Supporting Information

Protonolysis and Amide Exchange Reactions of a Three-Coordinate Cobalt Amide Complex Supported by an N-Heterocyclic Carbene Ligand

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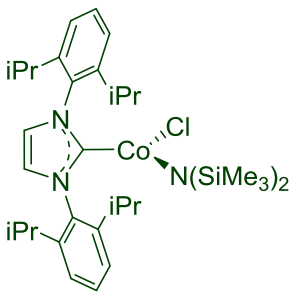
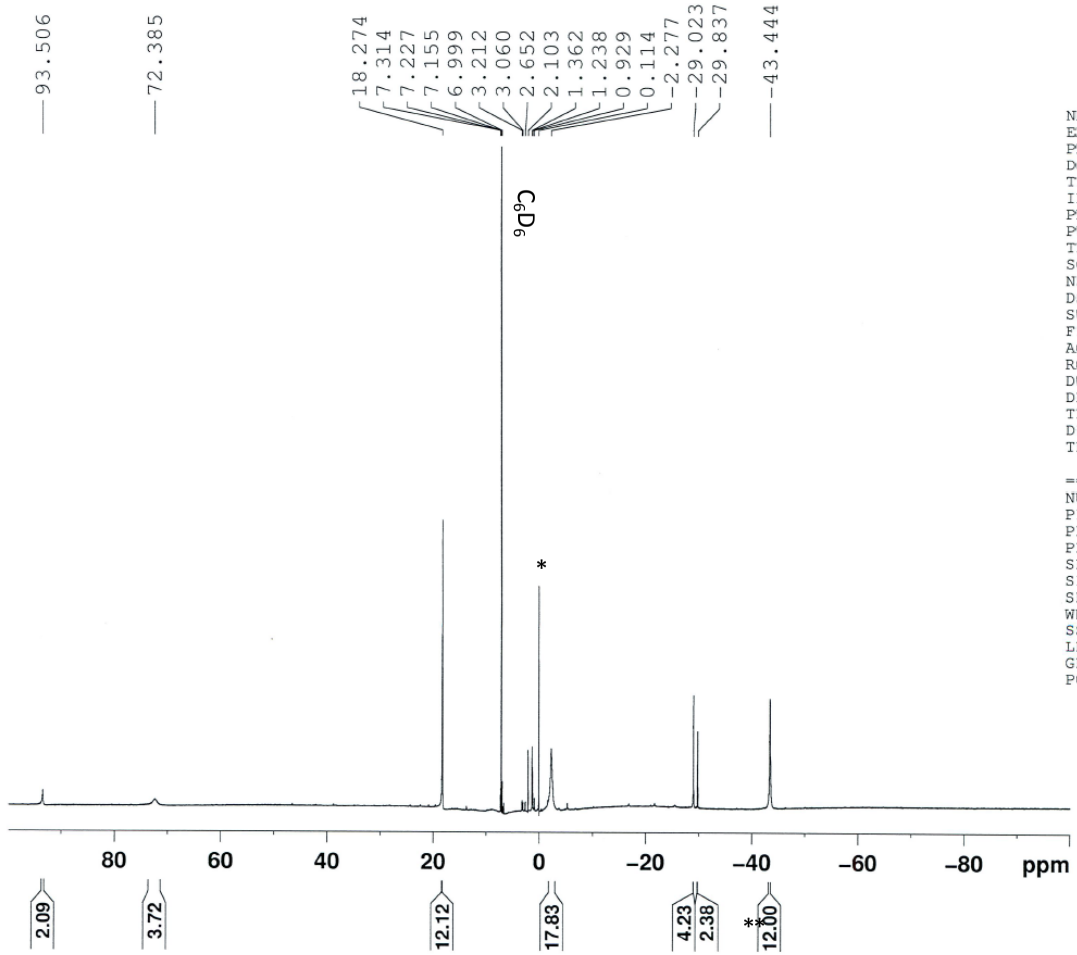


C_6D_6

500.13 MHz

* - trace amounts of free IPr and $HN(SiMe_3)_2$

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PROCNO                1
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Time               2.00
INSTRUM           spect
PROBHD   5 mm PAQNP 1H/
PULPROG              zg
TD               600000
SOLVENT            C6D6
NS                    16
DS                     0
SWH          100000.000 Hz
FIDRES         0.166667 Hz
AQ           3.0000501 sec
RG                  724
DW                5.000 usec
DE                71.43 usec
TE                295.5 K
D1           3.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 2.00 usec
PL1                0.00 dB
PL1W        24.54113007 W
SFO1        500.1300000 MHz
SI                16384
SF          500.1300497 MHz
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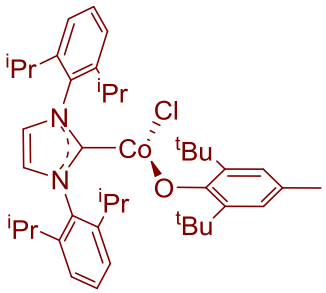
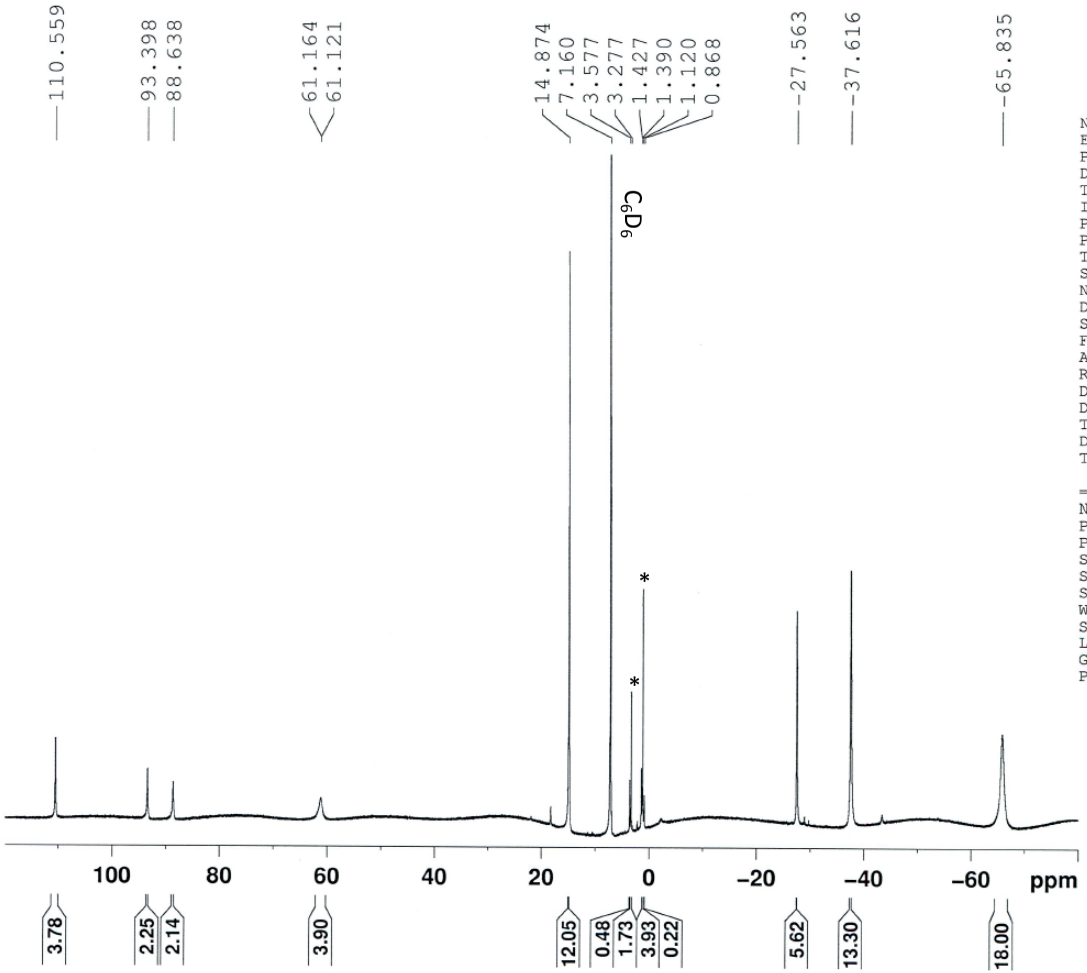
SSB                   0
LB                 0.30 Hz
GB                    0
PC                 1.00
```



C_6D_6

400.13 MHz

* - trace amounts of free IPr and free BHT-H

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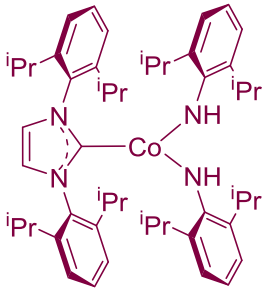
PROCNO                1
Date_          20140602
Time              19.59
INSTRUM           spect
PROBHD   5 mm BBO BB-1H
PULPROG              zg
TD               200000
SOLVENT         Acetone
NS                   16
DS                    0
SWH           80000.000 Hz
FIDRES         0.400000 Hz
AQ            1.2500499 sec
RG                645.1
DW                6.250 usec
DE               111.43 usec
TE                294.9 K
D1           1.00000000 sec
TD0                   1

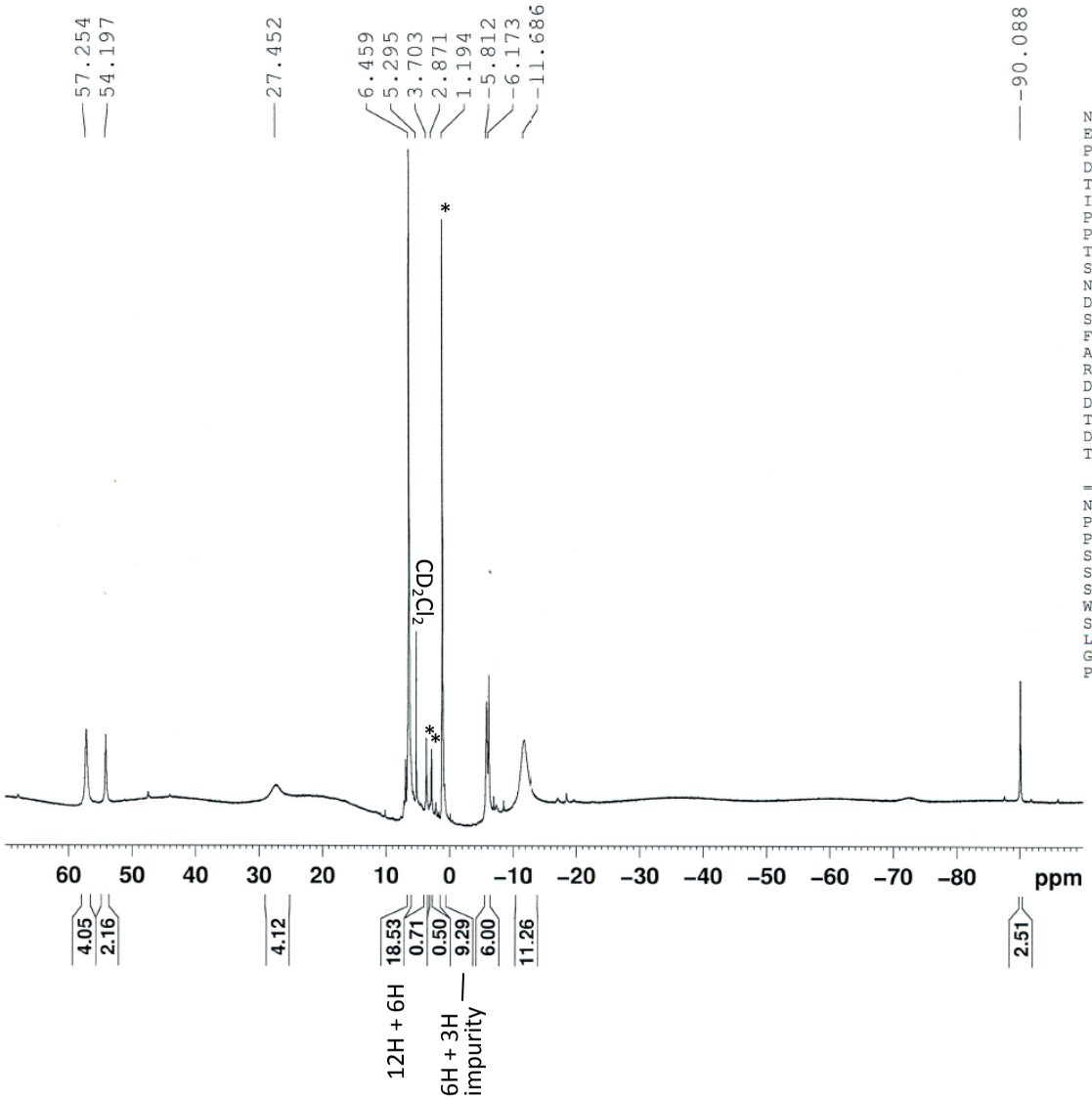
======== CHANNEL f1 ========
NUC1                 1H
P1                8.00 usec
PL1              -6.00 dB
SFO1        400.1380026 MHz
SI                32768
SF          400.1300438 MHz
WDW                  EM
SSB                   0
LB                0.00 Hz
GB                    0
PC                1.00
```



CD_2Cl_2

400.13 MHz

* - NH_2DIPP impurity. Note one set of NH_2DIPP resonances overlap with a product resonance at 1.194.

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PROCNO                1
Date_          20140722
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PULPROG               zg
TD               200000
SOLVENT          CD2Cl2
NS                    64
DS                     0
SWH          100000.000 Hz
FIDRES         0.500000 Hz
AQ            1.0000499 sec
RG                912.3
DW                5.000 usec
DE               111.43 usec
TE                294.5 K
D1           1.00000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 8.00 usec
PL1               -6.00 dB
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SI                32768
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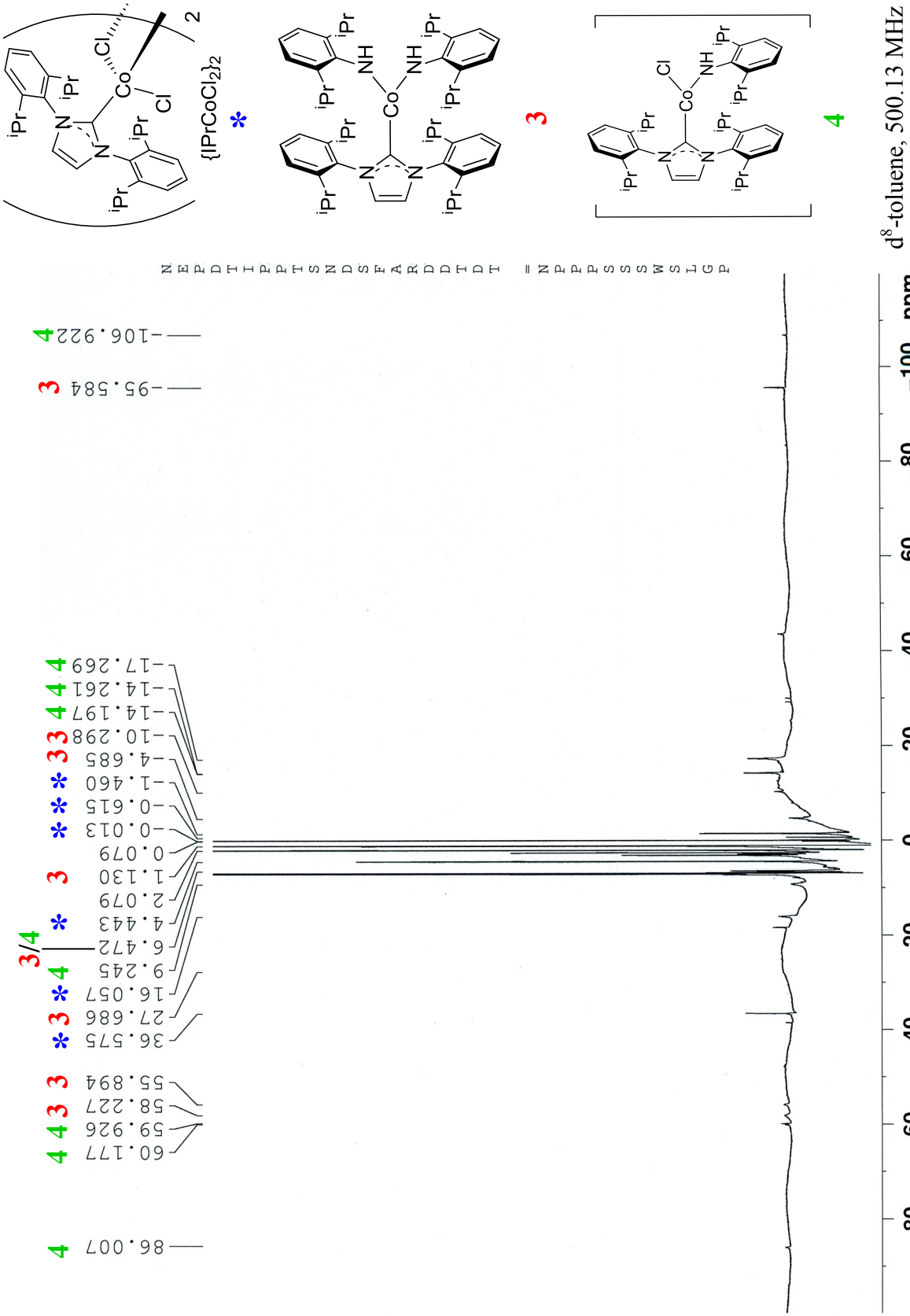
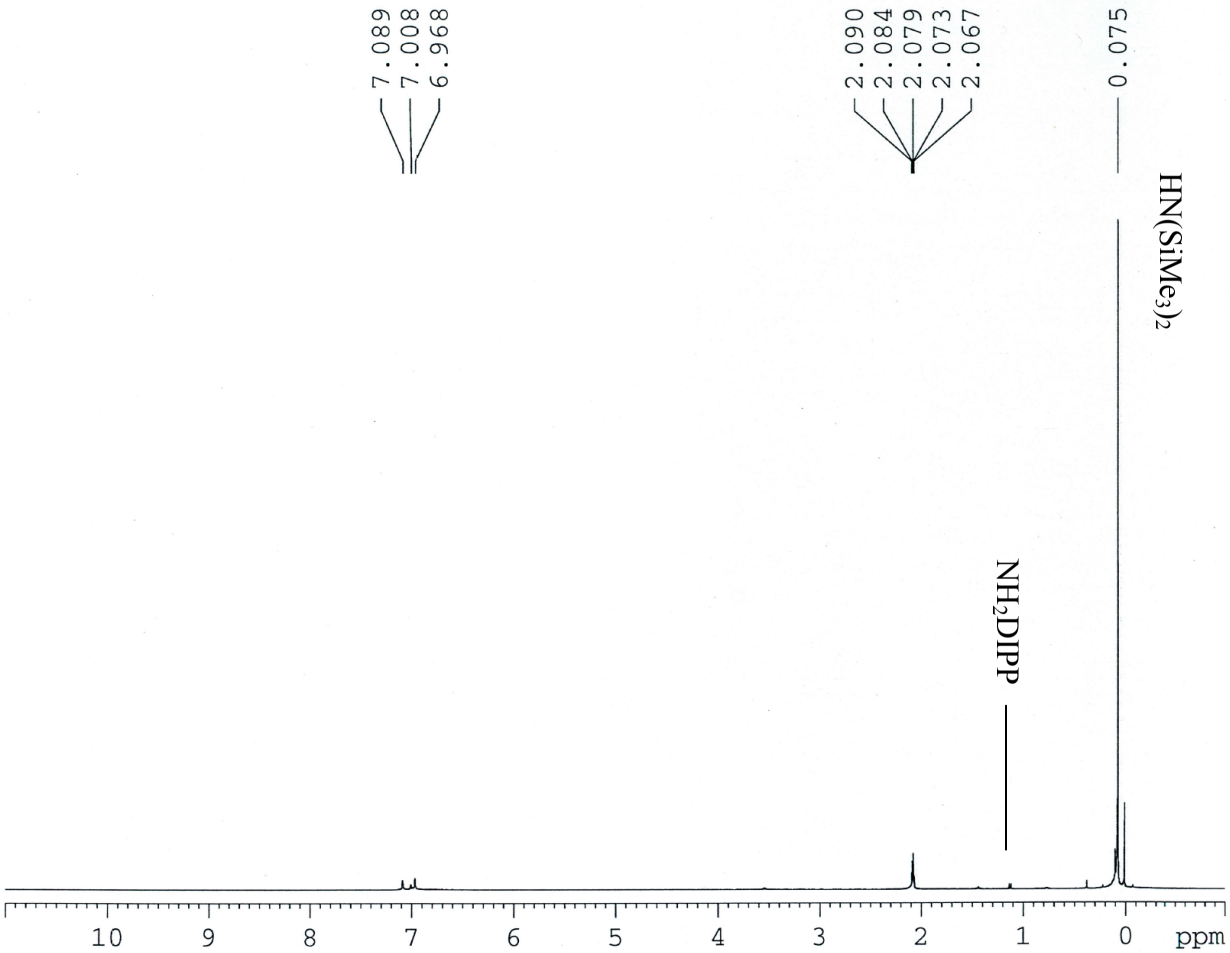
WDW                   EM
SSB                    0
LB                 0.00 Hz
GB                     0
PC                 1.00
```


2
{IPrCoCl2}2
*
3
4
d8-toluene, 500.13 MHz
ppm
80
60
40
20
0
−20
−40
−60
−80
−100
86.007
60.177
59.926
58.227
55.894
36.575
27.686
16.057
9.245
6.472
4.443
2.079
1.130
0.079
−0.013
−0.615
−1.460
−4.685
−10.298
−14.197
−14.261
−17.269
−95.584
−106.922

Volatiles after the reaction of **1** with NH_2DIPP.
$HN(SiMe_3)_2$ with trace of NH_2DIPP

d^8-toluene, 400.13 MHx




```
Current Data Parameters
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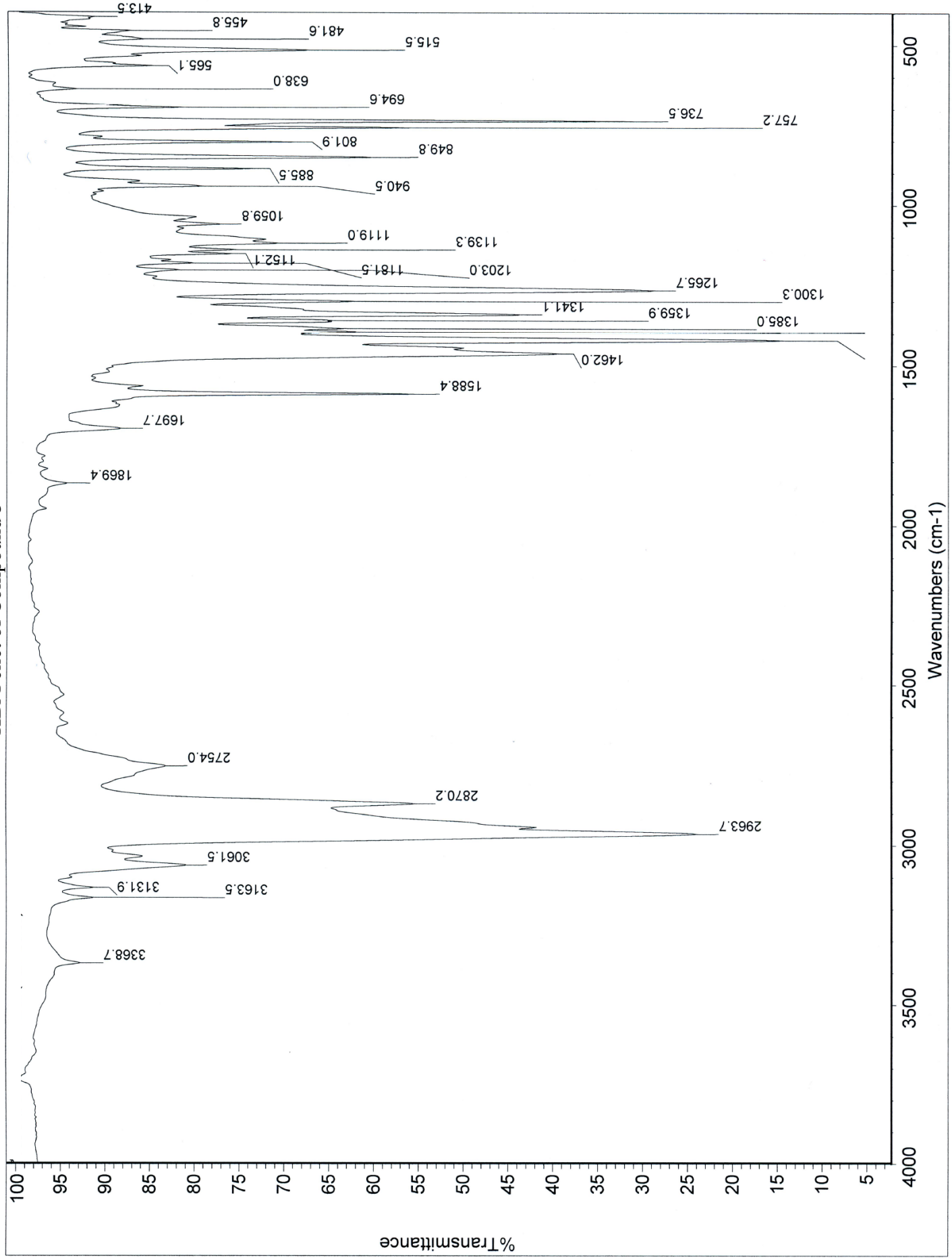
EXPNO                   5
PROCNO                  1

F2 - Acquisition Parameter:
Date_           20150402
Time               10.10
INSTRUM            spect
PROBHD   5 mm BBO BB-1H
PULPROG               zg
TD                38460
SOLVENT             Tol
NS                    8
DS                    0
SWH            6410.256 Hz
FIDRES         0.166673 Hz
AQ           2.9999299 se
RG                 2048
DW               78.000 us
DE               111.43 us
TE                295.2 K
D1           1.00000000 se
TD0                   1

======== CHANNEL f1 ======:
NUC1                 1H
P1                8.00 us
PL1              -6.00 dB
SFO1        400.1326008 MH:

F2 - Processing parameters
SI                32768
SF          400.1300190 MH:
WDW                  EM
SSB                   0
LB                 0.00 Hz
GB                    0
PC                 1.00
```

KBr Pellet of Compound **3**

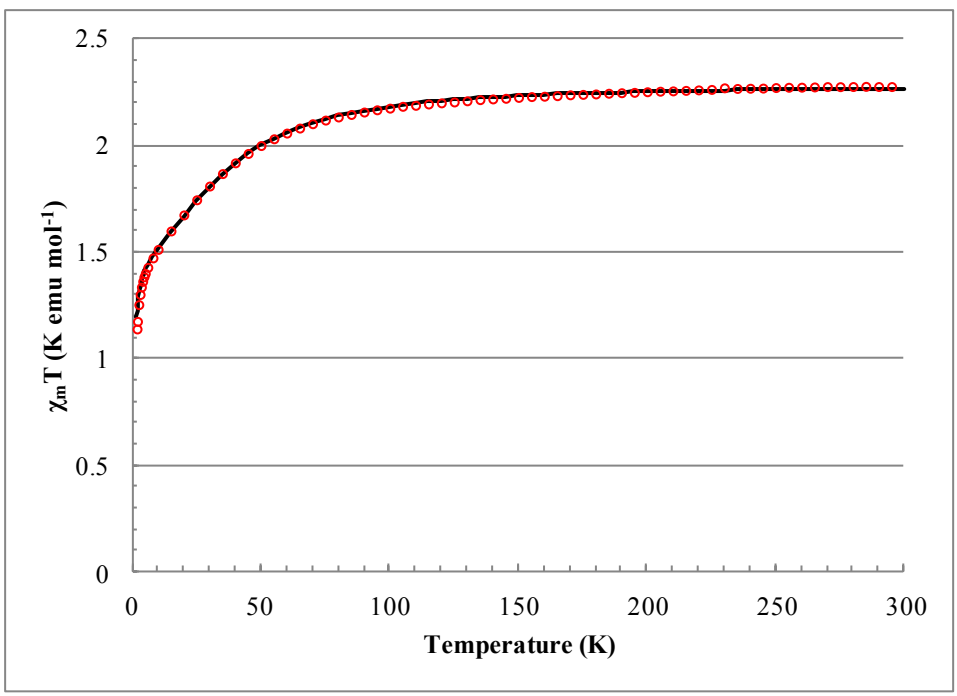


Magnetic Studies. Variable temperature dc magnetic susceptibility measurements were obtained on a solid sample of **3** under a field of 1.0 T to better probe the effect of the Co---H interactions. The variable temperature magnetic susceptibility of **3** is shown as a χT vs T plot. The experimental data were simulated using JulX[S1] using the spin Hamiltonian:

$$H = D\left[\hat{S}_z^{\,2} - {}^{1}/_{3}\left(S(S+1)\right) + \frac{E}{D}\left(\hat{S}_x^{\,2} - \hat{S}_y^{\,2}\right)\right] + \mu_B \cdot \hat{S} \cdot g \cdot B$$

(eq. 4)

Variables used to fit the data were the isotropic gyromagnetic ratio, g, and the axial zero field splitting parameter, D. Temperature independent paramagnetism (TIP), the rhombic zero field splitting parameter (E), intermolecular interactions (Weiss Temperature, Θ), and paramagnetic impurities were not considered in the fit to avoid over parameterization. Simulation (black line in plot) of the data at 1.0T provided g = 2.204(1), and $|D|$ = 42(1) cm^{-}.

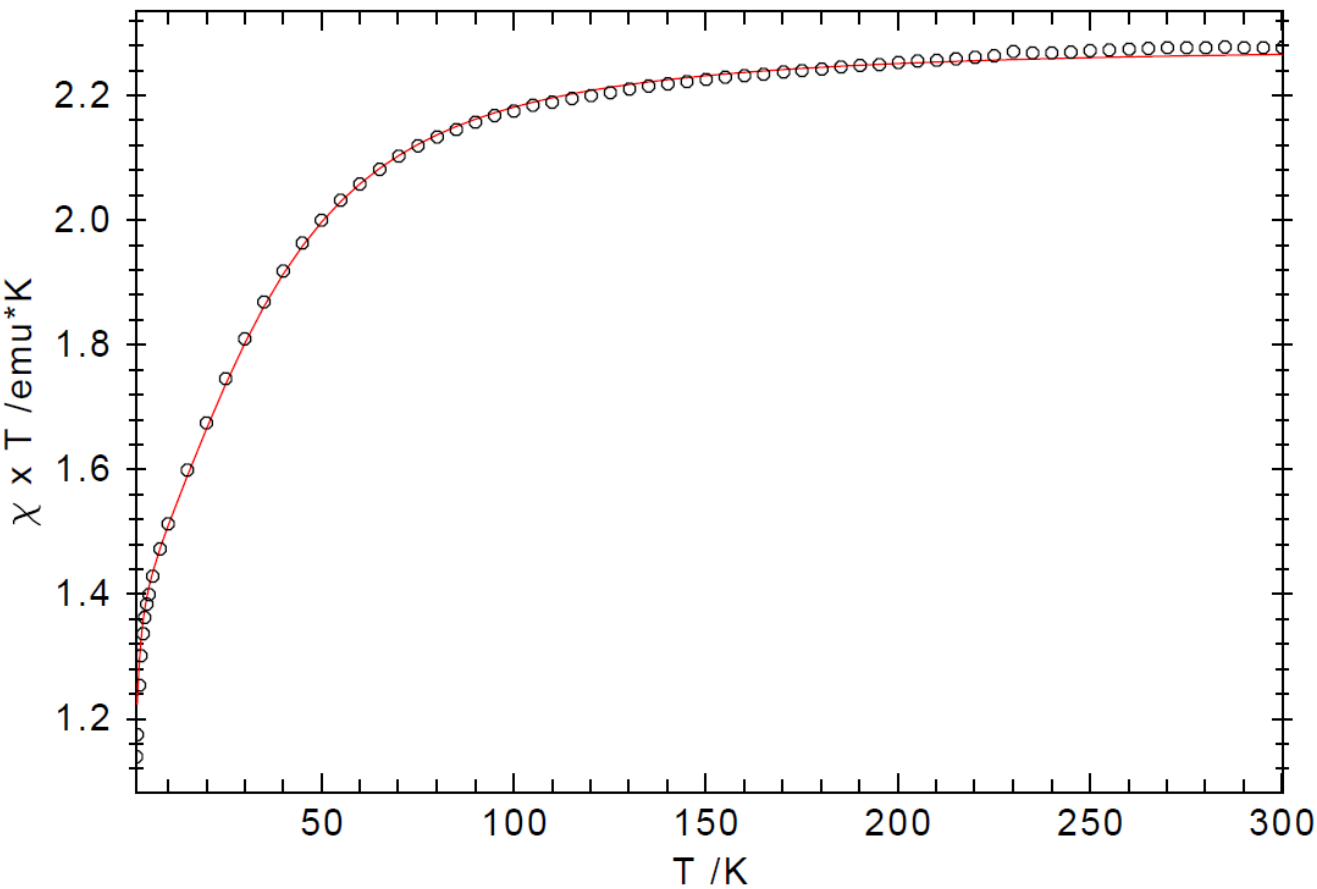


Red circles represent experimental data, and the black line corresponds to fit.

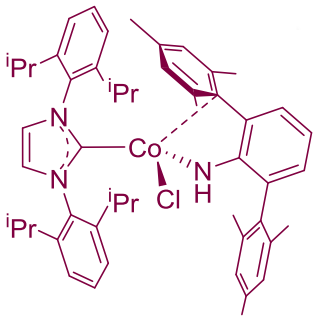
JulX fit output

C:\Users\Hopkins\Desktop\Chris Magnetism\IPrCoNHDIPP2.dc_004.PDF

sample2
cmnt: polyethylene baggy



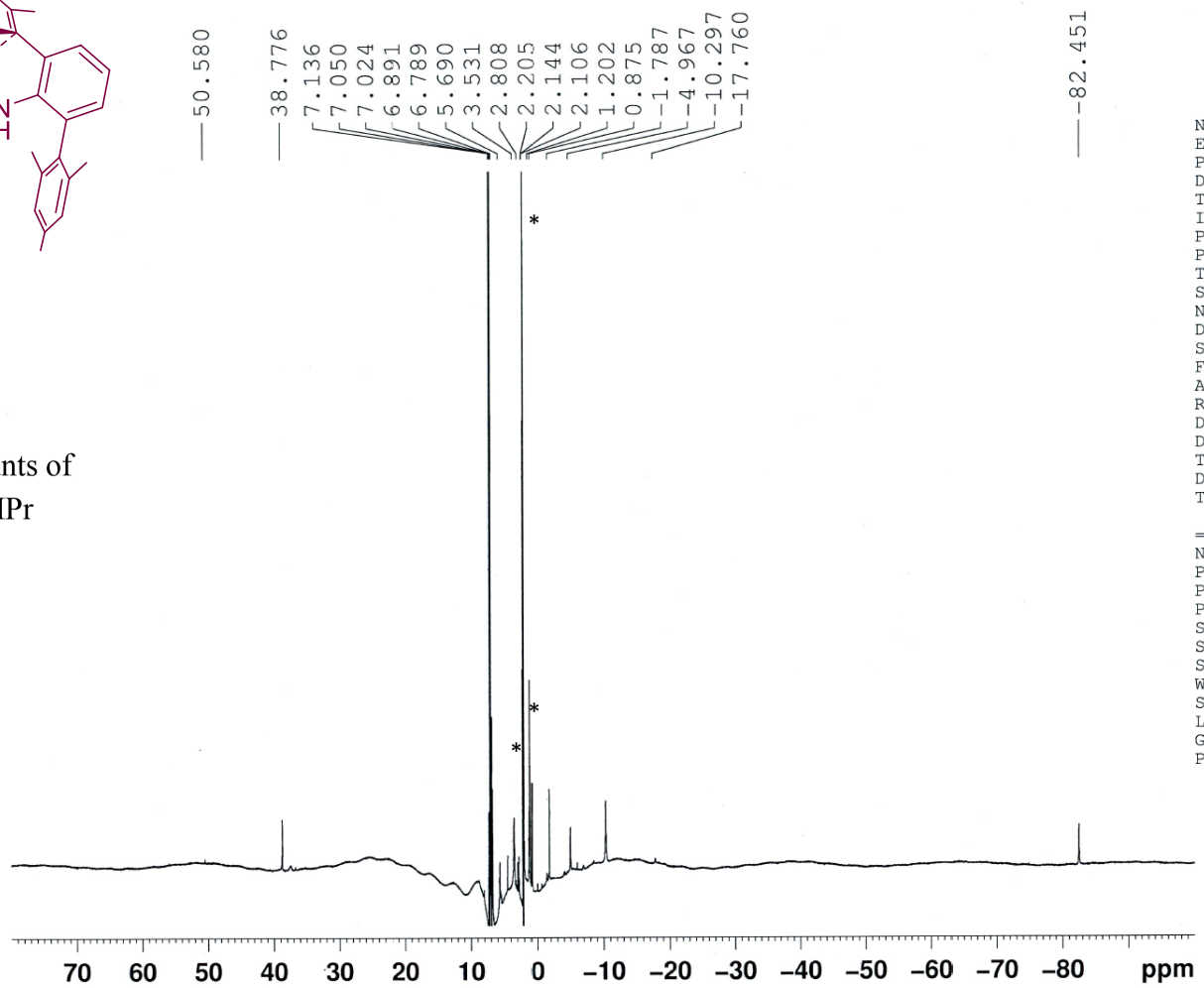

```
Spin 1 = 1.5
_var_______________value__ifit________
  g1                 2.204   f
  D1                41.965   f
E/D1                 0.000
----------------------------------------
PI [%] (S=1.5)        0.0
TIP [1e-6 emu]        0.0
T_W [K]              0.000   TW_TIP [K]=     0.000
-----------------------------------   fsum =   0.1267E-01
m[mg]=65.00;   M[g/mol]= 800.10;   chi(dia)=     0.0;   B-fields: 1
B[T]=    1.000
powder average: Lebedev grid  16pts  high_precission
efil:   sers\Hopkins\Desktop\Chris Magnetism\IPrCoNHDIPP2.dc.d
----------------------------------------
holder:     _file: none
baggy        22.00mg, d:-0.165E-07, s:-0.216E-07, p: 0.246E-07
----------------------------------------
  -
  -
```



C_6D_6

500.13 MHz

* - Trace amounts of NH_2DMP and IPr




```
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PROCNO                  1
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INSTRUM             spect
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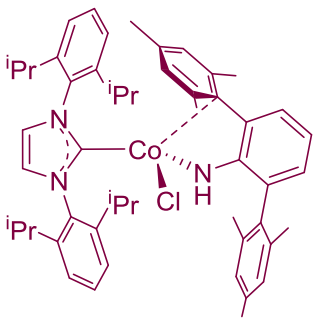
PULPROG                zg
TD                 700000
SOLVENT             C6D6
NS                     16
DS                      0
SWH           100000.000 Hz
FIDRES          0.142857 Hz
AQ            3.5000501 sec
RG                    456
DW                  5.000 usec
DE                  71.43 usec
TE                  294.9 K
D1            3.00000000 sec
TD0                     1

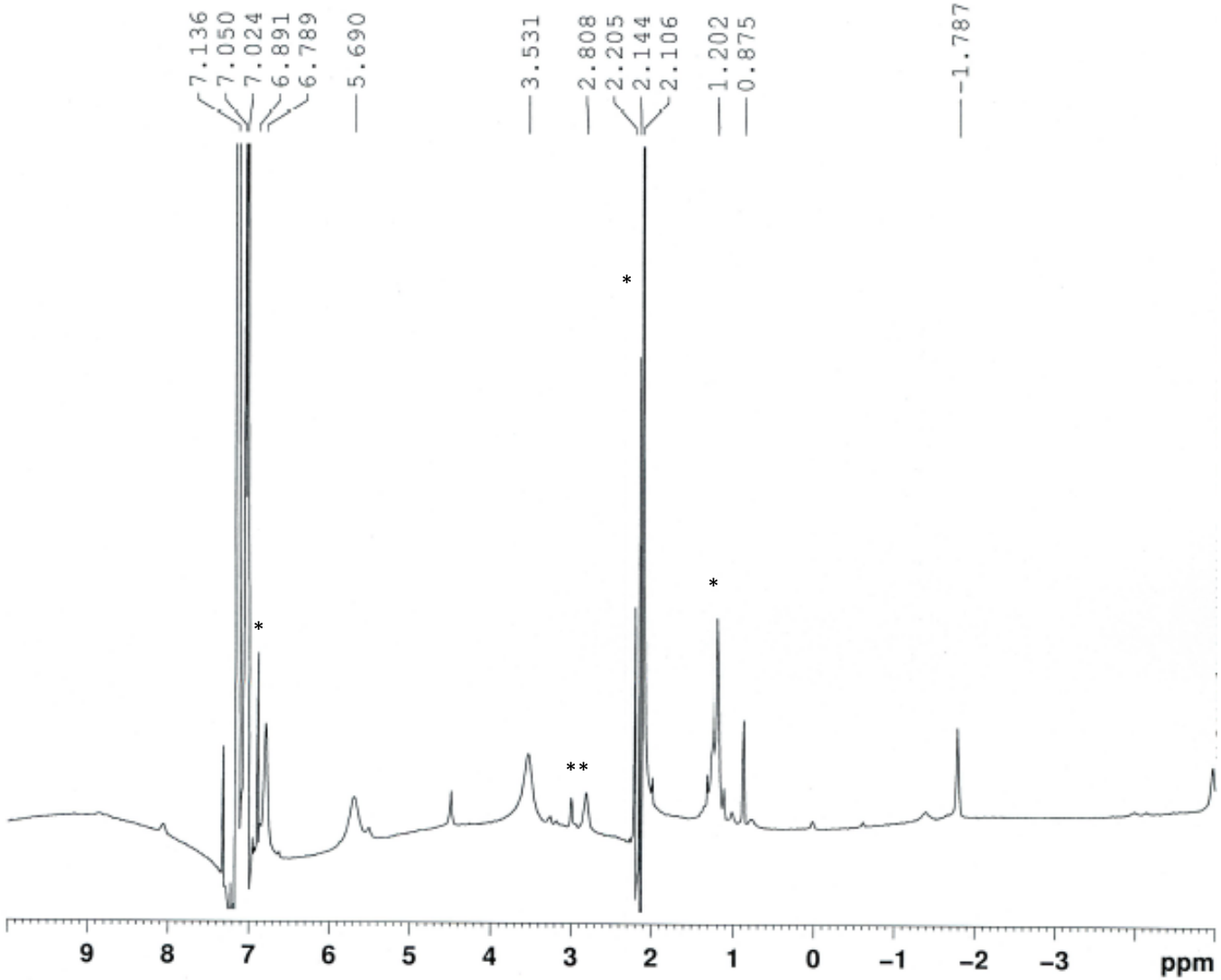
======== CHANNEL f1 ========
NUC1                   1H
P1                  12.00 usec
PL1                  0.00 dB
PL1W         24.54113007 W
SFO1         500.1300000 MHz
SI                 16384
SF           500.1300481 MHz
WDW                   EM
SSB                    0
LB                  0.30 Hz
GB                     0
PC                  1.00
```



C_6D_6

500.13 MHz

* - Trace amounts of NH_2DMP and IPr



References

S1 Bill, E. JulX 1.4.1, A Program for the Simulation and Analysis of Magnetic Susceptibility Data; Max Plank Institute for Bioinorganic Chemistry: Mülheim an der Ruhr, 2008.