Electronic Supplementary Information for

Catalytic Deuteration of Silanes Mediated by *N*-Heterocyclic Carbene-Ir(III) Complexes

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Experimental Section

General considerations. Unless stated otherwise all reactions were carried out inside an MBraun Glovebox under inert conditions. Solvents were distilled and dried as required. Silanes were purchased from Sigma-Aldrich and used as received. $[MCl(I^tBu')_2]$ and $[M(I^tBu')_2][PF_6]$ (M = Rh (**2a**/**3a**), Ir (**2b**/**3b**) and [IrHCl(ItBu)(ItBu')] (**1**) were prepared according to literature procedures.[1] The ^1H and ^{13}C NMR spectra were recorded on either a Burker 400 MHz or a Bruker 300 MHz NMR spectrometer. High-pressure ^1H NMR experiments were carried out using a 10 mm sapphire NMR tube. Elemental Analyses were performed at the London Metropolitan University.

General procedure for the isotopic exchange of silanes. In the glovebox a Schlenk tube was charged with a CD_2Cl_2 (0.7 mL) 0.22 mmol of the silane and 2.2 x 10^{-3} mmol of the catalyst. The flask was removed from the glovebox. Using Schlenk techniques, the flask was charged with 0.5 atm of D_2. The reaction was stirred for the appropriate time at room temperature. The reaction was eventually opened to air and examined by ^1H, ^{29}Si NMR and FTIR (Si-H ≈ 2200 cm^{-1}; Si-D ≈ 1500 cm^{-1}) spectroscopy. Yields were calculated from ^1H NMR data and are assigned an uncertainty of ± 5%.

Stiochiometric reaction between $[IrHCl(I^tBu)(I^tBu')]$ and $DSiEt_3$. A J-Young tap NMR tube was charged with 5.0 mg (8.5 x 10^{-3} mmol) $[IrHCl(I^tBu)(I^tBu')]$ which was dissolved in 0.7 mL CD_2Cl_2. 25.0 μL of the hydrosilane stock solution (13.7 μL $DSiEt_3$ (8.5 x 10^{-2} mmol) in 0.25 mL CD_2Cl_2) was added. Growth of the silane hydride peak was

monitored by ^{1}H NMR spectra recorded periodically over the course of 2 days and data are shown in Figure S3.

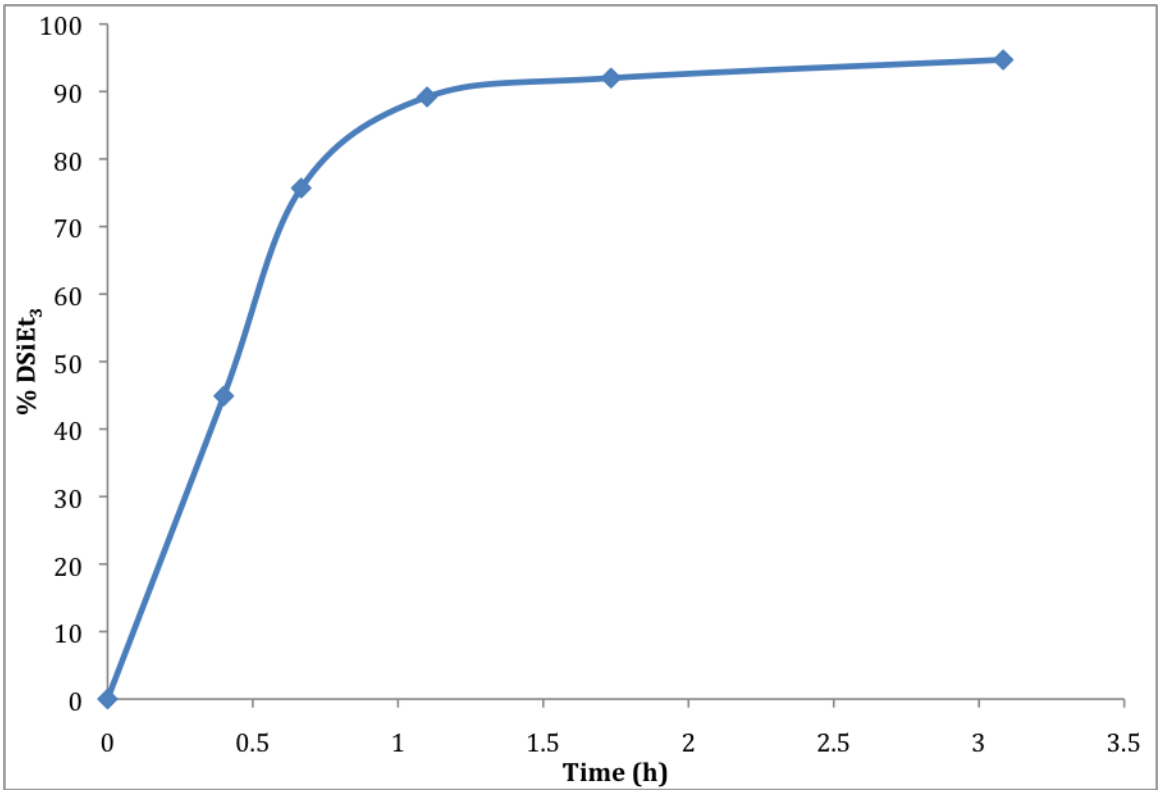


Figure S1. Conversion of $HSiEt_3$ to $DSiEt_3$ in CD_2Cl_2 with catalyst loading of 0.01% $IrCl(I^tBu')_2$ (**2b**) at 25 ^{o}C. Near complete conversion is reached in approximately 3 h.

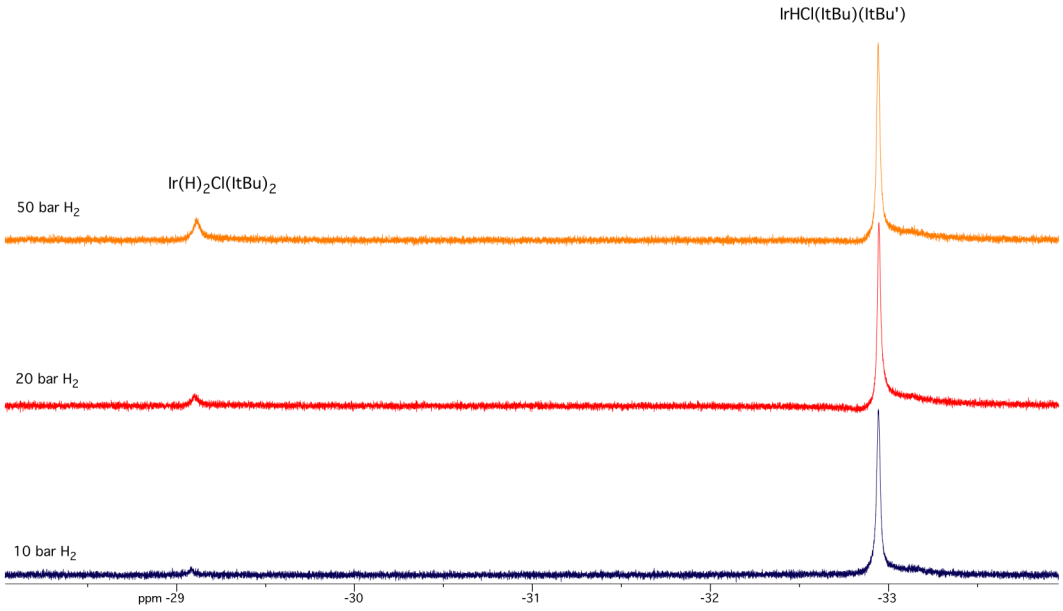


Figure S2. High pressure ^{1}H NMR spectra of hydride resonances of [IrHCl(I^{t}Bu)(I^{t}Bu')] and [Ir(H)$_2$Cl(I^{t}Bu)$_2$]. The spectra are the result of a prepared solution of [IrCl(I^{t}Bu')$_2$] in CD_2Cl_2 under the given amount of H_2 pressure. Growth of the shift attributed to the proposed [Ir(H)$_2$Cl(I^{t}Bu)$_2$] is seen to increase with higher H_2 pressure.

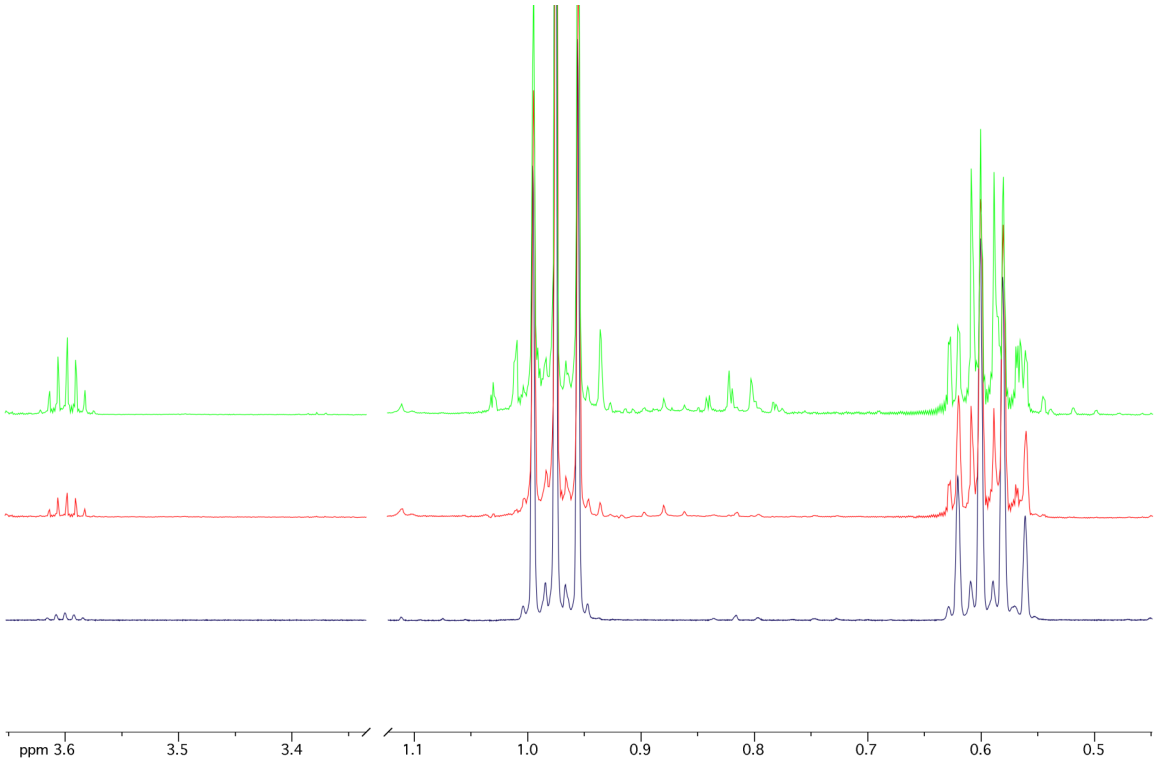


Figure S3. ^{1}H NMR spectra of $HSiEt_3$ in the stiochiometric reaction between [IrHCl(I^{t}Bu)(I^{t}Bu')] and $DSiEt_3$ in CD_2Cl_2. H-$SiEt_3$ shift at 3.60 ppm. Blue spectra – $DSiEt_3$ with no Ir (7 % $HSiEt_3$). Red spectra 7 h after the addition of [IrHCl(I^{t}Bu)(I^{t}Bu')] (32 % $HSiEt_3$). Green spectra – 5 days after the addition of [IrHCl(I^{t}Bu)(I^{t}Bu')] (70 % $HSiEt_3$) Equal molar amounts of each reactant give rise to > 50% $DSiEt_3$. This is believed to be the result of involvement of the *ortho*-metalated ^{t}Bu groups of the NHC and their ability to reversibly de-*ortho*-metalate which subsequently makes more than one H available per molecule of [IrHCl(I^{t}Bu)(I^{t}Bu')]. The conversion to only 70% $HSiEt_3$ indicates that this "proton shuffle" is quite slow compared to the rate of DSi/IrH exchange.

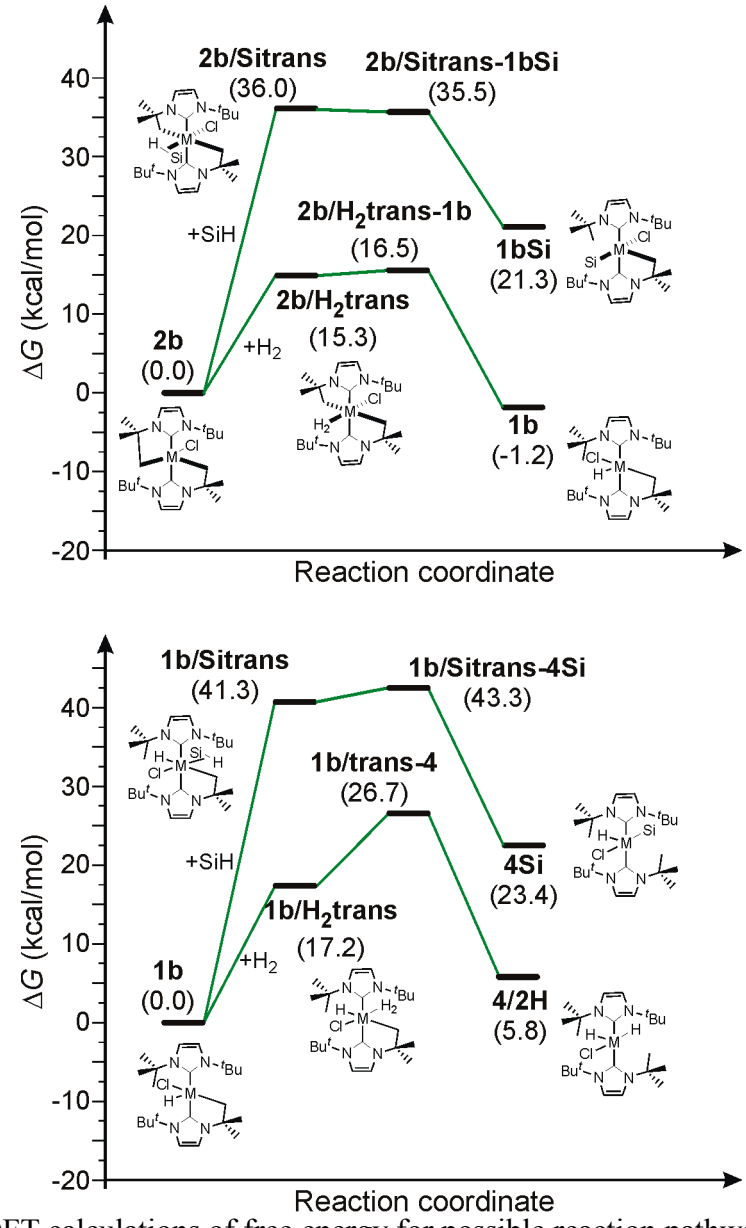
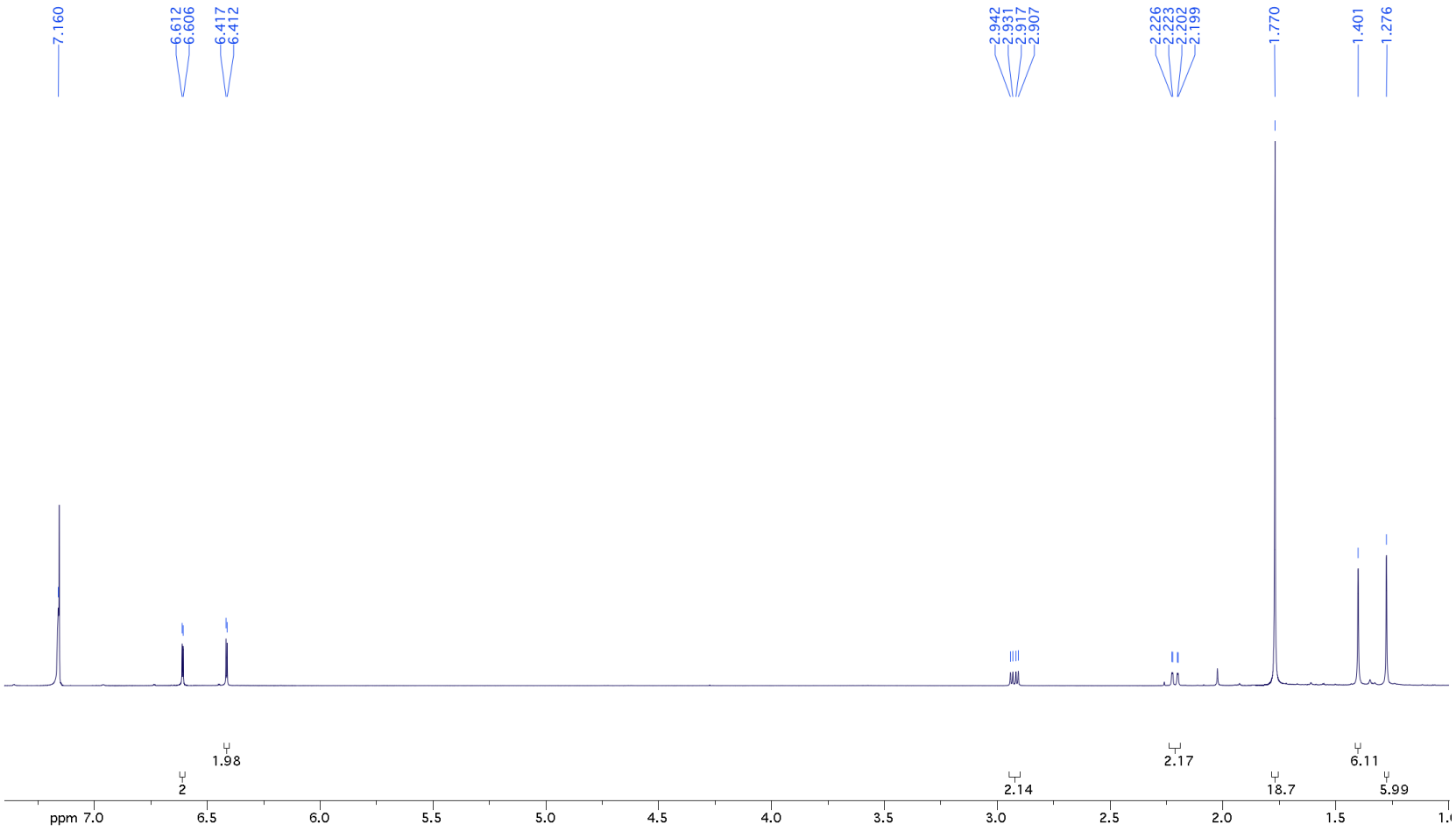


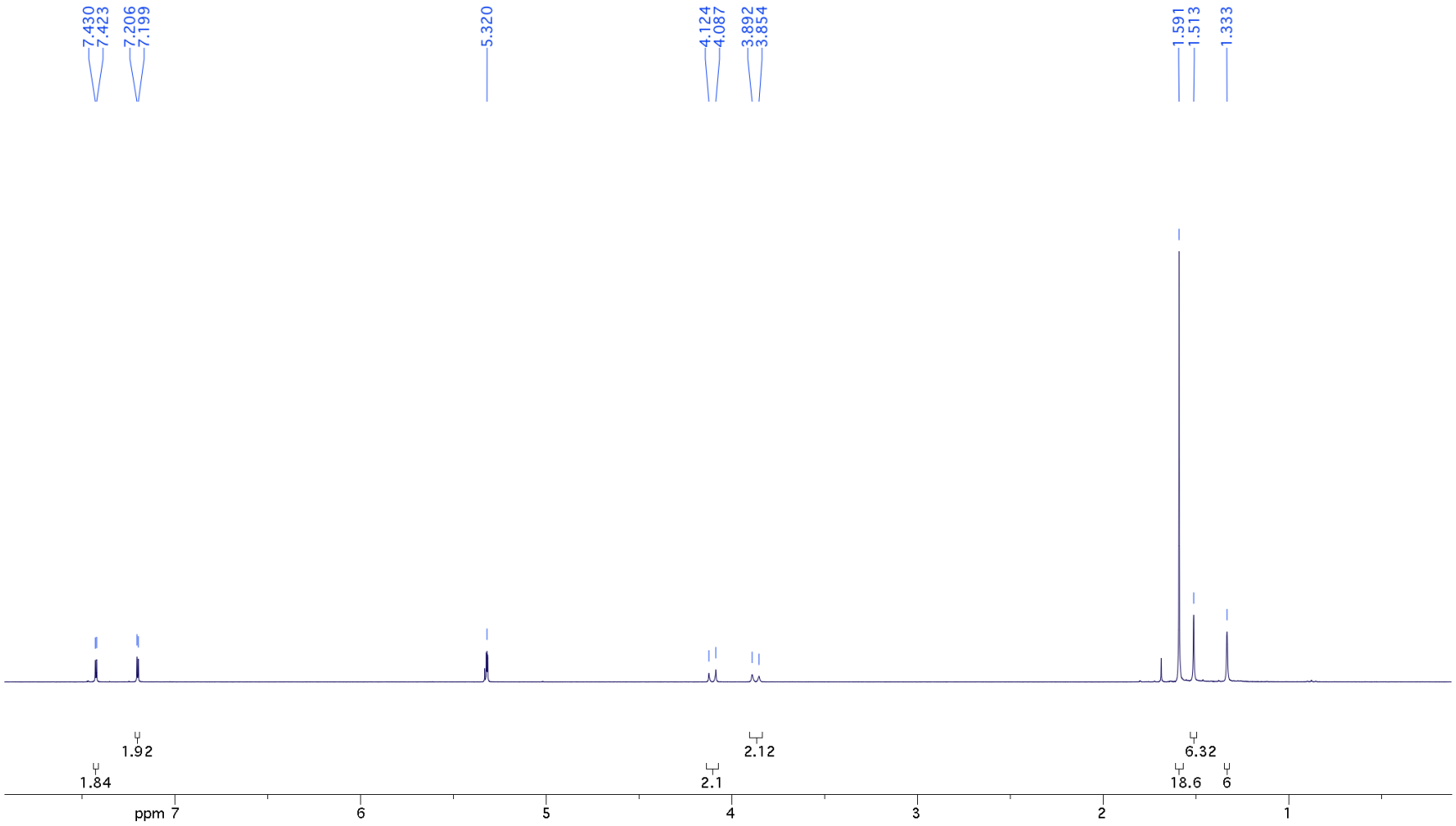
Figure S4. DFT calculations of free energy for possible reaction pathways for isotopic exchange of $HSiMe_3$ mediated by [IrHCl(I^tBu)(ItBu')] (**1**) and [IrCl(I^tBu')$_2$] (**2**).

$[RhCl(I^tBu')_2]$ **2a**
^1H 400 MHz NMR C_6D_6

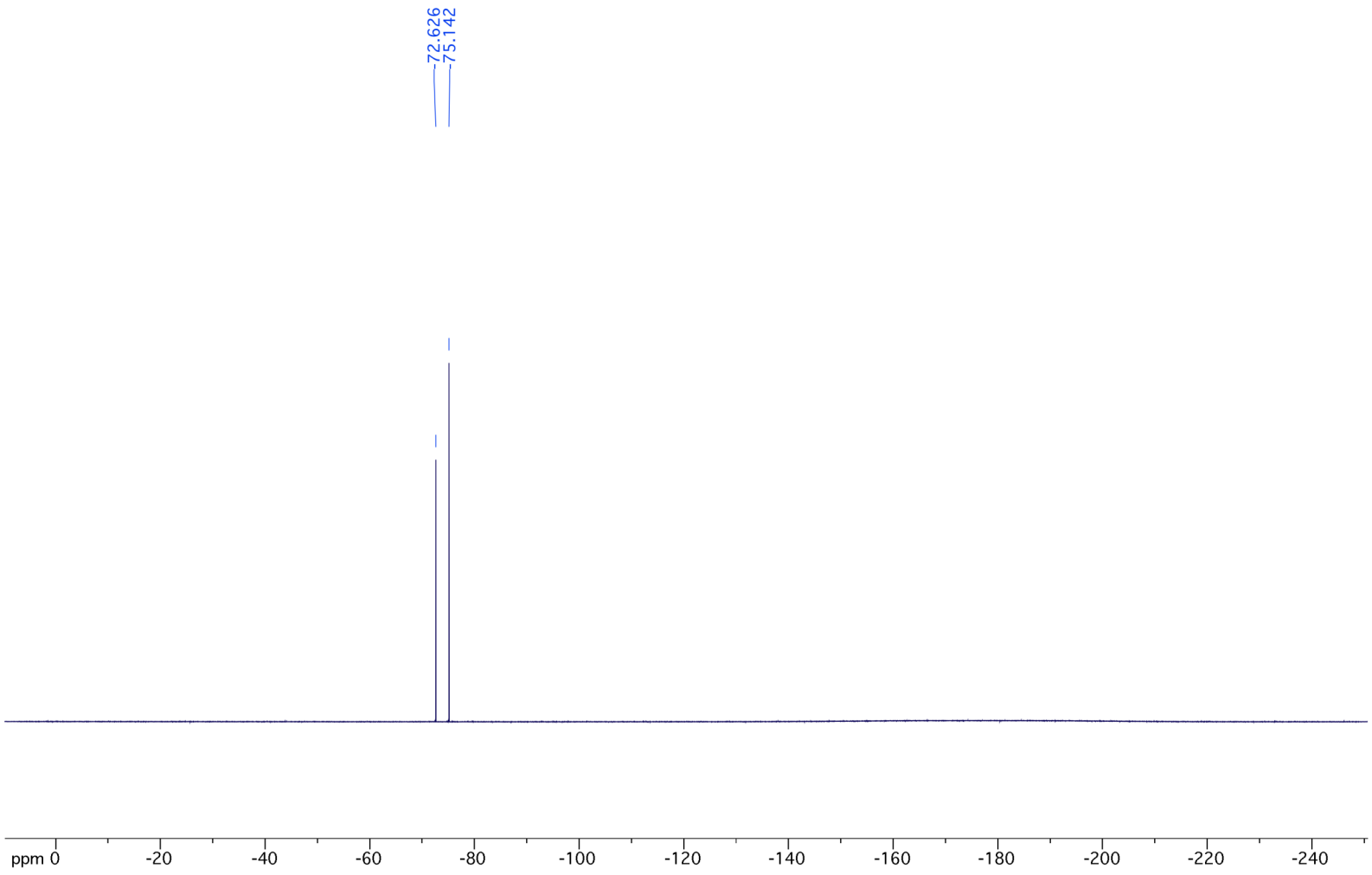


$[Rh(ItBu')_2][PF_6]$ **3a**

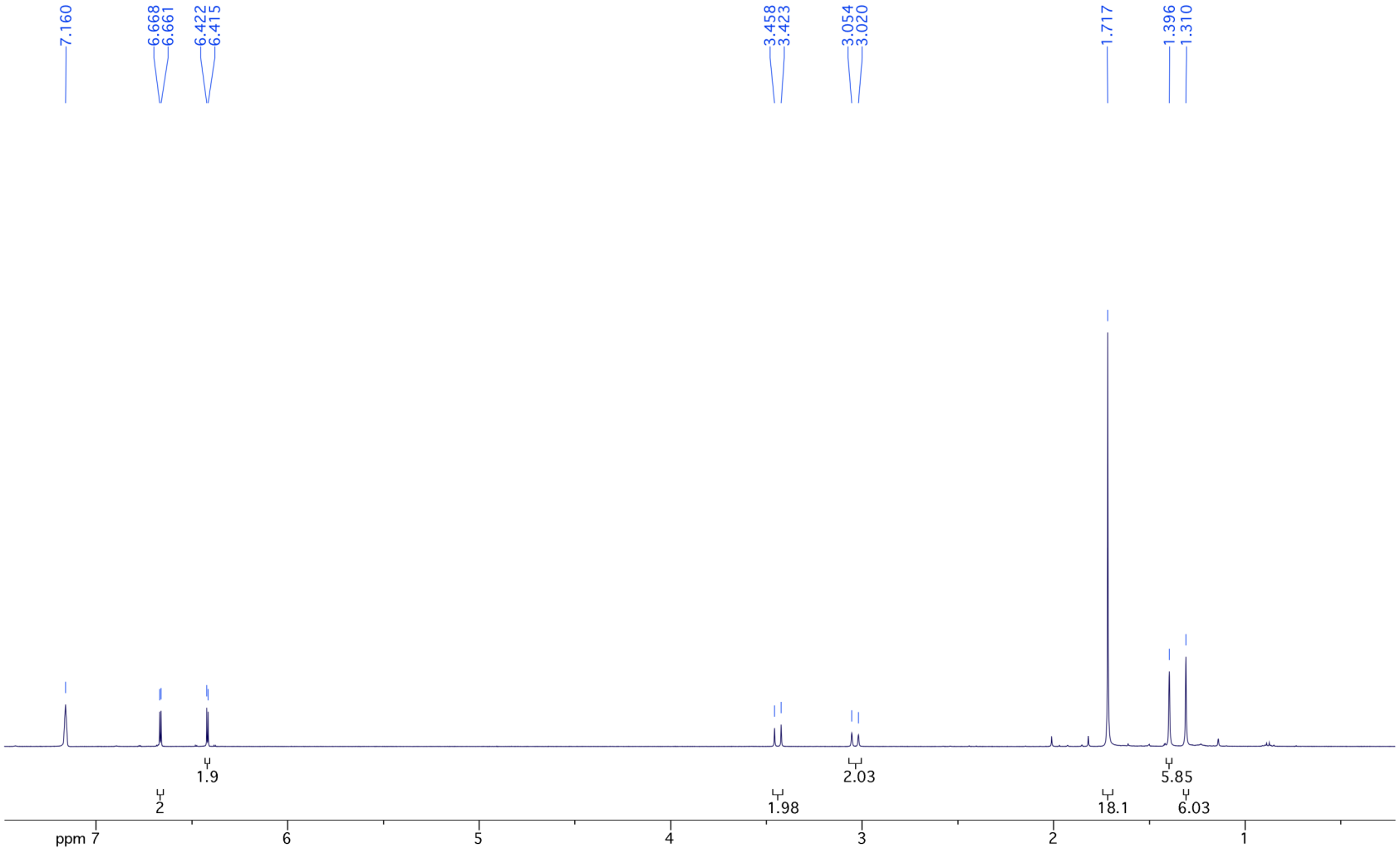
^1H NMR 300 MHz CD_2Cl_2



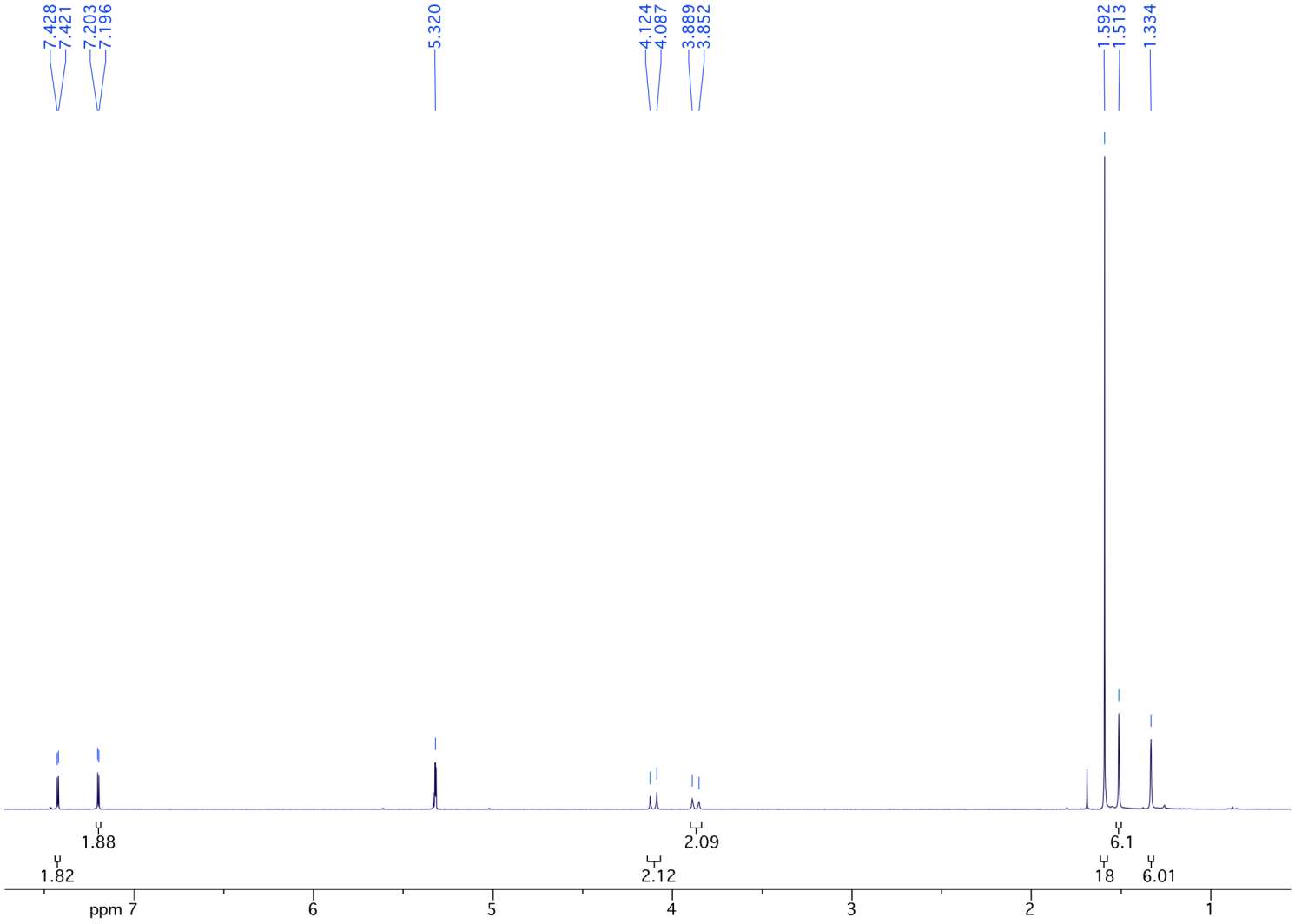
3a $^{19}F\{^{1}H\}$ NMR



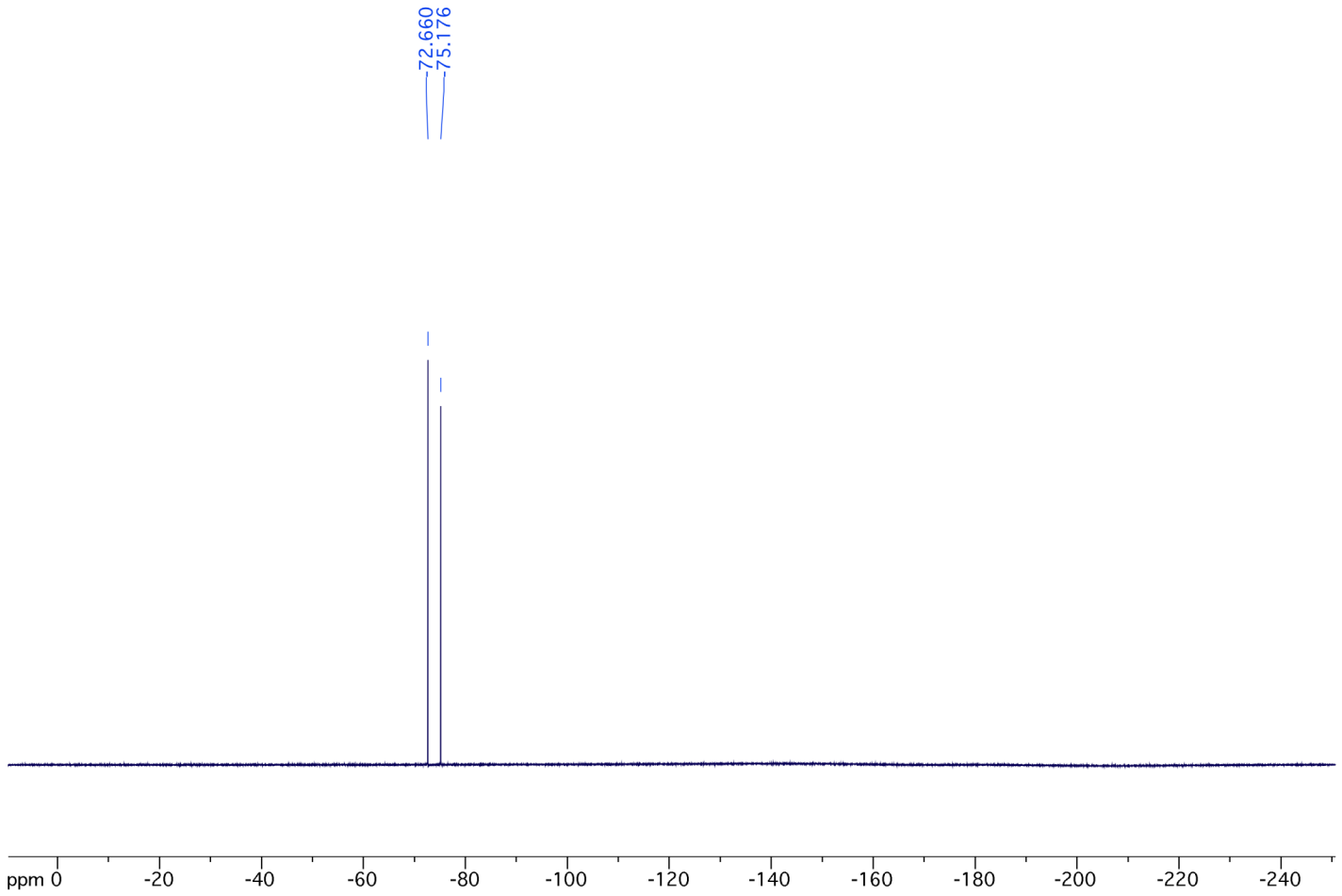
[IrCl(I^{t}Bu')$_2$] **2b**
^{1}H 300 MHz NMR C_6D_6



$[Ir(I^tBu')_2][PF_6]$ **3b**
^1H 300 MHz NMR CD_2Cl_2



3b $^{19}F\{^{1}H\}$ CD_2Cl_2



DFT structures and energies

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Information for structure h2


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Maximum Force     : 0.000008
Energy E(RB-P86)     -1.17758869 a.u.
ZPE-correction    :        0.009840 a.u.
Energy (298K)     :       -1.165389 a.u.
Enthalpy (298K)   :       -1.164445 a.u.
Free Energy (298K):       -1.179259 a.u.

Atom Coordinates (x,y,z) in Angstrom
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 H    0.000000   0.000000  -0.375809
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Information for structure 2b


SCF Convergence   : 0.4053D-08
Maximum Force     : 0.000010
Energy E(RB-P86)  -1645.40538757 a.u.
ZPE-correction    :        0.555619 a.u.
Energy (298K)     :    -1644.817012 a.u.
Enthalpy (298K)   :    -1644.816068 a.u.
Free Energy (298K):    -1644.911644 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir   0.023396   0.039920  -0.040299
 C    2.029517   0.056660   0.196987
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C	1.530621	-0.104561	2.598376
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Information for structure 2bh2cis

```
SCF Convergence   : 0.8970D-08
Maximum Force     : 0.000004
Energy E(RB-P86)  -1646.59510766 a.u.
ZPE-correction    :        0.572540 a.u.
Energy (298K)     :    -1645.989255 a.u.
Enthalpy (298K)   :    -1645.988311 a.u.
Free Energy (298K):    -1646.083405 a.u.

Atom Coordinates (x,y,z) in Angstrom
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 Cl   0.228498  -2.162509  -1.394806
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Information for structure 2bh2cis-1b

SCF Convergence : 0.4748D-08
Maximum Force : 0.000006
Energy E(RB-P86) -1646.54933070 a.u.
ZPE-correction : 0.572839 a.u.
Energy (298K) : -1645.943586 a.u.
Enthalpy (298K) : -1645.942641 a.u.
Free Energy (298K): -1646.037068 a.u.

Atom Coordinates (x,y,z) in Angstrom

Ir	0.046592	0.019871	-0.069737
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Cl	0.215173	-1.088008	-2.175564
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H	-4.803839	-3.219878	-1.095259
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Information for structure 2bh2trans

SCF Convergence : 0.1559D-08
Maximum Force : 0.000019
Energy E(RB-P86) -1646.57864650 a.u.
ZPE-correction : 0.573873 a.u.
Energy (298K) : -1645.971598 a.u.

Enthalpy (298K) : -1645.970654 a.u.
Free Energy (298K): -1646.065176 a.u.

Atom Coordinates (x,y,z) in Angstrom

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C	-2.054859	-0.534460	-0.112366
Cl	-0.000090	0.000024	2.456380
N	3.321526	-0.035052	-0.071908
N	2.319388	1.875316	-0.249184
N	-3.321522	0.034999	-0.072022
N	-2.319339	-1.875357	-0.249278
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C	3.672252	2.144495	-0.304971
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C	3.665861	-1.494945	0.064132
C	3.170983	-2.217114	-1.203831
C	-1.225250	-2.869238	-0.379613
C	1.225369	2.869277	-0.379467
C	1.048753	3.212003	-1.871690
C	-3.665880	1.494883	0.064057
C	-3.069239	2.017350	1.383063
H	2.117273	-1.998064	-1.404312
H	-2.026232	1.715665	1.517525
H	0.760741	2.319994	-2.446750
H	-5.360851	-0.725727	-0.168675
H	-4.073605	-3.145733	-0.402110
C	-3.170880	2.217152	-1.203803
C	-5.194073	1.680170	0.136712
C	-1.048648	-3.211890	-1.871853
C	-1.594935	-4.143465	0.405464
C	0.007019	-2.192891	0.226333
H	0.893344	-2.730286	-0.126552

H	-3.638391	1.608892	2.231966
H	-3.138333	3.115021	1.419711
H	-0.036348	-2.288419	1.319865
H	4.073687	3.145662	-0.401907
H	5.360875	0.725632	-0.168427
C	-0.006913	2.193018	0.226514
C	1.595141	4.143461	0.405647
C	3.069072	-2.017466	1.383052
C	5.194045	-1.680248	0.136946
H	3.296665	-3.304964	-1.096286
H	1.978588	3.615507	-2.302865
H	0.261160	3.971527	-1.988926
H	3.759855	-1.886866	-2.073848
H	0.036578	2.288300	1.320059
H	-0.893237	2.730548	-0.126182
H	0.728639	4.820523	0.408323
H	1.840582	3.898608	1.448997
H	2.440795	4.691247	-0.042349
H	-1.978485	-3.615364	-2.303052
H	-0.760615	-2.319845	-2.446845
H	-0.261060	-3.971412	-1.989131
H	-2.440582	-4.691273	-0.042520
H	-0.728402	-4.820487	0.408088
H	-1.840351	-3.898657	1.448832
H	3.138094	-3.115143	1.419632
H	3.638175	-1.609099	2.232032
H	2.026071	-1.715732	1.517440
H	5.391370	-2.754791	0.260750
H	5.705099	-1.355942	-0.782227
H	5.634286	-1.163696	1.002548
H	-3.296634	3.304989	-1.096201
H	-2.117134	1.998183	-1.404191
H	-3.759628	1.886932	-2.073914
H	-5.391426	2.754704	0.260546

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 H    -5.705021    1.355901   -0.782534
 H    -5.634402    1.163568    1.002239
 H     0.232854   -0.752483   -1.446570
 H    -0.233323    0.753732   -1.445752
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Information for structure 2bh2trans-1b


SCF Convergence   : 0.5244D-08
Maximum Force     : 0.000002
Energy E(RB-P86)  -1646.57511692 a.u.
ZPE-correction    :        0.573103 a.u.
Energy (298K)     :    -1645.969260 a.u.
Enthalpy (298K)   :    -1645.968316 a.u.
Free Energy (298K):    -1646.061924 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir  -0.015447   -0.006683   -0.071930
 C    2.050578    0.515217   -0.109201
 C   -2.056453   -0.543099   -0.113688
 Cl  -0.022558    0.095579    2.478180
 N    3.312276   -0.062066   -0.028988
 N    2.336623    1.853802   -0.273504
 N   -3.327422    0.017257   -0.053882
 N   -2.310657   -1.880834   -0.285617
 C    4.308072    0.904001   -0.151901
 C    3.694787    2.104903   -0.309224
 C   -4.301430   -0.970218   -0.201243
 C   -3.660882   -2.159752   -0.348660
 C    3.640569   -1.523397    0.129797
 C    3.174869   -2.247645   -1.149293
 C   -1.197423   -2.847482   -0.435705
 C    1.281035    2.877347   -0.465369
```

C	1.149029	3.176444	-1.972225
C	-3.686552	1.469548	0.117812
C	-3.034535	1.993374	1.408505
H	2.139916	-1.994608	-1.401130
H	-1.978224	1.718704	1.486357
H	0.863976	2.269906	-2.526276
H	-5.360746	-0.759252	-0.171924
H	-4.054554	-3.161308	-0.471609
C	-3.265642	2.222051	-1.159548
C	-5.212294	1.628478	0.268434
C	-0.999420	-3.143395	-1.935024
C	-1.544170	-4.150232	0.310567
C	0.013725	-2.154185	0.200485
H	0.911174	-2.676418	-0.145863
H	-3.542649	1.560041	2.283023
H	-3.133982	3.088335	1.460832
H	-0.048026	-2.280478	1.291984
H	4.111002	3.098133	-0.422321
H	5.362247	0.671963	-0.103100
C	0.010178	2.268999	0.121988
C	1.658743	4.162629	0.297271
C	3.010373	-2.027605	1.440972
C	5.165003	-1.721977	0.243812
H	3.258823	-3.337571	-1.023574
H	2.096630	3.551085	-2.389212
H	0.377336	3.944066	-2.135363
H	3.813134	-1.949463	-1.995890
H	0.056502	2.282513	1.219262
H	-0.850489	2.869414	-0.195640
H	0.812503	4.863547	0.253570
H	1.867046	3.941549	1.353736
H	2.531504	4.673213	-0.140787
H	-1.916434	-3.555111	-2.385780
H	-0.723049	-2.227923	-2.476767

```
 H    -0.194330  -3.882247  -2.065597
 H    -2.374303  -4.703026  -0.160010
 H    -0.663467  -4.808825   0.301143
 H    -1.802945  -3.941495   1.358693
 H     3.042082  -3.126851   1.477698
 H     3.583541  -1.638773   2.296426
 H     1.976960  -1.691555   1.565998
 H     5.347395  -2.796758   0.387322
 H     5.703162  -1.416005  -0.666060
 H     5.587889  -1.198352   1.113848
 H    -3.430913   3.302917  -1.034296
 H    -2.212208   2.050666  -1.402325
 H    -3.869130   1.878112  -2.013767
 H    -5.419527   2.695181   0.435781
 H    -5.763639   1.324258  -0.634085
 H    -5.600344   1.077228   1.137444
 H     0.140829  -0.484937  -1.580080
 H    -0.336491   1.158737  -1.109527
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Information for structure 1b


SCF Convergence   : 0.6580D-08
Maximum Force     : 0.000022
Energy E(RB-P86)  -1646.60720594 a.u.
ZPE-correction    :        0.575419 a.u.
Energy (298K)     :    -1645.998363 a.u.
Enthalpy (298K)   :    -1645.997419 a.u.
Free Energy (298K):    -1646.092902 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir   0.038880   0.040698  -0.018804
 C    -2.015288  -0.130891   0.096574
```

C	2.102654	0.363861	0.146903
Cl	-0.177233	-1.797353	-1.789191
N	-2.618140	-1.036511	0.959193
N	-3.087652	0.506565	-0.510075
N	3.340187	-0.158824	-0.205446
N	2.430504	1.473258	0.899541
C	-4.003275	-0.969338	0.869702
C	-4.295267	-0.006935	-0.038710
C	4.367833	0.626859	0.315709
C	3.795830	1.651625	1.004077
C	-1.940934	-2.129305	1.731340
C	-0.477194	-1.769559	2.005453
C	1.374134	2.383510	1.408726
C	-3.029615	1.553950	-1.600338
C	-2.317434	2.808556	-1.068906
C	3.609094	-1.363771	-1.076628
C	2.922070	-2.592980	-0.461558
H	0.126004	-1.683184	1.058255
H	1.831241	-2.477533	-0.468344
H	-1.291754	2.577550	-0.762929
H	5.414176	0.397337	0.173226
H	4.249794	2.465987	1.555754
C	3.105873	-1.057961	-2.496995
C	5.124452	-1.633970	-1.134366
C	1.254553	3.571965	0.435300
C	1.757961	2.892579	2.809939
C	0.083949	1.536248	1.450008
H	3.282874	-2.759351	0.565769
H	3.163531	-3.483026	-1.062064
H	-5.259959	0.348578	-0.370707
H	-4.666004	-1.595920	1.452266
C	-2.324047	0.963592	-2.832680
C	-4.459684	1.956411	-2.007105
C	-2.652475	-2.299206	3.088912

C	-2.023398	-3.427734	0.904429
H	0.004956	-2.615373	2.520734
H	-2.858841	3.224632	-0.205047
H	-2.285737	3.574912	-1.858193
H	-0.375898	-0.882224	2.640738
H	-4.380563	2.716737	-2.796737
H	-5.028193	1.110879	-2.421600
H	-5.024277	2.402416	-1.173975
H	2.205722	4.122613	0.360231
H	0.978910	3.217932	-0.567651
H	0.480417	4.270359	0.787138
H	2.639541	3.554386	2.796227
H	0.918063	3.472080	3.220741
H	1.958664	2.051875	3.490695
H	-2.095280	-3.026832	3.696759
H	-2.694224	-1.347765	3.639720
H	-3.675173	-2.687844	2.979486
H	-1.557955	-4.256577	1.460149
H	-3.071870	-3.695935	0.704080
H	-1.501066	-3.297111	-0.055998
H	3.310191	-1.917848	-3.153065
H	2.022050	-0.885015	-2.500223
H	3.629096	-0.178527	-2.904503
H	5.279124	-2.527403	-1.755199
H	5.681798	-0.809810	-1.604853
H	5.551438	-1.842231	-0.141183
H	-2.239760	1.737620	-3.611292
H	-1.324749	0.584197	-2.588062
H	-2.903966	0.121592	-3.238783
H	-0.780427	2.217890	1.395018
H	0.065273	1.107517	-1.142237
H	0.029000	1.057248	2.448580

Information for structure 1bh2cis

SCF Convergence : 0.4546D-08
Maximum Force : 0.000014
Energy E(RB-P86) -1647.77211864 a.u.
ZPE-correction : 0.593319 a.u.
Energy (298K) : -1647.144560 a.u.
Enthalpy (298K) : -1647.143616 a.u.
Free Energy (298K): -1647.240550 a.u.

Atom Coordinates (x,y,z) in Angstrom

Ir	-0.091546	0.077771	-0.110656
C	-2.145820	0.353664	0.183647
C	2.013638	-0.184246	0.048103
Cl	0.080619	-1.573178	-2.072451
N	-2.455435	1.366429	1.064489
N	-3.381990	-0.176031	-0.149766
N	2.690343	-1.121609	0.840144
N	3.056308	0.566214	-0.508488
C	-3.817855	1.490482	1.258709
C	-4.399606	0.521551	0.501886
C	4.063694	-0.920030	0.776654
C	4.290291	0.119568	-0.054661
C	-1.390890	2.222828	1.647418
C	-1.322516	3.532359	0.838172
C	2.990016	1.688970	-1.526710
C	-3.666000	-1.326526	-1.089988
C	-3.264037	-0.909958	-2.514220
C	2.151697	-2.287297	1.668045
C	1.371433	-1.759106	2.886557
H	-1.075079	3.332340	-0.213727
H	0.474215	-1.206952	2.591049
H	-2.181646	-0.741268	-2.586257

H	4.781405	-1.521106	1.313108
H	5.231407	0.557528	-0.350770
C	1.335105	-3.238248	0.777507
C	3.331585	-3.113905	2.228247
C	4.416575	2.117397	-1.936254
C	2.341754	2.933602	-0.888082
C	2.299480	1.184456	-2.810716
H	2.048166	2.039272	-3.457598
H	2.989950	0.530480	-3.364689
H	1.398077	0.593624	-2.620622
H	2.011078	-1.098976	3.492580
H	1.064325	-2.609883	3.513880
H	-5.445514	0.274020	0.391256
H	-4.260565	2.227885	1.917348
C	-2.904415	-2.567843	-0.600191
C	-5.173307	-1.643951	-1.076188
C	-0.090465	1.393994	1.544165
C	-1.728408	2.539709	3.115480
H	-0.551682	4.194773	1.259687
H	-3.811764	-0.002891	-2.815308
H	-3.519724	-1.717145	-3.217563
H	-2.285303	4.066498	0.865981
H	-5.336972	-2.503547	-1.740923
H	-5.532281	-1.927325	-0.074853
H	-5.783649	-0.812605	-1.460928
H	4.989488	2.548243	-1.101286
H	4.987073	1.292293	-2.386224
H	4.314331	2.899731	-2.701969
H	2.974201	3.302408	-0.065621
H	2.255628	3.732380	-1.640019
H	1.347890	2.736216	-0.476557
H	0.764504	2.090237	1.520962
H	0.016941	0.810377	2.472562
H	0.131130	1.600021	-1.097541

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 H    -0.878313    3.071284    3.567982
 H    -2.615385    3.186058    3.220472
 H    -1.896378    1.614847    3.686652
 H     0.907614   -4.036087    1.404594
 H     0.529501   -2.729341    0.240178
 H     1.987987   -3.701705    0.022937
 H     2.899917   -3.968159    2.768428
 H     3.972813   -3.520472    1.432748
 H     3.946752   -2.551546    2.947064
 H    -3.121364   -3.414193   -1.269135
 H    -1.821502   -2.398171   -0.615821
 H    -3.226214   -2.836546    0.418199
 H    -0.212553   -1.087771    0.938270
 H    -0.366269    1.111016   -1.566473
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Information for structure 1bh2cis-4


SCF Convergence   : 0.8190D-08
Maximum Force     : 0.000001
Energy E(RB-P86)  -1647.74314969 a.u.
ZPE-correction    :        0.591370 a.u.
Energy (298K)     :    -1647.117748 a.u.
Enthalpy (298K)   :    -1647.116804 a.u.
Free Energy (298K):    -1647.214375 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir  -0.112146   -0.012417   -0.000960
 C   -2.145596    0.331623   -0.221915
 C    1.991782   -0.221634   -0.097620
 Cl  -0.146205   -0.783950    2.438725
 N   -2.463661    1.493881   -0.891353
 N   -3.376324   -0.247121    0.041409
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N	2.985699	0.703053	0.245441
N	2.680977	-1.159093	-0.879440
C	-3.830268	1.642018	-1.050533
C	-4.401475	0.562489	-0.457183
C	4.180542	0.393459	-0.402351
C	3.993777	-0.753517	-1.088991
C	-1.419336	2.377581	-1.477965
C	-1.269684	2.034401	-2.973468
C	2.250107	-2.566267	-1.282724
C	-3.704578	-1.454861	0.899134
C	-2.700915	-2.592219	0.672068
C	3.114135	1.751999	1.354762
C	3.581988	3.072136	0.709257
H	-0.918930	1.000978	-3.100442
H	2.852006	3.416097	-0.037860
H	-1.706040	-2.331315	1.048345
H	5.074309	0.995676	-0.311574
H	4.694678	-1.297920	-1.704118
C	1.854242	2.022662	2.180189
C	4.179482	1.213437	2.341777
C	3.473219	-3.337352	-1.827414
C	1.202801	-2.545225	-2.410913
C	1.775256	-3.314443	-0.021764
H	1.407774	-4.311926	-0.308580
H	2.616180	-3.444686	0.676820
H	0.976195	-2.778487	0.502187
H	4.563564	2.988968	0.220543
H	3.664606	3.844177	1.488585
H	-5.447861	0.316397	-0.348214
H	-4.284013	2.486466	-1.554640
C	-3.706406	-1.006099	2.371727
C	-5.105190	-1.975102	0.510896
C	-0.103150	2.133545	-0.698585
C	-1.855769	3.846999	-1.325603

H	-0.541512	2.713426	-3.442007
H	-2.631156	-2.852366	-0.394534
H	-3.056145	-3.476702	1.222449
H	-2.230618	2.144222	-3.499738
H	-5.277347	-2.917296	1.049549
H	-5.915430	-1.290608	0.802049
H	-5.179620	-2.184342	-0.567213
H	3.851406	-2.924626	-2.775475
H	4.294433	-3.391617	-1.097940
H	3.145158	-4.366293	-2.030758
H	1.577076	-1.964470	-3.268573
H	1.025458	-3.577761	-2.750054
H	0.253678	-2.115129	-2.081523
H	0.755765	2.179895	-1.380065
H	0.022946	2.967264	0.010475
H	-0.053867	-0.083685	-1.589668
H	-1.039070	4.499081	-1.668348
H	-2.744309	4.089329	-1.929559
H	-2.068647	4.085044	-0.272929
H	2.168382	2.608338	3.058447
H	1.125576	2.635612	1.637115
H	1.370200	1.101651	2.534456
H	4.339073	1.953130	3.139992
H	3.826550	0.279797	2.803194
H	5.148783	1.020145	1.862839
H	-3.990297	-1.853452	3.015111
H	-2.703414	-0.667843	2.669755
H	-4.433787	-0.194264	2.530286
H	-0.029991	1.356611	0.845268
H	-0.297652	-1.603043	-0.217123

Information for structure 1bh2trans

```
SCF Convergence   : 0.4465D-08
Maximum Force     : 0.000026
Energy E(RB-P86)  -1647.77267990 a.u.
ZPE-correction    :        0.592066 a.u.
Energy (298K)     :    -1647.145947 a.u.
Enthalpy (298K)   :    -1647.145003 a.u.
Free Energy (298K):    -1647.244326 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir   0.089847   0.026017  -0.178080
 C    2.098390   0.075495   0.264985
 C   -2.069485   0.202797  -0.212132
 H    0.246999   0.639374  -1.802857
 N    2.413987  -0.109618   1.584071
 N    3.321335   0.256408  -0.356695
 N   -2.785339   1.386789   0.054883
 N   -3.074381  -0.764825  -0.232939
 C    3.780847  -0.078247   1.793345
 C    4.351833   0.154483   0.581374
 C   -4.131021   1.110034   0.263305
 C   -4.307871  -0.217166   0.087622
 C    1.370036  -0.386477   2.608507
 C    1.569243  -1.824688   3.123686
 C   -2.994845  -2.236371  -0.619756
 C    3.565682   0.509555  -1.821901
 C    3.051758  -0.687901  -2.640696
 C   -2.336408   2.844533   0.036202
 C   -1.529109   3.185305   1.303174
 H    1.457469  -2.534770   2.291619
 H   -0.611020   2.593692   1.378282
 H    2.003935  -0.920706  -2.424012
 H   -4.866303   1.860150   0.510213
 H   -5.216305  -0.796126   0.159360
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C	-1.580244	3.148905	-1.270501
C	-3.576258	3.769672	0.037365
C	-4.419115	-2.775609	-0.881685
C	-2.393052	-3.037359	0.543913
C	-2.218535	-2.372128	-1.938097
H	-2.218394	-3.428453	-2.245754
H	-2.708237	-1.780269	-2.727758
H	-1.172567	-2.069405	-1.828003
H	-2.138473	3.001028	2.201091
H	-1.257569	4.252074	1.286357
H	5.396111	0.252950	0.321489
H	4.235018	-0.221231	2.766462
C	2.889498	1.835265	-2.218894
C	5.076862	0.654656	-2.080926
C	-0.010059	-0.223873	1.914453
C	1.536389	0.626830	3.756572
H	0.808819	-2.047493	3.887313
H	3.633618	-1.589798	-2.401289
H	3.163877	-0.473762	-3.714910
H	2.561912	-1.959035	3.584292
H	5.218554	0.841310	-3.154927
H	5.514827	1.504482	-1.535921
H	5.629444	-0.262681	-1.830121
H	-5.033596	-2.828899	0.029707
H	-4.953322	-2.196944	-1.650443
H	-4.311634	-3.803915	-1.253525
H	-2.997139	-2.891008	1.453555
H	-2.401514	-4.109107	0.293162
H	-1.349321	-2.756410	0.726274
H	-0.606927	-1.130186	2.095845
H	-0.551792	0.611534	2.384700
Cl	0.761855	-2.535670	-0.406277
H	0.747860	0.460325	4.505261
H	2.508079	0.525196	4.266604

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 H     1.445850   1.657991   3.382698
 H    -1.303620   4.214081  -1.286791
 H    -0.670188   2.550948  -1.364309
 H    -2.226771   2.946697  -2.138092
 H    -3.214396   4.802672  -0.060711
 H    -4.246787   3.569597  -0.810920
 H    -4.147157   3.716979   0.975833
 H     3.023289   2.013271  -3.296557
 H     1.816807   1.822633  -1.995550
 H     3.341370   2.675380  -1.669334
 H     0.049294   1.565852   0.098055
 H     0.053745  -0.222499  -1.912269
-------------------------------------

Information for structure 1bh2trans-4


SCF Convergence   : 0.4734D-08
Maximum Force     : 0.000003
Energy E(RB-P86)  -1647.75710497 a.u.
ZPE-correction    :        0.591327 a.u.
Energy (298K)     :    -1647.131557 a.u.
Enthalpy (298K)   :    -1647.130613 a.u.
Free Energy (298K):    -1647.228783 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir    0.068982   0.014561  -0.018596
 C     2.118003   0.151395   0.076799
 C    -2.099704  -0.002584   0.143481
 H    -0.053674  -1.213721   1.028349
 N     2.726788   1.007525  -0.807394
 N     3.159995  -0.394510   0.799096
 N    -2.986837  -1.068954  -0.002499
 N    -2.870681   0.947068   0.846623
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C	4.102889	0.998207	-0.657400
C	4.375923	0.120292	0.343708
C	-4.187792	-0.819651	0.643922
C	-4.118285	0.423196	1.167386
C	1.965045	1.884165	-1.742450
C	2.035370	3.325863	-1.201000
C	-2.605446	2.420900	1.132535
C	3.071658	-1.431356	1.897158
C	2.205101	-0.884724	3.045502
C	-2.839167	-2.319777	-0.857276
C	-2.497792	-1.877921	-2.289114
H	1.566512	3.390650	-0.207711
H	-1.560975	-1.313408	-2.326546
H	1.181183	-0.688662	2.710102
H	-5.002400	-1.527114	0.682028
H	-4.865294	0.957339	1.733730
C	-1.817836	-3.276890	-0.226012
C	-4.188853	-3.067678	-0.922783
C	-3.888400	3.082593	1.688083
C	-2.280524	3.139367	-0.187201
C	-1.514383	2.629018	2.201089
H	-1.531569	3.680772	2.526448
H	-1.709434	1.996354	3.079761
H	-0.512080	2.400162	1.828858
H	-3.322025	-1.271881	-2.698449
H	-2.368747	-2.766861	-2.924282
H	5.330597	-0.176342	0.753371
H	4.770974	1.595318	-1.266001
C	2.503694	-2.736743	1.316128
C	4.480707	-1.711656	2.451654
C	0.513793	1.375672	-1.791323
C	2.601856	1.800828	-3.142846
H	1.507024	4.008766	-1.882957
H	2.634085	0.047554	3.444855

H	2.172062	-1.625432	3.858940
H	3.077021	3.671274	-1.111267
H	4.383013	-2.452763	3.257211
H	5.150453	-2.140935	1.691684
H	4.947038	-0.812541	2.882751
H	-4.743058	2.984685	1.003554
H	-4.168564	2.698773	2.680372
H	-3.678491	4.155158	1.802115
H	-3.137383	3.082175	-0.875600
H	-2.068767	4.200580	0.014152
H	-1.413621	2.700230	-0.685840
H	-0.144071	2.206178	-2.086202
H	0.403254	0.575817	-2.533770
H	0.011592	1.606777	-0.203498
H	1.990743	2.377978	-3.852228
H	3.621447	2.218718	-3.166072
H	2.633016	0.756002	-3.482064
H	-1.760398	-4.194105	-0.831240
H	-0.817300	-2.837191	-0.191636
H	-2.141026	-3.550701	0.790971
H	-4.049557	-3.920588	-1.601579
H	-4.499376	-3.477018	0.050866
H	-4.997786	-2.446171	-1.335445
H	2.418267	-3.486175	2.118165
H	1.517951	-2.576969	0.864749
H	3.168945	-3.132209	0.534668
Cl	0.763243	-1.778179	-1.791505
H	-0.046339	0.634374	1.421185

Information for structure 4-2h

SCF Convergence : 0.7763D-08

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Maximum Force     : 0.000012
Energy E(RB-P86)  -1647.78896012 a.u.
ZPE-correction    :        0.595303 a.u.
Energy (298K)     :    -1647.158733 a.u.
Enthalpy (298K)   :    -1647.157788 a.u.
Free Energy (298K):    -1647.257420 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir  -0.012512  -0.032676  -0.125990
 C    2.106713   0.027665  -0.141866
 C   -2.103102   0.013267  -0.180348
 Cl  -0.057598  -0.390186   2.404429
 N    3.004872  -1.000623  -0.437686
 N    2.957214   1.122132   0.065734
 N   -2.961585  -1.068031   0.003329
 N   -2.988260   1.079286  -0.367295
 C    4.317944  -0.554047  -0.421812
 C    4.287820   0.762079  -0.113435
 C   -4.292721  -0.675973  -0.032259
 C   -4.309383   0.656189  -0.267632
 C    2.680139  -2.455639  -0.654808
 C    1.708346  -2.576688  -1.839729
 C   -2.653491   2.530414  -0.621943
 C    2.605855   2.553232   0.424804
 C    1.930039   3.227812  -0.784271
 C   -2.613565  -2.493871   0.313303
 C   -1.204742  -2.793790  -0.185083
 H    0.852192  -1.897839  -1.726064
 H   -0.459184  -2.180977   0.359001
 H    1.031634   2.691810  -1.107436
 H   -5.116258  -1.363323   0.106442
 H   -5.154733   1.319707  -0.374571
 C   -2.723430  -2.715258   1.833585
 C   -3.589960  -3.425901  -0.437169
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C	-1.930802	3.098459	0.612331
C	-3.946329	3.348020	-0.816671
C	-1.843001	2.643234	-1.925461
H	-1.121687	-2.640486	-1.267222
H	-0.947123	-3.838603	0.046187
H	5.111295	1.451770	-0.006206
H	5.167263	-1.191097	-0.621189
C	1.761776	2.577353	1.708157
C	3.893146	3.353377	0.722811
C	2.151487	-3.027730	0.675078
C	3.953276	-3.240686	-1.030866
H	1.350042	-3.612931	-1.930595
H	2.626660	3.262178	-1.636438
H	1.649817	4.260025	-0.524953
H	2.222883	-2.302950	-2.774109
H	3.587268	4.361160	1.037996
H	4.473061	2.912724	1.546843
H	4.539089	3.470090	-0.160337
H	-2.614447	3.116591	1.474754
H	-1.065486	2.487193	0.890028
H	-1.597089	4.127906	0.411519
H	-4.581403	3.355178	0.081674
H	-3.651917	4.388312	-1.015707
H	-4.536290	3.002334	-1.678817
H	1.746454	-4.039568	0.522366
H	2.976801	-3.094773	1.400552
H	1.382195	-2.389143	1.127961
H	3.657388	-4.284340	-1.211198
H	4.417973	-2.863920	-1.954399
H	4.699106	-3.248666	-0.222506
H	-2.498351	-3.765978	2.074496
H	-2.012198	-2.064491	2.364499
H	-3.744034	-2.497025	2.184347
H	-3.242293	-4.463216	-0.325555

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 H    -4.610262  -3.385372  -0.029905
 H    -3.627217  -3.187935  -1.510782
 H     1.425525   3.606790   1.905313
 H     0.894756   1.910121   1.658736
 H     2.368709   2.242309   2.562596
 H    -1.535314   3.688129  -2.082188
 H    -0.954777   2.002387  -1.904503
 H    -2.463760   2.334779  -2.781144
 H     0.077001   1.488019  -0.237742
 H     0.017519   0.063856  -1.714695
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Information for structure 4-h2


SCF Convergence   : 0.6284D-08
Maximum Force     : 0.000032
Energy E(RB-P86)  -1647.79306126 a.u.
ZPE-correction    :        0.594352 a.u.
Energy (298K)     :    -1647.163704 a.u.
Enthalpy (298K)   :    -1647.162760 a.u.
Free Energy (298K):    -1647.262146 a.u.

Atom Coordinates (x,y,z) in Angstrom
 Ir    0.000012   0.000002  -0.079259
 C     2.105006  -0.069306  -0.132916
 C    -2.104951   0.069307  -0.132947
 Cl   -0.000166  -0.000100   2.402093
 N     2.913144  -1.202534  -0.252645
 N     3.036511   0.974162  -0.122139
 N    -3.036496  -0.974125  -0.122151
 N    -2.913059   1.202578  -0.252594
 C     4.256132  -0.857965  -0.334144
 C     4.332411   0.489552  -0.248138
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C	-4.332389	-0.489453	-0.248004
C	-4.256061	0.858062	-0.333955
C	2.491055	-2.649548	-0.361510
C	1.976161	-2.908104	-1.789931
C	-2.490916	2.649554	-0.361595
C	2.787247	2.454803	0.080513
C	1.860807	2.979928	-1.025103
C	-2.787365	-2.454793	0.080415
C	-1.860661	-2.979969	-1.024959
H	1.125354	-2.257382	-2.026505
H	-0.894963	-2.464364	-0.999766
H	0.895105	2.464295	-1.000054
H	-5.207507	-1.121547	-0.260433
H	-5.052276	1.581209	-0.434612
C	-2.220393	-2.677328	1.491482
C	-4.115427	-3.232591	-0.027586
C	-1.444698	2.969108	0.709825
C	-3.704905	3.569033	-0.111447
C	-1.976313	2.908010	-1.790143
H	-2.313619	-2.822045	-2.016015
H	-1.695059	-4.058750	-0.884077
H	5.207493	1.121690	-0.260615
H	5.052359	-1.581081	-0.434933
C	2.219894	2.677206	1.491453
C	4.115265	3.232715	-0.027040
C	1.445098	-2.969114	0.710168
C	3.705172	-3.568926	-0.111631
H	1.657249	-3.956727	-1.890923
H	2.313998	2.821967	-2.016043
H	1.695164	4.058716	-0.884336
H	2.773380	-2.717298	-2.525006
H	3.884179	4.298928	0.107418
H	4.831911	2.954524	0.759742
H	4.591877	3.120367	-1.012901

H	-1.853910	2.811971	1.717980
H	-0.567776	2.314764	0.604575
H	-1.126062	4.017762	0.610509
H	-4.181226	3.364129	0.858676
H	-3.340952	4.606138	-0.092533
H	-4.460715	3.507583	-0.908540
H	1.126441	-4.017771	0.610931
H	1.854592	-2.812014	1.718212
H	0.568144	-2.314771	0.605155
H	3.341358	-4.606081	-0.093043
H	4.461000	-3.507133	-0.908684
H	4.181448	-3.364253	0.858566
H	-1.960462	-3.738925	1.623851
H	-1.333623	-2.060570	1.681836
H	-2.973561	-2.409894	2.248559
H	-3.884510	-4.298812	0.107089
H	-4.832368	-2.954254	0.758880
H	-4.591616	-3.120304	-1.013657
H	1.959882	3.738784	1.623814
H	1.333062	2.060449	1.681554
H	2.972863	2.409759	2.248723
H	-1.657875	3.956742	-1.891436
H	-1.125223	2.257621	-2.026620
H	-2.773517	2.716701	-2.525101
H	0.014612	0.819433	-1.411568
H	-0.014449	-0.819668	-1.411430

References

[1] Scott, N. M.; Dorta, R.; Stevens, E. D.; Correa, A.; Cavallo, L.; Nolan, S. P. *J. Am. Chem. Soc.* **2005**, *127*, 3516-3526.