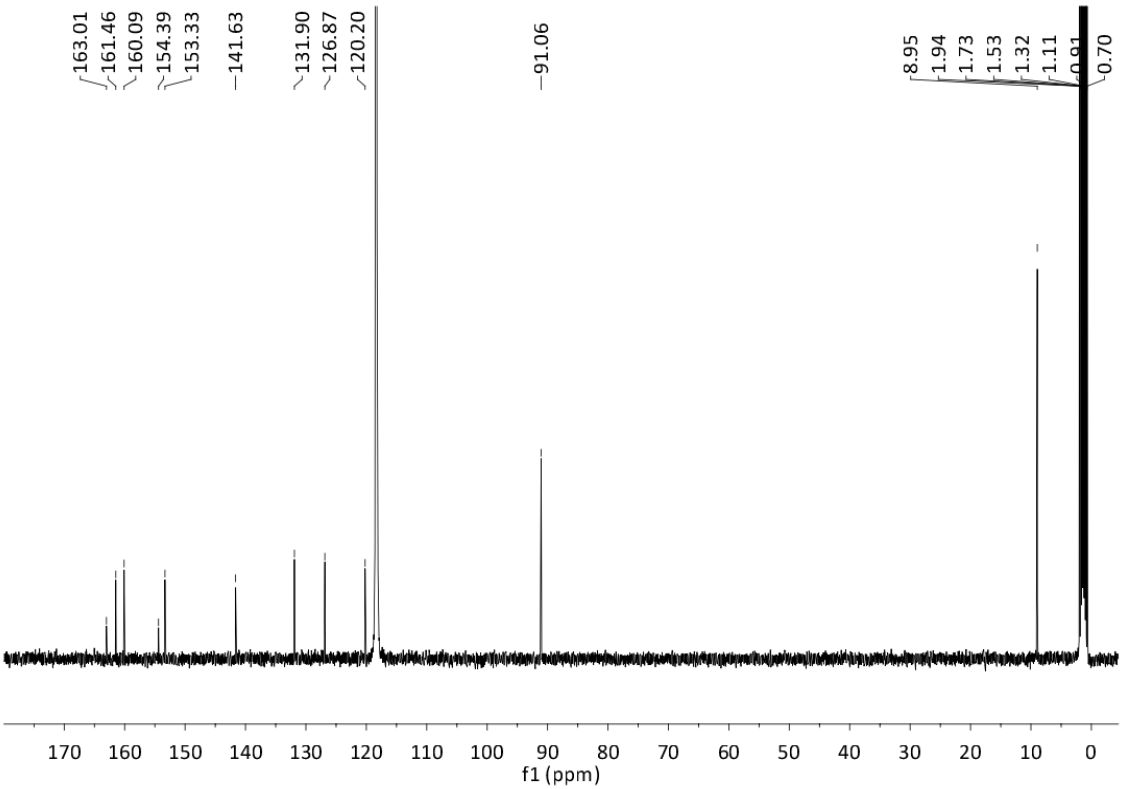


Chlorido(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)(2-pyrimidin-4-ylpyridine)iridium(III) tetrafluoroborate (4b): see Experimental Section.

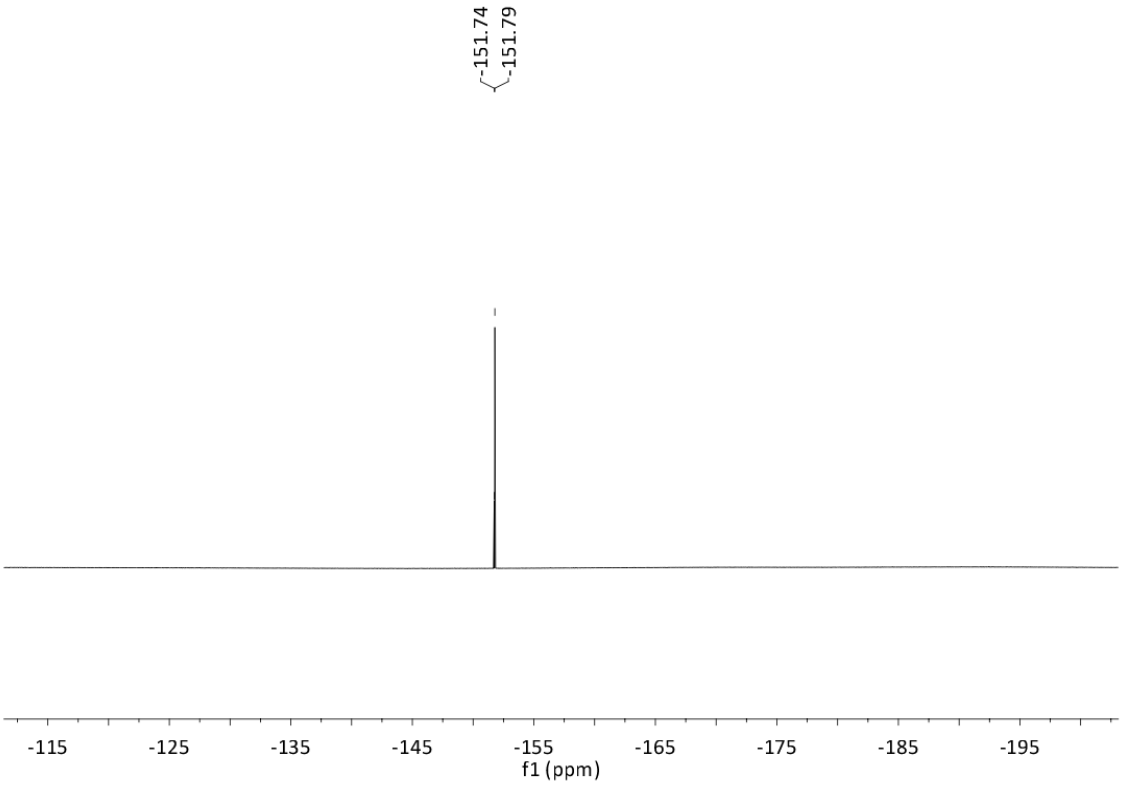
^{1}H NMR spectrum



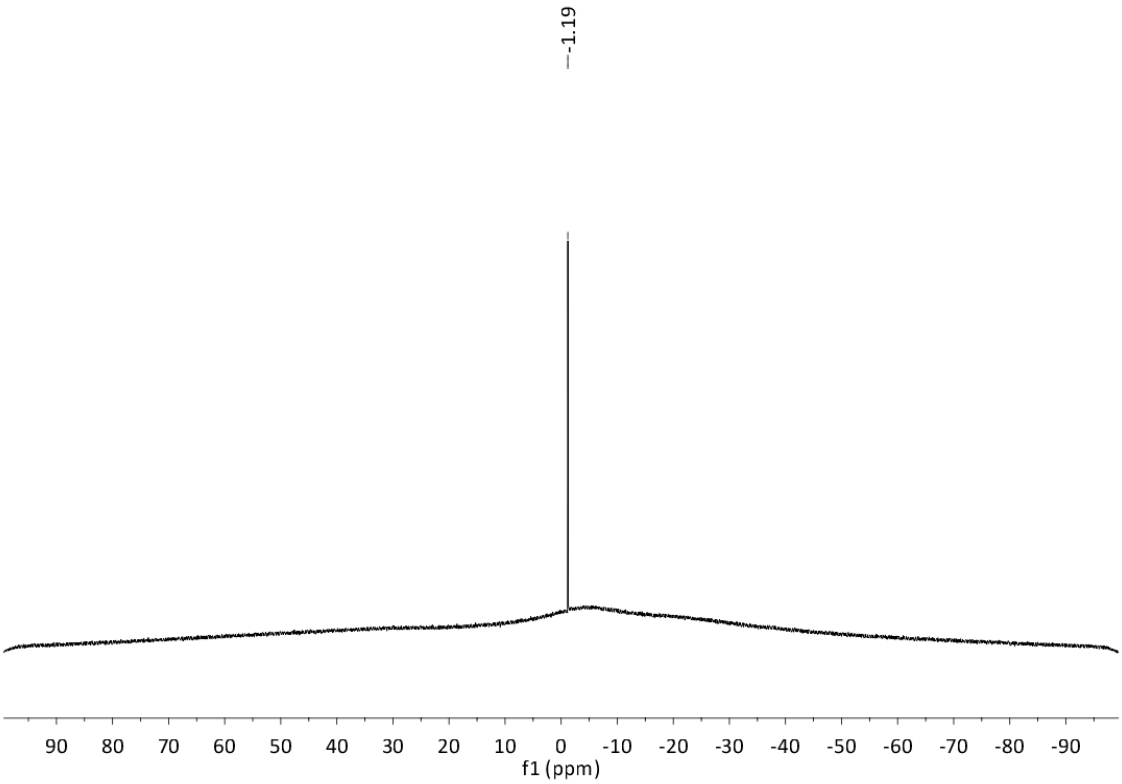
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

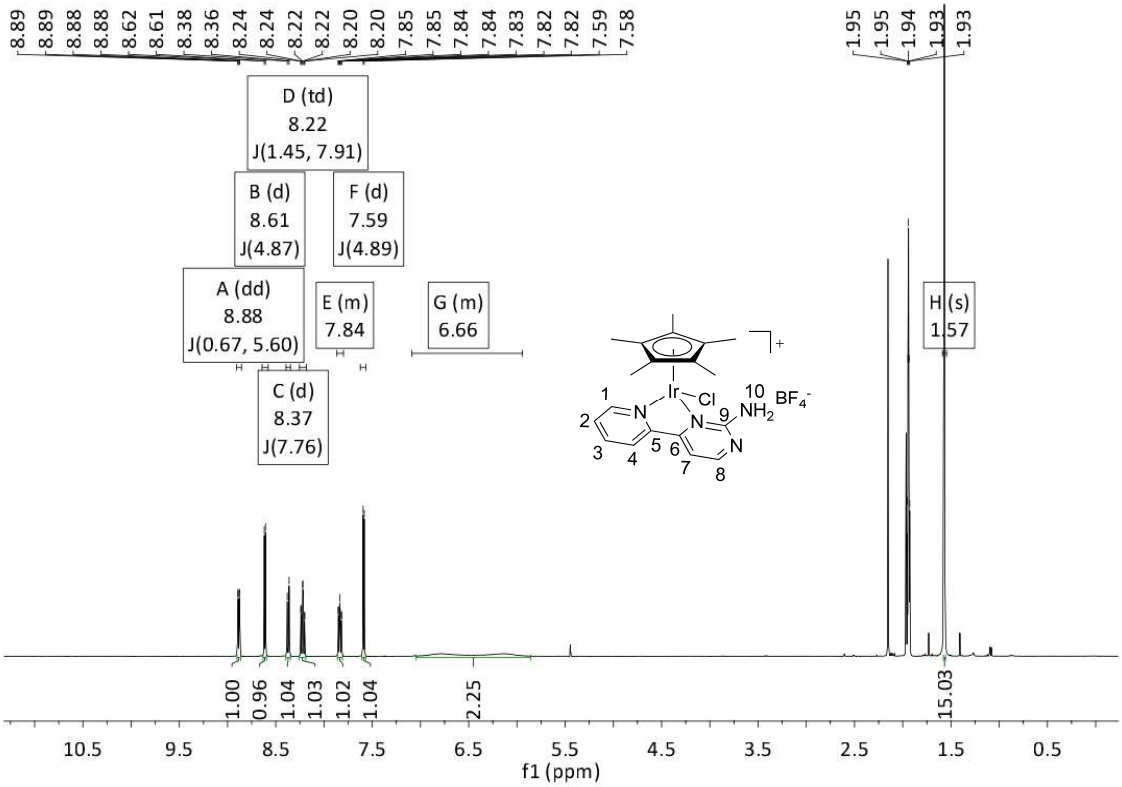


^{11}B NMR spectrum

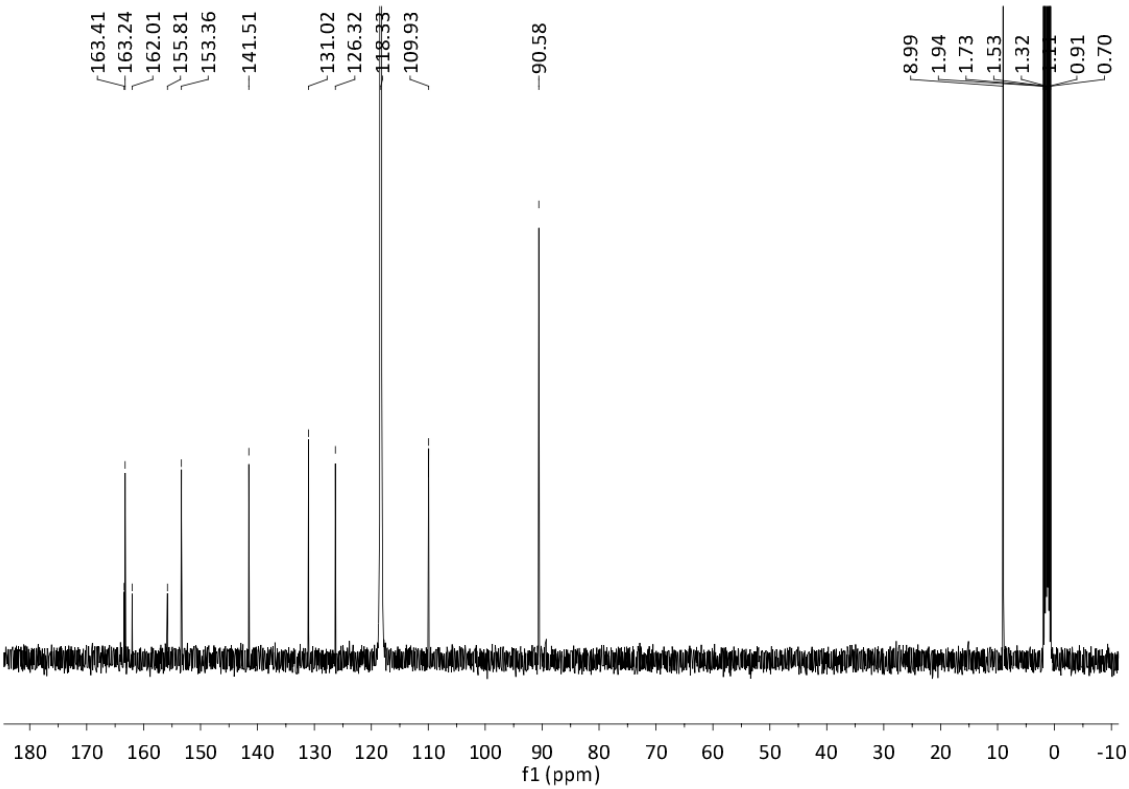


(2-(2-Aminopyrimidin-4-yl)pyridine)(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadien-yl)iridium(III) tetrafluoroborate (4c): see Experimental Section.

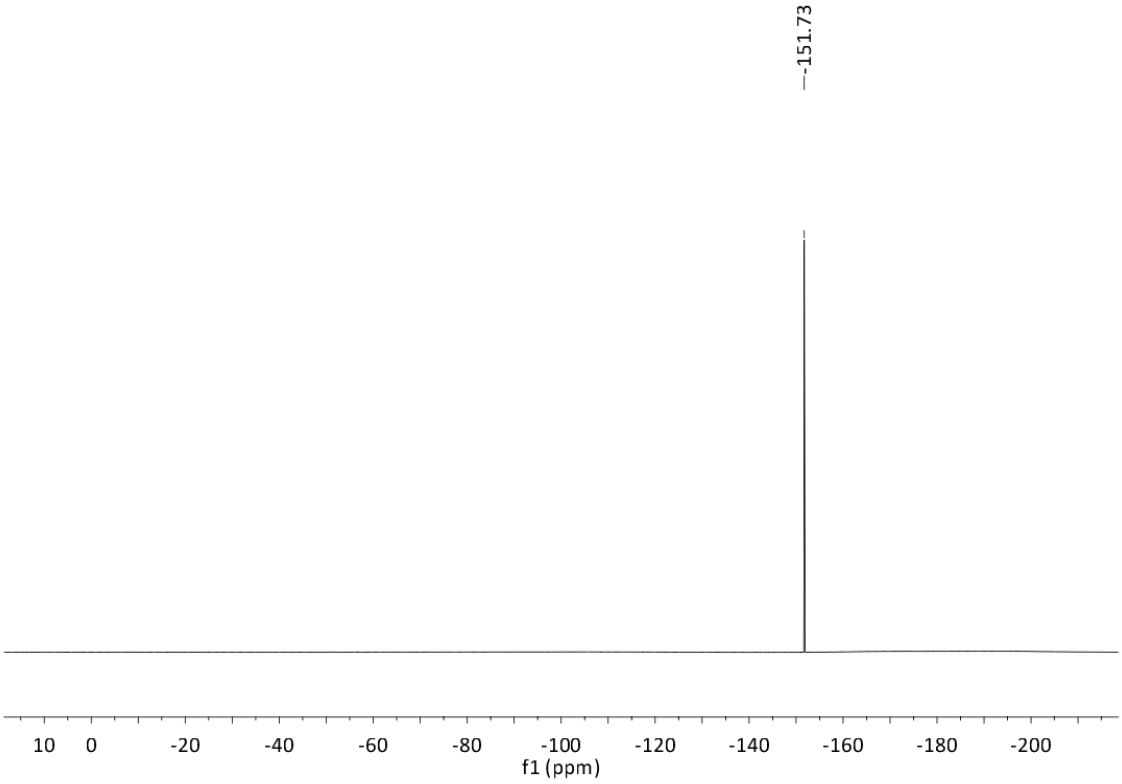
^{1}H NMR spectrum



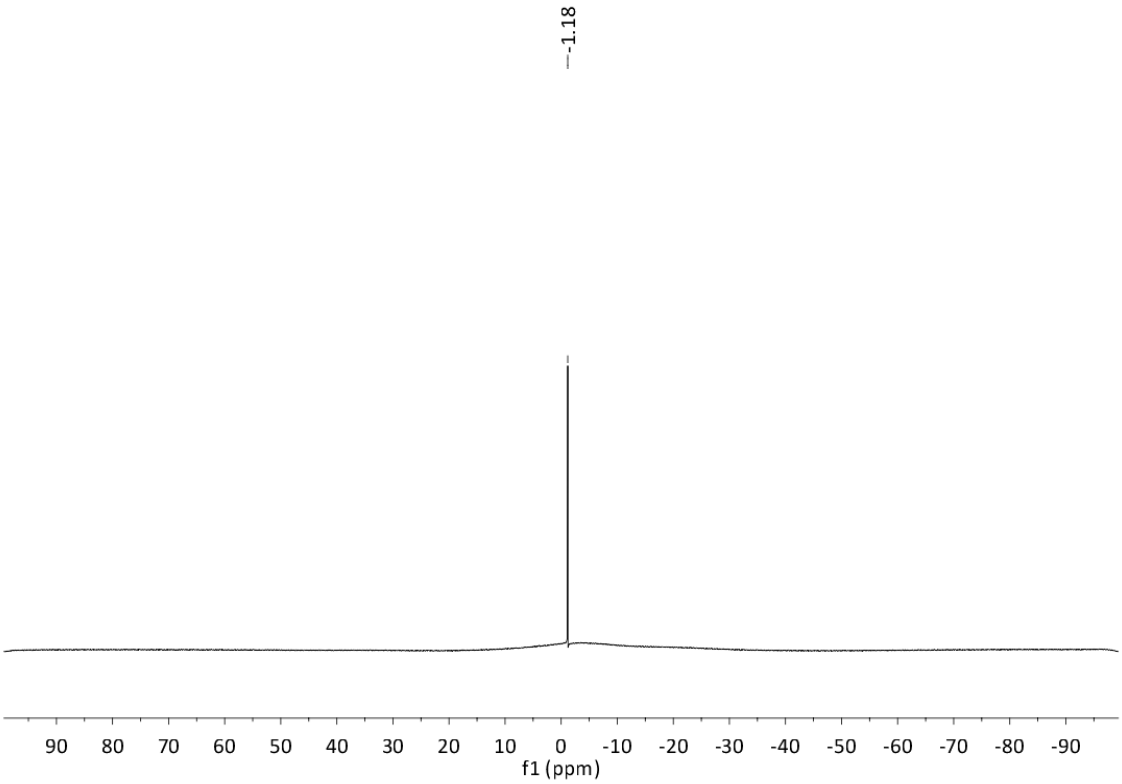
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

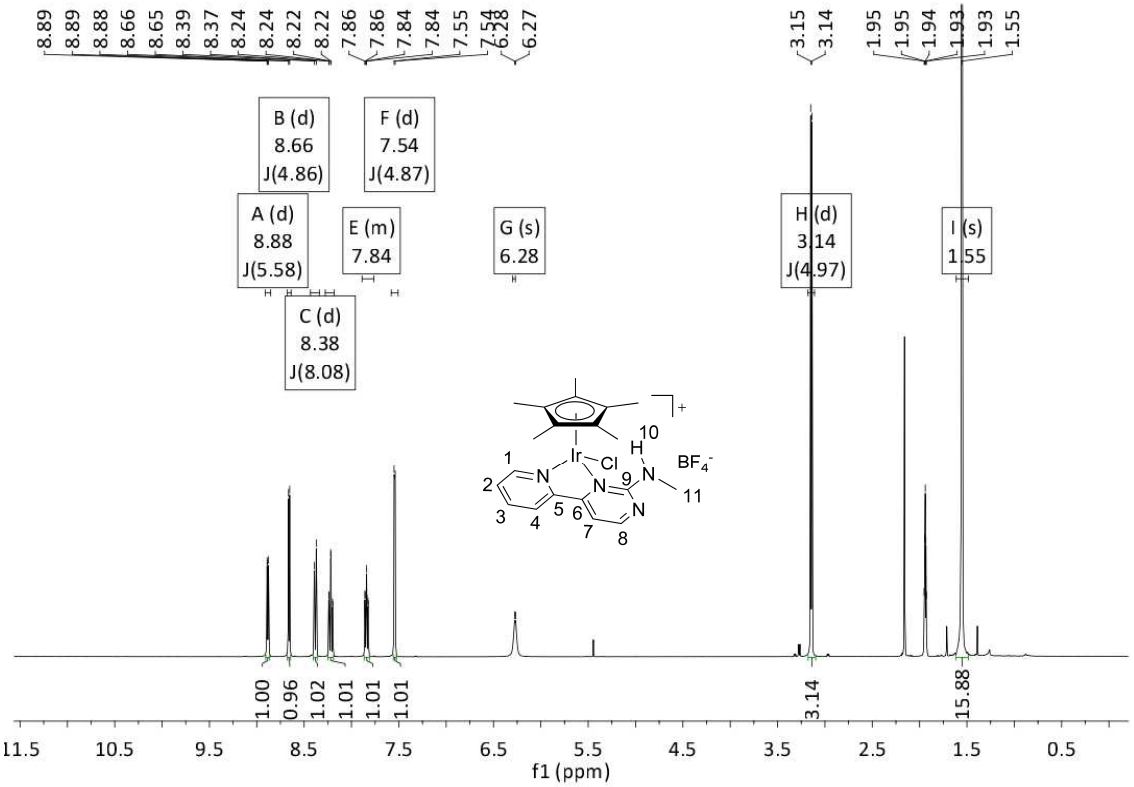


^{11}B NMR spectrum

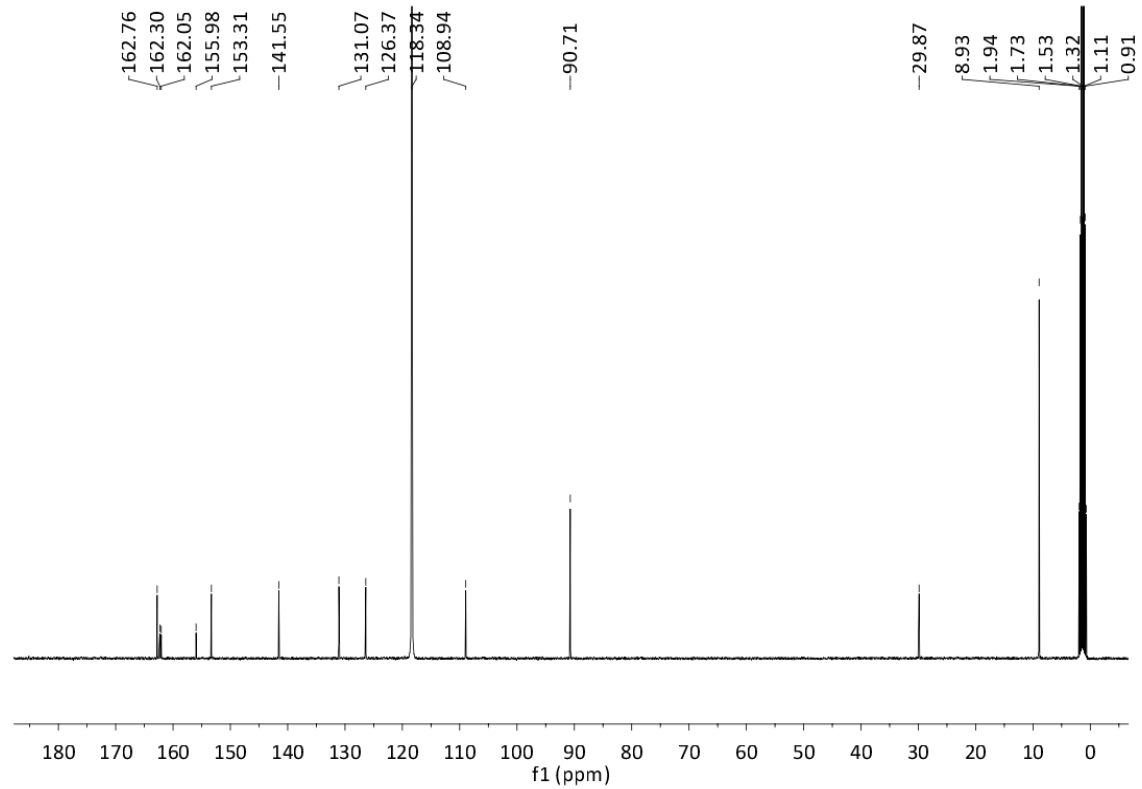


Chlorido(2-(2-methylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)iridium(III) tetrafluoroborate (4d): see Experimental Section

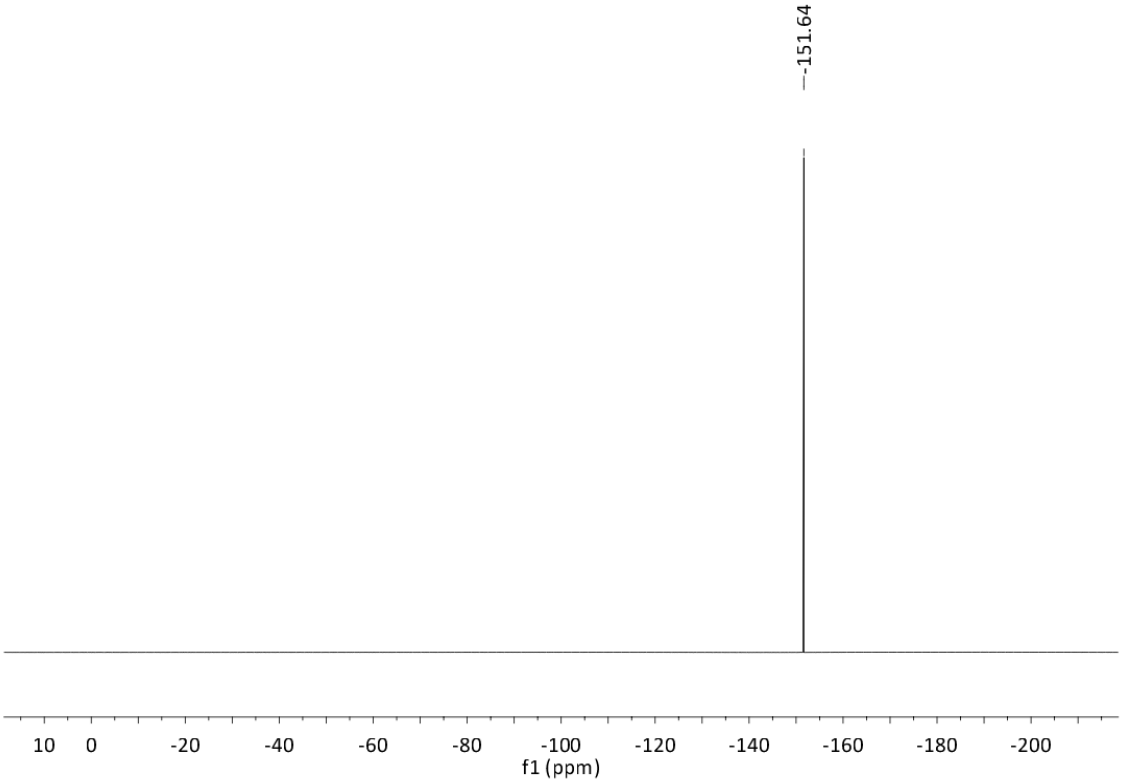
^{1}H NMR spectrum



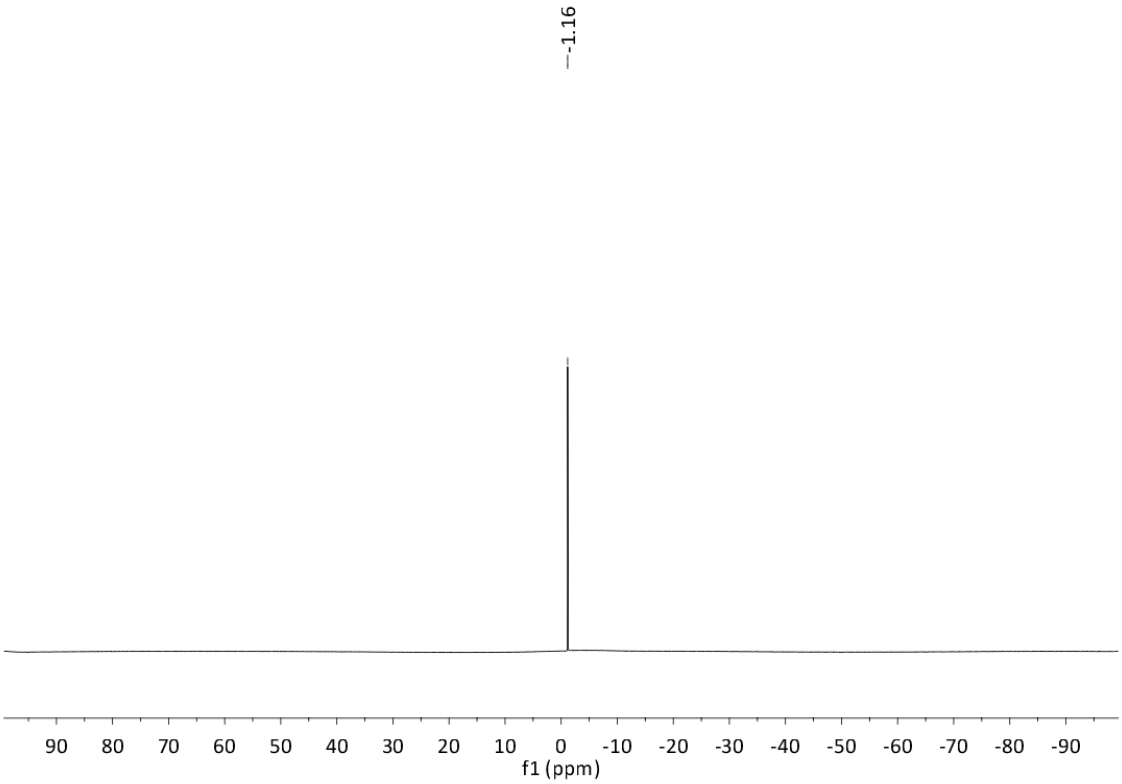
^{13}C{^{1}H} NMR spectrum



^{19}F NMR spectrum

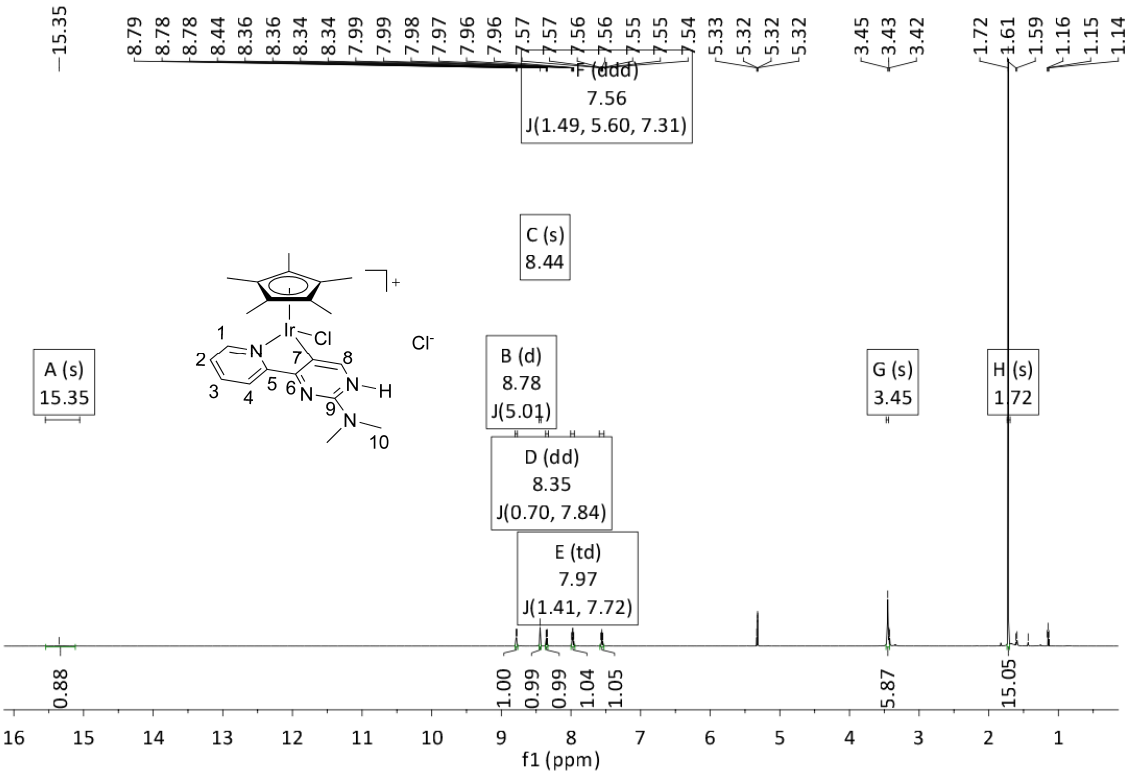


^{11}B NMR spectrum

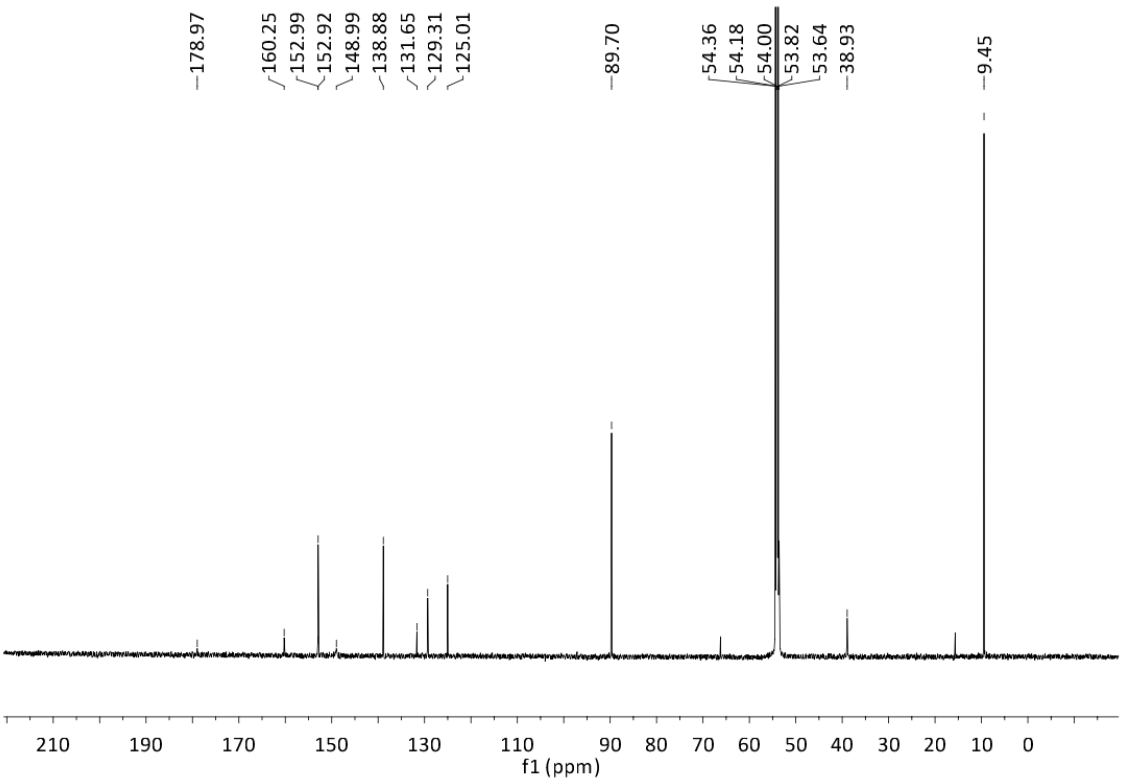


Chlorido(2-*N*,*N*-dimethylamino-4-(pyridin-2-yl-κ*N*)pyrimidine-κC5)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)iridium(III) hydrochloride (5): see Experimental Section

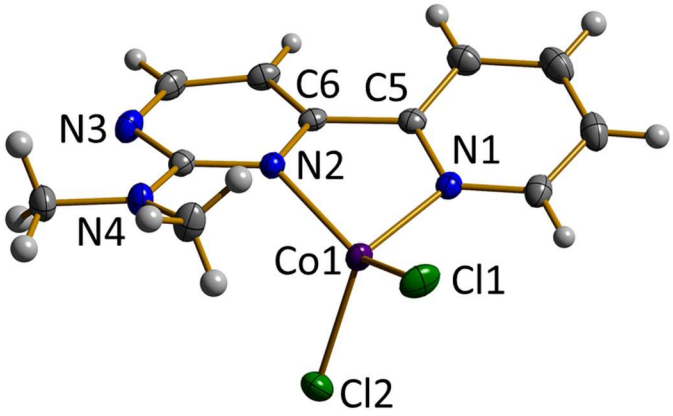
^{1}H NMR spectrum



^{13}C{^{1}H} NMR spectrum



2. X-Ray structure analysis of (2-(2-methylaminopyrimidin-4-yl)pyridine)cobalt(II) dichloride



Molecular structure of the compound in the solid state. Characteristic bond lengths [Å], angles [°] and dihedral angles [°]: Co1-Cl1 2.2273(5), Co1-Cl2 2.2513(5), Co1-N1 2.0223(14), Co1-N2 2.0559(13), Cl1-Co1-Cl2 111.43(2), Cl1-Co1-N1 107.04(4), Cl1-Co1-N2 136.70(4), Cl2-Co1-N1 113.84(4), Cl2-Co1-N2 102.50(4), N1-Co1-N2 81.60(5), N1-C5-C6-N2 16.8(2).

3. Quantum chemical calculations (optimized structures)

3.1 Hydrogen chloride

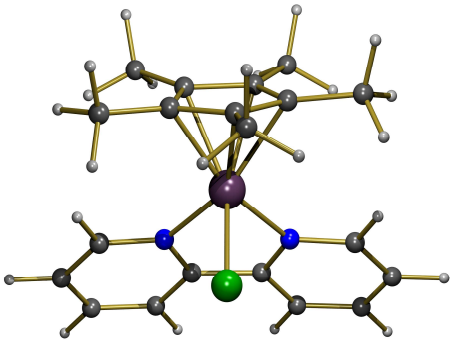
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	1	0	0.104009	0.000000	0.000000
2	17	0	1.395991	0.000000	0.000000

SCF Done: E(RB3LYP) = -460.826586507 A.U. after 1 cycles
Low frequencies --- 0.0027 0.0028 0.0052 55.9822 55.9822 2863.0747
Zero-point correction= 0.006523 (Hartree/Particle)
Thermal correction to Energy= 0.008883
Thermal correction to Enthalpy= 0.009827
Thermal correction to Gibbs Free Energy= -0.011374
Sum of electronic and zero-point Energies= -460.820064
Sum of electronic and thermal Energies= -460.817703
Sum of electronic and thermal Enthalpies= -460.816759
Sum of electronic and thermal Free Energies= -460.837960

3.2 Cobalt complexes

a1) [2,2'-Bipyridine(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III)]$^+$ (**2a**$^+$)



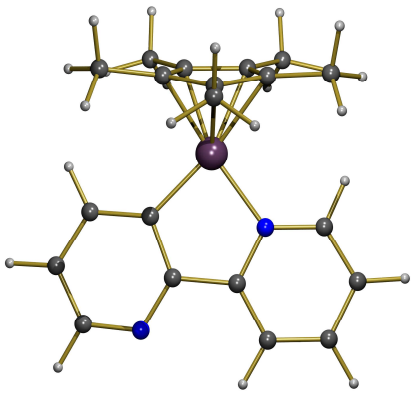
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.169166	-0.013384	0.358253
2	17	0	0.593093	-1.859097	1.574669
3	7	0	-1.140149	-1.032184	-0.716683
4	7	0	1.388553	-0.651061	-1.072897
5	6	0	3.506089	-1.012280	-2.127206
6	6	0	-2.399782	-1.310384	-0.356122
7	6	0	-3.263808	-2.038408	-1.163062
8	6	0	-2.800479	-2.503158	-2.389486
9	6	0	-1.481657	-2.253240	-2.747620
10	6	0	-0.663602	-1.525692	-1.883547
11	6	0	0.777011	-1.307414	-2.087222
12	6	0	1.501680	-1.799688	-3.172204
13	6	0	2.881591	-1.640905	-3.199103
14	6	0	2.722719	-0.536173	-1.083795
15	6	0	0.368141	2.068659	-0.004171
16	6	0	1.216634	1.690857	1.105743
17	6	0	0.385187	1.184203	2.140583
18	6	0	-0.970879	1.187047	1.670275
19	6	0	-0.978507	1.790588	0.362860

20	6	0	0.822839	2.747962	-1.258985
21	6	0	2.682118	1.974068	1.241850
22	6	0	0.826546	0.776217	3.505773
23	6	0	-2.153284	0.803159	2.508501
24	6	0	-2.189197	2.122695	-0.451745
25	1	0	4.582136	-0.895832	-2.086699
26	1	0	-2.710552	-0.955527	0.615844
27	1	0	-4.273164	-2.238819	-0.825293
28	1	0	-3.447887	-3.070397	-3.048315
29	1	0	-1.091553	-2.637930	-3.680764
30	1	0	1.000173	-2.317970	-3.978949
31	1	0	3.459780	-2.021369	-4.033315
32	1	0	3.171887	-0.065894	-0.221602
33	1	0	0.133961	2.586666	-2.089042
34	1	0	1.811516	2.412676	-1.575798
35	1	0	0.887860	3.829803	-1.098747
36	1	0	2.827399	2.877676	1.843758
37	1	0	3.164480	2.157248	0.281372
38	1	0	3.214986	1.168512	1.751589
39	1	0	0.784784	1.649892	4.168188
40	1	0	1.849063	0.400799	3.514472
41	1	0	0.186217	0.003475	3.927787
42	1	0	-2.042401	-0.201003	2.924704
43	1	0	-3.090468	0.847138	1.952523
44	1	0	-2.257792	1.491527	3.353248
45	1	0	-2.503217	3.149627	-0.234698
46	1	0	-3.037893	1.477277	-0.225856
47	1	0	-1.998339	2.065039	-1.524068

```
SCF Done:  E(RB3LYP) =  -2728.63404998     A.U. after    2 cycles
Low frequencies ---   -10.8699   -4.7297   -0.0056    0.0021    0.0022    2.2435
Zero-point correction=                           0.385829 (Hartree/Particle)
 Thermal correction to Energy=                    0.410271
 Thermal correction to Enthalpy=                  0.411216
 Thermal correction to Gibbs Free Energy=         0.332584
 Sum of electronic and zero-point Energies=          -2728.248221
 Sum of electronic and thermal Energies=             -2728.223779
 Sum of electronic and thermal Enthalpies=           -2728.222834
 Sum of electronic and thermal Free Energies=        -2728.301466
```

a2) Splitting of HCl from (**2a**$^{+}$); cyclometallation of the pyridine ring



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.834851	-0.945003	0.233232
2	7	0	-0.231829	0.955162	0.183640

3	7	0	3.142681	-0.134613	-0.352299
4	6	0	3.143340	-2.526708	-0.209121
5	6	0	-0.981545	2.052002	0.387357
6	6	0	-0.455696	3.335020	0.333387
7	6	0	0.901635	3.489939	0.056538
8	6	0	1.687731	2.359443	-0.136258
9	6	0	1.095757	1.103517	-0.058310
10	6	0	1.820975	-0.172289	-0.172407
11	6	0	1.041969	-1.340263	-0.029057
12	6	0	1.758978	-2.540817	-0.037807
13	6	0	3.788479	-1.301981	-0.379380
14	6	0	-1.923502	-2.559730	0.947493
15	6	0	-1.667916	-2.740482	-0.432632
16	6	0	-2.214554	-1.592508	-1.118131
17	6	0	-2.961466	-0.800924	-0.162718
18	6	0	-2.745209	-1.358355	1.107718
19	6	0	-1.523612	-3.460213	2.072829
20	6	0	-1.062083	-3.928352	-1.110891
21	6	0	-2.165260	-1.359499	-2.592764
22	6	0	-3.834019	0.361673	-0.522997
23	6	0	-3.253197	-0.864285	2.425210
24	1	0	3.715424	-3.448192	-0.213604
25	1	0	-2.028553	1.891039	0.601720
26	1	0	-1.100510	4.187990	0.505642
27	1	0	1.342019	4.479410	0.001521
28	1	0	2.750479	2.417718	-0.334082
29	1	0	1.264227	-3.495487	0.094259
30	1	0	4.862439	-1.253936	-0.533036
31	1	0	-1.174410	-2.898207	2.941809
32	1	0	-0.734324	-4.154157	1.786319
33	1	0	-2.383084	-4.055143	2.401795
34	1	0	-1.857703	-4.498183	-1.603035
35	1	0	-0.575229	-4.605913	-0.410618
36	1	0	-0.339987	-3.652046	-1.879906
37	1	0	-3.028424	-1.836915	-3.072827
38	1	0	-1.267724	-1.784243	-3.042891
39	1	0	-2.203630	-0.298918	-2.844764
40	1	0	-3.371862	1.022653	-1.258529
41	1	0	-4.119583	0.957761	0.344206
42	1	0	-4.762332	-0.007377	-0.971966
43	1	0	-4.048748	-1.521505	2.793075
44	1	0	-3.665834	0.142507	2.362427
45	1	0	-2.471457	-0.860589	3.188851

SCF Done: E(RB3LYP) = -2267.71776931 A.U. after 2 cycles

Low frequencies --- -6.2045 0.0005 0.0023 0.0048 8.4976 10.3445

Zero-point correction= 0.371500 (Hartree/Particle)

Thermal correction to Energy= 0.394163

Thermal correction to Enthalpy= 0.395107

Thermal correction to Gibbs Free Energy= 0.320349

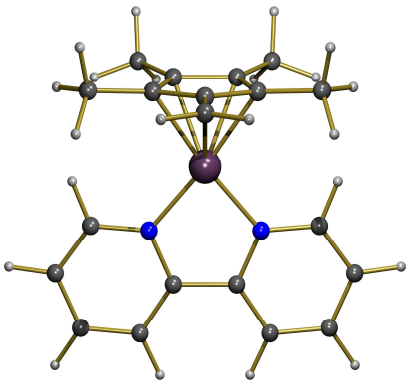
Sum of electronic and zero-point Energies= -2267.346269

Sum of electronic and thermal Energies= -2267.323606

Sum of electronic and thermal Enthalpies= -2267.322662

Sum of electronic and thermal Free Energies= -2267.397420

a3) Splitting of HCl from (**2a**$^{+}$); deprotonation of Cp*

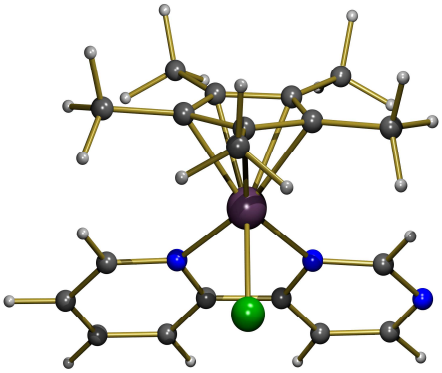


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.610936	0.680298	0.118566
2	7	0	-1.272770	-0.725789	1.313058
3	7	0	-0.935702	-0.694436	-1.240295
4	6	0	-0.995377	-1.614376	-3.459030
5	6	0	-1.458752	-0.637704	2.641660
6	6	0	-1.903080	-1.698835	3.417465
7	6	0	-2.169885	-2.916014	2.798503
8	6	0	-1.990044	-3.018572	1.424768
9	6	0	-1.546031	-1.911097	0.704214
10	6	0	-1.353812	-1.893213	-0.751992
11	6	0	-1.592180	-2.981538	-1.589591
12	6	0	-1.409787	-2.845274	-2.960056
13	6	0	-0.770897	-0.573712	-2.569126
14	6	0	-0.960152	2.595846	-0.638595
15	6	0	0.381201	2.260309	-0.909914
16	6	0	1.099185	2.118236	0.361991
17	6	0	0.075254	2.231970	1.407010
18	6	0	-1.150784	2.578180	0.805009
19	6	0	-2.009622	3.002762	-1.627265
20	6	0	1.083063	2.285692	-2.234771
21	6	0	2.399361	1.768323	0.529392
22	6	0	0.409150	2.223305	2.868836
23	6	0	-2.422199	2.964499	1.496891
24	1	0	-0.844882	-1.454915	-4.519779
25	1	0	-1.240143	0.318785	3.090531
26	1	0	-2.033462	-1.565508	4.484465
27	1	0	-2.515261	-3.768511	3.371899
28	1	0	-2.197917	-3.953590	0.921160
29	1	0	-1.920639	-3.927766	-1.179884
30	1	0	-1.591877	-3.682570	-3.623832
31	1	0	-0.446321	0.392624	-2.922680
32	1	0	-2.997295	2.627219	-1.354202
33	1	0	-1.787821	2.653464	-2.636307
34	1	0	-2.080645	4.095208	-1.674294
35	1	0	1.757529	3.147379	-2.275198
36	1	0	0.396210	2.389316	-3.075747
37	1	0	1.697967	1.397003	-2.399338
38	1	0	3.069596	1.648529	-0.313118
39	1	0	2.828359	1.626179	1.513843
40	1	0	0.963244	1.329060	3.165922
41	1	0	-0.472757	2.308711	3.504989

```
     42          1           0        1.047134    3.081728    3.103631
     43          1           0       -2.506706    4.055719    1.549739
     44          1           0       -2.468588    2.590696    2.520358
     45          1           0       -3.303929    2.598381    0.968112
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -2267.74290065     A.U. after    2 cycles
Low frequencies ---   -6.7584   -0.0044    0.0020    0.0052    3.4270    4.8333
Zero-point correction=                           0.372104 (Hartree/Particle)
 Thermal correction to Energy=                    0.394347
 Thermal correction to Enthalpy=                  0.395291
 Thermal correction to Gibbs Free Energy=         0.321887
 Sum of electronic and zero-point Energies=          -2267.370796
 Sum of electronic and thermal Energies=             -2267.348554
 Sum of electronic and thermal Enthalpies=           -2267.347609
 Sum of electronic and thermal Free Energies=        -2267.421013
```

b1) [Chlorido(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)(2-pyrimidin-4-ylpyridine)cobalt(III)]$^+$ (**2b**$^+$)



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                          Input orientation:
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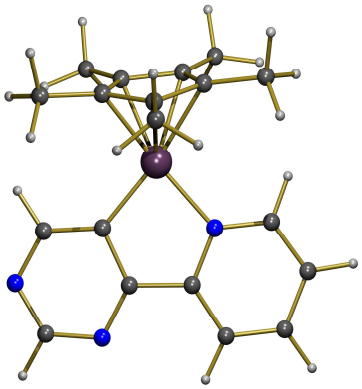
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1         27           0        0.575329    0.041994    0.315805
      2         17           0        1.296018   -1.651968    1.610632
      3          7           0       -0.766881   -1.175351   -0.515415
      4          7           0        1.673391   -0.649064   -1.179017
      5          7           0        3.695942   -0.916595   -2.386389
      6          6           0       -1.968308   -1.486498   -0.015098
      7          6           0       -2.832292   -2.378591   -0.640688
      8          6           0       -2.432663   -2.980369   -1.828054
      9          6           0       -1.170666   -2.688907   -2.333214
     10          6           0       -0.354378   -1.790925   -1.649318
     11          6           0        1.034620   -1.490070   -2.024249
     12          6           0        1.717197   -2.043229   -3.103842
     13          6           0        3.057876   -1.709304   -3.252033
     14          6           0        2.980990   -0.431804   -1.384119
     15          6           0        0.883020    2.100425   -0.159003
     16          6           0        1.619065    1.735316    1.026621
     17          6           0        0.669237    1.350179    2.027899
     18          6           0       -0.629330    1.381331    1.446499
     19          6           0       -0.497399    1.858681    0.086651
     20          6           0        1.459603    2.692971   -1.406657
     21          6           0        3.087139    1.906283    1.279447
     22          6           0        0.990780    1.030720    3.448457
     23          6           0       -1.908492    1.164960    2.197649
     24          6           0       -1.628777    2.152291   -0.849165
     25          1           0       -2.235206   -1.022332    0.922766
     26          1           0       -3.793532   -2.596498   -0.191464
```

27	1	0	-3.081406	-3.679207	-2.343298
28	1	0	-0.822982	-3.168905	-3.238860
29	1	0	1.238127	-2.718127	-3.800515
30	1	0	3.644876	-2.098220	-4.078224
31	1	0	3.492911	0.182775	-0.657010
32	1	0	0.877357	2.444080	-2.294698
33	1	0	2.491035	2.386381	-1.582257
34	1	0	1.464862	3.785256	-1.321415
35	1	0	3.252736	2.711197	2.002738
36	1	0	3.637899	2.178185	0.378520
37	1	0	3.533015	1.001768	1.699898
38	1	0	0.987732	1.961759	4.029109
39	1	0	1.973712	0.574122	3.552099
40	1	0	0.261509	0.356833	3.895877
41	1	0	-1.868469	0.281875	2.839387
42	1	0	-2.771850	1.077524	1.537397
43	1	0	-2.101066	2.021335	2.852708
44	1	0	-2.016736	3.159668	-0.662433
45	1	0	-2.463274	1.461343	-0.720920
46	1	0	-1.321268	2.114710	-1.894803

SCF Done: E(RB3LYP) = -2744.67143429 A.U. after 2 cycles
Low frequencies --- -14.1557 -7.8615 -2.3444 -0.0030 0.0058 0.0060
Zero-point correction= 0.373840 (Hartree/Particle)
Thermal correction to Energy= 0.398224
Thermal correction to Enthalpy= 0.399169
Thermal correction to Gibbs Free Energy= 0.320528
Sum of electronic and zero-point Energies= -2744.297595
Sum of electronic and thermal Energies= -2744.273210
Sum of electronic and thermal Enthalpies= -2744.272266
Sum of electronic and thermal Free Energies= -2744.350906

b2) Splitting of HCl from (**2b**$^{+}$); cyclometallation of the pyrimidine ring



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.931333	-0.922514	0.228898
2	7	0	-0.330155	0.985737	0.184285
3	7	0	3.045322	-0.123926	-0.334404
4	7	0	3.029814	-2.501793	-0.205607
5	6	0	-1.082142	2.080870	0.381112
6	6	0	-0.554648	3.365435	0.336906
7	6	0	0.804485	3.524069	0.078653
8	6	0	1.594362	2.393210	-0.109387
9	6	0	0.999847	1.140305	-0.043590
10	6	0	1.723688	-0.138172	-0.159721

11	6	0	0.946124	-1.303134	-0.028487
12	6	0	1.701438	-2.480333	-0.040316
13	6	0	3.632445	-1.322913	-0.363965
14	6	0	-1.996706	-2.549244	0.945141
15	6	0	-1.739456	-2.729168	-0.435404
16	6	0	-2.302005	-1.589657	-1.122621
17	6	0	-3.053441	-0.802101	-0.167216
18	6	0	-2.831545	-1.356835	1.104149
19	6	0	-1.582967	-3.443081	2.070414
20	6	0	-1.114083	-3.908799	-1.110564
21	6	0	-2.256200	-1.358686	-2.597295
22	6	0	-3.935534	0.353439	-0.526701
23	6	0	-3.343584	-0.866342	2.421113
24	1	0	-2.132202	1.919999	0.581095
25	1	0	-1.202655	4.217269	0.503043
26	1	0	1.244388	4.514103	0.032875
27	1	0	2.659349	2.453125	-0.295465
28	1	0	1.246438	-3.455609	0.096384
29	1	0	4.706361	-1.338020	-0.522146
30	1	0	-1.249796	-2.875927	2.942263
31	1	0	-0.778904	-4.120773	1.786249
32	1	0	-2.432264	-4.055532	2.393865
33	1	0	-1.901016	-4.494279	-1.598351
34	1	0	-0.612083	-4.574075	-0.409587
35	1	0	-0.399435	-3.623617	-1.883329
36	1	0	-3.115463	-1.846249	-3.074273
37	1	0	-1.355979	-1.776446	-3.048509
38	1	0	-2.306598	-0.299257	-2.852007
39	1	0	-3.482907	1.012868	-1.269594
40	1	0	-4.217975	0.952205	0.339694
41	1	0	-4.865107	-0.023146	-0.966611
42	1	0	-4.129009	-1.534353	2.791274
43	1	0	-3.770835	0.134210	2.356940
44	1	0	-2.561032	-0.850862	3.183800

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 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -2283.75861106     A.U. after    2 cycles
Low frequencies ---   -0.0046   -0.0045   -0.0036    4.1803    7.8915   10.3792
Zero-point correction=                           0.359835 (Hartree/Particle)
 Thermal correction to Energy=                    0.382389
 Thermal correction to Enthalpy=                  0.383333
 Thermal correction to Gibbs Free Energy=         0.308818
 Sum of electronic and zero-point Energies=          -2283.398776
 Sum of electronic and thermal Energies=             -2283.376222
 Sum of electronic and thermal Enthalpies=           -2283.375278
 Sum of electronic and thermal Free Energies=        -2283.449793
```
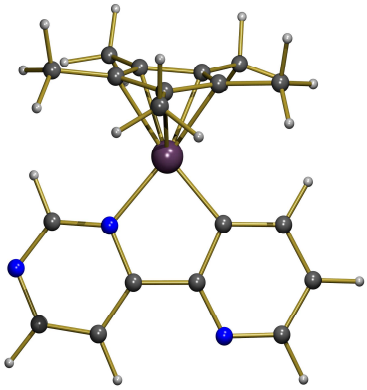

b3) Splitting of HCl from (**2b**$^{+}$); cyclometallation of the pyridine ring

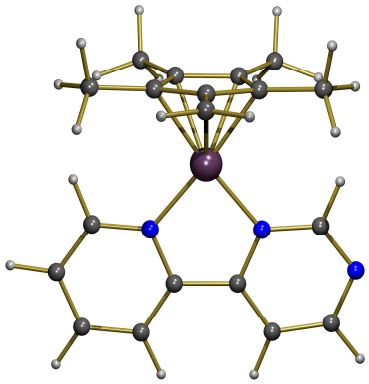


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.593424	0.808665	-0.372006
2	7	0	-0.927451	-3.010566	-0.341754
3	7	0	1.844979	-0.736964	-0.247569
4	7	0	3.969173	-1.787542	-0.143138
5	6	0	-2.245983	-2.916914	-0.514066
6	6	0	-2.900392	-1.694950	-0.683055
7	6	0	-2.156516	-0.516310	-0.638405
8	6	0	-0.773032	-0.568826	-0.435470
9	6	0	-0.236247	-1.868331	-0.316357
10	6	0	1.225495	-1.946446	-0.205384
11	6	0	1.973492	-3.112101	-0.107558
12	6	0	3.356470	-2.977541	-0.070592
13	6	0	3.187727	-0.724490	-0.230330
14	6	0	1.396026	2.699451	-0.971158
15	6	0	1.787658	2.462473	0.356743
16	6	0	0.587883	2.192310	1.122139
17	6	0	-0.558445	2.424252	0.273268
18	6	0	-0.066640	2.660394	-1.032640
19	6	0	2.274367	2.965666	-2.152081
20	6	0	3.168511	2.519992	0.933584
21	6	0	0.535985	1.895577	2.584744
22	6	0	-1.972308	2.505456	0.754898
23	6	0	-0.862714	2.919509	-2.271823
24	1	0	-2.798158	-3.851756	-0.527018
25	1	0	-3.972772	-1.672198	-0.844273
26	1	0	-2.672297	0.427252	-0.771029
27	1	0	1.475554	-4.072322	-0.072428
28	1	0	4.003667	-3.845477	0.011238
29	1	0	3.670324	0.241644	-0.296862
30	1	0	1.972521	2.382673	-3.025747
31	1	0	3.323102	2.749969	-1.949533
32	1	0	2.206977	4.020543	-2.440155
33	1	0	3.293489	3.462435	1.477483
34	1	0	3.945879	2.491584	0.169819
35	1	0	3.360586	1.718816	1.649433
36	1	0	0.517810	2.834497	3.151878
37	1	0	1.406942	1.333407	2.923887
38	1	0	-0.359329	1.335749	2.856223
39	1	0	-2.237487	1.685621	1.423286
40	1	0	-2.691509	2.528570	-0.062869
41	1	0	-2.101170	3.436462	1.317474
42	1	0	-0.853730	3.989971	-2.506085
43	1	0	-1.903399	2.615714	-2.165946
44	1	0	-0.449459	2.401079	-3.139765

SCF Done: E(RB3LYP) = -2283.75729728 A.U. after 2 cycles
Low frequencies --- -9.3932 -0.0019 -0.0018 0.0059 9.0193 10.4312
Zero-point correction= 0.359556 (Hartree/Particle)
Thermal correction to Energy= 0.382159
Thermal correction to Enthalpy= 0.383104
Thermal correction to Gibbs Free Energy= 0.308251
Sum of electronic and zero-point Energies= -2283.397741
Sum of electronic and thermal Energies= -2283.375138
Sum of electronic and thermal Enthalpies= -2283.374194
Sum of electronic and thermal Free Energies= -2283.449047

b4) Splitting of HCl from (**2b**$^{+}$); deprotonation of Cp*



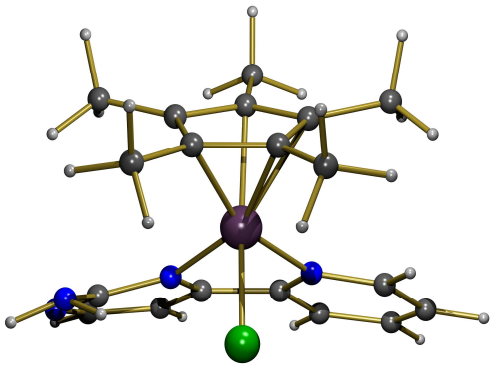
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.948426	0.496448	0.028484
2	7	0	-0.529373	-0.794126	0.063858
3	7	0	-0.531089	1.773984	0.065732
4	7	0	-1.490536	3.951862	0.109796
5	6	0	-0.434987	-2.134250	0.103271
6	6	0	-1.541774	-2.973149	0.094385
7	6	0	-2.813481	-2.411769	0.041541
8	6	0	-2.927145	-1.026919	0.008640
9	6	0	-1.774719	-0.245133	0.024956
10	6	0	-1.773078	1.221102	0.027790
11	6	0	-2.903995	2.031393	0.017459
12	6	0	-2.710375	3.406549	0.056743
13	6	0	-0.464806	3.117910	0.111299
14	6	0	2.612452	1.238729	1.060654
15	6	0	2.692512	1.678152	-0.275751
16	6	0	2.847733	0.507834	-1.147599
17	6	0	2.705921	-0.660972	-0.271208
18	6	0	2.621878	-0.217374	1.063638
19	6	0	2.614698	2.089023	2.294015
20	6	0	2.851218	3.084696	-0.770620
21	6	0	2.909791	0.506394	-2.503496
22	6	0	2.886310	-2.066673	-0.760635
23	6	0	2.635569	-1.061757	2.300825
24	1	0	0.563690	-2.541481	0.141308
25	1	0	-1.399172	-4.046467	0.127557
26	1	0	-3.698785	-3.036776	0.029959
27	1	0	-3.904445	-0.562708	-0.026251
28	1	0	-3.903455	1.618257	-0.015904
29	1	0	-3.550750	4.093452	0.050166
30	1	0	0.523973	3.550188	0.152527
31	1	0	1.967235	1.683252	3.073267
32	1	0	2.295812	3.112472	2.094325
33	1	0	3.626462	2.144110	2.711025
34	1	0	3.874440	3.231475	-1.131768
35	1	0	2.686806	3.828879	0.009312
36	1	0	2.186619	3.312637	-1.607965
37	1	0	2.948627	1.427534	-3.072106
38	1	0	2.959226	-0.415443	-3.070221
39	1	0	2.234713	-2.301691	-1.606215
40	1	0	2.720267	-2.810851	0.019368
41	1	0	3.915465	-2.204222	-1.108346

42	1	0	3.647763	-1.101750	2.718514
43	1	0	2.329804	-2.090282	2.105930
44	1	0	1.982556	-0.660540	3.077742

SCF Done: E(RB3LYP) = -2283.78110550 A.U. after 1 cycles
Low frequencies --- -7.4442 -2.4006 0.0044 0.0061 0.0067 5.7278
Zero-point correction= 0.360131 (Hartree/Particle)
Thermal correction to Energy= 0.382308
Thermal correction to Enthalpy= 0.383252
Thermal correction to Gibbs Free Energy= 0.309843
Sum of electronic and zero-point Energies= -2283.420975
Sum of electronic and thermal Energies= -2283.398797
Sum of electronic and thermal Enthalpies= -2283.397853
Sum of electronic and thermal Free Energies= -2283.471263

c1) [(2-(2-Aminopyrimidin-4-yl)pyridine)(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)-cobalt(III)]$^+$ (**2c$^+$**)



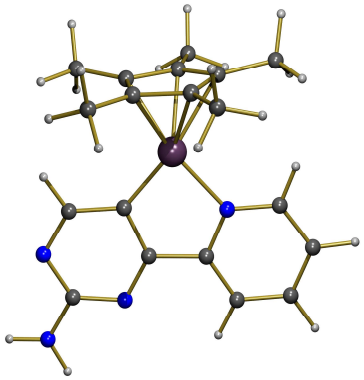
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.351772	-0.083643	0.457659
2	17	0	-0.506880	-1.753599	1.981039
3	7	0	-1.479759	-1.030844	-0.864219
4	7	0	1.058602	-1.047782	-0.550714
5	7	0	3.291610	-1.700123	-1.042305
6	7	0	2.669205	-1.168586	1.119698
7	6	0	-2.802164	-1.217424	-0.793650
8	6	0	-3.523195	-1.817061	-1.820501
9	6	0	-2.844688	-2.234591	-2.960346
10	6	0	-1.462459	-2.085263	-3.015206
11	6	0	-0.800781	-1.497348	-1.940270
12	6	0	0.664035	-1.470315	-1.777274
13	6	0	1.585354	-1.933586	-2.701145
14	6	0	2.921114	-1.964873	-2.283368
15	6	0	2.334721	-1.314845	-0.179661
16	6	0	-0.378162	1.868543	-0.319211
17	6	0	0.763881	1.756954	0.542796
18	6	0	0.307559	1.395263	1.840529
19	6	0	-1.143356	1.377710	1.813025
20	6	0	-1.557005	1.700194	0.497927
21	6	0	-0.359527	2.300075	-1.754100
22	6	0	2.178130	2.024791	0.137846
23	6	0	1.127744	1.233249	3.080960
24	6	0	-2.010112	1.157497	3.010229
25	6	0	-2.961482	1.932743	0.038652
26	1	0	1.924718	-1.311288	1.795821
27	1	0	3.583540	-1.517529	1.369586

28	1	0	-3.284681	-0.889491	0.116936
29	1	0	-4.592540	-1.954019	-1.716186
30	1	0	-3.377241	-2.696525	-3.783743
31	1	0	-0.906742	-2.449911	-3.869510
32	1	0	1.303604	-2.260491	-3.692162
33	1	0	3.712167	-2.248861	-2.971574
34	1	0	-1.227177	1.933877	-2.305133
35	1	0	0.536234	1.957299	-2.274397
36	1	0	-0.372072	3.393317	-1.826055
37	1	0	2.374824	3.099398	0.224509
38	1	0	2.374286	1.750680	-0.899739
39	1	0	2.896516	1.507237	0.770365
40	1	0	1.040730	2.130918	3.702987
41	1	0	2.185009	1.091506	2.859985
42	1	0	0.784178	0.387948	3.679634
43	1	0	-1.665162	0.308163	3.600163
44	1	0	-3.051203	0.977853	2.742208
45	1	0	-1.984798	2.045093	3.652265
46	1	0	-3.175152	3.006817	0.078006
47	1	0	-3.698288	1.441563	0.674473
48	1	0	-3.127361	1.616314	-0.991827

SCF Done: E(RB3LYP) = -2800.06709316 A.U. after 2 cycles Low frequencies --- -11.4248 -2.7889 -0.0054 -0.0051 0.0046 6.7255
Zero-point correction= 0.391007 (Hartree/Particle)
Thermal correction to Energy= 0.416533
Thermal correction to Enthalpy= 0.417477
Thermal correction to Gibbs Free Energy= 0.337470
Sum of electronic and zero-point Energies= -2799.676086
Sum of electronic and thermal Energies= -2799.650560
Sum of electronic and thermal Enthalpies= -2799.649616
Sum of electronic and thermal Free Energies= -2799.729623

c2) Splitting of HCl from (**2c**$^{+}$); cyclometallation of the pyrimidine ring



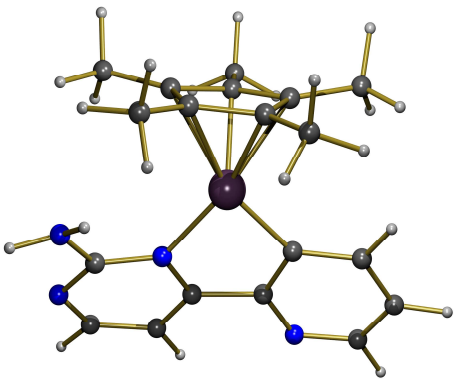
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.300563	1.218569	-0.259181
2	7	0	-1.494213	-0.208532	-1.035143
3	7	0	1.117255	-2.597738	-0.498763
4	7	0	2.996925	-1.398792	0.404193
5	7	0	3.090579	-3.664341	0.022386
6	6	0	-2.732197	-0.066170	-1.528665
7	6	0	-3.462435	-1.135069	-2.038682
8	6	0	-2.886690	-2.400913	-2.037963
9	6	0	-1.596308	-2.554907	-1.535648

10	6	0	-0.928271	-1.441759	-1.046478
11	6	0	0.449375	-1.453137	-0.514487
12	6	0	0.949448	-0.206594	-0.078799
13	6	0	2.281068	-0.283276	0.372105
14	6	0	2.380295	-2.522492	-0.024493
15	6	0	0.730590	3.005150	-0.311847
16	6	0	0.464646	2.647256	1.034495
17	6	0	-0.972078	2.542557	1.175455
18	6	0	-1.585260	2.950118	-0.055601
19	6	0	-0.548730	3.179642	-0.990442
20	6	0	2.062586	3.260423	-0.943899
21	6	0	1.438789	2.504412	2.163009
22	6	0	-1.687462	2.174731	2.434452
23	6	0	-3.056074	3.153870	-0.259217
24	6	0	-0.692647	3.576843	-2.425010
25	1	0	2.682673	-4.529606	-0.289690
26	1	0	4.037827	-3.648850	0.362779
27	1	0	-3.149166	0.930435	-1.514817
28	1	0	-4.459916	-0.966271	-2.425751
29	1	0	-3.430725	-3.254802	-2.426143
30	1	0	-1.092723	-3.512961	-1.517470
31	1	0	2.810413	0.597558	0.722412
32	1	0	2.127460	2.838884	-1.948613
33	1	0	2.884623	2.851326	-0.358377
34	1	0	2.229958	4.339482	-1.035638
35	1	0	1.309796	3.337884	2.861468
36	1	0	2.473281	2.530796	1.823702
37	1	0	1.291361	1.582664	2.727918
38	1	0	-1.886887	3.076502	3.026293
39	1	0	-1.096297	1.504003	3.058800
40	1	0	-2.649732	1.699170	2.239353
41	1	0	-3.659659	2.399431	0.248976
42	1	0	-3.336624	3.169228	-1.313278
43	1	0	-3.350778	4.123004	0.157108
44	1	0	-0.502037	4.650024	-2.539429
45	1	0	-1.692302	3.381089	-2.813143
46	1	0	0.024828	3.058158	-3.064238

SCF Done: E(RB3LYP) = -2339.15627217 A.U. after 2 cycles
Low frequencies --- -12.5078 -4.9314 0.0067 0.0070 0.0080 4.8361
Zero-point correction= 0.376397 (Hartree/Particle)
Thermal correction to Energy= 0.400651
Thermal correction to Enthalpy= 0.401595
Thermal correction to Gibbs Free Energy= 0.322687
Sum of electronic and zero-point Energies= -2338.779875
Sum of electronic and thermal Energies= -2338.755622
Sum of electronic and thermal Enthalpies= -2338.754677
Sum of electronic and thermal Free Energies= -2338.833585

c3) Splitting of HCl from (**2c**$^{+}$); cyclometallation of the pyridine ring



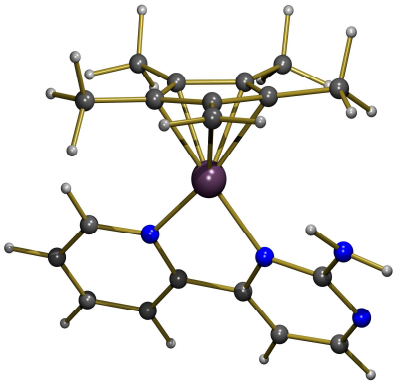
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.442973	0.963323	-0.370660
2	7	0	-1.432193	-2.622893	0.210017
3	7	0	1.558742	-0.647509	0.027094
4	7	0	3.511377	-1.828063	0.723628
5	7	0	3.717323	0.143641	-0.424857
6	6	0	-2.680220	-2.501147	-0.241100
7	6	0	-3.149649	-1.343565	-0.866317
8	6	0	-2.302020	-0.241560	-0.972490
9	6	0	-0.995708	-0.321003	-0.480482
10	6	0	-0.626687	-1.567400	0.061826
11	6	0	0.793761	-1.719486	0.401315
12	6	0	1.357645	-2.834947	0.986157
13	6	0	2.741899	-2.810285	1.172459
14	6	0	2.902960	-0.799340	0.115904
15	6	0	1.431985	2.864344	-0.724636
16	6	0	1.511272	2.563613	0.642807
17	6	0	0.158846	2.314443	1.113864
18	6	0	-0.759313	2.624388	0.044668
19	6	0	0.020754	2.867926	-1.110888
20	6	0	2.548973	3.201447	-1.664315
21	6	0	2.720399	2.532022	1.523076
22	6	0	-0.221227	1.990854	2.521975
23	6	0	-2.238996	2.777289	0.199972
24	6	0	-0.473935	3.181533	-2.487326
25	1	0	3.376304	0.704217	-1.187831
26	1	0	4.696374	-0.101515	-0.452034
27	1	0	-3.325531	-3.365017	-0.112545
28	1	0	-4.161962	-1.308703	-1.254383
29	1	0	-2.672434	0.658950	-1.448983
30	1	0	0.737069	-3.668996	1.282831
31	1	0	3.253510	-3.621645	1.682378
32	1	0	2.517121	2.606046	-2.582406
33	1	0	3.529307	3.078429	-1.204515
34	1	0	2.471667	4.247267	-1.979192
35	1	0	2.703531	3.401882	2.188781
36	1	0	3.650632	2.561061	0.960578
37	1	0	2.746521	1.645612	2.159568
38	1	0	-0.329568	2.917313	3.099248
39	1	0	0.535762	1.387159	3.024164
40	1	0	-1.172059	1.460428	2.576575
41	1	0	-2.683127	1.988913	0.807230
42	1	0	-2.759635	2.807086	-0.756334
43	1	0	-2.441548	3.729476	0.702535
44	1	0	-0.411017	4.259775	-2.673976
45	1	0	-1.512724	2.885454	-2.631315
46	1	0	0.123847	2.691184	-3.259064

SCF Done: E(RB3LYP) = -2339.14357082 A.U. after 2 cycles
Low frequencies --- -4.9349 0.0054 0.0059 0.0074 4.7265 7.4084
Zero-point correction= 0.376508 (Hartree/Particle)
Thermal correction to Energy= 0.400309
Thermal correction to Enthalpy= 0.401253
Thermal correction to Gibbs Free Energy= 0.324942
Sum of electronic and zero-point Energies= -2338.767063
Sum of electronic and thermal Energies= -2338.743262
Sum of electronic and thermal Enthalpies= -2338.742318

Sum of electronic and thermal Free Energies= -2338.818629

c4) Splitting of HCl from (**2c**$^{+}$); deprotonation of Cp*



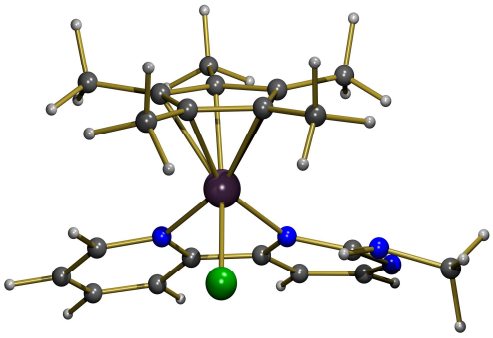
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.473116	-0.115917	-0.196412
2	7	0	-1.021402	-1.372573	-0.119921
3	7	0	-1.015946	1.174618	-0.445809
4	7	0	-2.023731	3.332235	-0.671305
5	7	0	0.044975	2.914617	-1.563909
6	6	0	-0.970743	-2.715544	-0.128122
7	6	0	-2.065091	-3.515540	0.172392
8	6	0	-3.269488	-2.907932	0.512899
9	6	0	-3.341192	-1.519794	0.503833
10	6	0	-2.211138	-0.777896	0.168223
11	6	0	-2.204043	0.683336	0.002269
12	6	0	-3.296792	1.509628	0.201557
13	6	0	-3.123376	2.862295	-0.107767
14	6	0	-1.020751	2.461805	-0.879172
15	6	0	1.944749	0.367117	1.227154
16	6	0	2.322410	1.030754	0.046392
17	6	0	2.612314	0.027923	-0.985670
18	6	0	2.222212	-1.263408	-0.397815
19	6	0	1.902231	-1.060247	0.962868
20	6	0	1.733863	0.998316	2.568231
21	6	0	2.710159	2.478877	-0.034758
22	6	0	3.004106	0.242168	-2.267711
23	6	0	2.411139	-2.567694	-1.113508
24	6	0	1.673162	-2.101355	2.016692
25	1	0	-0.020777	-3.155716	-0.392292
26	1	0	-1.965689	-4.593721	0.138496
27	1	0	-4.140307	-3.501277	0.766417
28	1	0	-4.271828	-1.021507	0.742241
29	1	0	-4.240844	1.145342	0.580774
30	1	0	-3.913546	3.583132	0.081775
31	1	0	0.998501	0.458194	3.166685
32	1	0	1.407232	2.035691	2.485263
33	1	0	2.672306	1.000366	3.135096
34	1	0	3.698307	2.612080	0.419955
35	1	0	2.016832	3.134680	0.491968
36	1	0	2.788457	2.838563	-1.060643
37	1	0	3.249914	1.231718	-2.634870
38	1	0	3.140442	-0.576232	-2.963865
39	1	0	1.844233	-2.615944	-2.047564
40	1	0	2.137326	-3.427559	-0.501404

41	1	0	3.465711	-2.697207	-1.376980
42	1	0	2.549563	-2.163747	2.670605
43	1	0	1.517836	-3.095861	1.599286
44	1	0	0.816701	-1.865689	2.651803
45	1	0	-0.010644	3.844151	-1.949784
46	1	0	0.702293	2.263620	-1.961674

SCF Done: E(RB3LYP) = -2339.16412647 A.U. after 2 cycles
Low frequencies --- -2.4207 0.0017 0.0049 0.0057 3.3490 7.1072
Zero-point correction= 0.376703 (Hartree/Particle)
Thermal correction to Energy= 0.400363
Thermal correction to Enthalpy= 0.401307
Thermal correction to Gibbs Free Energy= 0.325035
Sum of electronic and zero-point Energies= -2338.787423
Sum of electronic and thermal Energies= -2338.763764
Sum of electronic and thermal Enthalpies= -2338.762820
Sum of electronic and thermal Free Energies= -2338.839091

d1) [Chlorido(2-(2-methylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III)]$^+$ (**2d$^+$**)



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.171205	-0.550998	-0.192265
2	17	0	0.228376	-0.717101	-2.415292
3	7	0	-1.660773	0.725990	-0.437185
4	7	0	0.833144	1.153719	-0.057703
5	7	0	2.779846	2.485172	0.274277
6	7	0	2.916941	0.421460	-0.769347
7	6	0	-2.875795	0.450241	-0.923925
8	6	0	-3.888278	1.401953	-0.974037
9	6	0	-3.627299	2.683256	-0.500471
10	6	0	-2.350488	2.984500	-0.037155
11	6	0	-1.377283	1.988531	-0.035555
12	6	0	0.054323	2.221770	0.230518
13	6	0	0.609666	3.427494	0.629078
14	6	0	2.006532	3.470343	0.697663
15	6	0	2.174771	1.369720	-0.177828
16	6	0	4.339816	0.605198	-1.049289
17	6	0	-0.523957	-1.175608	1.784307
18	6	0	0.852397	-1.441631	1.480513
19	6	0	0.899119	-2.309203	0.353507
20	6	0	-0.464449	-2.668295	0.012188
21	6	0	-1.328511	-1.996330	0.909124
22	6	0	-1.034442	-0.366151	2.937255
23	6	0	2.020801	-0.917727	2.252599
24	6	0	2.110702	-2.915125	-0.281373

25	6	0	-0.842017	-3.659150	-1.040768
26	6	0	-2.809246	-2.177735	1.020471
27	1	0	2.393763	-0.217368	-1.360599
28	1	0	-3.027859	-0.554373	-1.294327
29	1	0	-4.855195	1.135692	-1.383044
30	1	0	-4.396617	3.446745	-0.516740
31	1	0	-2.109459	3.987998	0.289036
32	1	0	0.010535	4.290526	0.882776
33	1	0	2.515972	4.349729	1.082126
34	1	0	4.511626	1.418259	-1.758731
35	1	0	4.722593	-0.322611	-1.472069
36	1	0	4.881466	0.829983	-0.131599
37	1	0	-2.009125	0.077733	2.727634
38	1	0	-0.351379	0.440308	3.208135
39	1	0	-1.153738	-0.996676	3.825356
40	1	0	2.195590	-1.565182	3.119122
41	1	0	1.848515	0.088263	2.637854
42	1	0	2.936004	-0.905241	1.663711
43	1	0	2.219552	-3.956018	0.042296
44	1	0	3.026004	-2.392736	-0.004836
45	1	0	2.030791	-2.920532	-1.369945
46	1	0	-0.273519	-3.503096	-1.957600
47	1	0	-1.901216	-3.613318	-1.293645
48	1	0	-0.633236	-4.673928	-0.683549
49	1	0	-3.018080	-2.934911	1.784724
50	1	0	-3.259940	-2.534124	0.094031
51	1	0	-3.325184	-1.268116	1.329766

```
SCF Done:  E(RB3LYP) =  -2839.38311319     A.U. after    1 cycles
Low frequencies ---   -10.9725   -6.4596   -4.6163   -0.0054   -0.0054   -0.0037
Zero-point correction=                           0.418899 (Hartree/Particle)
 Thermal correction to Energy=                    0.446142
 Thermal correction to Enthalpy=                  0.447086
 Thermal correction to Gibbs Free Energy=         0.363181
 Sum of electronic and zero-point Energies=          -2838.964215
 Sum of electronic and thermal Energies=             -2838.936971
 Sum of electronic and thermal Enthalpies=           -2838.936027
 Sum of electronic and thermal Free Energies=        -2839.019932
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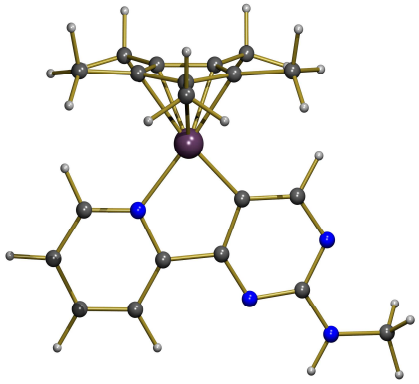
d2) Splitting of HCl from (**2d**$^{+}$); cyclometallation of the pyrimidine ring



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.645763	1.216797	-0.232050
2	7	0	-1.809102	-0.191990	-1.080286
3	7	0	0.785857	-2.586032	-0.516838

4	7	0	2.641935	-1.402552	0.461735
5	7	0	2.735136	-3.670579	0.031104
6	6	0	-3.031507	-0.038743	-1.609036
7	6	0	-3.744465	-1.095790	-2.165326
8	6	0	-3.168437	-2.361773	-2.175008
9	6	0	-1.894571	-2.526754	-1.636082
10	6	0	-1.242826	-1.424407	-1.101986
11	6	0	0.118593	-1.446160	-0.529259
12	6	0	0.603673	-0.203207	-0.053847
13	6	0	1.922056	-0.287615	0.430197
14	6	0	2.041642	-2.520222	-0.004076
15	6	0	4.094427	-3.796934	0.536834
16	6	0	0.354588	3.017187	-0.318845
17	6	0	0.127154	2.663393	1.036841
18	6	0	-1.302316	2.540695	1.213554
19	6	0	-1.951456	2.929043	-0.005159
20	6	0	-0.942040	3.171002	-0.966817
21	6	0	1.668426	3.284141	-0.982819
22	6	0	1.131459	2.559506	2.143199
23	6	0	-1.984769	2.172207	2.490789
24	6	0	-3.431324	3.099289	-0.170614
25	6	0	-1.125770	3.567153	-2.397801
26	1	0	2.257975	-4.483135	-0.327884
27	1	0	-3.449836	0.957201	-1.585979
28	1	0	-4.729382	-0.918208	-2.579755
29	1	0	-3.699676	-3.206490	-2.599272
30	1	0	-1.390886	-3.484865	-1.623358
31	1	0	2.439041	0.587703	0.811702
32	1	0	4.398344	-4.838107	0.441289
33	1	0	4.150352	-3.503767	1.586662
34	1	0	4.783467	-3.170011	-0.031960
35	1	0	1.703525	2.883053	-1.997275
36	1	0	2.506470	2.861933	-0.429607
37	1	0	1.834605	4.364856	-1.057882
38	1	0	1.022512	3.419510	2.812523
39	1	0	2.156659	2.572017	1.775734
40	1	0	0.999291	1.661147	2.748263
41	1	0	-2.174262	3.074208	3.085488
42	1	0	-1.375503	1.505539	3.101937
43	1	0	-2.949124	1.691523	2.320084
44	1	0	-4.003624	2.296780	0.299396
45	1	0	-3.731266	3.168434	-1.217009
46	1	0	-3.748089	4.031897	0.308018
47	1	0	-0.932270	4.638875	-2.519602
48	1	0	-2.137579	3.377286	-2.756161
49	1	0	-0.431344	3.042963	-3.057756

SCF Done: E(RB3LYP) = -2378.47327110 A.U. after 2 cycles

Low frequencies --- -7.4926 0.0013 0.0029 0.0048 2.5274 9.6481

Zero-point correction= 0.404745 (Hartree/Particle)

Thermal correction to Energy= 0.430532

Thermal correction to Enthalpy= 0.431477

Thermal correction to Gibbs Free Energy= 0.349022

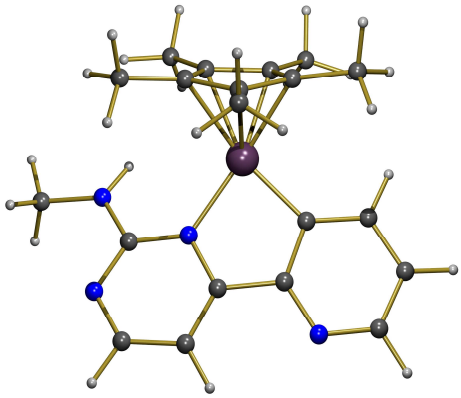
Sum of electronic and zero-point Energies= -2378.068526

Sum of electronic and thermal Energies= -2378.042739

Sum of electronic and thermal Enthalpies= -2378.041795

Sum of electronic and thermal Free Energies= -2378.124249

d3) Splitting of HCl from (**2d**$^{+}$); cyclometallation of the pyridine ring



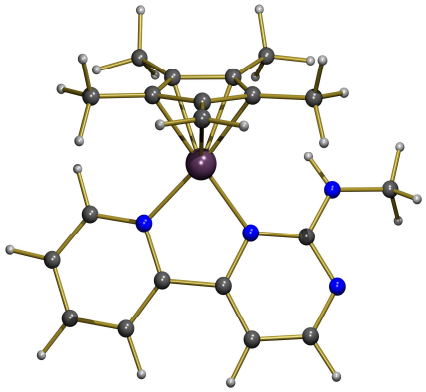
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.320628	0.271325	0.067960
2	7	0	2.757970	-2.178819	-1.035027
3	7	0	-0.139305	-1.498161	0.970377
4	7	0	-0.484563	-3.107404	2.705698
5	7	0	-2.178658	-1.684296	2.095343
6	6	0	3.245991	-1.716728	-2.186075
7	6	0	2.685448	-0.632973	-2.865550
8	6	0	1.606705	0.039258	-2.291990
9	6	0	1.089262	-0.396985	-1.068864
10	6	0	1.699747	-1.543265	-0.524712
11	6	0	1.039168	-2.115472	0.655984
12	6	0	1.501726	-3.199630	1.373964
13	6	0	0.708221	-3.621966	2.443279
14	6	0	-0.909518	-2.101703	1.922197
15	6	0	-3.099356	-2.305378	3.044566
16	6	0	0.209819	1.924849	1.116271
17	6	0	-1.096923	1.563540	1.638100
18	6	0	-1.994587	1.564832	0.560593
19	6	0	-1.271098	1.988600	-0.638508
20	6	0	0.058819	2.301300	-0.268269
21	6	0	1.452129	2.074895	1.932587
22	6	0	-1.369785	1.289769	3.084125
23	6	0	-3.461662	1.259909	0.575517
24	6	0	-1.901356	2.157076	-1.984996
25	6	0	1.098816	3.001006	-1.084497
26	1	0	-2.555893	-1.067453	1.395939
27	1	0	4.107659	-2.240691	-2.588921
28	1	0	3.093454	-0.321075	-3.820977
29	1	0	1.180707	0.886655	-2.817029
30	1	0	2.440110	-3.668372	1.112718
31	1	0	1.038813	-4.418771	3.103984
32	1	0	-3.308276	-3.344112	2.781119
33	1	0	-4.031229	-1.740881	3.032651
34	1	0	-2.681916	-2.283648	4.050452
35	1	0	2.354022	1.955612	1.332002
36	1	0	1.491734	1.358372	2.754108
37	1	0	1.485763	3.077349	2.376820
38	1	0	-1.227751	2.209720	3.660875
39	1	0	-0.689499	0.544543	3.501028
40	1	0	-2.387487	0.946867	3.260808
41	1	0	-4.034916	2.159850	0.330326

42	1	0	-3.807238	0.921257	1.552593
43	1	0	-3.740729	0.509470	-0.170853
44	1	0	-2.585754	1.339359	-2.221970
45	1	0	-1.162144	2.215142	-2.783587
46	1	0	-2.488180	3.082380	-2.014070
47	1	0	1.164828	4.042008	-0.749740
48	1	0	0.852983	3.024380	-2.145335
49	1	0	2.089557	2.560459	-0.973017

SCF Done: E(RB3LYP) = -2378.45947384 A.U. after 2 cycles
Low frequencies --- -5.1788 -0.0021 0.0019 0.0062 4.9116 9.5585
Zero-point correction= 0.404397 (Hartree/Particle)
Thermal correction to Energy= 0.429986
Thermal correction to Enthalpy= 0.430930
Thermal correction to Gibbs Free Energy= 0.350500
Sum of electronic and zero-point Energies= -2378.055077
Sum of electronic and thermal Energies= -2378.029488
Sum of electronic and thermal Enthalpies= -2378.028543
Sum of electronic and thermal Free Energies= -2378.108974

d4) Splitting of HCl from (**2d**$^{+}$); deprotonation of Cp*



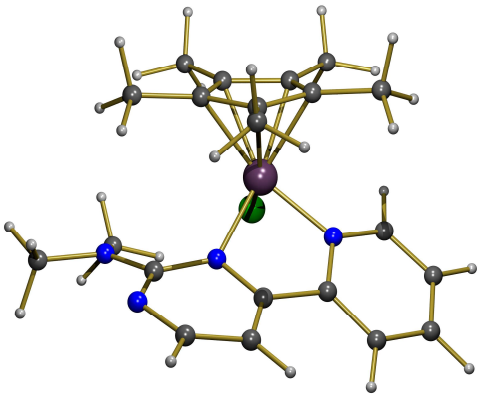
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.766005	-0.482306	-0.037880
2	7	0	-0.723302	-1.732704	-0.187007
3	7	0	-0.687150	0.834493	-0.382787
4	7	0	-1.559713	2.979821	-1.002631
5	7	0	0.131372	2.805547	0.541386
6	6	0	-0.746775	-3.033405	0.146461
7	6	0	-1.806779	-3.872917	-0.168694
8	6	0	-2.888489	-3.352938	-0.872677
9	6	0	-2.884618	-2.002542	-1.203671
10	6	0	-1.798518	-1.212775	-0.834672
11	6	0	-1.740853	0.248137	-1.010535
12	6	0	-2.684517	0.992420	-1.701126
13	6	0	-2.500447	2.376724	-1.710191
14	6	0	-0.718542	2.198252	-0.301104
15	6	0	2.512756	0.167230	0.948043
16	6	0	2.616127	0.551703	-0.401361
17	6	0	2.688191	-0.659185	-1.231556
18	6	0	2.414230	-1.774440	-0.316577
19	6	0	2.373156	-1.281688	1.003510
20	6	0	2.660881	1.031150	2.165960
21	6	0	2.871367	1.919536	-0.957064
22	6	0	2.829284	-0.719513	-2.577282

23	6	0	2.440504	-3.206118	-0.760803
24	6	0	2.331636	-2.071510	2.276544
25	6	0	0.166327	4.250175	0.744677
26	1	0	0.112590	-3.403726	0.685881
27	1	0	-1.776259	-4.912497	0.134091
28	1	0	-3.727968	-3.981938	-1.145539
29	1	0	-3.726557	-1.566956	-1.725617
30	1	0	-3.509116	0.537710	-2.231358
31	1	0	-3.152009	3.021487	-2.293431
32	1	0	1.858052	0.876701	2.892050
33	1	0	2.713670	2.093408	1.922633
34	1	0	3.596132	0.788135	2.681533
35	1	0	3.891475	1.969978	-1.351891
36	1	0	2.773735	2.706643	-0.211779
37	1	0	2.196865	2.158661	-1.782851
38	1	0	2.972599	0.172511	-3.174938
39	1	0	2.831910	-1.664328	-3.107397
40	1	0	1.720724	-3.408036	-1.558200
41	1	0	2.251116	-3.905761	0.053392
42	1	0	3.431786	-3.447019	-1.158421
43	1	0	3.329942	-2.118029	2.726094
44	1	0	2.010021	-3.101680	2.118647
45	1	0	1.665805	-1.623127	3.016893
46	1	0	-0.778049	4.620337	1.148290
47	1	0	0.365149	4.767057	-0.194174
48	1	0	0.965297	4.474320	1.450528
49	1	0	0.652958	2.209999	1.162603

```
SCF Done:  E(RB3LYP) =  -2378.48192938     A.U. after    2 cycles
Low frequencies ---   -0.0061   -0.0044   -0.0018    4.2113    7.4212   14.0559
Zero-point correction=                           0.405197 (Hartree/Particle)
 Thermal correction to Energy=                    0.430344
 Thermal correction to Enthalpy=                  0.431288
 Thermal correction to Gibbs Free Energy=         0.352180
 Sum of electronic and zero-point Energies=          -2378.076732
 Sum of electronic and thermal Energies=             -2378.051586
 Sum of electronic and thermal Enthalpies=           -2378.050641
 Sum of electronic and thermal Free Energies=        -2378.129749
```

e1) [Chlorido(2-(2-dimethylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)cobalt(III)]$^+$ (**2e$^+$**)



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.376025	-0.537431	-0.162239

2	17	0	-0.680384	-0.959562	-2.367395
3	7	0	-1.636238	0.950491	-0.362535
4	7	0	0.987259	1.041215	-0.257138
5	7	0	3.014249	2.004943	0.563010
6	7	0	3.125375	0.220623	-0.873555
7	6	0	-2.916735	0.834554	-0.739460
8	6	0	-3.745707	1.939152	-0.882776
9	6	0	-3.222402	3.206281	-0.643749
10	6	0	-1.884604	3.327450	-0.286062
11	6	0	-1.110149	2.175224	-0.158945
12	6	0	0.340439	2.181949	0.106657
13	6	0	0.990266	3.249787	0.700122
14	6	0	2.341608	3.047738	1.001080
15	6	0	2.358980	1.090820	-0.193070
16	6	0	2.669053	-0.491711	-2.064932
17	6	0	4.577424	0.210955	-0.663764
18	6	0	-0.069901	-0.984504	1.889240
19	6	0	0.796878	-1.845208	1.108613
20	6	0	-0.009895	-2.623380	0.249348
21	6	0	-1.393334	-2.260308	0.485684
22	6	0	-1.416658	-1.307435	1.552469
23	6	0	0.372987	-0.075644	2.994790
24	6	0	2.270750	-1.993437	1.317984
25	6	0	0.434063	-3.702069	-0.683117
26	6	0	-2.564239	-2.937451	-0.155083
27	6	0	-2.634783	-0.754899	2.221770
28	1	0	-3.263587	-0.166496	-0.955753
29	1	0	-4.773907	1.801236	-1.193908
30	1	0	-3.839662	4.090117	-0.757620
31	1	0	-1.440415	4.303824	-0.142066
32	1	0	0.472180	4.147529	1.006110
33	1	0	2.890946	3.756265	1.615543
34	1	0	1.660207	-0.204316	-2.334134
35	1	0	2.692115	-1.573475	-1.911645
36	1	0	3.343240	-0.251086	-2.891402
37	1	0	5.068007	0.983168	-1.263512
38	1	0	4.955600	-0.764553	-0.970816
39	1	0	4.820236	0.382904	0.380712
40	1	0	-0.352853	0.713828	3.193388
41	1	0	1.332207	0.397216	2.779976
42	1	0	0.495390	-0.641513	3.925080
43	1	0	2.442545	-2.747913	2.094433
44	1	0	2.741176	-1.072617	1.660293
45	1	0	2.790261	-2.331132	0.422360
46	1	0	0.181669	-4.680044	-0.257820
47	1	0	1.510819	-3.687080	-0.849448
48	1	0	-0.060766	-3.620753	-1.651235
49	1	0	-2.445818	-2.994756	-1.238003
50	1	0	-3.506452	-2.432113	0.060395
51	1	0	-2.658508	-3.961099	0.223453
52	1	0	-2.853618	-1.350222	3.115234
53	1	0	-3.519828	-0.798480	1.587645
54	1	0	-2.500730	0.276657	2.549665

SCF Done: E(RB3LYP) = -2878.68151227 A.U. after 2 cycles

Low frequencies --- -5.5703 -0.0066 -0.0064 -0.0040 6.0268 7.7136

Zero-point correction= 0.446672 (Hartree/Particle)

Thermal correction to Energy= 0.475431

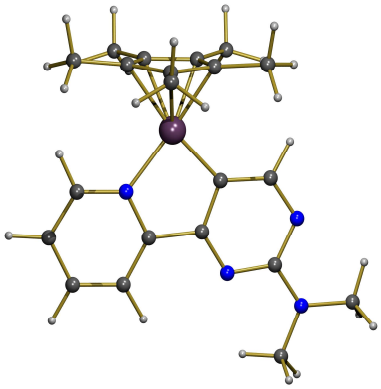
Thermal correction to Enthalpy= 0.476376

Thermal correction to Gibbs Free Energy= 0.389550

Sum of electronic and zero-point Energies= -2878.234841

```
Sum of electronic and thermal Energies=             -2878.206081
Sum of electronic and thermal Enthalpies=           -2878.205137
Sum of electronic and thermal Free Energies=        -2878.291962
```

e2) Splitting of HCl from (**2e**$^{+}$); cyclometallation of the pyrimidine ring



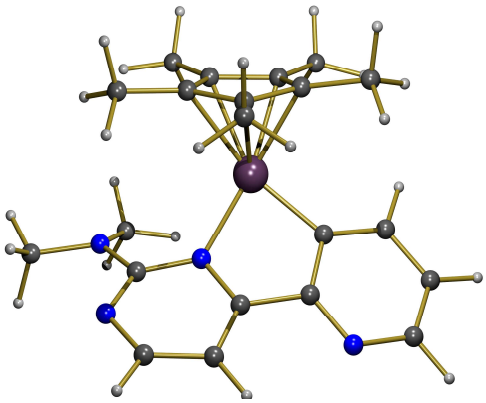
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-1.095024	-0.173628	0.025118
2	7	0	-0.497991	1.753206	0.027009
3	7	0	2.897354	0.629353	-0.000005
4	7	0	2.845623	-1.772348	0.067147
5	7	0	4.856368	-0.612053	0.034328
6	6	0	-1.263530	2.852725	0.056450
7	6	0	-0.730212	4.138071	0.045926
8	6	0	0.651159	4.289918	0.003511
9	6	0	1.453431	3.151146	-0.018395
10	6	0	0.850197	1.901974	-0.002014
11	6	0	1.575482	0.613984	0.003834
12	6	0	0.762853	-0.542505	0.025782
13	6	0	1.524475	-1.728467	0.061585
14	6	0	3.505997	-0.585437	0.030650
15	6	0	5.651069	0.609553	-0.038092
16	6	0	5.610081	-1.861569	-0.020872
17	6	0	-2.078576	-1.802873	0.824134
18	6	0	-1.929810	-1.971461	-0.576963
19	6	0	-2.602474	-0.862114	-1.219055
20	6	0	-3.247169	-0.073905	-0.212887
21	6	0	-2.883657	-0.610202	1.047360
22	6	0	-1.596979	-2.711897	1.910917
23	6	0	-1.314564	-3.125446	-1.307059
24	6	0	-2.689165	-0.650484	-2.696256
25	6	0	-4.192559	1.059528	-0.474980
26	6	0	-3.285874	-0.105110	2.396811
27	1	0	-2.332512	2.700156	0.089300
28	1	0	-1.394191	4.993574	0.070714
29	1	0	1.097936	5.277858	-0.008594
30	1	0	2.533996	3.206420	-0.044743
31	1	0	1.044766	-2.702535	0.091768
32	1	0	5.080600	1.455025	0.331816
33	1	0	5.958818	0.812918	-1.069728
34	1	0	6.548154	0.481858	0.570018
35	1	0	6.311084	-1.904412	0.816873
36	1	0	6.182545	-1.910256	-0.952675
37	1	0	4.932932	-2.706557	0.030224
38	1	0	-1.193799	-2.157911	2.760420

39	1	0	-0.825566	-3.399649	1.566809
40	1	0	-2.430520	-3.316236	2.286260
41	1	0	-2.104948	-3.725105	-1.771048
42	1	0	-0.759840	-3.788469	-0.644410
43	1	0	-0.641908	-2.805242	-2.104371
44	1	0	-3.538734	-1.211588	-3.104195
45	1	0	-1.794720	-1.002405	-3.211941
46	1	0	-2.841169	0.397834	-2.956393
47	1	0	-3.886610	1.678123	-1.320940
48	1	0	-4.324402	1.705074	0.394373
49	1	0	-5.182186	0.660222	-0.721089
50	1	0	-4.111666	-0.707230	2.792888
51	1	0	-3.623929	0.931027	2.370785
52	1	0	-2.469017	-0.174218	3.118013

SCF Done: E(RB3LYP) = -2417.78749338 A.U. after 2 cycles
Low frequencies --- -0.0048 -0.0040 -0.0029 1.4835 9.1370 10.9695
Zero-point correction= 0.432586 (Hartree/Particle)
Thermal correction to Energy= 0.459942
Thermal correction to Enthalpy= 0.460886
Thermal correction to Gibbs Free Energy= 0.374176
Sum of electronic and zero-point Energies= -2417.354908
Sum of electronic and thermal Energies= -2417.327551
Sum of electronic and thermal Enthalpies= -2417.326607
Sum of electronic and thermal Free Energies= -2417.413317

e3) Splitting of HCl from (**2e**$^{+}$); cyclometallation of the pyridine ring



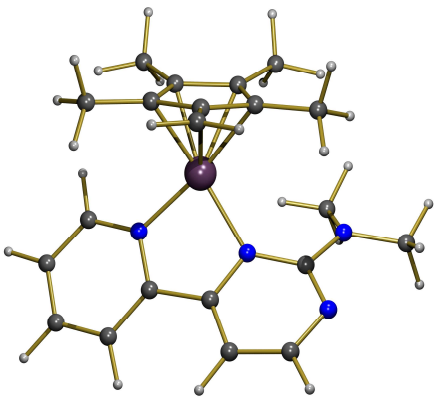
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	-0.308416	-0.541044	-0.237836
2	7	0	-2.185003	3.073943	-0.187886
3	7	0	0.812376	1.112310	-0.219910
4	7	0	2.748300	2.278402	0.518037
5	7	0	2.977041	0.441331	-0.863443
6	6	0	-3.431895	2.886287	-0.621958
7	6	0	-3.899415	1.652258	-1.081161
8	6	0	-3.051535	0.545660	-1.030996
9	6	0	-1.744531	0.703672	-0.564360
10	6	0	-1.376375	2.010945	-0.197706
11	6	0	0.046716	2.194802	0.120774
12	6	0	0.603245	3.320388	0.693664
13	6	0	1.973646	3.255816	0.964057
14	6	0	2.165369	1.285347	-0.176724
15	6	0	4.430673	0.575387	-0.725465
16	6	0	2.546563	-0.195408	-2.106209

17	6	0	0.857046	-1.905046	1.004501
18	6	0	0.437189	-2.603029	-0.136591
19	6	0	-1.018381	-2.513806	-0.229634
20	6	0	-1.489878	-1.818090	0.909089
21	6	0	-0.327226	-1.336599	1.623269
22	6	0	2.245610	-1.784944	1.550804
23	6	0	1.274402	-3.386501	-1.096269
24	6	0	-1.838352	-3.192071	-1.283263
25	6	0	-2.903444	-1.674102	1.374939
26	6	0	-0.354548	-0.558453	2.898918
27	1	0	-4.080674	3.757093	-0.612916
28	1	0	-4.912830	1.562675	-1.457527
29	1	0	-3.420380	-0.418043	-1.367401
30	1	0	-0.014926	4.165661	0.962186
31	1	0	2.468194	4.031260	1.542769
32	1	0	4.696713	0.784199	0.306424
33	1	0	4.819070	1.384024	-1.352627
34	1	0	4.891264	-0.363305	-1.036937
35	1	0	2.758519	-1.264889	-2.092833
36	1	0	3.087680	0.247914	-2.948947
37	1	0	1.481825	-0.044156	-2.270322
38	1	0	2.453730	-0.784569	1.933293
39	1	0	3.005901	-2.021528	0.807863
40	1	0	2.374958	-2.479761	2.387641
41	1	0	1.059177	-4.454537	-0.981388
42	1	0	2.341722	-3.252764	-0.925923
43	1	0	1.056186	-3.137971	-2.138074
44	1	0	-1.874228	-4.271601	-1.099101
45	1	0	-1.420950	-3.053767	-2.283219
46	1	0	-2.867390	-2.833985	-1.298849
47	1	0	-3.626845	-1.842147	0.578768
48	1	0	-3.102933	-0.695166	1.810229
49	1	0	-3.095783	-2.423641	2.150912
50	1	0	-0.425888	-1.245580	3.750764
51	1	0	-1.213106	0.111585	2.951346
52	1	0	0.549967	0.034204	3.039795

SCF Done: E(RB3LYP) = -2417.76667078 A.U. after 2 cycles
Low frequencies --- -8.5399 0.0034 0.0041 0.0067 0.7437 7.9376
Zero-point correction= 0.432228 (Hartree/Particle)
Thermal correction to Energy= 0.459190
Thermal correction to Enthalpy= 0.460134
Thermal correction to Gibbs Free Energy= 0.376739
Sum of electronic and zero-point Energies= -2417.334443
Sum of electronic and thermal Energies= -2417.307481
Sum of electronic and thermal Enthalpies= -2417.306537
Sum of electronic and thermal Free Energies= -2417.389932

e4) Splitting of HCl from (**2e**$^{+}$); deprotonation of Cp*



Input orientation:

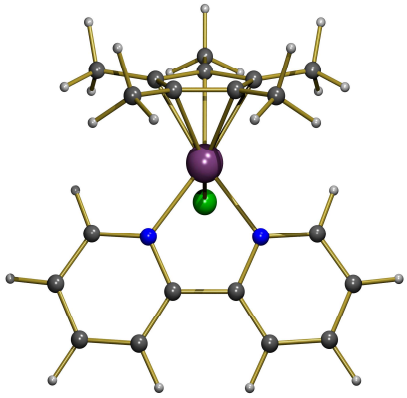
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	27	0	0.359828	-0.487611	-0.122984
2	7	0	1.678300	0.890836	-0.511728
3	7	0	-0.885408	1.097168	-0.205557
4	7	0	-2.857937	2.071813	0.713530
5	7	0	-3.032694	0.416716	-0.886652
6	6	0	2.931159	0.760621	-0.975196
7	6	0	3.817660	1.827634	-1.044787
8	6	0	3.399250	3.079272	-0.602415
9	6	0	2.098247	3.225928	-0.132192
10	6	0	1.257022	2.117051	-0.112509
11	6	0	-0.173118	2.167179	0.246009
12	6	0	-0.762158	3.183726	0.977239
13	6	0	-2.120932	3.017131	1.267568
14	6	0	-2.245676	1.202776	-0.116537
15	6	0	-0.281726	-2.488507	-0.375848
16	6	0	-0.780971	-2.028154	0.854096
17	6	0	0.351864	-1.778959	1.760155
18	6	0	1.545423	-1.862052	0.905088
19	6	0	1.167845	-2.370561	-0.358346
20	6	0	-1.048849	-3.129575	-1.490288
21	6	0	-2.207650	-2.030243	1.309622
22	6	0	0.301220	-1.422702	3.064417
23	6	0	2.934446	-1.662086	1.429934
24	6	0	2.063301	-2.861538	-1.455925
25	6	0	-4.488792	0.494269	-0.735595
26	6	0	-2.578467	-0.075368	-2.186704
27	1	0	3.219424	-0.228799	-1.302480
28	1	0	4.814766	1.672626	-1.438609
29	1	0	4.068475	3.931281	-0.637134
30	1	0	1.735325	4.193971	0.189049
31	1	0	-0.200116	4.018035	1.373088
32	1	0	-2.630693	3.685296	1.956378
33	1	0	-0.754849	-2.753729	-2.472708
34	1	0	-2.124612	-3.001800	-1.379887
35	1	0	-0.853611	-4.207895	-1.492155
36	1	0	-2.406775	-2.922415	1.913491
37	1	0	-2.910469	-2.032291	0.477465
38	1	0	-2.436082	-1.164324	1.935071
39	1	0	-0.639356	-1.338349	3.595359
40	1	0	1.200871	-1.237209	3.638915
41	1	0	3.035110	-0.719054	1.972543
42	1	0	3.691082	-1.681291	0.645885
43	1	0	3.183359	-2.463903	2.133293
44	1	0	2.072584	-3.957070	-1.473719
45	1	0	3.098380	-2.544231	-1.323045
46	1	0	1.729779	-2.529614	-2.441930
47	1	0	-4.900843	1.361082	-1.262308
48	1	0	-4.758851	0.569933	0.313485
49	1	0	-4.924055	-0.412089	-1.157933
50	1	0	-1.494981	-0.120584	-2.225852
51	1	0	-2.937180	0.588307	-2.982117
52	1	0	-2.982453	-1.071170	-2.367462

SCF Done: E(RB3LYP) = -2417.78757383 A.U. after 2 cycles

```
Low frequencies ---   -7.6504   -0.0017   -0.0005    0.0014    2.8561    6.6669
Zero-point correction=                           0.432752 (Hartree/Particle)
 Thermal correction to Energy=                    0.459408
 Thermal correction to Enthalpy=                  0.460352
 Thermal correction to Gibbs Free Energy=         0.377795
 Sum of electronic and zero-point Energies=          -2417.354822
 Sum of electronic and thermal Energies=             -2417.328166
 Sum of electronic and thermal Enthalpies=           -2417.327221
 Sum of electronic and thermal Free Energies=        -2417.409779
```

3.2 Rhodium complexes

a1) [2,2'-Bipyridine(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III)]$^+$ (**3a**$^+$)



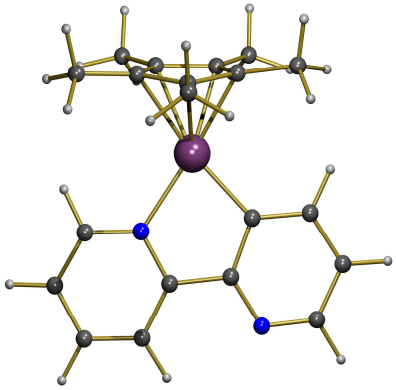
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.556845	-0.169018	0.860111
2	17	0	1.407783	-2.223037	1.744996
3	7	0	-1.121519	-1.322879	0.227566
4	7	0	1.153516	-0.927214	-1.041847
5	6	0	2.742514	-1.293361	-2.793431
6	6	0	-2.207847	-1.541797	0.980215
7	6	0	-3.263079	-2.338483	0.558125
8	6	0	-3.182316	-2.940714	-0.693092
9	6	0	-2.045340	-2.738008	-1.464164
10	6	0	-1.017008	-1.928295	-0.978542
11	6	0	0.255826	-1.706763	-1.688910
12	6	0	0.566265	-2.283088	-2.921933
13	6	0	1.818113	-2.070088	-3.483992
14	6	0	2.369370	-0.745555	-1.573959
15	6	0	0.847498	2.011337	0.580427
16	6	0	1.918401	1.462232	1.396077
17	6	0	1.334457	0.961295	2.605993
18	6	0	-0.088428	1.113298	2.515812
19	6	0	-0.383618	1.797275	1.267325
20	6	0	1.034082	2.745628	-0.710385
21	6	0	3.389180	1.582154	1.135531
22	6	0	2.082004	0.407827	3.773042
23	6	0	-1.058134	0.809002	3.616964
24	6	0	-1.739176	2.263694	0.837091
25	1	0	3.064070	-0.157073	-0.990502
26	1	0	3.738677	-1.117420	-3.180507
27	1	0	-2.216090	-1.075321	1.955747
28	1	0	-4.119488	-2.484894	1.204848
29	1	0	-3.985132	-3.570556	-1.058764
30	1	0	-1.957976	-3.218446	-2.429494

31	1	0	-0.155135	-2.903917	-3.436205
32	1	0	2.071022	-2.515882	-4.439101
33	1	0	0.119972	2.776738	-1.303089
34	1	0	1.817148	2.301303	-1.327311
35	1	0	1.331760	3.780825	-0.510608
36	1	0	3.811384	2.399815	1.729455
37	1	0	3.606146	1.808813	0.090878
38	1	0	3.924902	0.671850	1.409969
39	1	0	2.324905	1.226591	4.461287
40	1	0	3.014961	-0.067336	3.473445
41	1	0	1.497510	-0.329689	4.321107
42	1	0	-0.856410	-0.159071	4.078588
43	1	0	-2.092288	0.817320	3.270249
44	1	0	-0.983844	1.566796	4.404241
45	1	0	-1.986773	3.204508	1.340804
46	1	0	-2.521793	1.547819	1.094471
47	1	0	-1.791915	2.443786	-0.236527

SCF Done: E(RB3LYP) = -1456.43120216 A.U. after 2 cycles
Low frequencies --- -10.3353 -0.0012 -0.0010 0.0007 4.6071 6.8147
Zero-point correction= 0.384785 (Hartree/Particle)
Thermal correction to Energy= 0.409688
Thermal correction to Enthalpy= 0.410632
Thermal correction to Gibbs Free Energy= 0.330784
Sum of electronic and zero-point Energies= -1456.046417
Sum of electronic and thermal Energies= -1456.021514
Sum of electronic and thermal Enthalpies= -1456.020570
Sum of electronic and thermal Free Energies= -1456.100418

a2) Splitting of HCl from (**3a**$^{+}$); cyclometallation of the pyridine ring

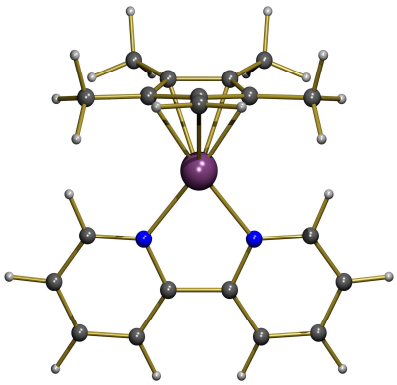


SCF Done: E(RB3LYP) = -995.528278910 A.U. after 2 cycles
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.838070	0.823120	0.252755
2	7	0	0.007229	-1.139257	0.161325
3	7	0	-3.318627	0.197062	-0.097216
4	6	0	-3.168511	2.589496	-0.055478
5	6	0	0.690282	-2.292517	0.249094
6	6	0	0.063994	-3.530367	0.220062
7	6	0	-1.324128	-3.572111	0.096684
8	6	0	-2.035848	-2.380799	0.012496
9	6	0	-1.344307	-1.173649	0.049103
10	6	0	-1.986974	0.152631	-0.009234
11	6	0	-1.138202	1.280835	0.050275
12	6	0	-1.778802	2.523592	0.029614

```
     13          6           0       -3.894384    1.399884   -0.124053
     14          6           0        2.163071    2.388647    1.001435
     15          6           0        1.853021    2.658227   -0.355348
     16          6           0        2.310281    1.512281   -1.123449
     17          6           0        3.070135    0.632637   -0.236932
     18          6           0        2.949520    1.139833    1.062075
     19          6           0        1.895082    3.269735    2.178634
     20          6           0        1.285278    3.916620   -0.932761
     21          6           0        2.227824    1.376575   -2.607279
     22          6           0        3.844433   -0.566338   -0.689180
     23          6           0        3.526886    0.581024    2.322532
     24          1           0       -3.684343    3.543508   -0.069913
     25          1           0        1.765512   -2.209905    0.343714
     26          1           0        0.654761   -4.435239    0.292668
     27          1           0       -1.844618   -4.523092    0.069495
     28          1           0       -3.114365   -2.354867   -0.076700
     29          1           0       -1.212149    3.446442    0.083706
     30          1           0       -4.977690    1.412115   -0.199257
     31          1           0        1.656211    2.692464    3.073314
     32          1           0        1.072518    3.960597    1.995226
     33          1           0        2.785333    3.867016    2.408193
     34          1           0        2.096368    4.522768   -1.350714
     35          1           0        0.787451    4.527546   -0.179996
     36          1           0        0.576413    3.722995   -1.738532
     37          1           0        3.115798    1.829422   -3.066132
     38          1           0        1.353727    1.884360   -3.014834
     39          1           0        2.196773    0.333145   -2.922979
     40          1           0        3.313901   -1.137420   -1.453518
     41          1           0        4.084911   -1.239424    0.134365
     42          1           0        4.795101   -0.251795   -1.132930
     43          1           0        4.376588    1.190763    2.649520
     44          1           0        3.886776   -0.439806    2.196793
     45          1           0        2.801699    0.585246    3.139353
 -------------------------------------------------------------------
Low frequencies ---   -7.7939   -0.0002    0.0006    0.0007    7.5296   11.7239
Zero-point correction=                           0.370808 (Hartree/Particle)
 Thermal correction to Energy=                    0.393690
 Thermal correction to Enthalpy=                  0.394634
 Thermal correction to Gibbs Free Energy=         0.318760
 Sum of electronic and zero-point Energies=           -995.157471
 Sum of electronic and thermal Energies=              -995.134589
 Sum of electronic and thermal Enthalpies=            -995.133645
 Sum of electronic and thermal Free Energies=         -995.209519
```

a3) Splitting of HCl from (**3a**$^{+}$); deprotonation of Cp*



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                          Input orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
```
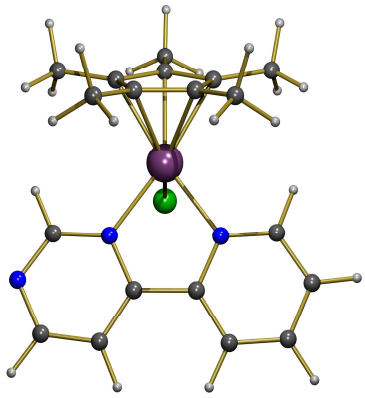

Number	Number	Type	X	Y	Z
1	45	0	-0.786195	-0.159437	0.187028
2	7	0	0.872746	1.132791	0.128845
3	6	0	3.169553	-1.629133	1.032501
4	6	0	1.776180	-3.563704	1.249809
5	6	0	0.825302	2.445124	-0.153602
6	6	0	1.951474	3.255520	-0.170026
7	6	0	3.186626	2.684913	0.120423
8	6	0	3.245583	1.328726	0.416429
9	6	0	2.075804	0.568304	0.416119
10	6	0	2.038718	-0.875388	0.716698
11	7	0	0.806501	-1.447666	0.665909
12	6	0	0.691544	-2.759675	0.929885
13	6	0	3.040832	-2.986136	1.301355
14	6	0	-2.707337	-1.224417	0.551589
15	6	0	-2.476031	-1.075536	-0.838439
16	6	0	-2.439190	0.354418	-1.135593
17	6	0	-2.648544	1.055647	0.077810
18	6	0	-3.039041	0.093488	1.125930
19	6	0	-2.923931	-2.507843	1.293230
20	6	0	-2.398538	-2.163203	-1.864670
21	6	0	-2.318865	0.938276	-2.509204
22	6	0	-2.794124	2.537229	0.244757
23	6	0	-3.491737	0.363214	2.367565
24	1	0	4.146445	-1.165691	1.070448
25	1	0	1.624668	-4.616771	1.453128
26	1	0	-0.154762	2.846910	-0.369987
27	1	0	1.854043	4.308340	-0.405228
28	1	0	4.090087	3.283795	0.118129
29	1	0	4.198820	0.871286	0.645830
30	1	0	-0.309268	-3.165638	0.881477
31	1	0	3.913600	-3.579898	1.547592
32	1	0	-2.438682	-2.497644	2.272192
33	1	0	-2.568814	-3.378676	0.740565
34	1	0	-3.994432	-2.660598	1.468692
35	1	0	-3.381335	-2.315533	-2.325369
36	1	0	-2.095801	-3.117249	-1.431960
37	1	0	-1.697811	-1.920822	-2.664826
38	1	0	-3.297937	0.944041	-3.001881
39	1	0	-1.640251	0.362374	-3.139936
40	1	0	-1.963838	1.969131	-2.489244
41	1	0	-2.402281	3.097300	-0.605348
42	1	0	-2.299959	2.893895	1.151688
43	1	0	-3.853961	2.799699	0.333918
44	1	0	-3.668146	1.378883	2.700849
45	1	0	-3.714712	-0.425646	3.075920

SCF Done: E(RB3LYP) = -995.548198416 A.U. after 2 cycles
Low frequencies --- -0.0006 0.0005 0.0009 2.1403 8.8802 10.1773
Zero-point correction= 0.371336 (Hartree/Particle)
Thermal correction to Energy= 0.393891
Thermal correction to Enthalpy= 0.394835
Thermal correction to Gibbs Free Energy= 0.320351
Sum of electronic and zero-point Energies= -995.176862
Sum of electronic and thermal Energies= -995.154308
Sum of electronic and thermal Enthalpies= -995.153364
Sum of electronic and thermal Free Energies= -995.227847

b1) [Chlorido(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)(2-pyrimidin-4-ylpyridine)rhodium(III)]$^+$ (**3b**$^+$)



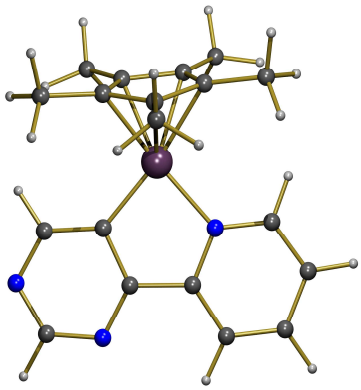
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.546294	-0.238099	0.833540
2	17	0	1.376266	-2.372670	1.529434
3	7	0	-1.144655	-1.339601	0.105341
4	7	0	1.127819	-0.842121	-1.129881
5	7	0	2.721189	-1.027188	-2.876258
6	6	0	-2.237026	-1.607388	0.830403
7	6	0	-3.279572	-2.392973	0.353472
8	6	0	-3.180133	-2.931029	-0.924411
9	6	0	-2.036684	-2.675187	-1.671791
10	6	0	-1.027043	-1.880285	-1.130483
11	6	0	0.244718	-1.599997	-1.819358
12	6	0	0.587496	-2.079858	-3.081549
13	6	0	1.844807	-1.754860	-3.574919
14	6	0	2.328125	-0.614606	-1.682695
15	6	0	0.865563	1.953864	0.743813
16	6	0	1.929328	1.318547	1.505515
17	6	0	1.338687	0.721324	2.668454
18	6	0	-0.082261	0.899160	2.592645
19	6	0	-0.368307	1.696082	1.410028
20	6	0	1.059700	2.801793	-0.473986
21	6	0	3.401546	1.437999	1.252477
22	6	0	2.077584	0.057736	3.781946
23	6	0	-1.055939	0.510272	3.662872
24	6	0	-1.715868	2.220849	1.024640
25	1	0	3.035642	-0.050447	-1.089093
26	1	0	-2.264142	-1.192399	1.828644
27	1	0	-4.141998	-2.579852	0.981645
28	1	0	-3.971901	-3.550214	-1.329899
29	1	0	-1.930936	-3.101883	-2.660581
30	1	0	-0.087216	-2.690954	-3.665740
31	1	0	2.166277	-2.092873	-4.555107
32	1	0	0.156077	2.867394	-1.079975
33	1	0	1.865210	2.433915	-1.111572
34	1	0	1.329666	3.821012	-0.176292
35	1	0	3.836746	2.189172	1.920260
36	1	0	3.621800	1.758422	0.233600
37	1	0	3.923047	0.497599	1.437696
38	1	0	2.303748	0.804375	4.552918
39	1	0	3.019029	-0.375479	3.447845
40	1	0	1.493382	-0.736565	4.244310
41	1	0	-0.861170	-0.494206	4.042129

42	1	0	-2.089660	0.555488	3.317596
43	1	0	-0.977156	1.199181	4.510694
44	1	0	-1.940683	3.125710	1.599942
45	1	0	-2.513001	1.504845	1.232408
46	1	0	-1.769395	2.483992	-0.031675

SCF Done: E(RB3LYP) = -1472.46916115 A.U. after 2 cycles
Low frequencies --- -10.3204 -3.5235 0.0005 0.0009 0.0010 8.2792
Zero-point correction= 0.372800 (Hartree/Particle)
Thermal correction to Energy= 0.397667
Thermal correction to Enthalpy= 0.398611
Thermal correction to Gibbs Free Energy= 0.318424
Sum of electronic and zero-point Energies= -1472.096362
Sum of electronic and thermal Energies= -1472.071494
Sum of electronic and thermal Enthalpies= -1472.070550
Sum of electronic and thermal Free Energies= -1472.150737

b2) Splitting of HCl from (**3b**$^{+}$); cyclometallation of the pyrimidine ring



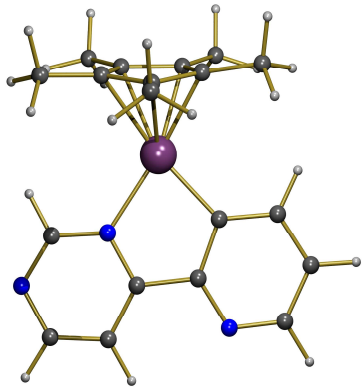
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.998170	0.813142	0.258065
2	7	0	0.156338	-1.154020	0.152694
3	7	0	-3.157627	0.224752	-0.104360
4	7	0	-2.981481	2.599730	-0.032746
5	6	0	0.831652	-2.311126	0.231685
6	6	0	0.196692	-3.546195	0.191024
7	6	0	-1.189928	-3.581778	0.064885
8	6	0	-1.895687	-2.384423	-0.011327
9	6	0	-1.195661	-1.185129	0.036632
10	6	0	-1.828883	0.147713	-0.011904
11	6	0	-0.977414	1.266821	0.061694
12	6	0	-1.651301	2.492481	0.057462
13	6	0	-3.667083	1.458250	-0.119067
14	6	0	2.305980	2.395553	0.995882
15	6	0	1.994153	2.650973	-0.363687
16	6	0	2.465653	1.504058	-1.123324
17	6	0	3.227723	0.635612	-0.228690
18	6	0	3.101483	1.153073	1.066777
19	6	0	2.028071	3.284073	2.164946
20	6	0	1.409118	3.896663	-0.951820
21	6	0	2.386326	1.358198	-2.605927
22	6	0	4.012114	-0.561610	-0.667938
23	6	0	3.681227	0.608187	2.331726
24	1	0	1.907446	-2.237298	0.328425
25	1	0	0.782985	-4.454526	0.257273

26	1	0	-1.714839	-4.529904	0.028892
27	1	0	-2.974043	-2.351952	-0.103054
28	1	0	-1.117924	3.435374	0.135187
29	1	0	-4.746143	1.540172	-0.205032
30	1	0	1.793337	2.713099	3.064743
31	1	0	1.200100	3.966230	1.973981
32	1	0	2.912937	3.891063	2.389780
33	1	0	2.211504	4.504411	-1.384076
34	1	0	0.910681	4.511779	-0.203294
35	1	0	0.695560	3.686838	-1.749277
36	1	0	3.272013	1.815604	-3.064801
37	1	0	1.510079	1.857966	-3.018633
38	1	0	2.364865	0.312897	-2.916128
39	1	0	3.496063	-1.132868	-1.441904
40	1	0	4.239432	-1.234478	0.159541
41	1	0	4.969828	-0.245059	-1.094686
42	1	0	4.531193	1.222729	2.649110
43	1	0	4.041923	-0.413603	2.216884
44	1	0	2.958369	0.622524	3.150386

```
SCF Done:  E(RB3LYP) =  -1011.56912784     A.U. after    2 cycles
Low frequencies ---   -6.7600   -0.0009   -0.0004    0.0007    6.5096   11.3409
Zero-point correction=                           0.359083 (Hartree/Particle)
 Thermal correction to Energy=                    0.381885
 Thermal correction to Enthalpy=                  0.382830
 Thermal correction to Gibbs Free Energy=         0.307134
 Sum of electronic and zero-point Energies=          -1011.210045
 Sum of electronic and thermal Energies=             -1011.187242
 Sum of electronic and thermal Enthalpies=           -1011.186298
 Sum of electronic and thermal Free Energies=        -1011.261994
```

b3) Splitting of HCl from (**3b**$^{+}$); cyclometallation of the pyridine ring



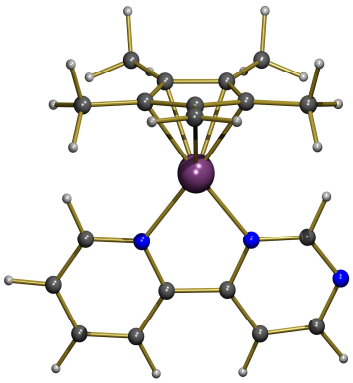
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.213303	0.070211	0.785306
2	7	0	-2.638025	-2.970983	0.075814
3	7	0	0.079980	-0.931791	-1.092390
4	7	0	0.767207	-1.412824	-3.308990
5	6	0	-3.339375	-3.120490	1.198877
6	6	0	-3.107263	-2.354663	2.343803
7	6	0	-2.110207	-1.381726	2.314081
8	6	0	-1.356913	-1.188291	1.151107
9	6	0	-1.682741	-2.036796	0.069238
10	6	0	-0.887673	-1.882703	-1.158690
11	6	0	-1.050247	-2.624555	-2.322306

12	6	0	-0.192853	-2.346103	-3.380268
13	6	0	0.861268	-0.750816	-2.168624
14	6	0	0.038923	2.183742	0.986809
15	6	0	1.378236	2.006795	0.426460
16	6	0	2.108287	1.217814	1.323867
17	6	0	1.254389	0.938135	2.495895
18	6	0	0.016671	1.608431	2.321023
19	6	0	-1.041786	3.017646	0.384879
20	6	0	1.845064	2.605862	-0.863866
21	6	0	3.519051	0.742683	1.189571
22	6	0	1.712390	0.194203	3.708085
23	6	0	-1.063601	1.812947	3.335923
24	1	0	-4.113169	-3.882140	1.185576
25	1	0	-3.699713	-2.521148	3.236992
26	1	0	-1.929940	-0.786957	3.202527
27	1	0	-1.819959	-3.383367	-2.375498
28	1	0	-0.268275	-2.884536	-4.320080
29	1	0	1.633162	0.005897	-2.089130
30	1	0	-2.029471	2.725465	0.741414
31	1	0	-1.040296	2.968154	-0.704526
32	1	0	-0.888971	4.068271	0.662499
33	1	0	2.075463	3.666907	-0.719785
34	1	0	1.084930	2.552191	-1.645578
35	1	0	2.751910	2.130415	-1.238235
36	1	0	4.171609	1.309223	1.863270
37	1	0	3.904609	0.869246	0.178396
38	1	0	3.621957	-0.310309	1.461185
39	1	0	2.323938	-0.671303	3.447955
40	1	0	0.878483	-0.153040	4.317537
41	1	0	2.330600	0.848573	4.333968
42	1	0	-0.955718	2.805624	3.786336
43	1	0	-1.008919	1.088005	4.147857
44	1	0	-2.061318	1.762103	2.898714

```
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1011.56793978     A.U. after    2 cycles
Low frequencies ---   -8.3739    0.0006    0.0006    0.0011    7.5958   11.1519
Zero-point correction=                           0.358904 (Hartree/Particle)
 Thermal correction to Energy=                    0.381719
 Thermal correction to Enthalpy=                  0.382664
 Thermal correction to Gibbs Free Energy=         0.306773
 Sum of electronic and zero-point Energies=          -1011.209036
 Sum of electronic and thermal Energies=             -1011.186220
 Sum of electronic and thermal Enthalpies=           -1011.185276
 Sum of electronic and thermal Free Energies=        -1011.261167
```

b4) Splitting of HCl from (**3b**$^{+}$); deprotonation of Cp*

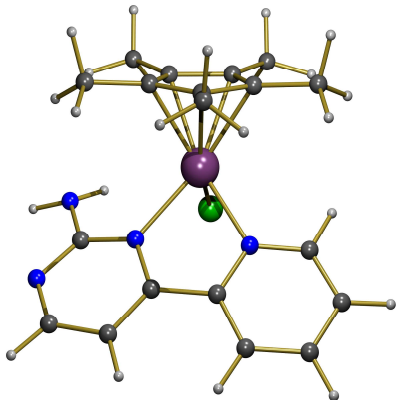


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.994320	0.517601	0.132869
2	7	0	-0.647698	1.824676	0.216480
3	7	0	-1.633672	3.987700	0.274899
4	7	0	-0.647361	-0.805586	0.200114
5	6	0	-3.041240	-0.996651	0.276047
6	6	0	-1.687151	-2.968587	0.216597
7	6	0	-0.597025	3.168745	0.226423
8	6	0	-2.843351	3.419746	0.315442
9	6	0	-3.016753	2.041024	0.307382
10	6	0	-1.875917	1.244156	0.255728
11	6	0	-1.878596	-0.228526	0.243579
12	6	0	-0.568580	-2.145602	0.185588
13	6	0	-2.948121	-2.383687	0.263238
14	6	0	2.841471	-0.638971	-0.313750
15	6	0	2.851264	-0.195342	1.032145
16	6	0	2.840247	1.264981	1.023078
17	6	0	2.826313	1.691793	-0.328518
18	6	0	3.043264	0.522291	-1.201390
19	6	0	2.949308	-2.054231	-0.792632
20	6	0	2.969952	-1.040153	2.262410
21	6	0	2.946460	2.127837	2.242157
22	6	0	2.913345	3.102227	-0.825235
23	6	0	3.263050	0.515896	-2.532537
24	1	0	-4.013168	-0.521816	0.310104
25	1	0	-1.562532	-4.044557	0.203274
26	1	0	0.390008	3.610931	0.190041
27	1	0	-3.694967	4.091651	0.354910
28	1	0	-4.011274	1.616598	0.340518
29	1	0	0.428797	-2.561126	0.145734
30	1	0	-3.843878	-2.993318	0.288042
31	1	0	2.310787	-2.239071	-1.659830
32	1	0	2.699575	-2.780582	-0.018002
33	1	0	3.978473	-2.265288	-1.102934
34	1	0	4.019563	-1.107035	2.570826
35	1	0	2.618332	-2.059216	2.098484
36	1	0	2.410615	-0.622378	3.100539
37	1	0	3.995558	2.218751	2.546112
38	1	0	2.397655	1.710984	3.087751
39	1	0	2.575323	3.137866	2.066338
40	1	0	2.654176	3.835273	-0.060552
41	1	0	2.271554	3.267894	-1.693641
42	1	0	3.939469	3.322505	-1.139383
43	1	0	3.360629	1.435131	-3.097504
44	1	0	3.371775	-0.408536	-3.086943

SCF Done: E(RB3LYP) = -1011.58635318 A.U. after 2 cycles
Low frequencies --- -5.8175 -0.0006 -0.0004 0.0005 8.7407 9.4158
Zero-point correction= 0.359361 (Hartree/Particle)
Thermal correction to Energy= 0.381836
Thermal correction to Enthalpy= 0.382781
Thermal correction to Gibbs Free Energy= 0.308373
Sum of electronic and zero-point Energies= -1011.226992
Sum of electronic and thermal Energies= -1011.204517
Sum of electronic and thermal Enthalpies= -1011.203573
Sum of electronic and thermal Free Energies= -1011.277980

c1) [(2-(2-Aminopyrimidin-4-yl)pyridine)(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)-rhodium(III)]$^+$ (**3c$^+$**)



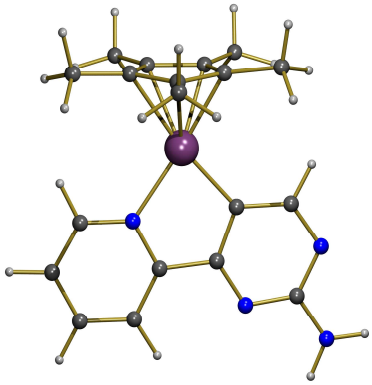
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.294972	-0.355594	0.858938
2	17	0	1.627727	-2.281989	1.421192
3	7	0	-1.349727	-1.640319	0.378547
4	7	0	0.601856	-0.890048	-1.189494
5	7	0	1.791792	-0.777038	-3.245063
6	7	0	2.888973	-0.479241	-1.230514
7	6	0	-2.183156	-2.184149	1.273070
8	6	0	-3.297465	-2.926745	0.899656
9	6	0	-3.553876	-3.110728	-0.454545
10	6	0	-2.667722	-2.579926	-1.385397
11	6	0	-1.559894	-1.859355	-0.941911
12	6	0	-0.477271	-1.395921	-1.832467
13	6	0	-0.476994	-1.529381	-3.212893
14	6	0	0.687992	-1.138158	-3.879138
15	6	0	1.741192	-0.728128	-1.904272
16	1	0	2.953355	-0.882289	-0.300986
17	1	0	3.726397	-0.527378	-1.793757
18	6	0	0.753858	1.813106	0.719077
19	6	0	1.578425	1.194658	1.720537
20	6	0	0.702650	0.688457	2.762130
21	6	0	-0.641441	0.957647	2.372667
22	6	0	-0.622301	1.632348	1.087227
23	6	0	1.246853	2.560895	-0.477827
24	6	0	3.071877	1.230527	1.808436
25	6	0	1.167100	0.071510	4.041442
26	6	0	-1.866249	0.707393	3.194219
27	6	0	-1.815064	2.204757	0.384468
28	1	0	-1.937636	-2.026019	2.314650
29	1	0	-3.939342	-3.352627	1.661151
30	1	0	-4.416794	-3.678140	-0.783712
31	1	0	-2.826225	-2.747657	-2.442646
32	1	0	-1.326336	-1.910532	-3.761636
33	1	0	0.737557	-1.147824	-4.964196
34	1	0	0.529703	2.546810	-1.299099
35	1	0	2.195272	2.169176	-0.842684
36	1	0	1.405694	3.610364	-0.205087
37	1	0	3.386436	2.038044	2.478788
38	1	0	3.534803	1.411768	0.839060
39	1	0	3.470131	0.297966	2.211066
40	1	0	1.536575	0.854490	4.713146

41	1	0	1.978597	-0.636335	3.871996
42	1	0	0.367710	-0.457238	4.559813
43	1	0	-1.730510	-0.108762	3.904327
44	1	0	-2.743021	0.493469	2.581940
45	1	0	-2.097840	1.604496	3.779213
46	1	0	-2.056828	3.194350	0.788009
47	1	0	-2.701241	1.580630	0.509668
48	1	0	-1.640565	2.325660	-0.685109

SCF Done: E(RB3LYP) = -1527.86342315 A.U. after 2 cycles
Low frequencies --- -14.0349 -10.4088 -7.1885 0.0009 0.0014 0.0016
Zero-point correction= 0.390265 (Hartree/Particle)
Thermal correction to Energy= 0.416149
Thermal correction to Enthalpy= 0.417093
Thermal correction to Gibbs Free Energy= 0.335678
Sum of electronic and zero-point Energies= -1527.473159
Sum of electronic and thermal Energies= -1527.447275
Sum of electronic and thermal Enthalpies= -1527.446330
Sum of electronic and thermal Free Energies= -1527.527745

c2) Splitting of HCl from (**3c**$^{+}$); cyclometallation of the pyrimidine ring



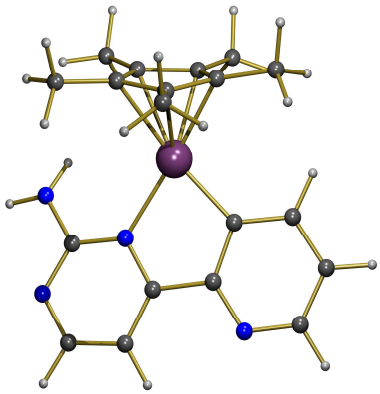
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.334794	0.827299	0.132206
2	7	0	0.503616	-1.157774	0.101595
3	7	0	-2.814550	0.203756	0.097447
4	7	0	-2.640313	2.602434	0.076231
5	7	0	-4.684176	1.548401	0.100201
6	6	0	1.185629	-2.310998	0.117018
7	6	0	0.553526	-3.549903	0.125823
8	6	0	-0.837293	-3.590101	0.121135
9	6	0	-1.549903	-2.393440	0.107596
10	6	0	-0.851814	-1.193087	0.097694
11	6	0	-1.489587	0.142217	0.087148
12	6	0	-0.628977	1.263057	0.071908
13	6	0	-1.319748	2.489271	0.065109
14	6	0	-3.341567	1.446932	0.090957
15	6	0	2.599565	2.391231	0.953961
16	6	0	2.364562	2.660674	-0.420570
17	6	0	2.900614	1.533625	-1.169330
18	6	0	3.585980	0.647458	-0.249766
19	6	0	3.367555	1.137821	1.051925
20	6	0	2.276658	3.272362	2.117675
21	6	0	1.806909	3.911647	-1.025748
22	6	0	2.904368	1.410446	-2.656849

23	6	0	4.389245	-0.551730	-0.651689
24	6	0	3.859699	0.559822	2.339222
25	1	0	-5.256232	0.720861	0.110627
26	1	0	-5.115421	2.457857	0.095831
27	1	0	2.265482	-2.234338	0.120056
28	1	0	1.146801	-4.456107	0.136767
29	1	0	-1.360695	-4.539740	0.128620
30	1	0	-2.631974	-2.365113	0.106143
31	1	0	-0.784115	3.434848	0.052306
32	1	0	1.950320	2.697302	2.985607
33	1	0	1.496973	3.995946	1.882564
34	1	0	3.169345	3.833639	2.417473
35	1	0	2.625885	4.537816	-1.396206
36	1	0	1.251881	4.506948	-0.301151
37	1	0	1.147496	3.706304	-1.869943
38	1	0	3.791651	1.910903	-3.064605
39	1	0	2.029892	1.879935	-3.107876
40	1	0	2.941500	0.370227	-2.982213
41	1	0	3.912572	-1.119715	-1.453381
42	1	0	4.567793	-1.228043	0.185156
43	1	0	5.370746	-0.240880	-1.024801
44	1	0	4.726622	1.126146	2.698488
45	1	0	4.169371	-0.479982	2.235655
46	1	0	3.100317	0.609768	3.121982

```
SCF Done:  E(RB3LYP) =  -1066.96615784     A.U. after    2 cycles
Low frequencies ---   -10.7019   -4.1439   -0.0002    0.0007    0.0009   10.7683
Zero-point correction=                           0.375687 (Hartree/Particle)
 Thermal correction to Energy=                    0.400148
 Thermal correction to Enthalpy=                  0.401092
 Thermal correction to Gibbs Free Energy=         0.321557
 Sum of electronic and zero-point Energies=          -1066.590471
 Sum of electronic and thermal Energies=             -1066.566010
 Sum of electronic and thermal Enthalpies=           -1066.565066
 Sum of electronic and thermal Free Energies=        -1066.644601
```

c3) Splitting of HCl from (**3c**$^{+}$); cyclometallation of the pyridine ring



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.298701	-0.032731	0.790620
2	7	0	-2.824847	-2.745557	-0.027890
3	7	0	0.244486	-1.162305	-1.034733
4	7	0	0.886384	-1.725655	-3.263629
5	7	0	2.323071	-0.552498	-1.917004
6	6	0	-3.544687	-2.861322	1.086498

7	6	0	-3.212953	-2.204503	2.273585
8	6	0	-2.103690	-1.362099	2.288995
9	6	0	-1.334802	-1.200433	1.131222
10	6	0	-1.749703	-1.952277	0.011539
11	6	0	-0.901605	-1.890156	-1.188591
12	6	0	-1.190160	-2.523409	-2.381140
13	6	0	-0.259953	-2.375006	-3.412240
14	6	0	1.121825	-1.167318	-2.067118
15	6	0	0.013306	2.067660	0.990240
16	6	0	1.358316	1.981138	0.406586
17	6	0	2.156800	1.254683	1.293918
18	6	0	1.335516	0.904099	2.466968
19	6	0	0.054352	1.505094	2.321373
20	6	0	-1.121997	2.834884	0.399135
21	6	0	1.741196	2.615067	-0.892885
22	6	0	3.611347	0.920577	1.171453
23	6	0	1.856865	0.185131	3.668100
24	6	0	-0.998567	1.669431	3.372064
25	1	0	2.691635	-0.428856	-0.988793
26	1	0	2.990964	-0.722517	-2.654307
27	1	0	-4.414118	-3.509818	1.032890
28	1	0	-3.816789	-2.350174	3.162809
29	1	0	-1.849216	-0.848198	3.208480
30	1	0	-2.103035	-3.092193	-2.488650
31	1	0	-0.438848	-2.806877	-4.392883
32	1	0	-2.085858	2.489840	0.772863
33	1	0	-1.132719	2.773577	-0.689657
34	1	0	-1.024783	3.895281	0.664149
35	1	0	1.717304	3.705455	-0.792038
36	1	0	1.051753	2.350742	-1.697078
37	1	0	2.743084	2.335945	-1.213899
38	1	0	4.191225	1.489826	1.905767
39	1	0	4.013640	1.169812	0.189081
40	1	0	3.813136	-0.135366	1.371516
41	1	0	2.527577	-0.631440	3.394765
42	1	0	1.055669	-0.226788	4.280960
43	1	0	2.430937	0.877272	4.295816
44	1	0	-0.901397	2.661844	3.825543
45	1	0	-0.897924	0.941820	4.177394
46	1	0	-2.008436	1.595320	2.968206

SCF Done: E(RB3LYP) = -1066.95570044 A.U. after 2 cycles

Low frequencies --- -11.2415 -2.6366 -0.0007 -0.0005 0.0004 4.2759

Zero-point correction= 0.375703 (Hartree/Particle)

Thermal correction to Energy= 0.399890

Thermal correction to Enthalpy= 0.400834

Thermal correction to Gibbs Free Energy= 0.322735

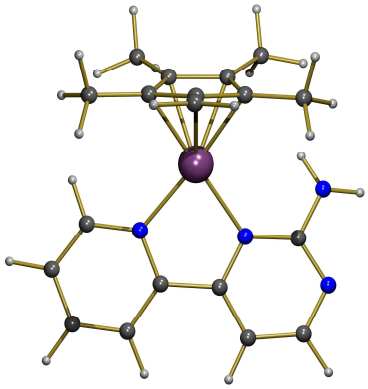
Sum of electronic and zero-point Energies= -1066.579998

Sum of electronic and thermal Energies= -1066.555811

Sum of electronic and thermal Enthalpies= -1066.554866

Sum of electronic and thermal Free Energies= -1066.632966

c4) Splitting of HCl from (**3c**$^{+}$); deprotonation of Cp*



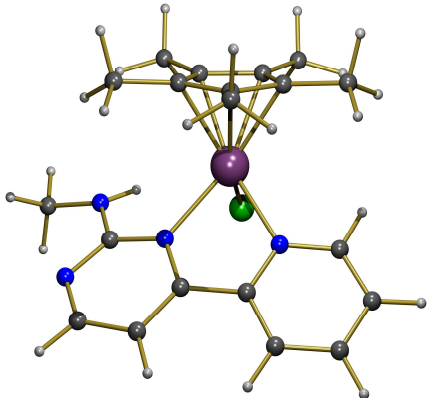
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.795105	0.160201	0.702428
2	7	0	-0.850818	1.467845	1.090841
3	7	0	-1.932880	3.600758	1.177092
4	7	0	-0.803653	-1.166632	1.028858
5	6	0	-3.192208	-1.393313	1.004100
6	6	0	-1.809763	-3.338068	1.193663
7	6	0	-0.851980	2.811434	1.285162
8	6	0	-3.091584	3.006474	0.947418
9	6	0	-3.228505	1.618520	0.876177
10	6	0	-2.065779	0.868276	0.962132
11	6	0	-2.040496	-0.607433	0.976346
12	6	0	-0.703977	-2.500545	1.143441
13	6	0	-3.078696	-2.774240	1.110114
14	6	0	2.366404	-1.064692	-0.258774
15	6	0	2.810847	-0.585018	1.000153
16	6	0	2.862615	0.872132	0.926018
17	6	0	2.439021	1.259252	-0.368580
18	6	0	2.343668	0.055476	-1.217989
19	6	0	2.286800	-2.496438	-0.691973
20	6	0	3.288441	-1.396721	2.164492
21	6	0	3.437306	1.749467	1.998006
22	6	0	2.409114	2.643771	-0.936350
23	6	0	2.182482	-0.000913	-2.554559
24	7	0	0.312236	3.418607	1.601105
25	1	0	-4.170644	-0.934389	0.956223
26	1	0	-1.670117	-4.407541	1.293981
27	1	0	-3.953769	3.657739	0.836174
28	1	0	-4.202503	1.168834	0.748442
29	1	0	0.299330	-2.898934	1.195151
30	1	0	-3.966204	-3.395883	1.136873
31	1	0	1.411205	-2.685654	-1.316996
32	1	0	2.269103	-3.192516	0.147313
33	1	0	3.168421	-2.747662	-1.291828
34	1	0	4.375492	-1.528452	2.110828
35	1	0	2.846536	-2.393858	2.182193
36	1	0	3.065435	-0.915253	3.117901
37	1	0	4.520570	1.596845	2.057821
38	1	0	3.033114	1.522855	2.987412
39	1	0	3.288796	2.810247	1.790750
40	1	0	2.321792	3.414784	-0.173308
41	1	0	1.576794	2.770649	-1.631489

42	1	0	3.331639	2.831478	-1.497239
43	1	0	2.146506	0.895077	-3.162324
44	1	0	2.101420	-0.945899	-3.078465
45	1	0	1.065226	2.861886	1.970404
46	1	0	0.255157	4.386447	1.878865

SCF Done: E(RB3LYP) = -1066.97340034 A.U. after 2 cycles
Low frequencies --- -7.2382 -0.0001 0.0007 0.0009 3.4754 10.1501
Zero-point correction= 0.376573 (Hartree/Particle)
Thermal correction to Energy= 0.400273
Thermal correction to Enthalpy= 0.401217
Thermal correction to Gibbs Free Energy= 0.324938
Sum of electronic and zero-point Energies= -1066.596827
Sum of electronic and thermal Energies= -1066.573127
Sum of electronic and thermal Enthalpies= -1066.572183
Sum of electronic and thermal Free Energies= -1066.648462

d1) [Chlorido(2-(2-methylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III)]$^+$ (**3d$^+$**)



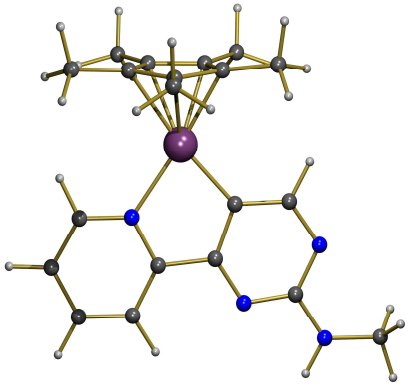
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.522161	0.238835	-0.168824
2	17	0	-0.454892	-0.186091	-2.539697
3	7	0	1.143150	1.561819	-0.359290
4	7	0	1.193162	-1.023741	0.007404
5	7	0	2.233191	-3.131293	0.393404
6	7	0	0.169087	-2.998216	-0.652902
7	6	0	1.070532	2.826363	-0.790754
8	6	0	2.170862	3.675605	-0.796939
9	6	0	3.390862	3.190411	-0.338444
10	6	0	3.476999	1.865082	0.073356
11	6	0	2.337818	1.062666	0.038677
12	6	0	2.352516	-0.391843	0.295082
13	6	0	3.466249	-1.106933	0.714155
14	6	0	3.315645	-2.492910	0.807761
15	6	0	1.217971	-2.384325	-0.076428
16	6	0	0.164555	-4.435753	-0.919737
17	1	0	-0.372397	-2.403685	-1.272155
18	6	0	-1.737683	-0.614434	1.482843
19	6	0	-2.489002	-0.624013	0.258715
20	6	0	-2.671295	0.755095	-0.158475
21	6	0	-1.998378	1.588421	0.781069
22	6	0	-1.387911	0.743796	1.791773
23	6	0	-1.414456	-1.809029	2.321959

24	6	0	-3.151596	-1.801154	-0.385552
25	6	0	-3.495614	1.190423	-1.326494
26	6	0	-2.010525	3.084049	0.804976
27	6	0	-0.694718	1.223133	3.030396
28	1	0	0.104033	3.153992	-1.149588
29	1	0	2.065062	4.690258	-1.160984
30	1	0	4.269299	3.825306	-0.322611
31	1	0	4.426200	1.455525	0.392978
32	1	0	4.402030	-0.631256	0.970868
33	1	0	4.114396	-3.111488	1.207603
34	1	0	0.947535	-4.720602	-1.626872
35	1	0	-0.805853	-4.697581	-1.339358
36	1	0	0.315864	-4.992654	0.003653
37	1	0	-0.503559	-1.670624	2.905018
38	1	0	-1.304621	-2.712950	1.724255
39	1	0	-2.230822	-1.981491	3.032374
40	1	0	-4.211351	-1.831375	-0.109488
41	1	0	-2.706638	-2.744240	-0.069218
42	1	0	-3.099182	-1.743164	-1.473873
43	1	0	-4.559099	1.113272	-1.073830
44	1	0	-3.311509	0.565478	-2.200569
45	1	0	-3.298762	2.224074	-1.609691
46	1	0	-2.172979	3.514050	-0.183602
47	1	0	-1.091643	3.501544	1.218328
48	1	0	-2.832509	3.428717	1.442276
49	1	0	-1.424957	1.428821	3.821019
50	1	0	-0.139206	2.146014	2.856999
51	1	0	0.003985	0.482156	3.420458

```
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1567.17920931     A.U. after    2 cycles
Low frequencies ---   -9.8832   -4.0520   -0.0014   -0.0011   -0.0007    9.4438
Zero-point correction=                           0.418129 (Hartree/Particle)
 Thermal correction to Energy=                    0.445822
 Thermal correction to Enthalpy=                  0.446766
 Thermal correction to Gibbs Free Energy=         0.361017
 Sum of electronic and zero-point Energies=          -1566.761080
 Sum of electronic and thermal Energies=             -1566.733387
 Sum of electronic and thermal Enthalpies=           -1566.732443
 Sum of electronic and thermal Free Energies=        -1566.818193
```

d2) Splitting of HCl from (**3d**$^{+}$); cyclometallation of the pyrimidine ring



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.685801	0.829331	0.120640
2	7	0	0.846453	-1.152381	0.125664

3	7	0	-2.462863	0.222266	0.094450
4	7	0	-2.276843	2.623739	0.057855
5	7	0	-4.328830	1.562321	0.084957
6	6	0	1.526125	-2.306554	0.159117
7	6	0	0.891728	-3.544117	0.175821
8	6	0	-0.499143	-3.581815	0.159789
9	6	0	-1.209163	-2.384004	0.129446
10	6	0	-0.508756	-1.185051	0.113135
11	6	0	-1.142526	0.152624	0.087865
12	6	0	-0.272366	1.270964	0.065698
13	6	0	-0.955779	2.499554	0.049322
14	6	0	-2.987180	1.473884	0.078551
15	6	0	-5.069886	2.815043	0.069838
16	6	0	2.958000	2.390324	0.934147
17	6	0	2.721441	2.656557	-0.441674
18	6	0	3.254807	1.527473	-1.188023
19	6	0	3.936049	0.640709	-0.267039
20	6	0	3.723154	1.136807	1.034129
21	6	0	2.637867	3.277533	2.094248
22	6	0	2.164245	3.906969	-1.048766
23	6	0	3.257546	1.403290	-2.675678
24	6	0	4.736571	-0.562070	-0.664663
25	6	0	4.223559	0.563187	2.320873
26	1	0	-4.827940	0.686464	0.099327
27	1	0	2.605851	-2.230197	0.171137
28	1	0	1.483153	-4.451261	0.201266
29	1	0	-1.024497	-4.530332	0.171979
30	1	0	-2.291148	-2.353784	0.119676
31	1	0	-0.412178	3.440635	0.030902
32	1	0	-6.133460	2.582349	0.088271
33	1	0	-4.846770	3.392399	-0.829320
34	1	0	-4.823416	3.426275	0.939910
35	1	0	2.345534	2.705583	2.976116
36	1	0	1.834087	3.976880	1.866961
37	1	0	3.521628	3.866125	2.367134
38	1	0	2.982219	4.529623	-1.427174
39	1	0	1.615158	4.506662	-0.323181
40	1	0	1.498039	3.699073	-1.887083
41	1	0	4.154957	1.885598	-3.082974
42	1	0	2.393148	1.890630	-3.126741
43	1	0	3.273045	0.362718	-3.001563
44	1	0	4.279993	-1.108174	-1.492474
45	1	0	4.877988	-1.256958	0.164237
46	1	0	5.734585	-0.258230	-0.997876
47	1	0	5.085397	1.138194	2.678414
48	1	0	4.544545	-0.472953	2.215216
49	1	0	3.466070	0.604099	3.106140

SCF Done: E(RB3LYP) = -1106.28304233 A.U. after 2 cycles

Low frequencies --- -0.0008 -0.0006 -0.0004 2.6754 10.6364 11.6146

Zero-point correction= 0.404138 (Hartree/Particle)

Thermal correction to Energy= 0.430146

Thermal correction to Enthalpy= 0.431090

Thermal correction to Gibbs Free Energy= 0.348074

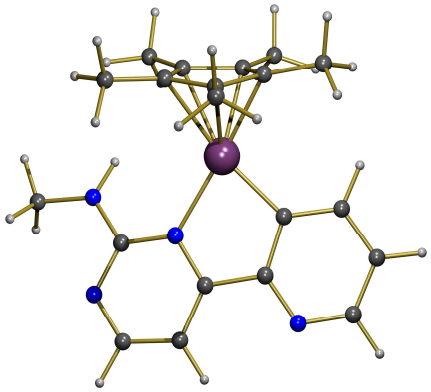
Sum of electronic and zero-point Energies= -1105.878904

Sum of electronic and thermal Energies= -1105.852897

Sum of electronic and thermal Enthalpies= -1105.851952

Sum of electronic and thermal Free Energies= -1105.934968

d3) Splitting of HCl from (**3d**$^{+}$); cyclometallation of the pyridine ring



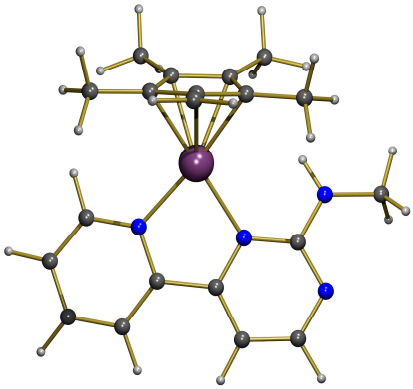
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.273778	-0.026655	0.742255
2	7	0	-2.843535	-2.766104	0.003278
3	7	0	0.179136	-1.147082	-1.084664
4	7	0	0.763103	-1.708737	-3.336397
5	7	0	2.230878	-0.537643	-2.014693
6	6	0	-3.534979	-2.887319	1.135183
7	6	0	-3.180457	-2.226550	2.313066
8	6	0	-2.078643	-1.374374	2.300225
9	6	0	-1.341160	-1.206089	1.123624
10	6	0	-1.775795	-1.962322	0.014850
11	6	0	-0.957183	-1.891836	-1.205796
12	6	0	-1.271322	-2.538019	-2.385407
13	6	0	-0.375959	-2.377508	-3.444459
14	6	0	1.033799	-1.142617	-2.148030
15	6	0	3.252134	-0.558219	-3.058361
16	6	0	0.014577	2.075684	0.970561
17	6	0	1.350987	1.983446	0.371939
18	6	0	2.150376	1.234923	1.240328
19	6	0	1.338873	0.878903	2.419056
20	6	0	0.064559	1.497387	2.294884
21	6	0	-1.118621	2.863668	0.402082
22	6	0	1.728752	2.636804	-0.920223
23	6	0	3.598792	0.881963	1.097179
24	6	0	1.868192	0.142556	3.606430
25	6	0	-0.975108	1.664522	3.358113
26	1	0	2.496955	-0.268086	-1.082206
27	1	0	-4.399395	-3.543951	1.103338
28	1	0	-3.760436	-2.376914	3.217270
29	1	0	-1.805127	-0.858998	3.213028
30	1	0	-2.178025	-3.121196	-2.462338
31	1	0	-0.579959	-2.814907	-4.418047
32	1	0	3.601818	-1.572918	-3.260509
33	1	0	4.093168	0.048415	-2.723448
34	1	0	2.859500	-0.139884	-3.984128
35	1	0	-2.082601	2.523662	0.780191
36	1	0	-1.141466	2.818146	-0.687392
37	1	0	-1.007700	3.919000	0.681519
38	1	0	1.682667	3.725426	-0.811490
39	1	0	1.050778	2.365966	-1.732181
40	1	0	2.740881	2.385037	-1.233987
41	1	0	4.190783	1.410700	1.851669

42	1	0	4.002352	1.164144	0.124148
43	1	0	3.783131	-0.184826	1.250160
44	1	0	2.530271	-0.674747	3.315330
45	1	0	1.071248	-0.272733	4.222794
46	1	0	2.452781	0.823248	4.236887
47	1	0	-0.868941	2.656614	3.810330
48	1	0	-0.867084	0.936589	4.162032
49	1	0	-1.989771	1.594427	2.966013

```
SCF Done:  E(RB3LYP) =  -1106.27150046     A.U. after    1 cycles
Low frequencies ---   -9.6375   -6.2931   -0.0007   -0.0006    0.0006    8.9322
Zero-point correction=                           0.403667 (Hartree/Particle)
 Thermal correction to Energy=                    0.429601
 Thermal correction to Enthalpy=                  0.430545
 Thermal correction to Gibbs Free Energy=         0.348122
 Sum of electronic and zero-point Energies=          -1105.867834
 Sum of electronic and thermal Energies=             -1105.841900
 Sum of electronic and thermal Enthalpies=           -1105.840956
 Sum of electronic and thermal Free Energies=        -1105.923378
```

d4) Splitting of HCl from (**3d**$^{+}$); deprotonation of Cp*



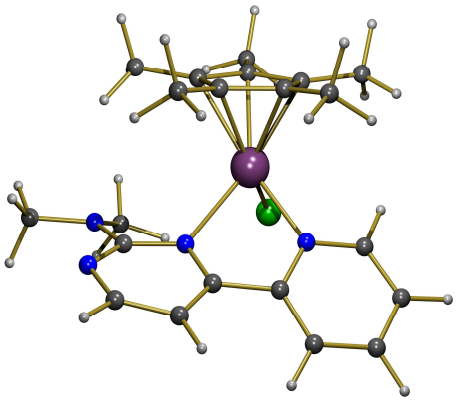
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	0.796234	-0.042502	0.630333
2	7	0	-0.864157	1.270411	0.932796
3	7	0	-1.974716	3.394513	0.848173
4	7	0	-0.784363	-1.362473	1.042311
5	6	0	-3.169484	-1.615035	1.065893
6	6	0	-1.762830	-3.527400	1.372913
7	6	0	-0.880105	2.633295	1.027133
8	6	0	-3.124275	2.765540	0.669568
9	6	0	-3.244334	1.375726	0.712233
10	6	0	-2.069067	0.650677	0.851129
11	6	0	-2.027517	-0.820696	0.967329
12	6	0	-0.667643	-2.684026	1.248262
13	6	0	-3.038972	-2.983703	1.267638
14	6	0	2.361792	-1.305182	-0.288505
15	6	0	2.798825	-0.797324	0.962455
16	6	0	2.869105	0.656978	0.849146
17	6	0	2.462947	1.013603	-0.459310
18	6	0	2.358999	-0.210922	-1.277286
19	6	0	2.261737	-2.746317	-0.685578
20	6	0	3.256972	-1.582031	2.153084
21	6	0	3.434275	1.554248	1.909418
22	6	0	2.460135	2.380491	-1.070552

23	6	0	2.204578	-0.300138	-2.612846
24	7	0	0.268646	3.258865	1.327445
25	6	0	0.371664	4.702213	1.513747
26	1	0	-4.153561	-1.170758	0.999896
27	1	0	-1.609791	-4.585609	1.546422
28	1	0	-3.995133	3.393247	0.502021
29	1	0	-4.211627	0.903996	0.619368
30	1	0	0.340920	-3.066660	1.313377
31	1	0	-3.919054	-3.610879	1.351096
32	1	0	1.368080	-2.944232	-1.281942
33	1	0	2.262442	-3.422301	0.169848
34	1	0	3.125110	-3.017479	-1.302875
35	1	0	4.346016	-1.704630	2.128019
36	1	0	2.824285	-2.582967	2.179208
37	1	0	3.005958	-1.085185	3.091542
38	1	0	4.518523	1.410733	1.975423
39	1	0	3.024202	1.339900	2.898551
40	1	0	3.278169	2.612060	1.690579
41	1	0	2.486155	3.179984	-0.332171
42	1	0	1.581881	2.535527	-1.700705
43	1	0	3.342108	2.498251	-1.709677
44	1	0	2.179188	0.580418	-3.243417
45	1	0	2.115539	-1.257130	-3.113016
46	1	0	1.039923	2.667422	1.591880
47	1	0	-0.236130	5.042502	2.354618
48	1	0	0.045108	5.229645	0.617671
49	1	0	1.415246	4.946330	1.709352

```
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1106.28972711     A.U. after    2 cycles
Low frequencies ---   -7.6752   -0.0009    0.0004    0.0006    5.4278    9.6629
Zero-point correction=                           0.404260 (Hartree/Particle)
 Thermal correction to Energy=                    0.429896
 Thermal correction to Enthalpy=                  0.430840
 Thermal correction to Gibbs Free Energy=         0.349340
 Sum of electronic and zero-point Energies=          -1105.885467
 Sum of electronic and thermal Energies=             -1105.859831
 Sum of electronic and thermal Enthalpies=           -1105.858887
 Sum of electronic and thermal Free Energies=        -1105.940387
```

e1) [Chlorido(2-(2-dimethylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)rhodium(III)]$^+$ (**3e$^+$**)



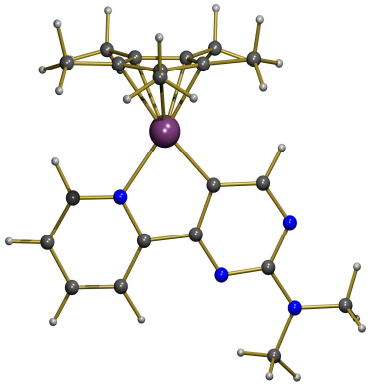
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.444989	-0.493263	-0.150418
2	17	0	-0.822576	-0.586714	-2.516182
3	7	0	-1.448528	1.370021	-0.287202
4	7	0	1.211076	1.042829	-0.223774
5	7	0	3.348584	1.640372	0.660049
6	7	0	3.189613	-0.093553	-0.842935
7	6	0	-2.735363	1.498846	-0.636919
8	6	0	-3.356754	2.737485	-0.728869
9	6	0	-2.609497	3.881154	-0.466316
10	6	0	-1.266498	3.747452	-0.133382
11	6	0	-0.706993	2.472346	-0.053862
12	6	0	0.727719	2.234176	0.210621
13	6	0	1.520808	3.152238	0.881230
14	6	0	2.826854	2.741444	1.162806
15	6	0	2.568251	0.874726	-0.136965
16	6	0	2.658770	-0.613208	-2.104736
17	6	0	4.624806	-0.321241	-0.643068
18	6	0	0.050639	-1.356526	1.830199
19	6	0	0.463336	-2.290345	0.788995
20	6	0	-0.695790	-2.688354	0.064686
21	6	0	-1.828350	-1.963808	0.598030
22	6	0	-1.359553	-1.187894	1.733009
23	6	0	0.952032	-0.802110	2.888301
24	6	0	1.837618	-2.866238	0.657299
25	6	0	-0.765976	-3.697710	-1.033084
26	6	0	-3.253188	-2.177522	0.191350
27	6	0	-2.226132	-0.390646	2.654904
28	1	0	-3.260636	0.582399	-0.870113
29	1	0	-4.398977	2.795281	-1.017931
30	1	0	-3.058369	4.865090	-0.540835
31	1	0	-0.652662	4.623732	0.030032
32	1	0	1.135665	4.092166	1.250272
33	1	0	3.469687	3.328377	1.813644
34	1	0	1.673661	-0.214902	-2.315974
35	1	0	2.597592	-1.703025	-2.078536
36	1	0	3.338713	-0.329947	-2.914169
37	1	0	5.224268	0.412670	-1.190430
38	1	0	4.862378	-1.317276	-1.017922
39	1	0	4.885040	-0.257210	0.409797
40	1	0	0.543751	0.097373	3.349517
41	1	0	1.941347	-0.561623	2.496866
42	1	0	1.092474	-1.541608	3.684672
43	1	0	2.004449	-3.600366	1.453463
44	1	0	2.613626	-2.105991	0.747270
45	1	0	1.974876	-3.381289	-0.292521
46	1	0	-1.102857	-4.656309	-0.621749
47	1	0	0.201511	-3.859537	-1.506183
48	1	0	-1.466664	-3.398278	-1.811533
49	1	0	-3.354496	-2.257636	-0.891804
50	1	0	-3.905790	-1.375401	0.538400
51	1	0	-3.632802	-3.108394	0.627049
52	1	0	-2.641766	-1.046566	3.427751
53	1	0	-3.069349	0.065981	2.135600
54	1	0	-1.672040	0.399982	3.160925

SCF Done: E(RB3LYP) = -1606.47993994 A.U. after 2 cycles

```
Low frequencies ---  -19.4278   -9.9077   -5.1734   -0.0015   -0.0011    0.0005
Zero-point correction=                           0.445527 (Hartree/Particle)
 Thermal correction to Energy=                    0.474896
 Thermal correction to Enthalpy=                  0.475840
 Thermal correction to Gibbs Free Energy=         0.386209
 Sum of electronic and zero-point Energies=          -1606.034413
 Sum of electronic and thermal Energies=             -1606.005044
 Sum of electronic and thermal Enthalpies=           -1606.004100
 Sum of electronic and thermal Free Energies=        -1606.093731
```

e2) Splitting of HCl from (**3e**$^{+}$); cyclometallation of the pyrimidine ring



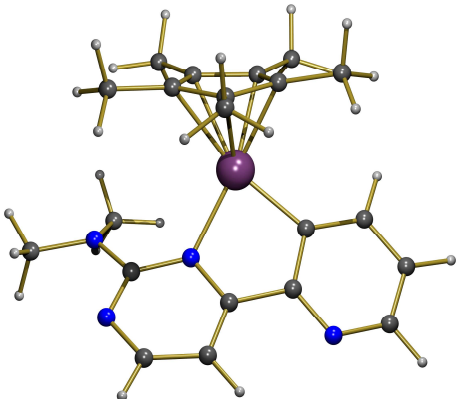
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	1.028710	-0.115475	-0.046963
2	7	0	0.194504	1.870045	-0.021090
3	7	0	-3.117838	0.501348	-0.019967
4	7	0	-2.935536	-1.895575	-0.007084
5	7	0	-5.004528	-0.838543	-0.060761
6	6	0	0.875901	3.023039	-0.031658
7	6	0	0.243669	4.262145	-0.024129
8	6	0	-1.146875	4.301678	-0.006760
9	6	0	-1.858662	3.104299	-0.000581
10	6	0	-1.160553	1.904075	-0.009133
11	6	0	-1.795740	0.565897	-0.010174
12	6	0	-0.926859	-0.550090	-0.000402
13	6	0	-1.619407	-1.777754	0.007071
14	6	0	-3.657484	-0.744884	-0.026947
15	6	0	-5.842037	0.357287	-0.046679
16	6	0	-5.698359	-2.119438	0.041065
17	6	0	2.295498	-1.666591	-0.888071
18	6	0	2.062367	-1.952093	0.485040
19	6	0	2.603874	-0.837208	1.246383
20	6	0	3.281908	0.061687	0.335880
21	6	0	3.063061	-0.414465	-0.972343
22	6	0	1.969535	-2.536641	-2.059665
23	6	0	1.502996	-3.209459	1.075466
24	6	0	2.615051	-0.736645	2.736010
25	6	0	4.085737	1.257773	0.747191
26	6	0	3.562360	0.176240	-2.252012
27	1	0	1.955420	2.944581	-0.045126
28	1	0	0.836616	5.168624	-0.031602
29	1	0	-1.670742	5.251097	0.000768
30	1	0	-2.940555	3.075694	0.010338
31	1	0	-1.080451	-2.721892	0.024410
32	1	0	-5.393672	1.145986	-0.645268

33	1	0	-5.984910	0.730768	0.973044
34	1	0	-6.816360	0.100569	-0.462035
35	1	0	-6.397328	-2.226230	-0.792347
36	1	0	-6.264801	-2.166826	0.976796
37	1	0	-4.980228	-2.931426	0.016105
38	1	0	1.682382	-1.951062	-2.934255
39	1	0	1.160027	-3.232504	-1.842029
40	1	0	2.848814	-3.128708	-2.339482
41	1	0	2.319577	-3.841019	1.441992
42	1	0	0.948759	-3.796081	0.343104
43	1	0	0.840628	-3.010750	1.919069
44	1	0	3.511490	-1.230411	3.131518
45	1	0	1.749887	-1.225684	3.183903
46	1	0	2.638082	0.298591	3.077999
47	1	0	3.636535	1.788707	1.588856
48	1	0	4.218298	1.967497	-0.070552
49	1	0	5.087186	0.949219	1.065376
50	1	0	4.419177	-0.398221	-2.622213
51	1	0	3.890487	1.208511	-2.131164
52	1	0	2.801613	0.153304	-3.034892

```
SCF Done:  E(RB3LYP) =  -1145.59697320     A.U. after    2 cycles
Low frequencies ---   -5.6065   -0.0008   -0.0003    0.0007    5.0951    7.0680
Zero-point correction=                           0.431706 (Hartree/Particle)
 Thermal correction to Energy=                    0.459387
 Thermal correction to Enthalpy=                  0.460331
 Thermal correction to Gibbs Free Energy=         0.373056
 Sum of electronic and zero-point Energies=          -1145.165267
 Sum of electronic and thermal Energies=             -1145.137586
 Sum of electronic and thermal Enthalpies=           -1145.136642
 Sum of electronic and thermal Free Energies=        -1145.223918
```

e3) Splitting of HCl from (**3e**$^{+}$); cyclometallation of the pyridine ring



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.392135	-0.433628	-0.218821
2	7	0	-1.548413	3.604006	-0.148474
3	7	0	1.073369	1.148193	-0.194478
4	7	0	3.171600	2.002981	0.530735
5	7	0	3.101216	0.056027	-0.708638
6	6	0	-2.836934	3.647617	-0.485355
7	6	0	-3.567165	2.512024	-0.844541
8	6	0	-2.939642	1.268283	-0.809343
9	6	0	-1.591566	1.186792	-0.449004
10	6	0	-0.952051	2.407970	-0.159606

11	6	0	0.493929	2.348568	0.107646
12	6	0	1.230198	3.392109	0.635376
13	6	0	2.570085	3.119289	0.915401
14	6	0	2.434319	1.084855	-0.116711
15	6	0	2.629674	-0.539406	-1.957571
16	6	0	4.550826	-0.048147	-0.512704
17	6	0	-0.549551	-1.510454	1.599729
18	6	0	0.522802	-2.242837	0.924684
19	6	0	-0.001455	-2.737459	-0.271520
20	6	0	-1.427917	-2.366358	-0.352084
21	6	0	-1.784105	-1.710090	0.851879
22	6	0	-0.448594	-0.909249	2.962655
23	6	0	1.901346	-2.426236	1.478145
24	6	0	0.684717	-3.570288	-1.304565
25	6	0	-2.348356	-2.815362	-1.442583
26	6	0	-3.156329	-1.374715	1.344329
27	1	0	-3.303971	4.627970	-0.475316
28	1	0	-4.607839	2.604937	-1.136094
29	1	0	-3.505797	0.381224	-1.073597
30	1	0	0.755384	4.334523	0.869458
31	1	0	3.186742	3.832868	1.455144
32	1	0	1.602273	-0.250623	-2.164624
33	1	0	2.689392	-1.627320	-1.914683
34	1	0	3.256926	-0.196408	-2.788089
35	1	0	5.094639	0.660833	-1.145243
36	1	0	4.857333	-1.061575	-0.775999
37	1	0	4.810601	0.149358	0.523163
38	1	0	-1.199361	-0.136407	3.126933
39	1	0	0.535951	-0.478508	3.148085
40	1	0	-0.609287	-1.688933	3.717801
41	1	0	1.884395	-3.159391	2.291754
42	1	0	2.305757	-1.500246	1.889825
43	1	0	2.602466	-2.788176	0.727016
44	1	0	0.257286	-4.578989	-1.309865
45	1	0	1.752437	-3.670983	-1.115498
46	1	0	0.549680	-3.169085	-2.312217
47	1	0	-1.877809	-2.751121	-2.425221
48	1	0	-3.267627	-2.230578	-1.471643
49	1	0	-2.632343	-3.862868	-1.288200
50	1	0	-3.486362	-2.149023	2.045650
51	1	0	-3.888109	-1.337569	0.538298
52	1	0	-3.186448	-0.420507	1.870541

SCF Done: E(RB3LYP) = -1145.57717465 A.U. after 2 cycles

Low frequencies --- -0.0007 -0.0006 0.0001 4.4909 5.0393 11.6827

Zero-point correction= 0.431690 (Hartree/Particle)

Thermal correction to Energy= 0.458884

Thermal correction to Enthalpy= 0.459828

Thermal correction to Gibbs Free Energy= 0.375457

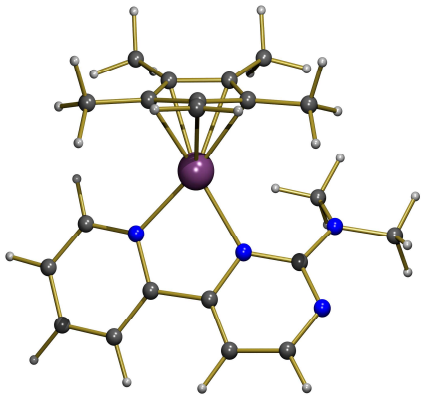
Sum of electronic and zero-point Energies= -1145.145485

Sum of electronic and thermal Energies= -1145.118291

Sum of electronic and thermal Enthalpies= -1145.117347

Sum of electronic and thermal Free Energies= -1145.201717

e4) Splitting of HCl from (**3e**$^{+}$); deprotonation of Cp*



Input orientation:

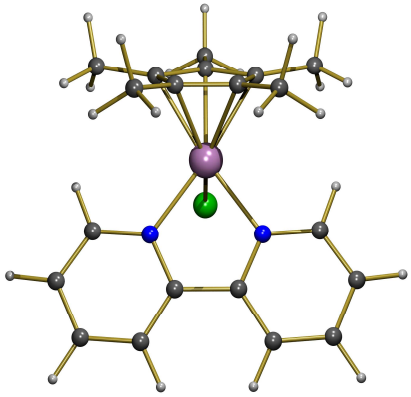
Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	45	0	-0.440777	-0.378308	0.133231
2	7	0	1.217922	1.032533	0.171855
3	7	0	3.354613	1.507963	-0.778100
4	6	0	-1.160766	3.828841	0.055421
5	6	0	-3.226654	2.938723	0.880369
6	6	0	2.560951	0.805059	0.055624
7	6	0	2.854055	2.598869	-1.328163
8	6	0	1.571584	3.073767	-1.036653
9	6	0	0.764478	2.228428	-0.292741
10	6	0	-0.641800	2.535227	0.046096
11	7	0	-1.391436	1.468948	0.420058
12	6	0	-2.652056	1.675917	0.831748
13	6	0	-2.470087	4.034362	0.475170
14	6	0	-1.946370	-1.611516	-0.854216
15	6	0	-1.699449	-2.092773	0.463238
16	6	0	-0.315689	-2.548611	0.508808
17	6	0	0.265506	-2.315829	-0.759602
18	6	0	-0.805446	-1.974862	-1.719164
19	6	0	-3.256139	-1.134924	-1.401061
20	6	0	-2.695346	-2.269788	1.568350
21	6	0	0.296728	-3.264201	1.672073
22	6	0	1.652163	-2.682113	-1.188661
23	6	0	-0.731277	-1.914819	-3.062036
24	7	0	3.145128	-0.164028	0.799197
25	6	0	2.593734	-0.562804	2.093267
26	6	0	4.578848	-0.421963	0.632841
27	1	0	-0.542237	4.667590	-0.236867
28	1	0	-4.245120	3.053160	1.231033
29	1	0	3.501445	3.131133	-2.019892
30	1	0	1.215759	4.009515	-1.443918
31	1	0	-3.203565	0.795924	1.134650
32	1	0	-2.886804	5.034771	0.498090
33	1	0	-3.120897	-0.318354	-2.113287
34	1	0	-3.941454	-0.798107	-0.623212
35	1	0	-3.753180	-1.951947	-1.935905
36	1	0	-3.073837	-3.298415	1.575532
37	1	0	-3.561290	-1.616549	1.451365
38	1	0	-2.257311	-2.077433	2.549319
39	1	0	-0.103458	-4.283398	1.721725
40	1	0	0.068733	-2.784918	2.626170
41	1	0	1.378379	-3.350537	1.580507

42	1	0	2.350744	-2.723356	-0.353713
43	1	0	2.044983	-1.972251	-1.919387
44	1	0	1.648421	-3.668404	-1.666467
45	1	0	0.178664	-2.166164	-3.593881
46	1	0	-1.584360	-1.631322	-3.666989
47	1	0	1.515592	-0.436968	2.110410
48	1	0	3.038341	0.038057	2.895523
49	1	0	2.830500	-1.609596	2.282435
50	1	0	5.184678	0.321977	1.160384
51	1	0	4.849401	-0.400687	-0.418629
52	1	0	4.797439	-1.407724	1.044273

SCF Done: E(RB3LYP) = -1145.59515560 A.U. after 2 cycles
Low frequencies --- -7.2498 -0.0009 -0.0008 0.0002 5.8327 9.6645
Zero-point correction= 0.432317 (Hartree/Particle)
Thermal correction to Energy= 0.459182
Thermal correction to Enthalpy= 0.460126
Thermal correction to Gibbs Free Energy= 0.376880
Sum of electronic and zero-point Energies= -1145.162839
Sum of electronic and thermal Energies= -1145.135974
Sum of electronic and thermal Enthalpies= -1145.135030
Sum of electronic and thermal Free Energies= -1145.218275

3.3 Iridium complexes

a1) [2,2'-Bipyridine(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)iridium(III)]$^+$ (**4a**$^+$)



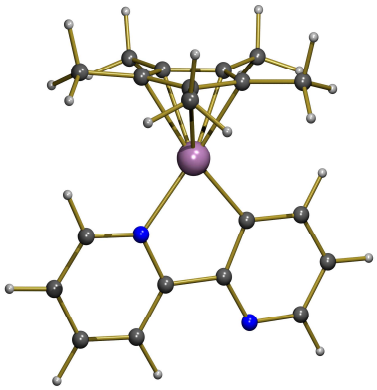
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.298232	-0.368214	0.189846
2	17	0	-0.051055	-2.609414	1.037257
3	7	0	-1.311428	-1.323915	-1.417511
4	7	0	1.258135	-0.936945	-1.143471
5	6	0	3.563000	-1.185223	-1.738888
6	6	0	-2.635762	-1.544983	-1.431656
7	6	0	-3.269322	-2.214230	-2.467554
8	6	0	-2.501726	-2.685591	-3.528481
9	6	0	-1.128853	-2.482973	-3.504238
10	6	0	-0.549744	-1.804657	-2.431010
11	6	0	0.895711	-1.586983	-2.276850
12	6	0	1.855649	-2.033538	-3.185918
13	6	0	3.202112	-1.826597	-2.920140
14	6	0	2.562541	-0.762058	-0.877268
15	6	0	0.076525	1.794679	0.444827
16	6	0	0.517463	1.076284	1.634416
17	6	0	-0.640275	0.462803	2.224702

18	6	0	-1.779065	0.729833	1.389808
19	6	0	-1.331757	1.582246	0.294870
20	6	0	0.937152	2.683653	-0.399395
21	6	0	1.877386	1.142504	2.263675
22	6	0	-0.661713	-0.301594	3.508364
23	6	0	-3.198237	0.376757	1.723072
24	6	0	-2.221048	2.206789	-0.736043
25	1	0	4.600895	-1.019660	-1.477373
26	1	0	-3.187892	-1.185092	-0.575224
27	1	0	-4.341009	-2.366455	-2.430990
28	1	0	-2.962145	-3.214422	-4.354940
29	1	0	-0.513321	-2.861760	-4.309281
30	1	0	1.557076	-2.550038	-4.088434
31	1	0	3.956725	-2.172490	-3.616990
32	1	0	2.796772	-0.283686	0.063027
33	1	0	0.524888	2.826793	-1.398291
34	1	0	1.950188	2.292832	-0.510142
35	1	0	1.022683	3.671150	0.066728
36	1	0	1.881776	1.873438	3.079025
37	1	0	2.643663	1.459356	1.554565
38	1	0	2.177266	0.181586	2.684627
39	1	0	-0.854218	0.393931	4.333576
40	1	0	0.286534	-0.800619	3.703080
41	1	0	-1.442344	-1.060941	3.519170
42	1	0	-3.284827	-0.642849	2.101757
43	1	0	-3.860537	0.479275	0.862106
44	1	0	-3.583182	1.048117	2.497775
45	1	0	-2.686337	3.110705	-0.328401
46	1	0	-3.029481	1.540282	-1.041761
47	1	0	-1.671632	2.495917	-1.632024

SCF Done: E(RB3LYP) = -1450.22379053 A.U. after 2 cycles
Low frequencies --- -12.9315 -6.9554 0.0013 0.0017 0.0020 6.7579
Zero-point correction= 0.384700 (Hartree/Particle)
Thermal correction to Energy= 0.409661
Thermal correction to Enthalpy= 0.410606
Thermal correction to Gibbs Free Energy= 0.329945
Sum of electronic and zero-point Energies= -1449.839090
Sum of electronic and thermal Energies= -1449.814129
Sum of electronic and thermal Enthalpies= -1449.813185
Sum of electronic and thermal Free Energies= -1449.893845

a2) Splitting of HCl from (**4a**$^{+}$); cyclometallation of the pyridine ring

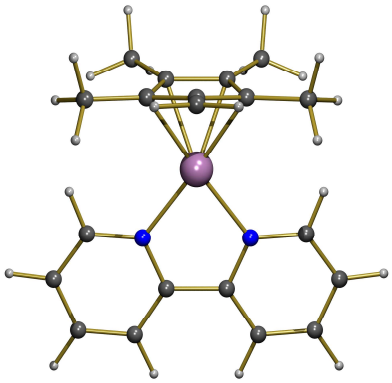


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.760877	-0.937801	0.001283
2	7	0	-0.091225	1.013574	0.005179
3	7	0	-3.431310	-0.318449	-0.000137
4	6	0	-3.267533	-2.713336	-0.005735
5	6	0	0.600130	2.167290	0.008280
6	6	0	-0.025318	3.405141	0.010719
7	6	0	-1.418464	3.450083	0.009928
8	6	0	-2.137592	2.259430	0.006713
9	6	0	-1.449919	1.051618	0.004366
10	6	0	-2.098076	-0.275168	0.000837
11	6	0	-1.237563	-1.395561	-0.001262
12	6	0	-1.876921	-2.642868	-0.004653
13	6	0	-4.001300	-1.525488	-0.003368
14	6	0	1.896994	-2.650415	-0.713340
15	6	0	1.896093	-2.654126	0.708552
16	6	0	2.573033	-1.425995	1.151069
17	6	0	3.056684	-0.724247	0.003374
18	6	0	2.574480	-1.419972	-1.148606
19	6	0	1.429085	-3.736257	-1.631173
20	6	0	1.427003	-3.744747	1.620100
21	6	0	2.820685	-1.063699	2.578901
22	6	0	3.925332	0.497359	0.007255
23	6	0	2.823919	-1.050323	-2.574242
24	1	0	-3.781509	-3.668244	-0.008364
25	1	0	1.678158	2.080633	0.008769
26	1	0	0.571848	4.308587	0.013177
27	1	0	-1.937364	4.402266	0.011788
28	1	0	-3.219790	2.235232	0.005954
29	1	0	-1.300974	-3.562630	-0.006465
30	1	0	-5.087094	-1.542900	-0.004149
31	1	0	0.949442	-3.336037	-2.525323
32	1	0	0.721774	-4.407935	-1.145562
33	1	0	2.282442	-4.340701	-1.957358
34	1	0	2.279986	-4.350621	1.944599
35	1	0	0.720675	-4.414135	1.129917
36	1	0	0.945785	-3.349219	2.515493
37	1	0	3.729807	-1.563717	2.933690
38	1	0	2.003031	-1.380369	3.227301
39	1	0	2.964009	0.008759	2.712160
40	1	0	3.766409	1.115316	0.892542
41	1	0	3.768948	1.119125	-0.875807
42	1	0	4.981428	0.207932	0.008168
43	1	0	3.733081	-1.549077	-2.930700
44	1	0	2.968077	0.022723	-2.701709
45	1	0	2.006739	-1.363031	-3.225163

SCF Done: E(RB3LYP) = -989.325600286 A.U. after 2 cycles
Low frequencies --- -22.5697 -9.9808 -5.7447 0.0002 0.0006 0.0008
Zero-point correction= 0.370652 (Hartree/Particle)
Thermal correction to Energy= 0.392790
Thermal correction to Enthalpy= 0.393734
Thermal correction to Gibbs Free Energy= 0.320569
Sum of electronic and zero-point Energies= -988.954949
Sum of electronic and thermal Energies= -988.932811
Sum of electronic and thermal Enthalpies= -988.931867
Sum of electronic and thermal Free Energies= -989.005031

a3) Splitting of HCl from (**4a**$^{+}$); deprotonation of Cp*



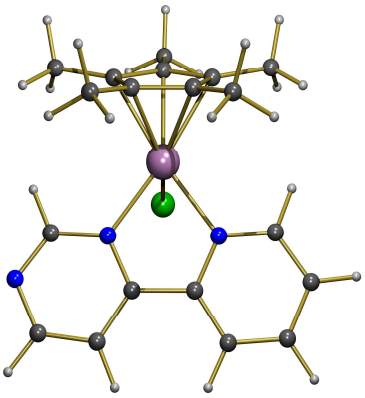
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.761155	-0.171895	0.130206
2	7	0	0.892593	1.112326	0.106278
3	6	0	3.180374	-1.626930	1.076183
4	6	0	1.778034	-3.560954	1.229269
5	6	0	0.835880	2.423839	-0.194724
6	6	0	1.952799	3.244352	-0.191657
7	6	0	3.188115	2.695222	0.140903
8	6	0	3.256721	1.343994	0.455390
9	6	0	2.098527	0.568655	0.431813
10	6	0	2.061600	-0.869858	0.732205
11	7	0	0.827197	-1.438403	0.638538
12	6	0	0.702917	-2.756322	0.886535
13	6	0	3.042140	-2.986040	1.327582
14	6	0	-2.684663	-1.221605	0.560473
15	6	0	-2.475209	-1.080157	-0.839928
16	6	0	-2.438184	0.356518	-1.139322
17	6	0	-2.625905	1.055374	0.086024
18	6	0	-3.039625	0.094801	1.129591
19	6	0	-2.898367	-2.504978	1.305389
20	6	0	-2.435525	-2.169960	-1.866428
21	6	0	-2.355526	0.942601	-2.515053
22	6	0	-2.768753	2.538246	0.254364
23	6	0	-3.514211	0.363911	2.362248
24	1	0	4.154933	-1.162289	1.147813
25	1	0	1.619111	-4.615733	1.417035
26	1	0	-0.143250	2.808801	-0.439834
27	1	0	1.847857	4.292620	-0.443041
28	1	0	4.082603	3.307007	0.156107
29	1	0	4.207987	0.899305	0.716401
30	1	0	-0.296383	-3.158568	0.805486
31	1	0	3.905500	-3.583830	1.595692
32	1	0	-2.410636	-2.491000	2.282927
33	1	0	-2.542051	-3.376426	0.754088
34	1	0	-3.968344	-2.659497	1.481475
35	1	0	-3.434763	-2.322164	-2.290200
36	1	0	-2.117248	-3.122812	-1.441962
37	1	0	-1.762103	-1.929607	-2.690107
38	1	0	-3.350621	0.963409	-2.973949
39	1	0	-1.704451	0.359773	-3.167832
40	1	0	-1.984977	1.968255	-2.503166
41	1	0	-2.375896	3.098467	-0.595422

42	1	0	-2.272223	2.891886	1.161037
43	1	0	-3.828000	2.802485	0.343274
44	1	0	-3.698647	1.379465	2.691592
45	1	0	-3.745172	-0.425278	3.067707

SCF Done: E(RB3LYP) = -989.328370125 A.U. after 1 cycles
Low frequencies --- -0.0001 0.0004 0.0006 7.2684 10.1595 11.0514
Zero-point correction= 0.371461 (Hartree/Particle)
Thermal correction to Energy= 0.393897
Thermal correction to Enthalpy= 0.394841
Thermal correction to Gibbs Free Energy= 0.320570
Sum of electronic and zero-point Energies= -988.956909
Sum of electronic and thermal Energies= -988.934473
Sum of electronic and thermal Enthalpies= -988.933529
Sum of electronic and thermal Free Energies= -989.007800

b1) [Chlorido(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)(2-pyrimidin-4-ylpyridine)iridium(III)]$^+$ (**4b**$^+$)



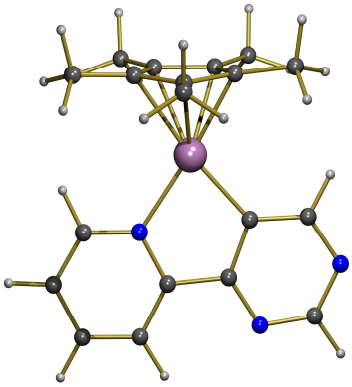
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.058243	-0.363728	0.185037
2	17	0	0.301963	-2.608457	1.024196
3	7	0	-0.963492	-1.330544	-1.422832
4	7	0	1.602645	-0.942639	-1.155537
5	7	0	3.895667	-1.155581	-1.719268
6	6	0	-2.288554	-1.538316	-1.444154
7	6	0	-2.918487	-2.237852	-2.464477
8	6	0	-2.148417	-2.754901	-3.501115
9	6	0	-0.773153	-2.562493	-3.471805
10	6	0	-0.202107	-1.852180	-2.417158
11	6	0	1.241713	-1.632308	-2.264364
12	6	0	2.221681	-2.089641	-3.142054
13	6	0	3.546121	-1.815325	-2.828873
14	6	0	2.915628	-0.761000	-0.927811
15	6	0	0.458727	1.793207	0.456942
16	6	0	0.883908	1.058672	1.642475
17	6	0	-0.286552	0.456912	2.222501
18	6	0	-1.415538	0.743771	1.381574
19	6	0	-0.950845	1.598966	0.295312
20	6	0	1.332469	2.680948	-0.374652
21	6	0	2.242060	1.098718	2.278256
22	6	0	-0.327325	-0.315921	3.500282
23	6	0	-2.840874	0.405666	1.702599
24	6	0	-1.824456	2.247545	-0.734105
25	1	0	-2.847650	-1.143778	-0.607684
26	1	0	-3.992196	-2.377039	-2.433085

27	1	0	-2.607408	-3.308450	-4.311900
28	1	0	-0.151220	-2.972166	-4.256978
29	1	0	1.973533	-2.645828	-4.036028
30	1	0	4.354601	-2.138110	-3.477047
31	1	0	3.179216	-0.254261	-0.009138
32	1	0	0.946641	2.807708	-1.386295
33	1	0	2.353747	2.304610	-0.450902
34	1	0	1.391561	3.674691	0.082215
35	1	0	2.250599	1.817860	3.103973
36	1	0	3.015932	1.415880	1.577933
37	1	0	2.529119	0.128325	2.685766
38	1	0	-0.551066	0.371831	4.324094
39	1	0	0.623634	-0.800628	3.715820
40	1	0	-1.096385	-1.087001	3.487226
41	1	0	-2.940616	-0.611159	2.085242
42	1	0	-3.494718	0.511617	0.835559
43	1	0	-3.225721	1.084171	2.471095
44	1	0	-2.266551	3.161782	-0.323548
45	1	0	-2.650154	1.603297	-1.041234
46	1	0	-1.267921	2.526128	-1.629052

SCF Done: E(RB3LYP) = -1466.26141895 A.U. after 2 cycles
Low frequencies --- -10.7751 -6.4664 -0.0004 0.0002 0.0014 9.5621
Zero-point correction= 0.372855 (Hartree/Particle)
Thermal correction to Energy= 0.397697
Thermal correction to Enthalpy= 0.398641
Thermal correction to Gibbs Free Energy= 0.317930
Sum of electronic and zero-point Energies= -1465.888564
Sum of electronic and thermal Energies= -1465.863722
Sum of electronic and thermal Enthalpies= -1465.862778
Sum of electronic and thermal Free Energies= -1465.943489

b2) Splitting of HCl from (**4b**$^{+}$); cyclometallation of the pyrimidine ring



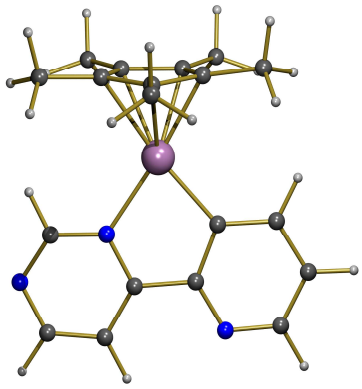
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.930078	-0.944816	-0.032148
2	7	0	0.071573	1.004492	-0.195029
3	7	0	-3.229361	-0.301296	0.399959
4	7	0	-3.038909	-2.659505	0.696399
5	6	0	0.750864	2.135924	-0.448666
6	6	0	0.122143	3.369870	-0.548632
7	6	0	-1.258805	3.434575	-0.380309
8	6	0	-1.967221	2.264261	-0.119056
9	6	0	-1.276836	1.063651	-0.032545
10	6	0	-1.908536	-0.245855	0.233174

11	6	0	-1.049384	-1.360404	0.286845
12	6	0	-1.716858	-2.569396	0.525892
13	6	0	-3.729156	-1.518918	0.628449
14	6	0	2.118501	-2.569719	-0.845808
15	6	0	2.029934	-2.729912	0.568205
16	6	0	2.624973	-1.538991	1.161936
17	6	0	3.212538	-0.730468	0.105885
18	6	0	2.867385	-1.328749	-1.124485
19	6	0	1.680403	-3.545909	-1.890490
20	6	0	1.546711	-3.928436	1.325552
21	6	0	2.770514	-1.290119	2.626625
22	6	0	4.045055	0.496309	0.324198
23	6	0	3.234833	-0.860699	-2.496134
24	1	0	1.821331	2.036693	-0.569306
25	1	0	0.710118	4.255897	-0.754011
26	1	0	-1.777689	4.383952	-0.451919
27	1	0	-3.041088	2.254632	0.018858
28	1	0	-1.176826	-3.510304	0.584895
29	1	0	-4.803044	-1.586696	0.771365
30	1	0	1.301729	-3.045044	-2.782531
31	1	0	0.901009	-4.214252	-1.525845
32	1	0	2.530877	-4.164643	-2.198823
33	1	0	2.403329	-4.531354	1.644970
34	1	0	0.912075	-4.570555	0.715229
35	1	0	0.987836	-3.654752	2.221325
36	1	0	3.690292	-1.765431	2.988739
37	1	0	1.939976	-1.710545	3.193952
38	1	0	2.839239	-0.226592	2.856895
39	1	0	3.650480	1.127263	1.123094
40	1	0	4.130179	1.102482	-0.578548
41	1	0	5.062264	0.213372	0.614133
42	1	0	4.108659	-1.414744	-2.857127
43	1	0	3.488218	0.199276	-2.517295
44	1	0	2.429600	-1.029545	-3.212869

```
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1005.36630080     A.U. after    2 cycles
Low frequencies ---  -10.7190    0.0007    0.0008    0.0009    4.9599   10.2231
Zero-point correction=                           0.359198 (Hartree/Particle)
 Thermal correction to Energy=                    0.382040
 Thermal correction to Enthalpy=                  0.382984
 Thermal correction to Gibbs Free Energy=         0.306914
 Sum of electronic and zero-point Energies=          -1005.007103
 Sum of electronic and thermal Energies=             -1004.984261
 Sum of electronic and thermal Enthalpies=           -1004.983317
 Sum of electronic and thermal Free Energies=        -1005.059387
```

b3) Splitting of HCl from (**4b**$^{+}$); cyclometallation of the pyridine ring

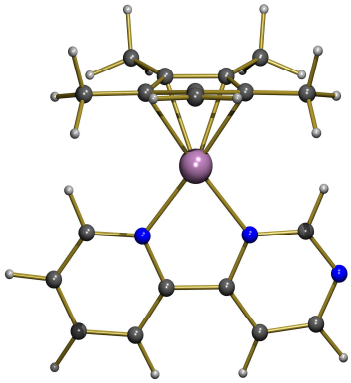


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.419688	0.033554	0.014471
2	7	0	3.610691	1.362682	-0.150346
3	7	0	1.218499	-1.317976	-0.091775
4	7	0	2.176382	-3.481415	-0.206567
5	6	0	3.582711	2.695594	-0.120087
6	6	0	2.394652	3.427335	-0.043378
7	6	0	1.182388	2.744283	0.008417
8	6	0	1.165182	1.342744	-0.018020
9	6	0	2.436286	0.730556	-0.101280
10	6	0	2.449560	-0.741048	-0.139889
11	6	0	3.582198	-1.539148	-0.221424
12	6	0	3.391493	-2.916373	-0.251584
13	6	0	1.145581	-2.659881	-0.129068
14	6	0	-2.086573	0.038314	1.381736
15	6	0	-2.306515	-1.150728	0.569605
16	6	0	-2.396295	-0.733506	-0.773726
17	6	0	-2.299379	0.738681	-0.810057
18	6	0	-2.180898	1.214710	0.530168
19	6	0	-1.975239	0.058208	2.870229
20	6	0	-2.430231	-2.544766	1.105279
21	6	0	-2.615178	-1.590346	-1.979805
22	6	0	-2.461686	1.564721	-2.045529
23	6	0	-2.269424	2.630763	1.009965
24	1	0	4.544474	3.197951	-0.159271
25	1	0	2.427560	4.511207	-0.024154
26	1	0	0.258544	3.308672	0.070526
27	1	0	4.562117	-1.081599	-0.259804
28	1	0	4.234247	-3.597943	-0.314463
29	1	0	0.153236	-3.092737	-0.090368
30	1	0	-1.420317	0.926949	3.224743
31	1	0	-1.491293	-0.838993	3.257125
32	1	0	-2.978683	0.105664	3.310713
33	1	0	-3.425806	-2.693180	1.536314
34	1	0	-1.706898	-2.750736	1.896533
35	1	0	-2.305225	-3.298543	0.327200
36	1	0	-3.670462	-1.559219	-2.273149
37	1	0	-2.357713	-2.633671	-1.797880
38	1	0	-2.033952	-1.244238	-2.836120
39	1	0	-1.970551	1.108906	-2.906241
40	1	0	-2.059359	2.570008	-1.923204
41	1	0	-3.526095	1.659982	-2.289185
42	1	0	-3.276966	2.829746	1.389842
43	1	0	-2.082324	3.345919	0.208972
44	1	0	-1.568517	2.837080	1.819956

SCF Done: E(RB3LYP) = -1005.36505542 A.U. after 1 cycles
Low frequencies --- -10.7735 0.0001 0.0003 0.0006 3.0730 10.2988
Zero-point correction= 0.358991 (Hartree/Particle)
Thermal correction to Energy= 0.381862
Thermal correction to Enthalpy= 0.382806
Thermal correction to Gibbs Free Energy= 0.306707
Sum of electronic and zero-point Energies= -1005.006064
Sum of electronic and thermal Energies= -1004.983194
Sum of electronic and thermal Enthalpies= -1004.982250
Sum of electronic and thermal Free Energies= -1005.058349

b4) Splitting of HCl from (**4b**$^{+}$); deprotonation of Cp*

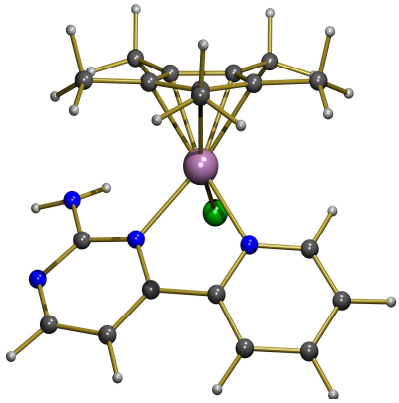


Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.978594	0.517942	0.191204
2	7	0	-0.662115	1.808148	0.244091
3	7	0	-1.627934	3.979777	0.292377
4	7	0	-0.660671	-0.789168	0.229593
5	6	0	-3.056856	-1.004469	0.240542
6	6	0	-1.680598	-2.961599	0.246265
7	6	0	-0.597937	3.156356	0.268036
8	6	0	-2.846315	3.425654	0.288917
9	6	0	-3.033348	2.049609	0.264559
10	6	0	-1.900514	1.241579	0.242281
11	6	0	-1.902338	-0.225374	0.232295
12	6	0	-0.568672	-2.132283	0.234647
13	6	0	-2.949801	-2.389976	0.247958
14	6	0	2.818545	-0.637694	-0.320411
15	6	0	2.848959	-0.201227	1.033378
16	6	0	2.839068	1.266465	1.027546
17	6	0	2.804912	1.691696	-0.329899
18	6	0	3.040493	0.524854	-1.204711
19	6	0	2.924272	-2.052541	-0.804613
20	6	0	3.001474	-1.050578	2.257089
21	6	0	2.980603	2.128564	2.243844
22	6	0	2.890521	3.103817	-0.825568
23	6	0	3.278115	0.521330	-2.532473
24	1	0	-4.032701	-0.536209	0.241517
25	1	0	-1.544772	-4.036212	0.250570
26	1	0	0.394690	3.585922	0.265536
27	1	0	-3.690548	4.107378	0.305691
28	1	0	-4.031645	1.632524	0.263665
29	1	0	0.433124	-2.536702	0.225981
30	1	0	-3.839129	-3.009174	0.254185
31	1	0	2.282088	-2.232988	-1.669851
32	1	0	2.675451	-2.781248	-0.031685
33	1	0	3.952569	-2.263523	-1.117146
34	1	0	4.060216	-1.125367	2.530208
35	1	0	2.636916	-2.066404	2.100701
36	1	0	2.470204	-0.631901	3.112633
37	1	0	4.038918	2.225862	2.511437
38	1	0	2.461055	1.707392	3.105424
39	1	0	2.596247	3.135923	2.080905
40	1	0	2.633714	3.835901	-0.058949
41	1	0	2.244198	3.269537	-1.690458

```
     42          1           0        3.915542    3.324570   -1.142252
     43          1           0        3.382584    1.442006   -3.093843
     44          1           0        3.392823   -0.402170   -3.087217
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1005.36604651     A.U. after    1 cycles
Low frequencies ---   -0.5893   -0.0005   -0.0004   -0.0003    9.7853   10.8216
Zero-point correction=                           0.359438 (Hartree/Particle)
 Thermal correction to Energy=                    0.381806
 Thermal correction to Enthalpy=                  0.382750
 Thermal correction to Gibbs Free Energy=         0.308501
 Sum of electronic and zero-point Energies=          -1005.006609
 Sum of electronic and thermal Energies=             -1004.984241
 Sum of electronic and thermal Enthalpies=           -1004.983296
 Sum of electronic and thermal Free Energies=        -1005.057545
```

c1) [(2-(2-Aminopyrimidin-4-yl)pyridine)(chlorido)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)-iridium(III)]$^+$ (**4c**$^+$)



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                          Input orientation:
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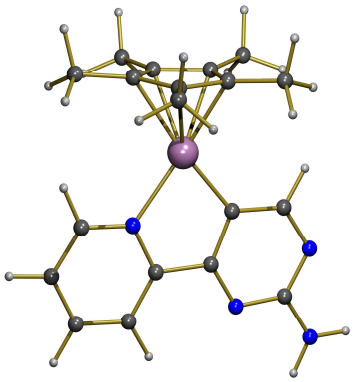
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1         77           0       -0.345635   -0.472745    0.307875
      2         17           0        0.355423   -2.553748    1.327333
      3          7           0       -1.458450   -1.649737   -1.083111
      4          7           0        1.044037   -0.973379   -1.241441
      5          7           0        3.194696   -0.886566   -2.254451
      6          7           0        2.969721   -0.663528    0.032321
      7          6           0       -2.672009   -2.163398   -0.833972
      8          6           0       -3.404623   -2.842943   -1.798391
      9          6           0       -2.859841   -3.000320   -3.068547
     10          6           0       -1.584780   -2.506306   -3.317407
     11          6           0       -0.895163   -1.847478   -2.301550
     12          6           0        0.511849   -1.426161   -2.404623
     13          6           0        1.293555   -1.541344   -3.543330
     14          6           0        2.640212   -1.190937   -3.416491
     15          6           0        2.395536   -0.853412   -1.177610
     16          6           0        0.179840    1.660679    0.600838
     17          6           0        0.291436    0.951187    1.850010
     18          6           0       -1.034417    0.454380    2.191261
     19          6           0       -1.929454    0.828966    1.143474
     20          6           0       -1.178793    1.560364    0.132556
     21          6           0        1.274620    2.429918   -0.069363
     22          6           0        1.479807    0.906252    2.761769
     23          6           0       -1.380416   -0.250641    3.464549
     24          6           0       -3.413645    0.629818    1.135679
     25          6           0       -1.763735    2.256622   -1.059201
```

26	1	0	2.486466	-1.066210	0.827180
27	1	0	3.977084	-0.740369	0.037083
28	1	0	-3.050383	-2.028965	0.169618
29	1	0	-4.379063	-3.243090	-1.546421
30	1	0	-3.406996	-3.519216	-3.847044
31	1	0	-1.123273	-2.654006	-4.284965
32	1	0	0.895213	-1.878849	-4.489473
33	1	0	3.298570	-1.186738	-4.280314
34	1	0	1.146000	2.472794	-1.151464
35	1	0	2.257471	2.011519	0.141846
36	1	0	1.265794	3.461399	0.299726
37	1	0	1.383516	1.669645	3.541208
38	1	0	2.410319	1.100321	2.229013
39	1	0	1.565815	-0.060401	3.260769
40	1	0	-1.461749	0.478731	4.277849
41	1	0	-0.617191	-0.978443	3.739889
42	1	0	-2.331245	-0.778887	3.397618
43	1	0	-3.721319	-0.222333	1.742460
44	1	0	-3.811887	0.500205	0.128597
45	1	0	-3.898591	1.516135	1.558878
46	1	0	-2.138765	3.246629	-0.777349
47	1	0	-2.601566	1.702345	-1.484701
48	1	0	-1.025992	2.401241	-1.849180

```
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1521.65455192     A.U. after    2 cycles
Low frequencies ---   -15.4136   -9.8299   -8.2781   -0.0011   -0.0008   -0.0004
Zero-point correction=                           0.390376 (Hartree/Particle)
 Thermal correction to Energy=                    0.416222
 Thermal correction to Enthalpy=                  0.417166
 Thermal correction to Gibbs Free Energy=         0.335462
 Sum of electronic and zero-point Energies=          -1521.264176
 Sum of electronic and thermal Energies=             -1521.238330
 Sum of electronic and thermal Enthalpies=           -1521.237386
 Sum of electronic and thermal Free Energies=        -1521.319090
```

c2) Splitting of HCl from (**4c**$^{+}$); cyclometallation of the pyrimidine ring



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                          Input orientation:
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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type              X           Y           Z
 ---------------------------------------------------------------------
      1         77           0        1.262345   -0.950183    0.000338
      2          7           0        0.420696    1.022361    0.003386
      3          7           0       -2.905730   -0.319477    0.000586
      4          7           0       -2.723455   -2.720179   -0.004030
      5          7           0       -4.769470   -1.671398   -0.001890
      6          6           0        1.113941    2.171022    0.005328
      7          6           0        0.491452    3.414199    0.007245
```

8	6	0	-0.898456	3.468255	0.007165
9	6	0	-1.622006	2.277377	0.005130
10	6	0	-0.936621	1.071779	0.003241
11	6	0	-1.582596	-0.259928	0.000791
12	6	0	-0.714585	-1.374680	-0.001108
13	6	0	-1.405264	-2.604530	-0.003617
14	6	0	-3.428868	-1.565970	-0.001786
15	6	0	2.409682	-2.651471	-0.715294
16	6	0	2.407668	-2.655901	0.708690
17	6	0	3.081865	-1.428899	1.153359
18	6	0	3.558145	-0.725024	0.004107
19	6	0	3.085603	-1.421969	-1.150659
20	6	0	1.952667	-3.746008	-1.628887
21	6	0	1.948499	-3.756220	1.614254
22	6	0	3.336499	-1.072359	2.582215
23	6	0	4.417554	0.503499	0.009277
24	6	0	3.344535	-1.057324	-2.576704
25	1	0	-5.344445	-0.845580	-0.000826
26	1	0	-5.198125	-2.582312	-0.003807
27	1	0	2.191883	2.083959	0.005359
28	1	0	1.093998	4.314220	0.008764
29	1	0	-1.412929	4.422706	0.008652
30	1	0	-2.704293	2.257950	0.004949
31	1	0	-0.864067	-3.547751	-0.005403
32	1	0	1.488641	-3.356617	-2.535956
33	1	0	1.236244	-4.410096	-1.146120
34	1	0	2.809802	-4.356271	-1.934209
35	1	0	2.805007	-4.368067	1.918145
36	1	0	1.233714	-4.417590	1.125377
37	1	0	1.481818	-3.372646	2.522440
38	1	0	4.240028	-1.582143	2.937060
39	1	0	2.514640	-1.380517	3.229572
40	1	0	3.490548	-0.001633	2.717478
41	1	0	4.253633	1.120240	0.894717
42	1	0	4.258462	1.124246	-0.874227
43	1	0	5.475701	0.221829	0.011505
44	1	0	4.248050	-1.566595	-2.932305
45	1	0	3.500786	0.013901	-2.705314
46	1	0	2.523806	-1.360203	-3.227989

SCF Done: E(RB3LYP) = -1060.76468101 A.U. after 2 cycles

Low frequencies --- -12.3141 -8.8136 -0.0007 -0.0005 0.0005 6.6733

Zero-point correction= 0.375894 (Hartree/Particle)

Thermal correction to Energy= 0.400329

Thermal correction to Enthalpy= 0.401273

Thermal correction to Gibbs Free Energy= 0.320781

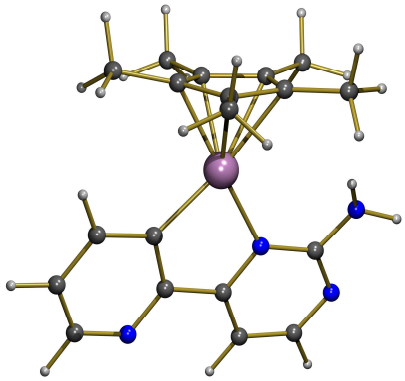
Sum of electronic and zero-point Energies= -1060.388787

Sum of electronic and thermal Energies= -1060.364352

Sum of electronic and thermal Enthalpies= -1060.363408

Sum of electronic and thermal Free Energies= -1060.443900

c3) Splitting of HCl from (**4c**$^{+}$); cyclometallation of the pyridine ring



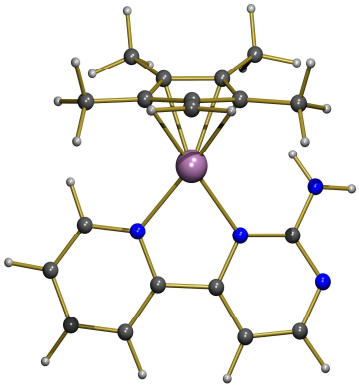
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.409516	-0.118081	-0.050356
2	7	0	-3.577321	-1.544547	-0.046415
3	7	0	-1.259654	1.204119	-0.234724
4	7	0	-2.353730	3.329041	-0.243303
5	7	0	-0.104254	3.200020	-0.631878
6	6	0	-3.515357	-2.873913	-0.104330
7	6	0	-2.308883	-3.572267	-0.201976
8	6	0	-1.115008	-2.857674	-0.211048
9	6	0	-1.135400	-1.457109	-0.135946
10	6	0	-2.420546	-0.877531	-0.077608
11	6	0	-2.478178	0.591764	-0.091870
12	6	0	-3.639251	1.326615	0.005812
13	6	0	-3.510768	2.718254	-0.043368
14	6	0	-1.262884	2.556643	-0.369345
15	6	0	1.928442	-0.360750	1.450549
16	6	0	2.247588	0.947697	0.870292
17	6	0	2.511207	0.752711	-0.494923
18	6	0	2.373854	-0.682827	-0.787065
19	6	0	2.127454	-1.376485	0.441536
20	6	0	1.674189	-0.607189	2.902201
21	6	0	2.316379	2.217959	1.658951
22	6	0	2.960930	1.765684	-1.504182
23	6	0	2.656589	-1.302886	-2.117397
24	6	0	2.215345	-2.851785	0.683306
25	1	0	0.665277	2.688555	-1.028289
26	1	0	-0.185760	4.179711	-0.858708
27	1	0	-4.464007	-3.401779	-0.078990
28	1	0	-2.312671	-4.655000	-0.265186
29	1	0	-0.179703	-3.399543	-0.281142
30	1	0	-4.589873	0.826067	0.124745
31	1	0	-4.377106	3.363748	0.070762
32	1	0	1.150258	-1.547567	3.071894
33	1	0	1.091201	0.195008	3.356278
34	1	0	2.630430	-0.659727	3.436687
35	1	0	3.229304	2.228359	2.264210
36	1	0	1.474063	2.317944	2.345614
37	1	0	2.331119	3.103539	1.025768
38	1	0	4.004761	1.577974	-1.776676
39	1	0	2.918314	2.785129	-1.118850
40	1	0	2.386390	1.717880	-2.433148
41	1	0	2.304967	-0.678121	-2.939617

42	1	0	2.191524	-2.283207	-2.217764
43	1	0	3.737724	-1.433928	-2.244526
44	1	0	3.211065	-3.096962	1.067669
45	1	0	2.076155	-3.428106	-0.231447
46	1	0	1.488808	-3.197207	1.419149

SCF Done: E(RB3LYP) = -1060.75314114 A.U. after 1 cycles
Low frequencies --- -16.6464 -8.2296 -0.0001 0.0004 0.0007 4.0843
Zero-point correction= 0.375954 (Hartree/Particle)
Thermal correction to Energy= 0.400113
Thermal correction to Enthalpy= 0.401057
Thermal correction to Gibbs Free Energy= 0.322859
Sum of electronic and zero-point Energies= -1060.377187
Sum of electronic and thermal Energies= -1060.353028
Sum of electronic and thermal Enthalpies= -1060.352084
Sum of electronic and thermal Free Energies= -1060.430282

c4) Splitting of HCl from (**4c**$^{+}$); deprotonation of Cp*



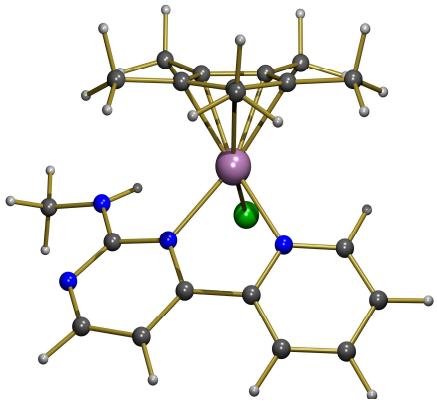
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.789051	0.159947	0.740268
2	7	0	-0.853046	1.451970	1.093535
3	7	0	-1.912531	3.593938	1.202703
4	7	0	-0.812801	-1.148535	1.051875
5	6	0	-3.200189	-1.396627	0.959997
6	6	0	-1.805677	-3.324241	1.226541
7	6	0	-0.840748	2.795408	1.318326
8	6	0	-3.075229	3.018933	0.945453
9	6	0	-3.229090	1.633494	0.855701
10	6	0	-2.077866	0.869222	0.945744
11	6	0	-2.055704	-0.601415	0.958459
12	6	0	-0.704625	-2.482590	1.194650
13	6	0	-3.077501	-2.774121	1.090602
14	6	0	2.343811	-1.062873	-0.262480
15	6	0	2.802522	-0.584338	0.999568
16	6	0	2.847302	0.878789	0.922039
17	6	0	2.403319	1.255900	-0.376145
18	6	0	2.353652	0.051221	-1.232860
19	6	0	2.264258	-2.497466	-0.690808
20	6	0	3.306650	-1.396361	2.152900
21	6	0	3.443729	1.761873	1.977649
22	6	0	2.357810	2.641048	-0.944235
23	6	0	2.233868	-0.009334	-2.571984
24	7	0	0.319436	3.379666	1.673303
25	1	0	-4.179471	-0.944867	0.873061

26	1	0	-1.660400	-4.390423	1.350138
27	1	0	-3.926030	3.683477	0.826770
28	1	0	-4.206102	1.194723	0.712868
29	1	0	0.300265	-2.868900	1.281065
30	1	0	-3.959064	-3.404498	1.097015
31	1	0	1.396085	-2.684208	-1.326763
32	1	0	2.230235	-3.189592	0.151358
33	1	0	3.153524	-2.755660	-1.275904
34	1	0	4.391270	-1.532573	2.070846
35	1	0	2.860174	-2.391407	2.182645
36	1	0	3.107482	-0.912981	3.110501
37	1	0	4.531148	1.629270	1.995565
38	1	0	3.078706	1.522498	2.978954
39	1	0	3.268208	2.820701	1.780903
40	1	0	2.241999	3.408737	-0.181202
41	1	0	1.534067	2.750544	-1.652429
42	1	0	3.285715	2.847749	-1.488923
43	1	0	2.209215	0.885248	-3.182545
44	1	0	2.174419	-0.956249	-3.095420
45	1	0	1.069860	2.807015	2.023611
46	1	0	0.275293	4.346888	1.955086

SCF Done: E(RB3LYP) = -1060.75400602 A.U. after 1 cycles
Low frequencies --- -7.3053 -0.0007 -0.0005 0.0002 3.0256 10.2663
Zero-point correction= 0.376657 (Hartree/Particle)
Thermal correction to Energy= 0.400232
Thermal correction to Enthalpy= 0.401176
Thermal correction to Gibbs Free Energy= 0.325142
Sum of electronic and zero-point Energies= -1060.377349
Sum of electronic and thermal Energies= -1060.353774
Sum of electronic and thermal Enthalpies= -1060.352830
Sum of electronic and thermal Free Energies= -1060.428864

d1) [Chlorido(2-(2-methylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopentadienyl)iridium(III)]$^+$ (**4d$^+$**)



Input orientation:

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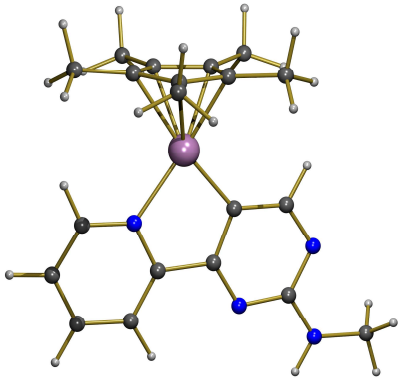
1	77	0	-0.485850	0.130390	-0.133404
2	17	0	-0.195239	-0.203975	-2.514211
3	7	0	0.936634	1.708939	-0.287809
4	7	0	1.419908	-0.821532	0.057267
5	7	0	2.808454	-2.727946	0.401723
6	7	0	0.729426	-2.948099	-0.587130
7	6	0	0.640070	2.951538	-0.696424

8	6	0	1.576479	3.976520	-0.698988
9	6	0	2.870350	3.704446	-0.266366
10	6	0	3.190701	2.408253	0.119232
11	6	0	2.208315	1.420359	0.085038
12	6	0	2.471000	-0.009369	0.322112
13	6	0	3.696923	-0.531468	0.708113
14	6	0	3.781863	-1.922627	0.794087
15	6	0	1.671020	-2.162383	-0.036811
16	6	0	0.966504	-4.364969	-0.859846
17	6	0	-1.594728	-0.928366	1.467985
18	6	0	-2.286142	-1.074674	0.212166
19	6	0	-2.692249	0.255294	-0.221531
20	6	0	-2.220219	1.196720	0.741694
21	6	0	-1.512211	0.473052	1.788707
22	6	0	-1.096367	-2.044165	2.331798
23	6	0	-2.720682	-2.352080	-0.440488
24	6	0	-3.523166	0.539567	-1.432672
25	6	0	-2.511107	2.665509	0.762106
26	6	0	-0.993792	1.065590	3.064787
27	1	0	0.066987	-2.460175	-1.178590
28	1	0	-0.373730	3.112599	-1.035017
29	1	0	1.289208	4.963013	-1.041708
30	1	0	3.624946	4.482276	-0.249825
31	1	0	4.200752	2.164375	0.421034
32	1	0	4.545784	0.093589	0.945151
33	1	0	4.682026	-2.402474	1.167849
34	1	0	1.758259	-4.508812	-1.599198
35	1	0	0.041031	-4.794715	-1.240871
36	1	0	1.250874	-4.882722	0.054638
37	1	0	-0.221717	-1.753318	2.914505
38	1	0	-0.839256	-2.928891	1.751325
39	1	0	-1.880703	-2.328828	3.041585
40	1	0	-3.765354	-2.565781	-0.190532
41	1	0	-2.127878	-3.203550	-0.106332
42	1	0	-2.651461	-2.291134	-1.528054
43	1	0	-4.570776	0.294401	-1.226753
44	1	0	-3.198871	-0.054372	-2.287344
45	1	0	-3.479747	1.588445	-1.725139
46	1	0	-2.711411	3.063045	-0.233279
47	1	0	-1.701533	3.243563	1.209611
48	1	0	-3.406055	2.847938	1.366718
49	1	0	-1.800263	1.147268	3.801857
50	1	0	-0.589566	2.067784	2.915383
51	1	0	-0.208385	0.453990	3.510147

SCF Done: E(RB3LYP) = -1560.97058896 A.U. after 2 cycles
Low frequencies --- -6.6349 0.0010 0.0012 0.0015 5.4385 9.6164
Zero-point correction= 0.418473 (Hartree/Particle)
Thermal correction to Energy= 0.445965
Thermal correction to Enthalpy= 0.446910
Thermal correction to Gibbs Free Energy= 0.361825
Sum of electronic and zero-point Energies= -1560.552116
Sum of electronic and thermal Energies= -1560.524624
Sum of electronic and thermal Enthalpies= -1560.523679
Sum of electronic and thermal Free Energies= -1560.608764

d2) Splitting of HCl from (**4d**$^{+}$); cyclometallation of the pyrimidine ring



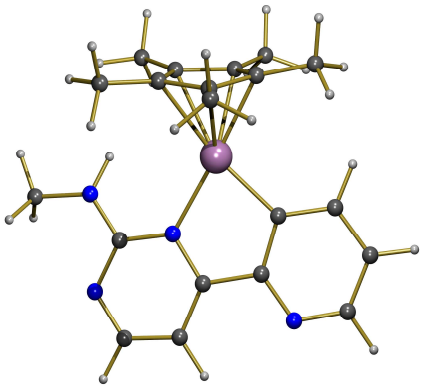
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	1.602223	-0.950172	0.006442
2	7	0	0.751803	1.018323	-0.009176
3	7	0	-2.565160	-0.339546	-0.002878
4	7	0	-2.369110	-2.742883	0.016089
5	7	0	-4.424278	-1.688906	0.004752
6	6	0	1.441282	2.169224	-0.017302
7	6	0	0.815010	3.410334	-0.027457
8	6	0	-0.575172	3.460232	-0.029304
9	6	0	-1.294656	2.267143	-0.020991
10	6	0	-0.605567	1.063636	-0.011051
11	6	0	-1.246593	-0.270887	-0.001671
12	6	0	-0.368286	-1.382394	0.008007
13	6	0	-1.050648	-2.615391	0.016896
14	6	0	-3.084688	-1.594908	0.006057
15	6	0	-5.160753	-2.945051	0.013543
16	6	0	2.755490	-2.651025	-0.697516
17	6	0	2.748637	-2.648879	0.726979
18	6	0	3.421663	-1.420593	1.167863
19	6	0	3.899733	-0.721364	0.016396
20	6	0	3.434648	-1.425068	-1.136625
21	6	0	2.296830	-3.746761	-1.609190
22	6	0	2.282798	-3.742206	1.637994
23	6	0	3.679773	-1.062984	2.596178
24	6	0	4.755151	0.510222	0.019494
25	6	0	3.707328	-1.073885	-2.563894
26	1	0	-4.927259	-0.814994	-0.002524
27	1	0	2.519254	2.084011	-0.015474
28	1	0	1.414824	4.312179	-0.033723
29	1	0	-1.092679	4.413003	-0.037118
30	1	0	-2.376890	2.244188	-0.022019
31	1	0	-0.501628	-3.554291	0.025295
32	1	0	-6.225186	-2.716016	0.009599
33	1	0	-4.924798	-3.530868	0.903682
34	1	0	-4.921364	-3.545165	-0.866080
35	1	0	1.823472	-3.356497	-2.511124
36	1	0	1.586287	-4.413960	-1.122265
37	1	0	3.153669	-4.353325	-1.922432
38	1	0	3.137482	-4.346075	1.962079
39	1	0	1.578525	-4.412624	1.146352
40	1	0	1.799618	-3.349510	2.533640
41	1	0	4.579152	-1.580253	2.950841

42	1	0	2.856039	-1.363378	3.244813
43	1	0	3.844021	0.006367	2.731507
44	1	0	4.580935	1.131930	0.899335
45	1	0	4.599293	1.123688	-0.869493
46	1	0	5.814569	0.233528	0.031709
47	1	0	4.608408	-1.595147	-2.908162
48	1	0	3.875967	-0.005572	-2.701980
49	1	0	2.888833	-1.374429	-3.219092

SCF Done: E(RB3LYP) = -1100.08176541 A.U. after 1 cycles
Low frequencies --- -0.0006 -0.0004 -0.0003 1.0990 5.1689 5.5657
Zero-point correction= 0.404489 (Hartree/Particle)
Thermal correction to Energy= 0.430419
Thermal correction to Enthalpy= 0.431364
Thermal correction to Gibbs Free Energy= 0.346976
Sum of electronic and zero-point Energies= -1099.677277
Sum of electronic and thermal Energies= -1099.651346
Sum of electronic and thermal Enthalpies= -1099.650402
Sum of electronic and thermal Free Energies= -1099.734789

d3) Splitting of HCl from (**4d**$^{+}$); cyclometallation of the pyridine ring



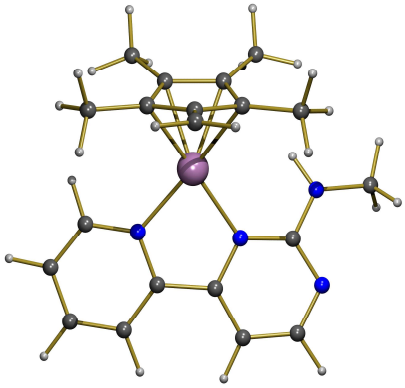
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.885704	-0.492850	-0.634146
2	7	0	-1.462005	3.671819	-1.143621
3	7	0	0.743799	0.827218	-1.040737
4	7	0	3.047715	1.454913	-1.259031
5	7	0	2.449791	-0.755081	-1.264046
6	6	0	-2.776684	3.886007	-1.143667
7	6	0	-3.711342	2.853497	-1.034483
8	6	0	-3.257538	1.545582	-0.894822
9	6	0	-1.880575	1.278658	-0.874741
10	6	0	-1.048404	2.407403	-1.024824
11	6	0	0.398623	2.151303	-1.086055
12	6	0	1.350929	3.140815	-1.196627
13	6	0	2.684907	2.726781	-1.252509
14	6	0	2.072867	0.530255	-1.185346
15	6	0	3.833366	-1.172009	-1.473879
16	6	0	-1.345182	-1.785676	1.022608
17	6	0	-0.189242	-2.446422	0.412812
18	6	0	-0.533613	-2.765199	-0.911395
19	6	0	-1.922513	-2.332361	-1.140371
20	6	0	-2.451677	-1.835469	0.093080
21	6	0	-1.422402	-1.359774	2.452846
22	6	0	1.082906	-2.741812	1.147008

23	6	0	0.281597	-3.500959	-1.931556
24	6	0	-2.685230	-2.582942	-2.401638
25	6	0	-3.887219	-1.569522	0.425974
26	1	0	1.715193	-1.440364	-1.313395
27	1	0	-3.096364	4.919310	-1.240571
28	1	0	-4.772357	3.077378	-1.055912
29	1	0	-3.984215	0.747618	-0.806215
30	1	0	1.053096	4.179334	-1.225105
31	1	0	3.492181	3.452603	-1.301389
32	1	0	4.211712	-0.826931	-2.437782
33	1	0	3.867538	-2.260643	-1.446919
34	1	0	4.477617	-0.776103	-0.689585
35	1	0	-2.187404	-0.599971	2.611723
36	1	0	-0.470785	-0.966748	2.812907
37	1	0	-1.679360	-2.222913	3.078920
38	1	0	0.889027	-3.455859	1.953753
39	1	0	1.511257	-1.847225	1.603775
40	1	0	1.842943	-3.184057	0.503529
41	1	0	-0.158713	-4.486160	-2.117116
42	1	0	1.307845	-3.672922	-1.603932
43	1	0	0.311148	-2.983563	-2.893463
44	1	0	-2.061996	-2.445842	-3.286405
45	1	0	-3.547934	-1.923771	-2.494254
46	1	0	-3.053653	-3.615417	-2.415997
47	1	0	-4.308604	-2.444443	0.932287
48	1	0	-4.491984	-1.395113	-0.463908
49	1	0	-4.008357	-0.717376	1.095220

```
SCF Done:  E(RB3LYP) =  -1100.06940728     A.U. after    2 cycles
Low frequencies ---   -11.7327   -0.0003    0.0008    0.0009    7.9261    9.2559
Zero-point correction=                           0.404157 (Hartree/Particle)
 Thermal correction to Energy=                    0.429977
 Thermal correction to Enthalpy=                  0.430921
 Thermal correction to Gibbs Free Energy=         0.348773
 Sum of electronic and zero-point Energies=          -1099.665251
 Sum of electronic and thermal Energies=             -1099.639431
 Sum of electronic and thermal Enthalpies=           -1099.638486
 Sum of electronic and thermal Free Energies=        -1099.720635
```

d4) Splitting of HCl from (**4d**$^{+}$); deprotonation of Cp*



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.789263	-0.037314	0.663721
2	7	0	-0.866590	1.257522	0.929363
3	7	0	-1.951664	3.393528	0.856475

4	7	0	-0.795984	-1.339531	1.066193
5	6	0	-3.180444	-1.617018	1.012998
6	6	0	-1.763847	-3.506073	1.409336
7	6	0	-0.869190	2.622387	1.055853
8	6	0	-3.104384	2.782266	0.640609
9	6	0	-3.243522	1.393220	0.668776
10	6	0	-2.081501	0.653466	0.822398
11	6	0	-2.044619	-0.812766	0.942393
12	6	0	-0.672064	-2.658340	1.304982
13	6	0	-3.042362	-2.979634	1.245053
14	6	0	2.338056	-1.306340	-0.290121
15	6	0	2.794149	-0.787235	0.957289
16	6	0	2.850981	0.671794	0.826722
17	6	0	2.418658	1.005099	-0.487262
18	6	0	2.363113	-0.228612	-1.300653
19	6	0	2.236216	-2.753951	-0.667837
20	6	0	3.292944	-1.558563	2.140545
21	6	0	3.440593	1.586195	1.858924
22	6	0	2.397034	2.368404	-1.108889
23	6	0	2.248491	-0.335937	-2.637198
24	7	0	0.272270	3.225551	1.410880
25	6	0	0.388901	4.664722	1.622151
26	1	0	-4.164910	-1.182258	0.901921
27	1	0	-1.606514	-4.558722	1.610099
28	1	0	-3.961624	3.423183	0.454812
29	1	0	-4.213785	0.931814	0.555064
30	1	0	0.337792	-3.026767	1.409490
31	1	0	-3.917330	-3.616176	1.307094
32	1	0	1.346616	-2.955073	-1.269264
33	1	0	2.224238	-3.417463	0.197414
34	1	0	3.104575	-3.038153	-1.271816
35	1	0	4.382906	-1.662632	2.088937
36	1	0	2.877676	-2.566351	2.179500
37	1	0	3.053613	-1.062228	3.082247
38	1	0	4.528896	1.461232	1.882321
39	1	0	3.071658	1.371744	2.864021
40	1	0	3.258264	2.639375	1.637703
41	1	0	2.352000	3.170862	-0.374540
42	1	0	1.546654	2.486006	-1.783623
43	1	0	3.305976	2.517116	-1.702078
44	1	0	2.233161	0.536545	-3.279342
45	1	0	2.181624	-1.300057	-3.127091
46	1	0	1.030320	2.616570	1.676706
47	1	0	-0.257903	5.002147	2.434149
48	1	0	0.119600	5.209946	0.717539
49	1	0	1.424000	4.887498	1.878036

SCF Done: E(RB3LYP) = -1100.07067393 A.U. after 2 cycles

Low frequencies --- -8.1154 -0.0006 -0.0004 0.0003 6.8348 10.7095

Zero-point correction= 0.404510 (Hartree/Particle)

Thermal correction to Energy= 0.429950

Thermal correction to Enthalpy= 0.430894

Thermal correction to Gibbs Free Energy= 0.349922

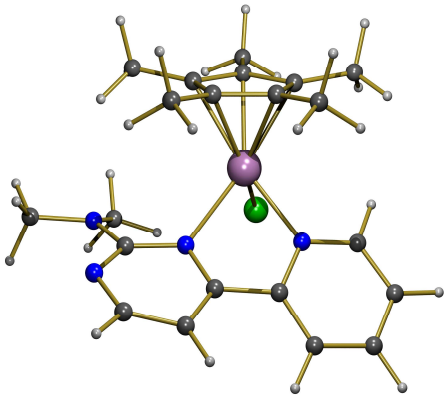
Sum of electronic and zero-point Energies= -1099.666164

Sum of electronic and thermal Energies= -1099.640724

Sum of electronic and thermal Enthalpies= -1099.639780

Sum of electronic and thermal Free Energies= -1099.720752

e1) [Chlorido(2-(2-dimethylaminopyrimidin-4-yl)pyridine)(η^5-1,2,3,4,5-pentamethylcyclopenta-dienyl)cobalt(III)]$^+$ (**4e$^+$**)



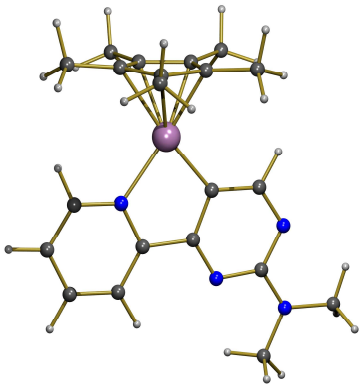
Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.392594	-0.428640	-0.122122
2	17	0	-0.722672	-0.380336	-2.511285
3	7	0	-1.397667	1.439602	-0.234959
4	7	0	1.236969	1.094733	-0.178674
5	7	0	3.384302	1.686512	0.679646
6	7	0	3.211592	-0.072359	-0.788032
7	6	0	-2.693923	1.562736	-0.561266
8	6	0	-3.319580	2.798299	-0.649594
9	6	0	-2.572538	3.947961	-0.412367
10	6	0	-1.223263	3.821524	-0.105078
11	6	0	-0.657622	2.549940	-0.025425
12	6	0	0.775759	2.310442	0.221014
13	6	0	1.586212	3.234188	0.860383
14	6	0	2.883540	2.808422	1.156319
15	6	0	2.597722	0.912953	-0.099519
16	6	0	2.713600	-0.562345	-2.075781
17	6	0	4.640044	-0.318280	-0.558025
18	6	0	0.193372	-1.404140	1.774334
19	6	0	0.488050	-2.305979	0.664030
20	6	0	-0.747352	-2.614199	0.010455
21	6	0	-1.806299	-1.874623	0.659178
22	6	0	-1.214317	-1.158346	1.783753
23	6	0	1.188347	-0.940134	2.792778
24	6	0	1.807362	-2.972258	0.422928
25	6	0	-0.931210	-3.557959	-1.133782
26	6	0	-3.271326	-2.024337	0.378790
27	6	0	-1.973014	-0.364169	2.801431
28	1	0	-3.221159	0.643261	-0.773929
29	1	0	-4.367830	2.849077	-0.917215
30	1	0	-3.027013	4.929259	-0.486030
31	1	0	-0.609136	4.700739	0.040113
32	1	0	1.215574	4.189680	1.203100
33	1	0	3.535542	3.398474	1.794834
34	1	0	1.740866	-0.147815	-2.309972
35	1	0	2.638643	-1.650804	-2.071217
36	1	0	3.422709	-0.271097	-2.857001
37	1	0	5.260861	0.415279	-1.081217
38	1	0	4.873877	-1.312296	-0.940320
39	1	0	4.876280	-0.271638	0.501537
40	1	0	0.874056	-0.020328	3.286680

41	1	0	2.171708	-0.766577	2.354225
42	1	0	1.310913	-1.703535	3.568874
43	1	0	1.934781	-3.801611	1.127394
44	1	0	2.644600	-2.289436	0.565792
45	1	0	1.875755	-3.388225	-0.581645
46	1	0	-1.175592	-4.552763	-0.744470
47	1	0	-0.031153	-3.646321	-1.740692
48	1	0	-1.739758	-3.244281	-1.792365
49	1	0	-3.472121	-2.140079	-0.686934
50	1	0	-3.848481	-1.173395	0.743699
51	1	0	-3.661906	-2.914161	0.884307
52	1	0	-2.372808	-1.032990	3.571166
53	1	0	-2.820519	0.164537	2.362362
54	1	0	-1.341268	0.370460	3.300988

```
SCF Done:  E(RB3LYP) =  -1600.26970402     A.U. after    2 cycles
Low frequencies ---  -16.7766  -12.7658   -0.0011    0.0012    0.0016    9.2441
Zero-point correction=                           0.446268 (Hartree/Particle)
 Thermal correction to Energy=                    0.475246
 Thermal correction to Enthalpy=                  0.476191
 Thermal correction to Gibbs Free Energy=         0.388046
 Sum of electronic and zero-point Energies=          -1599.823436
 Sum of electronic and thermal Energies=             -1599.794458
 Sum of electronic and thermal Enthalpies=           -1599.793513
 Sum of electronic and thermal Free Energies=        -1599.881658
```

e2) Splitting of HCl from (**4e**$^{+}$); cyclometallation of the pyrimidine ring



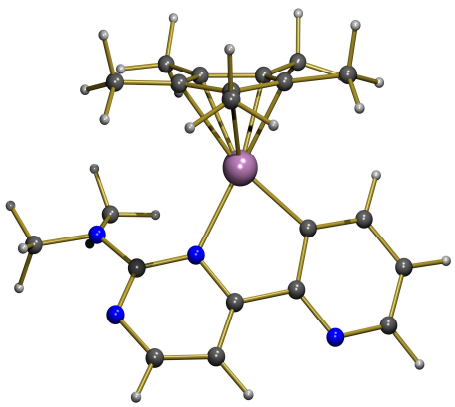
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	0.897379	-0.107359	-0.000107
2	7	0	0.053560	1.864142	0.002654
3	7	0	-3.267223	0.516792	-0.010030
4	7	0	-3.077449	-1.882040	0.001178
5	7	0	-5.148737	-0.830243	-0.042215
6	6	0	0.747331	3.011789	0.008176
7	6	0	0.125765	4.255591	0.012877
8	6	0	-1.264033	4.310149	0.012320
9	6	0	-1.987747	3.119282	0.006139
10	6	0	-1.303368	1.913227	0.000699
11	6	0	-1.947063	0.578952	-0.005174
12	6	0	-1.070888	-0.531053	0.001445
13	6	0	-1.763632	-1.762340	0.008065
14	6	0	-3.803770	-0.732704	-0.015197
15	6	0	-5.991859	0.362363	-0.033712
16	6	0	-5.839641	-2.113563	0.056055

17	6	0	2.047267	-1.804491	-0.717295
18	6	0	2.046954	-1.808715	0.707804
19	6	0	2.724101	-0.583756	1.151243
20	6	0	3.196592	0.120320	0.000460
21	6	0	2.726425	-0.577838	-1.153909
22	6	0	1.580965	-2.893792	-1.632763
23	6	0	1.581733	-2.903787	1.616947
24	6	0	2.990970	-0.232697	2.579759
25	6	0	4.052054	1.352068	0.004566
26	6	0	2.994134	-0.219348	-2.580431
27	1	0	1.824816	2.920752	0.008925
28	1	0	0.728757	5.155326	0.017391
29	1	0	-1.778238	5.264751	0.016778
30	1	0	-3.069923	3.100446	0.006730
31	1	0	-1.219930	-2.704770	0.021193
32	1	0	-5.542699	1.153316	-0.628386
33	1	0	-6.143203	0.733384	0.985489
34	1	0	-6.961975	0.101283	-0.456080
35	1	0	-6.515523	-2.234265	-0.794447
36	1	0	-6.430586	-2.149395	0.976618
37	1	0	-5.117795	-2.922507	0.060805
38	1	0	1.098306	-2.495600	-2.526347
39	1	0	0.874955	-3.564925	-1.144483
40	1	0	2.434568	-3.497653	-1.959691
41	1	0	2.436630	-3.505292	1.944791
42	1	0	0.880963	-3.576183	1.122865
43	1	0	1.093702	-2.511446	2.510217
44	1	0	3.896456	-0.745582	2.925113
45	1	0	2.174211	-0.541779	3.233052
46	1	0	3.148717	0.837137	2.719415
47	1	0	3.885600	1.967927	0.890105
48	1	0	3.888337	1.971868	-0.878715
49	1	0	5.111556	1.075458	0.005671
50	1	0	3.899102	-0.731305	-2.928457
51	1	0	3.152987	0.851082	-2.714162
52	1	0	2.177220	-0.523912	-3.235662

```
 ---------------------------------------------------------------------
SCF Done:  E(RB3LYP) =  -1139.39582202     A.U. after    1 cycles
Low frequencies ---   -5.8753   -0.0004    0.0006    0.0007    1.9922    9.5912
Zero-point correction=                           0.432104 (Hartree/Particle)
 Thermal correction to Energy=                    0.459674
 Thermal correction to Enthalpy=                  0.460618
 Thermal correction to Gibbs Free Energy=         0.373208
 Sum of electronic and zero-point Energies=          -1138.963718
 Sum of electronic and thermal Energies=             -1138.936148
 Sum of electronic and thermal Enthalpies=           -1138.935204
 Sum of electronic and thermal Free Energies=        -1139.022614
```

e3) Splitting of HCl from (**4e**$^{+}$); cyclometallation of the pyridine ring



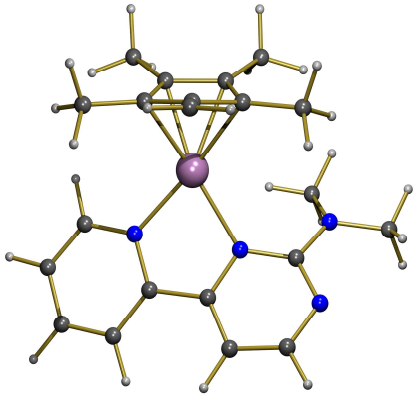
Standard orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.391622	-0.317356	-0.099931
2	7	0	-1.053456	3.844294	-0.138375
3	7	0	1.241382	1.074000	-0.154012
4	7	0	3.418812	1.661540	0.605450
5	7	0	3.143916	-0.220880	-0.696776
6	6	0	-2.331496	4.035694	-0.464870
7	6	0	-3.199520	2.988528	-0.788630
8	6	0	-2.727945	1.680247	-0.735900
9	6	0	-1.390501	1.437859	-0.392624
10	6	0	-0.611988	2.583938	-0.135466
11	6	0	0.815810	2.346868	0.134837
12	6	0	1.670178	3.287061	0.670990
13	6	0	2.956930	2.841427	0.986802
14	6	0	2.590605	0.850206	-0.073910
15	6	0	2.630450	-0.711014	-1.975815
16	6	0	4.567611	-0.503523	-0.482056
17	6	0	-0.585227	-1.624965	1.600579
18	6	0	0.334267	-2.362201	0.757183
19	6	0	-0.318969	-2.586721	-0.472871
20	6	0	-1.686534	-2.049757	-0.396199
21	6	0	-1.873362	-1.519719	0.912328
22	6	0	-0.333534	-1.232876	3.019773
23	6	0	1.700166	-2.820669	1.167893
24	6	0	0.192114	-3.348494	-1.652659
25	6	0	-2.727987	-2.238719	-1.455253
26	6	0	-3.149357	-1.049549	1.538243
27	1	0	-2.676704	5.065297	-0.473028
28	1	0	-4.226146	3.202604	-1.065323
29	1	0	-3.402849	0.863598	-0.970405
30	1	0	1.314504	4.281954	0.899009
31	1	0	3.643123	3.464290	1.554163
32	1	0	1.627627	-0.338963	-2.162885
33	1	0	2.611489	-1.800716	-1.987398
34	1	0	3.287443	-0.373601	-2.785306
35	1	0	5.202545	0.153472	-1.084644
36	1	0	4.754646	-1.537961	-0.773248
37	1	0	4.829335	-0.368566	0.563237
38	1	0	-0.941270	-0.380192	3.322923
39	1	0	0.714062	-0.987403	3.196473
40	1	0	-0.590345	-2.069826	3.680502
41	1	0	1.623448	-3.711859	1.799726
42	1	0	2.232926	-2.062364	1.742900
43	1	0	2.320251	-3.080754	0.311058
44	1	0	-0.366465	-4.286299	-1.746834
45	1	0	1.245094	-3.607438	-1.557360
46	1	0	0.052781	-2.804425	-2.589492
47	1	0	-2.317272	-2.107747	-2.457594
48	1	0	-3.558616	-1.542398	-1.341314
49	1	0	-3.142342	-3.251638	-1.399707
50	1	0	-3.587162	-1.860761	2.129828
51	1	0	-3.888381	-0.753953	0.794716
52	1	0	-2.991660	-0.202343	2.206460

SCF Done: E(RB3LYP) = -1139.37251253 A.U. after 2 cycles
Low frequencies --- -5.6487 -0.0008 -0.0006 0.0003 3.2792 12.0509
Zero-point correction= 0.432115 (Hartree/Particle)

Thermal correction to Energy=	0.459205
Thermal correction to Enthalpy=	0.460150
Thermal correction to Gibbs Free Energy=	0.376030
Sum of electronic and zero-point Energies=	-1138.940397
Sum of electronic and thermal Energies=	-1138.913307
Sum of electronic and thermal Enthalpies=	-1138.912363
Sum of electronic and thermal Free Energies=	-1138.996482

e4) Splitting of HCl from (**4e**$^{+}$); deprotonation of Cp*



Input orientation:

Center Number	Atomic Number	Atomic Type	Coordinates (Angstroms) X	Y	Z
1	77	0	-0.420990	-0.273021	0.129510
2	7	0	1.376104	0.902625	0.119336
3	7	0	3.566121	1.089224	-0.798901
4	6	0	-0.624773	3.984860	-0.016511
5	6	0	-2.754386	3.352001	0.881530
6	6	0	2.685313	0.503103	0.033848
7	6	0	3.223478	2.234321	-1.360020
8	6	0	2.018279	2.883806	-1.074321
9	6	0	1.096241	2.157580	-0.341248
10	6	0	-0.253819	2.642053	-0.001343
11	7	0	-1.111789	1.673347	0.413314
12	6	0	-2.332169	2.031801	0.852786
13	6	0	-1.891119	4.346443	0.426991
14	6	0	-2.087294	-1.314688	-0.838087
15	6	0	-1.856915	-1.836192	0.474429
16	6	0	-0.520674	-2.434714	0.466967
17	6	0	0.032156	-2.249794	-0.829647
18	6	0	-1.047671	-1.836145	-1.754391
19	6	0	-3.358588	-0.693967	-1.332830
20	6	0	-2.839307	-1.937295	1.601228
21	6	0	0.053289	-3.232482	1.595429
22	6	0	1.361307	-2.750502	-1.305559
23	6	0	-1.037704	-1.824469	-3.098486
24	7	0	3.134232	-0.514544	0.802542
25	6	0	2.560104	-0.785860	2.121902
26	6	0	4.519087	-0.969313	0.634783
27	1	0	0.076361	4.740178	-0.347371
28	1	0	-3.743818	3.589184	1.252947
29	1	0	3.940026	2.666645	-2.052938
30	1	0	1.797405	3.861072	-1.479669
31	1	0	-2.970288	1.225749	1.187295
32	1	0	-2.193745	5.387143	0.430795
33	1	0	-3.162558	0.094469	-2.062473
34	1	0	-3.962483	-0.271041	-0.529435

35	1	0	-3.971926	-1.452751	-1.831040
36	1	0	-3.337598	-2.913357	1.580587
37	1	0	-3.622850	-1.180958	1.532011
38	1	0	-2.357851	-1.835720	2.575270
39	1	0	-0.428675	-4.216506	1.623009
40	1	0	-0.115601	-2.762899	2.566089
41	1	0	1.122194	-3.403546	1.475633
42	1	0	2.089839	-2.817912	-0.498222
43	1	0	1.777198	-2.099233	-2.077131
44	1	0	1.254691	-3.748566	-1.744767
45	1	0	-0.189456	-2.191159	-3.664380
46	1	0	-1.884338	-1.464711	-3.671144
47	1	0	1.515337	-0.493062	2.161473
48	1	0	3.118897	-0.239118	2.890507
49	1	0	2.634767	-1.850653	2.339914
50	1	0	5.224372	-0.302396	1.140842
51	1	0	4.780591	-1.010586	-0.418365
52	1	0	4.604083	-1.965481	1.069579

SCF Done: E(RB3LYP) = -1139.37489313 A.U. after 2 cycles

Low frequencies --- -6.4402 -0.0007 0.0004 0.0006 4.5887 7.2257

Zero-point correction= 0.432250 (Hartree/Particle)

Thermal correction to Energy= 0.459076

Thermal correction to Enthalpy= 0.460020

Thermal correction to Gibbs Free Energy= 0.376589

Sum of electronic and zero-point Energies= -1138.942643

Sum of electronic and thermal Energies= -1138.915817

Sum of electronic and thermal Enthalpies= -1138.914873

Sum of electronic and thermal Free Energies= -1138.998304

3.4 Energy calculations

Calculations for cobalt complexes														
	Bipy	Fulven	Pypm	Pypm2	Fulven	NH2Pypm	NH2Pypm2	Fulven	MeNHPypm	MeNHPypm2	Fulven	Me2NPypm	Me2NPypm2	Fulven
NN (Hartrees)														
E	-2.728,634050	-2.728,634050	-2.744,671434	-2.744,671434	-2.744,671434	-2.800,067093	-2.800,067093	-2.800,067093	-2.839,383113	-2.839,383113	-2.839,383113	-2878,681512	-2878,681512	-2878,681512
H	-2.728,222834	-2.728,222834	-2.744,272266	-2.744,272266	-2.744,272266	-2.799,649616	-2.799,649616	-2.799,649616	-2.838,936027	-2.838,936027	-2.838,936027	-2878,205137	-2878,205137	-2878,205137
G	-2.728,301466	-2.728,301466	-2.744,350906	-2.744,350906	-2.744,350906	-2.799,729623	-2.799,729623	-2.799,729623	-2.839,019932	-2.839,019932	-2.839,019932	-2878,291962	-2878,291962	-2878,291962
NC (Hartrees)														
E	-2.267,717769	-2.267,742901	-2.283,758611	-2.283,75730	-2.283,781106	-2.339,156272	-2.339,143571	-2.339,164126	-2.378,473271	-2.378,459474	-2.378,481929	-2417,787493	-2.417,766671	-2.417,787574
H	-2.267,322662	-2.267,347609	-2.283,375278	-2.283,37419	-2.283,397853	-2.338,754677	-2.338,742318	-2.338,762820	-2.378,041795	-2.378,028543	-2.378,050641	-2417,326607	-2.417,306537	-2.417,327221
G	-2.267,397420	-2.267,421013	-2.283,449793	-2.283,44905	-2.283,471263	-2.338,833585	-2.338,818629	-2.338,839091	-2.378,124249	-2.378,108974	-2.378,129749	-2417,413317	-2.417,389932	-2.417,409779
HCl (Hartrees)														
E	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587
H	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759
G	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960
Diff (kcal/mol)														
E	56,28	40,51	54,11	54,94	40,00	52,86	60,83	47,93	52,24	60,90	46,81	42,31	55,38	42,26
H	52,34	36,69	50,34	51,02	36,18	49,06	56,81	43,95	48,61	56,93	43,06	38,76	51,36	38,38
G	41,47	26,66	39,63	40,10	26,16	36,44	45,83	32,99	36,22	45,81	32,77	25,53	40,20	27,75

Calculations for rhodium complexes														
	Ligand **1a**		Ligand **1b**			Ligand **1c**			Ligand **1d**			Ligand **1e**		
	Bipy	Fulven	Pypm	Pypm2	Fulven	NH2Pypm	NH2Pypm2	Fulven	MeNHPypm	MeNHPypm2	Fulven	Me2NPypm	Me2NPypm2	Fulven
NN (Hartrees)														
E	-1.456,431202	-1.456,431202	-1.472,469161	-1.472,469161	-1.472,469161	-1.527,863423	-1.527,863423	-1.527,863423	-1.567,179209	-1.567,179209	-1.567,179209	-1.606,479940	-1.606,479940	-1.606,479940
H	-1.456,020570	-1.456,020570	-1.472,070550	-1.472,070550	-1.472,070550	-1.527,446330	-1.527,446330	-1.527,446330	-1.566,732443	-1.566,732443	-1.566,732443	-1.606,004100	-1.606,004100	-1.606,004100
G	-1.456,100418	-1.456,100418	-1.472,150737	-1.472,150737	-1.472,150737	-1.527,527745	-1.527,527745	-1.527,527745	-1.566,818193	-1.566,818193	-1.566,818193	-1.606,093731	-1.606,093731	-1.606,093731
NC (Hartrees)														
E	-995,528279	-995,548198	-1.011,569128	-1.011,567940	-1.011,586353	-1.066,966158	-1.066,955700	-1.066,97340	-1.106,283042	-1.106,271500	-1.106,289727	-1.145,596973	-1.145,577175	-1.145,595156
H	-995,133645	-995,153364	-1.011,186298	-1.011,185276	-1.011,203573	-1.066,565066	-1.066,554866	-1.066,57218	-1.105,851952	-1.105,840956	-1.105,858887	-1.145,136642	-1.145,117347	-1.145,135030
G	-995,209519	-995,227847	-1.011,261994	-1.011,261167	-1.011,277980	-1.066,644601	-1.066,632966	-1.066,64846	-1.105,934968	-1.105,923378	-1.105,940387	-1.145,223918	-1.145,201717	-1.145,218275
HCl (Hartrees)														
E	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587
H	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759
G	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960
Diff (kcal/mol)														
E	47,90	35,40	46,09	46,83	35,28	44,35	50,91	39,81	43,66	50,90	39,47	35,38	47,80	36,52
H	44,03	31,66	42,35	42,99	31,51	40,48	46,88	36,01	39,99	46,89	35,64	31,81	43,92	32,83
G	33,22	21,72	31,87	32,39	21,84	28,35	35,65	25,93	28,40	35,68	25,00	19,99	33,92	23,53

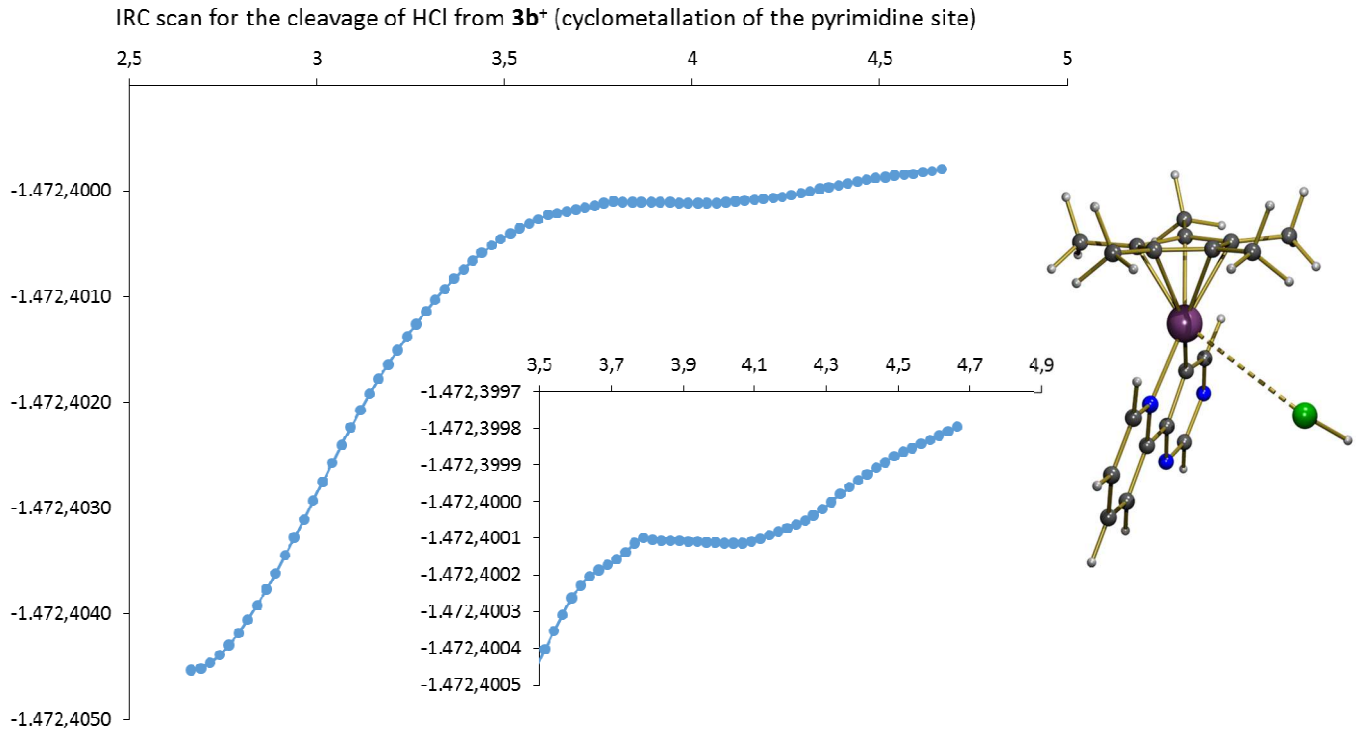
Calculations for iridium complexes

	Ligand **1a**		Ligand **1b**			Ligand **1c**			Ligand **1d**			Ligand **1e**		
	Bipy	Fulven	Pypm	Pypm2	Fulven	NH2Pypm	NH2Pypm2	Fulven	MeNHPypm	MeNHPypm2	Fulven	Me2NPypm	Me2NPypm2	Fulven
NN (Hartrees)														
E	-1.450,223791	-1.450,223791	-1.466,261419	-1.466,261419	-1.466,261419	-1.521,654552	-1.521,654552	-1.521,654552	-1.560,970589	-1.560,970589	-1.560,970589	-1.600,269704	-1.600,269704	-1.600,269704
H	-1.449,813185	-1.449,813185	-1.465,862778	-1.465,862778	-1.465,862778	-1.521,237386	-1.521,237386	-1.521,237386	-1.560,523679	-1.560,523679	-1.560,523679	-1.599,793513	-1.599,793513	-1.599,793513
G	-1.449,893845	-1.449,893845	-1.465,943489	-1.465,943489	-1.465,943489	-1.521,319090	-1.521,319090	-1.521,319090	-1.560,608764	-1.560,608764	-1.560,608764	-1.599,881658	-1.599,881658	-1.599,881658
NC (Hartrees)														
E	-989,325600	-989,328370	-1.005,366301	-1.005,365055	-1.005,366047	-1.060,764681	-1.060,753141	-1.060,754006	-1.100,081765	-1.100,069407	-1.100,070674	-1.139,395822	-1.139,372513	-1.139,374893
H	-988,931867	-988,933529	-1.004,983317	-1.004,982250	-1.004,983296	-1.060,363408	-1.060,352084	-1.060,352830	-1.099,650402	-1.099,638486	-1.099,639780	-1.138,935204	-1.138,912363	-1.138,914873
G	-989,005031	-989,007800	-1.005,059387	-1.005,058349	-1.005,057545	-1.060,443900	-1.060,430282	-1.060,428864	-1.099,734789	-1.099,720635	-1.099,720752	-1.139,022614	-1.138,996482	-1.138,998304
HCl (Hartrees)														
E	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587	-460,826587
H	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759	-460,816759
G	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960	-460,837960
Diff (kcal/mol)														
E	44,93	43,19	43,00	43,79	43,16	39,71	46,95	46,41	39,05	46,81	46,01	29,68	44,30	42,81
H	40,51	39,47	39,35	40,02	39,36	35,90	43,01	42,54	35,47	42,94	42,13	26,07	40,41	38,83
G	31,91	30,17	28,95	29,61	30,11	23,36	31,91	32,80	22,60	31,48	31,41	13,23	29,63	28,48

4. Quantum chemical calculations (transition states)

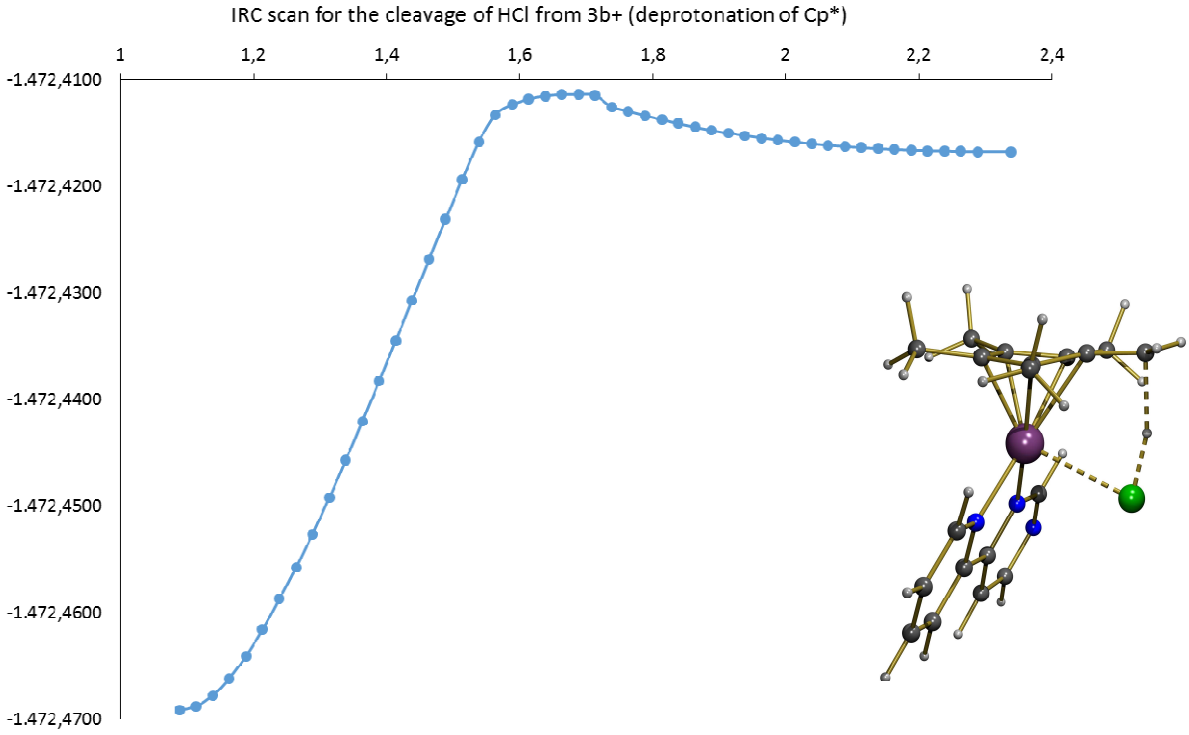
4.1 Cyclometallation reactions

Only a part of the crucial transition states was calculated. Typical IRC curves calculated for the elongation of the M-Cl bond look like the one presented. Here the energy profile for the HCl splitting from the pyrimidine site of the rhodium complex **3b**$^{+}$ was calculated. A transition state with a Rh-Cl distance of approx. 3.79 Å was found followed by another tiny minimum at a Rh-Cl distance of approx. 4.06 Å (the inset presents the IRC curve for a Rh-Cl distance d of 3.50 ≤ d ≤ 4.68 Å). The following release of the HCl molecule requires just a few kcal/mol. The structure of this transition state is exemplarily shown on the right side. This makes clear, that the final 16 VE species resulting from the cyclometallation are energetically located on top of thy energy hypersurface.



4.1 Deprotonation of a Cp* methyl group

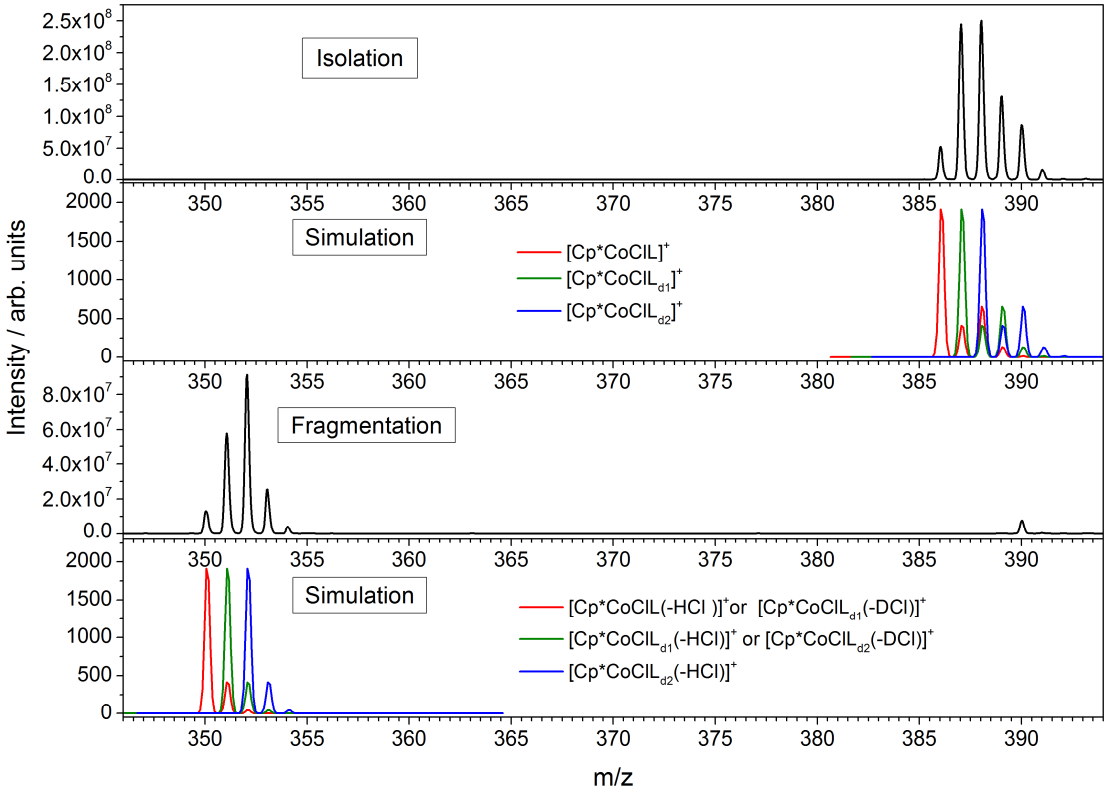
Only a part of the crucial transition states was calculated. Typical IRC curves were calculated for the elongation of the critical Cp* C-H distance. Here the energy of the final product is slightly below the transition state. This is due to the stability of the square planar, d^8, 16 VE nature of the corresponding products. However, the energy difference to the transition state is just a few kcal/mol. The energy profile presented exemplarily below is for the Cp* deprotonation occurring at **3b**$^+$, the according transition state structure is shown on the right side.



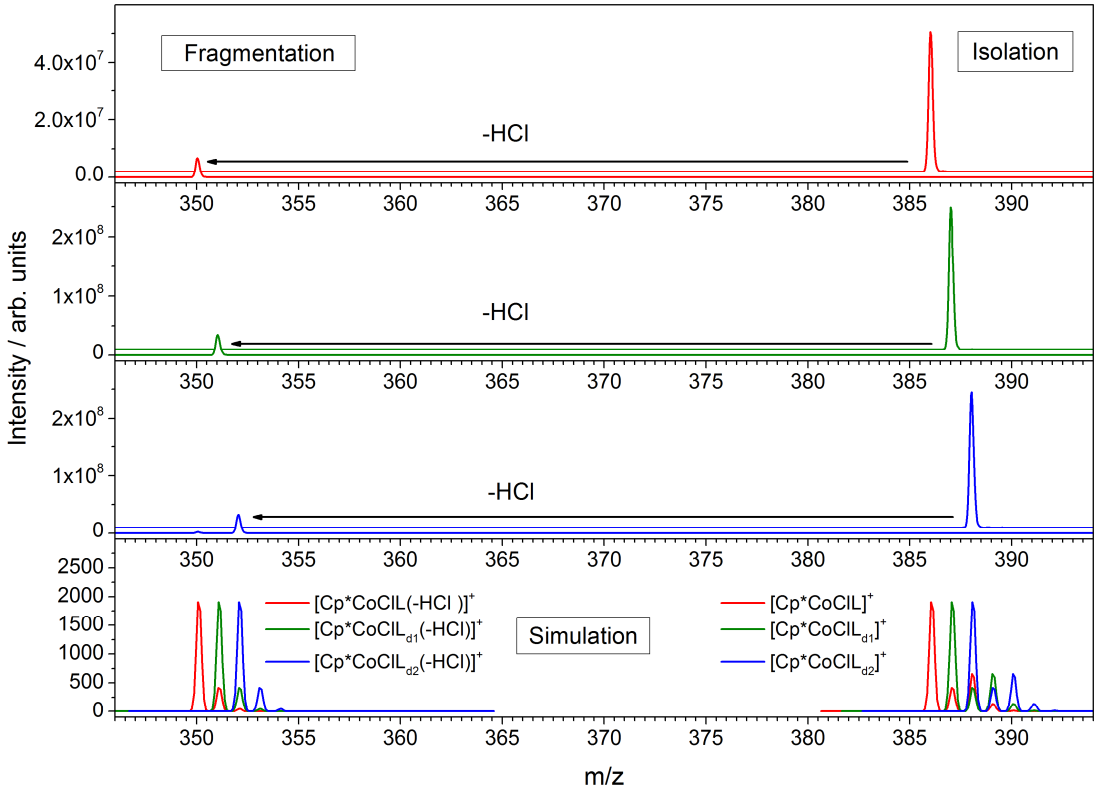
5. CID ESI-MS experiments with deuterated compounds

5.1 Cobalt complex **[2b-D]$^+$**

overall spectra

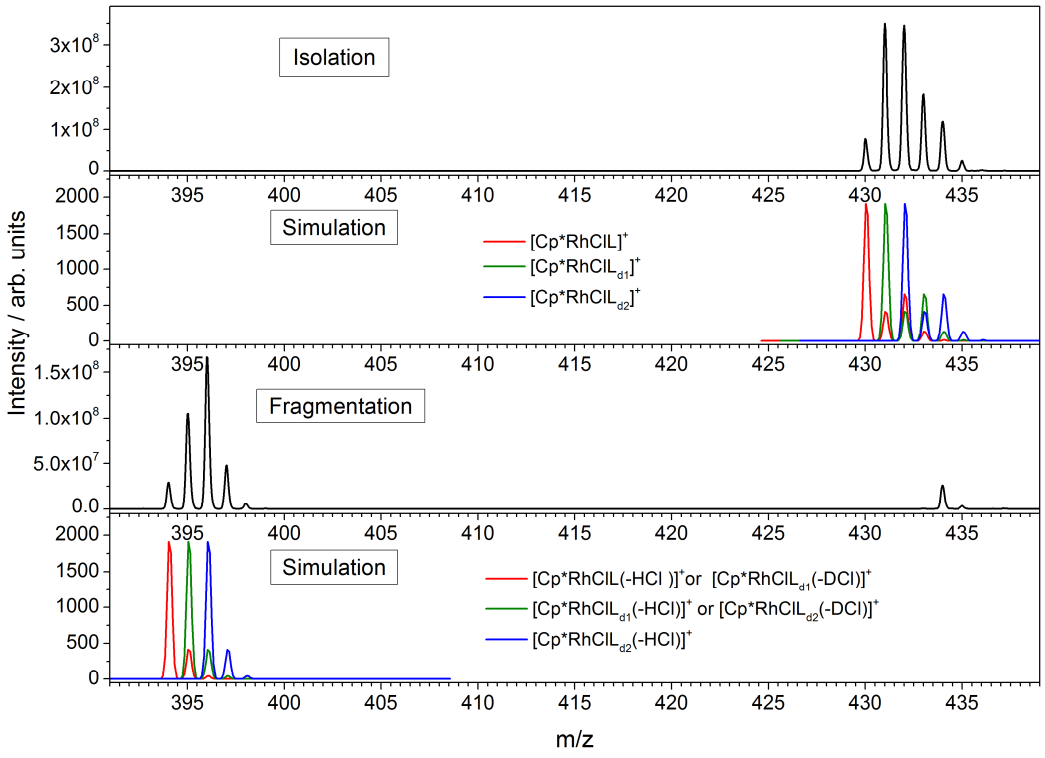


fragmentation of the isolated isotopomers

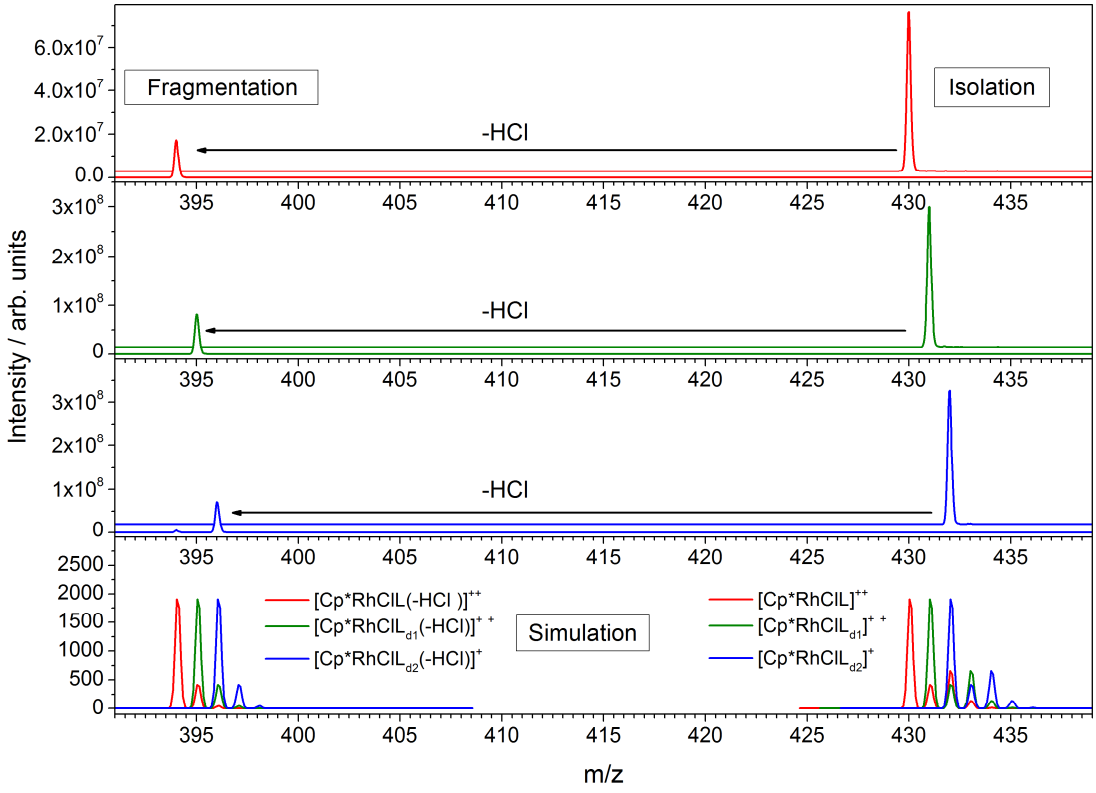


5.2 Rhodium complex **[3b-D]⁺**

overall spectra

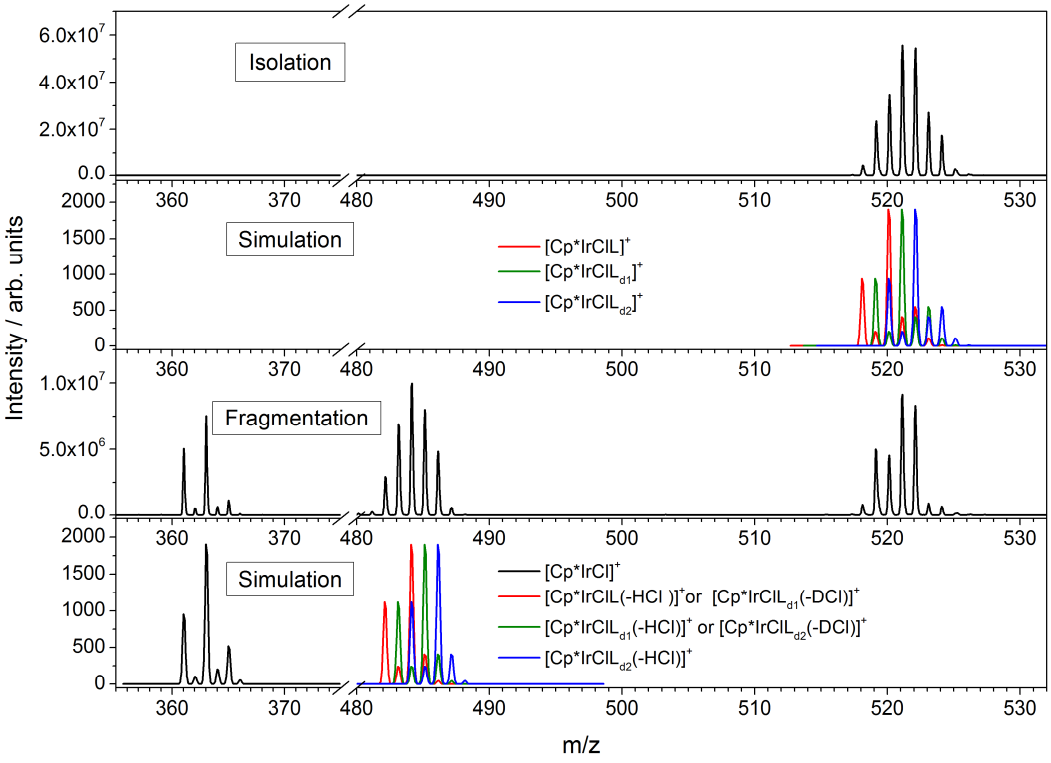


fragmentation of the isolated isotopomers



5.3 Iridium complex **[4b-D]$^+$**

overall spectra



fragmentation of the isolated isotopomers