Electronic Supplementary Information for Dalton Transactions

Electronic Supplemental Information

Synthesis and Characterization of Palladium Fluorides with Nitrogen Ligands

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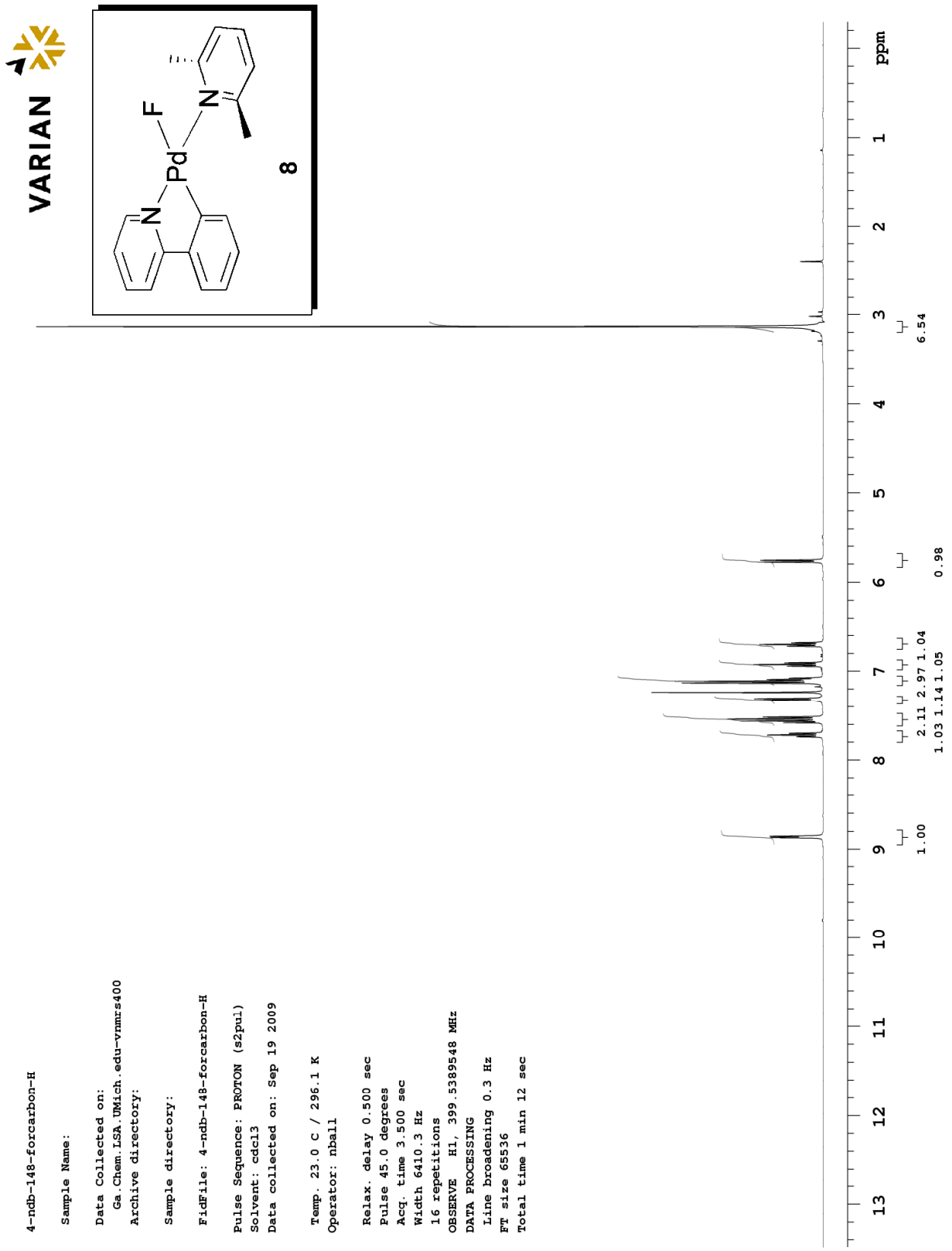

4-ndb-148-forcarbon-H
Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: 4-ndb-148-forcarbon-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 19 2009
Temp. 23.0 C / 296.1 K
Operator: nball
Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.5389548 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
VARIAN
F
Pd
N
N
8
ppm
1.00
2.11
2.97
1.04
1.03
1.14
1.05
0.98
6.54

VARIAN

```
4-ndb-148-forF-F

 Sample Name:

 Data Collected on:
   Zr.Chem.LSA.UMich.edu-inova400
 Archive directory:

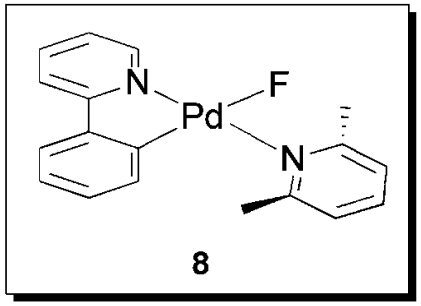
 Sample directory:

 FidFile: FLUORINE

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Sep 19 2009

 Temp. 25.0 C / 298.1 K
Operator: nball

 Relax. delay 1.000 sec
 Pulse 30.0 degrees
 Acq. time 1.053 sec
 Width 124.4 kHz
 64 repetitions
OBSERVE  F19, 376.3430777 MHz
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 262144
Total time 2 min 16 sec
```



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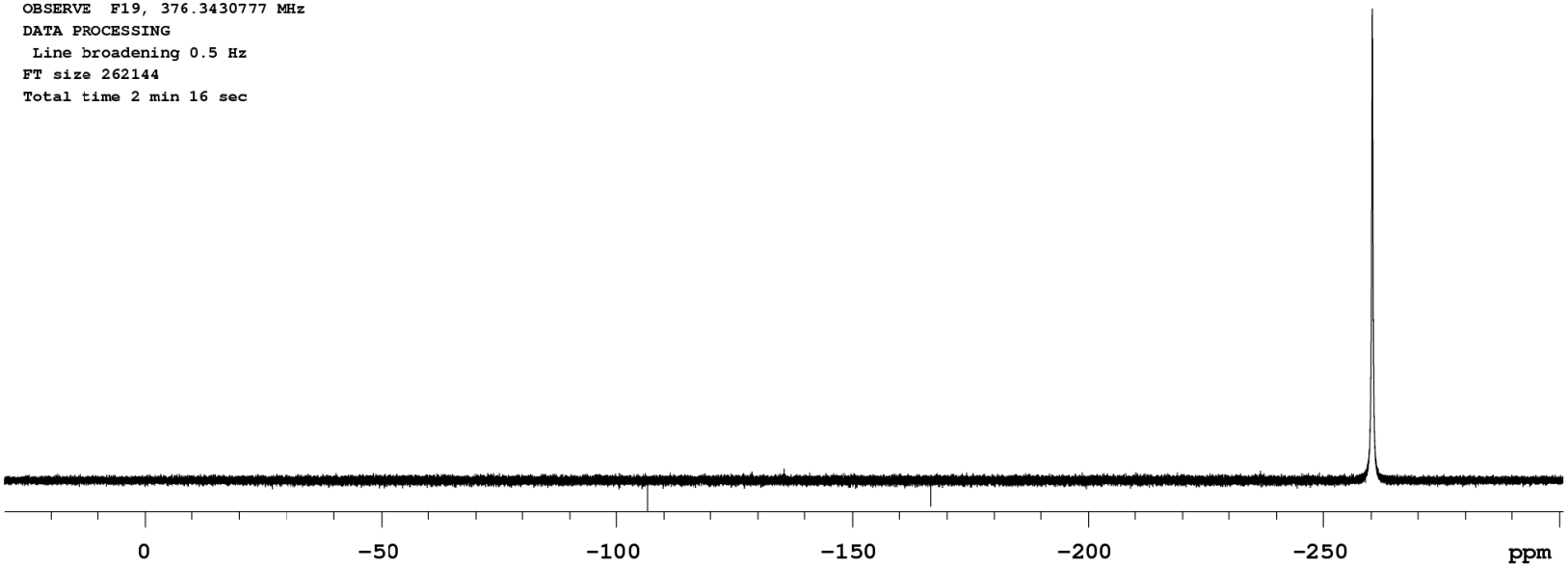
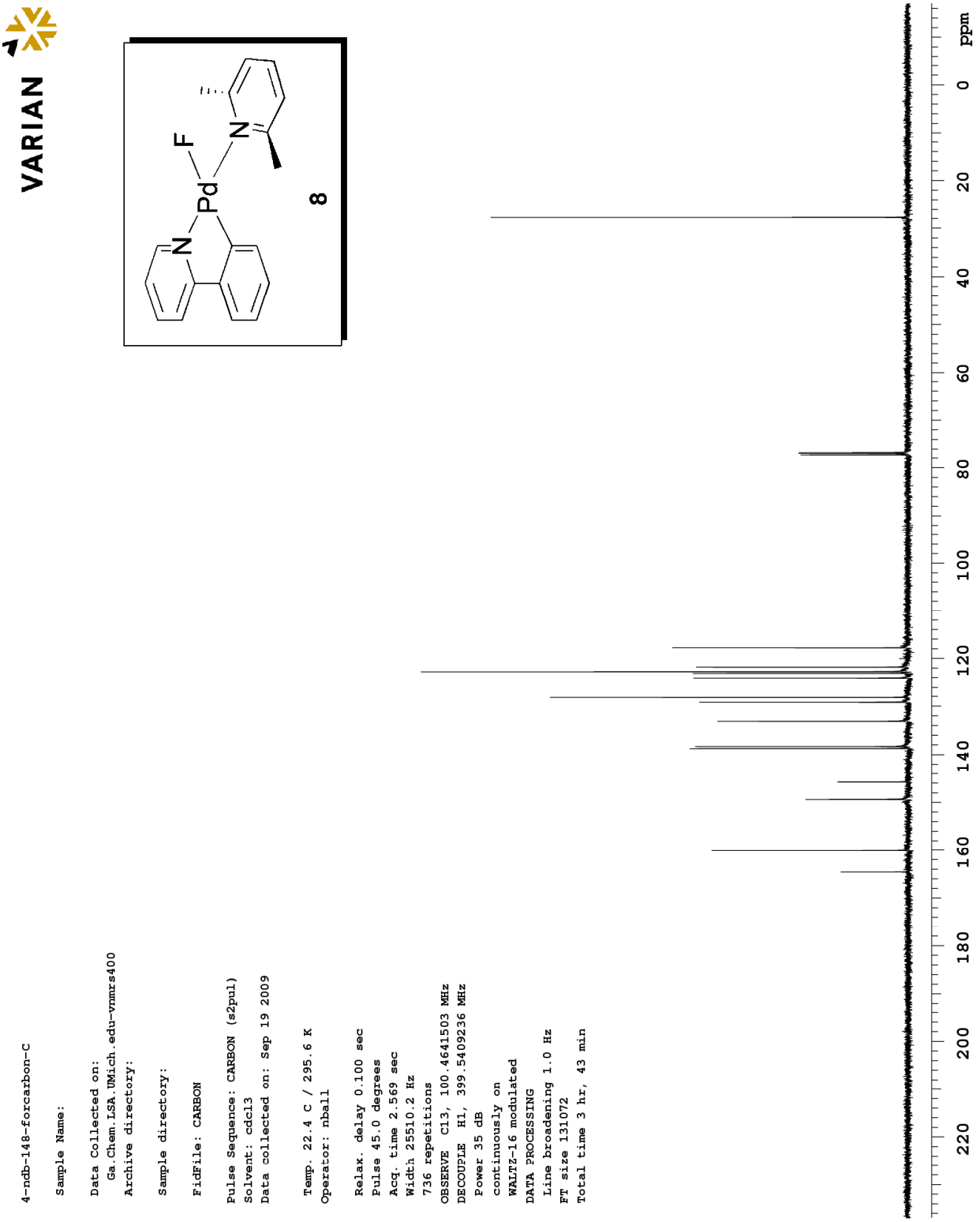



VARIAN
F
Pd
N
N
8
4-ndb-148-forcarbon-C
Sample Name:
Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: CARBON
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 19 2009
Temp. 22.4 C / 295.6 K
Operator: nball
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
736 repetitions
OBSERVE C13, 100.4641503 MHz
DECOUPLE H1, 399.5409236 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 hr, 43 min
220
200
180
160
140
120
100
80
60
40
20
0
ppm

Electronic Supplementary Information for Dalton Transactions

VARIAN

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
co.chem.lsa.umich.edu-vnmrs400
Archive directory:

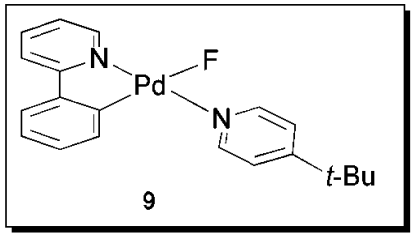
Sample directory:

FidFile: 4-ndb-63-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Mar 10 2009

Operator: nball

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.5297671 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 5 sec



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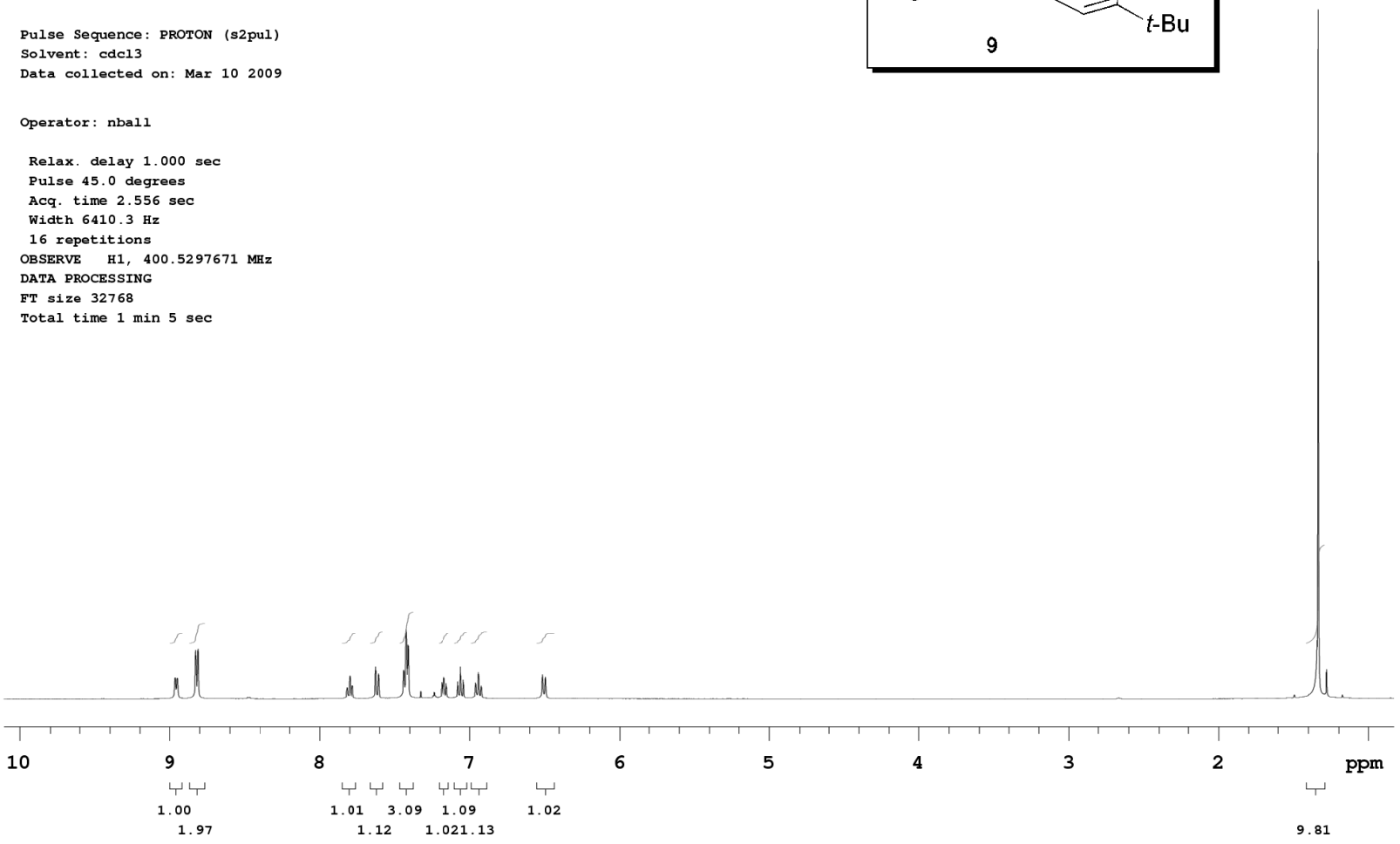


4-ndb-63-F

Sample Name:

Data Collected on:
co.chem.lsa.umich.edu-vnmrs400
Archive directory:

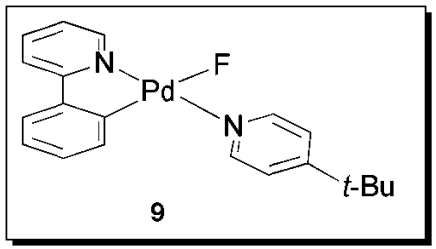
Sample directory:

FidFile: 4-ndb-63-F

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Mar 10 2009

Operator: nball

Relax. delay 1.000 sec
Pulse 35.0 degrees
Acq. time 0.996 sec
Width 131.6 kHz
64 repetitions
OBSERVE F19, 376.8745231 MHz
DATA PROCESSING
FT size 262144
Total time 2 min 9 sec



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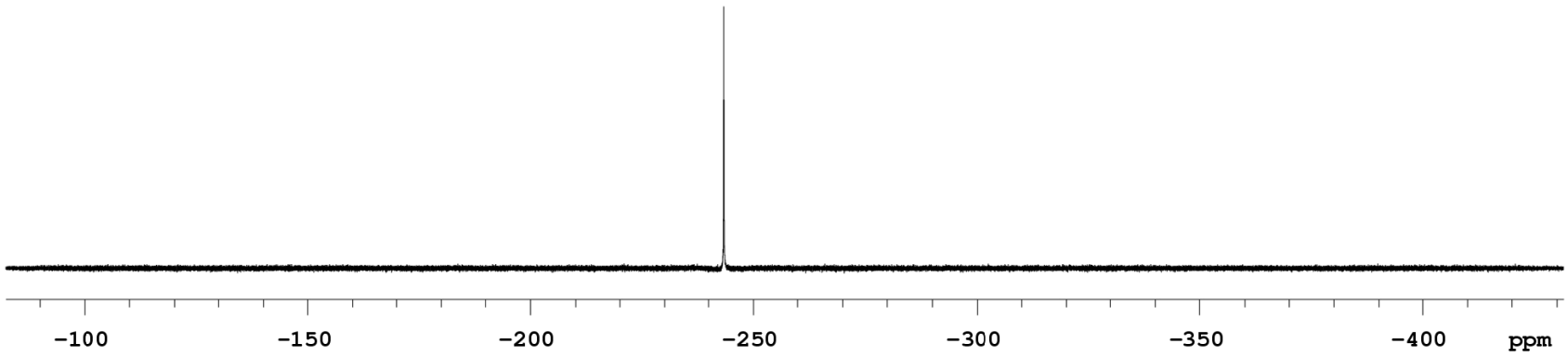
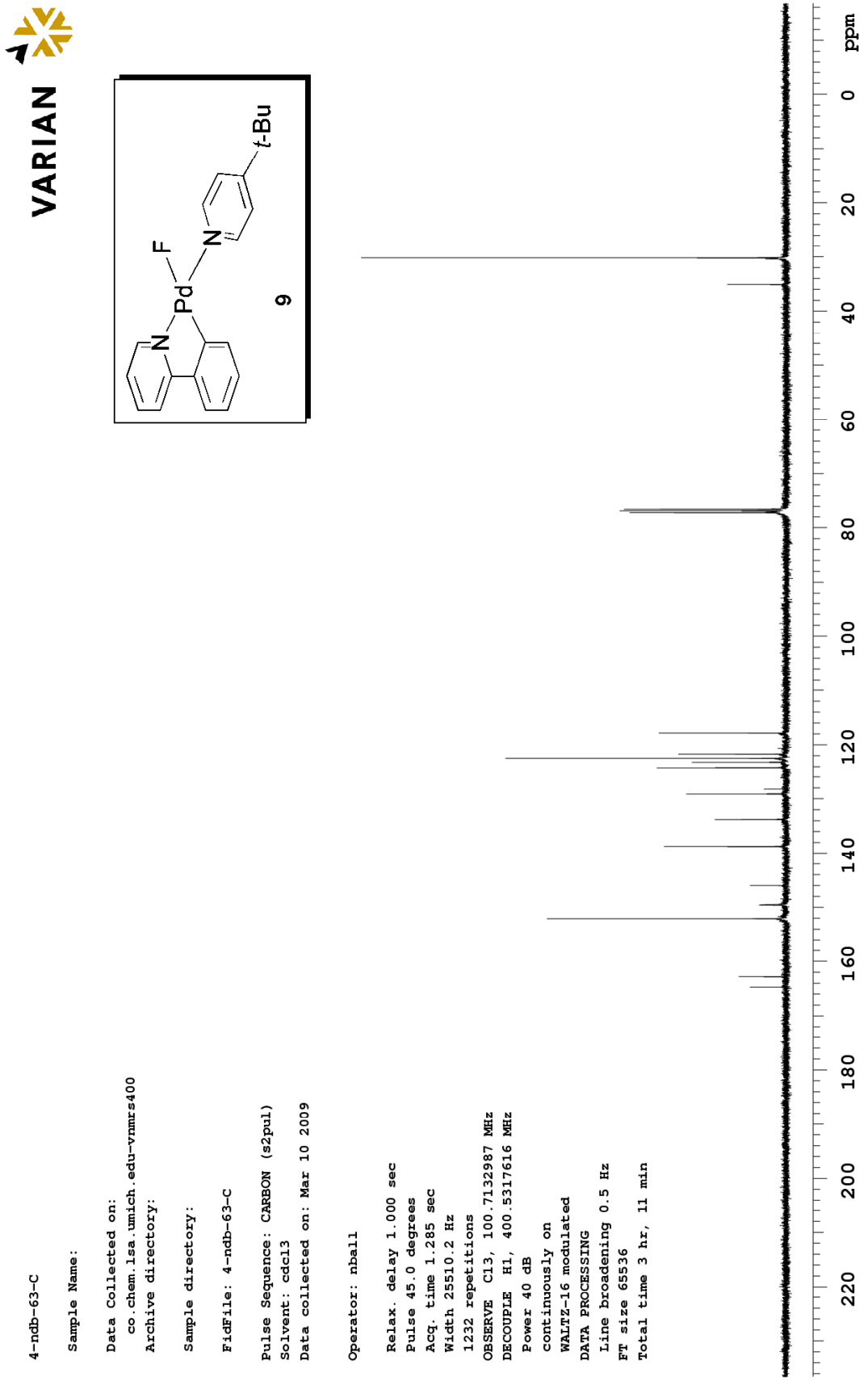



VARIAN
4-ndb-63-C
Sample Name:
Data Collected on:
co.chem.lsa.umich.edu-vnmrs400
Archive directory:
Sample directory:
FidFile: 4-ndb-63-C
Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Mar 10 2009
Operator: nball
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
1232 repetitions
OBSERVE C13, 100.7132987 MHz
DECOUPLE H1, 400.5317616 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 11 min
F
Pd
N
N
t-Bu
9
220
200
180
160
140
120
100
80
60
40
20
0
ppm

2-ndb-192-pumped21907-H

Sample Name:

Archive directory:

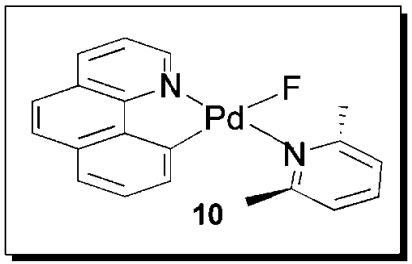
Sample directory:

FidFile: 2-ndb-192-pumped21907-H

Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Feb 19 2007

Operator: nball
VNMRS-500 "Dy.Chem.LSA.UMich.edu"

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.000 sec
Width 6399.5 Hz
16 repetitions
OBSERVE H1, 399.9649896 MHz
DATA PROCESSING
Line broadening 0.2 Hz
FT size 65536
Total time 0 min 24 sec



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VARIAN

```
2-ndb-192-pumped21907-H

 Sample Name:

 Archive directory:

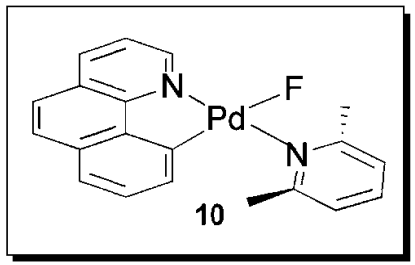
 Sample directory:

 FidFile: 2-ndb-192-pumped21907-H

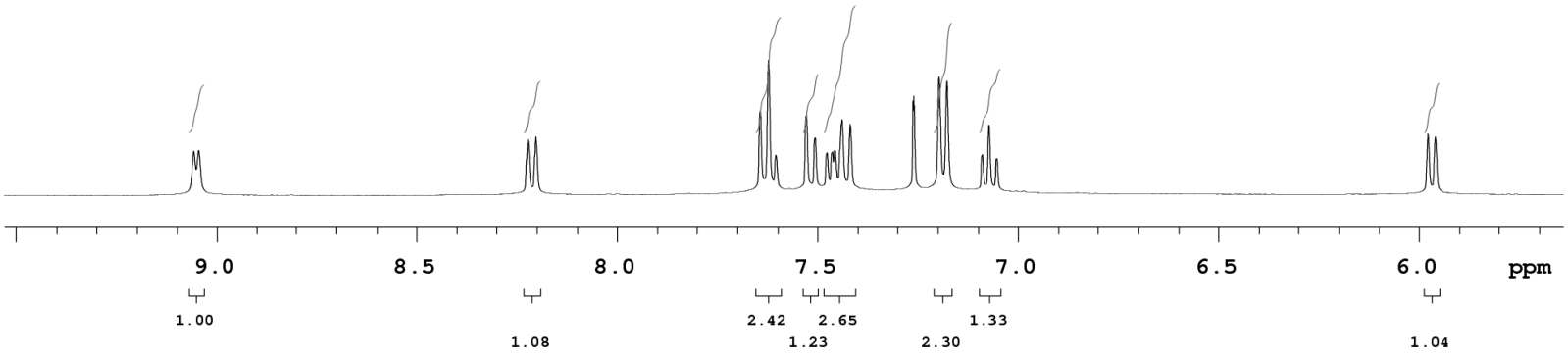
Pulse Sequence: Proton (s2pul)
Solvent: cdcl3
Data collected on: Feb 19 2007


Operator: nball
VNMRS-500  "Dy.Chem.LSA.UMich.edu"


 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.000 sec
 Width 6399.5 Hz
 16 repetitions
OBSERVE   H1, 399.9649810 MHz
DATA PROCESSING
 Line broadening 0.2 Hz
FT size 65536
Total time 0 min 24 sec
```



Aromatic Region



VARIAN

2-ndb-192-pumped21907-F

Sample Name:

Archive directory:

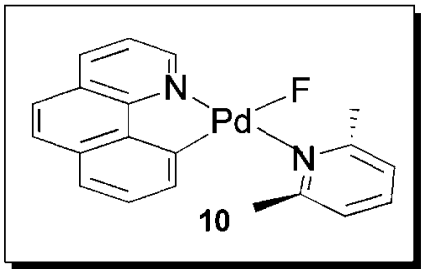
Sample directory:

FidFile: 2-ndb-192-pumped21907-F

Pulse Sequence: Fluorine (s2pul)
Solvent: cdcl3
Data collected on: Feb 19 2007

Operator: nball
VNMRS-500 "Dy.Chem.LSA.UMich.edu"

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.049 sec
Width 250.0 kHz
128 repetitions
OBSERVE F19, 376.3430932 MHz
DATA PROCESSING
Line broadening 0.9 Hz
Gauss apodization 0.462 sec
FT size 524288
Total time 0 min 24 sec



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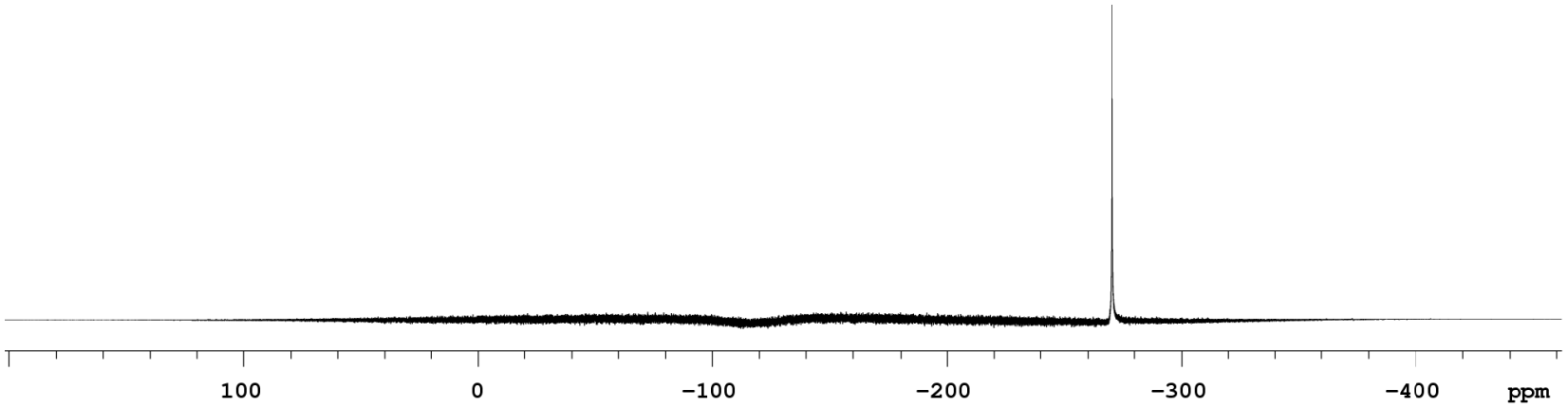
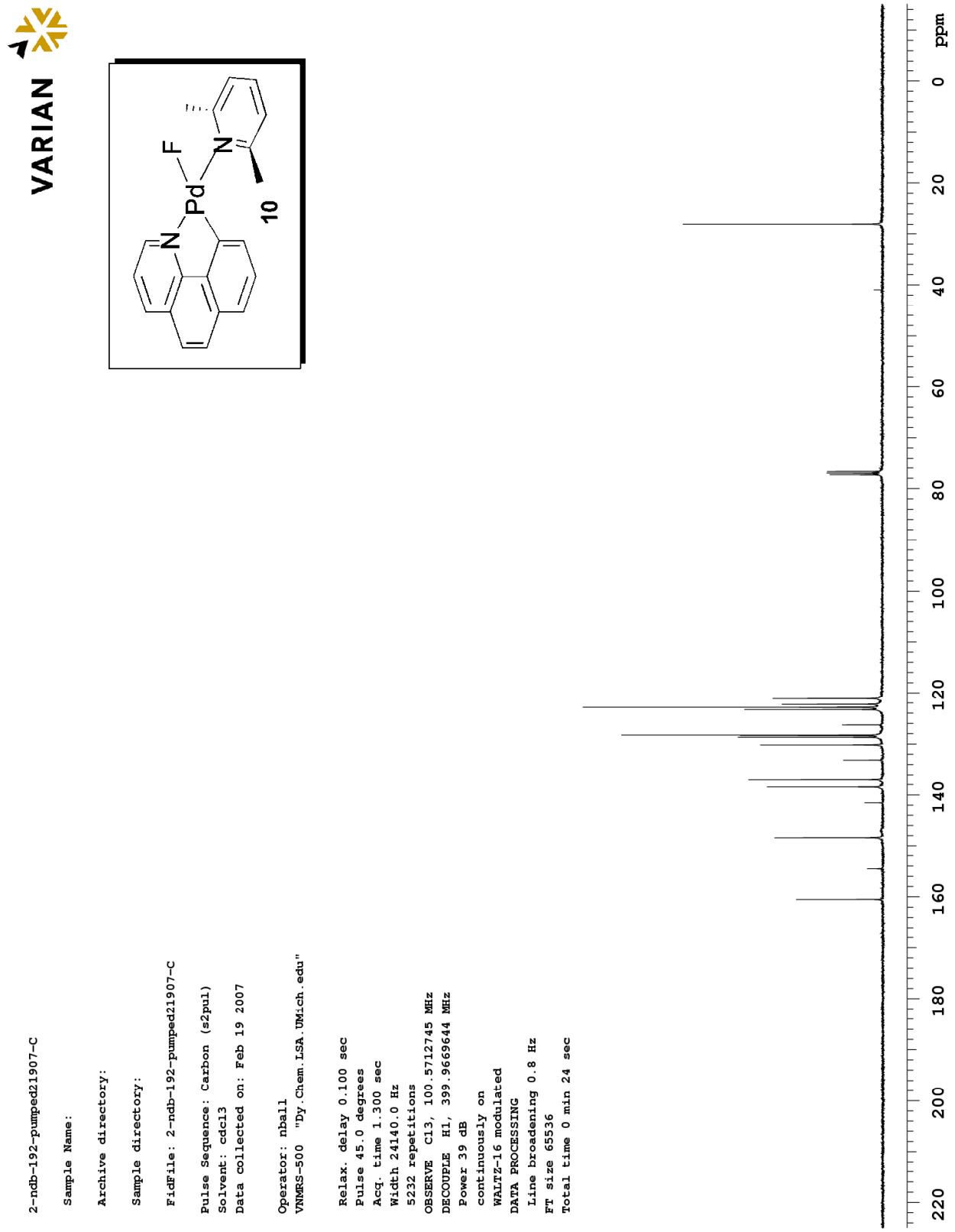



VARIAN
F
Pd
N
N
10
2-ndb-192-pumped21907-C
Sample Name:
Archive directory:
Sample directory:
FidFile: 2-ndb-192-pumped21907-C
Pulse Sequence: Carbon (s2pul)
Solvent: cdcl3
Data collected on: Feb 19 2007
Operator: nball
VNMRS-500 "Dy.Chem.LSA.UMich.edu"
Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 1.300 sec
Width 24140.0 Hz
5232 repetitions
OBSERVE C13, 100.5712745 MHz
DECOUPLE H1, 399.9669644 MHz
Power 39 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.8 Hz
FT size 65536
Total time 0 min 24 sec
220
200
180
160
140
120
100
80
60
40
20
0
ppm

4-ndb-2phpyrPdIlut-H

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

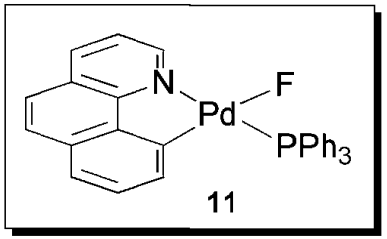
FidFile: 4-ndb-192-PPh3lutPdI-forcarbon-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 18 2009

Temp. 23.0 C / 296.1 K
Operator: nball

Relax. delay 0.500 sec
Pulse 45.0 degrees
Acq. time 3.500 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 399.5389274 MHz
DATA PROCESSING
Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec

VARIAN



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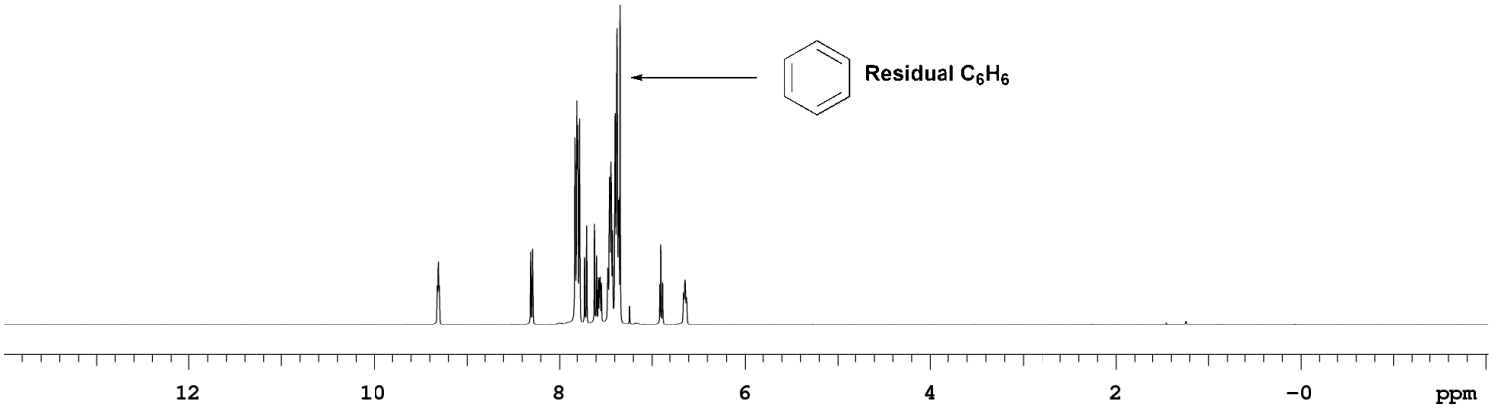


```
4-ndb-2phpyrPdIlut-H

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

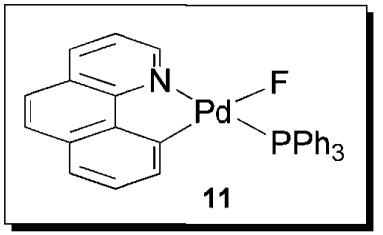
 FidFile: 4-ndb-192-PPh3lutPdI-forcarbon-H

Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Sep 18 2009

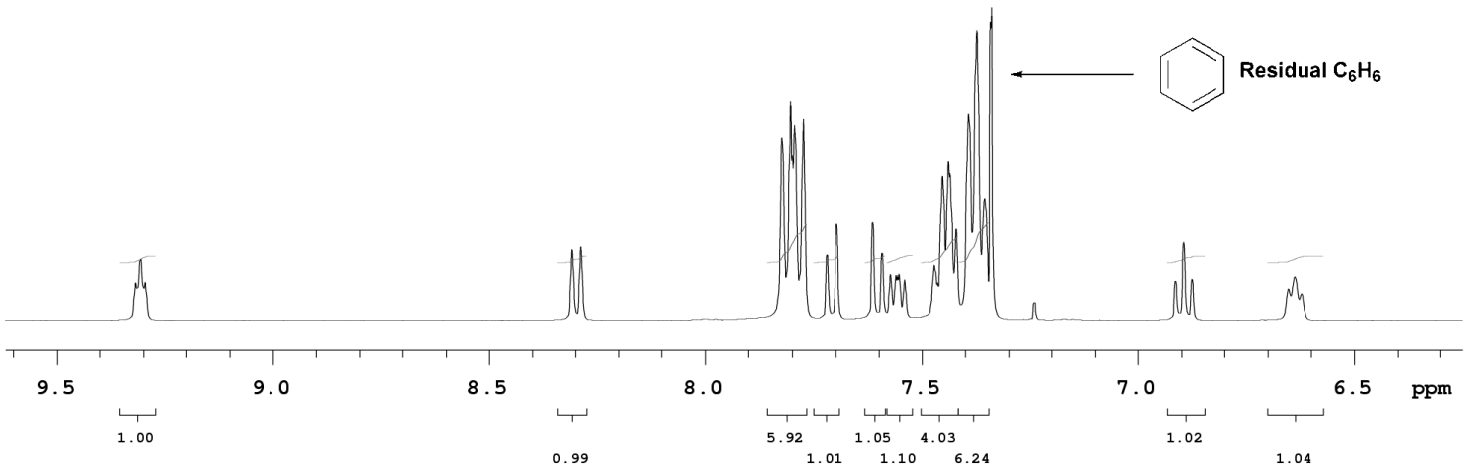

 Temp. 23.0 C / 296.1 K
Operator: nball

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 3.500 sec
 Width 6410.3 Hz
 16 repetitions
OBSERVE   H1, 399.5389274 MHz
DATA PROCESSING
 Line broadening 0.3 Hz
FT size 65536
Total time 1 min 12 sec
```

VARIAN



Aromatic Region



4-ndb-192-Freal

Sample Name:

Data Collected on:
Zr.Chem.LSA.UMich.edu-inova400
Archive directory:

Sample directory:

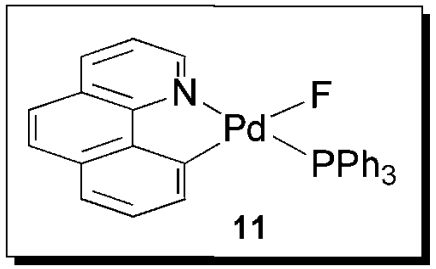
FidFile: FLUORINE

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Sep 18 2009

Temp. 25.0 C / 298.1 K
Operator: nball

Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 1.024 sec
Width 128.0 kHz
64 repetitions
OBSERVE F19, 376.3430710 MHz
DATA PROCESSING
Line broadening 0.5 Hz
FT size 262144
Total time 2 min 14 sec

VARIAN



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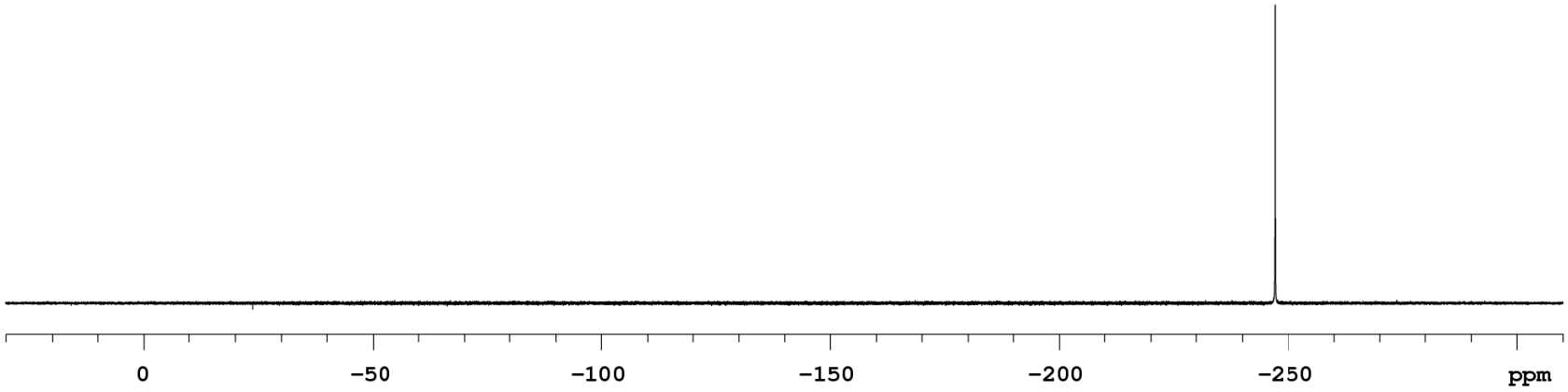


```
4-ndb-192-PPh3lutPdI-forcarbon-P

 Sample Name:

 Data Collected on:
   Ga.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

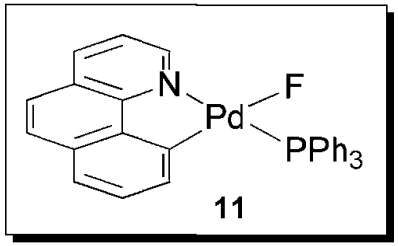
 FidFile: PHOSPHORUS

Pulse Sequence: PHOSPHORUS (s2pul)
Solvent: cdcl3
Data collected on: Sep 18 2009


 Temp. 23.0 C / 296.1 K
Operator: nball

 Relax. delay 0.500 sec
 Pulse 45.0 degrees
 Acq. time 1.573 sec
 Width 41666.7 Hz
 64 repetitions
OBSERVE  P31, 161.7363218 MHz
DECOUPLE  H1, 399.5409236 MHz
 Power 35 dB
 on during acquisition
 off during delay
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 131072
Total time 2 min 13 sec
```

VARIAN



4-ndb-192-PPh3lutPdI-forcarbon-C

Sample Name:

Data Collected on:
Ga.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

Sample directory:

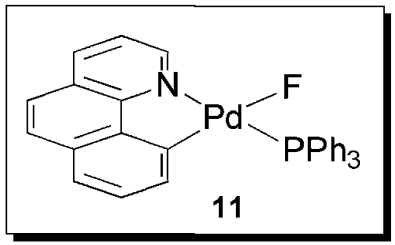
FidFile: CARBON

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Sep 18 2009

Temp. 23.0 C / 296.1 K
Operator: nball

Relax. delay 0.100 sec
Pulse 45.0 degrees
Acq. time 2.569 sec
Width 25510.2 Hz
1952 repetitions
OBSERVE C13, 100.4641448 MHz
DECOUPLE H1, 399.5409236 MHz
Power 35 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 1.0 Hz
FT size 131072
Total time 3 hr, 43 min

VARIAN



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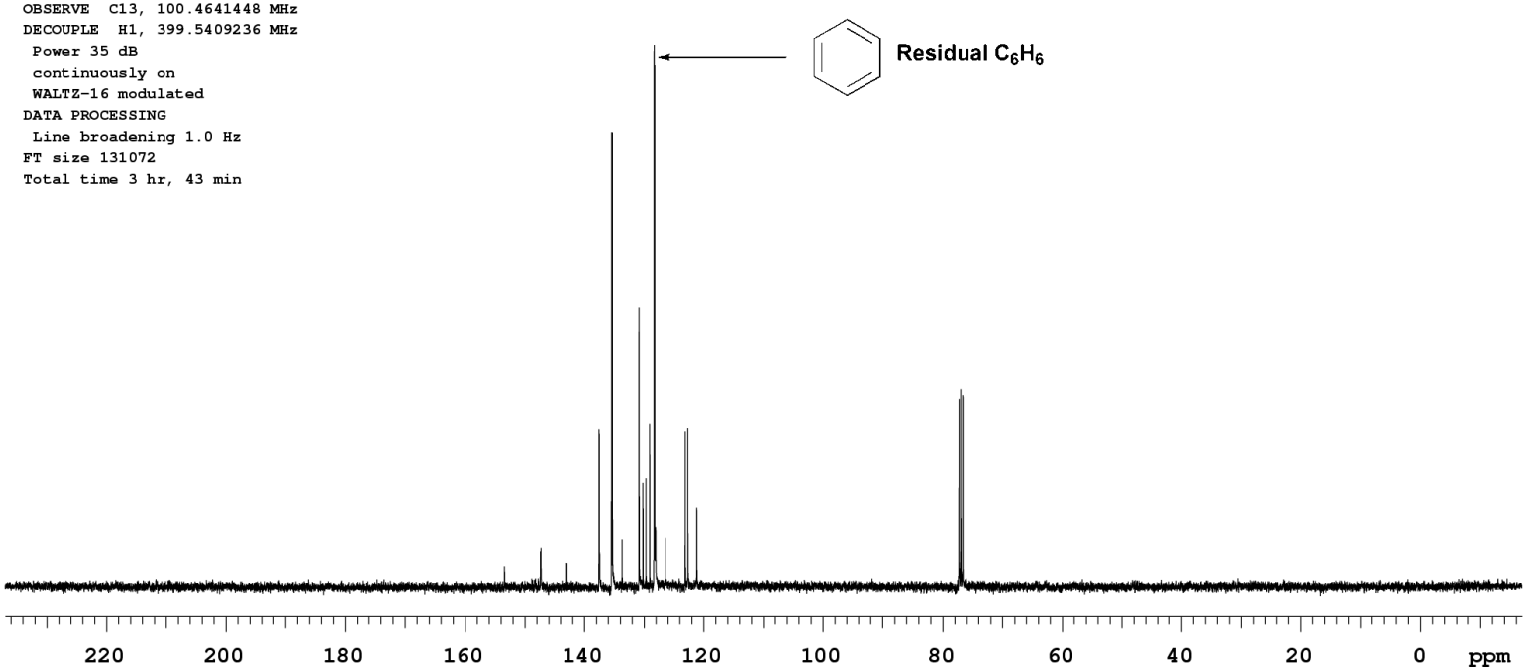
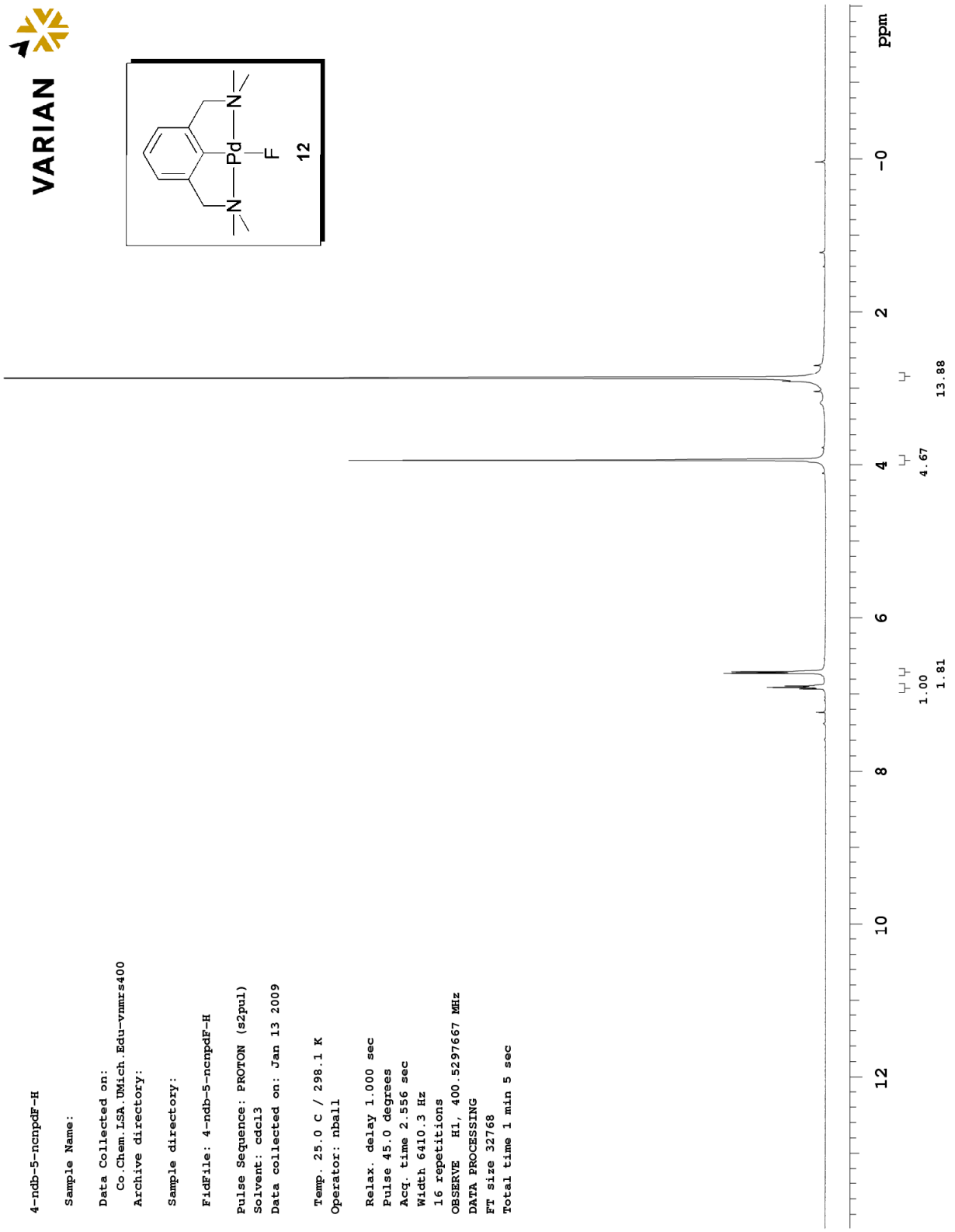



4-ndb-5-ncnpdF-H
Sample Name:
Data Collected on:
Co.Chem.LSA.UMich.Edu-vnmrs400
Archive directory:
Sample directory:
FidFile: 4-ndb-5-ncnpdF-H
Pulse Sequence: PROTON (s2pul)
Solvent: cdcl3
Data collected on: Jan 13 2009
Temp. 25.0 C / 298.1 K
Operator: nball
Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.5297667 MHz
DATA PROCESSING
FT size 32768
Total time 1 min 5 sec
VARIAN
Pd
F
12
ppm
1.00
1.81
4.67
13.88

4-ndb-5-ncnpdF-F

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.Edu-vnmrs400
Archive directory:

Sample directory:

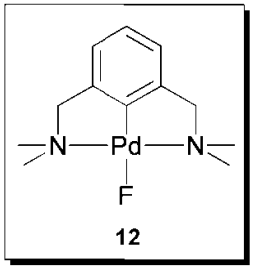
FidFile: 4-ndb-5-ncnpdF-F

Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: Jan 13 2009

Temp. 25.0 C / 298.1 K
Operator: nball

Relax. delay 1.000 sec
Pulse 35.0 degrees
Acq. time 0.734 sec
Width 89285.7 Hz
64 repetitions
OBSERVE F19, 376.8745228 MHz
DATA PROCESSING
FT size 131072
Total time 1 min 52 sec

VARIAN



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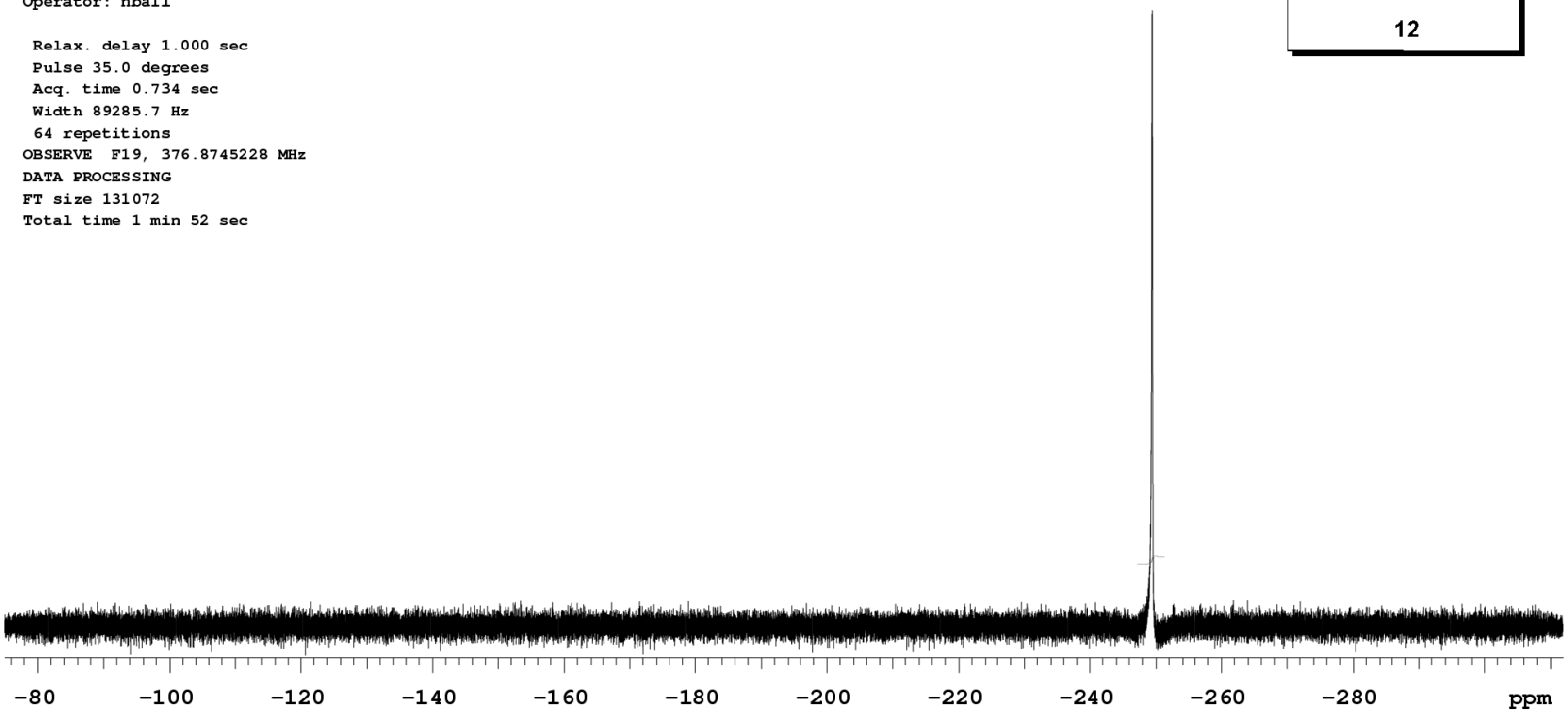


```
4-ndb-5-ncnpdF-C

 Sample Name:

 Data Collected on:
   Co.Chem.LSA.UMich.Edu-vnmrs400
 Archive directory:

 Sample directory:

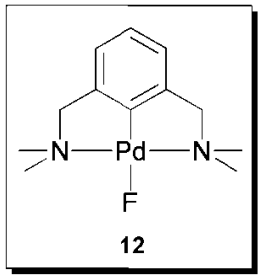
 FidFile: 4-ndb-5-ncnpdF-C

Pulse Sequence: CARBON (s2pul)
Solvent: cdcl3
Data collected on: Jan 13 2009


 Temp. 25.0 C / 298.1 K
Operator: nball

 Relax. delay 1.000 sec
 Pulse 45.0 degrees
 Acq. time 1.285 sec
 Width 25510.2 Hz
 3664 repetitions
OBSERVE  C13, 100.7132880 MHz
DECOUPLE  H1, 400.5317616 MHz
 Power 40 dB
 continuously on
 WALTZ-16 modulated
DATA PROCESSING
 Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 11 min
```

VARIAN



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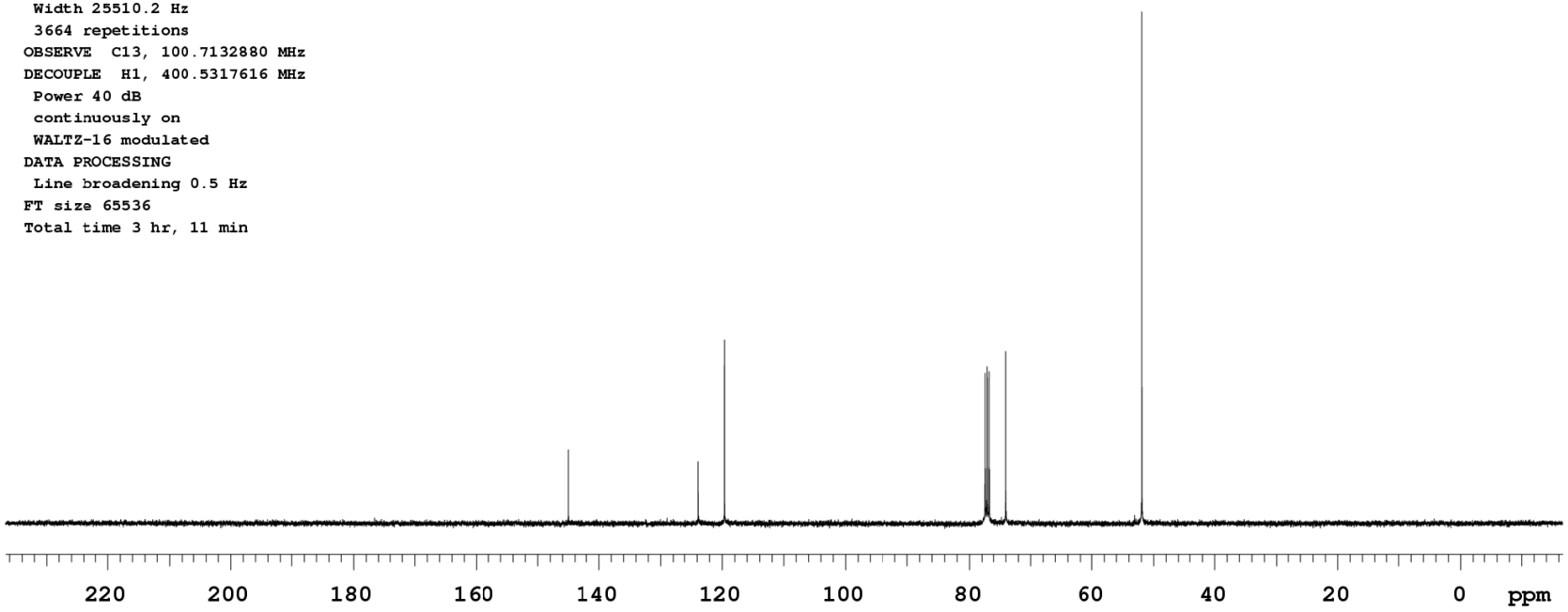


STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

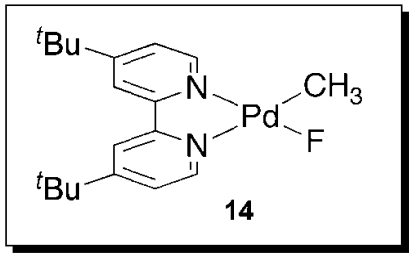
Sample directory:

FidFile: 4-ndb-134-forcarbon-H

Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: May 28 2009

Operator: nball

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.5305758 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 57 sec



14

VARIAN

VARIAN

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

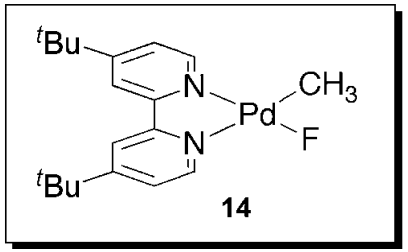
Sample directory:

FidFile: 4-ndb-134-forcarbon-H

Pulse Sequence: PROTON (s2pul)
Solvent: cd2cl2
Data collected on: May 28 2009

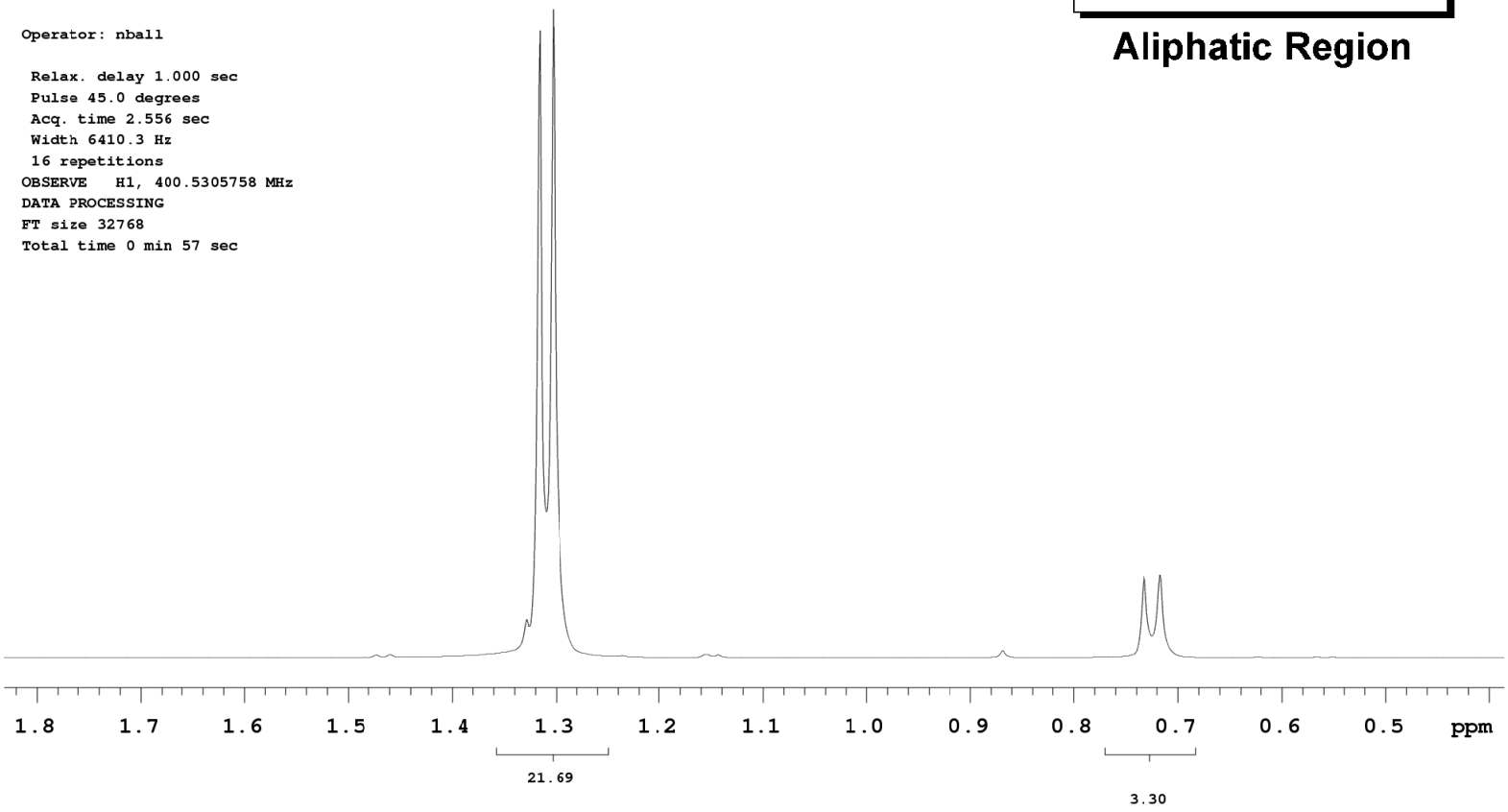
Operator: nball

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 2.556 sec
Width 6410.3 Hz
16 repetitions
OBSERVE H1, 400.5305758 MHz
DATA PROCESSING
FT size 32768
Total time 0 min 57 sec



14

Aliphatic Region



VARIAN

```
4-ndb-134-forcarbon-F

 Sample Name:

 Data Collected on:
   Co.Chem.LSA.UMich.edu-vnmrs400
 Archive directory:

 Sample directory:

 FidFile: 4-ndb-134-forcarbon-F

Pulse Sequence: FLUORINE (s2pul)
Solvent: cd2cl2
Data collected on: May 28 2009


Operator: nball

 Relax. delay 1.000 sec
 Pulse 35.0 degrees
 Acq. time 1.101 sec
 Width 119.0 kHz
 32 repetitions
OBSERVE  F19, 376.8752435 MHz
DATA PROCESSING
FT size 262144
Total time 1 min 8 sec
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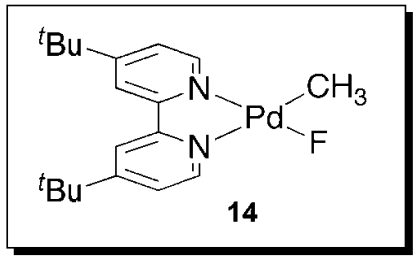
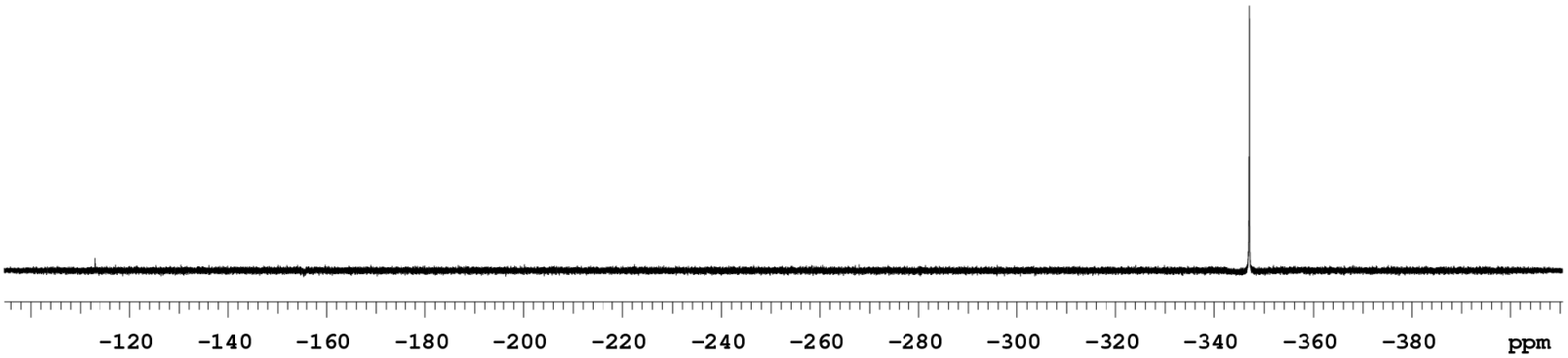


14



4-ndb-134-forcarbon-C

Sample Name:

Data Collected on:
Co.Chem.LSA.UMich.edu-vnmrs400
Archive directory:

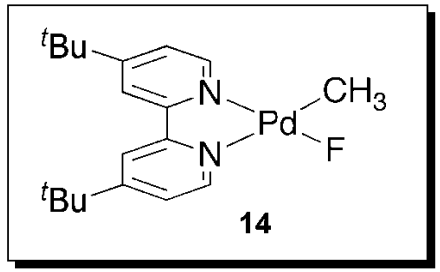
Sample directory:

FidFile: 4-ndb-134-forcarbon-C

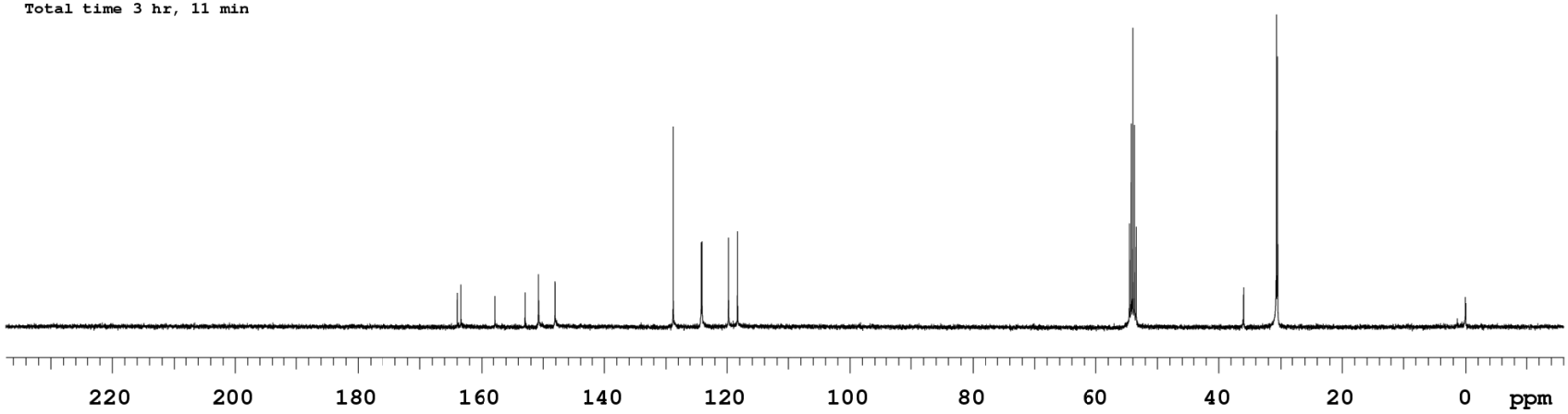
Pulse Sequence: CARBON (s2pul)
Solvent: cd2cl2
Data collected on: May 28 2009

Operator: nball

Relax. delay 1.000 sec
Pulse 45.0 degrees
Acq. time 1.285 sec
Width 25510.2 Hz
3776 repetitions
OBSERVE C13, 100.7134238 MHz
DECOUPLE H1, 400.5325306 MHz
Power 40 dB
continuously on
WALTZ-16 modulated
DATA PROCESSING
Line broadening 0.5 Hz
FT size 65536
Total time 3 hr, 11 min



14



Structure Determination of 8.

Colorless needles of **8** were crystallized from a pentane/tetrahydrofuran solution at -35 deg. C. A crystal of dimensions 0.33 x 0.14 x 0.07 mm was mounted on a standard Bruker SMART-APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3630 frames were collected with a scan width of 0.5° in ω and 0.45° in ϕ with an exposure time of 20 s/frame. Indexing was performed by use of the CELL_NOW program which indicated that the crystal was a non-merohedral twin. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 39833 reflections to a maximum 2θ value of 52.88° of which 4339 were independent and 3953 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9958 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with TWINABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{18}H_{17}N_2FPd$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The twin domains are related by a 4.2 degree rotation about the direct (0.900 0.100 1) axis or reciprocal (0.048 0.031 1) axis and a refined twin volume fraction of 0.281(1). Full-matrix least-squares refinement based on F^2 converged at R1 = 0.0323 and wR2 = 0.0797 [based on I > 2sigma(I)], R1 = 0.0383 and wR2 = 0.0842 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Sheldrick, G.M. CELL_NOW, Program for Indexing Twins and Other Problem Crystals, University of Gottingen: Gottingen, Germany, 2007.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. TWINABS, v. 2007/5. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2007.

Table S1. Crystal data and structure refinement for **8**.

Identification code	nb272
Empirical formula	C18 H17 F N2 Pd
Formula weight	386.74
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 9.6607(11) A alpha = 90 deg. b = 9.2742(10) A beta = 96.023(2) deg. c = 17.810(2) A gamma = 90 deg.
Volume	1586.9(3) A^3
Z, Calculated density	4, 1.619 Mg/m^3
Absorption coefficient	1.177 mm^-1
F(000)	776
Crystal size	0.33 x 0.14 x 0.07 mm
Theta range for data collection	2.12 to 28.44 deg.
Limiting indices	-12<=h<=11, -12<=k<=12, -23<=l<=23
Reflections collected / unique	39833 / 4339 [R(int) = 0.0578]
Completeness to theta = 28.44	99.4 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9222 and 0.6974
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4339 / 0 / 211
Goodness-of-fit on F^2	1.142

Final R indices [I>2sigma(I)] R1 = 0.0323, wR2 = 0.0797

R indices (all data) R1 = 0.0383, wR2 = 0.0842

Largest diff. peak and hole 1.264 and -0.786 e.A^-3

Table S2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **8**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	7004(1)	2363(1)	4012(1)	13(1)
F(1)	8723(2)	3537(2)	4509(1)	21(1)
N(1)	5753(3)	4108(3)	3981(1)	16(1)
N(2)	8136(2)	484(2)	4040(1)	15(1)
C(1)	6147(3)	5398(3)	4258(2)	20(1)
C(2)	5225(3)	6530(3)	4266(2)	24(1)
C(3)	3847(3)	6298(3)	3993(2)	26(1)
C(4)	3434(3)	4962(3)	3704(2)	22(1)
C(5)	4420(3)	3876(3)	3692(1)	16(1)
C(6)	4178(3)	2422(3)	3383(2)	17(1)
C(7)	2939(3)	1997(3)	2972(2)	20(1)
C(8)	2803(3)	604(3)	2686(2)	21(1)
C(9)	3899(3)	-356(3)	2828(2)	21(1)
C(10)	5150(3)	63(3)	3227(1)	18(1)
C(11)	5321(3)	1465(3)	3505(1)	15(1)
C(12)	8102(3)	-437(3)	4626(2)	18(1)
C(13)	8834(3)	-1716(3)	4651(2)	22(1)
C(14)	9608(3)	-2070(3)	4068(2)	25(1)
C(15)	9642(3)	-1109(3)	3474(2)	22(1)
C(16)	8911(3)	171(3)	3473(2)	18(1)
C(17)	7237(3)	-14(3)	5241(2)	22(1)
C(18)	8941(3)	1259(3)	2851(2)	22(1)

Table S3. Bond lengths [A] and angles [deg] for **8**.

Pd(1)-C(11)	1.960(3)
Pd(1)-N(1)	2.017(2)
Pd(1)-N(2)	2.055(2)
Pd(1)-F(1)	2.1024(17)
N(1)-C(1)	1.335(4)
N(1)-C(5)	1.353(4)
N(2)-C(16)	1.351(3)
N(2)-C(12)	1.351(3)
C(1)-C(2)	1.378(4)
C(2)-C(3)	1.384(5)
C(3)-C(4)	1.385(4)
C(4)-C(5)	1.388(4)
C(5)-C(6)	1.466(4)
C(6)-C(7)	1.394(4)
C(6)-C(11)	1.416(4)
C(7)-C(8)	1.389(4)
C(8)-C(9)	1.386(4)
C(9)-C(10)	1.392(4)
C(10)-C(11)	1.395(4)
C(12)-C(13)	1.380(4)
C(12)-C(17)	1.498(4)
C(13)-C(14)	1.381(4)
C(14)-C(15)	1.386(4)
C(15)-C(16)	1.381(4)
C(16)-C(18)	1.501(4)
C(11)-Pd(1)-N(1)	82.13(11)
C(11)-Pd(1)-N(2)	93.68(10)
N(1)-Pd(1)-N(2)	175.36(9)
C(11)-Pd(1)-F(1)	173.88(9)
N(1)-Pd(1)-F(1)	92.32(8)
N(2)-Pd(1)-F(1)	91.95(8)
C(1)-N(1)-C(5)	120.4(2)
C(1)-N(1)-Pd(1)	124.2(2)
C(5)-N(1)-Pd(1)	115.25(19)
C(16)-N(2)-C(12)	120.2(2)
C(16)-N(2)-Pd(1)	119.92(18)
C(12)-N(2)-Pd(1)	119.91(18)
N(1)-C(1)-C(2)	121.8(3)
C(1)-C(2)-C(3)	118.5(3)
C(2)-C(3)-C(4)	119.9(3)
C(3)-C(4)-C(5)	118.9(3)
N(1)-C(5)-C(4)	120.4(3)

N(1)-C(5)-C(6)	113.4(2)
C(4)-C(5)-C(6)	126.2(3)
C(7)-C(6)-C(11)	121.1(3)
C(7)-C(6)-C(5)	123.5(3)
C(11)-C(6)-C(5)	115.4(2)
C(8)-C(7)-C(6)	119.9(3)
C(9)-C(8)-C(7)	119.3(3)
C(8)-C(9)-C(10)	121.3(3)
C(9)-C(10)-C(11)	120.4(3)
C(10)-C(11)-C(6)	117.9(3)
C(10)-C(11)-Pd(1)	128.4(2)
C(6)-C(11)-Pd(1)	113.6(2)
N(2)-C(12)-C(13)	120.9(3)
N(2)-C(12)-C(17)	117.4(2)
C(13)-C(12)-C(17)	121.7(3)
C(12)-C(13)-C(14)	119.7(3)
C(13)-C(14)-C(15)	118.7(3)
C(16)-C(15)-C(14)	120.0(3)
N(2)-C(16)-C(15)	120.5(3)
N(2)-C(16)-C(18)	117.6(2)
C(15)-C(16)-C(18)	122.0(3)

Symmetry transformations used to generate equivalent atoms:

Table S4. Anisotropic displacement parameters (A^2 x 10^3) for **8**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	15(1)	15(1)	10(1)	0(1)	1(1)	0(1)
F(1)	21(1)	24(1)	18(1)	0(1)	-2(1)	-3(1)
N(1)	21(1)	18(1)	11(1)	2(1)	3(1)	1(1)
N(2)	16(1)	15(1)	12(1)	-1(1)	0(1)	0(1)
C(1)	24(2)	19(1)	15(1)	2(1)	3(1)	-1(1)
C(2)	33(2)	17(1)	21(1)	0(1)	5(1)	1(1)
C(3)	29(2)	22(1)	26(1)	2(1)	5(1)	8(1)
C(4)	24(2)	21(1)	20(1)	2(1)	3(1)	5(1)
C(5)	19(1)	19(1)	10(1)	3(1)	3(1)	1(1)
C(6)	21(1)	19(1)	10(1)	2(1)	3(1)	-1(1)
C(7)	18(1)	28(1)	14(1)	4(1)	1(1)	0(1)
C(8)	20(2)	32(2)	12(1)	0(1)	1(1)	-5(1)
C(9)	25(2)	23(1)	15(1)	-2(1)	6(1)	-5(1)
C(10)	20(1)	21(1)	13(1)	-1(1)	5(1)	-1(1)
C(11)	17(1)	20(1)	9(1)	1(1)	2(1)	-1(1)
C(12)	18(1)	18(1)	18(1)	0(1)	-1(1)	-3(1)
C(13)	20(2)	19(1)	26(1)	2(1)	-2(1)	-1(1)
C(14)	22(2)	20(1)	33(2)	-3(1)	-1(1)	3(1)
C(15)	20(1)	25(2)	22(1)	-7(1)	4(1)	1(1)
C(16)	19(1)	20(1)	13(1)	-3(1)	-1(1)	-2(1)
C(17)	28(2)	22(1)	15(1)	4(1)	4(1)	1(1)
C(18)	25(2)	30(2)	14(1)	1(1)	6(1)	1(1)

Table S5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **8**.

	x	y	z	U(eq)
H(1A)	7090	5541	4456	23
H(2A)	5527	7449	4453	28
H(3A)	3187	7055	4005	31
H(4A)	2490	4791	3518	26
H(7A)	2188	2658	2886	24
H(8A)	1968	313	2397	26
H(9A)	3795	-1319	2648	25
H(10A)	5891	-609	3311	22
H(13A)	8807	-2350	5068	26
H(14A)	10105	-2954	4074	30
H(15A)	10169	-1331	3068	27
H(17A)	7613	871	5485	32
H(17B)	7256	-790	5616	32
H(17C)	6275	154	5025	32
H(18A)	7989	1444	2623	34
H(18B)	9499	885	2465	34
H(18C)	9353	2159	3058	34

Structure Determination of 10.

Yellow blocks of **10** were crystallized from a dichloromethane/pentane solution at -35 deg. C. A crystal of dimensions 0.34 x 0.20 x 0.16 mm was mounted on a standard Bruker SMART 1K CCD-based X-ray diffractometer equipped with a LT-2 low temperature device and normal focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 40 mA). The X-ray intensities were measured at 108(2) K; the detector was placed at a distance 4.912 cm from the crystal. A total of 3000 frames were collected with a scan width of 0.5° in ω and phi with an exposure time of 25 s/frame. The integration of the data yielded a total of 44848 reflections to a maximum 2θ value of 56.72° of which 5037 were independent and 4299 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9227 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group P2(1)/c with Z = 4 for the formula $C_{20}H_{17}N_2FPd\bullet(CH_2Cl_2)$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0214 and wR2 = 0.0508 [based on I > 2sigma(I)], R1 = 0.0307 and wR2 = 0.0551 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. SADABS, v. 2.10. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2003.

Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Table S6. Crystal data and structure refinement for **10**.

Identification code	nb192
Empirical formula	C21 H19 Cl2 F N2 Pd
Formula weight	495.68
Temperature	108(2) K
Wavelength	0.71073 A
Crystal system, space group	Monoclinic, P2(1)/c
Unit cell dimensions	a = 13.904(4) A alpha = 90 deg. b = 11.409(3) A beta = 117.158(3) deg. c = 14.366(4) A gamma = 90 deg.
Volume	2027.8(9) A^3
Z, Calculated density	4, 1.624 Mg/m^3
Absorption coefficient	1.195 mm^-1
F(000)	992
Crystal size	0.34 x 0.20 x 0.16 mm
Theta range for data collection	2.39 to 28.36 deg.
Limiting indices	-18<=h<=18, -15<=k<=15, -19<=l<=19
Reflections collected / unique	44848 / 5037 [R(int) = 0.0379]
Completeness to theta = 28.36	99.3 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8318 and 0.6867
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5037 / 0 / 246
Goodness-of-fit on F^2	1.073

Final R indices [I>2sigma(I)] R1 = 0.0214, wR2 = 0.0508

R indices (all data) R1 = 0.0307, wR2 = 0.0551

Largest diff. peak and hole 0.436 and -0.586 e.A^-3

Table S7. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **10**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	2261(1)	8571(1)	4042(1)	18(1)
Cl(1)	2090(1)	155(1)	7084(1)	31(1)
Cl(2)	1368(1)	2362(1)	5926(1)	44(1)
F(1)	1042(1)	9608(1)	4028(1)	26(1)
N(1)	3018(1)	9990(1)	3824(1)	20(1)
N(2)	1551(1)	7048(1)	4178(1)	19(1)
C(1)	2720(2)	11107(2)	3747(2)	25(1)
C(2)	3307(2)	11999(2)	3562(2)	29(1)
C(3)	4207(2)	11724(2)	3448(2)	28(1)
C(4)	4544(2)	10547(2)	3528(1)	24(1)
C(5)	5473(2)	10133(2)	3432(2)	28(1)
C(6)	5738(2)	8979(2)	3540(2)	28(1)
C(7)	5108(2)	8113(2)	3745(1)	23(1)
C(8)	5347(2)	6906(2)	3862(2)	27(1)
C(9)	4683(2)	6144(2)	4040(2)	27(1)
C(10)	3760(2)	6540(2)	4125(2)	24(1)
C(11)	3488(2)	7721(2)	4016(1)	20(1)
C(12)	4186(2)	8491(2)	3830(1)	19(1)
C(13)	3922(2)	9705(2)	3722(1)	20(1)
C(14)	1880(2)	6517(2)	5119(2)	24(1)
C(15)	1476(2)	5428(2)	5193(2)	30(1)
C(16)	717(2)	4882(2)	4296(2)	29(1)
C(17)	365(2)	5444(2)	3342(2)	24(1)
C(18)	790(2)	6533(2)	3304(1)	20(1)
C(19)	2699(2)	7143(2)	6065(2)	34(1)
C(20)	413(2)	7175(2)	2289(2)	26(1)
C(21)	1090(2)	843(2)	5941(2)	28(1)

Table S8. Bond lengths [A] and angles [deg] for **10**.

Pd(1)-C(11)	1.9769(19)
Pd(1)-N(1)	2.0325(15)
Pd(1)-N(2)	2.0519(15)
Pd(1)-F(1)	2.0604(12)
Cl(1)-C(21)	1.778(2)
Cl(2)-C(21)	1.778(2)
N(1)-C(1)	1.328(2)
N(1)-C(13)	1.370(2)
N(2)-C(18)	1.352(2)
N(2)-C(14)	1.355(2)
C(1)-C(2)	1.404(3)
C(2)-C(3)	1.370(3)
C(3)-C(4)	1.410(3)
C(4)-C(13)	1.404(3)
C(4)-C(5)	1.439(3)
C(5)-C(6)	1.357(3)
C(6)-C(7)	1.437(3)
C(7)-C(8)	1.408(3)
C(7)-C(12)	1.410(3)
C(8)-C(9)	1.375(3)
C(9)-C(10)	1.418(3)
C(10)-C(11)	1.388(3)
C(11)-C(12)	1.422(2)
C(12)-C(13)	1.423(3)
C(14)-C(15)	1.388(3)
C(14)-C(19)	1.497(3)
C(15)-C(16)	1.386(3)
C(16)-C(17)	1.384(3)
C(17)-C(18)	1.387(3)
C(18)-C(20)	1.496(3)
C(11)-Pd(1)-N(1)	82.89(7)
C(11)-Pd(1)-N(2)	92.46(7)
N(1)-Pd(1)-N(2)	174.46(6)
C(11)-Pd(1)-F(1)	174.14(6)
N(1)-Pd(1)-F(1)	91.29(6)
N(2)-Pd(1)-F(1)	93.32(5)
C(1)-N(1)-C(13)	119.09(16)
C(1)-N(1)-Pd(1)	127.79(14)
C(13)-N(1)-Pd(1)	113.09(12)
C(18)-N(2)-C(14)	119.82(16)
C(18)-N(2)-Pd(1)	119.09(12)

C(14)-N(2)-Pd(1)	120.96(12)
N(1)-C(1)-C(2)	121.62(19)
C(3)-C(2)-C(1)	119.88(19)
C(2)-C(3)-C(4)	119.78(18)
C(13)-C(4)-C(3)	117.11(18)
C(13)-C(4)-C(5)	117.10(18)
C(3)-C(4)-C(5)	125.79(18)
C(6)-C(5)-C(4)	121.06(18)
C(5)-C(6)-C(7)	122.11(19)
C(8)-C(7)-C(12)	117.61(18)
C(8)-C(7)-C(6)	124.27(19)
C(12)-C(7)-C(6)	118.12(18)
C(9)-C(8)-C(7)	119.85(18)
C(8)-C(9)-C(10)	121.77(18)
C(11)-C(10)-C(9)	120.68(18)
C(10)-C(11)-C(12)	116.50(17)
C(10)-C(11)-Pd(1)	131.84(14)
C(12)-C(11)-Pd(1)	111.65(13)
C(7)-C(12)-C(11)	123.58(17)
C(7)-C(12)-C(13)	119.13(17)
C(11)-C(12)-C(13)	117.28(16)
N(1)-C(13)-C(4)	122.53(17)
N(1)-C(13)-C(12)	115.00(16)
C(4)-C(13)-C(12)	122.47(18)
N(2)-C(14)-C(15)	120.78(18)
N(2)-C(14)-C(19)	117.60(17)
C(15)-C(14)-C(19)	121.62(18)
C(16)-C(15)-C(14)	119.62(18)
C(17)-C(16)-C(15)	119.15(18)
C(16)-C(17)-C(18)	119.32(18)
N(2)-C(18)-C(17)	121.26(17)
N(2)-C(18)-C(20)	118.01(16)
C(17)-C(18)-C(20)	120.72(17)
Cl(1)-C(21)-Cl(2)	111.03(11)

Symmetry transformations used to generate equivalent atoms:

Table S9. Anisotropic displacement parameters (A^2 x 10^3) for **10**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	19(1)	17(1)	18(1)	0(1)	9(1)	-2(1)
Cl(1)	33(1)	27(1)	35(1)	4(1)	18(1)	-2(1)
Cl(2)	47(1)	28(1)	41(1)	6(1)	6(1)	1(1)
F(1)	25(1)	28(1)	28(1)	2(1)	14(1)	4(1)
N(1)	22(1)	19(1)	17(1)	1(1)	7(1)	-2(1)
N(2)	20(1)	19(1)	20(1)	0(1)	10(1)	-2(1)
C(1)	28(1)	21(1)	22(1)	2(1)	9(1)	0(1)
C(2)	38(1)	19(1)	22(1)	3(1)	7(1)	-3(1)
C(3)	32(1)	25(1)	21(1)	2(1)	7(1)	-10(1)
C(4)	26(1)	27(1)	16(1)	1(1)	6(1)	-7(1)
C(5)	24(1)	37(1)	21(1)	1(1)	10(1)	-12(1)
C(6)	22(1)	40(1)	23(1)	-1(1)	12(1)	-5(1)
C(7)	22(1)	31(1)	16(1)	-1(1)	8(1)	-2(1)
C(8)	26(1)	33(1)	23(1)	-1(1)	13(1)	4(1)
C(9)	33(1)	25(1)	24(1)	0(1)	14(1)	5(1)
C(10)	29(1)	22(1)	22(1)	1(1)	13(1)	-1(1)
C(11)	22(1)	21(1)	16(1)	0(1)	8(1)	-2(1)
C(12)	20(1)	22(1)	14(1)	-1(1)	6(1)	-3(1)
C(13)	21(1)	24(1)	13(1)	1(1)	5(1)	-4(1)
C(14)	27(1)	27(1)	21(1)	1(1)	12(1)	-4(1)
C(15)	37(1)	28(1)	23(1)	4(1)	14(1)	-7(1)
C(16)	34(1)	23(1)	31(1)	0(1)	17(1)	-7(1)
C(17)	26(1)	22(1)	24(1)	-3(1)	12(1)	-5(1)
C(18)	19(1)	21(1)	21(1)	-1(1)	10(1)	0(1)
C(19)	41(1)	37(1)	21(1)	2(1)	10(1)	-13(1)
C(20)	30(1)	22(1)	20(1)	0(1)	8(1)	-3(1)
C(21)	27(1)	30(1)	28(1)	-6(1)	12(1)	-5(1)

Table S10. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **10**.

	x	y	z	U(eq)
H(1A)	2093	11306	3818	30
H(2A)	3081	12792	3516	35
H(3A)	4602	12324	3316	33
H(5A)	5909	10677	3292	33
H(6A)	6359	8735	3477	33
H(8A)	5967	6619	3818	32
H(9A)	4847	5331	4108	32
H(10A)	3322	5992	4257	28
H(15A)	1718	5059	5855	35
H(16A)	442	4131	4335	35
H(17A)	-162	5088	2720	29
H(19A)	3393	7162	6044	52
H(19B)	2785	6731	6697	52
H(19C)	2454	7947	6073	52
H(20A)	1	7870	2296	39
H(20B)	-50	6660	1712	39
H(20C)	1039	7417	2196	39
H(21A)	372	743	5917	34
H(21B)	1070	462	5313	34

Structure Determination of 11.

Colorless plates **11** were grown from a pentanes/dichloromethane solution at -35 deg. C. A crystal of dimensions 0.25 x 0.24 x 0.05 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 5190 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 25 s/frame. The integration of the data yielded a total of 128348 reflections to a maximum 2θ value of 56.66° of which 14487 were independent and 13303 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9709 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/3) software package, using the space group P1bar with Z = 4 for the formula $C_{31}H_{23}NFPPd$, $CHCl_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. There are two independent palladium complexes and two independent dichloromethane solvates in the asymmetric unit. One of the solvates is disordered over three sites. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0376 and wR2 = 0.0934 [based on I > 2sigma(I)], R1 = 0.0403 and wR2 = 0.0961 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 2008/3; Bruker Analytical X-ray, Madison, WI, 2008.

Sheldrick, G.M. SADABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.

Saint Plus, v. 7.60a, Bruker Analytical X-ray, Madison, WI, 2009.

Table 1. Crystal data and structure refinement for nb143.

Identification code	nb143
Empirical formula	C32 H25 Cl2 F N P Pd
Formula weight	650.80
Temperature	85(2) K

Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.7399(5) A alpha = 96.861(1) deg. b = 17.2959(9) A beta = 98.293(1) deg. c = 20.3468(11) A gamma = 104.123(1)deg.
Volume	2913.0(3) A^3
Z, Calculated density	4, 1.484 Mg/m^3
Absorption coefficient	0.904 mm^-1
F(000)	1312
Crystal size	0.25 x 0.24 x 0.05 mm
Theta range for data collection	1.72 to 28.33 deg.
Limiting indices	-11<=h<=11, -23<=k<=23, -27<=l<=27
Reflections collected / unique	128348 / 14487 [R(int) = 0.0328]
Completeness to theta = 28.33	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9562 and 0.8056
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	14487 / 45 / 79
Goodness-of-fit on F^2	1.055
Final R indices [I>2sigma(I)]	R1 = 0.0367, wR2 = 0.0934
R indices (all data)	R1 = 0.0403, wR2 = 0.0961
Largest diff. peak and hole	0.950 and -0.859 e.A^-3

Table S11. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **11**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	2644(1)	6622(1)	2975(1)	18(1)
Pd(2)	5538(1)	1764(1)	421(1)	19(1)
P(1)	3689(1)	5945(1)	3719(1)	18(1)
P(2)	5019(1)	2401(1)	1358(1)	18(1)
F(1)	2329(2)	7447(1)	3705(1)	33(1)
F(2)	6471(2)	987(1)	919(1)	26(1)
C(1)	991(3)	7836(2)	2402(1)	24(1)
C(2)	254(3)	8152(2)	1878(2)	29(1)
C(3)	60(3)	7784(2)	1225(1)	28(1)
C(4)	630(3)	7101(2)	1086(1)	24(1)
C(5)	505(3)	6665(2)	428(1)	28(1)
C(6)	1155(3)	6033(2)	341(1)	27(1)
C(7)	1987(3)	5769(2)	898(1)	22(1)
C(8)	2777(3)	5154(2)	820(1)	26(1)
C(9)	3578(3)	4953(2)	1378(1)	26(1)
C(10)	3573(3)	5322(2)	2035(1)	22(1)
C(11)	2820(3)	5929(1)	2142(1)	18(1)
C(12)	2055(3)	6156(1)	1557(1)	19(1)
C(13)	1377(3)	6826(1)	1637(1)	19(1)
C(14)	3250(3)	6210(2)	4553(1)	24(1)
C(15)	3850(4)	7018(2)	4859(1)	35(1)
C(16)	3530(5)	7263(2)	5487(2)	44(1)
C(17)	2616(4)	6712(3)	5814(2)	45(1)
C(18)	2030(4)	5914(2)	5520(1)	40(1)
C(19)	2344(3)	5659(2)	4883(1)	29(1)
C(20)	5865(3)	6175(2)	3883(1)	23(1)
C(21)	6721(3)	6446(2)	3391(1)	26(1)
C(22)	8391(3)	6667(2)	3523(2)	32(1)
C(23)	9208(3)	6613(2)	4146(2)	39(1)
C(24)	8372(4)	6338(2)	4631(2)	43(1)
C(25)	6705(3)	6119(2)	4505(2)	34(1)
C(26)	2933(3)	4851(2)	3546(1)	21(1)
C(27)	3856(3)	4326(2)	3715(1)	24(1)
C(28)	3169(4)	3497(2)	3591(1)	29(1)
C(29)	1561(4)	3188(2)	3307(1)	31(1)

C(30)	631(3)	3705(2)	3138(1)	30(1)
C(31)	1314(3)	4532(2)	3254(1)	25(1)
C(32)	6496(3)	527(2)	-533(1)	24(1)
C(33)	6689(3)	181(2)	-1164(1)	27(1)
C(34)	6219(3)	493(2)	-1726(1)	28(1)
C(35)	5559(3)	1158(2)	-1662(1)	24(1)
C(36)	4974(3)	1518(2)	-2214(1)	30(1)
C(37)	4347(3)	2156(2)	-2100(1)	29(1)
C(38)	4263(3)	2508(2)	-1435(1)	24(1)
C(39)	3679(3)	3189(2)	-1305(1)	26(1)
C(40)	3623(3)	3482(2)	-652(1)	25(1)
C(41)	4107(3)	3110(2)	-112(1)	23(1)
C(42)	4700(3)	2440(1)	-209(1)	19(1)
C(43)	4787(3)	2157(2)	-884(1)	21(1)
C(44)	5431(3)	1480(2)	-1013(1)	22(1)
C(45)	5310(3)	1903(2)	2088(1)	22(1)
C(46)	6796(3)	1747(2)	2281(1)	28(1)
C(47)	7046(4)	1359(2)	2828(1)	32(1)
C(48)	5821(4)	1112(2)	3186(1)	34(1)
C(49)	4351(4)	1275(2)	3005(1)	32(1)
C(50)	4093(3)	1670(2)	2457(1)	26(1)
C(51)	2935(3)	2439(2)	1269(1)	20(1)
C(52)	1806(3)	1814(2)	818(1)	24(1)
C(53)	193(3)	1798(2)	731(1)	27(1)
C(54)	-287(3)	2422(2)	1066(1)	27(1)
C(55)	810(3)	3034(2)	1493(1)	27(1)
C(56)	2434(3)	3048(2)	1613(1)	23(1)
C(57)	6249(3)	3430(1)	1671(1)	19(1)
C(58)	7135(3)	3861(2)	1248(1)	22(1)
C(59)	8069(3)	4651(2)	1480(1)	25(1)
C(60)	8114(3)	5017(2)	2131(1)	25(1)
C(61)	7250(3)	4590(2)	2556(1)	22(1)
C(62)	6331(3)	3799(2)	2331(1)	21(1)
N(1)	1534(2)	7191(1)	2280(1)	19(1)
N(7)	5903(2)	1164(1)	-461(1)	21(1)
Cl(1)	8924(1)	-412(1)	751(1)	39(1)
Cl(2)	10077(1)	448(1)	2123(1)	40(1)
C(63)	8369(3)	-35(2)	1501(2)	32(1)
Cl(3)	6921(8)	400(1)	6258(2)	103(2)
Cl(4)	5204(9)	657(4)	4962(3)	105(2)
C(64)	6842(13)	932(5)	5589(4)	77(2)
Cl(5)	1400(40)	1330(20)	5200(20)	250(30)
Cl(6)	4289(8)	780(3)	5686(3)	98(2)
C(65)	3040(20)	1397(13)	5838(13)	140(9)
Cl(7)	2941(14)	1225(6)	4885(5)	161(4)
Cl(8)	-258(13)	1592(6)	4506(5)	154(3)

C(66)	1270(30)	1510(20)	5106(9)	165(10)

Table S12. Bond lengths [A] and angles [deg] for **11**.

Pd(1)-C(11)	2.004(2)
Pd(1)-F(1)	2.0301(15)
Pd(1)-N(1)	2.0762(19)
Pd(1)-P(1)	2.2458(6)
Pd(2)-C(42)	2.012(2)
Pd(2)-F(2)	2.0290(15)
Pd(2)-N(7)	2.070(2)
Pd(2)-P(2)	2.2448(6)
P(1)-C(26)	1.816(3)
P(1)-C(20)	1.818(2)
P(1)-C(14)	1.823(3)
P(2)-C(45)	1.822(3)
P(2)-C(51)	1.822(2)
P(2)-C(57)	1.825(2)
C(1)-N(1)	1.327(3)
C(1)-C(2)	1.402(4)
C(2)-C(3)	1.371(4)
C(3)-C(4)	1.404(4)
C(4)-C(13)	1.408(3)
C(4)-C(5)	1.430(4)
C(5)-C(6)	1.355(4)
C(6)-C(7)	1.440(3)
C(7)-C(8)	1.407(4)
C(7)-C(12)	1.411(3)
C(8)-C(9)	1.373(4)
C(9)-C(10)	1.412(3)
C(10)-C(11)	1.381(3)
C(11)-C(12)	1.424(3)
C(12)-C(13)	1.427(3)
C(13)-N(1)	1.356(3)
C(14)-C(19)	1.387(4)
C(14)-C(15)	1.398(4)
C(15)-C(16)	1.386(4)
C(16)-C(17)	1.386(6)
C(17)-C(18)	1.376(5)
C(18)-C(19)	1.405(4)
C(20)-C(21)	1.392(4)
C(20)-C(25)	1.395(4)
C(21)-C(22)	1.392(4)
C(22)-C(23)	1.387(5)
C(23)-C(24)	1.373(5)
C(24)-C(25)	1.390(4)

C(26)-C(27)	1.395(3)
C(26)-C(31)	1.399(3)
C(27)-C(28)	1.389(4)
C(28)-C(29)	1.386(4)
C(29)-C(30)	1.388(4)
C(30)-C(31)	1.385(4)
C(32)-N(7)	1.328(3)
C(32)-C(33)	1.401(4)
C(33)-C(34)	1.374(4)
C(34)-C(35)	1.408(4)
C(35)-C(44)	1.402(3)
C(35)-C(36)	1.436(4)
C(36)-C(37)	1.358(4)
C(37)-C(38)	1.436(4)
C(38)-C(39)	1.406(4)
C(38)-C(43)	1.409(4)
C(39)-C(40)	1.376(4)
C(40)-C(41)	1.402(4)
C(41)-C(42)	1.386(3)
C(42)-C(43)	1.421(3)
C(43)-C(44)	1.431(3)
C(44)-N(7)	1.362(3)
C(45)-C(50)	1.396(4)
C(45)-C(46)	1.400(4)
C(46)-C(47)	1.386(4)
C(47)-C(48)	1.390(5)
C(48)-C(49)	1.390(4)
C(49)-C(50)	1.395(4)
C(51)-C(56)	1.388(3)
C(51)-C(52)	1.402(3)
C(52)-C(53)	1.389(3)
C(53)-C(54)	1.390(4)
C(54)-C(55)	1.356(4)
C(55)-C(56)	1.399(3)
C(57)-C(58)	1.400(3)
C(57)-C(62)	1.401(3)
C(58)-C(59)	1.395(3)
C(59)-C(60)	1.389(4)
C(60)-C(61)	1.391(4)
C(61)-C(62)	1.391(3)
Cl(1)-C(63)	1.767(3)
Cl(2)-C(63)	1.767(3)
Cl(3)-C(64)	1.734(7)
Cl(4)-C(64)	1.702(8)
Cl(4)-Cl(4)#1	2.240(13)
Cl(5)-C(65)	1.757(10)

Cl(6)-C(65)	1.737(10)
Cl(7)-C(66)	1.751(10)
Cl(8)-C(66)	1.720(10)

C(11)-Pd(1)-F(1)	169.77(8)
C(11)-Pd(1)-N(1)	82.52(9)
F(1)-Pd(1)-N(1)	87.36(7)
C(11)-Pd(1)-P(1)	96.97(7)
F(1)-Pd(1)-P(1)	93.23(5)
N(1)-Pd(1)-P(1)	176.20(6)
C(42)-Pd(2)-F(2)	170.46(8)
C(42)-Pd(2)-N(7)	82.57(9)
F(2)-Pd(2)-N(7)	87.91(7)
C(42)-Pd(2)-P(2)	96.08(7)
F(2)-Pd(2)-P(2)	93.46(5)
N(7)-Pd(2)-P(2)	177.32(6)
C(26)-P(1)-C(20)	107.02(11)
C(26)-P(1)-C(14)	103.43(12)
C(20)-P(1)-C(14)	102.23(12)
C(26)-P(1)-Pd(1)	116.10(8)
C(20)-P(1)-Pd(1)	115.30(8)
C(14)-P(1)-Pd(1)	111.25(8)
C(45)-P(2)-C(51)	104.15(11)
C(45)-P(2)-C(57)	102.19(11)
C(51)-P(2)-C(57)	106.64(11)
C(45)-P(2)-Pd(2)	113.53(8)
C(51)-P(2)-Pd(2)	112.23(8)
C(57)-P(2)-Pd(2)	116.85(8)
N(1)-C(1)-C(2)	121.3(2)
C(3)-C(2)-C(1)	119.9(2)
C(2)-C(3)-C(4)	119.6(2)
C(3)-C(4)-C(13)	117.2(2)
C(3)-C(4)-C(5)	125.0(2)
C(13)-C(4)-C(5)	117.7(2)
C(6)-C(5)-C(4)	120.8(2)
C(5)-C(6)-C(7)	122.0(2)
C(8)-C(7)-C(12)	118.0(2)
C(8)-C(7)-C(6)	123.3(2)
C(12)-C(7)-C(6)	118.7(2)
C(9)-C(8)-C(7)	119.5(2)
C(8)-C(9)-C(10)	121.7(2)
C(11)-C(10)-C(9)	121.2(2)
C(10)-C(11)-C(12)	116.5(2)
C(10)-C(11)-Pd(1)	132.79(18)
C(12)-C(11)-Pd(1)	110.69(16)
C(7)-C(12)-C(11)	123.0(2)

C(7)-C(12)-C(13)	118.3(2)
C(11)-C(12)-C(13)	118.6(2)
N(1)-C(13)-C(4)	122.2(2)
N(1)-C(13)-C(12)	115.5(2)
C(4)-C(13)-C(12)	122.3(2)
C(19)-C(14)-C(15)	119.6(3)
C(19)-C(14)-P(1)	123.4(2)
C(15)-C(14)-P(1)	117.0(2)
C(16)-C(15)-C(14)	119.9(3)
C(17)-C(16)-C(15)	120.4(3)
C(18)-C(17)-C(16)	120.3(3)
C(17)-C(18)-C(19)	119.9(3)
C(14)-C(19)-C(18)	120.0(3)
C(21)-C(20)-C(25)	119.0(2)
C(21)-C(20)-P(1)	119.67(19)
C(25)-C(20)-P(1)	121.2(2)
C(22)-C(21)-C(20)	120.3(3)
C(23)-C(22)-C(21)	120.0(3)
C(24)-C(23)-C(22)	120.1(3)
C(23)-C(24)-C(25)	120.4(3)
C(24)-C(25)-C(20)	120.2(3)
C(27)-C(26)-C(31)	119.2(2)
C(27)-C(26)-P(1)	123.59(19)
C(31)-C(26)-P(1)	117.19(19)
C(28)-C(27)-C(26)	120.1(2)
C(29)-C(28)-C(27)	120.3(3)
C(28)-C(29)-C(30)	120.1(3)
C(31)-C(30)-C(29)	119.8(3)
C(30)-C(31)-C(26)	120.5(2)
N(7)-C(32)-C(33)	121.7(3)
C(34)-C(33)-C(32)	119.4(2)
C(33)-C(34)-C(35)	119.8(2)
C(44)-C(35)-C(34)	117.4(2)
C(44)-C(35)-C(36)	117.7(2)
C(34)-C(35)-C(36)	124.9(2)
C(37)-C(36)-C(35)	120.4(2)
C(36)-C(37)-C(38)	122.2(3)
C(39)-C(38)-C(43)	118.1(2)
C(39)-C(38)-C(37)	123.1(2)
C(43)-C(38)-C(37)	118.9(2)
C(40)-C(39)-C(38)	119.3(2)
C(39)-C(40)-C(41)	121.8(2)
C(42)-C(41)-C(40)	121.5(2)
C(41)-C(42)-C(43)	116.0(2)
C(41)-C(42)-Pd(2)	133.27(18)
C(43)-C(42)-Pd(2)	110.67(17)

C(38)-C(43)-C(42)	123.3(2)
C(38)-C(43)-C(44)	118.1(2)
C(42)-C(43)-C(44)	118.6(2)
N(7)-C(44)-C(35)	122.1(2)
N(7)-C(44)-C(43)	115.3(2)
C(35)-C(44)-C(43)	122.6(2)
C(50)-C(45)-C(46)	119.4(2)
C(50)-C(45)-P(2)	121.81(19)
C(46)-C(45)-P(2)	118.8(2)
C(47)-C(46)-C(45)	120.1(3)
C(46)-C(47)-C(48)	120.4(3)
C(47)-C(48)-C(49)	119.9(3)
C(48)-C(49)-C(50)	120.0(3)
C(49)-C(50)-C(45)	120.1(3)
C(56)-C(51)-C(52)	119.7(2)
C(56)-C(51)-P(2)	123.75(19)
C(52)-C(51)-P(2)	116.58(18)
C(53)-C(52)-C(51)	119.7(2)
C(52)-C(53)-C(54)	119.9(2)
C(55)-C(54)-C(53)	120.2(2)
C(54)-C(55)-C(56)	121.1(2)
C(51)-C(56)-C(55)	119.2(2)
C(58)-C(57)-C(62)	119.2(2)
C(58)-C(57)-P(2)	119.76(18)
C(62)-C(57)-P(2)	121.09(18)
C(59)-C(58)-C(57)	120.2(2)
C(60)-C(59)-C(58)	120.2(2)
C(61)-C(60)-C(59)	119.9(2)
C(62)-C(61)-C(60)	120.3(2)
C(61)-C(62)-C(57)	120.3(2)
C(1)-N(1)-C(13)	119.7(2)
C(1)-N(1)-Pd(1)	127.68(17)
C(13)-N(1)-Pd(1)	112.60(15)
C(32)-N(7)-C(44)	119.6(2)
C(32)-N(7)-Pd(2)	127.57(18)
C(44)-N(7)-Pd(2)	112.81(16)
Cl(2)-C(63)-Cl(1)	111.06(15)
C(64)-Cl(4)-Cl(4)#1	92.8(5)
Cl(4)-C(64)-Cl(3)	120.1(6)
Cl(6)-C(65)-Cl(5)	117.5(10)
Cl(8)-C(66)-Cl(7)	121.5(12)

Symmetry transformations used to generate equivalent atoms:
#1 -x+1,-y,-z+1

Table S13. Anisotropic displacement parameters (A^2 x 10^3) for **11**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	18(1)	22(1)	16(1)	3(1)	2(1)	10(1)
Pd(2)	17(1)	19(1)	19(1)	0(1)	1(1)	7(1)
P(1)	16(1)	24(1)	16(1)	5(1)	2(1)	8(1)
P(2)	16(1)	19(1)	19(1)	1(1)	1(1)	6(1)
F(1)	44(1)	36(1)	24(1)	-2(1)	4(1)	23(1)
F(2)	26(1)	24(1)	30(1)	5(1)	3(1)	12(1)
C(1)	23(1)	24(1)	28(1)	6(1)	5(1)	10(1)
C(2)	25(1)	26(1)	38(2)	11(1)	2(1)	12(1)
C(3)	22(1)	28(1)	33(1)	15(1)	-1(1)	7(1)
C(4)	18(1)	26(1)	25(1)	10(1)	-1(1)	2(1)
C(5)	26(1)	36(1)	21(1)	12(1)	-1(1)	4(1)
C(6)	28(1)	33(1)	17(1)	5(1)	2(1)	2(1)
C(7)	22(1)	24(1)	18(1)	4(1)	3(1)	2(1)
C(8)	29(1)	28(1)	20(1)	0(1)	7(1)	6(1)
C(9)	30(1)	25(1)	25(1)	2(1)	9(1)	12(1)
C(10)	23(1)	26(1)	22(1)	6(1)	6(1)	11(1)
C(11)	18(1)	20(1)	16(1)	3(1)	2(1)	6(1)
C(12)	17(1)	21(1)	18(1)	3(1)	2(1)	3(1)
C(13)	15(1)	22(1)	19(1)	7(1)	2(1)	4(1)
C(14)	23(1)	36(1)	17(1)	4(1)	0(1)	16(1)
C(15)	42(2)	39(2)	23(1)	0(1)	-3(1)	17(1)
C(16)	57(2)	54(2)	24(1)	-7(1)	-6(1)	33(2)
C(17)	46(2)	82(3)	18(1)	0(1)	1(1)	42(2)
C(18)	30(1)	77(2)	22(1)	16(1)	7(1)	27(2)
C(19)	22(1)	47(2)	22(1)	10(1)	3(1)	16(1)
C(20)	17(1)	25(1)	27(1)	6(1)	1(1)	8(1)
C(21)	23(1)	26(1)	30(1)	2(1)	6(1)	7(1)
C(22)	24(1)	26(1)	47(2)	0(1)	13(1)	5(1)
C(23)	18(1)	34(2)	65(2)	5(1)	-1(1)	10(1)
C(24)	25(1)	48(2)	51(2)	16(2)	-10(1)	9(1)
C(25)	23(1)	45(2)	36(2)	16(1)	-2(1)	9(1)
C(26)	21(1)	26(1)	17(1)	6(1)	4(1)	8(1)
C(27)	23(1)	29(1)	21(1)	5(1)	2(1)	10(1)
C(28)	35(1)	27(1)	28(1)	7(1)	4(1)	14(1)
C(29)	36(2)	26(1)	27(1)	3(1)	5(1)	5(1)

C(30)	24(1)	34(1)	29(1)	4(1)	3(1)	3(1)
C(31)	22(1)	31(1)	24(1)	6(1)	3(1)	9(1)
C(32)	20(1)	22(1)	29(1)	-1(1)	2(1)	5(1)
C(33)	25(1)	23(1)	34(1)	-2(1)	9(1)	6(1)
C(34)	25(1)	27(1)	29(1)	-6(1)	9(1)	3(1)
C(35)	18(1)	26(1)	23(1)	-2(1)	4(1)	1(1)
C(36)	30(1)	36(1)	21(1)	1(1)	7(1)	5(1)
C(37)	28(1)	34(1)	22(1)	4(1)	4(1)	5(1)
C(38)	19(1)	29(1)	22(1)	4(1)	4(1)	3(1)
C(39)	22(1)	31(1)	25(1)	9(1)	4(1)	8(1)
C(40)	21(1)	26(1)	30(1)	5(1)	4(1)	10(1)
C(41)	20(1)	26(1)	22(1)	2(1)	3(1)	8(1)
C(42)	15(1)	20(1)	20(1)	2(1)	2(1)	4(1)
C(43)	16(1)	24(1)	23(1)	1(1)	3(1)	4(1)
C(44)	14(1)	25(1)	23(1)	0(1)	3(1)	2(1)
C(45)	25(1)	20(1)	19(1)	0(1)	0(1)	7(1)
C(46)	28(1)	32(1)	25(1)	1(1)	2(1)	13(1)
C(47)	38(2)	35(1)	25(1)	1(1)	-3(1)	21(1)
C(48)	52(2)	28(1)	23(1)	3(1)	-2(1)	14(1)
C(49)	40(2)	31(1)	24(1)	5(1)	6(1)	6(1)
C(50)	28(1)	23(1)	24(1)	1(1)	2(1)	6(1)
C(51)	17(1)	23(1)	21(1)	5(1)	3(1)	5(1)
C(52)	18(1)	19(1)	34(1)	4(1)	1(1)	5(1)
C(53)	19(1)	25(1)	32(1)	5(1)	-1(1)	2(1)
C(54)	17(1)	38(1)	29(1)	13(1)	6(1)	10(1)
C(55)	24(1)	36(1)	27(1)	10(1)	11(1)	17(1)
C(56)	20(1)	27(1)	22(1)	1(1)	2(1)	6(1)
C(57)	14(1)	19(1)	24(1)	2(1)	1(1)	7(1)
C(58)	19(1)	24(1)	22(1)	0(1)	4(1)	6(1)
C(59)	21(1)	24(1)	30(1)	4(1)	6(1)	4(1)
C(60)	20(1)	21(1)	29(1)	-2(1)	0(1)	4(1)
C(61)	21(1)	23(1)	22(1)	-2(1)	-1(1)	8(1)
C(62)	18(1)	23(1)	22(1)	3(1)	2(1)	8(1)
N(1)	18(1)	22(1)	20(1)	6(1)	2(1)	9(1)
N(7)	16(1)	20(1)	23(1)	-3(1)	2(1)	4(1)
Cl(1)	44(1)	30(1)	43(1)	-1(1)	-3(1)	18(1)
Cl(2)	30(1)	41(1)	43(1)	-4(1)	-1(1)	11(1)
C(63)	23(1)	34(1)	39(2)	8(1)	1(1)	10(1)
Cl(3)	212(5)	24(1)	59(2)	12(1)	35(2)	-5(2)
Cl(4)	151(6)	79(4)	60(3)	3(3)	12(3)	-9(4)
C(64)	128(6)	32(3)	64(4)	7(3)	7(4)	13(4)
Cl(5)	180(30)	150(30)	360(60)	-170(40)	-60(30)	100(20)
Cl(6)	115(5)	51(3)	88(4)	-10(2)	-12(3)	-24(3)
C(65)	152(19)	65(14)	160(20)	-60(15)	42(15)	-25(10)
Cl(7)	237(10)	103(6)	103(6)	-24(5)	4(7)	2(7)
Cl(8)	186(8)	119(6)	98(5)	-12(5)	2(6)	-41(6)

C(66)	278(16)	38(11)	180(20)	14(13)	1(9)	62(15)

Table S14. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **11**.

	x	y	z	U(eq)
H(1A)	1104	8090	2854	29
H(2A)	-112	8620	1975	34
H(3A)	-456	7990	868	33
H(5A)	-39	6821	49	34
H(6A)	1058	5756	-101	32
H(8A)	2757	4881	383	31
H(9A)	4149	4555	1321	31
H(10A)	4098	5150	2411	27
H(15A)	4476	7398	4637	42
H(16A)	3941	7812	5695	53
H(17A)	2392	6886	6242	54
H(18A)	1415	5537	5747	48
H(19A)	1935	5109	4678	34
H(21A)	6163	6481	2964	32
H(22A)	8971	6855	3187	39
H(23A)	10347	6767	4237	47
H(24A)	8937	6297	5055	51
H(25A)	6136	5930	4844	41
H(27A)	4956	4536	3914	29
H(28A)	3804	3141	3702	35
H(29A)	1094	2621	3227	37
H(30A)	-471	3493	2942	36
H(31A)	678	4885	3135	30
H(32A)	6797	301	-147	29
H(33A)	7141	-266	-1203	33
H(34A)	6339	261	-2157	34
H(36A)	5025	1307	-2661	36
H(37A)	3951	2378	-2474	35
H(39A)	3326	3444	-1664	31
H(40A)	3247	3948	-565	30
H(41A)	4027	3323	331	27
H(46A)	7634	1909	2036	34
H(47A)	8060	1261	2960	38
H(48A)	5989	832	3552	41
H(49A)	3521	1118	3256	38
H(50A)	3087	1781	2334	31
H(52A)	2143	1403	572	29

H(53A)	-582	1362	443	32
H(54A)	-1387	2420	995	32
H(55A)	470	3461	1714	32
H(56A)	3186	3469	1926	28
H(58A)	7100	3614	801	26
H(59A)	8675	4939	1192	30
H(60A)	8735	5559	2286	30
H(61A)	7288	4839	3003	27
H(62A)	5755	3508	2626	25
H(63A)	7735	355	1406	38
H(63B)	7686	-486	1671	38
H(64A)	6979	1504	5779	93
H(64B)	7787	912	5377	93
H(65A)	3701	1964	5934	168
H(65B)	2617	1276	6251	168
H(66A)	783	1120	5385	197
H(66B)	1681	2041	5403	197

Structure Determination of 12.

Colorless plates **12** were grown from a pentanes/dichloromethane solution at -35 deg. C. A crystal of dimensions 0.32 x 0.30 x 0.22 mm was mounted on a Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low temperature device and fine focus Mo-target X-ray tube (λ = 0.71073 A) operated at 1500 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(1) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 5190 frames were collected with a scan width of 0.5° in ω and 0.45° in phi with an exposure time of 10 s/frame. The integration of the data yielded a total of 38567 reflections to a maximum 2θ value of 60.18° of which 4384 were independent and 4326 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9935 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with SADABS and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/3) software package, using the space group P1bar with Z = 2 for the formula $C_{12}H_{19}N_2FPd$, $CHCl_2$. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. Full matrix least-squares refinement based on F^2 converged at R1 = 0.0147 and wR2 = 0.0386 [based on I > 2sigma(I)], R1 = 0.0150 and wR2 = 0.0387 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 2008/3; Bruker Analytical X-ray, Madison, WI, 2008.

Sheldrick, G.M. SADABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.

Saint Plus, v. 7.60a, Bruker Analytical X-ray, Madison, WI, 2009.

Table S15. Crystal data and structure refinement for **12**.

Identification code	nb4s
Empirical formula	C13 H21 Cl2 F N2 Pd
Formula weight	401.62
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 8.4407(6) A alpha = 105.314(1)deg. b = 9.5451(6) A beta = 95.629(1) deg. c = 11.5693(8) A gamma = 116.010(1)deg.
Volume	782.97(9) A^3
Z, Calculated density	2, 1.704 Mg/m^3
Absorption coefficient	1.525 mm^-1
F(000)	404
Crystal size	0.32 x 0.30 x 0.22 mm
Theta range for data collection	1.88 to 29.59 deg.
Limiting indices	-11<=h<=11, -13<=k<=13, -16<=l<=16
Reflections collected / unique	38567 / 4384 [R(int) = 0.0282]
Completeness to theta = 29.59	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7157 and 0.6283
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4384 / 0 / 176

Goodness-of-fit on F^2	1.096
Final R indices [I>2sigma(I)]	R1 = 0.0147, wR2 = 0.0386
R indices (all data)	R1 = 0.0150, wR2 = 0.0387
Largest diff. peak and hole	0.566 and -0.863 e.A^-3

Table S16. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **12**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	7397(1)	7930(1)	1983(1)	10(1)
Cl(1)	4209(1)	8447(1)	7413(1)	19(1)
Cl(2)	1384(1)	6301(1)	8377(1)	17(1)
F(1)	6461(1)	8361(1)	436(1)	16(1)
N(1)	10182(1)	9337(1)	2131(1)	11(1)
N(2)	4894(1)	6338(1)	2246(1)	13(1)
C(1)	11211(2)	9761(1)	3429(1)	13(1)
C(2)	10163(2)	8381(1)	3898(1)	13(1)
C(3)	10842(2)	7976(2)	4836(1)	16(1)
C(4)	9653(2)	6681(2)	5186(1)	17(1)
C(5)	7792(2)	5771(1)	4604(1)	16(1)
C(6)	7112(2)	6162(1)	3658(1)	14(1)
C(7)	8306(2)	7470(1)	3331(1)	12(1)
C(8)	5214(2)	5216(1)	2830(1)	15(1)
C(9)	10660(2)	8245(1)	1234(1)	14(1)
C(10)	10650(2)	10864(1)	1825(1)	16(1)
C(11)	3427(2)	5324(2)	1090(1)	19(1)
C(12)	4330(2)	7374(2)	3117(1)	18(1)
C(13)	3402(2)	8238(1)	8759(1)	16(1)

Table S17. Bond lengths [A] and angles [deg] for **12**.

Pd(1)-C(7)	1.9068(11)
Pd(1)-N(1)	2.0954(9)
Pd(1)-F(1)	2.0959(7)
Pd(1)-N(2)	2.1019(9)
Cl(1)-C(13)	1.7833(12)
Cl(2)-C(13)	1.7810(12)
N(1)-C(10)	1.4835(14)
N(1)-C(9)	1.4853(14)
N(1)-C(1)	1.5127(14)
N(2)-C(11)	1.4824(15)
N(2)-C(12)	1.4836(14)
N(2)-C(8)	1.5094(15)
C(1)-C(2)	1.5042(15)
C(2)-C(7)	1.3945(15)
C(2)-C(3)	1.3958(15)
C(3)-C(4)	1.3978(17)
C(4)-C(5)	1.4010(18)
C(5)-C(6)	1.3953(16)
C(6)-C(7)	1.3927(15)
C(6)-C(8)	1.5080(16)
C(7)-Pd(1)-N(1)	81.69(4)
C(7)-Pd(1)-F(1)	176.62(4)
N(1)-Pd(1)-F(1)	96.89(3)
C(7)-Pd(1)-N(2)	81.61(4)
N(1)-Pd(1)-N(2)	163.27(4)
F(1)-Pd(1)-N(2)	99.74(3)
C(10)-N(1)-C(9)	108.90(9)
C(10)-N(1)-C(1)	110.67(8)
C(9)-N(1)-C(1)	109.54(8)
C(10)-N(1)-Pd(1)	113.19(7)
C(9)-N(1)-Pd(1)	105.98(6)
C(1)-N(1)-Pd(1)	108.42(6)
C(11)-N(2)-C(12)	108.92(9)
C(11)-N(2)-C(8)	109.73(9)
C(12)-N(2)-C(8)	109.14(9)
C(11)-N(2)-Pd(1)	113.84(7)
C(12)-N(2)-Pd(1)	107.88(7)
C(8)-N(2)-Pd(1)	107.24(7)
C(2)-C(1)-N(1)	108.49(9)
C(7)-C(2)-C(3)	118.76(10)
C(7)-C(2)-C(1)	114.04(9)

C(3)-C(2)-C(1)	127.17(10)
C(2)-C(3)-C(4)	119.50(11)
C(3)-C(4)-C(5)	121.18(11)
C(6)-C(5)-C(4)	119.45(11)
C(7)-C(6)-C(5)	118.80(11)
C(7)-C(6)-C(8)	113.67(10)
C(5)-C(6)-C(8)	127.25(10)
C(6)-C(7)-C(2)	122.30(10)
C(6)-C(7)-Pd(1)	118.68(8)
C(2)-C(7)-Pd(1)	118.88(8)
C(6)-C(8)-N(2)	108.87(9)
Cl(2)-C(13)-Cl(1)	110.41(6)

Symmetry transformations used to generate equivalent atoms:

Table S18. Anisotropic displacement parameters (A^2 x 10^3) for **12**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	9(1)	11(1)	10(1)	4(1)	2(1)	5(1)
Cl(1)	16(1)	19(1)	21(1)	10(1)	5(1)	6(1)
Cl(2)	15(1)	16(1)	19(1)	6(1)	6(1)	6(1)
F(1)	17(1)	19(1)	15(1)	8(1)	1(1)	9(1)
N(1)	10(1)	11(1)	11(1)	4(1)	2(1)	4(1)
N(2)	11(1)	14(1)	14(1)	4(1)	4(1)	5(1)
C(1)	11(1)	15(1)	11(1)	4(1)	1(1)	5(1)
C(2)	14(1)	14(1)	11(1)	4(1)	3(1)	8(1)
C(3)	19(1)	19(1)	12(1)	4(1)	2(1)	12(1)
C(4)	27(1)	19(1)	12(1)	6(1)	5(1)	16(1)
C(5)	26(1)	15(1)	14(1)	7(1)	9(1)	12(1)
C(6)	18(1)	12(1)	14(1)	5(1)	7(1)	8(1)
C(7)	14(1)	13(1)	11(1)	5(1)	4(1)	7(1)
C(8)	15(1)	13(1)	18(1)	7(1)	6(1)	6(1)
C(9)	14(1)	15(1)	13(1)	3(1)	5(1)	7(1)
C(10)	17(1)	13(1)	16(1)	7(1)	4(1)	5(1)
C(11)	12(1)	21(1)	18(1)	4(1)	1(1)	3(1)
C(12)	17(1)	18(1)	21(1)	6(1)	9(1)	10(1)
C(13)	14(1)	15(1)	15(1)	4(1)	1(1)	6(1)

Table S19. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **12**.

	x	y	z	U(eq)
H(1A)	12439	9889	3425	16
H(1B)	11348	10820	3974	16
H(3A)	12104	8575	5233	19
H(4A)	10116	6414	5829	21
H(5A)	6999	4896	4853	20
H(8A)	4313	4838	3319	18
H(8B)	5070	4226	2179	18
H(9A)	9927	7906	400	22
H(9B)	10415	7259	1454	22
H(9C)	11954	8850	1255	22
H(10A)	11930	11386	1797	23
H(10B)	10449	11639	2459	23
H(10C)	9878	10576	1018	23
H(11A)	2285	4671	1287	29
H(11B)	3748	4575	534	29
H(11C)	3278	6056	686	29
H(12A)	4220	8171	2772	27
H(12B)	5243	7975	3910	27
H(12C)	3153	6661	3244	27
H(13A)	4350	8307	9382	19
H(13B)	3146	9156	9122	19

Structure Determination of 15.

Yellow cubes of **15** were crystallized from a pentane/dichloromethane solution at -30 deg. C. A crystal of dimensions 0.10 x 0.10 x 0.10 mm was mounted on a standard Bruker SMART APEX CCD-based X-ray diffractometer equipped with a low-temperature device and fine- focus Mo-target X-ray tube (λ = 0.71073 A) operated at 2000 W power (50 kV, 30 mA). The X-ray intensities were measured at 85(2) K; the detector was placed at a distance 5.055 cm from the crystal. A total of 3100 frames were collected with a scan width of 0.5° in ω and 0.45° in ϕ with an exposure time of 25 s/frame. Indexing was performed by use of the CELL_NOW program which indicated that the crystal was a two-component, non-merohedral twin. The frames were integrated with the Bruker SAINT software package with a narrow frame algorithm. The integration of the data yielded a total of 92957 reflections to a maximum 2θ value of 56.66° of which 6735 were independent and 3768 were greater than $2\sigma(I)$. The final cell constants (Table 1) were based on the xyz centroids of 9448 reflections above $10\sigma(I)$. Analysis of the data showed negligible decay during data collection; the data were processed with TWINABS and corrected for absorption. For this refinement, reflections from both components were used in the refinement and well as reflections containing contributions from both domains. Merging of the data was performed in TWINABS and an HKLF 5 format file used for refinement. The structure was solved and refined with the Bruker SHELXTL (version 6.12) software package, using the space group Pccn with Z = 4 for the formula $C_{18}H_{24}N_2F_2Pd{\bullet}CH_2Cl_2$. The complex lies on a two-fold axis of the crystal lattice. The dichloromethane is disordered over an alternate two-fold axis. All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The twin domains are related by a 180 degree rotation about the direct (1 1 0) axis) and a refined twin volume fraction of 0.886(2). Full-matrix least-squares refinement based on F^2 converged at R1 = 0.0386 and wR2 = 0.1032 [based on I > 2sigma(I)], R1 = 0.0507 and wR2 = 0.102 for all data. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.
Saint Plus, v. 7.34, Bruker Analytical X-ray, Madison, WI, 2006.

Sheldrick, G.M. CELL_NOW, Program for Indexing Twins and Other Problem Crystals, University of Gottingen: Gottingen, Germany, 2003.

Sheldrick, G.M. SHELXTL, v. 6.12; Bruker Analytical X-ray, Madison, WI, 2001.

Sheldrick, G.M. TWINABS, v. 2008/1. Program for Empirical Absorption Correction of Area Detector Data, University of Gottingen: Gottingen, Germany, 2008.

Table S20. Crystal data and structure refinement for **15**.

Identification code	nb153
Empirical formula	C19 H26 Cl2 F2 N2 Pd
Formula weight	497.72
Temperature	85(2) K
Wavelength	0.71073 A
Crystal system, space group	Orthorhombic, Pccn
Unit cell dimensions	a = 11.1616(9) A alpha = 90 deg. b = 11.9919(9) A beta = 90 deg. c = 15.6096(10) A gamma = 90 deg.
Volume	2089.3(3) A^3
Z, Calculated density	4, 1.582 Mg/m^3
Absorption coefficient	1.166 mm^-1
F(000)	1008
Crystal size	0.10 x 0.10 x 0.10 mm
Theta range for data collection	2.49 to 28.33 deg.
Limiting indices	-14<=h<=14, -16<=k<=16, -20<=l<=20
Reflections collected / unique	92957 / 6735 [R(int) = 0.0631]
Completeness to theta = 28.33	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8923 and 0.8923
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	6735 / 0 / 128

Goodness-of-fit on F^2 1.095

Final R indices [I>2sigma(I)] R1 = 0.0386, wR2 = 0.1032

R indices (all data) R1 = 0.0507, wR2 = 0.1102

Largest diff. peak and hole 1.143 and -1.091 e.A^-3

Table S21. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters (A^2 x 10^3) for **15**.
U(eq) is defined as one third of the trace of the orthogonalized Uij tensor.

	x	y	z	U(eq)
Pd(1)	7500	2500	5166(1)	13(1)
N(1)	6697(2)	1737(1)	4205(1)	14(1)
C(2)	6485(2)	1639(2)	2687(1)	18(1)
C(3)	5579(2)	849(2)	2767(1)	19(1)
C(4)	5272(2)	504(2)	3594(1)	20(1)
C(5)	5839(2)	963(2)	4293(1)	17(1)
C(1)	7028(2)	2068(2)	3413(1)	14(1)
C(6)	4902(2)	369(2)	2003(1)	27(1)
C(9)	3565(2)	639(3)	2112(2)	39(1)
C(7)	5342(2)	865(2)	1158(1)	34(1)
C(8)	5086(3)	-898(2)	1992(2)	37(1)
Cl(1)	2568(1)	1270(1)	4712(1)	57(1)
C(10)	3114(6)	2514(3)	5133(4)	62(2)
F(1)	6643(1)	1631(1)	6045(1)	23(1)

Table S22. Bond lengths [A] and angles [deg] for **15**.

Pd(1)-F(1)	1.9708(11)
Pd(1)-F(1)#1	1.9708(11)
Pd(1)-N(1)#1	1.9722(15)
Pd(1)-N(1)	1.9722(15)
N(1)-C(5)	1.341(3)
N(1)-C(1)	1.351(2)
C(2)-C(1)	1.384(3)
C(2)-C(3)	1.391(3)
C(3)-C(4)	1.398(3)
C(3)-C(6)	1.525(3)
C(4)-C(5)	1.376(3)
C(1)-C(1)#1	1.478(4)
C(6)-C(7)	1.528(3)
C(6)-C(8)	1.533(4)
C(6)-C(9)	1.536(4)
Cl(1)-C(10)	1.740(4)
Cl(1)-C(10)#2	1.772(4)
C(10)-Cl(1)#2	1.772(4)
F(1)-Pd(1)-F(1)#1	91.70(7)
F(1)-Pd(1)-N(1)#1	174.52(6)
F(1)#1-Pd(1)-N(1)#1	93.64(6)
F(1)-Pd(1)-N(1)	93.64(6)
F(1)#1-Pd(1)-N(1)	174.52(6)
N(1)#1-Pd(1)-N(1)	81.04(9)
C(5)-N(1)-C(1)	119.49(16)
C(5)-N(1)-Pd(1)	124.67(12)
C(1)-N(1)-Pd(1)	115.80(13)
C(1)-C(2)-C(3)	119.91(18)
C(2)-C(3)-C(4)	117.50(18)
C(2)-C(3)-C(6)	123.20(18)
C(4)-C(3)-C(6)	119.29(19)
C(5)-C(4)-C(3)	120.10(19)
N(1)-C(5)-C(4)	121.63(17)
N(1)-C(1)-C(2)	121.34(17)
N(1)-C(1)-C(1)#1	113.66(11)
C(2)-C(1)-C(1)#1	124.97(11)
C(3)-C(6)-C(7)	111.63(18)
C(3)-C(6)-C(8)	108.4(2)
C(7)-C(6)-C(8)	109.5(2)
C(3)-C(6)-C(9)	108.32(19)
C(7)-C(6)-C(9)	109.0(2)

C(8)-C(6)-C(9)	109.9(2)
C(10)-Cl(1)-C(10)#2	45.9(4)
Cl(1)-C(10)-Cl(1)#2	114.5(3)

Symmetry transformations used to generate equivalent atoms:
#1 -x+3/2,-y+1/2,z #2 -x+1/2,-y+1/2,z

Table S23. Anisotropic displacement parameters (A^2 x 10^3) for **15**.
The anisotropic displacement factor exponent takes the form:
-2 pi^2 [h^2 a*^2 U11 + ... + 2 h k a* b* U12]

	U11	U22	U33	U23	U13	U12
Pd(1)	16(1)	17(1)	7(1)	0	0	-1(1)
N(1)	17(1)	19(1)	6(1)	0(1)	0(1)	1(1)
C(2)	16(1)	26(1)	10(1)	0(1)	-1(1)	-3(1)
C(3)	17(1)	26(1)	13(1)	-3(1)	-1(1)	-4(1)
C(4)	20(1)	26(1)	15(1)	0(1)	0(1)	-6(1)
C(5)	17(1)	25(1)	10(1)	2(1)	1(1)	-3(1)
C(1)	11(1)	18(1)	11(1)	1(1)	2(1)	2(1)
C(6)	25(1)	44(1)	12(1)	-6(1)	0(1)	-16(1)
C(9)	23(1)	74(2)	21(1)	-3(1)	-5(1)	-15(1)
C(7)	35(1)	56(2)	11(1)	-6(1)	-3(1)	-21(1)
C(8)	43(2)	46(2)	23(1)	-11(1)	4(1)	-21(1)
Cl(1)	45(1)	67(1)	60(1)	0(1)	2(1)	10(1)
C(10)	62(4)	49(4)	76(5)	-10(4)	-33(4)	4(3)
F(1)	30(1)	29(1)	11(1)	2(1)	1(1)	-12(1)

Table S24. Hydrogen coordinates (x 10^4) and isotropic displacement parameters (A^2 x 10^3) for **15**.

	x	y	z	U(eq)
H(2A)	6730	1883	2136	21
H(4A)	4671	-47	3673	24
H(5A)	5616	725	4851	21
H(9A)	3454	1450	2115	59
H(9B)	3277	327	2654	59
H(9C)	3112	314	1636	59
H(7A)	5223	1675	1165	51
H(7B)	4889	539	682	51
H(7C)	6196	700	1086	51
H(8A)	5940	-1064	1923	56
H(8B)	4636	-1223	1515	56
H(8C)	4800	-1216	2533	56
H(10A)	3986	2553	5024	74
H(10B)	2996	2505	5762	74