Supporting Online Material for

Synthesis of a Chloro Protected Iridium Nitrido Complex.

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1) Experimental Section

a) IR spectra of 4-Cl and 4-Cl-15N:

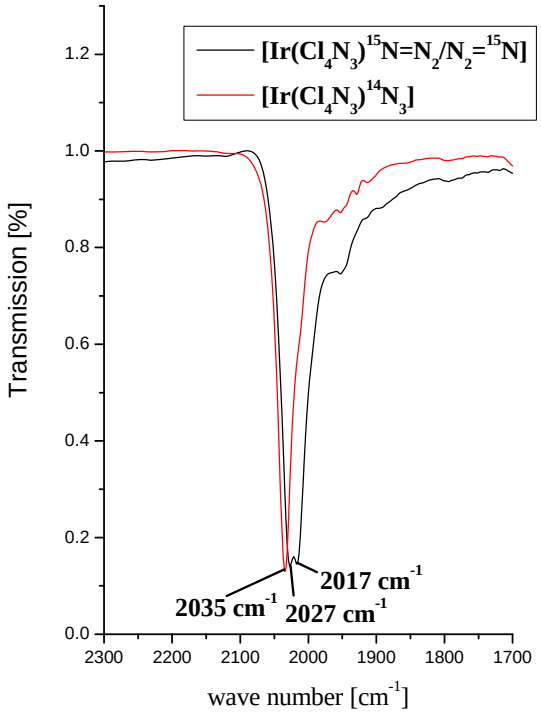

Figure S1: Azido region of the IR spectra of complexes **4-Cl** and **4-Cl-^{15}N**.

b) UV/vis and ^{1}H NMR spectra of 4-Me after thermolysis at 90 °C:

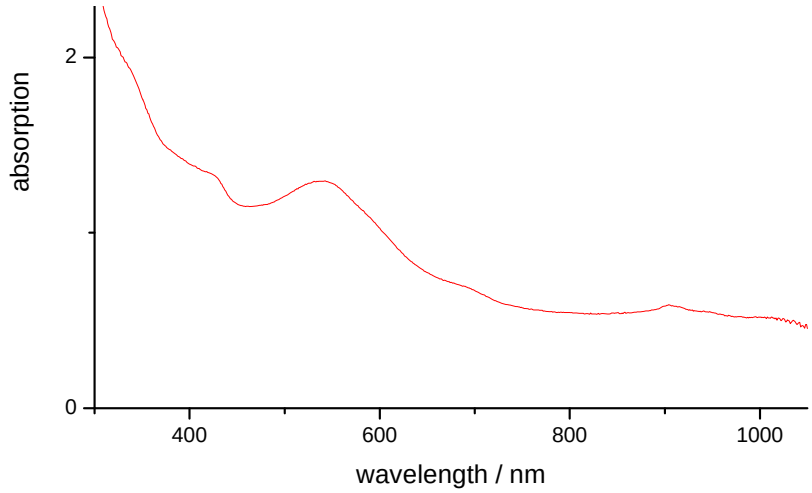

Figure S2: UV/vis spectrum (THF) of **4-Me** after thermolysis at 90 °C.

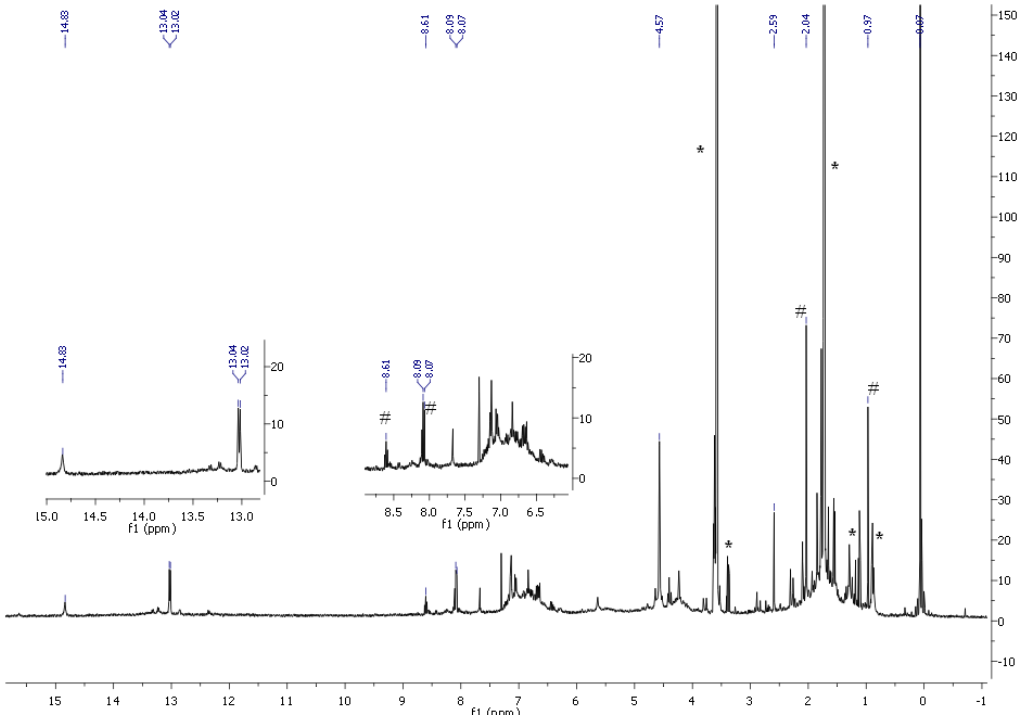

Figure S3: Room temperature ^{1}H NMR spectrum (400 MHz; THF-d_8) of **4-Me** after thermolysis at 90 °C. *: THF-d_8 and solvent impurities; #: residual **4-Me**.

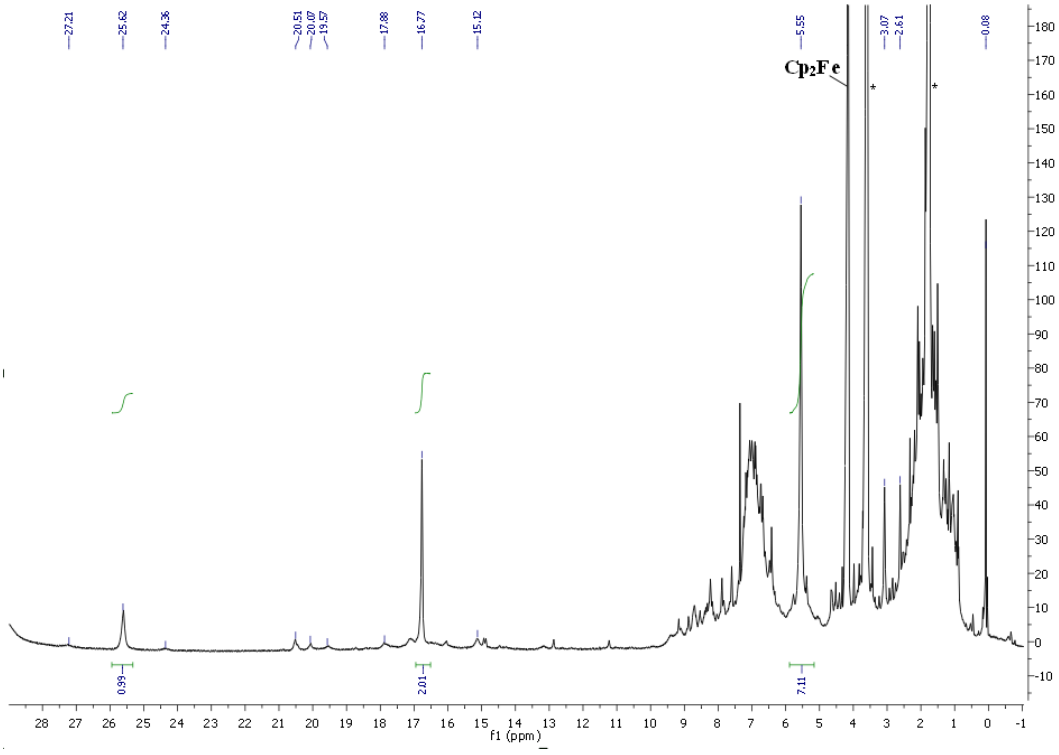

Figure S4: -80 °C ^{1}H NMR spectrum (500 MHz; THF-d_8) of **4-Me** after thermolysis at 90 °C (range: -1 to 28 ppm). *: THF-d_8, Cp_2Fe was used as an internal standard.

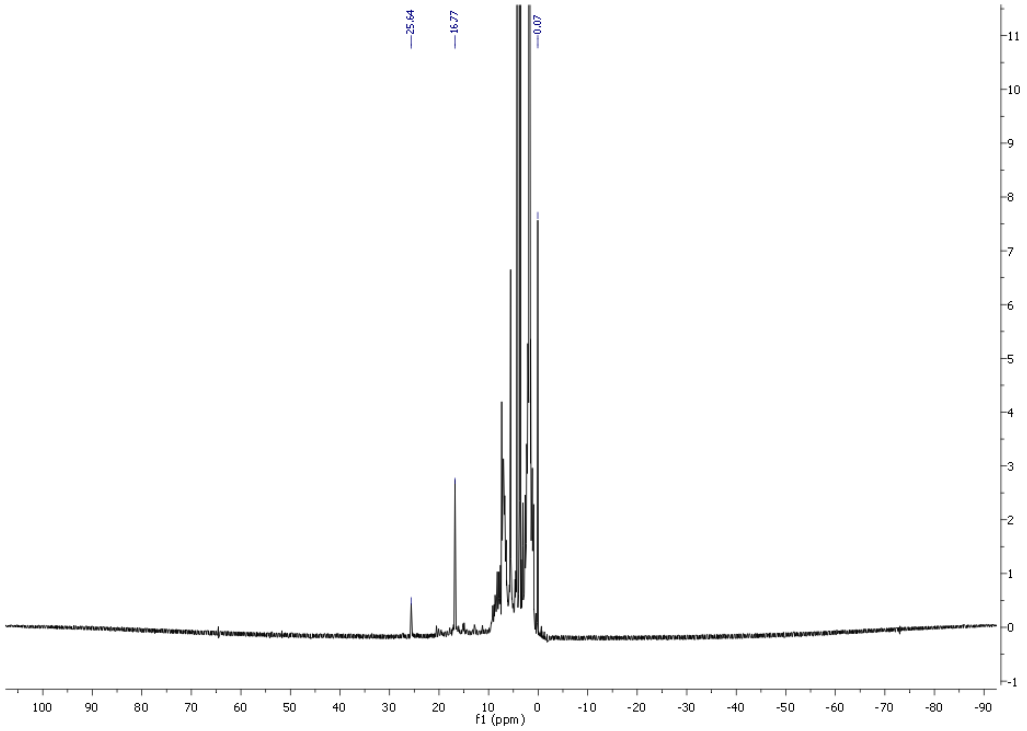

Figure S5: -80 °C ^{1}H NMR spectrum (500 MHz; THF-d_8) of **4-Me** after thermolysis at 90 °C (range: -90 – 100 ppm).

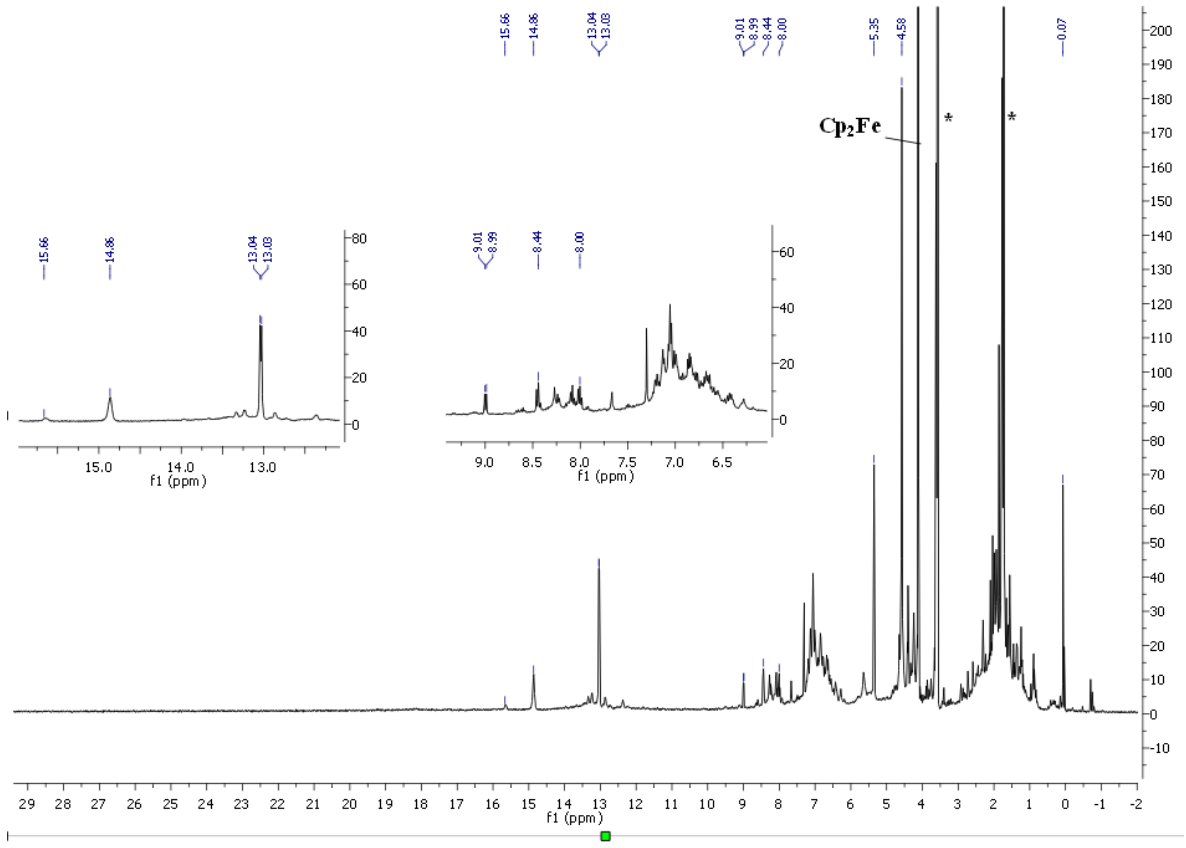

Figure S6: ^{1}H NMR spectrum (400 MHz; THF-d_8) of the same sample used in Figs. S4 and S5 after the probe was allowed to warm to room temperature. *: THF-d_8, Cp_2Fe was used as an internal standard.

c) DSC measurement of 4-Cl:

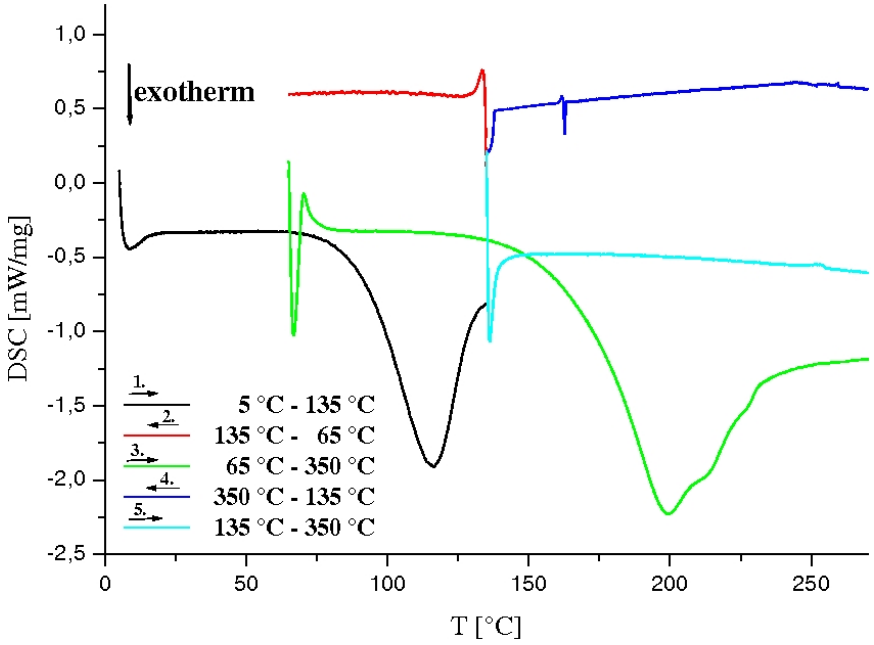

Figure S7: DSC test of the thermolysis steps of **4-Cl** for reversibility.

d) IR and UV/vis spectra of 6-Cl after thermolysis at 150 °C:

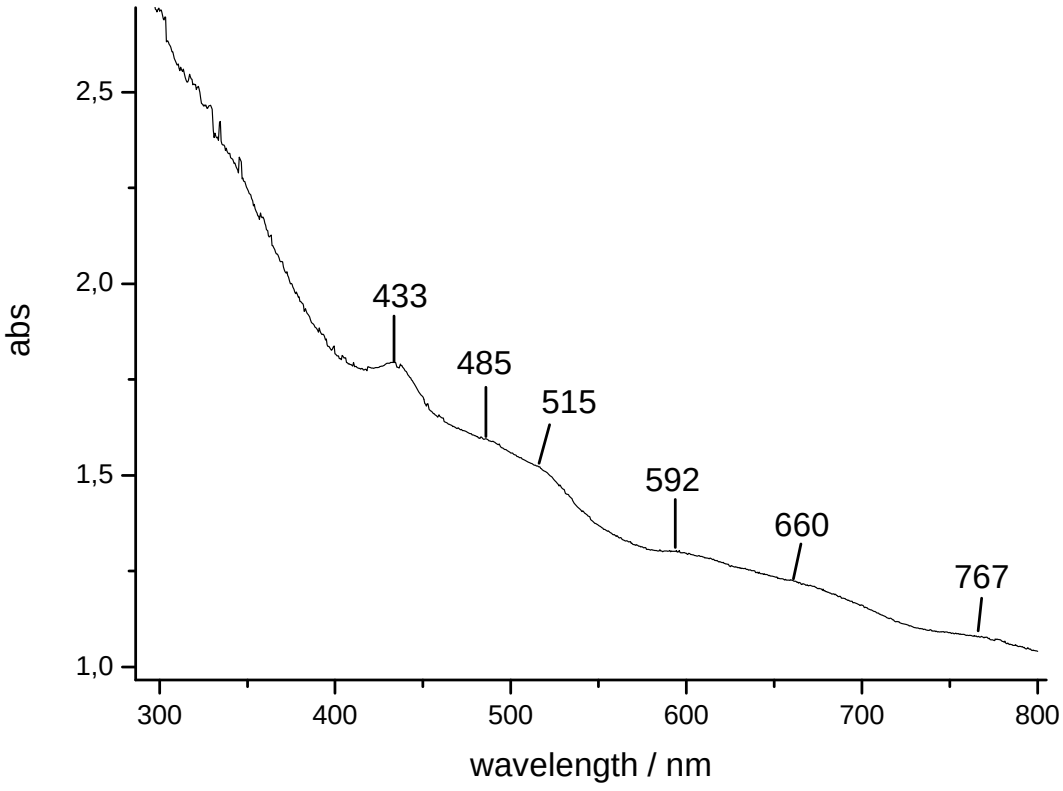

Figure S8: UV/vis spectrum (KBr) of **6-Cl** after thermolysis at 150 °C.

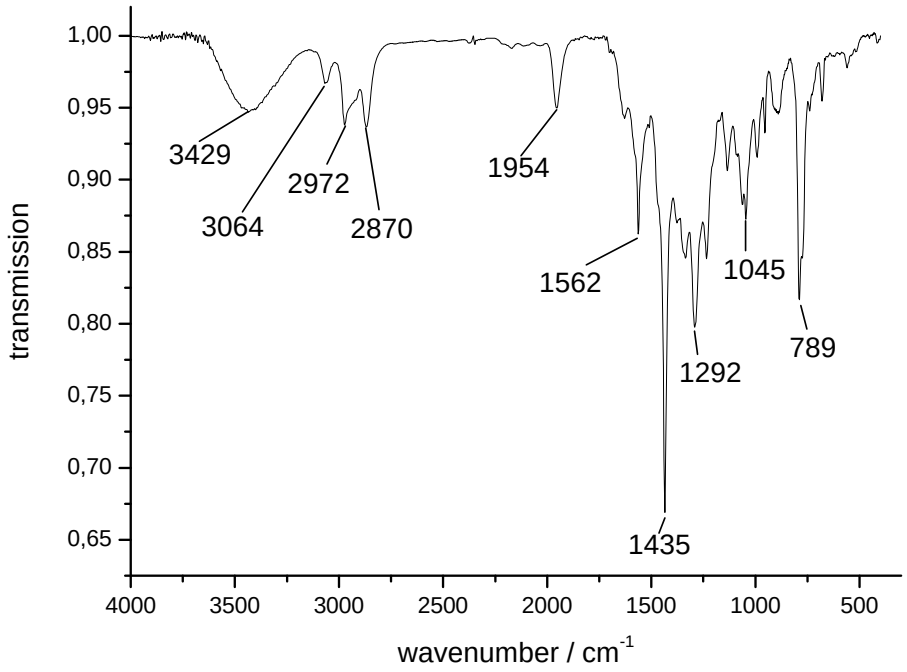

Figure S9: IR spectrum (KBr) of 6-Cl after thermolysis at 150 °C.

e) Comparison of the UV/vis and IR spectra of 6-Cl. Original solid material and dissolved material:

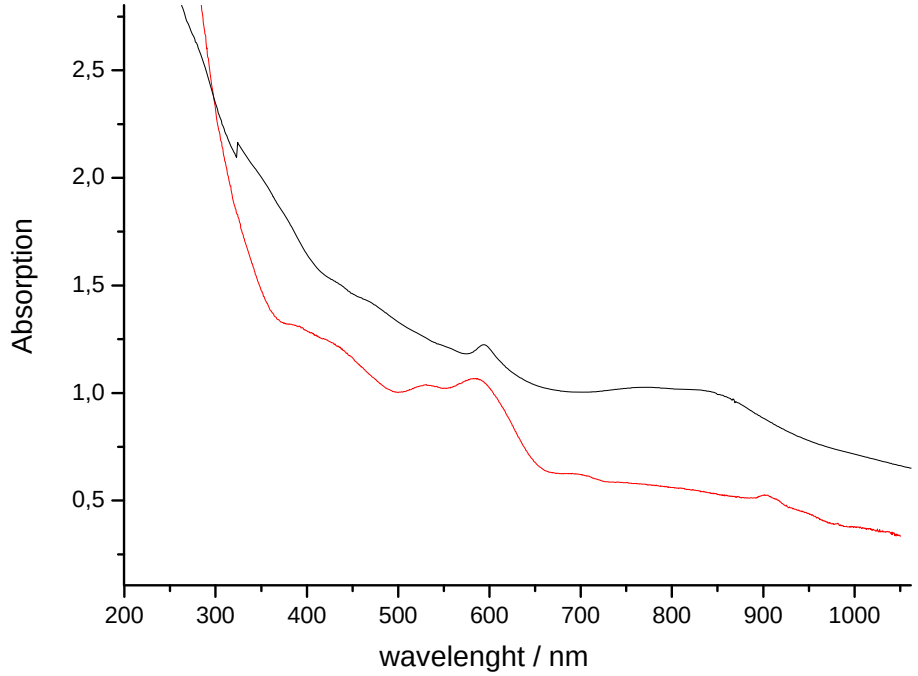

Figure S10: UV/vis spectra of **6-Cl**. Red: originally solid material (KBr); Black: THF extracted material (THF).

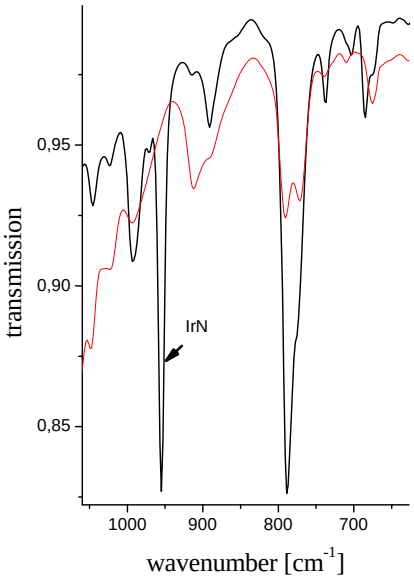

Figure S11: Section of the IR spectra of **6-Cl**. Black: original solid material (KBr); red: THF extracted material (KBr).

f) NMR spectra of 9 and 10:

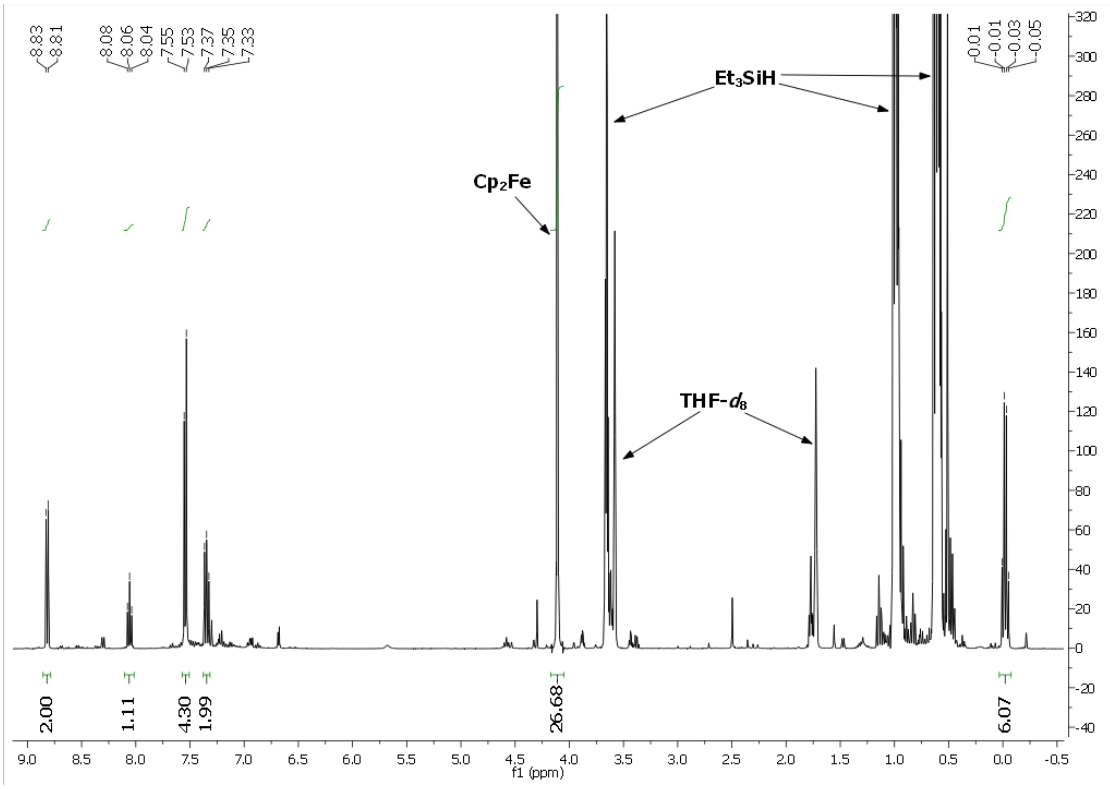

Figure S12: Exemplary raw ^{1}H NMR spectrum of the reaction of **5-Cl** with Et_3SiH with Cp_2Fe as an internal standard (400 MHz; THF-d_8). Initial quantities: **5-Cl**: 19.7 mg (30.0 µmol); Et_3SiH: 48.0 µl (34.9 mg, 300 µmol); Cp_2Fe: 7.6 mg (40.9 µmol).

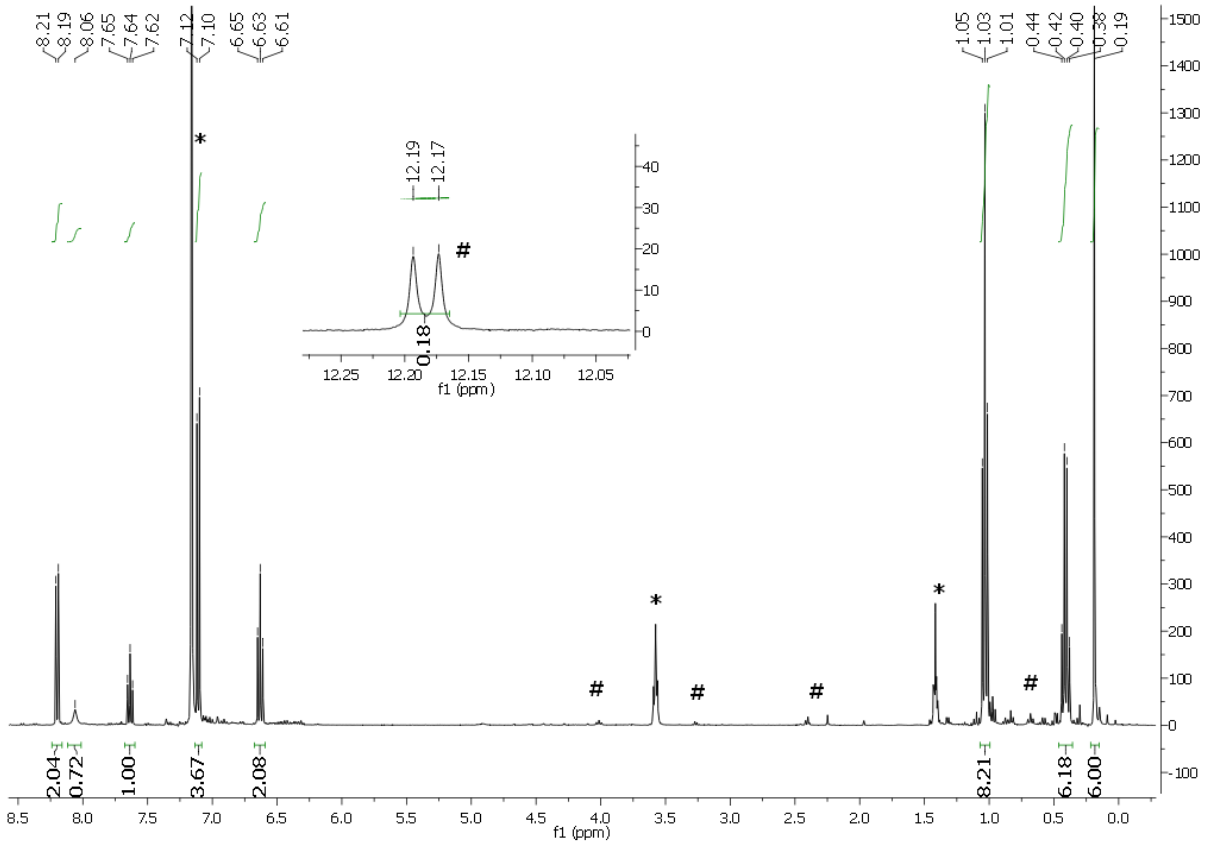

Figure S13: Room temperature ^{1}H NMR spectrum of **9** (400 MHz; C_6D_6). *: C_6D_6 and residual solvents; #: unidentified impurities.

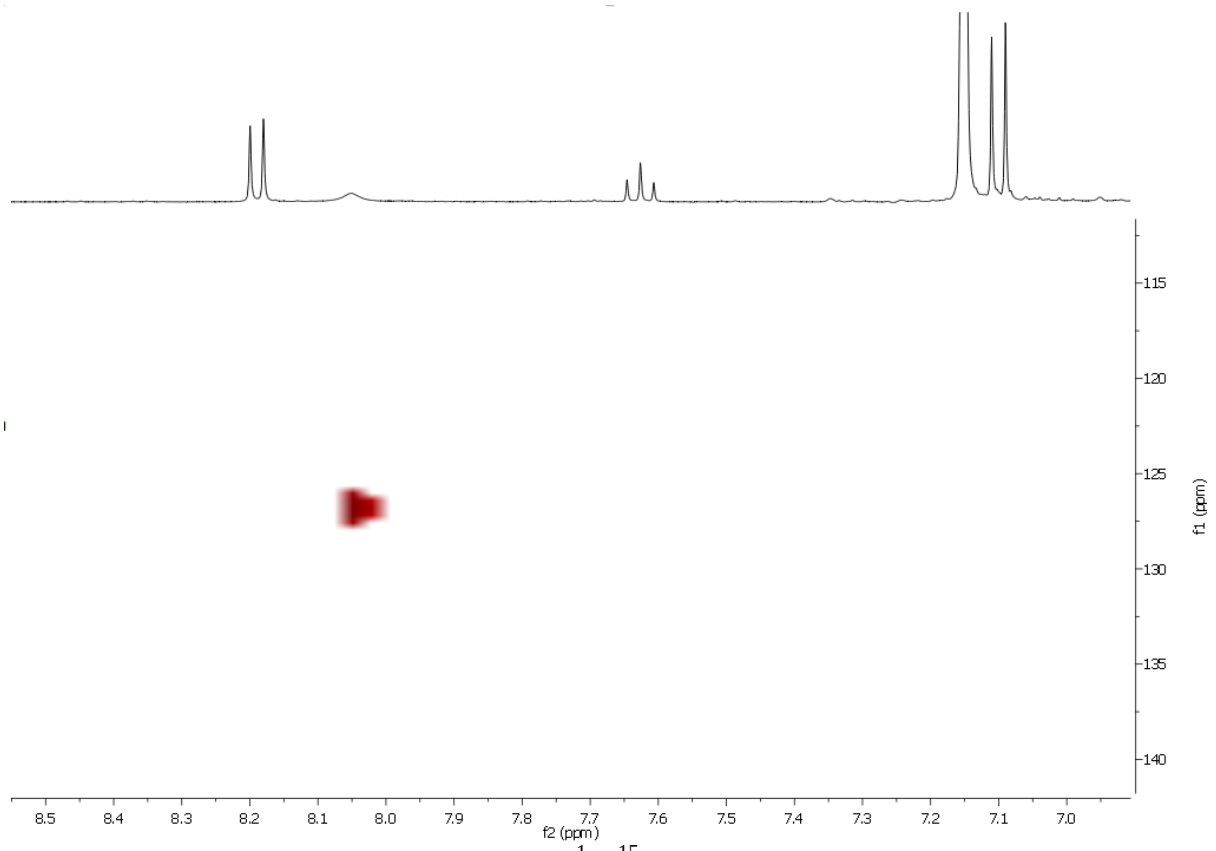

Figure S14: Part of the ^{1}H,^{15}N-HSQC spectrum of **9**.

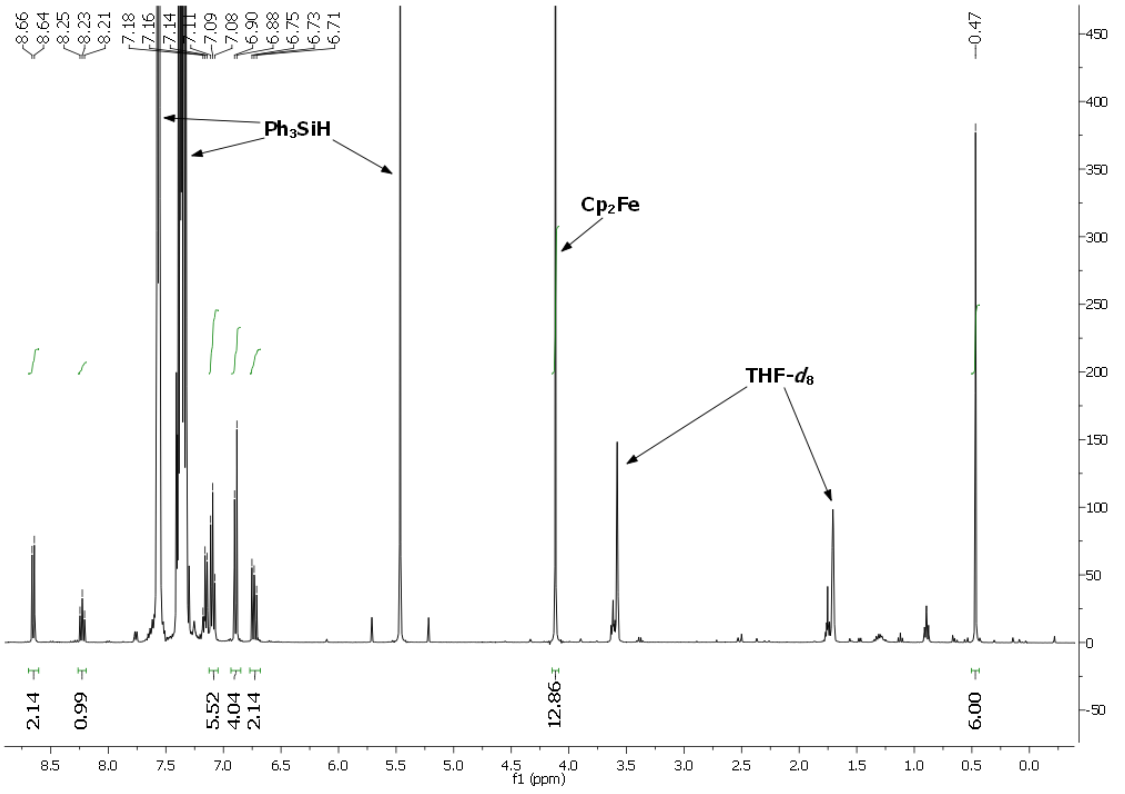

Figure S15: Exemplary raw ^{1}H NMR spectrum of the reaction of **5-Cl** with Ph_3SiH with Cp_2Fe as an internal standard (400 MHz; THF-d_8). Initial quantities: **5-Cl**: 15.7 mg (23.9 µmol); Ph_3SiH: 68.6 mg (263 µmol); Cp_2Fe: 4.8 mg (25.8 µmol).

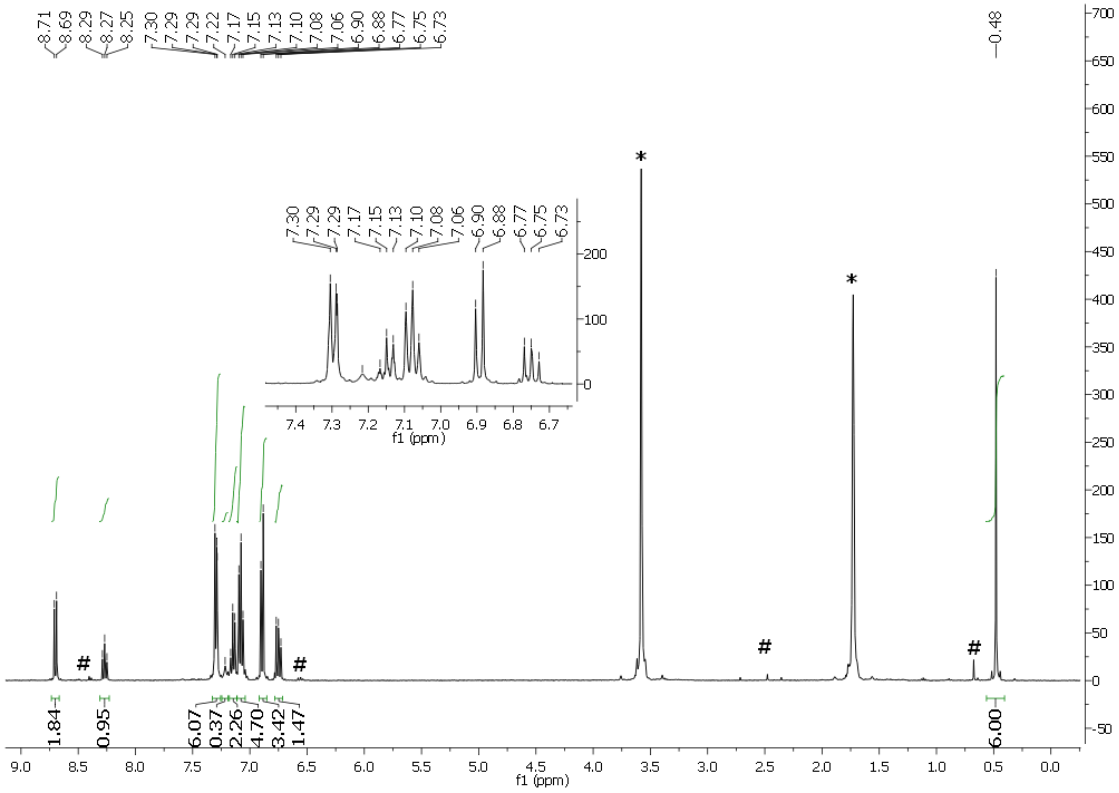

Figure S16: Room temperature ^{1}H NMR spectrum of **10** (400 MHz; THF-d_8). *: THF-d_8; #: unidentified impurities.

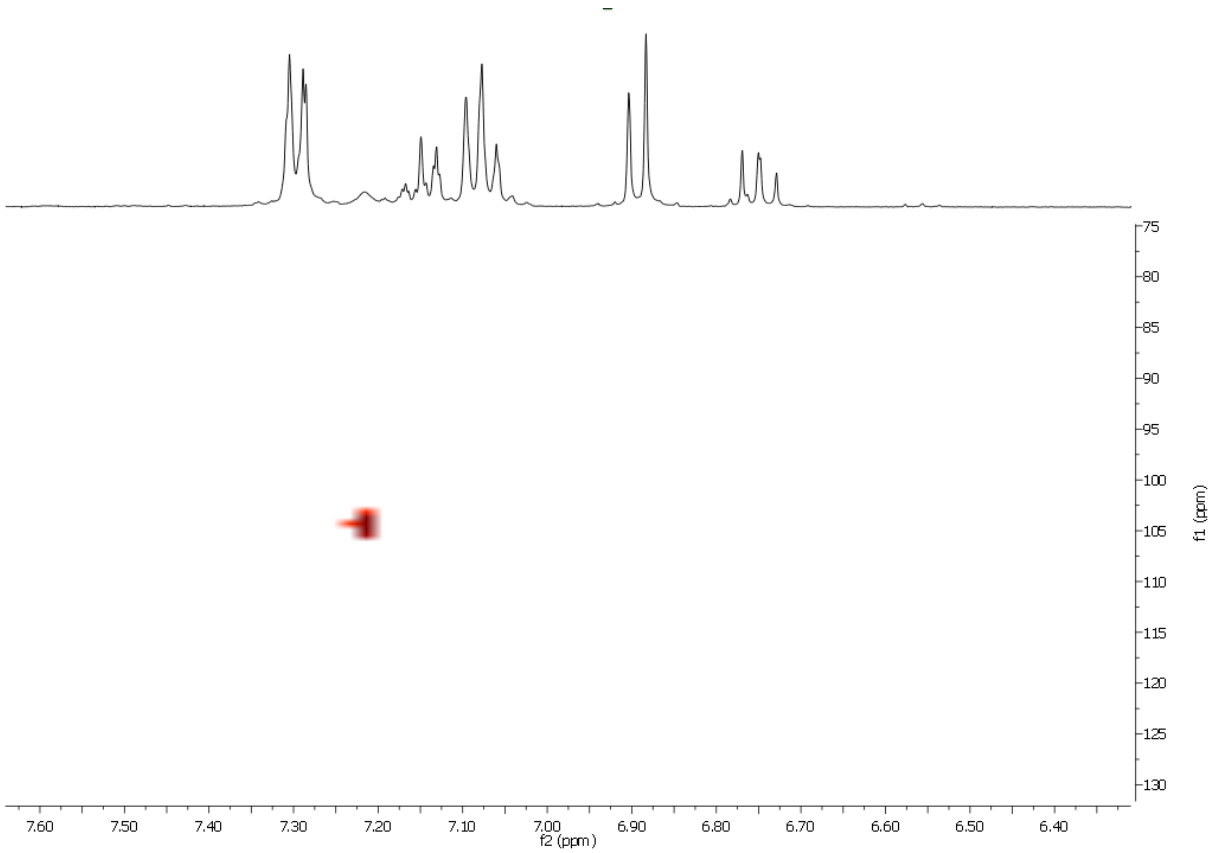

Figure S17: Part of the $^{1}H,^{15}N$-HSQC spectrum of **10**.

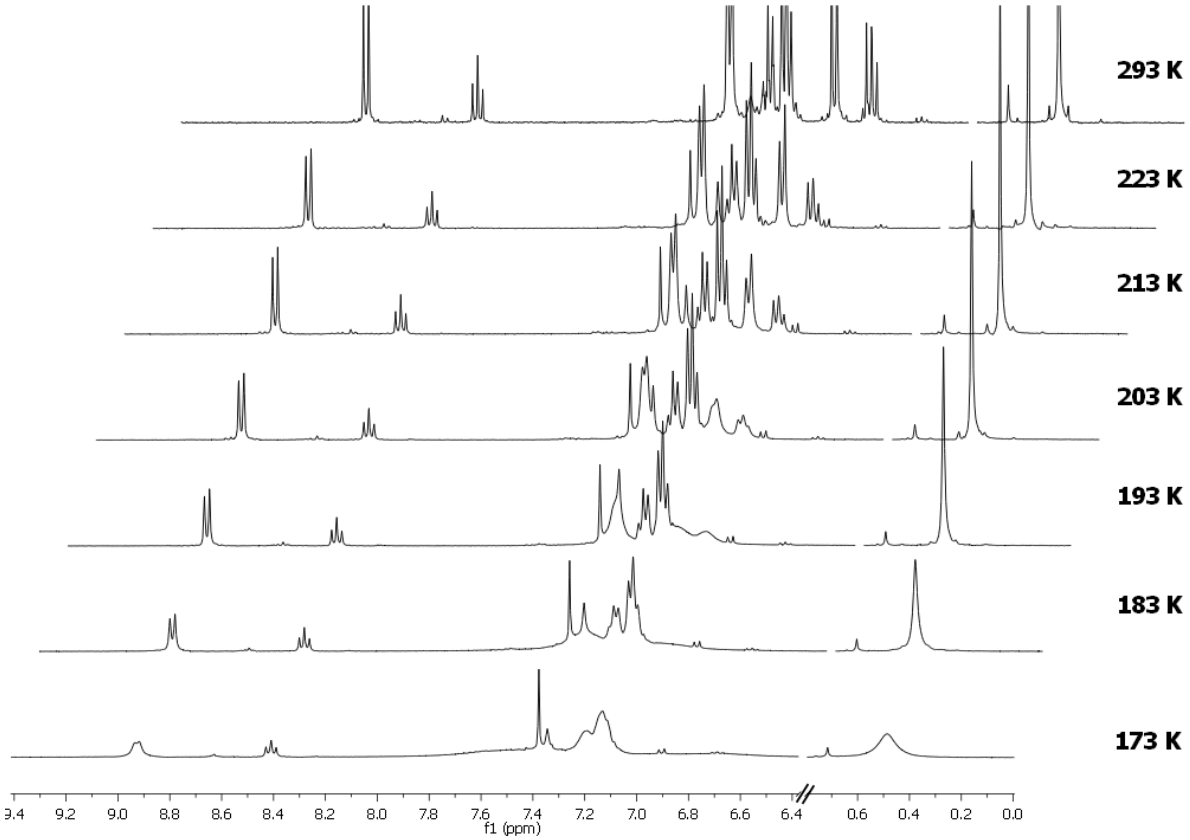

Figure S18: VT NMR spectra of **10** (400 MHz; THF-d_8).

2. **Computational Results**

Table S1. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the azido complex **4-Me** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atoms of the azido ligand; the basis set of the latter N atoms was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.

```
59
Energy = -1401.360037229
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C     0.1126708    4.0647065   -2.2843695
C     0.0976454    4.0608396   -0.8763625
N     0.0435969    1.6463381   -0.9039904
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H     0.1129527    5.0050999   -0.3140198
C     0.0336707    0.2811032   -2.8086622
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N     0.0110234    1.2986055    1.5935297
N     0.0021429   -0.6763661   -1.8605915
Ir   -0.0032581   -0.0054692    0.0447713
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H     0.9497039    0.4324602   -4.7623440
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H     0.9678573    4.3578771    2.0960562
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C    -0.0783510   -4.7919015   -2.8595236
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C    -1.2787104   -2.7100435   -2.3924987
C    -1.2781334   -4.0822405   -2.7104808
C     1.1482228   -4.1359031   -2.6849423
H    -2.2428755   -4.5994569   -2.8324459
H     2.0914893   -4.6953781   -2.7867139
H    -0.0995314   -5.8655191   -3.0997797
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C     1.1719216    0.2088789    4.9725917
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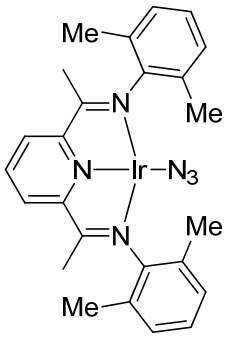

4-Me

C	2.5211605	-2.0599484	-2.1576419
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H	2.7040111	-1.2809910	-2.9284092
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H	-2.5875422	-1.4258427	-1.2309494
H	-3.4417962	-2.6247417	-2.2677909
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H	2.7042586	1.8866679	2.6131231
H	2.5537939	0.2306428	1.9820697
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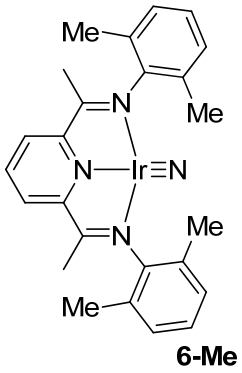
H	-2.6721707	1.9950407	2.5604372
H	-3.4250974	0.6632797	3.4923574
H	-2.5805812	0.3319981	1.9367403
N	-0.0717483	-2.8529354	0.9501075
N	-0.0923871	-4.0101681	0.9015500

Table S2. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the azido complex **6-Me** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atom of the nitrido ligand; the basis set of the latter N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.



6-Me

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C     0.1083366    1.2501157    1.7384811
C     0.0922811    1.2517253    3.1463639
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C     0.0407770   -2.8679687   -0.2281982
H     0.9202245   -3.4897749   -0.4975644
H     0.0630936   -1.9567488   -0.8527226
H    -0.8553673   -3.4575529   -0.5143958
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H     0.9234861    0.8173860    6.9641936
H    -0.8526061    0.8576007    6.9393454
H     0.0752549    1.8960015    5.8119091
N    -0.0288074   -4.3943216    5.0260668
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C    -0.0681245   -7.5593483    1.0528526
C     1.2080219   -5.5525543    1.6372214
C    -1.2736142   -5.5030936    1.6149390
C    -1.2699798   -6.8604759    1.2353622
C     1.1571522   -6.9088028    1.2570900
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H     2.1021422   -7.4597873    1.1282862
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C    -0.0225557   -1.8538640    7.0050965
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C    -1.2760859   -2.3659774    9.0137912
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H	-2.6607944	-0.8156129	6.4520752
H	-3.4425428	-2.0011337	7.5472468
H	-2.6231331	-2.5409372	6.0374404

Table S3. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for dinitrogen, N_2, in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis augmented with diffuse functions taken from the aug-cc-pVTZ basis set.

2
Energy = -109.5811435406

N	0.0000000	0.0000000	-0.5510195
N	0.0000000	0.0000000	0.5510195

Table S4. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the tuckin complex **7** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atom of the amido ligand; the basis set of the amido N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.

```
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Energy = -1291.825138075
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C     0.1756177    1.3168920    1.7115766
C     0.0474055    1.3315237    3.1168471
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C     1.1991367   -1.9597661    7.6347466
C     1.1870021   -2.4536304    8.9554312
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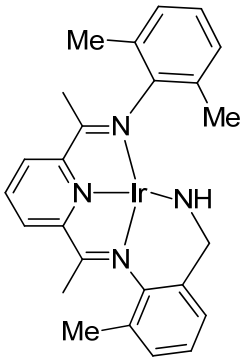

7

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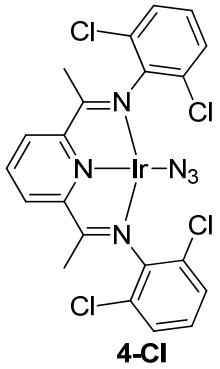
H	3.3666138	-1.8736558	7.5616266
H	2.5594542	-0.4505130	6.8400062
H	2.5699678	-1.9873121	5.9472632
C	-2.5634127	-2.1419809	6.7966176
H	-2.7974165	-1.0959177	6.5067453
H	-3.4090002	-2.5284499	7.3972094
H	-2.5017298	-2.7170629	5.8476203
N	0.7618005	-4.3653065	4.7767424
H	1.1178760	-4.4331044	5.7336626

Table S5. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the azido complex **4-Cl** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atoms of the azido ligand; the basis set of the latter N atoms was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.



4-Cl

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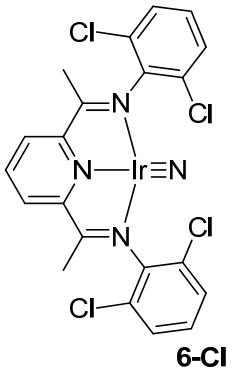
47
Energy = -3082.231843246
H     1.9648257    4.7507075   -0.0015344
C     1.0310993    4.1713466   -0.0026914
C    -1.3544997    2.6778765   -0.0044016
C     1.0790486    2.7649907   -0.0030891
C    -0.2127402    4.8271122   -0.0035461
C    -1.4069369    4.0837127   -0.0043166
N    -0.1127691    2.0421418   -0.0042676
H    -0.2521932    5.9257425   -0.0032869
H    -2.3796195    4.5949007   -0.0045395
C     2.2259636    1.8872791   -0.0025959
C    -2.4406378    1.7231691   -0.0037262
N    -2.0417499    0.4372125   -0.0025303
N     1.9142780    0.5747704   -0.0017264
Ir   -0.0506083    0.1367079   -0.0008003
C     3.6452082    2.3721277   -0.0032366
H     4.1883852    2.0094756    0.8939581
H     3.6962228    3.4755203   -0.0108073
H     4.1916397    1.9971382   -0.8932618
C    -3.8900822    2.1082733   -0.0035863
H    -4.4063442    1.6999731    0.8898567
H    -4.4064564    1.7008035   -0.8973399
H    -4.0199533    3.2051190   -0.0031117
N    -0.1229439   -1.8476950    0.0094674
C     2.9592814   -0.3947227   -0.0013718
C     4.9099340   -2.4511679    0.0000360
C     3.4715536   -0.9223036    1.2091329
C     3.4639735   -0.9310774   -1.2112513
C     4.4296758   -1.9485355   -1.2173480
C     4.4375303   -1.9394531    1.2166709
H     4.7890923   -2.3402282   -2.1785665
H     4.8027837   -2.3243122    2.1784338
H     5.6583712   -3.2570261    0.0006508
C    -3.0003080   -0.6158530   -0.0026545
C    -4.7193259   -2.8695945   -0.0033355
C    -3.4503446   -1.1965671   -1.2126935
C    -3.4446020   -1.2016496    1.2070555
C    -4.2966942   -2.3163227    1.2141108
C    -4.3023923   -2.3112590   -1.2204575
H    -4.6157966   -2.7403633    2.1759468
H    -4.6259645   -2.7313174   -2.1825481
H    -5.3819301   -3.7476807   -0.0036169
N     0.7119332   -2.7308004    0.0268322
N     1.4052580   -3.6583667    0.0436175
Cl   -2.9424218   -0.4982753   -2.7328462
```

Cl	-2.9300710	-0.5092737	2.7275515
Cl	2.8766708	-0.3009594	-2.7330313
Cl	2.8921926	-0.2826141	2.7300607

Table S6. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the nitrido complex **6-Cl** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atom of the nitrido ligand; the basis set of the nitrido N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.



6-Cl

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45
Energy = -2972.646457422
H     0.1694290    0.0619598   -0.0825534
C     0.1539425    0.0660129    1.0166650
C     0.1112449    0.0649946    3.8262035
C     0.0978455   -1.1474889    1.7230640
C     0.1892737    1.2839636    1.7217006
C     0.1675212    1.2840022    3.1291925
N     0.0775200   -1.1349863    3.1169713
H     0.2330745    2.2354698    1.1728684
H     0.1935587    2.2331441    3.6832640
C     0.0541298   -2.4781287    1.2049607
C     0.0793683   -0.1530892    5.2375941
N     0.0261590   -1.4645900    5.5850027
N     0.0053436   -3.4354570    2.1661317
Ir    0.0096516   -2.9041218    4.1376552
C     0.0580761   -2.8324942   -0.2523551
H     0.9322276   -3.4663118   -0.5107512
H     0.0993903   -1.9252630   -0.8815007
H    -0.8546402   -3.3994286   -0.5320454
C     0.0987295    0.9306434    6.2742238
H     0.1447637    1.9291180    5.8035852
H     0.9765648    0.8303630    6.9465672
H    -0.8100513    0.8963405    6.9111706
N    -0.0213885   -4.3720213    4.9770751
C    -0.0498626   -4.8086741    1.7953224
C    -0.1632130   -7.5762040    1.1890640
C     1.1308499   -5.5769539    1.6403807
C    -1.2891859   -5.4733697    1.6197040
C    -1.3514980   -6.8436680    1.3213795
C     1.0809128   -6.9478174    1.3422643
H    -2.3335788   -7.3207493    1.2002198
H     2.0205310   -7.5071786    1.2374722
H    -0.2072701   -8.6517056    0.9617676
C    -0.0204800   -1.8305977    6.9597953
C    -0.1182434   -2.6853732    9.6614810
C    -1.2557044   -2.0011268    7.6334349
C     1.1643884   -2.0885834    7.6932353
C     1.1221137   -2.5138478    9.0303932
C    -1.3103300   -2.4258885    8.9702912
H     2.0646156   -2.7088386    9.5599493
H    -2.2894557   -2.5516279    9.4522324
H    -0.1562975   -3.0245326   10.7073562
Cl    2.7131404   -1.8634362    6.9204219
Cl   -2.7441519   -1.6666178    6.7854280
Cl    2.6841457   -4.8001131    1.8150477
```
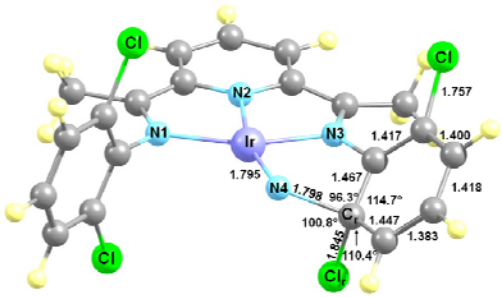

Cl	-2.7731606	-4.5666953	1.7686201

Table S7. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the transition state for C-Cl activation in **6-Cl,** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atoms of the former nitrido ligand; the basis set of the latter N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.

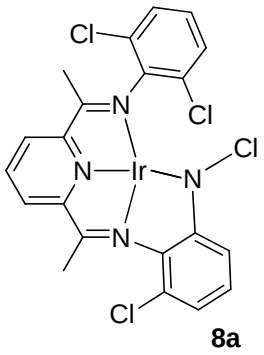


45
Energy = -2972.601246673

H	0.2130742	4.6808897	-1.9842027
C	0.1427072	4.1007299	-1.0531791
C	0.0932806	2.6039359	1.3304465
C	0.0079538	2.6983705	-1.1057498
C	0.2089167	4.7487864	0.1913299
C	0.1923567	4.0035347	1.3898940
N	-0.0428094	1.9887106	0.0922449
H	0.3001067	5.8437583	0.2318464
H	0.2630368	4.5090314	2.3629709
C	-0.0621127	1.8319502	-2.2491843
C	0.1678781	1.6561465	2.4206313
N	0.0863057	0.3726802	2.0181765
N	-0.0683172	0.5103275	-1.9421243
Ir	0.0024089	-0.0020563	0.0423097
C	-0.1362935	2.3093768	-3.6692079
H	0.6924738	1.8913640	-4.2777396
H	-0.0802680	3.4113882	-3.7252744
H	-1.0882038	1.9948755	-4.1467943
C	0.4745598	2.0731401	3.8290973
H	1.2622150	2.8540077	3.8235167
H	0.8439018	1.2143540	4.4207056
H	-0.4108622	2.4831989	4.3555162
N	0.0926201	-1.6924199	0.5205173
C	-0.2334295	-0.4703037	-2.9546550
C	-0.5504454	-2.5495174	-4.8585170
C	0.8877255	-1.0814243	-3.5728576
C	-1.5199635	-0.9297605	-3.3376934
C	-1.6823736	-1.9600866	-4.2762630
C	0.7366421	-2.1099423	-4.5153854
H	-2.6968650	-2.2900912	-4.5385351
H	1.6325093	-2.5576766	-4.9668321
H	-0.6731849	-3.3610014	-5.5910396
C	0.0644165	-0.8042762	2.7957206
C	-0.2526724	-3.4357661	3.7949780
C	-0.8441629	-1.0783491	3.8475880
C	0.7894563	-1.9121437	2.1637230
C	0.6168800	-3.2279307	2.7399859
C	-0.9981523	-2.3709500	4.3615119
H	1.2032905	-4.0541652	2.3143652
H	-1.7420426	-2.5506620	5.1487154
H	-0.3761938	-4.4506399	4.2032349
Cl	2.5743655	-1.5859803	1.8284623

Cl	-1.9687408	0.1520785	4.4039289
Cl	2.4913630	-0.5309462	-3.1570392
Cl	-2.9346200	-0.1912505	-2.6279887

Table S8. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the tuckin complex **8a** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atoms of the amido ligand; the basis set of the amido N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.

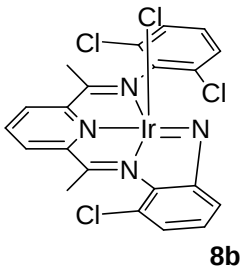


8a

```
45
Energy = -2972.675544026
H     -0.0934781    0.2364476   -0.0578069
C     -0.1537259    0.2179902    1.0396578
C     -0.2498644    0.1674627    3.8553149
C     -0.1596324   -1.0232368    1.7219223
C     -0.2090387    1.4123086    1.7651544
C     -0.2374273    1.3945555    3.1831056
N     -0.2587225   -1.0139804    3.1133812
H     -0.2095063    2.3750683    1.2343141
H     -0.2482940    2.3339448    3.7527171
C     -0.0669115   -2.3660207    1.2229841
N     -0.0320808   -3.3169881    2.1931630
C     -0.1935804   -0.0770153    5.2976563
N     -0.2988877   -1.3789361    5.6307232
Ir    -0.1222019   -2.6323382    4.1017715
C     -0.0261371   -2.7166565   -0.2347973
H      0.9121564   -3.2512099   -0.4922496
H     -0.0898765   -1.8133677   -0.8681882
H     -0.8704406   -3.3838503   -0.5072574
C      0.1602846    1.0428006    6.2284531
H      0.5631454    0.6657394    7.1848126
H     -0.7055693    1.6959983    6.4628665
H      0.9353665    1.6739246    5.7471726
N      0.2627450   -3.8849047    5.5294535
C      0.0352251   -4.6911966    1.8463530
C      0.1840023   -7.4823283    1.3501880
C     -1.1342814   -5.4853369    1.7385863
C      1.2808987   -5.3473262    1.6808044
C      1.3621281   -6.7263533    1.4362151
C     -1.0674431   -6.8658845    1.4955486
H      2.3501619   -7.1925160    1.3202919
H     -1.9999354   -7.4423840    1.4242410
H      0.2414992   -8.5651712    1.1646971
C     -0.3115598   -2.0104305    6.9027791
C     -0.0847352   -3.5601063    9.2522611
C      0.1288276   -3.3921363    6.8323596
C     -0.8411172   -1.5509775    8.1283680
C     -0.7001909   -2.3064268    9.3135504
C      0.3074384   -4.1190097    8.0235925
H     -1.1034407   -1.9054056   10.2527792
H      0.7077931   -5.1383088    7.9688338
H      0.0435576   -4.1448976   10.1757993
Cl     2.7528661   -4.4095599    1.7779263
```

Cl	-2.6985821	-4.7233529	1.8988860
Cl	-1.8476019	-0.1160425	8.2300102
Cl	0.8561680	-5.5895523	5.4645554

Table S9. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the tuckin complex **8b** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for iridium and the nitrogen atom of the imido ligand; the basis set of the imido N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.



8b

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45
Energy = -2972.697885597
N     0.8908456    0.6928112   -1.3908007
Ir   -0.4652697    0.0870171   -2.5739460
N    -0.1407020    0.0655173   -4.4427346
C     0.1149589    0.0076281   -7.2017685
C    -0.2946428    1.2705999   -5.1522134
C     0.1340054   -1.1633454   -5.0637248
C     0.2586545   -1.1838683   -6.4596832
C    -0.1626284    1.2229246   -6.5535848
H     0.4432981   -2.1375315   -6.9737086
H    -0.2767589    2.1473642   -7.1373478
H     0.2117002   -0.0174742   -8.2962723
C    -0.4580322    2.4074830   -4.2967730
C     0.1897469   -2.2568597   -4.1339464
N    -0.0645412   -1.9130242   -2.8502987
N    -0.5632087    2.0820256   -2.9769931
C    -0.2880903    3.8125224   -4.7887350
H     0.1198893    3.8231926   -5.8159955
H     0.4173320    4.3671633   -4.1346891
H    -1.2388249    4.3817019   -4.7779778
C     0.4993464   -3.6711266   -4.5272019
H     0.7928577   -3.7419743   -5.5897601
H    -0.3797831   -4.3293745   -4.3655232
H     1.3320632   -4.0726289   -3.9143182
C    -0.0934583   -2.8956217   -1.8240176
C    -0.2212629   -4.6803698    0.3755456
C     1.0258063   -3.1029000   -0.9788146
C    -1.2621392   -3.6534498   -1.5577248
C    -1.3333784   -4.5318688   -0.4655308
C     0.9650952   -3.9795486    0.1159925
H    -2.2625851   -5.0902551   -0.2879924
H     1.8536756   -4.1053647    0.7495707
H    -0.2761195   -5.3615730    1.2376658
Cl    2.5266295   -2.2909471   -1.3381919
Cl   -2.6335894   -3.5320163   -2.6343894
Cl   -2.3824344   -0.1454208   -1.2587060
C    -0.1582532    2.8267707   -1.8596531
C     0.9981581    3.8626276    0.5001986
C     0.7095807    2.0086672   -1.0428654
C    -0.4838583    4.1296399   -1.4227412
C     0.0971812    4.6466129   -0.2531789
C     1.3075514    2.5546742    0.1246619
H    -0.1839700    5.6563688    0.0757916
H     1.9675182    1.9146792    0.7270427
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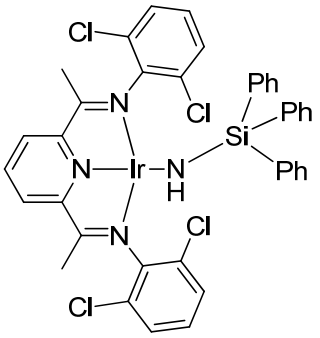
H	1.4379241	4.2886831	1.4147735
Cl	-1.7342880	5.0788698	-2.2124051

Table S10. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the silyl amido complex **10** in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for the iridium, Si and the nitrogen atom of the amido ligand; the basis set of the amido N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.



R = Ph: **10**

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80
Energy = -3957.373512208
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C     1.2727100    1.7239311   -4.6958793
C    -1.1009102    1.1296221   -3.3152367
C     1.3225772    1.0439647   -3.4657210
C     0.0317803    2.1044886   -5.2372519
C    -1.1555472    1.8078984   -4.5471235
N     0.1347910    0.7498359   -2.7875424
H    -0.0089365    2.6337261   -6.1999810
H    -2.1284710    2.1030498   -4.9642892
C     2.4767296    0.5700362   -2.7507106
C    -2.1742254    0.7457922   -2.4449303
N    -1.7777335    0.0905074   -1.3266539
N     2.1891017   -0.0629377   -1.5926840
Ir    0.2273212   -0.1996937   -1.1231517
C     3.8872589    0.7510274   -3.2296744
H     4.5012543    1.2772298   -2.4699009
H     3.9247774    1.3393991   -4.1636278
H     4.3711723   -0.2292305   -3.4231611
C    -3.6154175    1.0560226   -2.7279269
H    -4.0568719    1.6761045   -1.9204962
H    -4.2191339    0.1278665   -2.8004684
H    -3.7262688    1.6085780   -3.6780214
C    -2.7995549   -0.2815245   -0.4074172
C    -4.7974047   -1.0323513    1.4591811
C    -3.4973292   -1.5080653   -0.5278736
C    -3.1857351    0.5821861    0.6474565
C    -4.1690452    0.2158611    1.5768775
C    -4.4736543   -1.8953670    0.4025438
H    -4.4259430    0.9100335    2.3877780
H    -4.9781077   -2.8631225    0.2782652
H    -5.5583233   -1.3311872    2.1949531
C     3.2612538   -0.5758794   -0.8071361
C     5.2650282   -1.6657702    0.8812632
C     3.7551285   -1.8904325   -1.0000763
C     3.8112061    0.1715723    0.2642394
C     4.8026924   -0.3613415    1.1027872
C     4.7485989   -2.4340584   -0.1717353
H     5.1982180    0.2523428    1.9231857
H     5.1012320   -3.4574323   -0.3580169
H     6.0330539   -2.0918475    1.5426776
N     0.5736955   -1.2145541    0.5480615
H     1.5926744   -1.3144714    0.6298465
Si   -0.0299596   -2.1172308    1.9238014
Cl    3.1247887   -2.8531996   -2.3166637
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Cl	3.2604346	1.8086092	0.5319078
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C	1.5061828	-2.5828896	2.9482971
C	3.8425034	-3.2942735	4.4104903
C	2.2488135	-3.7454121	2.6259866
C	1.9673077	-1.7887645	4.0251795
C	3.1217496	-2.1360628	4.7481354
C	3.4030518	-4.0992069	3.3455120
H	1.9093576	-4.3954071	1.8035478
H	1.4056185	-0.8866304	4.3148970
H	3.4543859	-1.5043822	5.5871698
H	3.9564926	-5.0141023	3.0800950
H	4.7408064	-3.5745402	4.9832726
C	-1.1296658	-1.0753993	3.0538335
C	-2.4977912	0.5189879	4.9699620
C	-2.1529645	-1.6228366	3.8630171
C	-0.8217635	0.2971272	3.2175355
C	-1.4967075	1.0873484	4.1640892
C	-2.8283154	-0.8384532	4.8131504
H	-2.4340555	-2.6807944	3.7495468
H	-0.0476206	0.7544254	2.5810870
H	-1.2415655	2.1533422	4.2698445
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C	-1.8341079	-6.2998637	0.6438876
C	-0.9114244	-4.1233081	0.0551544
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C	-1.4160474	-5.3786617	-0.3297142
H	-0.5757175	-3.4098196	-0.7135760
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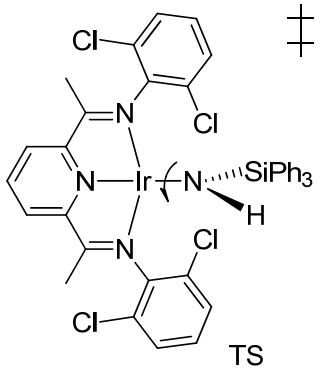
H	-1.4813137	-5.6371464	-1.3981573
H	-2.2280769	-7.2837639	0.3437832

Table S11. Total energy in [H] and cartesian coordinates of the optimized geometry (DFT/BP86) for the transition state shown in Fig. 11 in [Å] (xmol xyz format). Basis set: Ahlrichs def2-TZVPP basis for Ir and Si and the nitrogen atom of the amido ligand; the basis set of the latter N atom was augmented with diffuse functions taken from the aug-cc-pVTZ basis set. For the residual atoms Ahlrichs def2-SVP basis sets were used. For the iridium center a Stuttgart-Dresden ECP-60-MWB pseudo-potential was employed.

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80
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C     0.3459959    3.2080595   -4.4060486
C     1.5220674    2.8394502   -3.7300020
N     0.2440535    1.2881733   -2.3845563
H     0.3852054    3.9673642   -5.2003238
H     2.4858223    3.2977602   -3.9915236
C    -2.0478049    0.8490465   -2.5907241
C     2.5333602    1.3406889   -1.8936857
N     2.1501221    0.3883372   -1.0241769
N    -1.7454525   -0.0421461   -1.6295883
Ir    0.1985096   -0.1351691   -1.0962962
C    -3.4317695    1.0599989   -3.1257506
H    -3.4045510    1.3064404   -4.2049979
H    -3.9333836    1.9013821   -2.5997918
H    -4.0604875    0.1605360   -2.9895310
C     3.9367429    1.8544854   -2.0045022
H     4.1985481    2.0571054   -3.0617661
H     4.6664979    1.1300856   -1.5981510
H     4.0557887    2.8048815   -1.4401848
C     3.0910376   -0.1221221   -0.0834004
C     4.8303268   -1.2366764    1.8530691
C     3.4279715    0.5866663    1.0951762
C     3.6740038   -1.3986901   -0.2676449
C     4.5382739   -1.9549813    0.6848418
C     4.2839618    0.0377180    2.0613666
H     4.9616390   -2.9526486    0.5106743
H     4.5110171    0.6167567    2.9667863
H     5.4928590   -1.6786659    2.6110371
C    -2.7901935   -0.8097597   -1.0375969
C    -4.8000603   -2.3835445    0.1858709
C    -3.6318054   -0.2735403   -0.0341013
C    -2.9845828   -2.1642305   -1.4003757
C    -3.9799750   -2.9480445   -0.8009632
C    -4.6327039   -1.0463248    0.5726528
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H    -5.5741078   -2.9987232    0.6658628
N     0.1885479   -1.8723560    0.0128979
H     0.3773201   -2.6234874   -0.6566826
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C	-3.5853142	-4.2680436	2.8809875
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H	-2.5773938	-2.3772123	3.1862260
H	-4.4293306	-3.9967753	3.5357957
H	-2.4418643	-6.8357740	0.9206951
H	-4.3823438	-6.2403040	2.4042720
C	1.5748943	-3.5392932	2.0621504
C	3.7879669	-5.2424001	2.6675451
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C	2.2212491	-3.4923863	3.3196383
C	3.3125001	-4.3275929	3.6215494
C	3.1715695	-5.3019819	1.4049792
H	1.6455675	-4.5073036	0.1028788
H	1.8734514	-2.7813815	4.0846872
H	3.7920287	-4.2649925	4.6117651
H	3.5378941	-6.0095007	0.6438696
H	4.6353351	-5.9050464	2.9046840
C	-0.1555115	-1.0620543	2.8567663
C	-0.4950045	1.0447361	4.7439076
C	-0.3338056	-1.3310201	4.2382247
C	-0.1614853	0.2912546	2.4526558
C	-0.3302484	1.3343714	3.3796416
C	-0.4971250	-0.2941612	5.1724732
H	-0.3616925	-2.3733658	4.5951451
H	-0.0389270	0.5343242	1.3783340
H	-0.3325621	2.3790081	3.0316557
H	-0.6327265	-0.5325958	6.2394262
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