Supplementary Material (ESI) for Dalton Transactions

Supporting Information

for

Flexible Cycloalkyl-substituted *N*-heterocyclic Carbenes.

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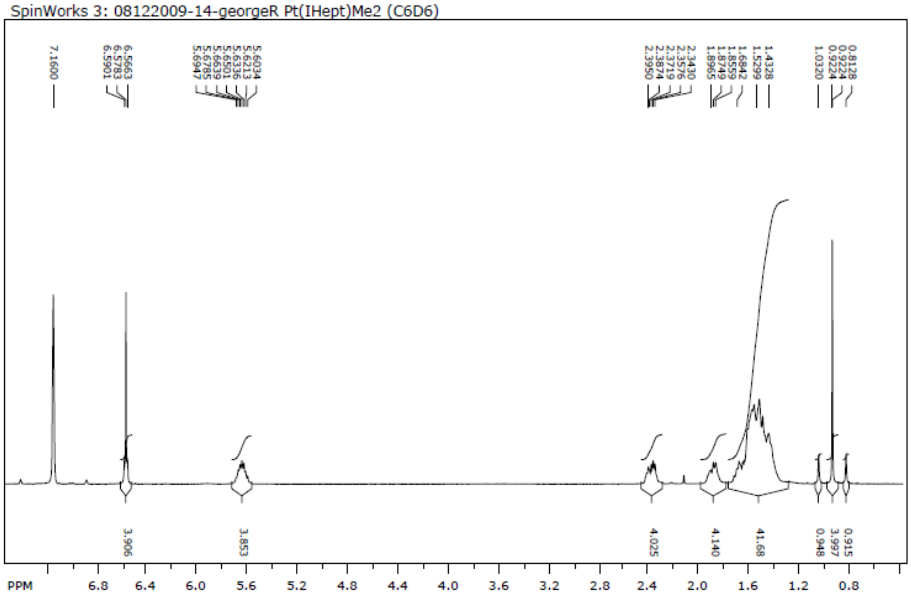
^{1}H & ^{13}C NMR

cis-Pt(ICy^{7})$_2$Me$_2$



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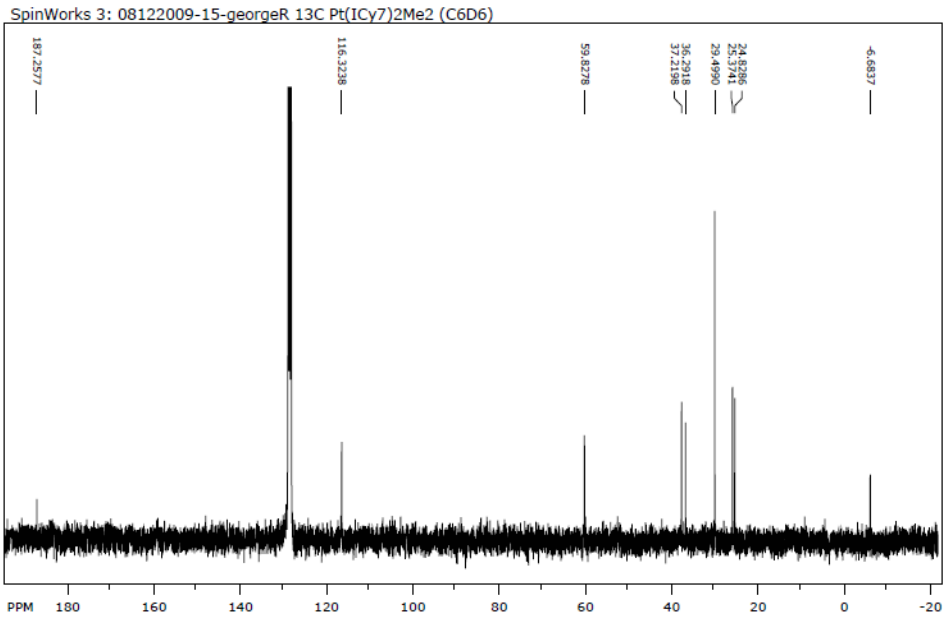

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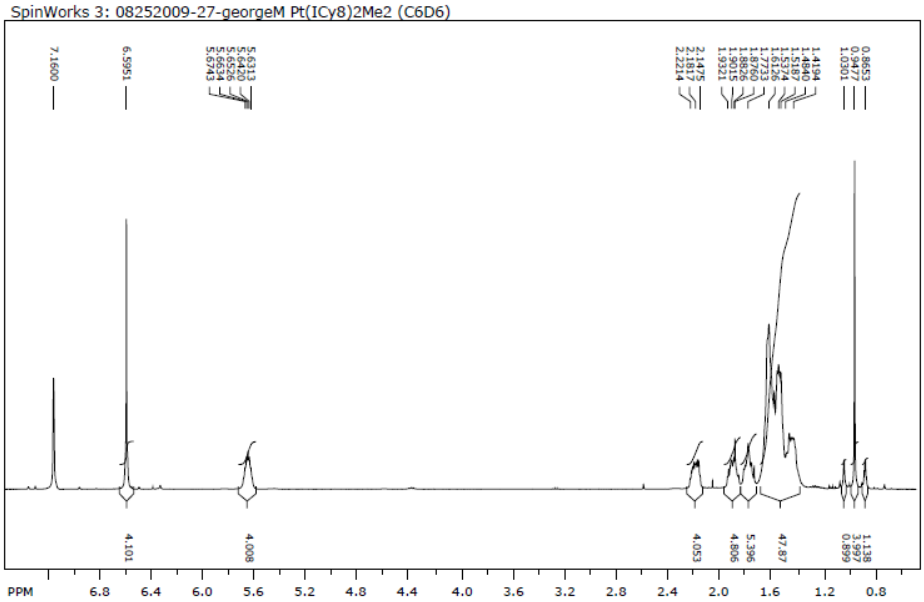
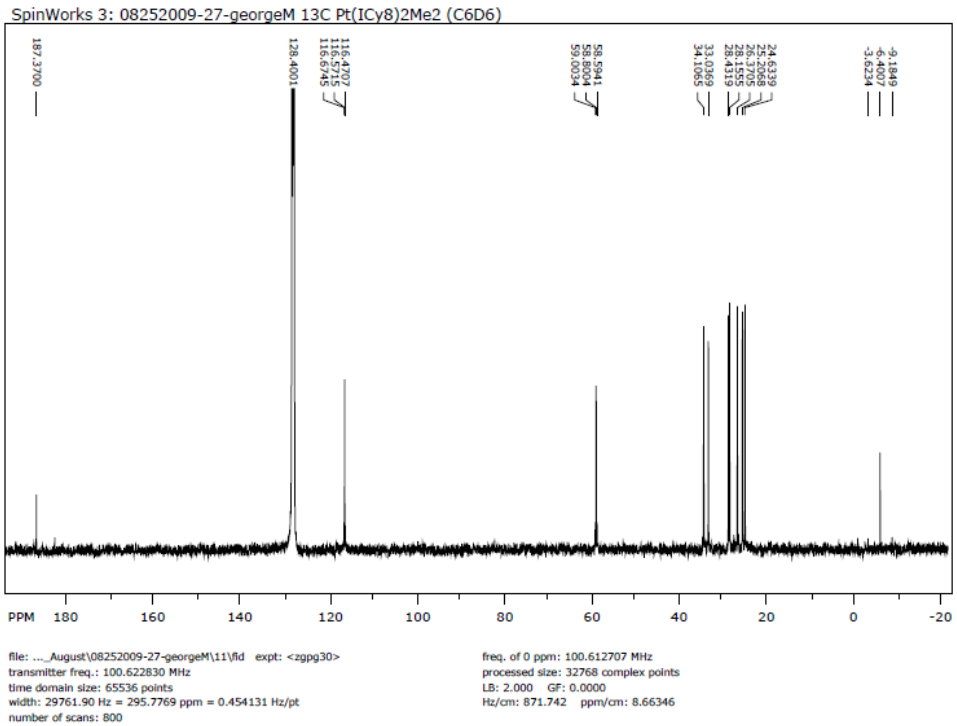
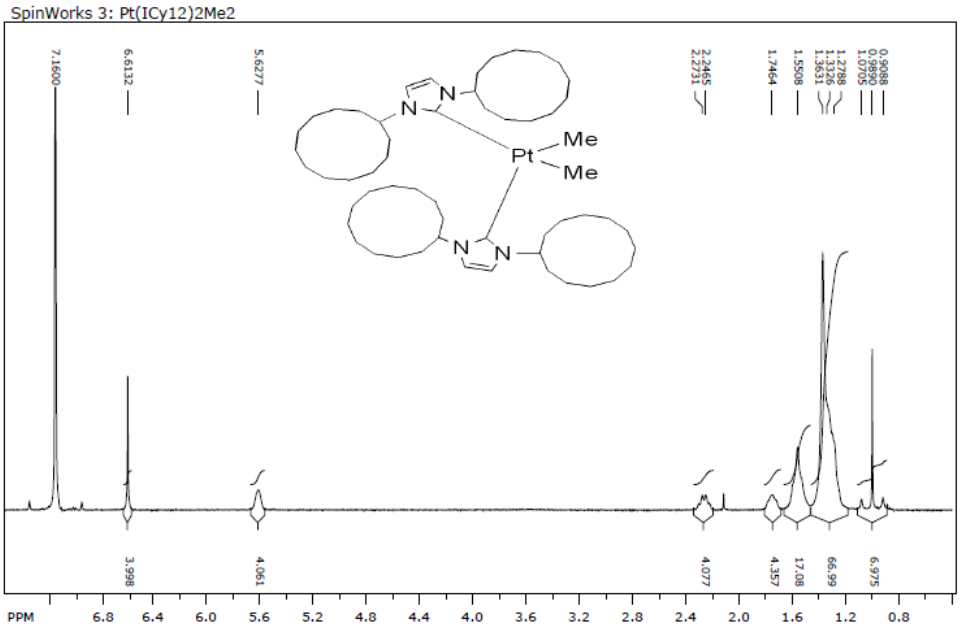
cis-Pt(ICy^{8})$_2$Me$_2$





cis-Pt(ICy^{12})$_2$Me$_2$



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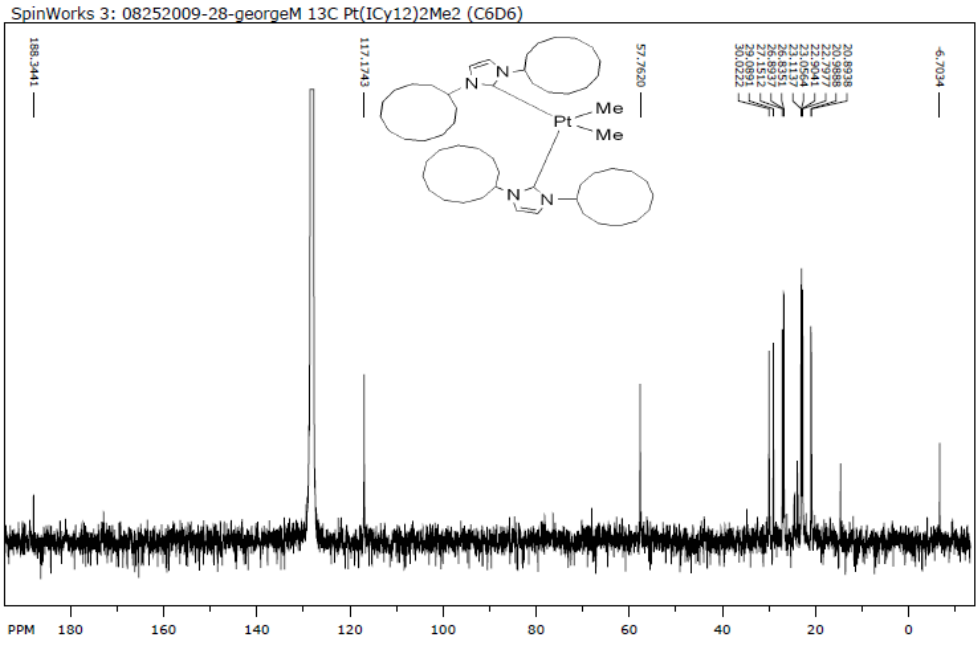

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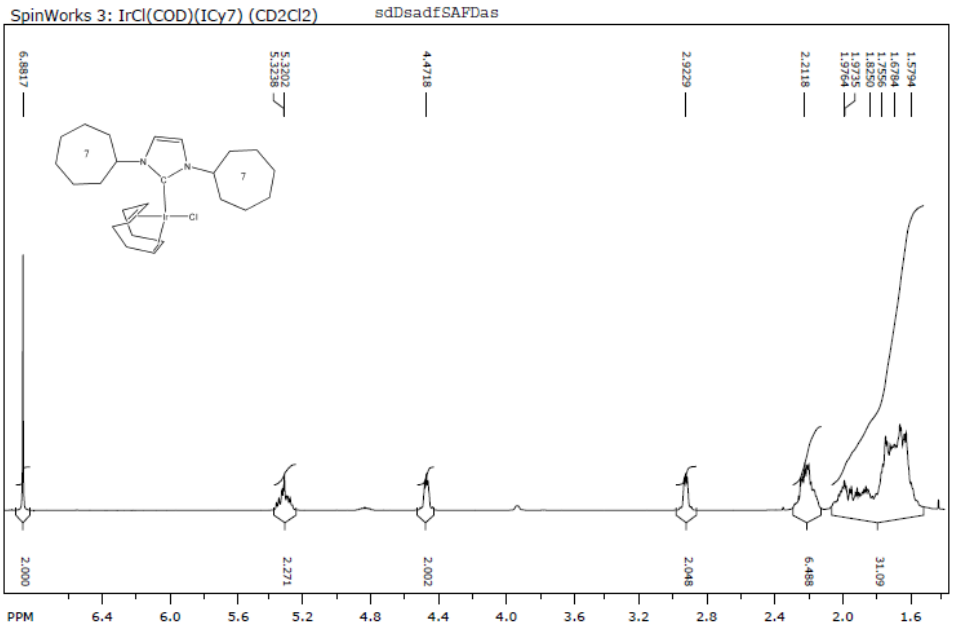
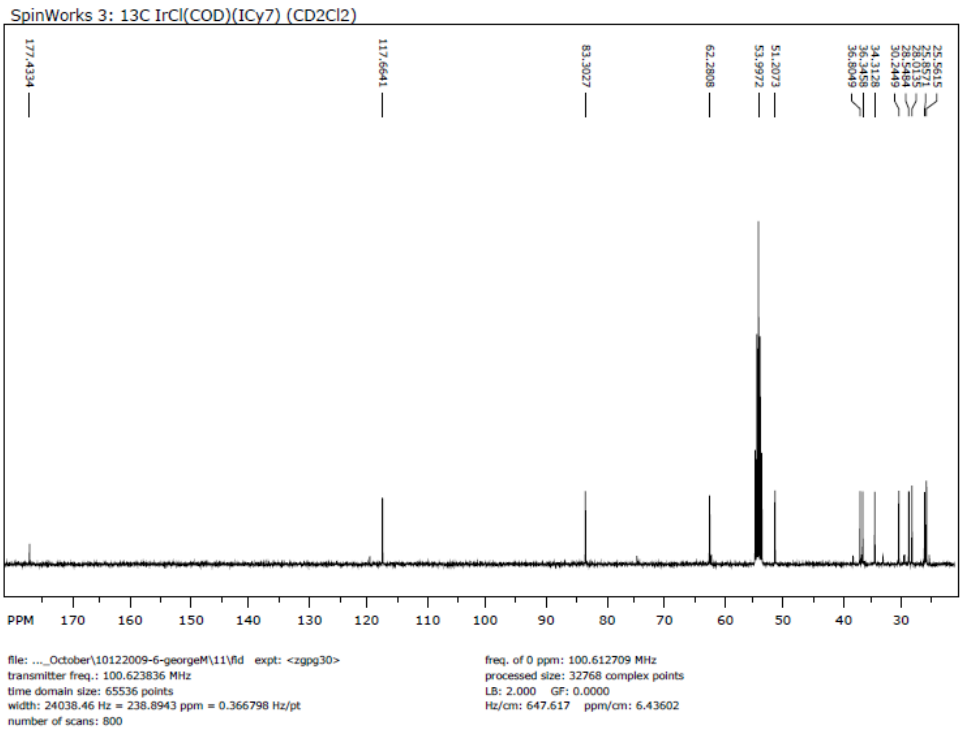
$Ir(ICy^7)(cod)Cl$





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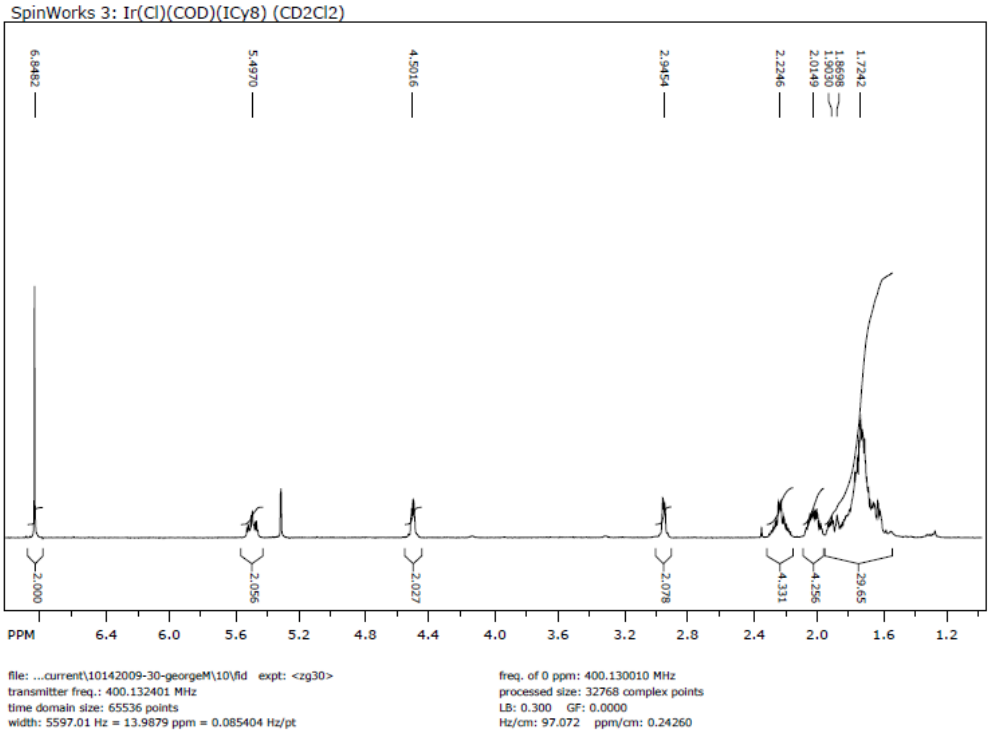
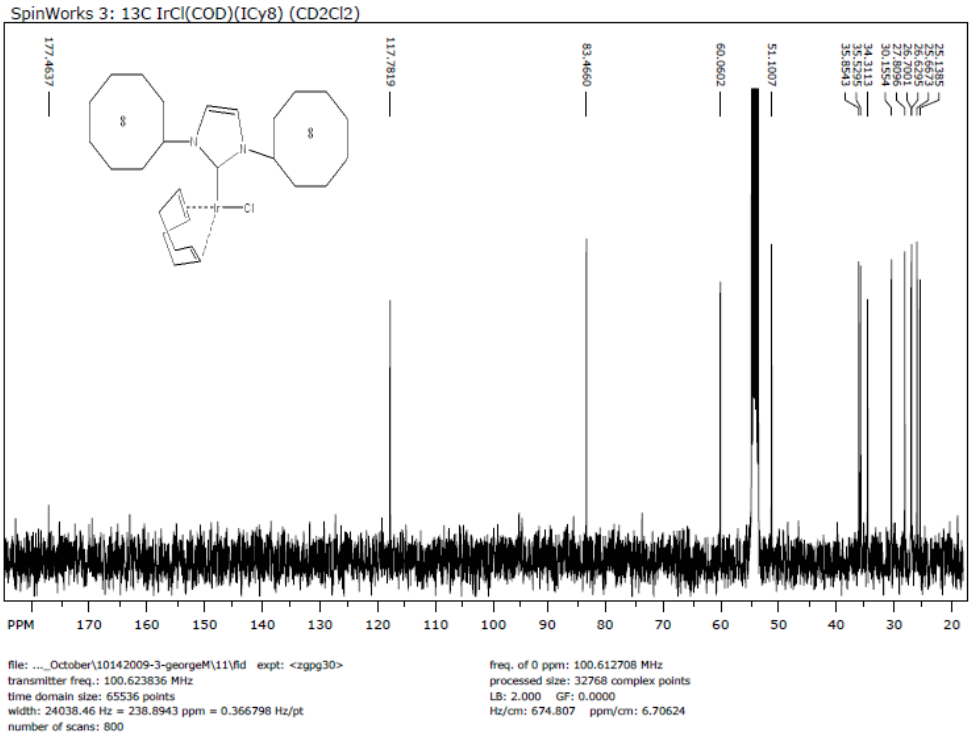
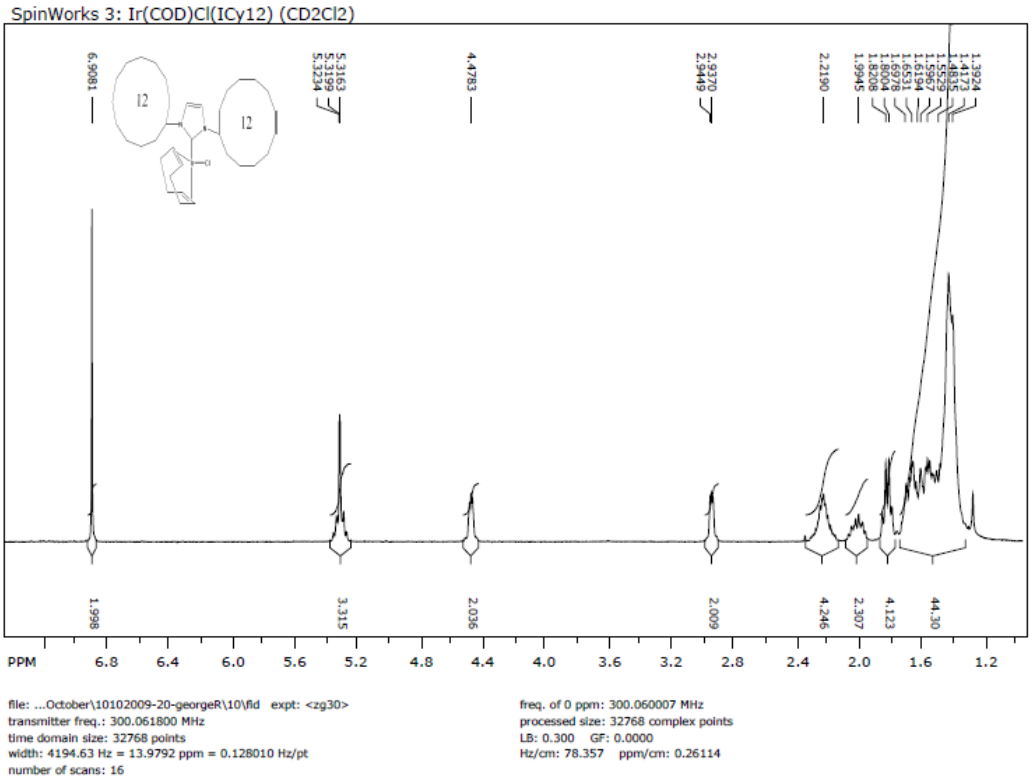




$Ir(ICy^{12})(cod)Cl$



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time domain size: 32768 points
width: 4194.63 Hz = 13.9792 ppm = 0.128010 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.060007 MHz
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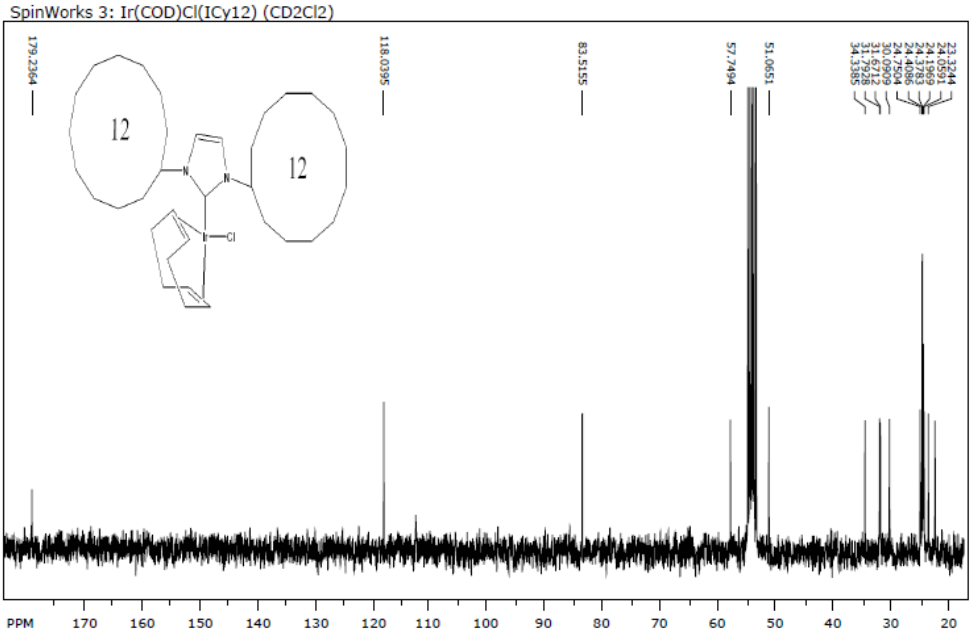

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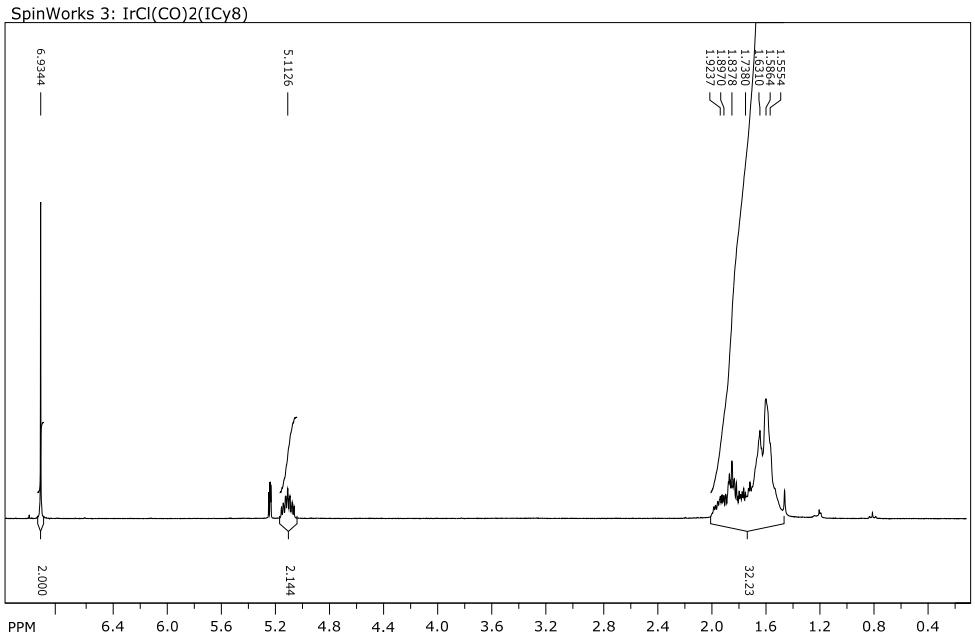
time domain size: 65536 points
width: 18115.94 Hz = 240.0785 ppm = 0.276427 Hz/pt
number of scans: 800

freq. of 0 ppm: 75.450101 MHz
processed size: 65536 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 504.204 ppm/cm: 6.68188

$Ir(ICy^8)(CO)_2Cl$



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time domain size: 32768 points
width: 4194.63 Hz = 13.9760 ppm = 0.128010 Hz/pt
number of scans: 16

freq. of 0 ppm: 300.130035 MHz
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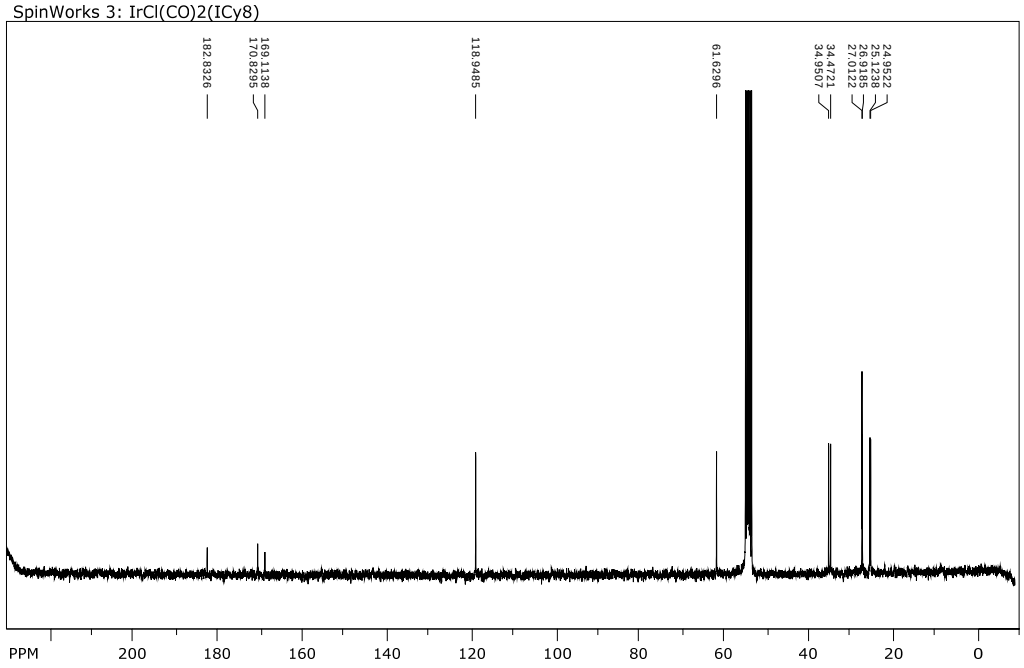
Hz/cm: 85.115 ppm/cm: 0.28359



file: ...November\11142009-4-georgeI\11\fid expt: <zgpg30>
transmitter freq.: 75.476050 MHz
time domain size: 65536 points
width: 18115.94 Hz = 240.0224 ppm = 0.276427 Hz/pt
number of scans: 2400

freq. of 0 ppm: 75.467703 MHz
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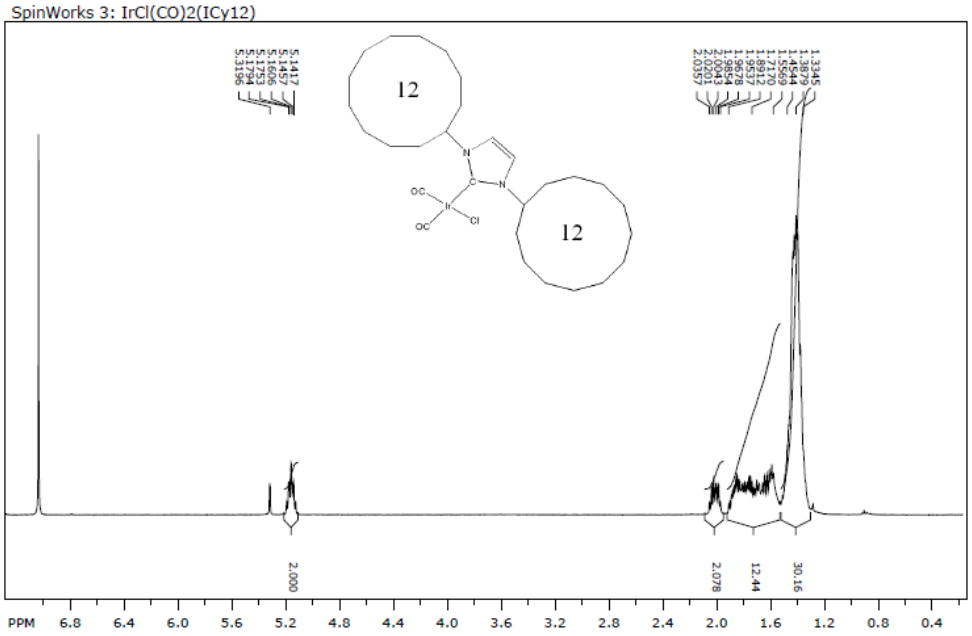
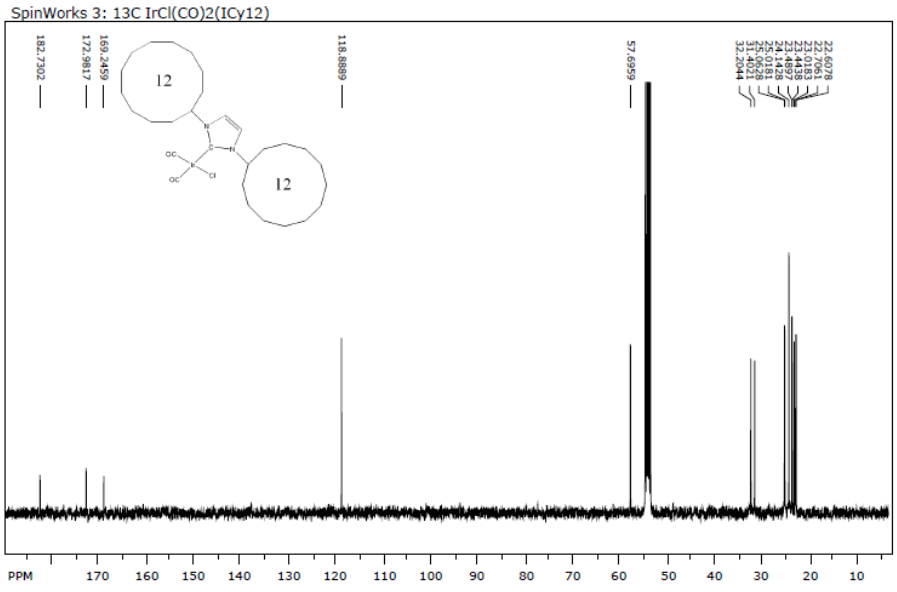
LB: 2.000 GF: 0.0000
Hz/cm: 724.638 ppm/cm: 9.60090

$Ir(ICy^{12})(CO)_2Cl$



file: ..._October\10132009-8-georgeM\10\fid expt: <zg30>
transmitter freq.: 400.132401 MHz
time domain size: 65536 points
width: 5597.01 Hz = 13.9879 ppm = 0.085404 Hz/pt
number of scans: 8

freq. of 0 ppm: 400.130010 MHz
processed size: 32768 complex points
LB: 0.300 GF: 0.0000
Hz/cm: 114.530 ppm/cm: 0.28623



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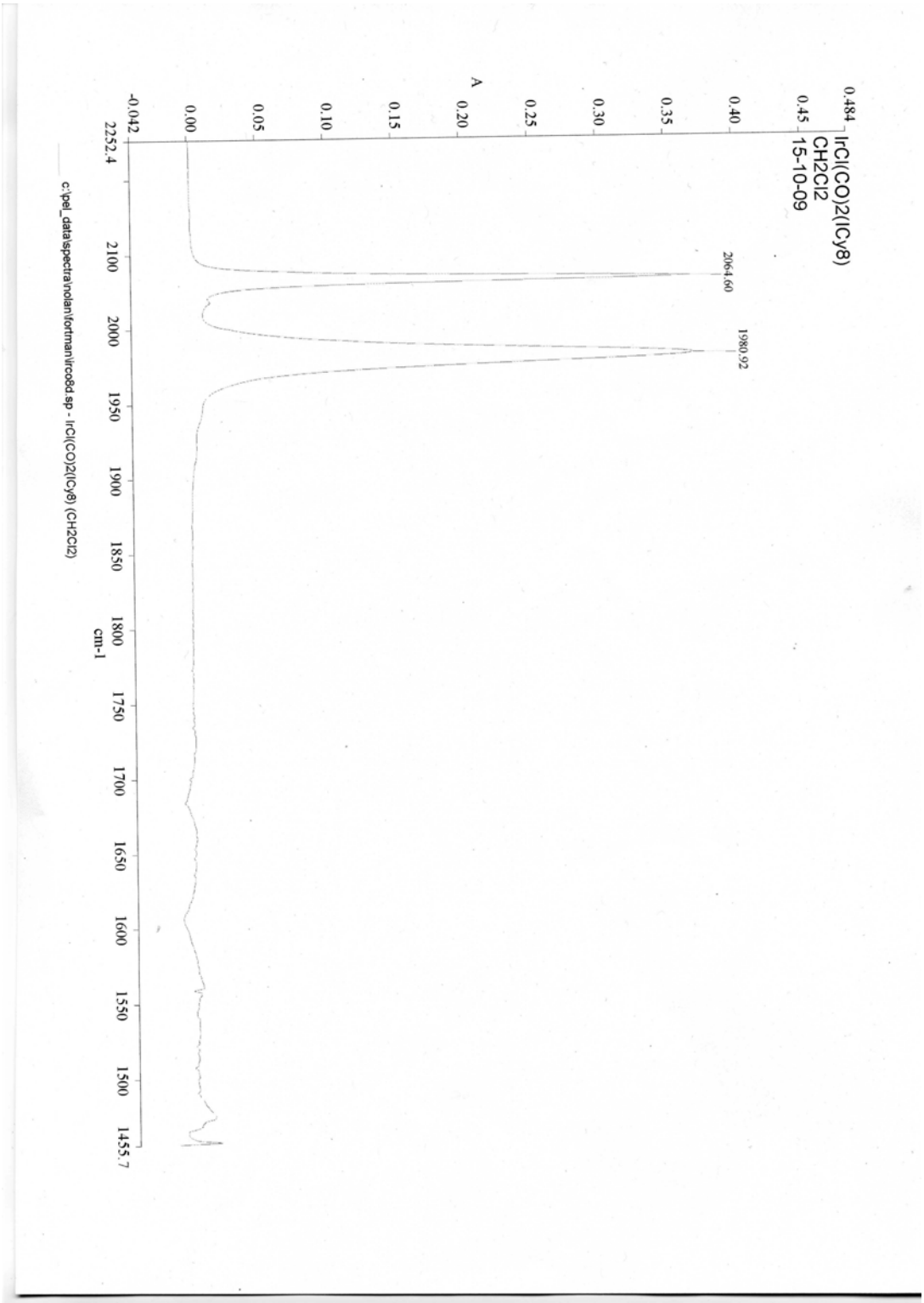
time domain size: 65536 points
width: 24038.46 Hz = 238.8943 ppm = 0.366798 Hz/pt
number of scans: 800

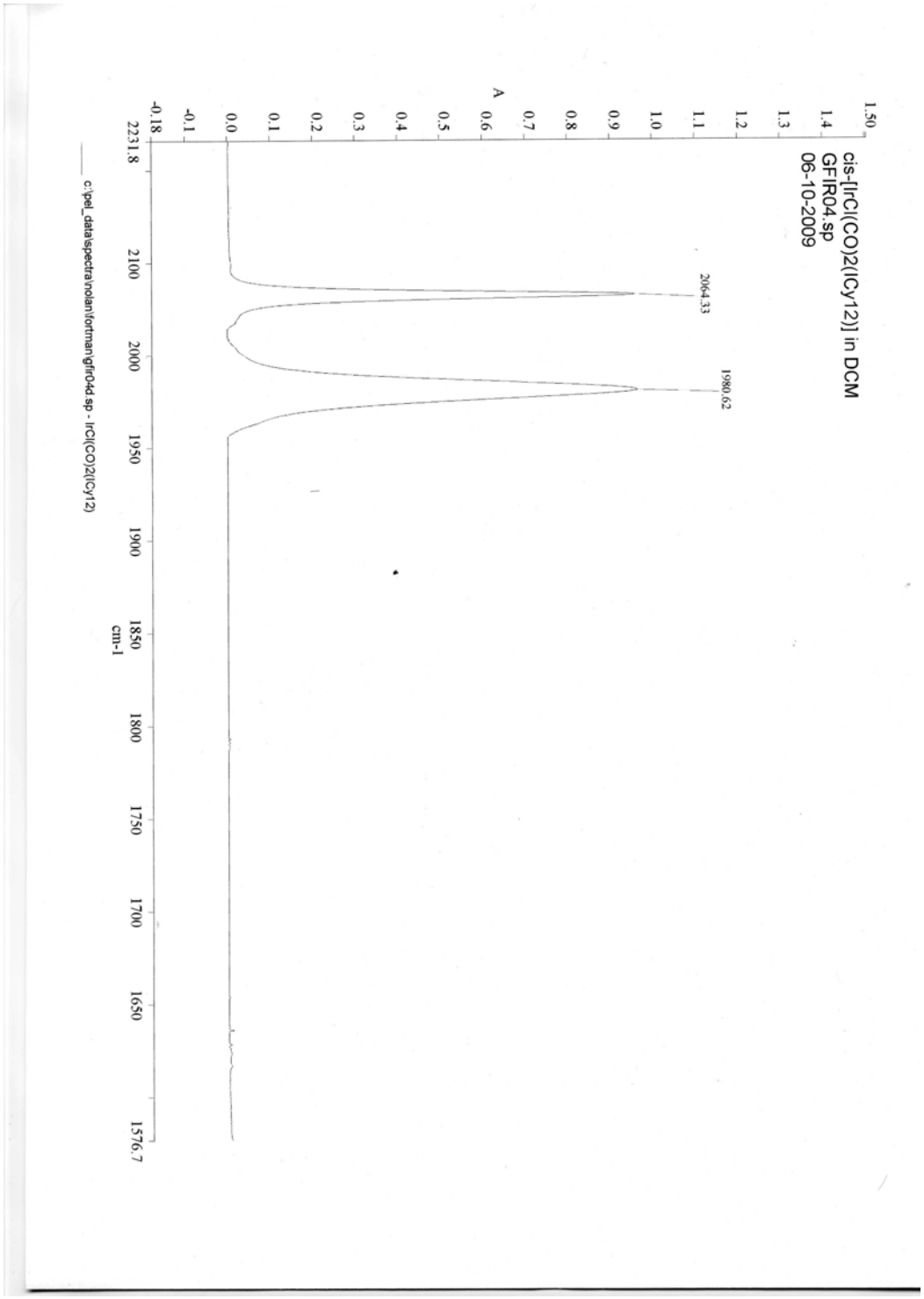
freq. of 0 ppm: 100.612708 MHz
processed size: 32768 complex points
LB: 2.000 GF: 0.0000
Hz/cm: 753.082 ppm/cm: 7.48413

FTIR

cis-Ir(ICy^{8})(CO)$_2$Cl

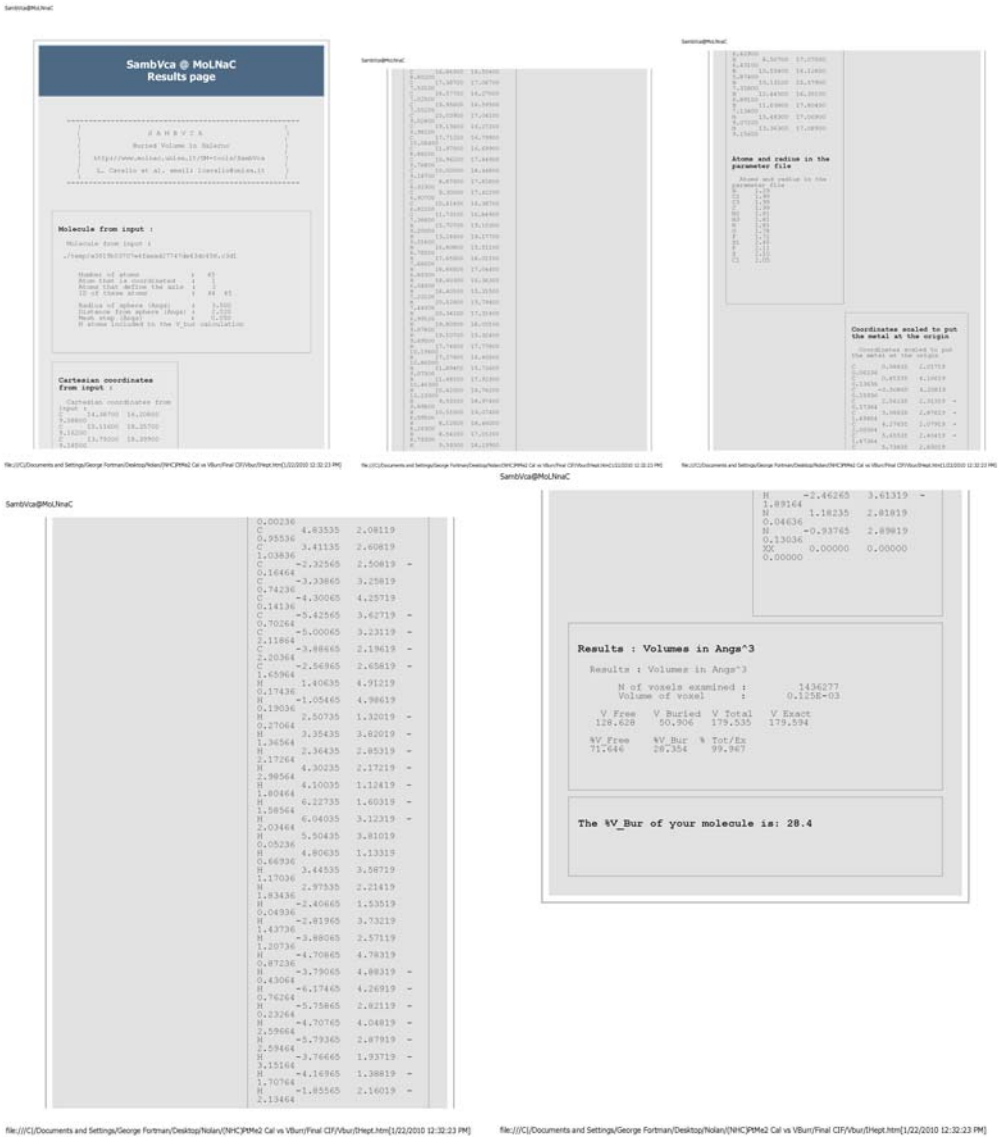


cis-Ir(ICy^{12})(CO)$_2$Cl

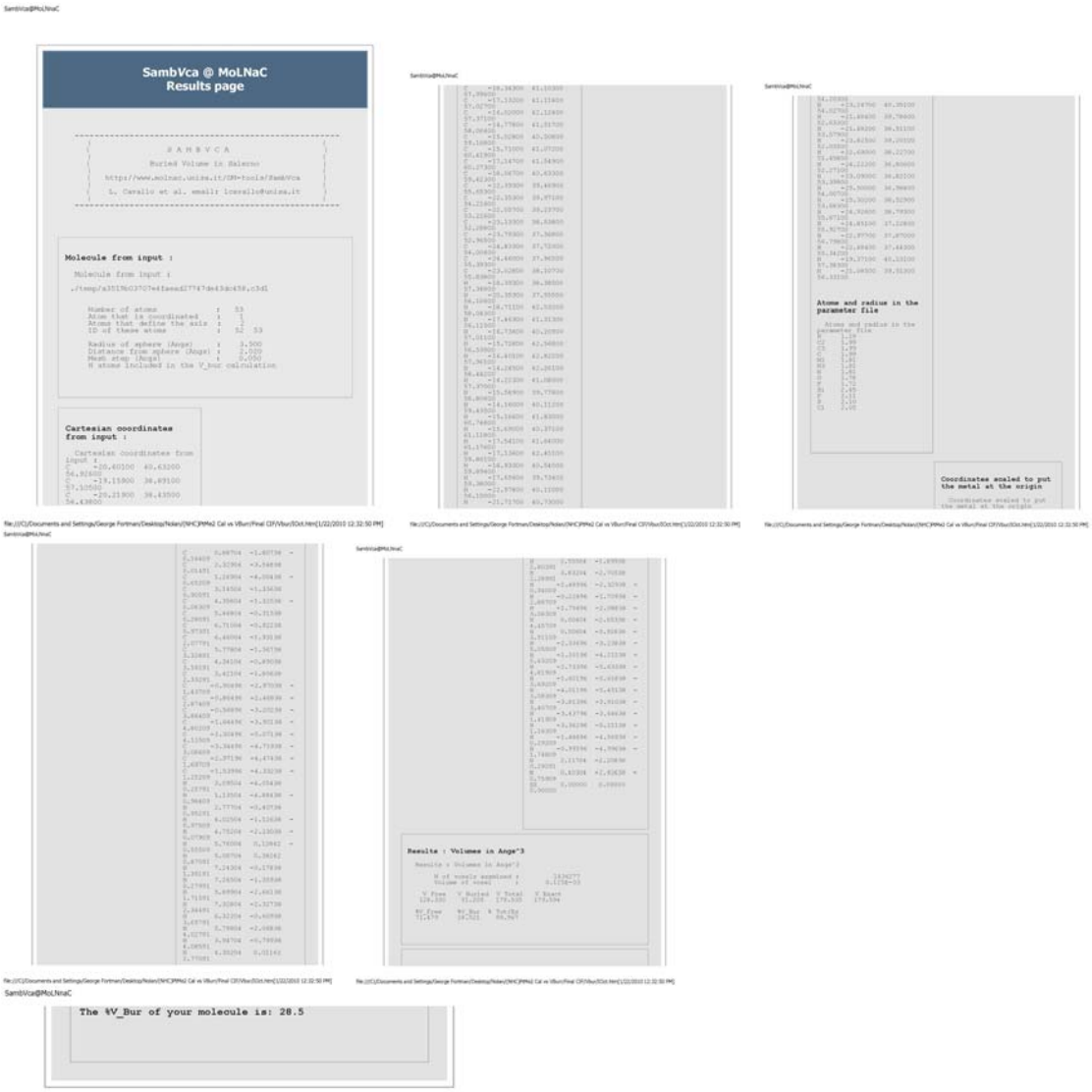


SambVca Output

cis-Pt(ICy^7)$_2$Me$_2$



cis-Pt(ICy^{8})$_2$Me$_2$



cis-Pt(ICy[12])$_2$Me$_2$

cis-Ir(ICy)$(CO)_2$Cl

SambVca@MoLNnaC

SambVca @ MoLNaC
Results page

```
-------------------------------------------------
|                                               |
|                  S A M B V C A                |
|                                               |
|             Buried Volume in Salerno          |
|                                               |
|    http://www.molnac.unisa.it/OM-tools/SambVca|
|                                               |
|     L. Cavallo et al. email: lcavallo@unisa.it|
|                                               |
-------------------------------------------------
```

Molecule from input :

Molecule from input :

./temp/09b7707f0d3d40350%875f3fd3c749c.c3d1

```
    Number of atoms             :   41
    Atom that is coordinated    :    2
    Atoms that define the axis  :    2
    ID of these atoms           :   40   41

    Radius of sphere (Angs)     :    3.500
    Distance from sphere (Angs) :    2.020
    Mesh step (Angs)            :    0.050
    H atoms included in the V_bur calculation
```

Cartesian coordinates from input :

Cartesian coordinates from input :

```
C       3.52600   -2.11600    7.04600
C       4.90800   -2.12700    7.08000
C       4.26400   -4.20700    6.86000
C       6.75200   -3.83700    6.96400
C       7.50000   -3.31100    8.05900
C       8.96300   -3.71100    8.07900
C       9.61100   -3.97300    6.72600
C       8.80700   -3.90800    5.61300
C       7.37100   -3.52900    5.61300
C       1.79700   -3.94700    7.02300
C       0.86000   -3.14600    6.20100
C      -0.53600   -3.67900    6.32900
C      -0.97500   -3.74800    7.70100
C      -0.06500   -4.57400    8.57800
C       1.37500   -4.09600    8.44800
H       2.95500   -1.38400    7.69000
H       5.46100   -1.38600    7.18600
H       6.75300   -4.81300    7.06100
H       7.44400   -2.94300    8.03400
H       7.08800   -3.60800    8.88500
H       9.42200   -3.23500    8.79000
H       9.04200   -4.66200    8.25100
H      10.51900   -3.71600    6.70200
H       9.64900   -2.41100    6.61100
H       9.21300   -2.75500    4.76500
H       8.83200   -4.95400    5.70100
H       6.88000   -3.98700    4.91400
H       7.33100   -2.57600    5.44200
H       1.80000   -4.84800    6.64000
H       0.98200   -2.22200    6.49100
H       1.13600   -3.17900    5.27100
H      -0.57600   -4.56600    5.93800
```

file:///C|/Documents and Settings/George Fortman/Desktop/Nolan/Ir NHC/Cif/Final/Vbur/ICy.htm[1/22/2010 12:13:54 PM]

SambVca@MoLNnaC

```
H      -1.14100   -3.10800    5.83000
H      -1.02500   -2.84800    8.05900
H      -1.86700   -4.12800    7.72700
H      -0.35100   -4.49900    9.50300
H      -0.12300   -5.50400    8.11900
H       1.94100   -4.73000    8.88900
H       1.46700   -3.24100    8.89900
H       3.19900   -3.44700    6.92800
H       5.31100   -3.39900    6.93600
```

Atoms and radius in the parameter file

Atoms and radius in the parameter file

```
H     1.29
C12   1.99
C3    1.99
C7    1.99
N2    1.81
N3    1.81
N     1.81
O     1.78
P     1.72
Ir1   2.45
S     2.11
Br    2.10
Cl    2.05
```

Coordinates scaled to put the metal at the origin

Coordinates scaled to put the metal at the origin

```
C      -0.76879    4.10230    0.37071
C       0.61321    4.09139    0.40471
C      -0.03879    2.01138    0.18471
C       2.45721    2.38138    0.26871
C       3.20521    2.90738    1.38371
C       4.66821    2.50738    1.40371
C       5.31621    2.84538    0.05071
C       4.91221    2.23038   -1.06229
C       3.07421    2.68938   -1.04229
C      -2.49779    3.07138    0.34771
C      -3.63479    3.07238   -0.47429
C      -4.83679    2.53938   -0.34629
C      -5.26979    2.47038    1.02571
C      -4.35979    1.64438    1.90271
C      -2.91979    2.12238    1.77271
H      -1.33979    4.83438    0.41471
H       1.16621    4.85238    0.51071
H       2.45821    1.40538    0.38571
H       2.51921    3.67538    1.35871
H       2.79321    2.61038    2.20971
H       5.12721    2.98038    2.11471
H       5.14721    1.55638    1.57571
H       6.12421    2.50238    0.02671
H       5.35421    3.90738   -0.66429
H       4.91821    2.46338   -1.91029
H       4.53721    1.26438   -0.97429
H       2.58521    2.23138   -1.76129
H       3.03621    3.64238   -1.23329
H      -2.49479    1.37038   -0.03529
H      -3.81279    2.99638   -0.18429
H      -3.15879    3.03938   -1.40429
H      -4.87079    1.68238   -0.53729
H      -5.43579    3.11038   -0.84529
H      -5.31979    3.37038    1.98271
H      -4.14179    2.09038    1.85171
H      -4.64579    1.71938    2.82771
H      -4.41679    0.71238    1.64371
H      -2.33379    1.48838    2.21371
H      -2.82779    2.97738    2.02271
H      -1.10179    2.77138    0.25271
```

file:///C|/Documents and Settings/George Fortman/Desktop/Nolan/Ir NHC/Cif/Final/Vbur/ICy.htm[1/22/2010 12:13:54 PM]

SambVca@MoLNnaC

```
N       1.01621   2.81938   0.24071
Xx      0.00000   0.00000   0.00000
```

Results : Volumes in Angs^3

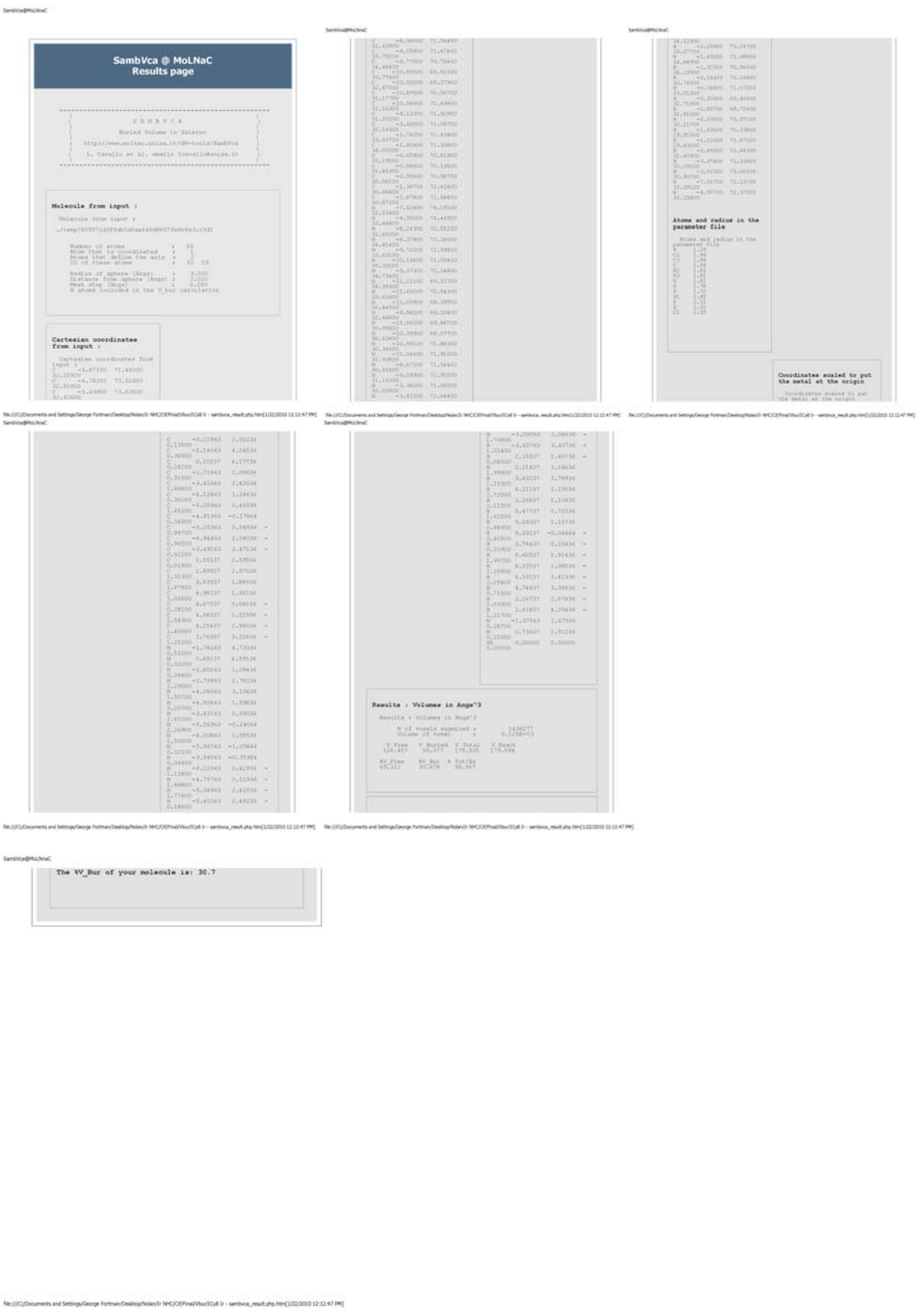
Results : Volumes in Angs^3

```
      N of voxels examined :          1426277
      Volume of voxel      :        0.125E+00

   V_Free   V_Buried  V_Total   V_Exact
  127.074    51.940   179.535   179.594

  %V_Free    %V_Bur   % Tot/By
   71.058    28.942    99.987
```

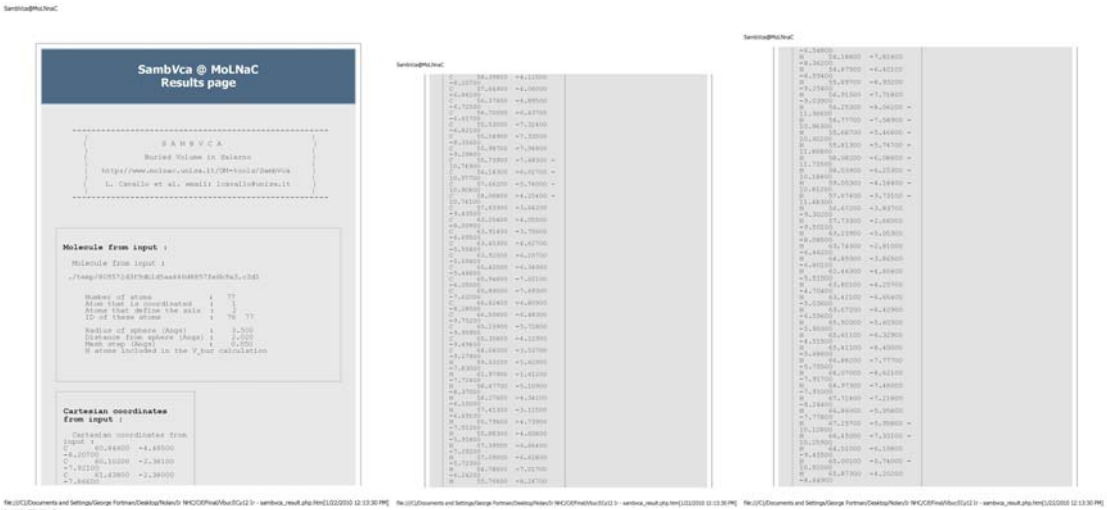
The %V_Bur of your molecule is: 28.9

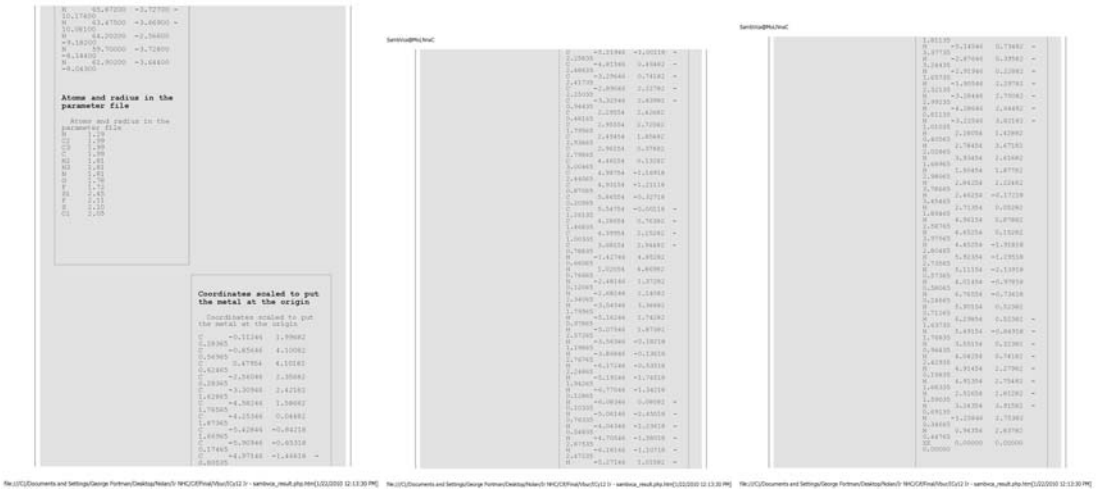
file:///C|/Documents and Settings/George Fortman/Desktop/Nolan/Ir NHC/Cif/Final/Vbur/ICy.htm[1/22/2010 12:13:54 PM]

cis-Ir(ICy^{8})(CO)$_2$Cl



cis-Ir(ICy^{12})(CO)$_2$Cl





cis-Ir(IMes)(CO)$_2$Cl

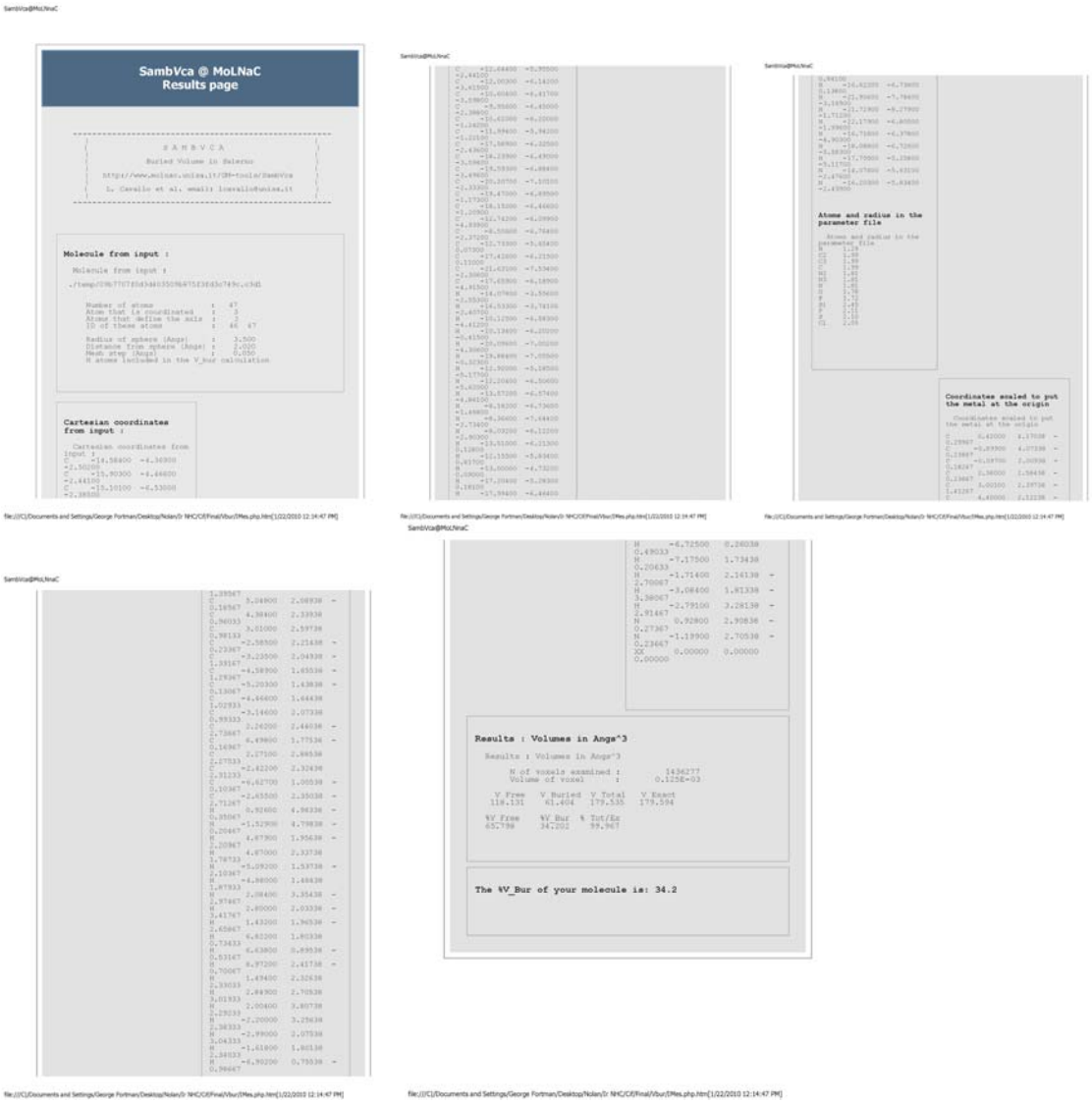


Table S1. Crystallographic data for *cis*-Pt(NHC)$_2$Me$_2$ (NHC = ICy[7], ICy[8], ICy[12])complexes.

Compound reference	*cis*-Pt(ICy[7])$_2$Me$_2$ (**3e**)	*cis*-Pt(ICy[8])$_2$Me$_2$ (**3f**)	*cis*-Pt(ICy[12])$_2$Me$_2$ (**3g**)
Chemical formula	$C_{36}H_{62}N_4Pt$	$C_{40}H_{70}N_4Pt$	$C_{56}H_{102}N_4Pt•C_4H_8O_2$
Formula Mass	745.99	802.09	1114.61
CCDC number	762962	762961	762963
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
a/Å	19.481(4)	12.924(3)	17.712(5)
b/Å	15.267(3)	14.532(3)	15.351(4)
c/Å	22.882(5)	19.717(4)	23.005(7)
α/°	90.00	90.00	90.00
β/°	90.00	90.00	111.436(7)
γ/°	90.00	90.00	90.00
Unit cell volume/Å^3	6806(2)	3703.3(14)	5822(3)
Temperature/K	93(2)	93(2)	93(2)
Space group	*Pbca*	*P2(1)2(1)2(1)*	*P2(1)/n*
No. of formula units per unit cell, *Z*	8	4	4
Absorption coefficient, μ/mm^{-1}	4.153	3.822	2.453
No. of reflections measured	41103	23569	36606
No. of independent reflections	6210	6756	10549
R_{int}	0.1494	0.0764	0.1599
Final R_1 values ($I > 2\sigma(I)$)	0.0582	0.0408	0.0641
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1034	0.0651	0.1005
Final R_1 values (all data)	0.1082	0.0486	0.1321
Final $wR(F^2)$ values (all data)	0.1191	0.0680	0.1192

Table S2. Crystallographic data for *cis*-Ir(NHC)$(CO)_2$Cl (NHC = ICy^8, ICy^{12}) complexes.

Compound reference	*cis*-Ir(ICy^8)$(CO)_2$Cl (**6f**)	*cis*-Ir(ICy^{12})$(CO)_2$Cl (**6g**)
Chemical formula	$C_{21}H_{32}ClIrN_2O_2$	$C_{29}H_{48}ClIrN_2O_2$
Formula Mass	572.14	684.34
CCDC number	762964	762965
Crystal system	Orthorhombic	Triclinic
a/Å	17.878(6)	7.815(4)
b/Å	19.052(6)	9.552(5)
c/Å	13.392(4)	20.760(9)
α/°	90.00	92.160(9)
β/°	90.00	92.229(10)
γ/°	90.00	111.059(15)
Unit cell volume/Å^3	4561(2)	1442.8(12)
Temperature/K	93(2)	93(2)
Space group	*Pccn*	$P\bar{1}$
No. of formula units per unit cell, *Z*	8	2
Absorption coefficient, μ/mm^{-1}	5.988	4.747
No. of reflections measured	27093	9296
No. of independent reflections	4135	5089
R_{int}	0.1448	0.0837
Final R_1 values ($I > 2\sigma(I)$)	0.0821	0.0681
Final $wR(F^2)$ values ($I > 2\sigma(I)$)	0.1559	0.1215
Final R_1 values (all data)	0.1330	0.1059
Final $wR(F^2)$ values (all data)	0.1745	0.1375