

## Supporting Information for:

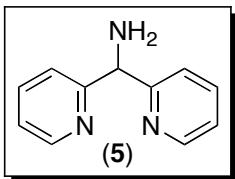
### Facial Tridentate Ligands for Stabilizing Palladium(IV) Complexes

Ansis Maleckis and Melanie S. Sanford\*

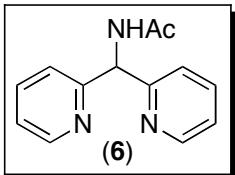
Department of Chemistry, University of Michigan, 930 N. University Ave, Ann Arbor, MI 48109

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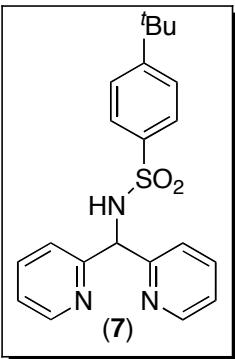
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**Di(pyridin-2-yl)methylamine (5)** was obtained as described in *Inorg. Chem.*, **2004**, *5*, 1735-1742.

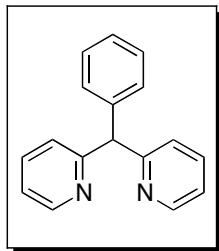


**N-Di(2-pyridyl)methylacetamide (dpaa) (6).** To a solution of di(pyridin-2-yl)methylamine (5) (0.75 g; 4.05 mmol) in pyridine (5 mL) was added acetic anhydride (1.0 mL). The reaction mixture was stirred at rt for 2 h, then water (1 mL) was added, and stirring was continued for 30 min. The reaction mixture was poured into a saturated aq.  $\text{NaHCO}_3$  solution (50 mL), and the resulting solution was extracted with  $\text{EtOAc}$  ( $6 \times 50$  mL). The combined organic phases were washed with brine (100 mL) and dried over anhydrous  $\text{MgSO}_4$ . The volatiles were evaporated under reduced pressure, and the resulting residue was suspended in diethyl ether (15 mL) and collected by filtration. The solid was washed with hexanes and dried under reduced pressure. Yield: 0.74 g (80%) of white crystals.  $\text{Mp} = 77\text{-}79$  °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.51 (d,  $J = 3.6$  Hz, 2H), 7.88 (bs, 1H), 7.60 (t,  $J = 7.4$  Hz, 2H), 7.39 (d,  $J = 7.6$  Hz, 2H), 7.12 (t,  $J = 5.9$  Hz, 2H), 6.19 (d,  $J = 6.8$  Hz, 1H), 2.09 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  169.55, 158.88, 149.20, 136.81, 122.45, 122.20, 59.06, 23.36. HRMS electrospray (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{13}\text{H}_{14}\text{N}_3\text{O}$ , 228.1131; found, 228.1131.

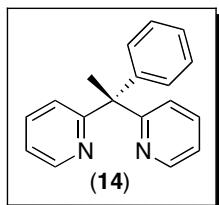


**4-*tert*-Butyl-N-[di(pyridin-2-yl)methyl]benzenesulfonamide (dpfa) (7).** 4-*tert*-Butylbenzenesulfonyl chloride (1.05 g; 4.50 mmol) was added to a solution of di(pyridin-2-yl)methylamine (5) (0.75 g; 4.05 mmol) in pyridine (5 mL). The reaction mixture was stirred at rt for 2 h and then water (1 mL) was added. The solution was allowed to stir for 30 min. The reaction mixture was poured into water (100 mL), and the resulting suspension was extracted with  $\text{EtOAc}$  (100 mL). The organic phase was washed with water ( $3 \times 50$  mL) and brine (100 mL) and dried over anhydrous  $\text{MgSO}_4$ . The solvent was evaporated under reduced pressure and the residue was suspended in hexane (100 mL) and collected by filtration. Yield: 1.20 g (78%) of yellow crystals.  $\text{Mp} = 178$  °C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.41 (d,  $J = 4.4$  Hz, 2H), 7.61 (d,  $J = 8.5$  Hz,

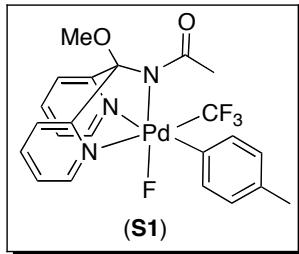
2H), 7.49 (t,  $J$  = 6.4 Hz, 2H), 7.24 (multiple peaks, 5H), 7.05 (dd,  $J$  = 7.2, 5.0 Hz, 2H), 5.62 (d,  $J$  = 6.2 Hz, 1H), 1.23 (s, 9H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  157.84, 155.86, 148.75, 136.87, 136.71, 126.99, 125.59, 122.52, 122.17, 62.08, 34.93, 31.00. HRMS electrospray (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{21}\text{H}_{24}\text{N}_3\text{O}_2\text{S}$ , 382.1584; found, 382.1584.



**Di-(2-pyridyl)phenylmethane** was obtained as described in *J. Organomet. Chem.* **1999**, *574*, 40–49.



**1,1-Di(2-pyridyl)phenylethane (dppe) (14).** Butyllithium (2.5 M in hexanes, 4.8 mL, 12.0 mmol) was slowly added to a cooled ( $-78^\circ\text{C}$ ) solution of dipyridylphenylmethane (2.50 g; 10.15 mmol) in dry THF (50 mL). The resulting suspension was warmed to  $-20^\circ\text{C}$  over the period of 1 h, and then methyl iodide (1.25 mL; 20.0 mmol) was added. The reaction mixture was stirred at rt for 3 h, then the volatiles were removed under reduced pressure. The resulting residue was suspended in diethyl ether, this suspension was filtered, and the filtrate was collected and concentrated under vacuum. The crude product was purified on a silica gel column (mobile phase: hexanes/EtOAc with gradient from 4/1 to 1/1) to yield thick oil that crystallized upon standing. Yield: 2.04 g (77%) of a colorless solid.  $\text{Mp} = 69\text{--}71^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.60 (d,  $J$  = 4.7 Hz, 2H), 7.55 (td,  $J$  = 8.0 and 1.6 Hz, 2H), 7.27 (m, 2H), 7.21 (m, 1H), 7.10 (multiple peaks, 4H), 7.05 (d,  $J$  = 8.0 Hz, 2H), 2.30 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  166.48, 148.77, 147.61, 135.85, 128.47, 128.06, 126.21, 123.48, 121.07, 57.56, 28.33. HRMS electrospray (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{18}\text{H}_{17}\text{N}_2$ , 261.1386; found, 261.1386.



**(MeO-dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1).** When the reaction of **8** with NFTPT was carried out under slightly different conditions, compound **S1** was formed as a minor by-product. The procedure that generated **S1** is as follows: (dpaa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (**8**) (150 mg; 0.30 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> (5 mL), and NFTPT (110 mg; 0.38 mmol) was added. The reaction mixture was stirred at rt for 20 min. The solvent was then removed under reduced pressure, and

the crude mixture was purified on a silica gel column that was eluted first with ethyl acetate, then with THF, and finally with 10 % methanol in THF. The major isomer **13a** eluted first followed by the minor side product **S1**. Both products **13a** (60 mg; 39%) and **S1** (38 mg; 24%) were obtained as yellow powders. Analytical data for **S1**:  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  8.88 (d,  $J = 5.2$  Hz, 1H), 8.25 (d,  $J = 5.2$  Hz, 1H), 7.93 (multiple peaks, 3H), 7.74 (d,  $J = 7.9$  Hz, 1H), 7.41 (m, 1H), 7.28 (multiple peaks, 3H), 6.92 (d,  $J = 8.1$  Hz, 2H), 3.16 (s, 3H), 2.32 (s, 3H), 1.86 (s, 3H).  $^{13}\text{C}\{\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  182.17, 158.95, 158.58, 152.52 (m), 147.98, 147.86, 140.42, 140.11, 135.98, 132.04, 132.00, 129.12, 125.04, 124.50, 121.34, 120.94, 116.81 (q,  $J = 378$  Hz), 99.87, 52.69, 26.11 (m), 20.56.  $^{19}\text{F}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  -284.40 (s), -25.58 (s). HRMS electrospray (m/z):  $[\text{M} + \text{H}]^+$  calcd for  $\text{C}_{22}\text{H}_{22}\text{F}_4\text{N}_3\text{O}_2\text{Pd}$ , 542.0678; found, 542.0678.

<sup>1</sup>H NMR of (4-MePy)<sub>2</sub>Pd(4-MeC<sub>6</sub>H<sub>4</sub>)(I) (2)

STANDARD 1H OBSERVE - profile

Sample Name:

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Ga.Chem.LSA.UMich.edu-vnmrs400  
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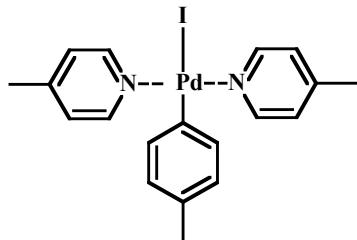
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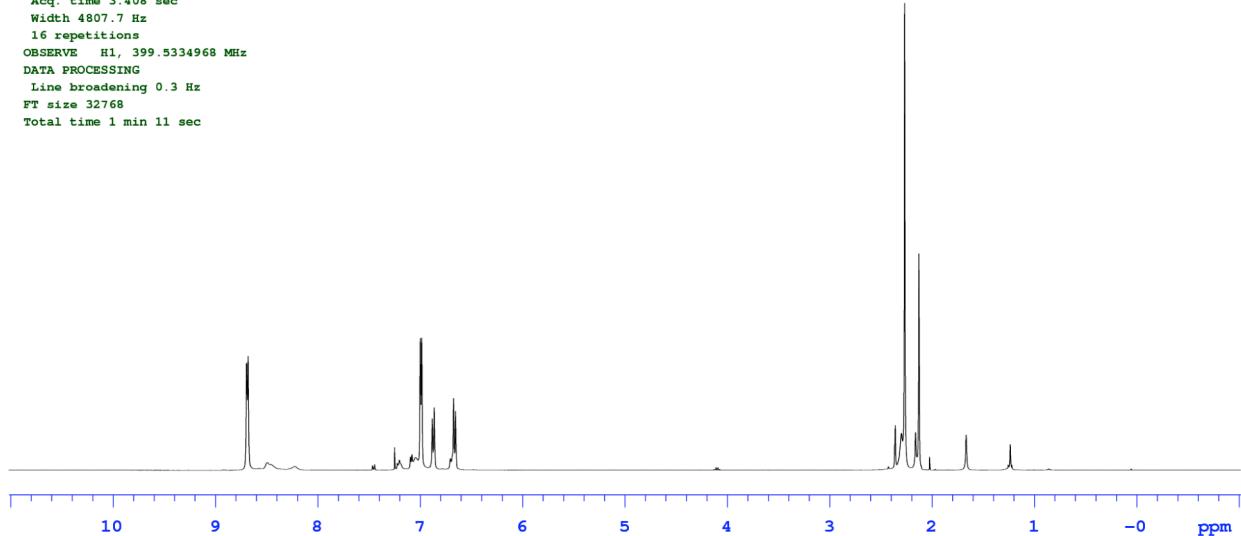
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Solvent: cdcl3  
Data collected on: May 8 2011

Operator: maleckis

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Width 4807.7 Hz  
16 repetitions  
OBSERVE H1, 399.5334968 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 32768  
Total time 1 min 11 sec



VARIAN



$^{13}\text{C}\{\text{H}\}$  NMR of  $(\text{4-MePy})_2\text{Pd}(\text{4-MeC}_6\text{H}_4)(\text{I})$  (2)

STANDARD 1H OBSERVE - profile

Sample Name:

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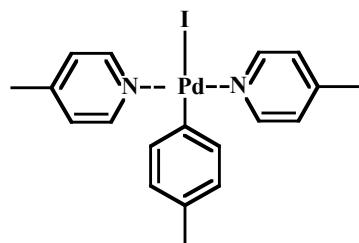
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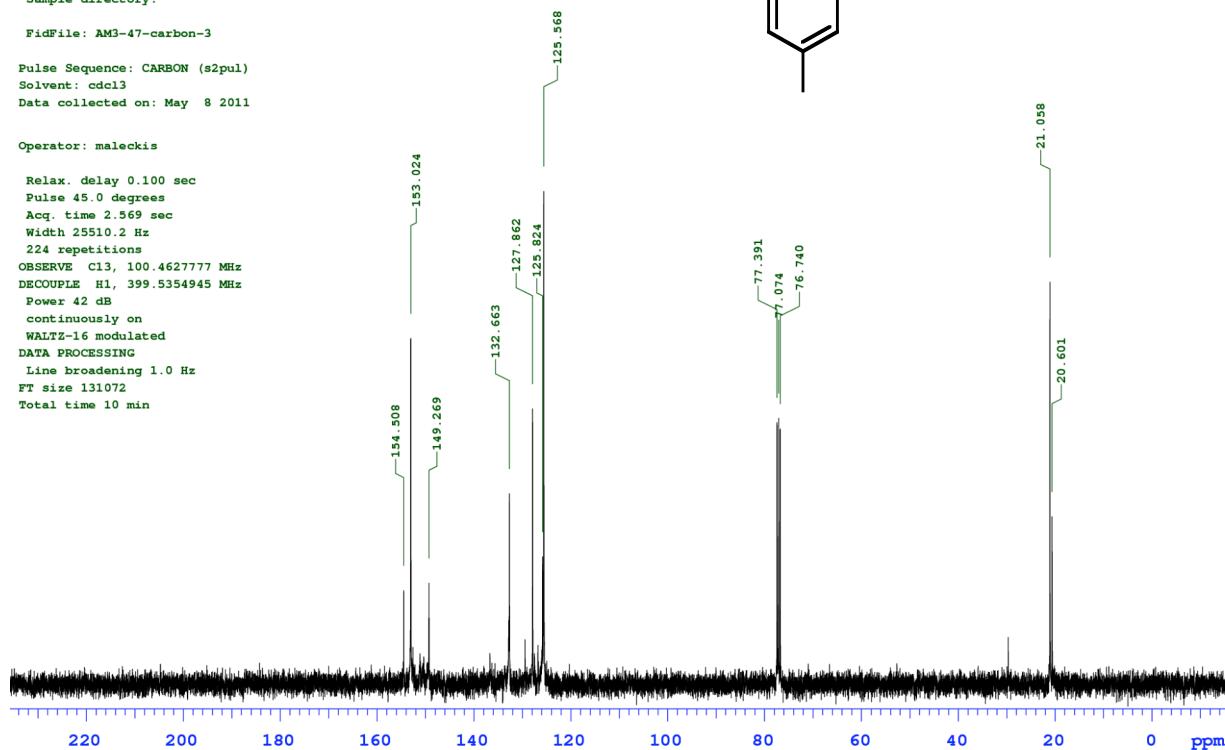
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Data collected on: May 8 2011

Operator: malekis

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224 repetitions  
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DECOUPLE H1, 399.5354945 MHz  
Power 42 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 10 min



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<sup>1</sup>H NMR of (4-MePy)<sub>2</sub>Pd(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (1)

STANDARD PROTON PARAMETERS

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Data Collected on:  
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Archive directory:

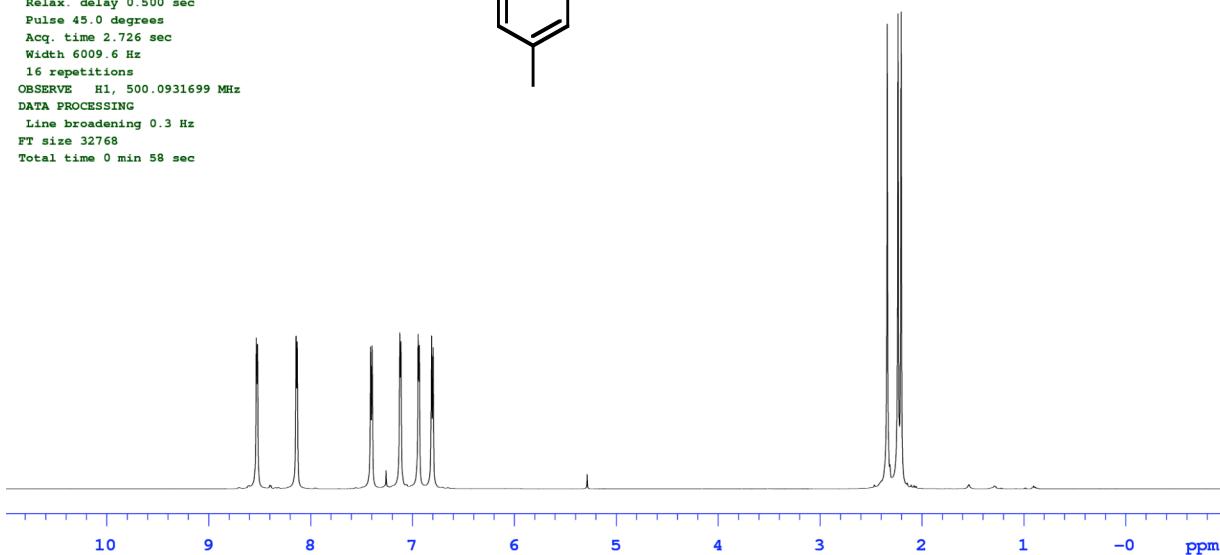
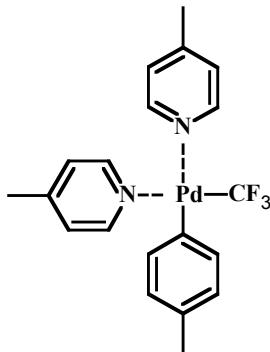
Sample directory:

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Solvent: cdcl3  
Data collected on: May 4 2011

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Operator: maleckis

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Width 6009.6 Hz  
16 repetitions  
OBSERVE H1, 500.0931699 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 32768  
Total time 0 min 58 sec



### $^{13}\text{C}\{\text{H}\}$ NMR of $(\text{4-MePy})_2\text{Pd}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)$ (**1**)

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
Te.Chem.LSA.UMich.edu-vnmrs500  
Archive directory:

Sample directory:

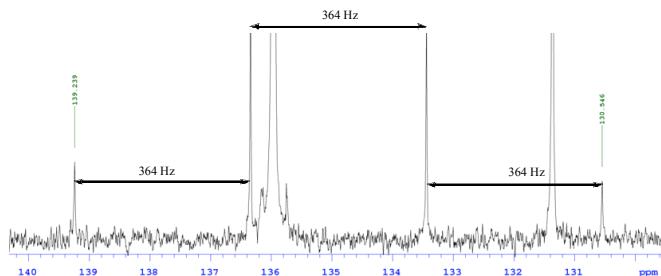
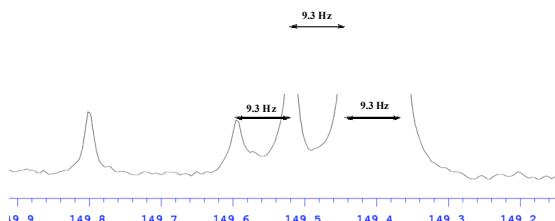
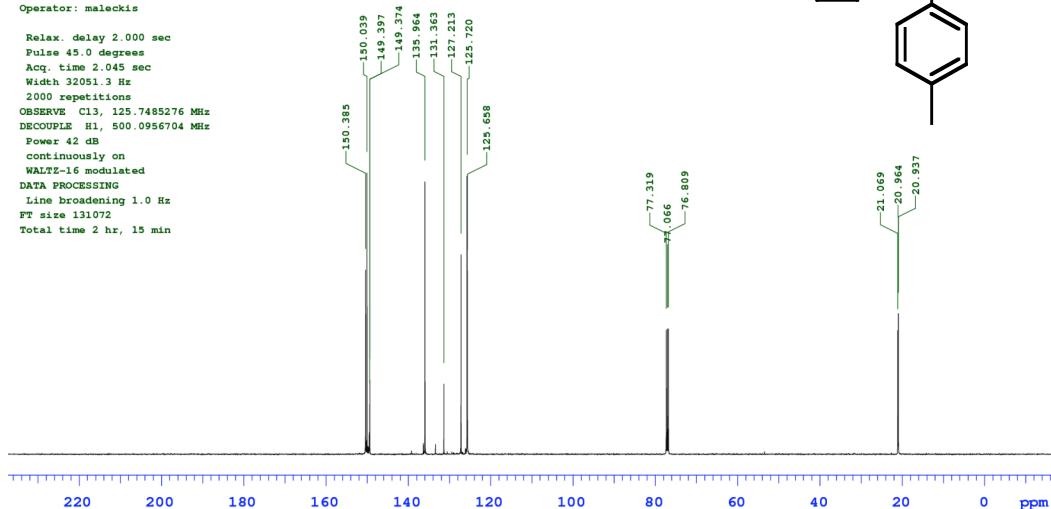
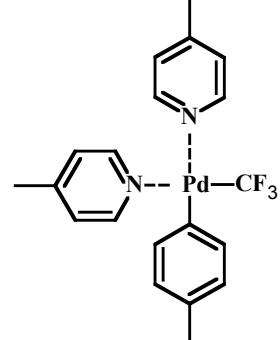
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Data collected on: May 4 2011

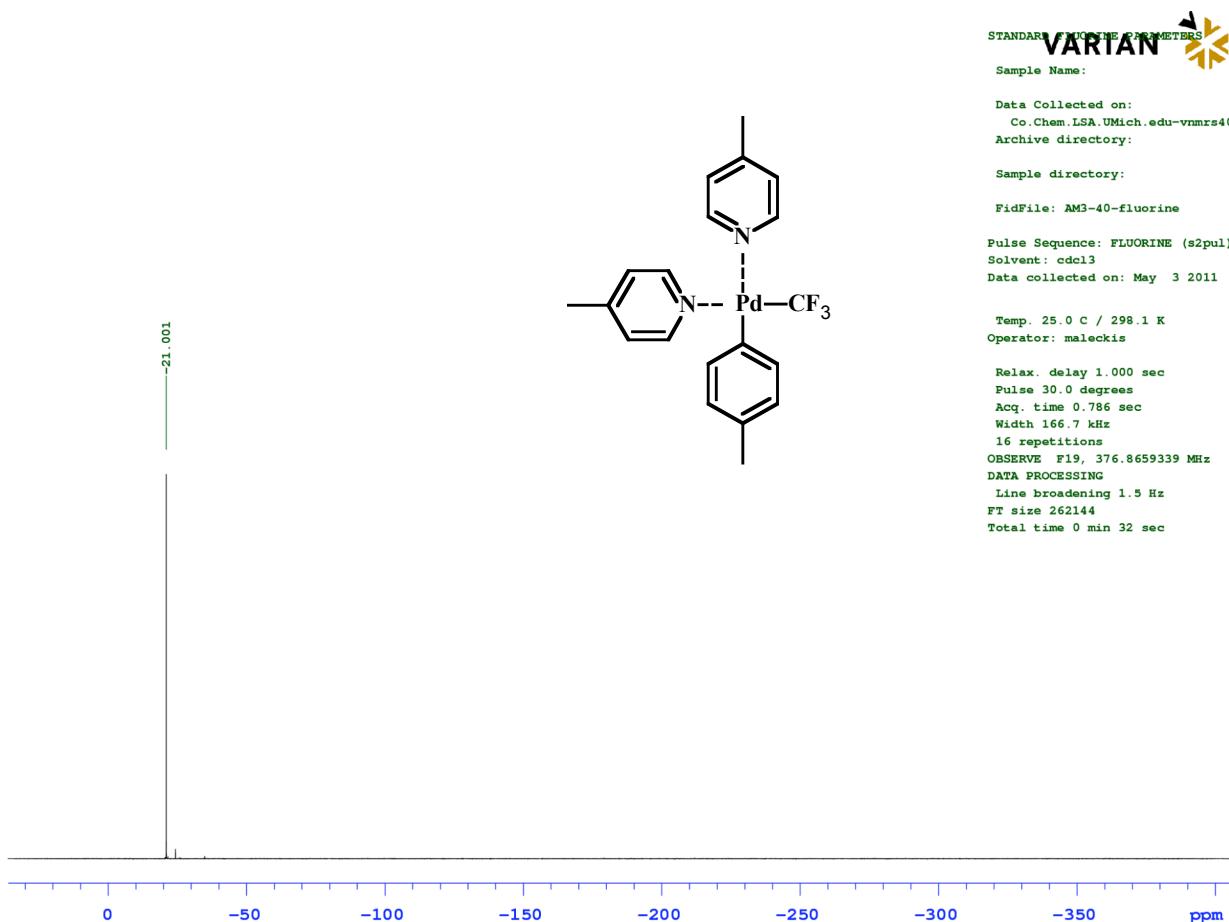
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continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 2 hr, 15 min

VARIAN



<sup>19</sup>F NMR of (4-MePy)<sub>2</sub>Pd(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (**1**)



<sup>1</sup>H NMR of (Tp)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (4)

VARIAN

STANDARD PROTON PARAMETERS  
Atropine

Sample Name:

Data Collected on:

Yb-vnmrs700

Archive directory:

Sample directory:

FidFile: AM3-114

Pulse Sequence: PROTON (s2pul)

Solvent: cdc13

Data collected on: Jun 9 2011

Temp. 26.0 C / 299.1 K

Operator: maleckis

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 11261.3 Hz

16 repetitions

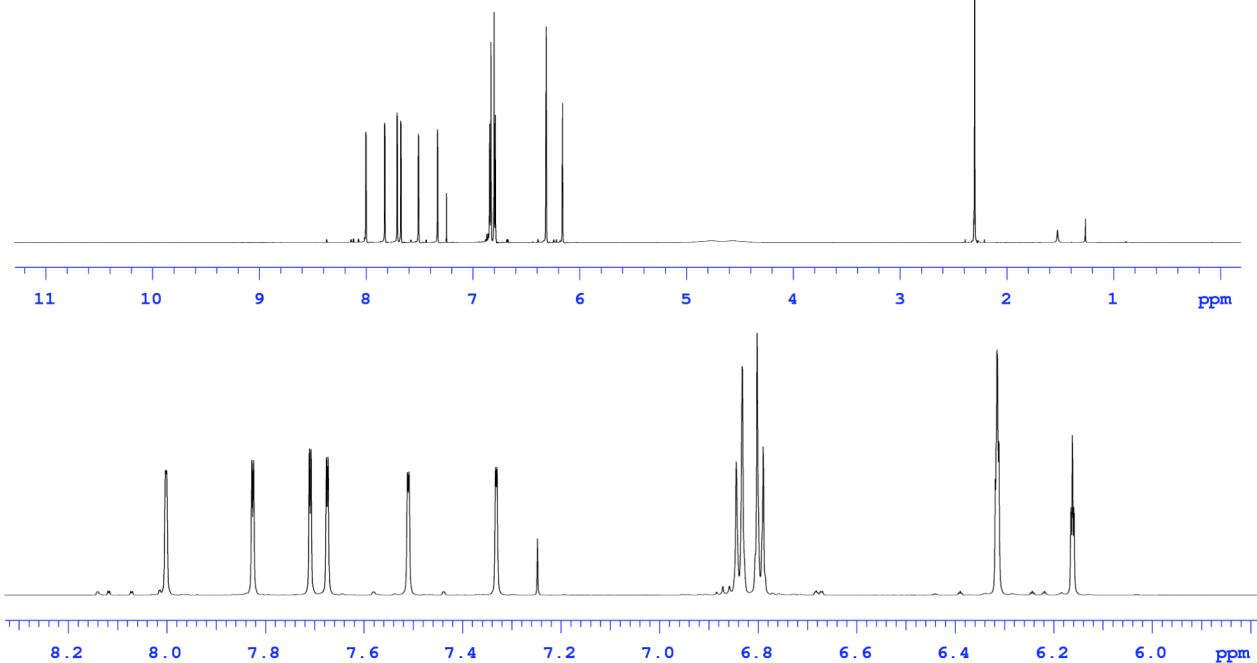
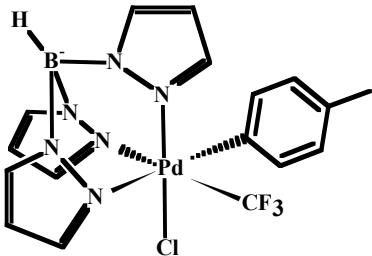
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DATA PROCESSING

Line broadening 0.3 Hz

FT size 131072

Total time 1 min 12 sec



$^{13}\text{C}\{\text{H}\}$  NMR of (Tp)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**4**)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN

Sample Name:

Data Collected on:  
Yb-vnmrs700

Archive directory:

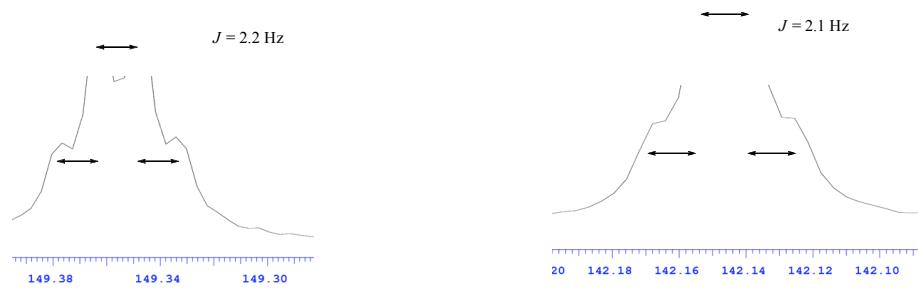
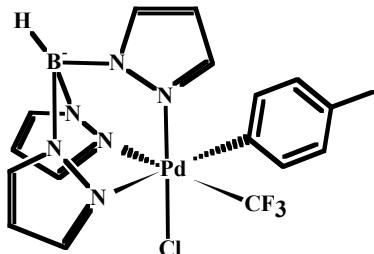
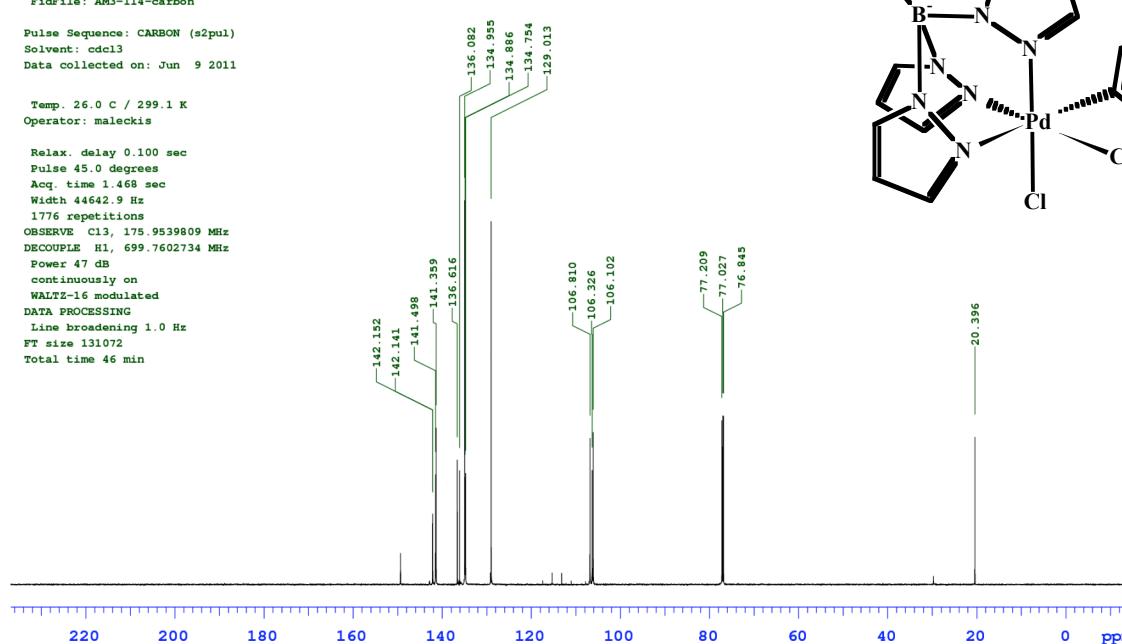
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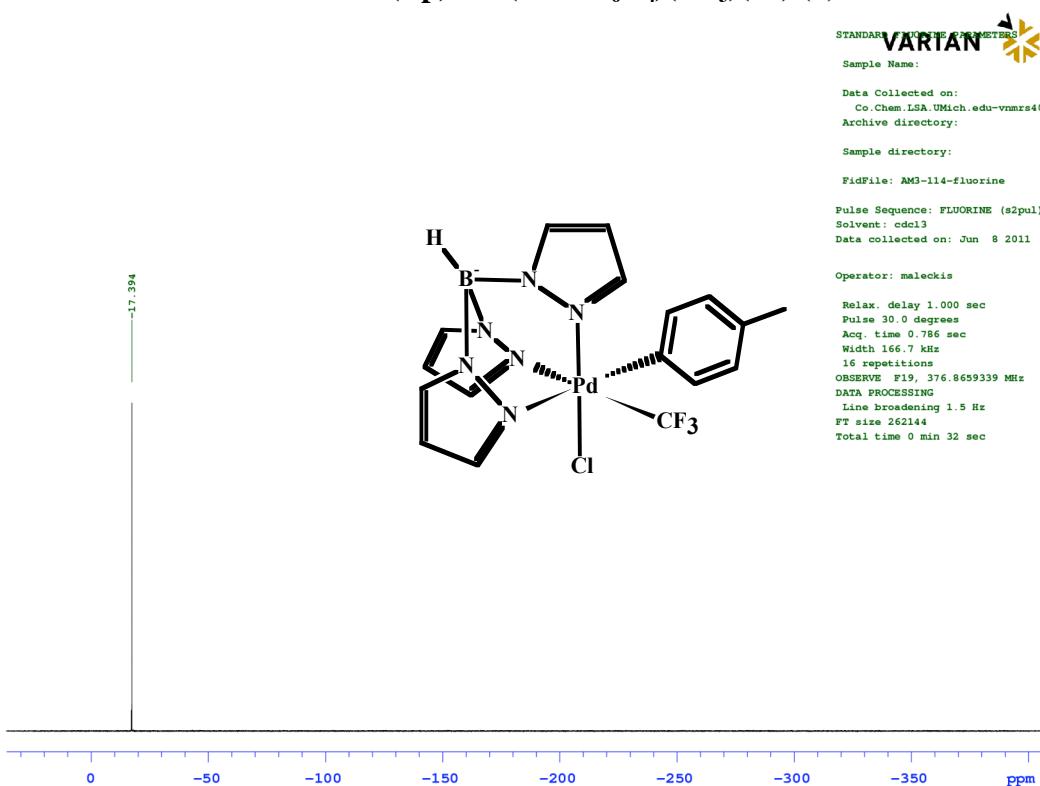
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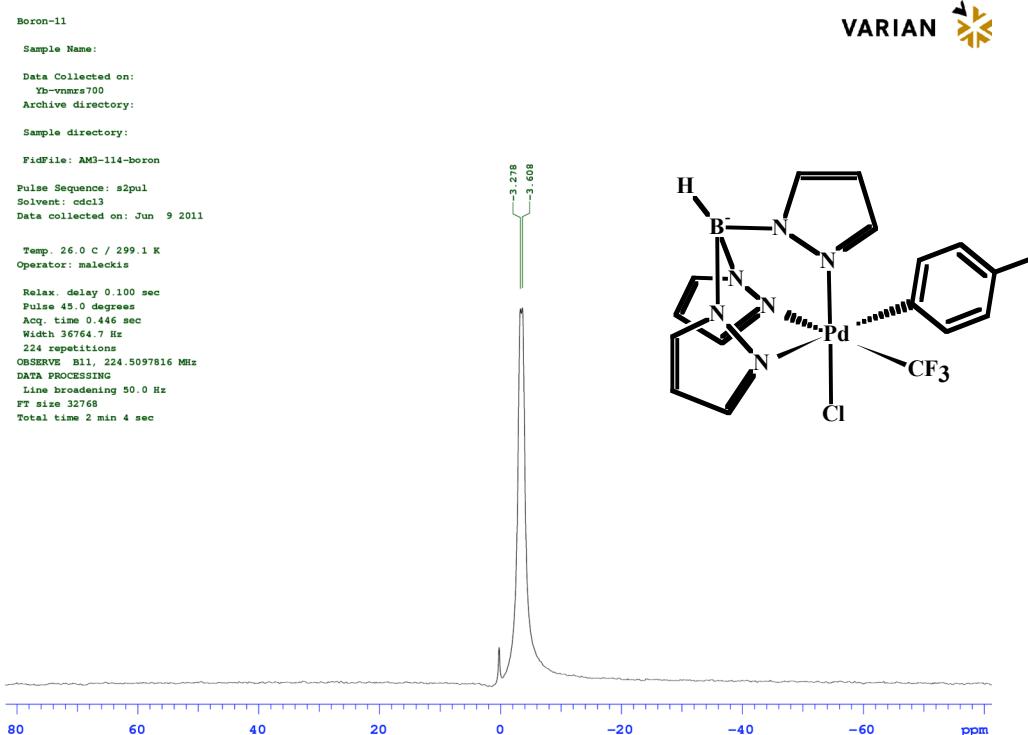


$J = 376 \text{ Hz}$

**<sup>19</sup>F NMR of (Tp)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (4)**



**<sup>11</sup>B NMR of (Tp)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (4)**



# <sup>1</sup>H NMR of *N*-di(2-pyridyl)methylacetamide (dpaa) (6)

STANDARD 1H OBSERVE - profile

Sample Name:

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

Sample directory:

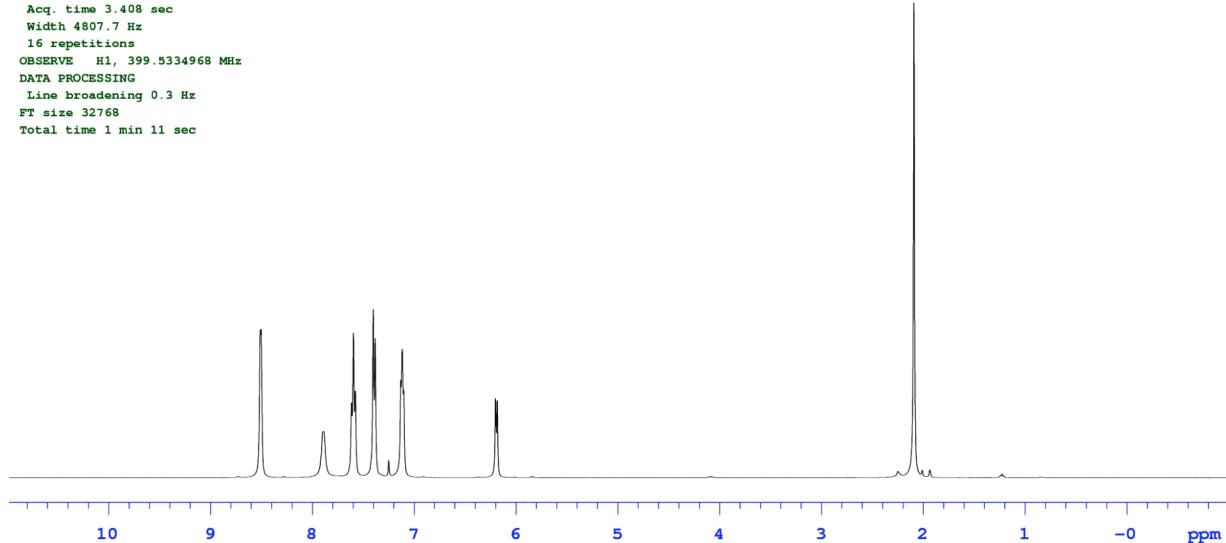
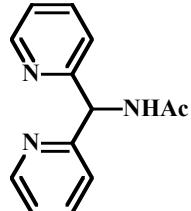
FidFile: AM3-31

Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: Apr 29 2011

Operator: maleckis

Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 3.408 sec  
Width 4807.7 Hz  
16 repetitions  
OBSERVE H1, 399.5334968 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
Ft size 32768  
Total time 1 min 11 sec

VARIAN 



<sup>13</sup>C{<sup>1</sup>H} NMR of *N*-di(2-pyridyl)methylacetamide (dpaa) (6)

STANDARD 1H OBSERVE - profile

Sample Name:

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

Archive directory:

Sample directory:

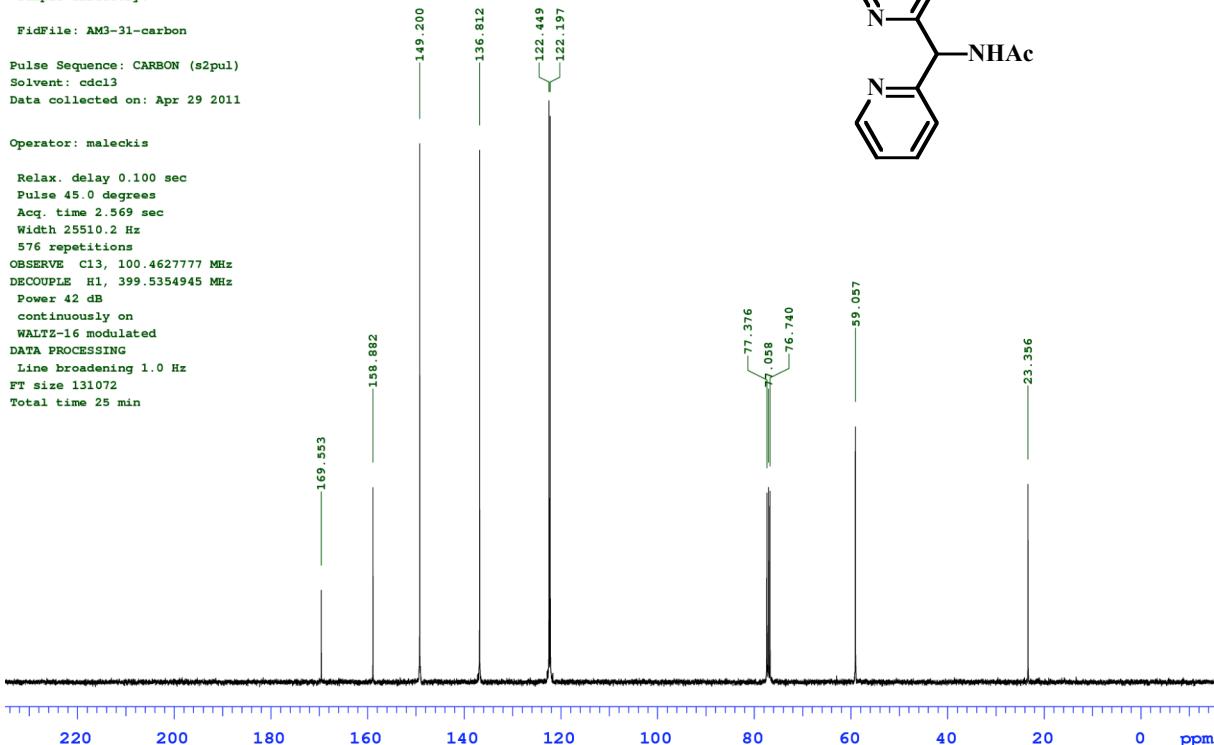
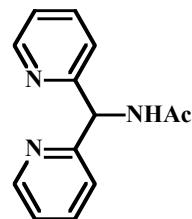
FidFile: AM3-31-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Apr 29 2011

Operator: maleckis

Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 2.569 sec  
Width 25510.2 Hz  
576 repetitions  
OBSERVE Cl3, 100.4627777 MHz  
DECOUPLE H1, 399.5354945 MHz  
Power 42 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 25 min

VARIAN 



**<sup>1</sup>H NMR of 4-*tert*-Butyl-N-[di(pyridin-2-yl)methyl]benzenesulfonamide (dpsa) (7)**

STANDARD 1H OBSERVE - profile

Sample Name:

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

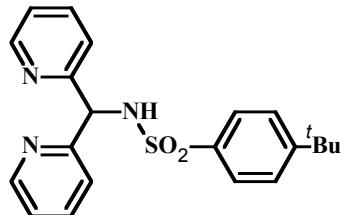
Sample directory:

FidFile: AM3-160

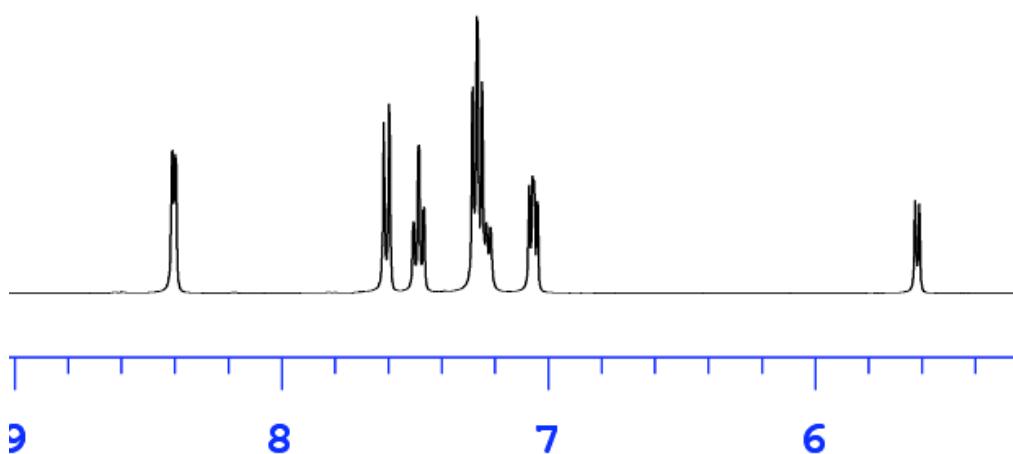
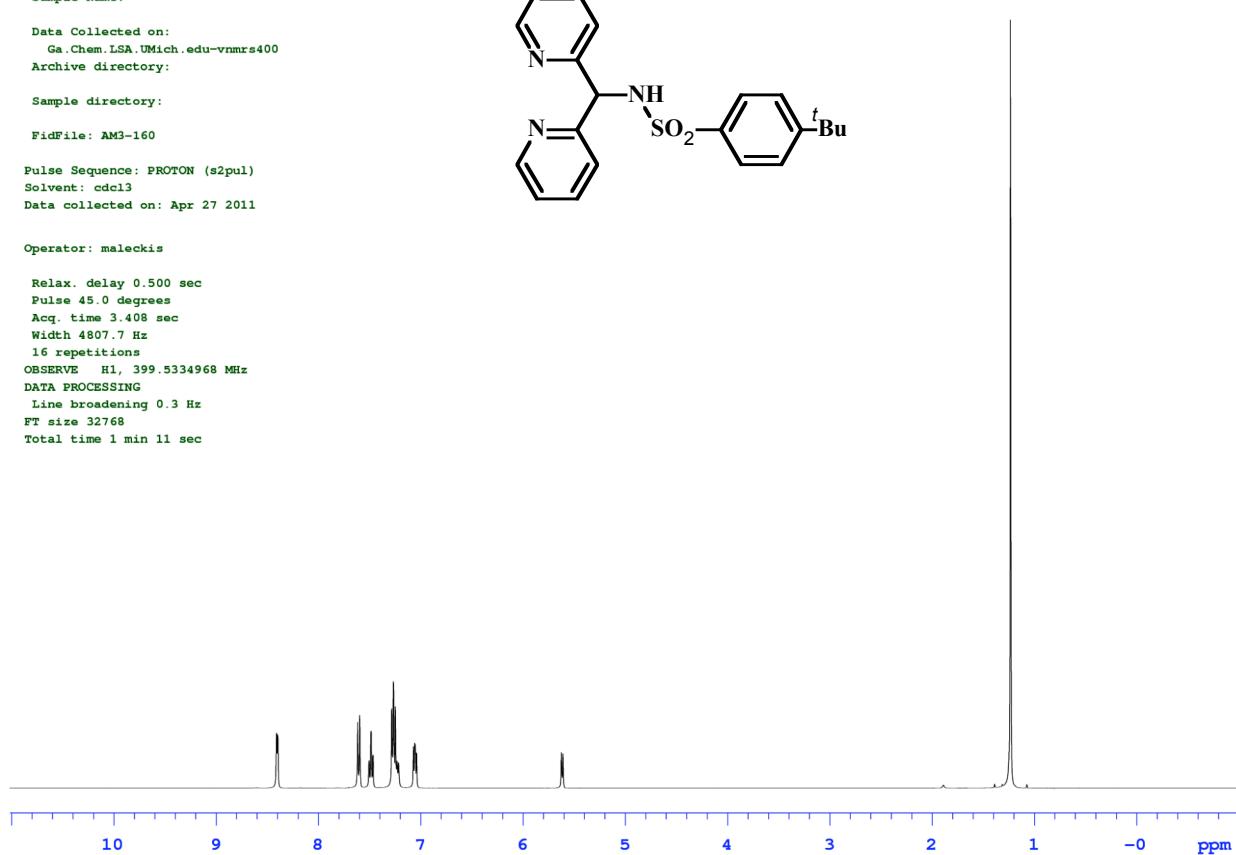
Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: Apr 27 2011

Operator: malekis

Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 3.408 sec  
Width 4807.7 Hz  
16 repetitions  
OBSERVE H1, 399.5334968 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 32768  
Total time 1 min 11 sec



VARIAN 



$^{13}\text{C}\{^1\text{H}\}$  NMR of 4-*tert*-Butyl-N-[di(pyridin-2-yl)methyl]benzenesulfonamide (dpsa) (7)

STANDARD 1H OBSERVE - profile

VARIAN 

Sample Name:

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

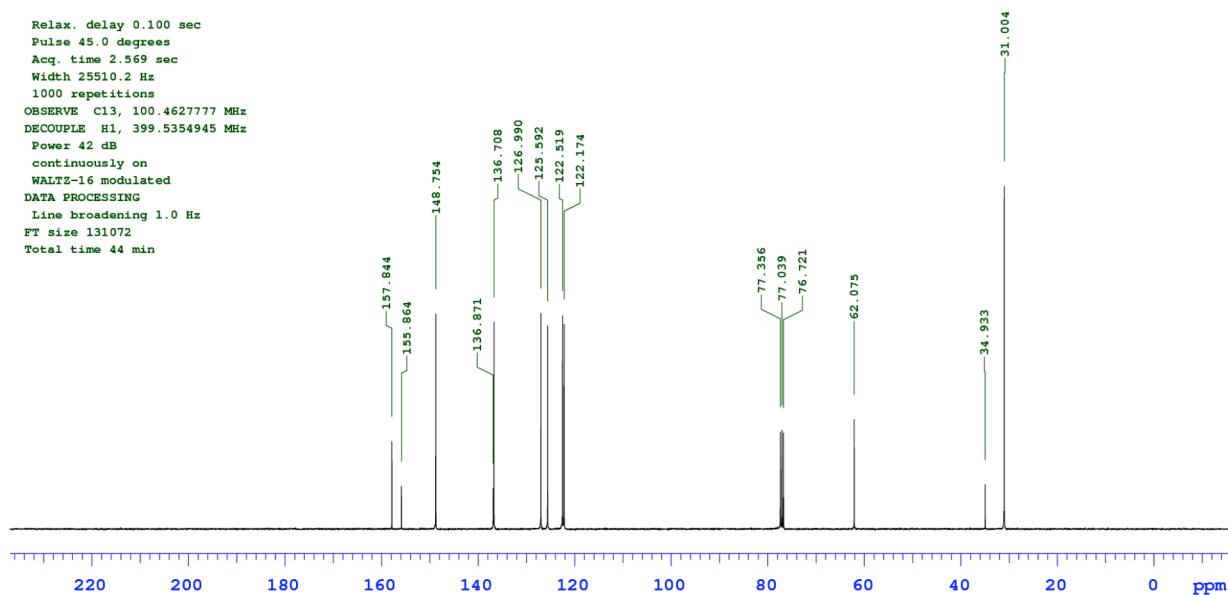
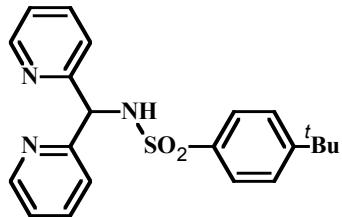
Sample directory:

FidFile: AM3-160-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Date collected on: Apr 27 2011

Operator: maleckis

Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acc. time 2.569 sec  
Width 25510.2 Hz  
1000 repetitions  
OBSERVE C13, 100.4627777 MHz  
DECOUPLE H1, 399.5354945 MHz  
Power 42 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 44 min



<sup>1</sup>H NMR of (dpaa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (8)

STANDARD FLUORINE PARAMETERS

Sample Name:

Data Collected on:

Te-vnmrs500

Archive directory:

Sample directory:

FidFile: AM3-43

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl<sub>3</sub>

Data collected on: May 15 2011

Temp. 25.0 C / 298.1 K

Operator: maleckis

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 2.726 sec

Width 6009.6 Hz

16 repetitions

OBSERVE H1, 500.0931699 MHz

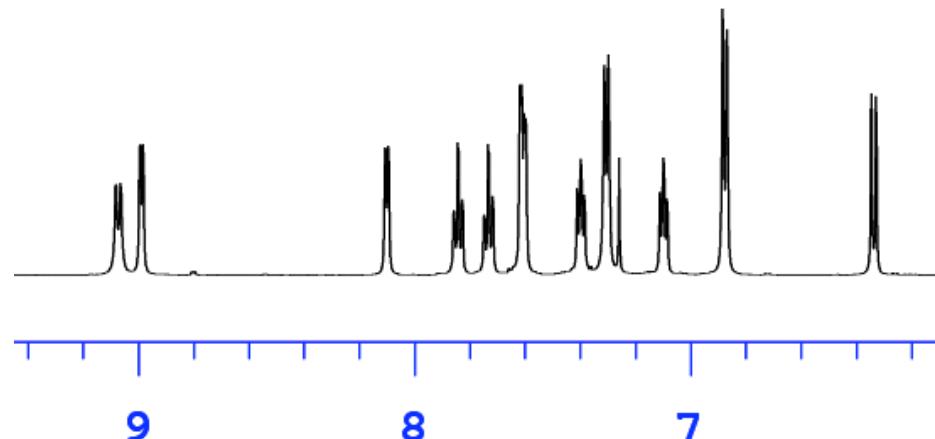
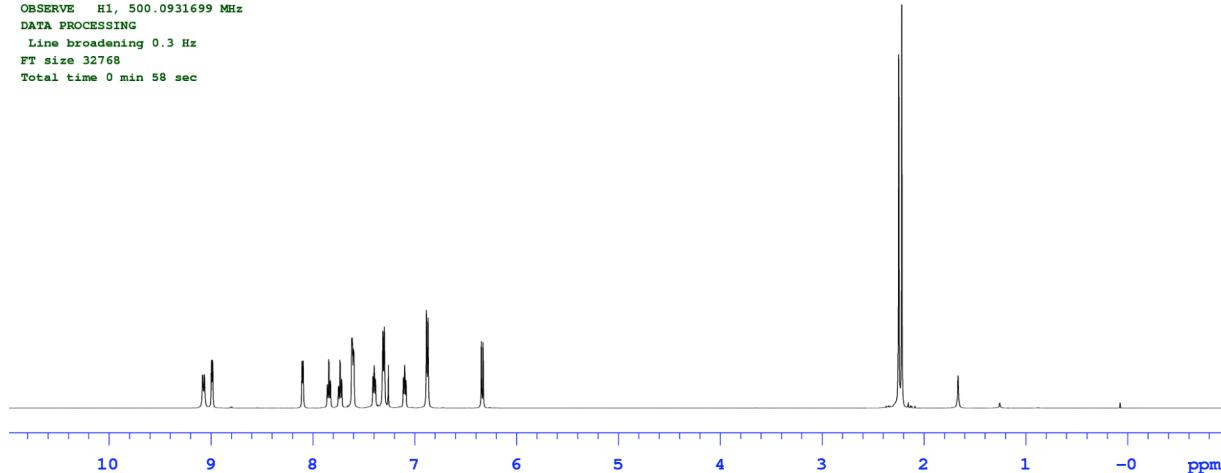
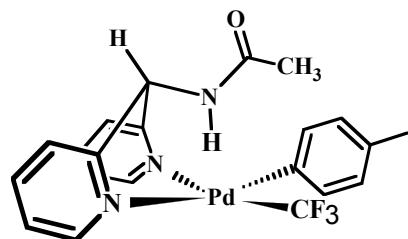
DATA PROCESSING

Line broadening 0.3 Hz

FT size 32768

Total time 0 min 58 sec

VARIAN 



<sup>13</sup>C{<sup>1</sup>H} NMR of (dpaa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (8)

STANDARD FLUORINE PARAMETERS

Sample Name:

Data Collected on:

Te-vnmrs500

Archive directory:

Sample directory:

FidFile: AM3-43-carbon

Pulse Sequence: CARBON (s2pul)

Solvent: cdcl<sub>3</sub>

Data collected on: May 15 2011

Temp: 25.0 C / 298.1 K

Operator: maleckis

Relax. delay 0.100 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 32051.3 Hz

3104 repetitions

OBSERVE C13, 125.7485276 MHz

DECOUPLE H1, 500.0956704 MHz

Power 42 dB

continuously on

WALTZ-16 modulated

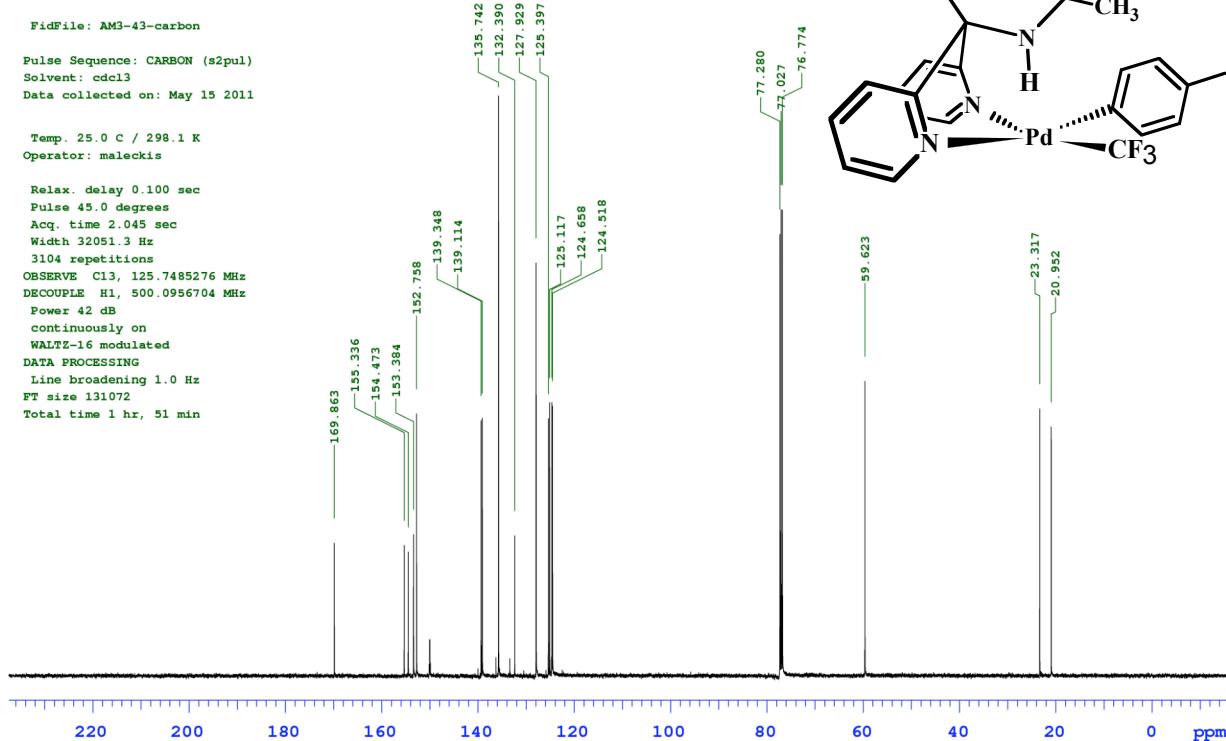
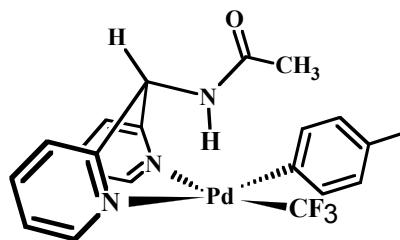
DATA PROCESSING

Line broadening 1.0 Hz

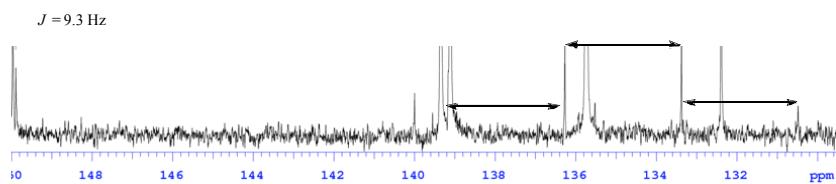
FT size 131072

Total time 1 hr, 51 min

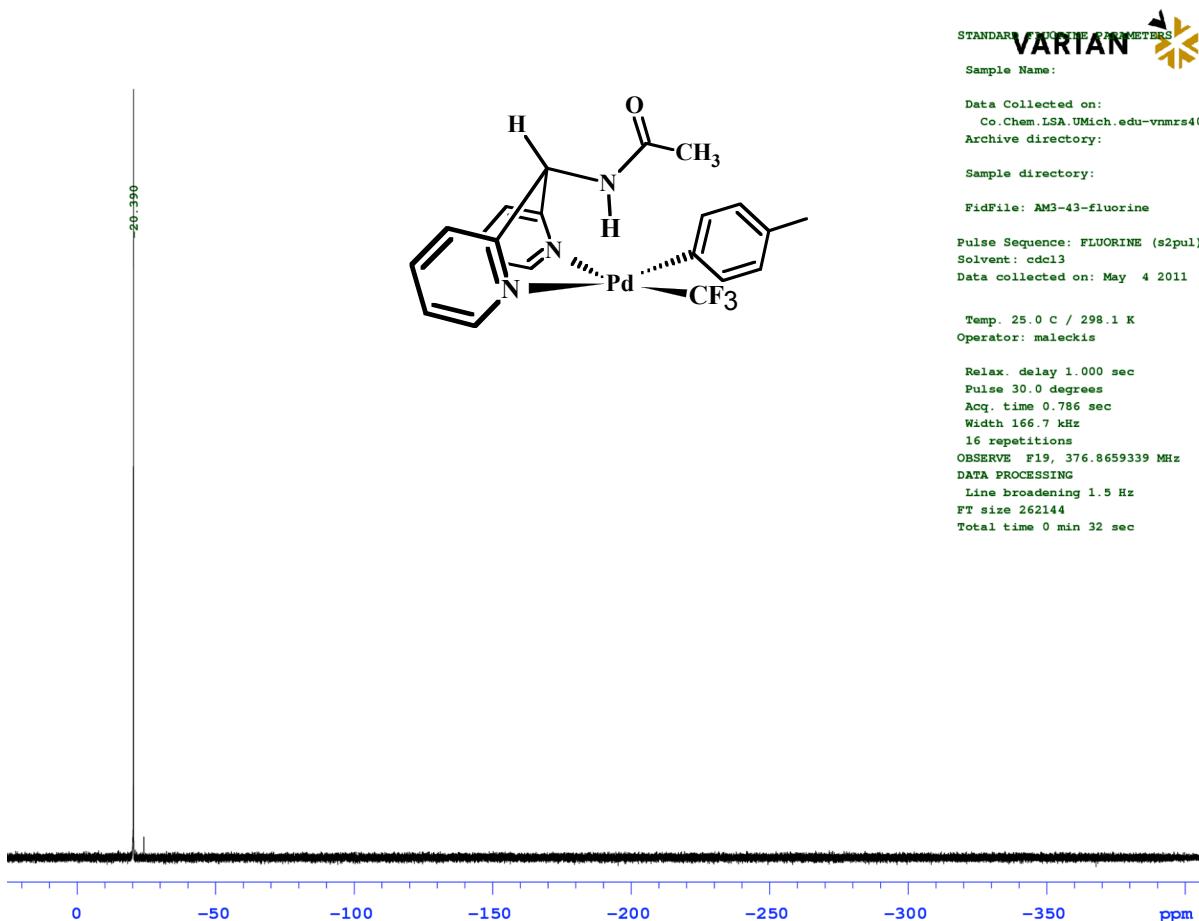
VARIAN



*J* = 363 Hz



<sup>19</sup>F NMR of (dpaa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (8)



<sup>1</sup>H/<sup>1</sup>H COSY NMR of (dpaa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (8)

STANDARD PROTON PARAMETERS  
Atropine

Sample Name:

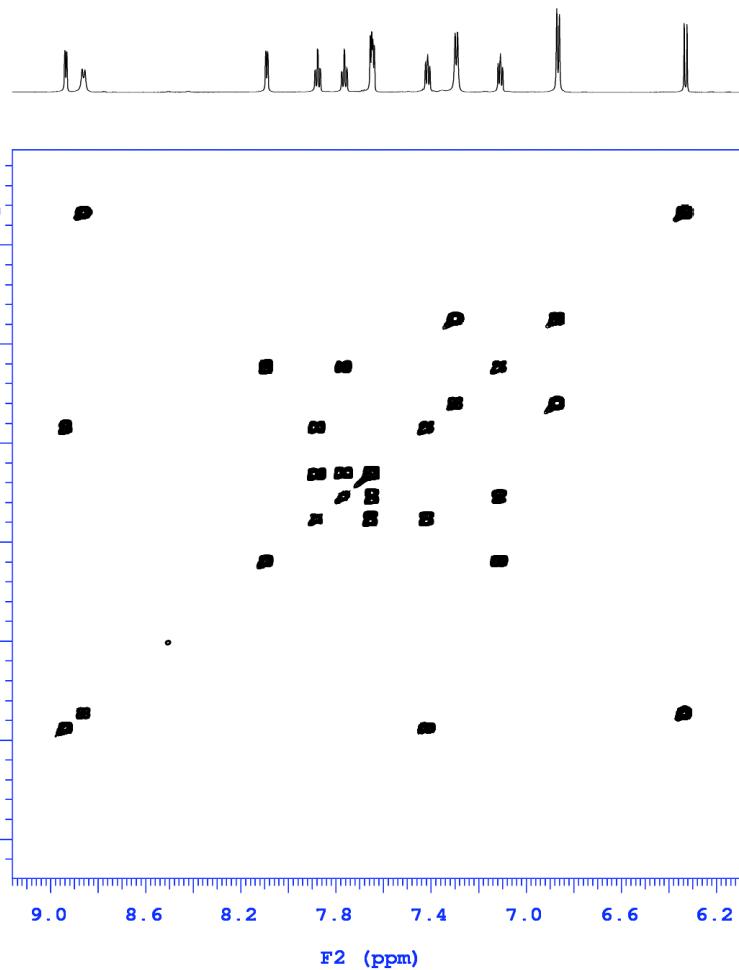
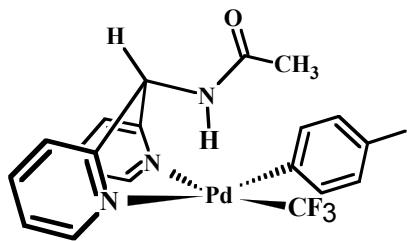
Data Collected on:  
Yb-vnmrs700  
Archive directory:

Sample directory:

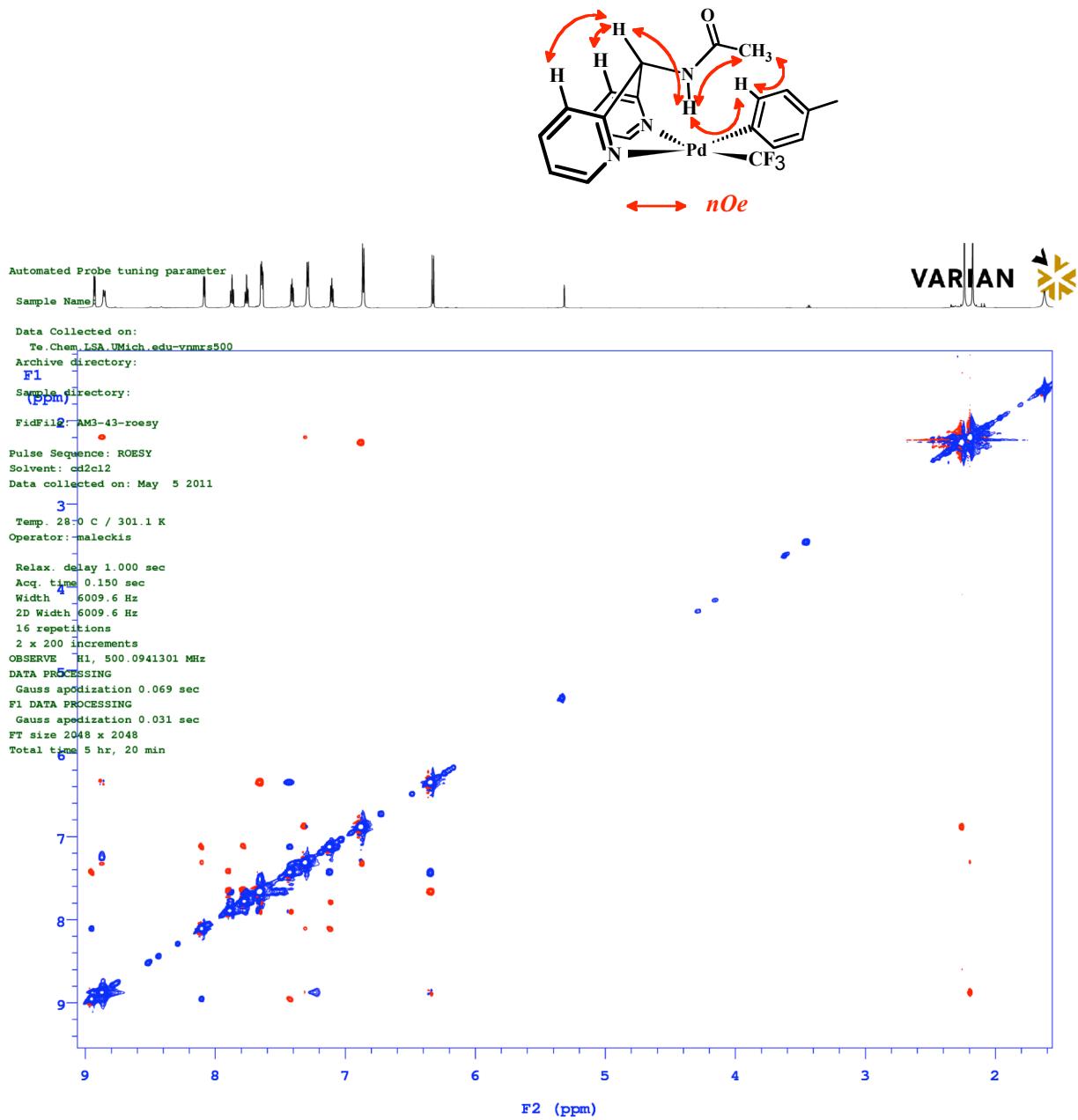
FidFile: AM3-43-cosy

Pulse Sequence: COSY  
Solvent: cd2cl2  
Data collected on: May 5 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis  
Relax. delay 1.000 sec  
Mixing 0.080 sec  
Acq. time 0.150 sec  
Width 8445.9 Hz  
2D Width 8445.9 Hz  
2 repetitions  
512 increments  
OBSERVE H1, 699.7581182 MHz  
DATA PROCESSING  
Sq. sine bell 0.061 sec  
F1 DATA PROCESSING  
Sq. sine bell 0.061 sec  
FT size 4096 x 4096  
Total time 21 min



<sup>1</sup>H/<sup>1</sup>H ROESY NMR of (dpaa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (8)

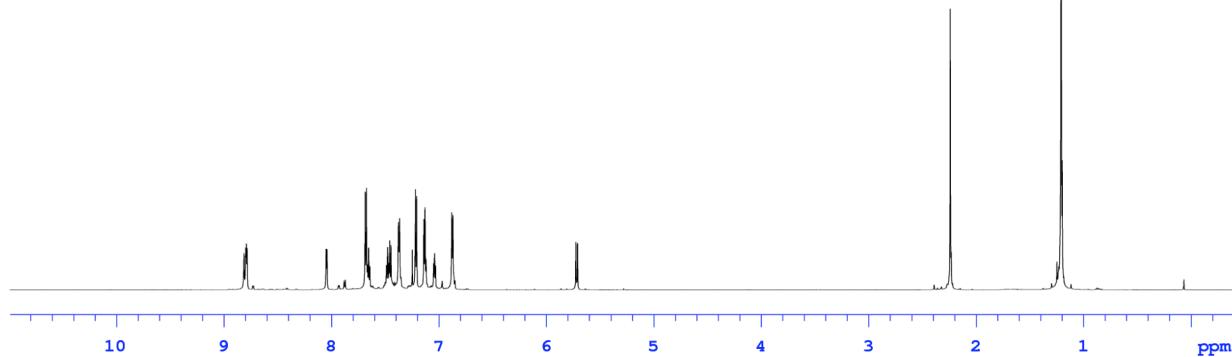
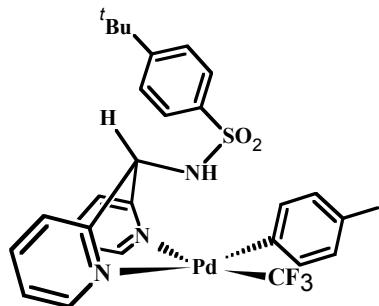


<sup>1</sup>H NMR of (dpsa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (**9**) (in CDCl<sub>3</sub> solvent)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN 

Sample Name:  
Data Collected on:  
Yb-vnmrs700  
Archive directory:  
Sample directory:  
FidFile: AM3-62  
Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: May 16 2011  
  
Temp. 24.0 C / 297.1 K  
Operator: maleckis  
  
Relax. delay 5.000 sec  
Pulse 45.0 degrees  
Acq. time 3.500 sec  
Width 11261.3 Hz  
16 repetitions  
OBSERVE H1, 699.7567747 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 131072  
Total time 2 min 33 sec



$^{13}\text{C}\{^1\text{H}\}$  NMR of (dpsa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (9) (in CDCl<sub>3</sub> solvent)

STANDARD FLUORINE PARAMETERS

Sample Name:

Data Collected on:  
Te-vnmrs500

Archive directory:

Sample directory:

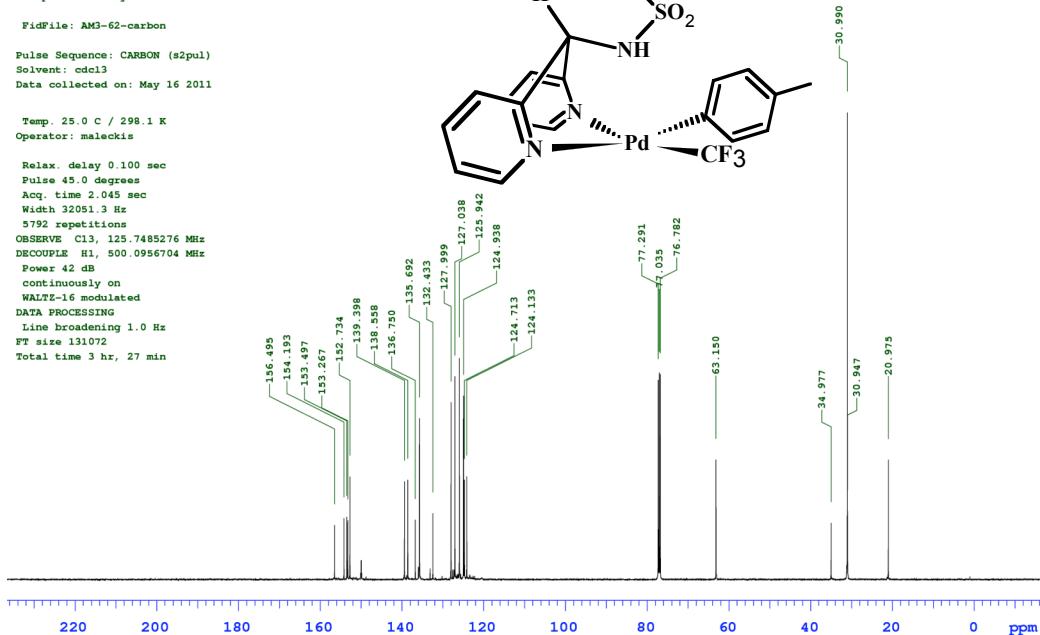
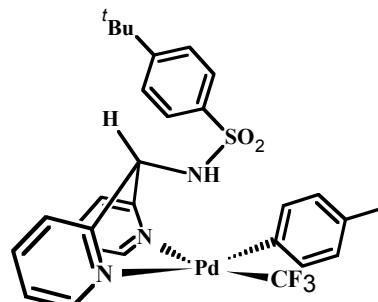
FidFile: AM3-62-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdc13  
Data collected on: May 16 2011

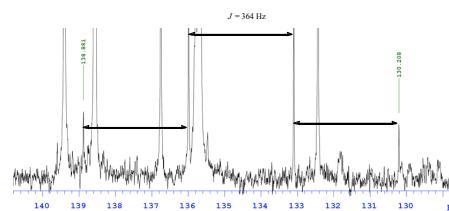
Temp. 25.0 C / 298.1 K  
Operator: maleckis

Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acc. time 2.045 sec  
Width 32051.3 Hz  
5792 repetitions  
OBSERVE Cl3, 125.7485276 MHz  
DECOUPLE H1, 500.0956704 MHz  
Power 42 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 3 hr, 27 min

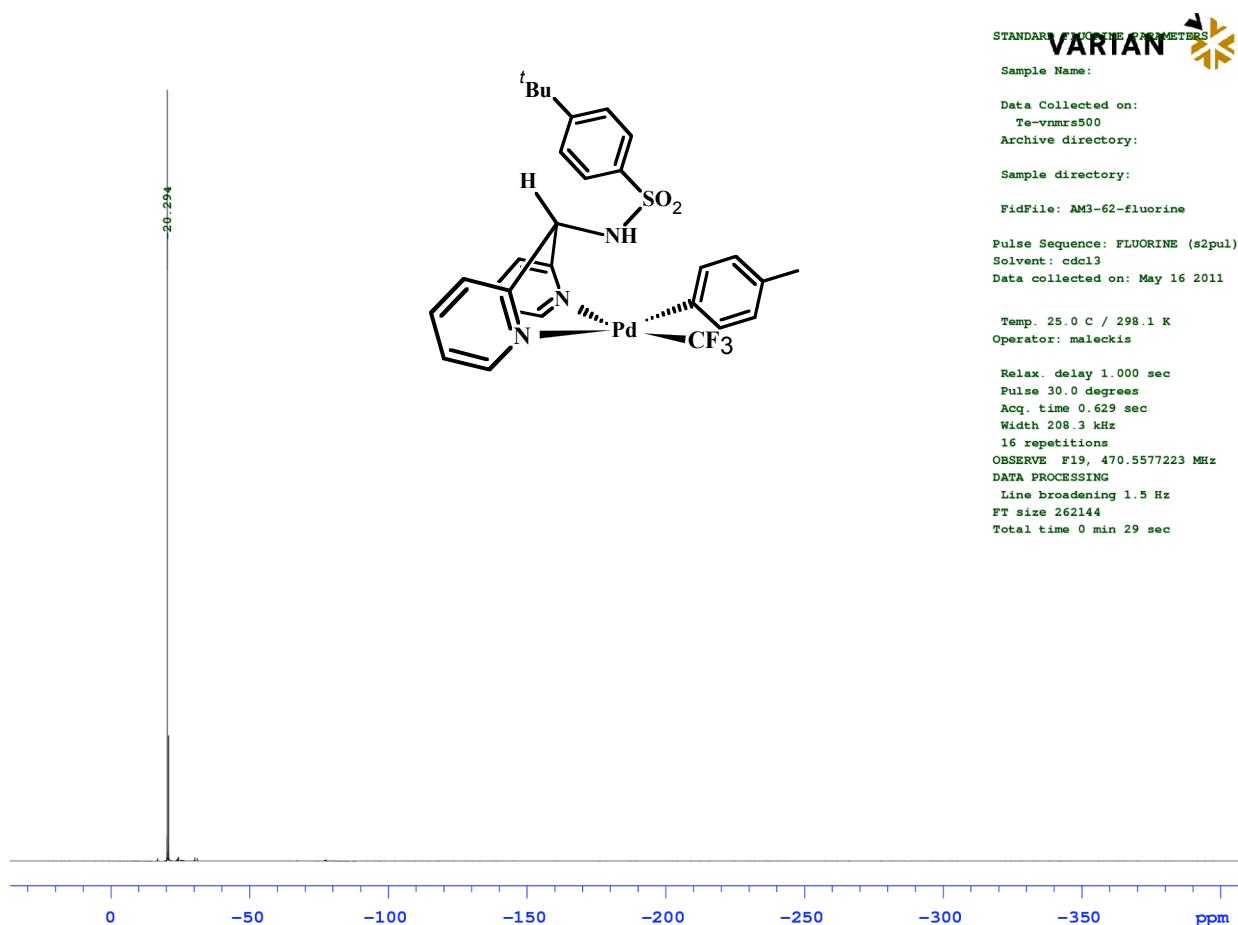
VARIAN



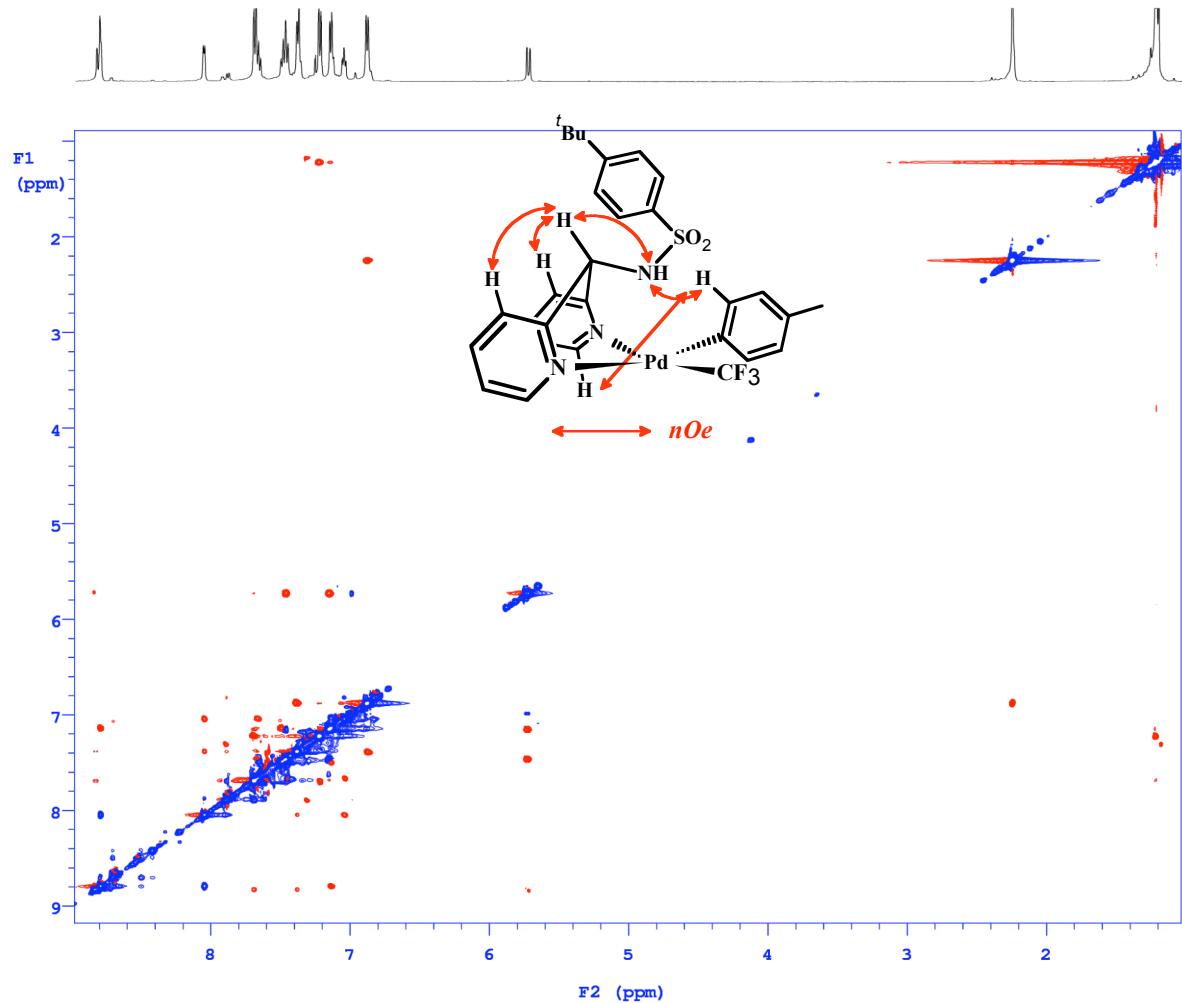
$J = 9.4 \text{ Hz}$



<sup>19</sup>F NMR of (dpsa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (9)



<sup>1</sup>H/<sup>1</sup>H ROESY of (dpsa)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (9)



<sup>1</sup>H NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (10)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN 

Sample Name:

Data Collected on:

Yb-vnmrs700

Archive directory:

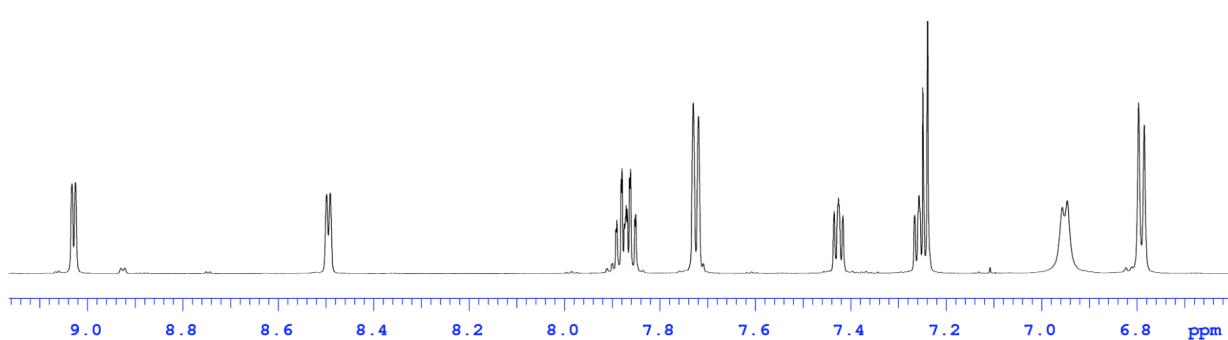
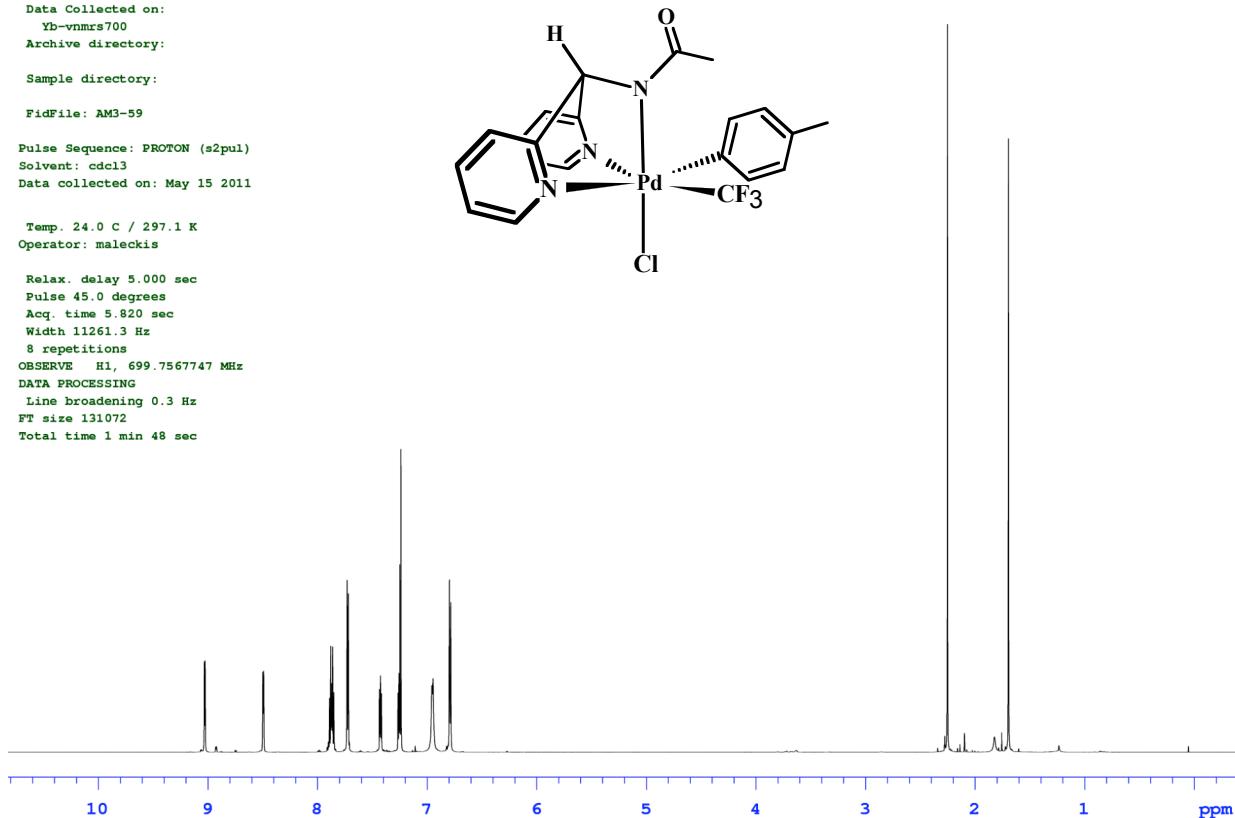
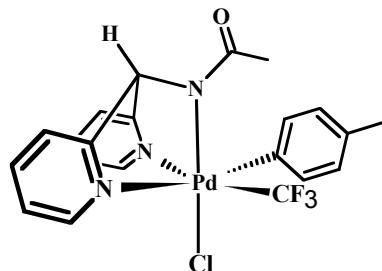
Sample directory:

FidFile: AM3-59

Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: May 15 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

Relax. delay 5.000 sec  
Pulse 45.0 degrees  
Acq. time 5.820 sec  
Width 11261.3 Hz  
8 repetitions  
OBSERVE H1, 699.7567747 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 131072  
Total time 1 min 48 sec



<sup>13</sup>C{<sup>1</sup>H} NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (10)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN \*

Sample Name:

Data Collected on:  
Yb-vnmrs700

Archive directory:

Sample directory:

File: AM3-59-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: May 15 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

Relax. delay 0.100 sec

Pulse 45.0 degrees

Acq. time 1.468 sec

Width 44642.9 Hz

4320 repetitions

OBSERVE: C13, 175.9839809

DECOUPLE: H1, 699.7602734 MHz

Power 47 dB

continuously on

WALTZ-16 modulation

DATA PROCESSING

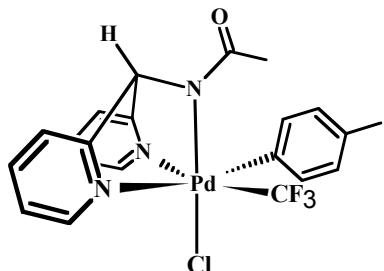
Line broadening 1.3

FT size 131072

Total time 1 hr, 53 min

<sup>19</sup>F NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (10)

STANDARD FOR DETERMINING PARAMETERS  
**VARIAN**   
Sample Name:



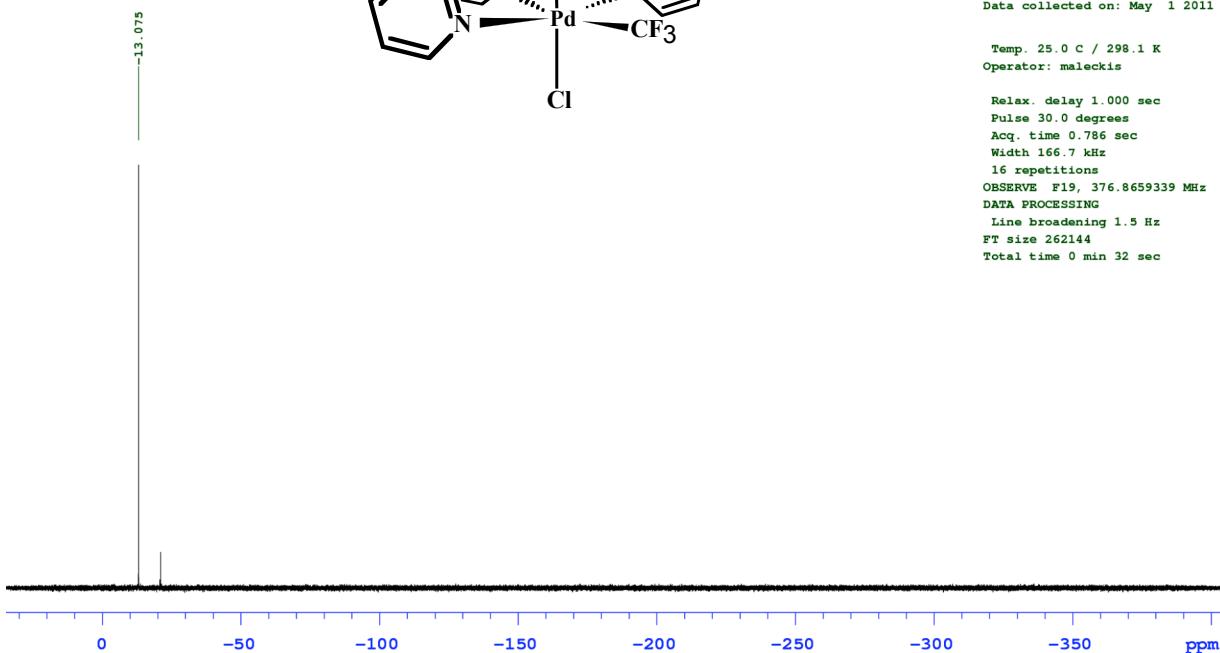
Data Collected on:  
Co.Chem.LSA.UMich.edu-vnmrs400  
Archive directory:

Sample directory:  
FidFile: AM3-37-fluorine

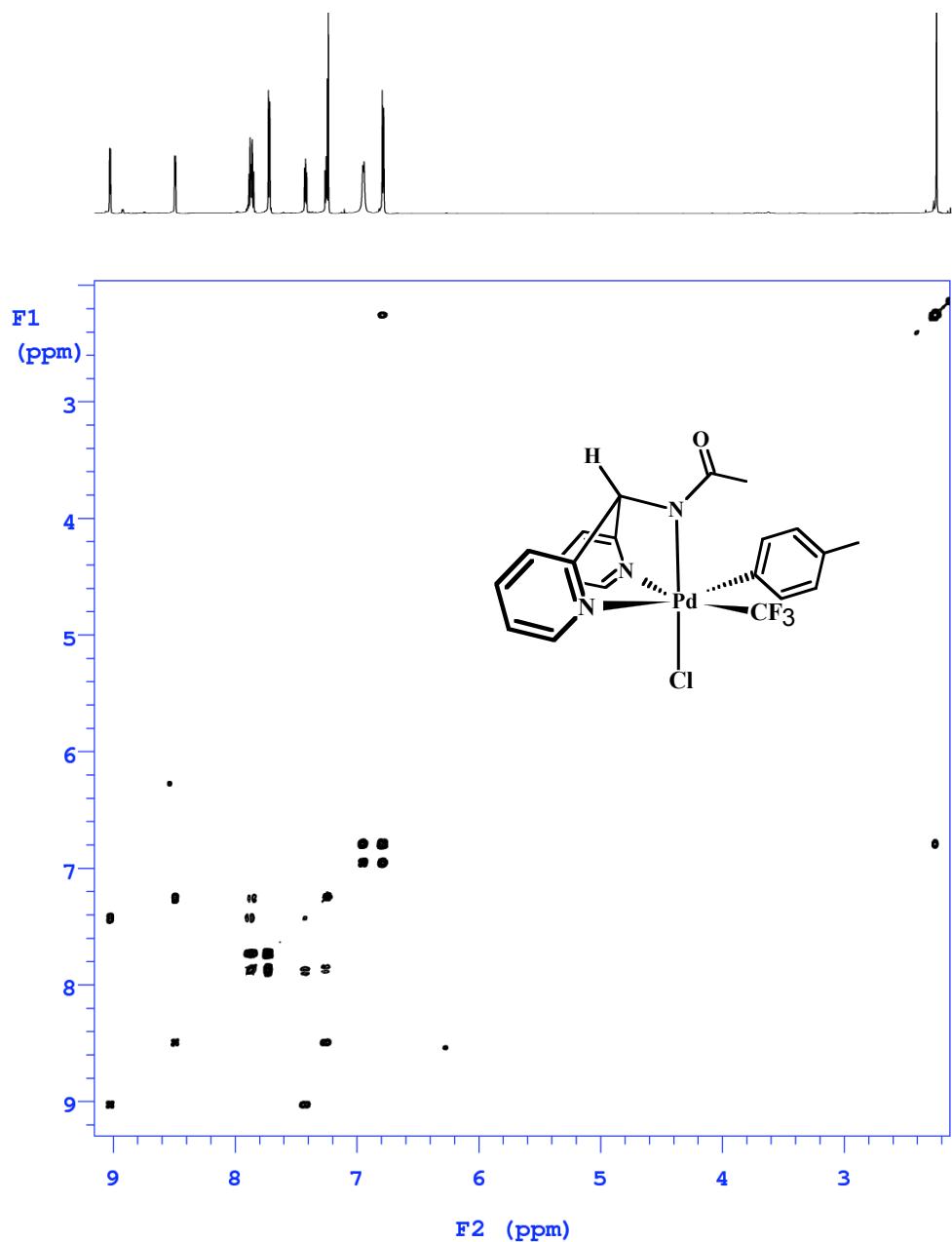
Pulse Sequence: FLUORINE (s2pul)  
Solvent: cdcl3  
Data collected on: May 1 2011

Temp. 25.0 C / 298.1 K  
Operator: maleckis

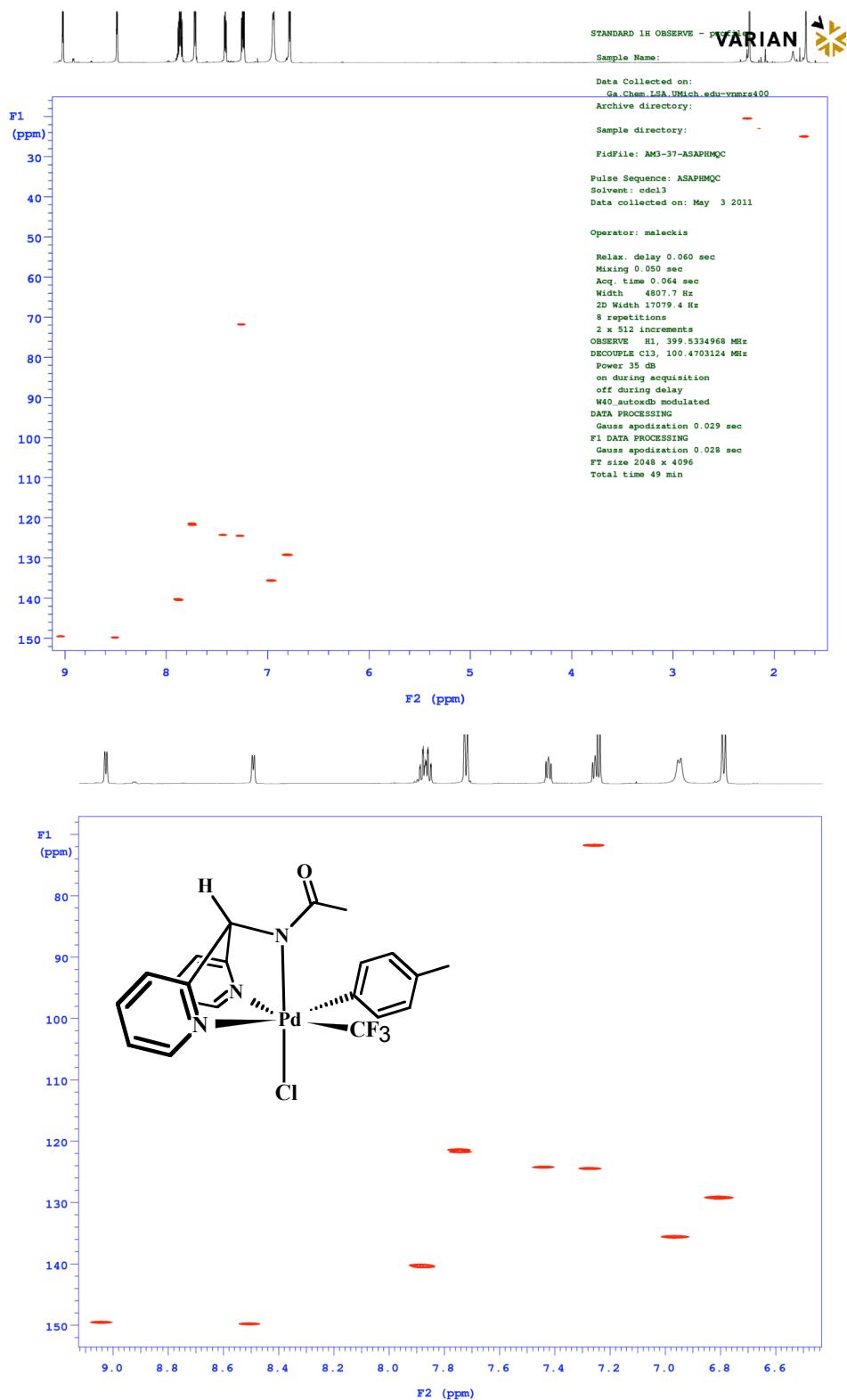
Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acq. time 0.786 sec  
Width 166.7 kHz  
16 repetitions  
OBSERVE F19, 376.8659339 MHz  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 262144  
Total time 0 min 32 sec



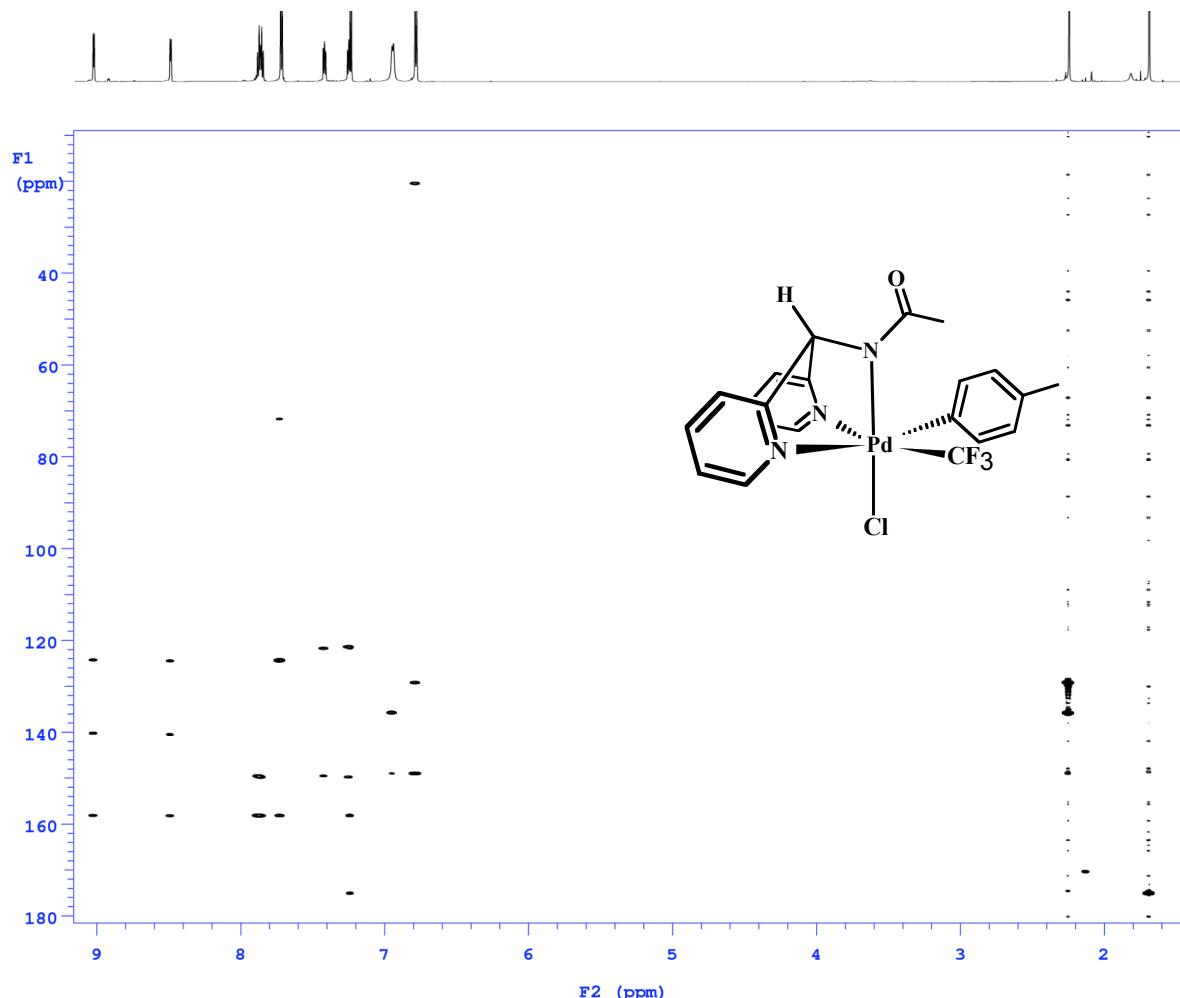
<sup>1</sup>H/<sup>1</sup>H COSY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**10**)



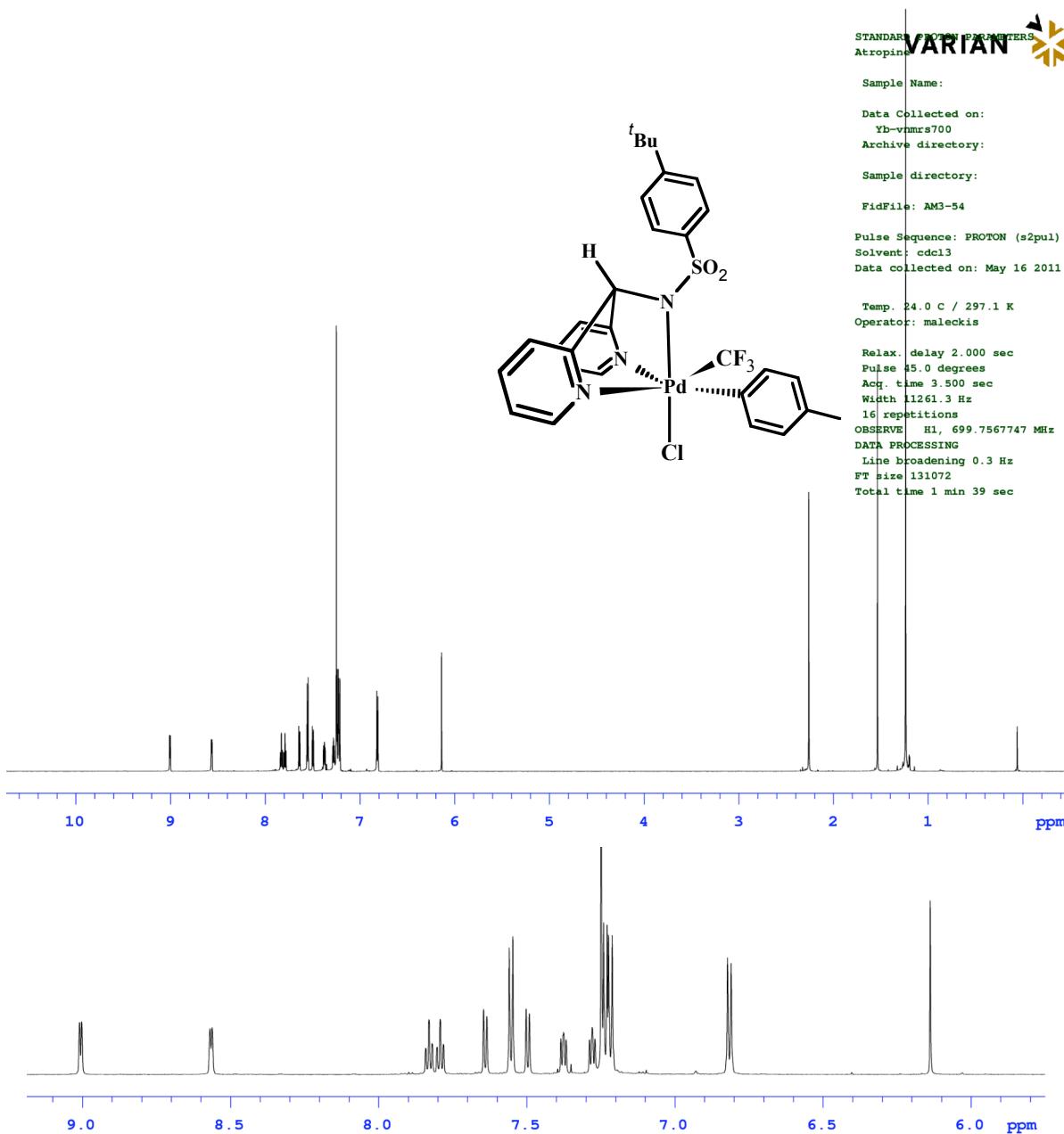
**$^1\text{H}/^{13}\text{C}$  ASAPHMQC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (10)**



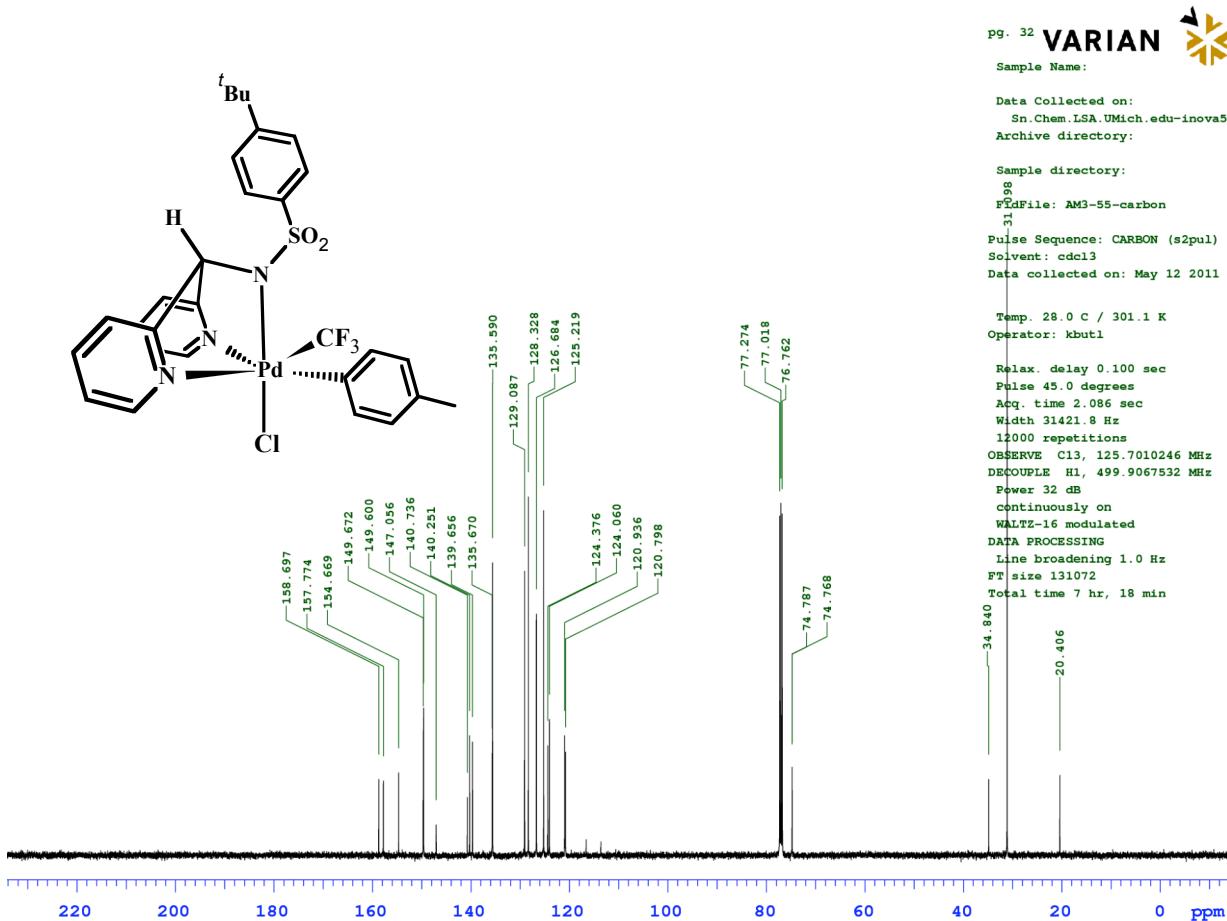
$^1\text{H}/^{13}\text{C}$  HMBC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**10**)



<sup>1</sup>H NMR of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



<sup>13</sup>C{<sup>1</sup>H} NMR of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



$$J = 378 \text{ Hz}$$

<sup>19</sup>F NMR of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)

STANDARD VARIANCE METERS  
VARTAN

Sample Name:

Data Collected on:  
Te=vmr500

Archive directory:

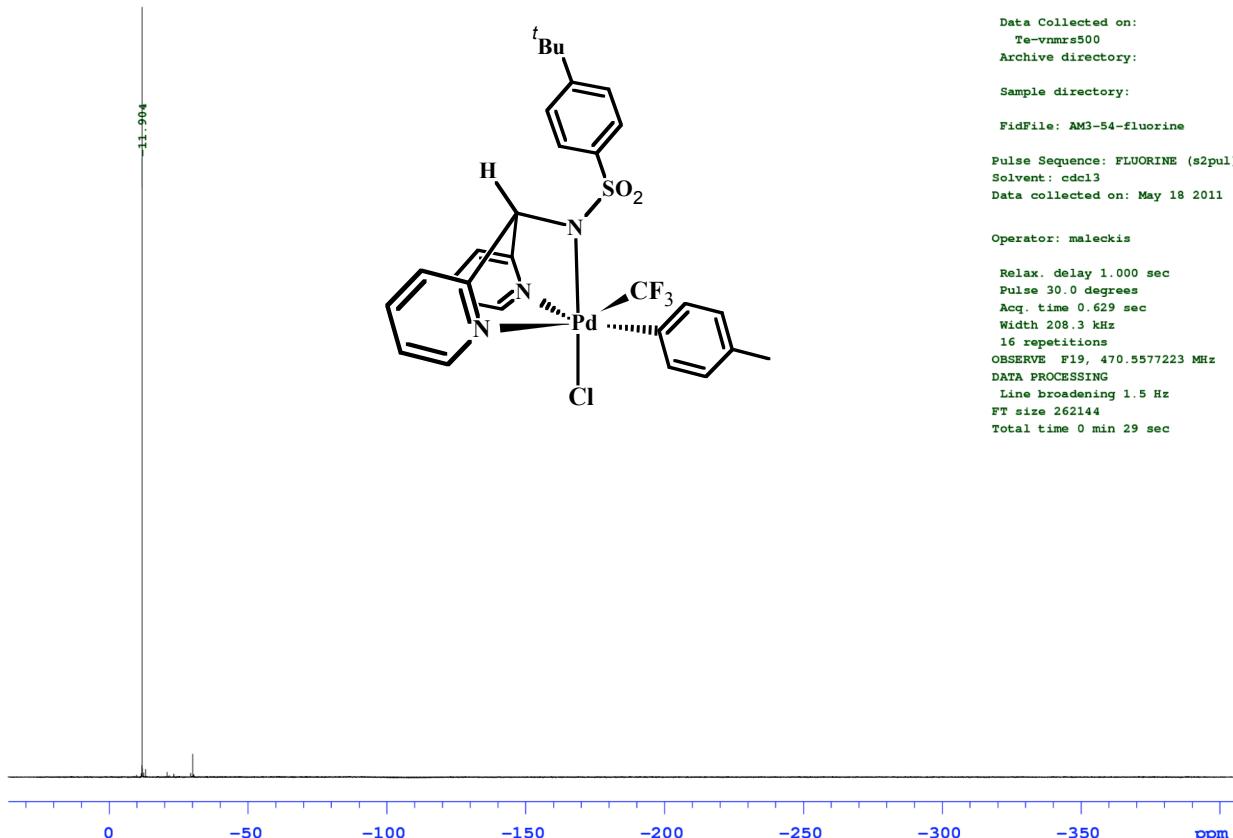
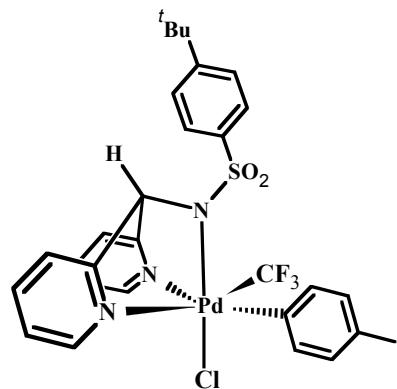
Sample directory:

FidFile: AM3-54-fluorine

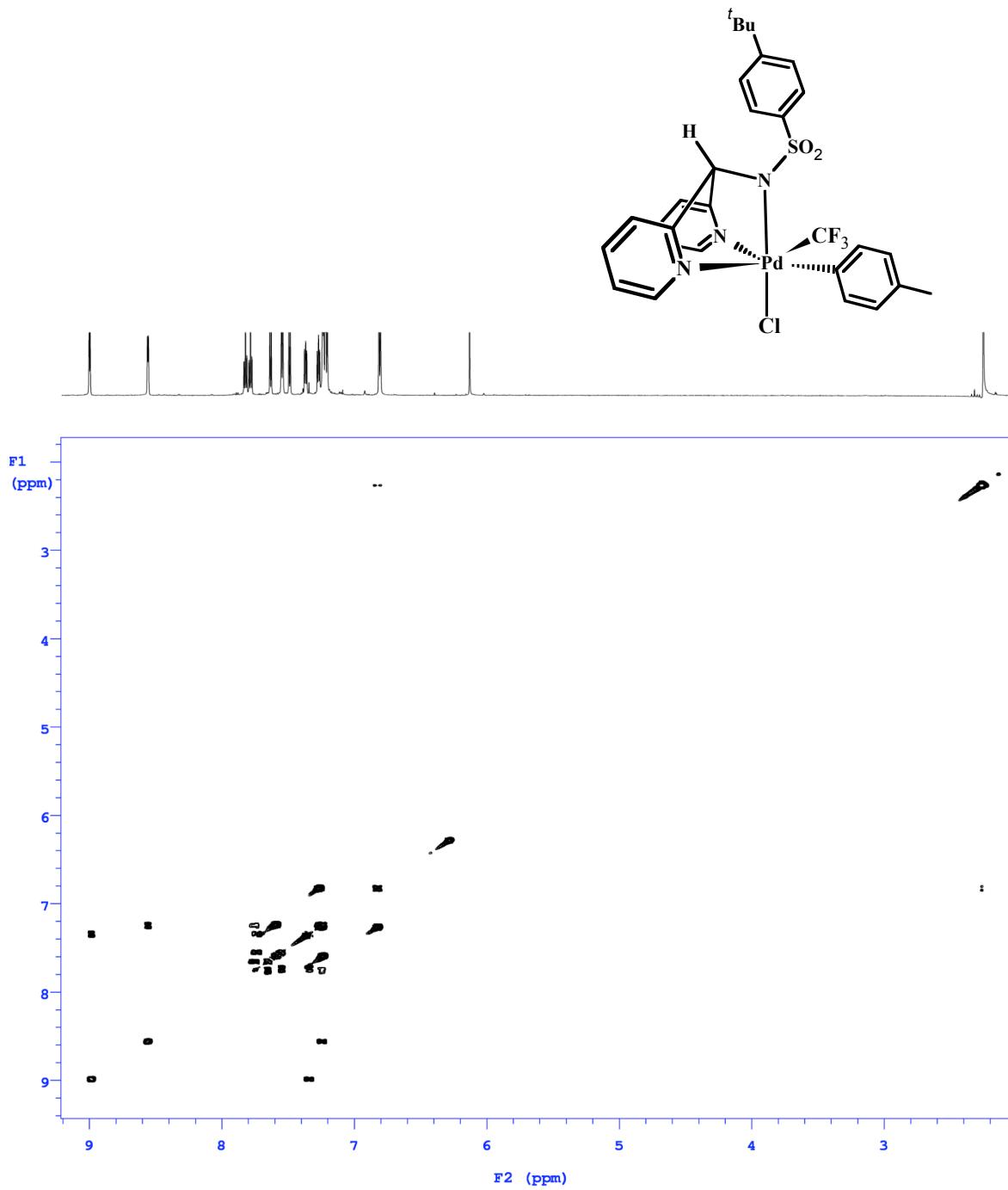
Pulse Sequence: FLUORINE (s2pul)  
Solvent: cdcl3  
Data collected on: May 18 2011

Operator: maleckis

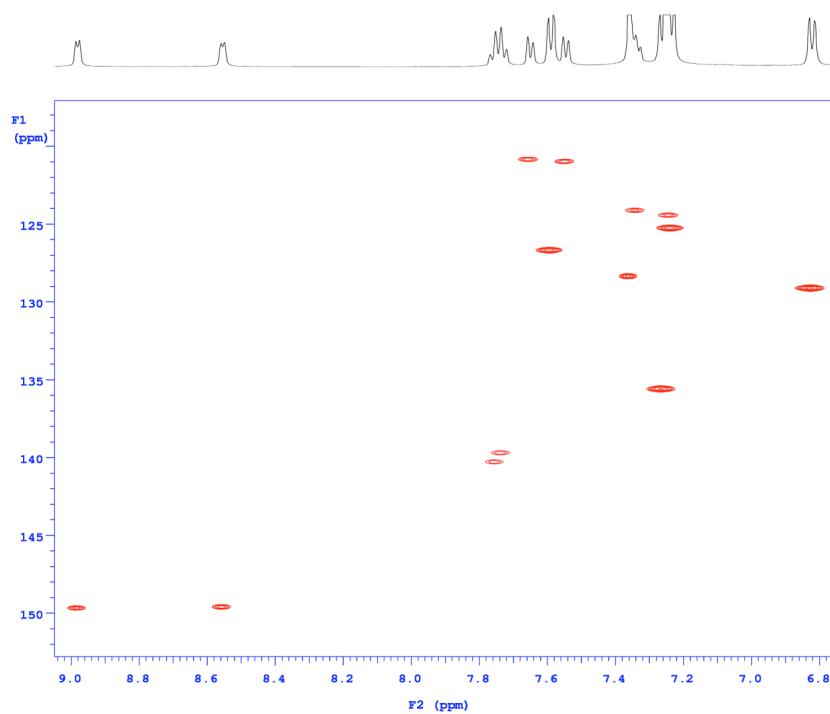
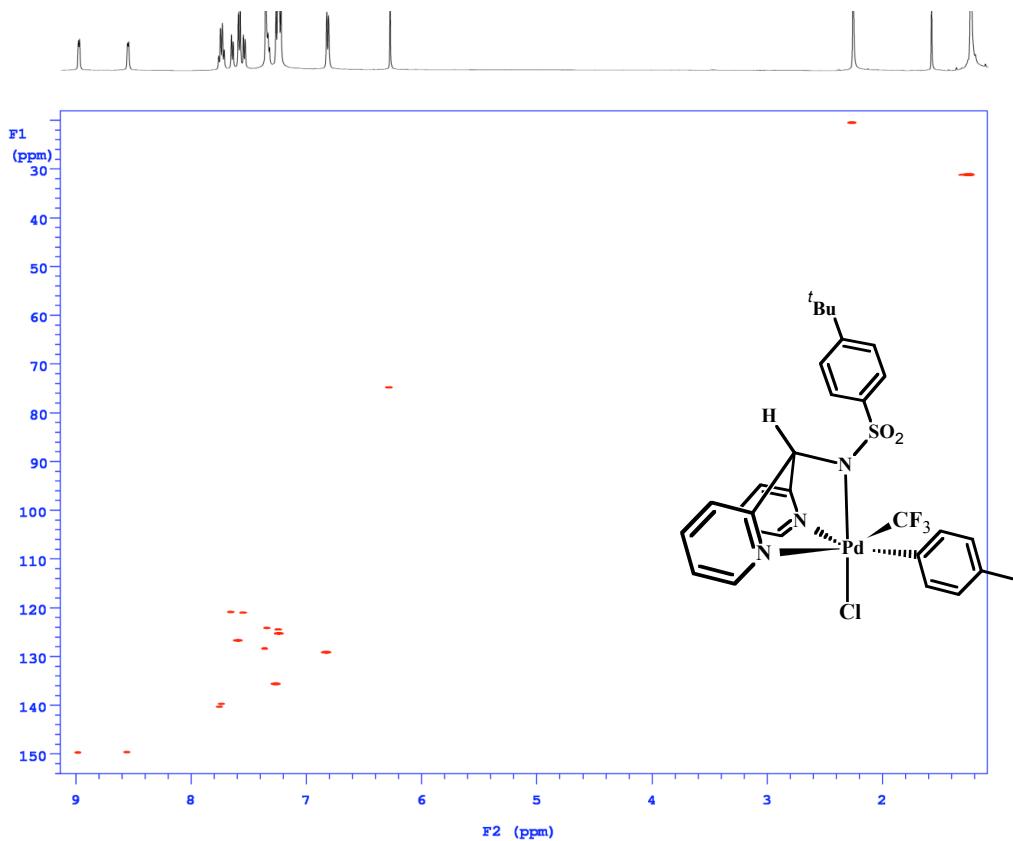
Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acc. time 0.629 sec  
Width 208.3 kHz  
16 repetitions  
OBSERVE F19, 470.5577223 MHz  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 262144  
Total time 0 min 29 sec



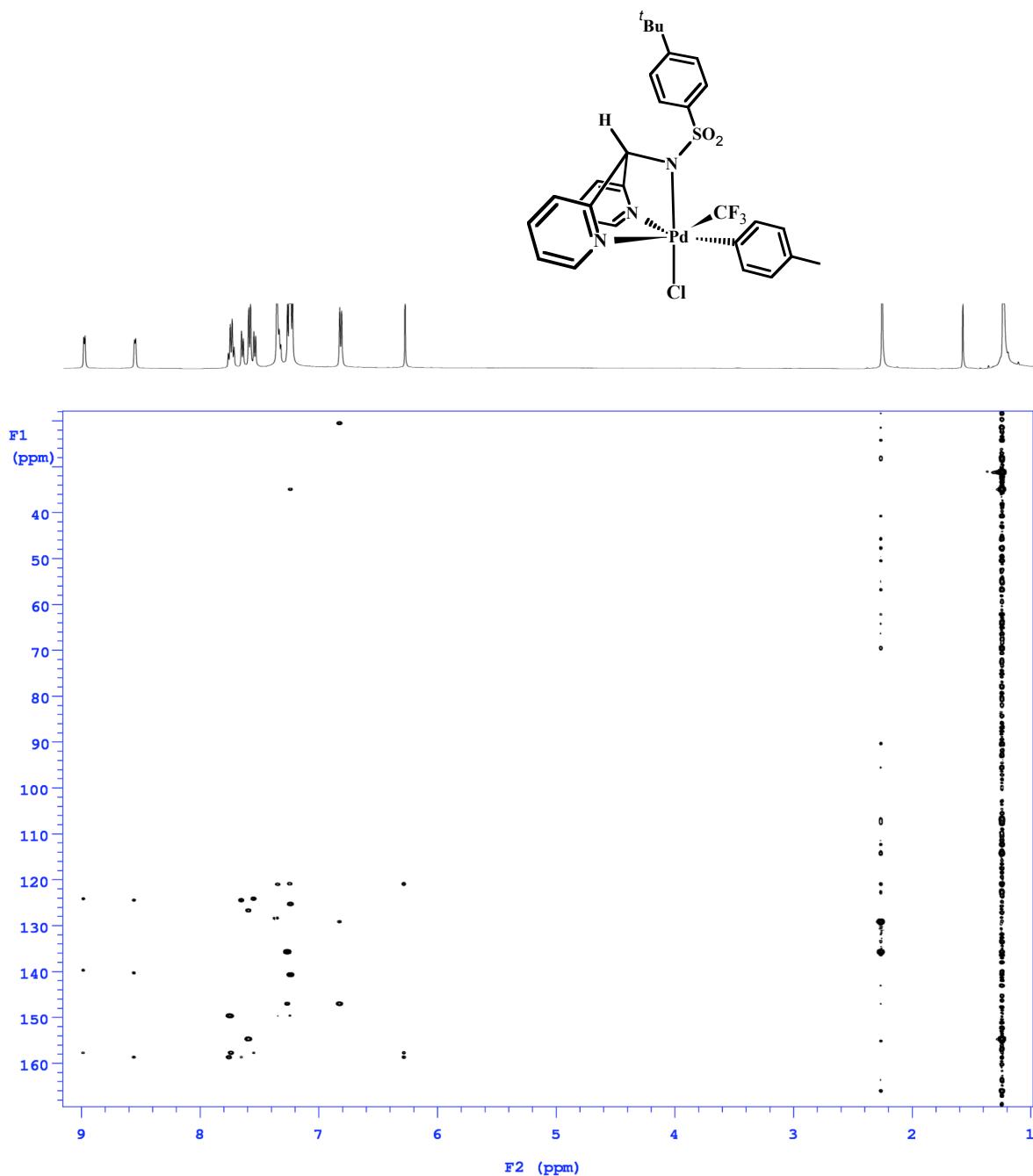
<sup>1</sup>H/<sup>1</sup>H COSY of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



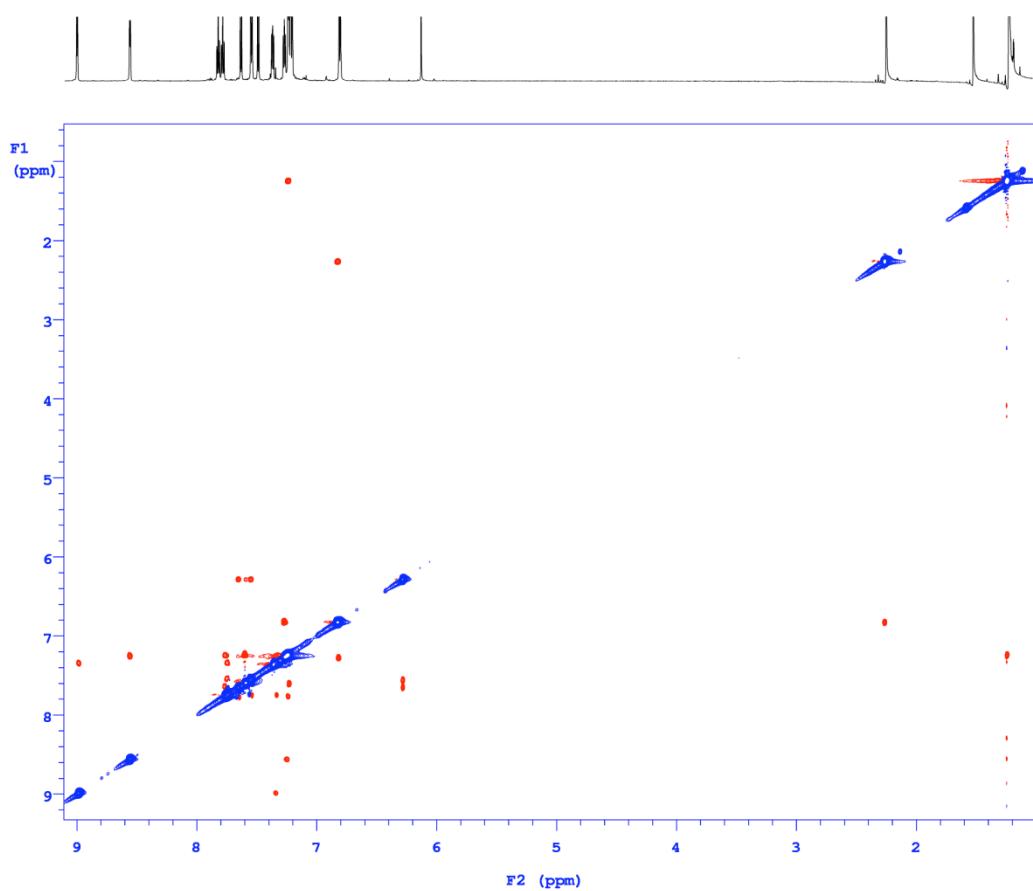
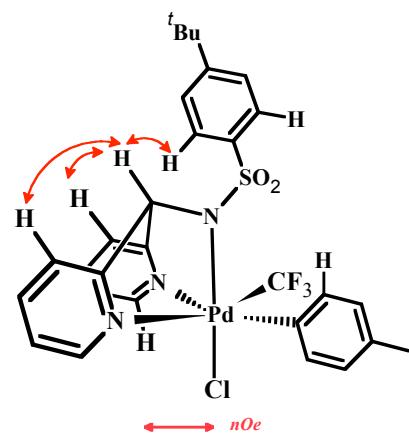
$^1\text{H}/^{13}\text{C}$  ASAHMQC of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



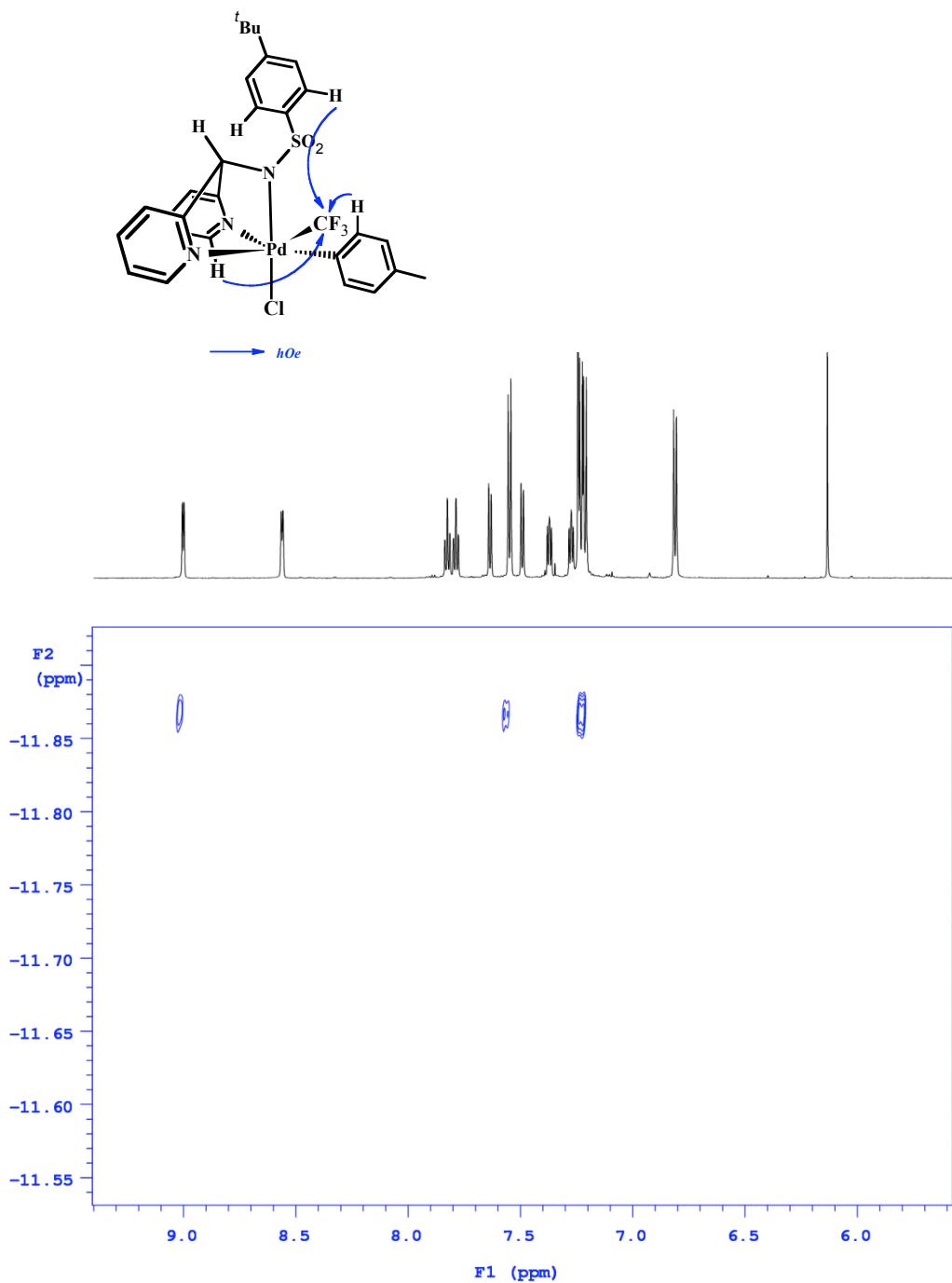
$^1\text{H}/^{13}\text{C}$  HMBC of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



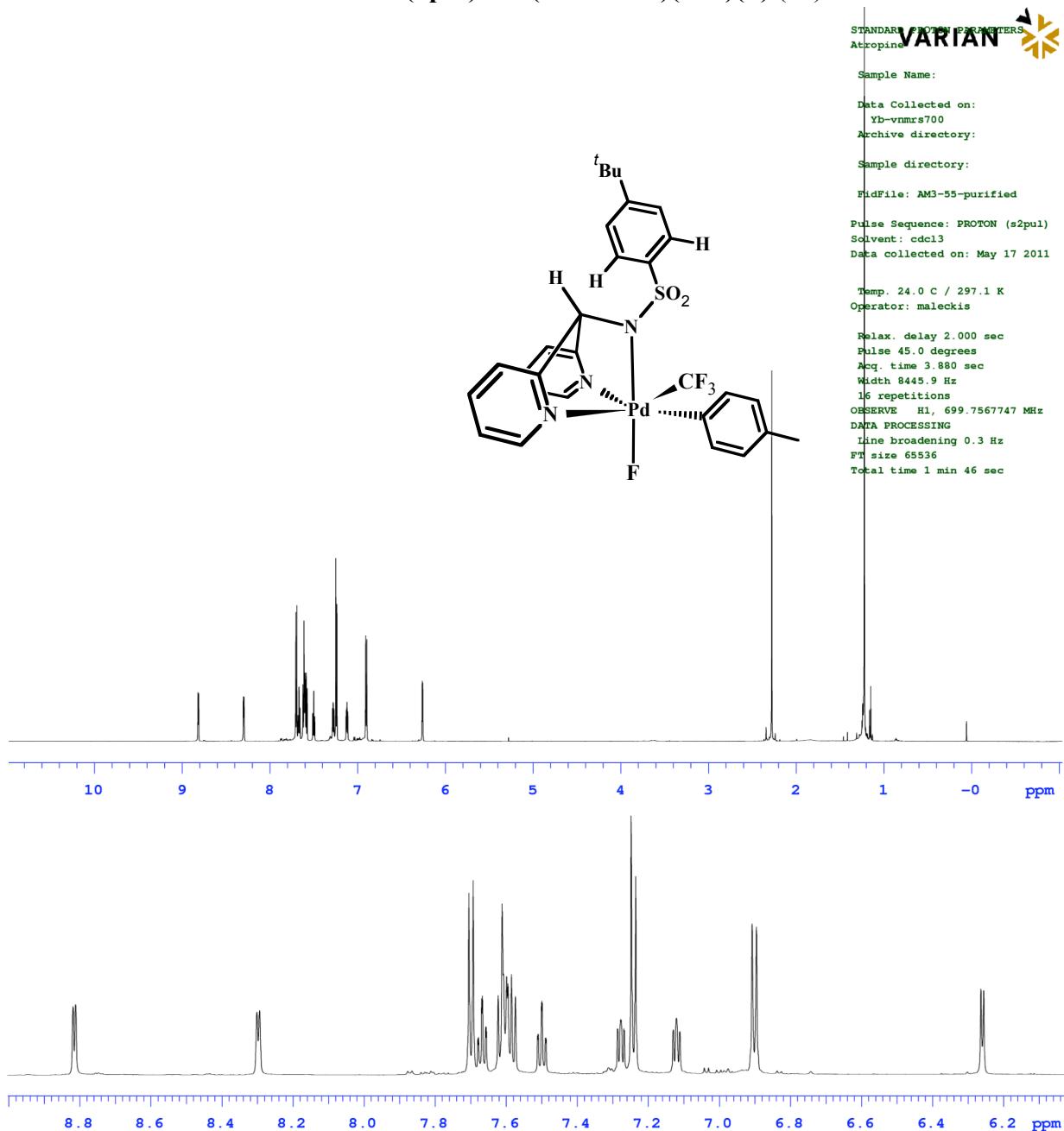
$^1\text{H}/^1\text{H}$  ROESY of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



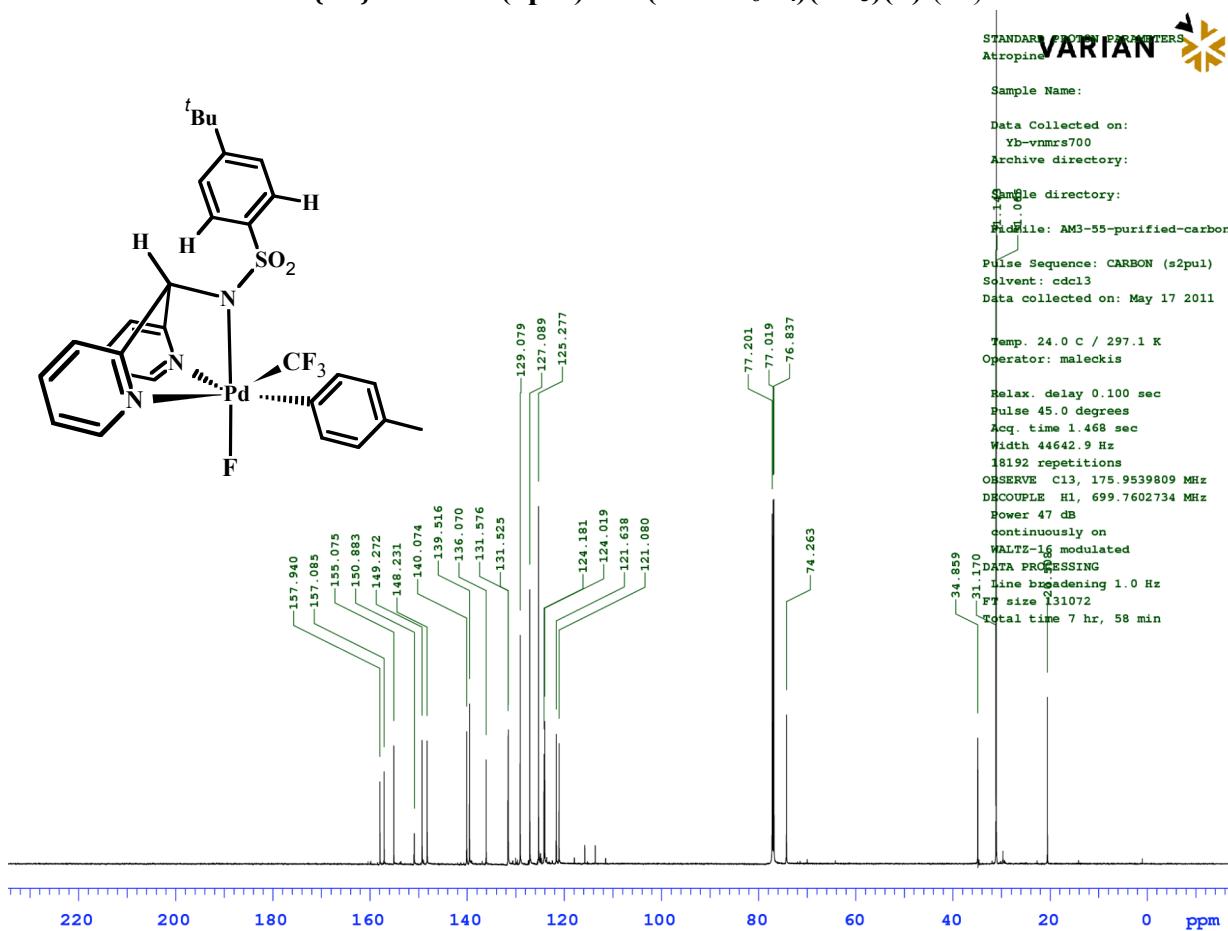
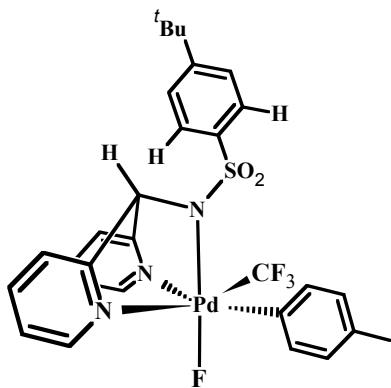
<sup>19</sup>F/<sup>1</sup>H HOESY of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)



<sup>1</sup>H NMR of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)

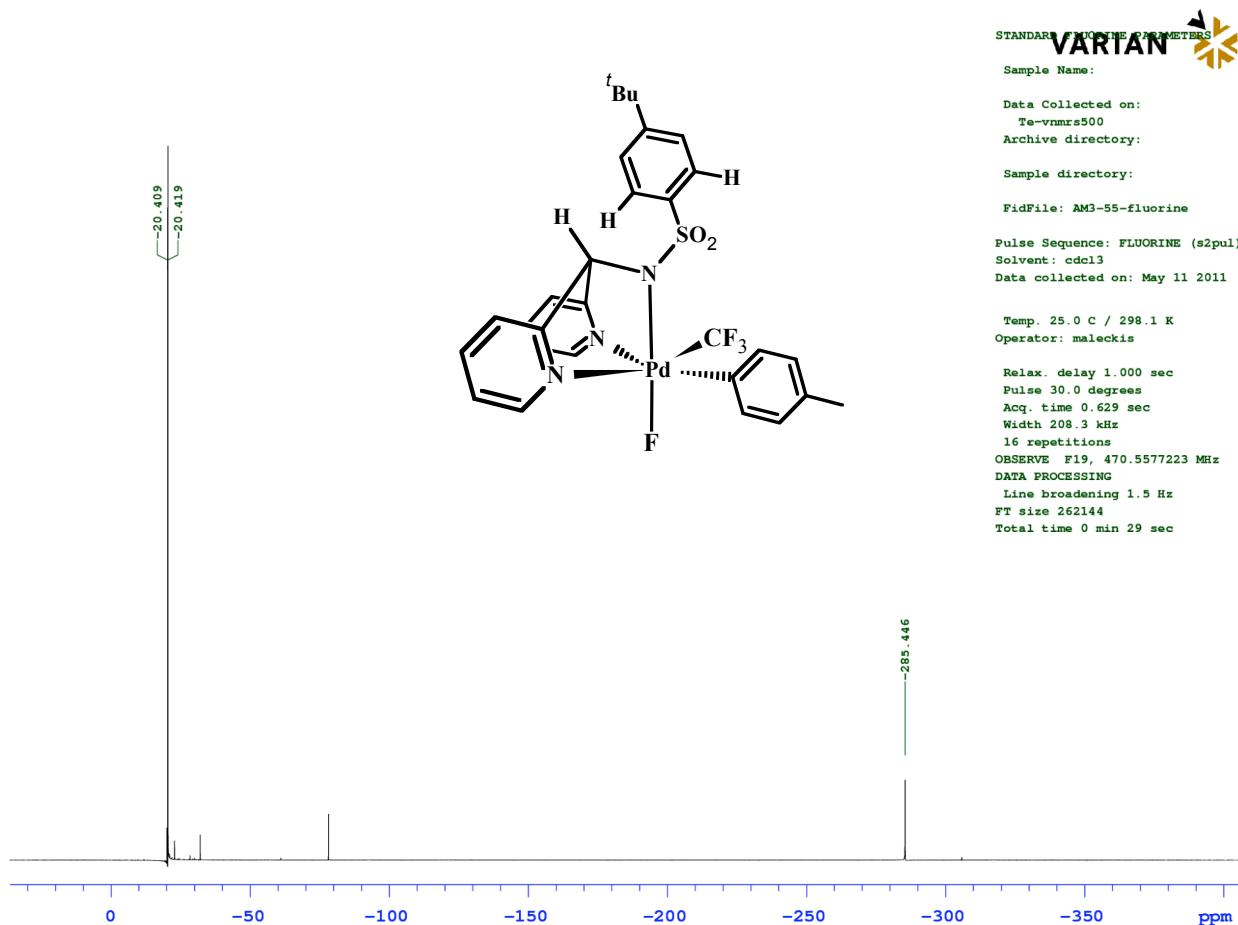


<sup>13</sup>C{<sup>1</sup>H} NMR of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)

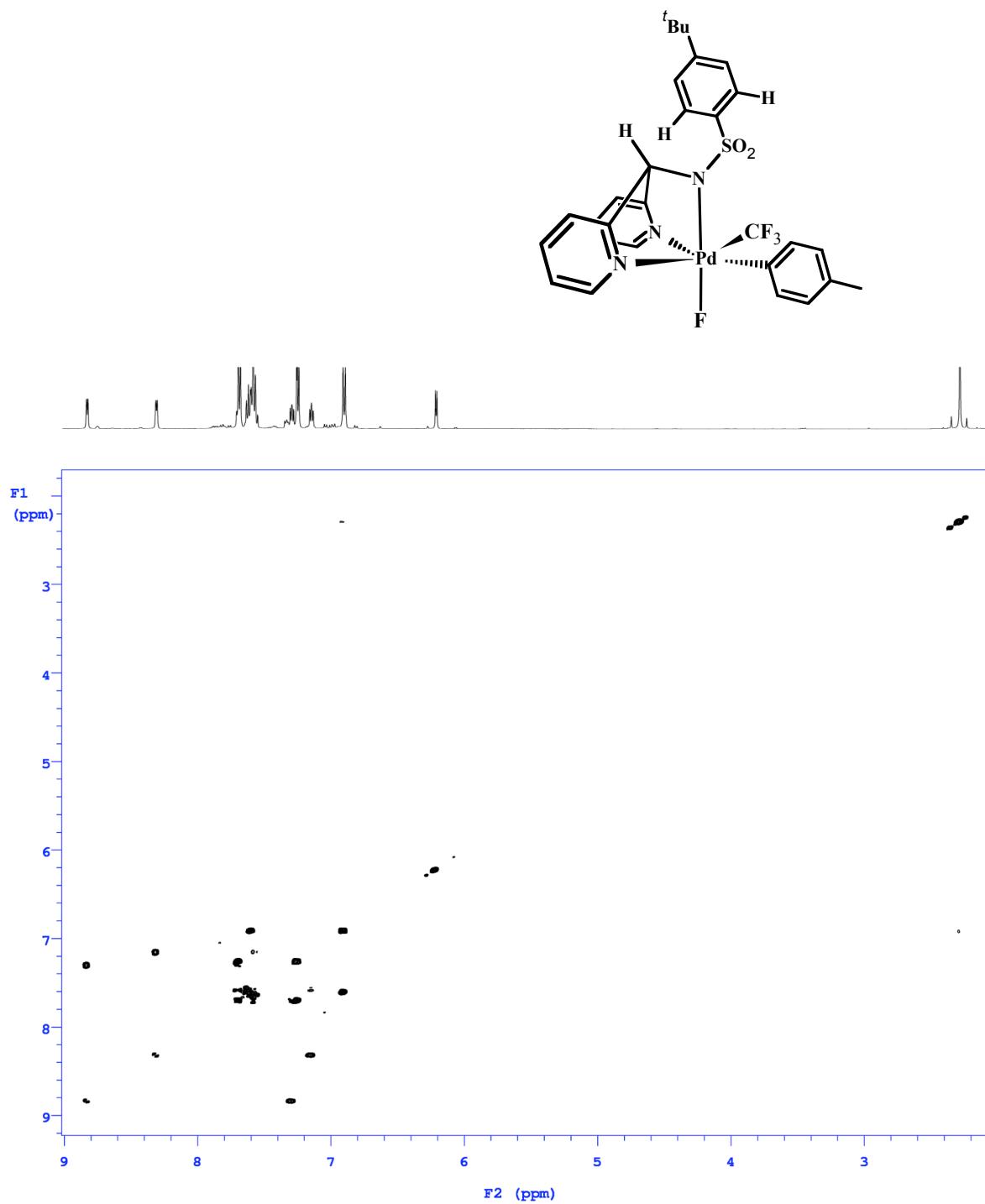


$$J = 378 \text{ Hz}$$

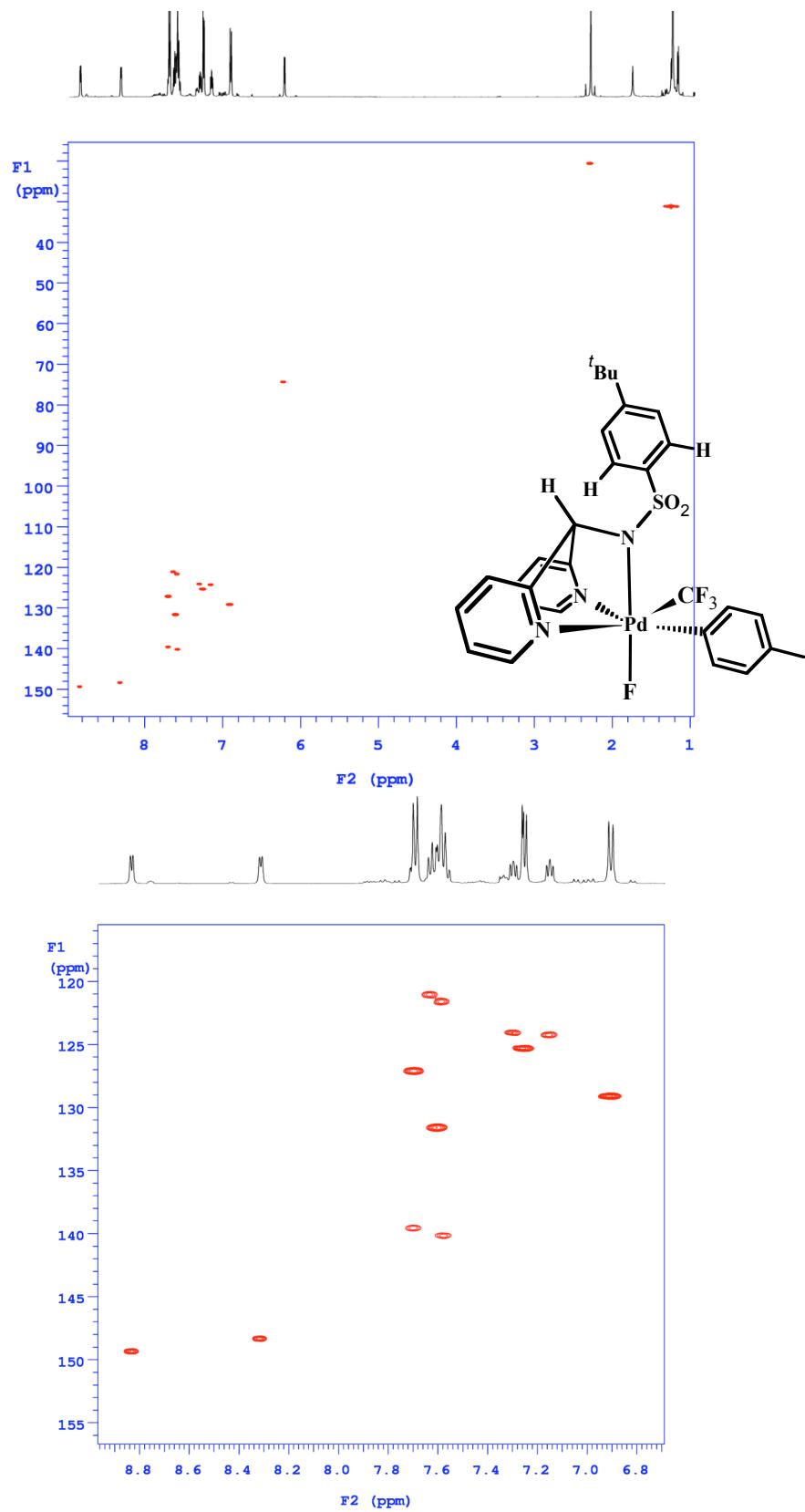
<sup>19</sup>F NMR of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)



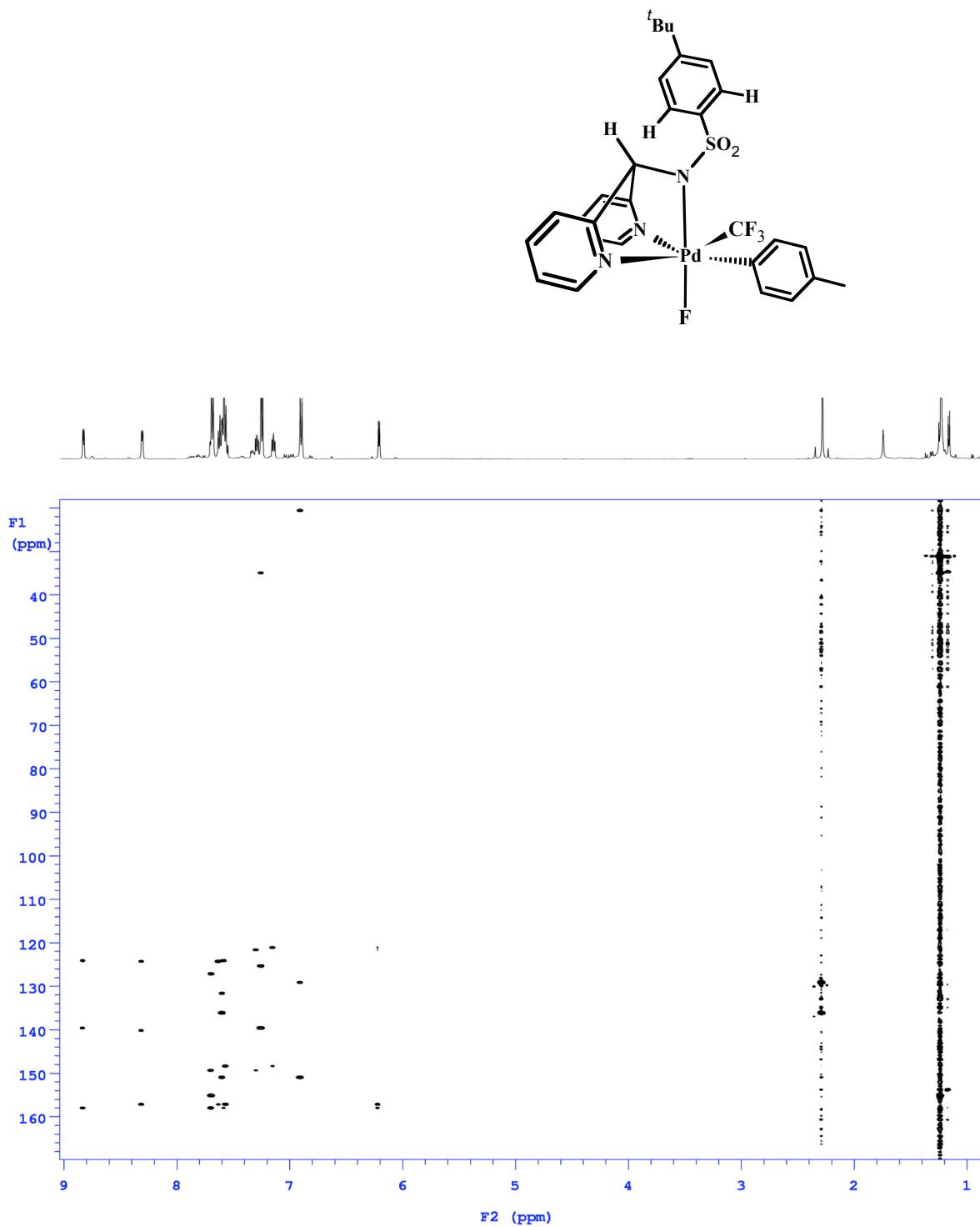
$^1\text{H}/^1\text{H}$  gCOSY of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)



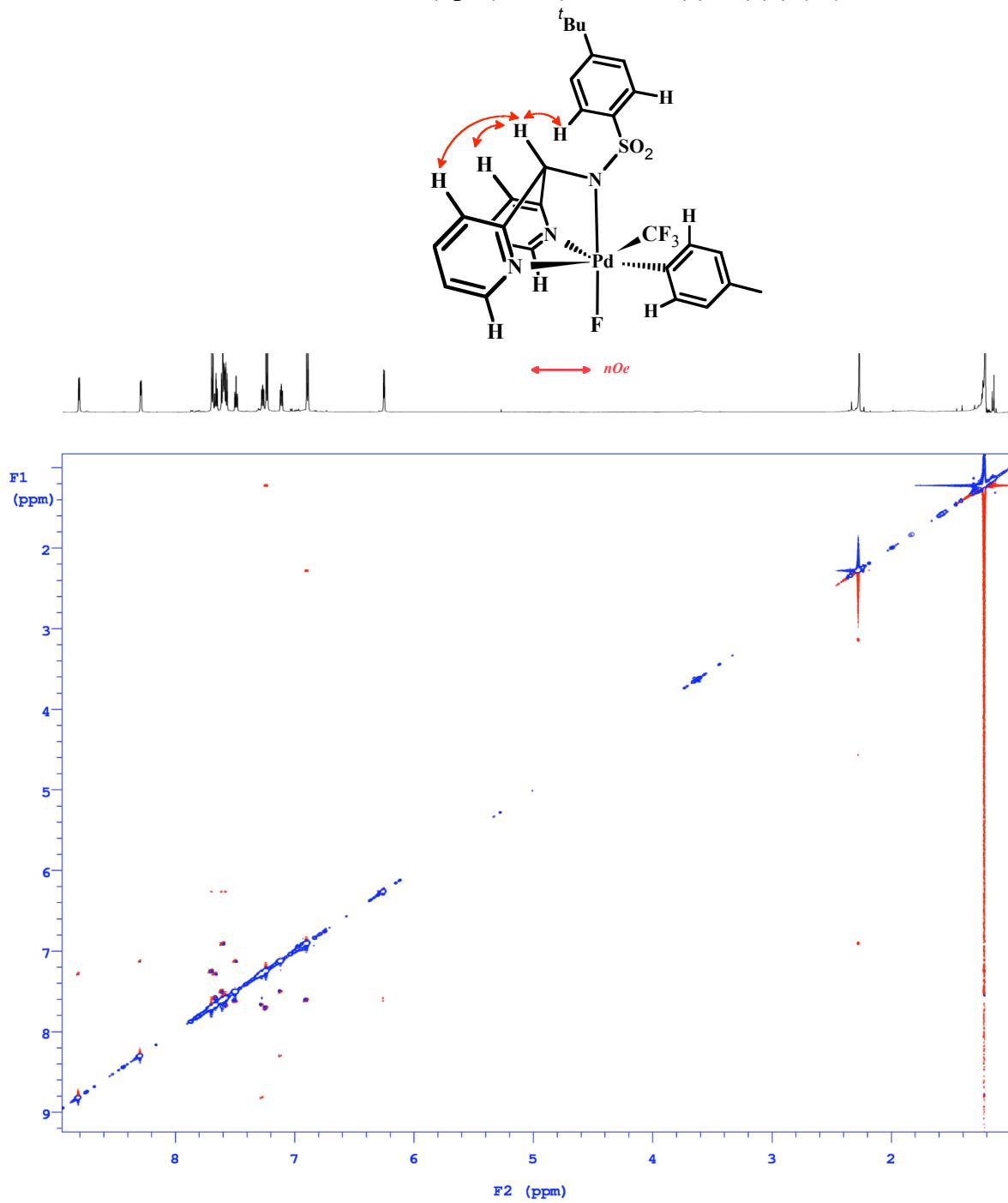
$^1\text{H}/^{13}\text{C}$  ASAPHMQC of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)



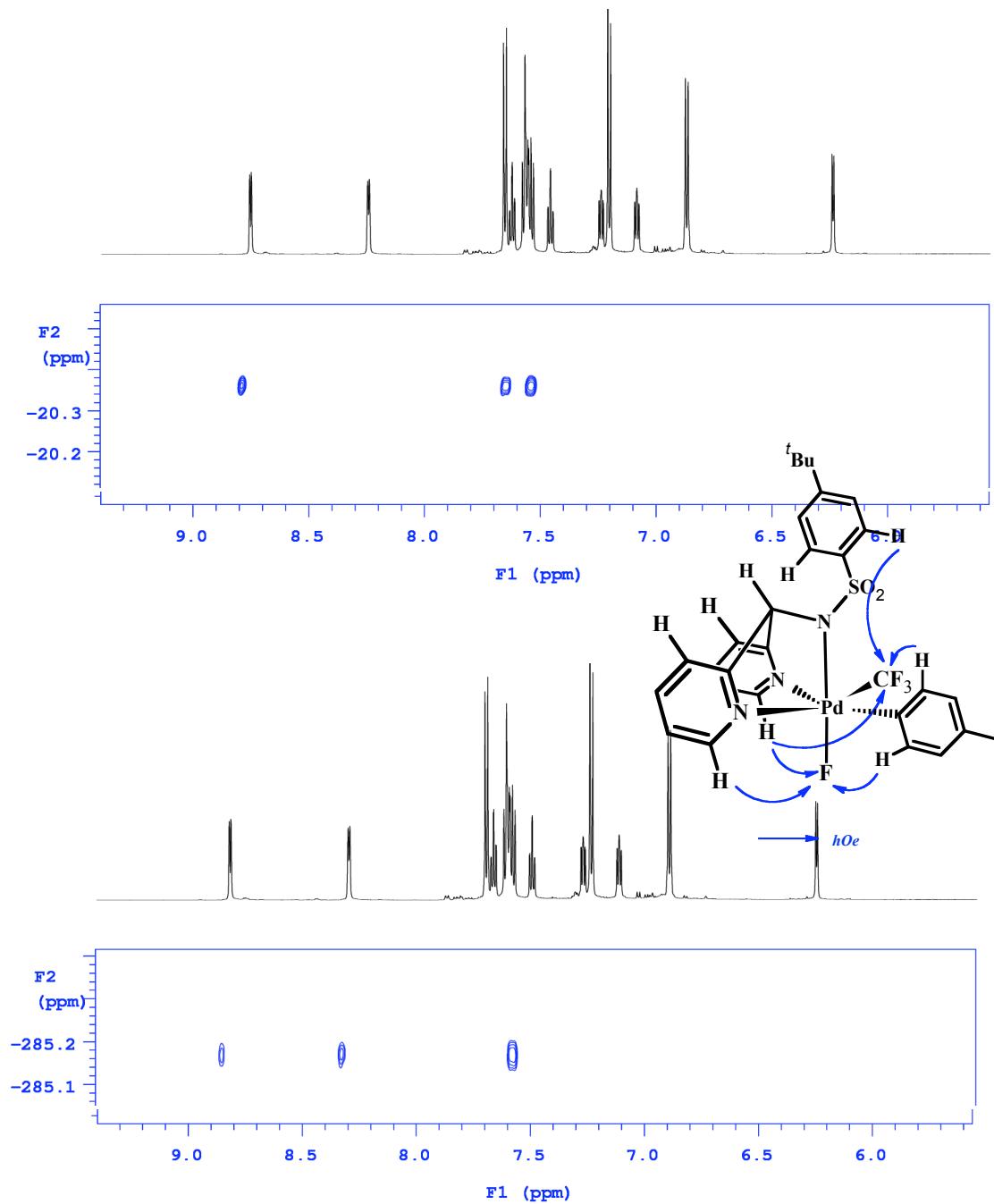
$^1\text{H}/^{13}\text{C}$  HMBC of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)



$^1\text{H}/^1\text{H}$  NOESY of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)



<sup>19</sup>F/<sup>1</sup>H HOESY of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)



<sup>1</sup>H NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13a)

STANDARD Deuterium PARAMETERS  
Using lock coil

VARIAN 

Sample Name:

Data Collected on:  
Sn.Chem.LSA.UMich.edu-inova500

Archive directory:

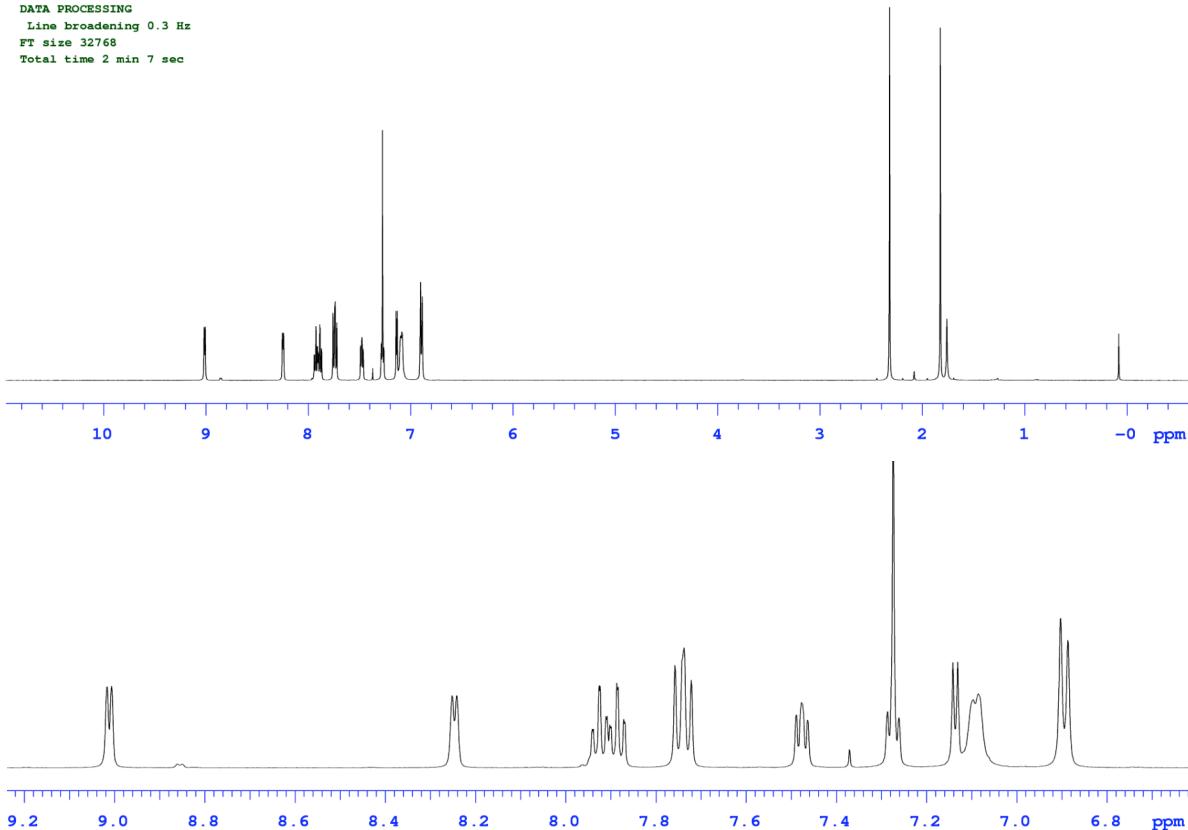
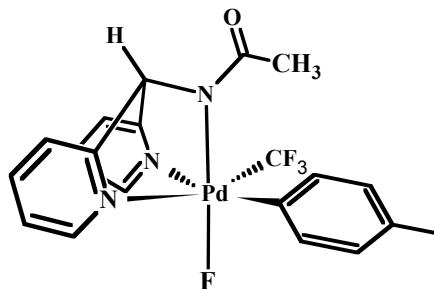
Sample directory:

FidFile: AM3-60

Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: May 15 2011

Operator: maleckis

Relax. delay 5.000 sec  
Pulse 45.0 degrees  
Acq. time 2.048 sec  
Width 7998.4 Hz  
16 repetitions  
OBSERVE H1, 499.9042537 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 32768  
Total time 2 min 7 sec



# <sup>1</sup>H NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13a)

STANDARD 1H OBSERVE - profile

Sample Name:

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

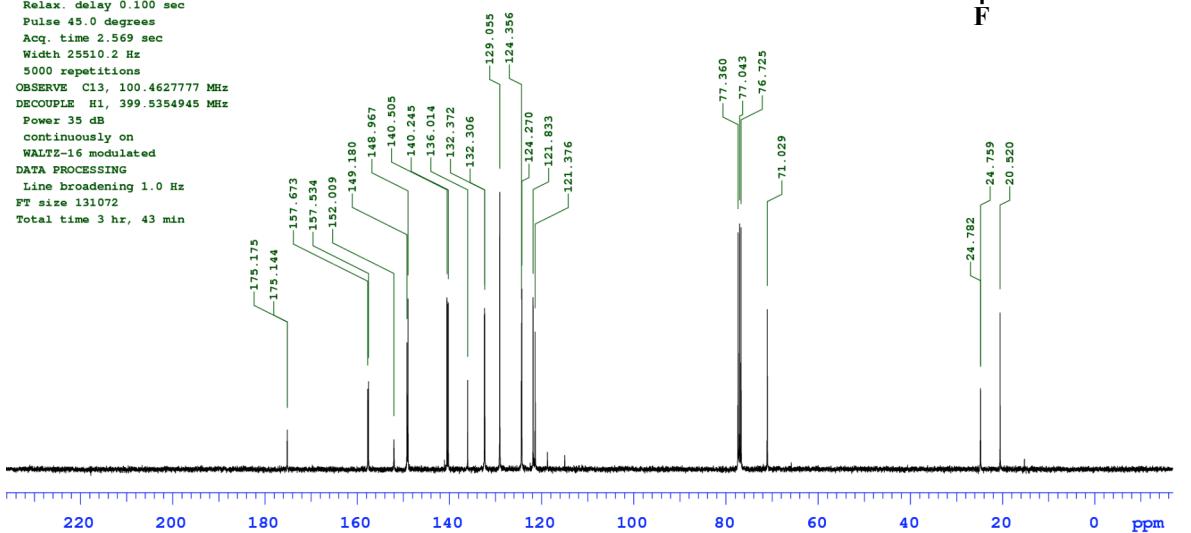
Sample directory:

FidFile: AM3-60-carbon

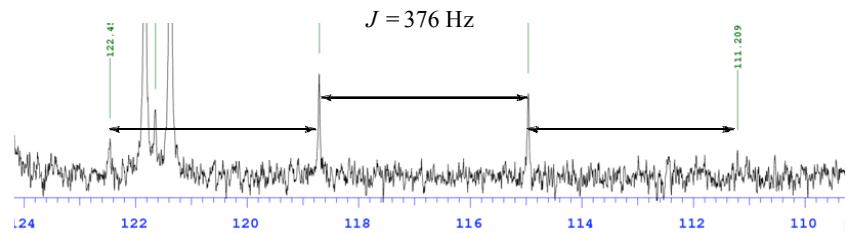
Pulse Sequence: CARBON (s2pul)  
Solvent: cdc13  
Data collected on: May 14 2011

Temp. 52.0 C / 325.1 K  
Operator: maleckis

Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 2.569 sec  
Width 25510.2 Hz  
5000 repetitions  
OBSERVE C13, 100.4627777 MHz  
DECOPPLE H1, 399.5354945 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



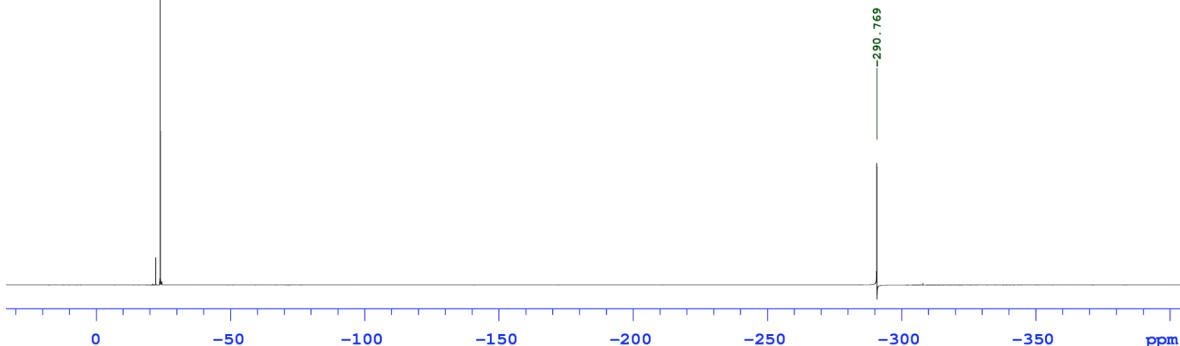
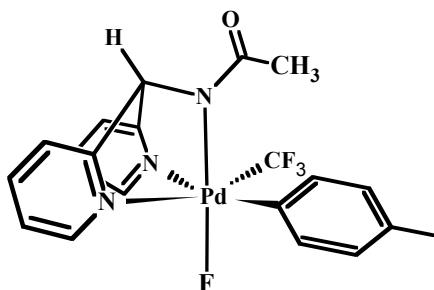
**<sup>19</sup>F NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13a)**

STANDARD FLUORINE PARAMETERS

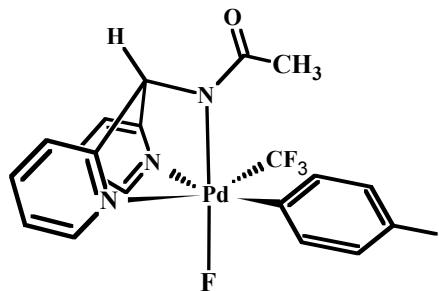
Sample Name:

```
Data Collected on:
  Te-vnmrs500
Archive directory:
Sample directory:
FidFile: AM3-60-fluorine
Pulse Sequence: FLUORINE (s2pul)
Solvent: cdcl3
Data collected on: May 14 2011
Temp. 25.0 C / 298.1 K
Operator: maleckis
Relax. delay 1.000 sec
Pulse 30.0 degrees
Acq. time 0.629 sec
Width 208.3 kHz
16 repetitions
OBSERVE F19, 470.5577223 MHz
DATA PROCESSING
Line broadening 1.5 Hz
FT size 262144
Total time 0 min 29 sec
```

VARIAN 



<sup>19</sup>F/<sup>13</sup>C HSQC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13a)



STANDARD FLUORINE PARAMETERS

Sample Name:

VARIAN

Data Collected on:  
Tm-varnmas500

Archive directory:  
**F1**

Sample directory:  
**(ppm)**

FidFile: AM3-60-FH-HSQC

Pulse Sequence: HSQC

Solvent: cdcl3

Data collected on: May 14 2011

Temp 115.0 C / 298.1 K  
Operator: haleckis

Relax. delay 1.000 sec  
Acc 128 ms 0.150 sec

Width 9328.4 Hz

2D Width 7545.0 Hz

2 repetitions

2 x 125 increments

OBSERVE F1, 470.5577223 MHz

DECOUPLE C13, 125.7648749 MHz

Power 39 dB

on during acquisition

off during delay

W40\_OneNMR\_W010 modulated

DATA PROCESSING

Gauss apodization 0.069 sec

F1 DATA PROCESSING

Gauss apodization 0.023 sec

FT size 4096 x 2048

Total time 15 min

**140**

**145**

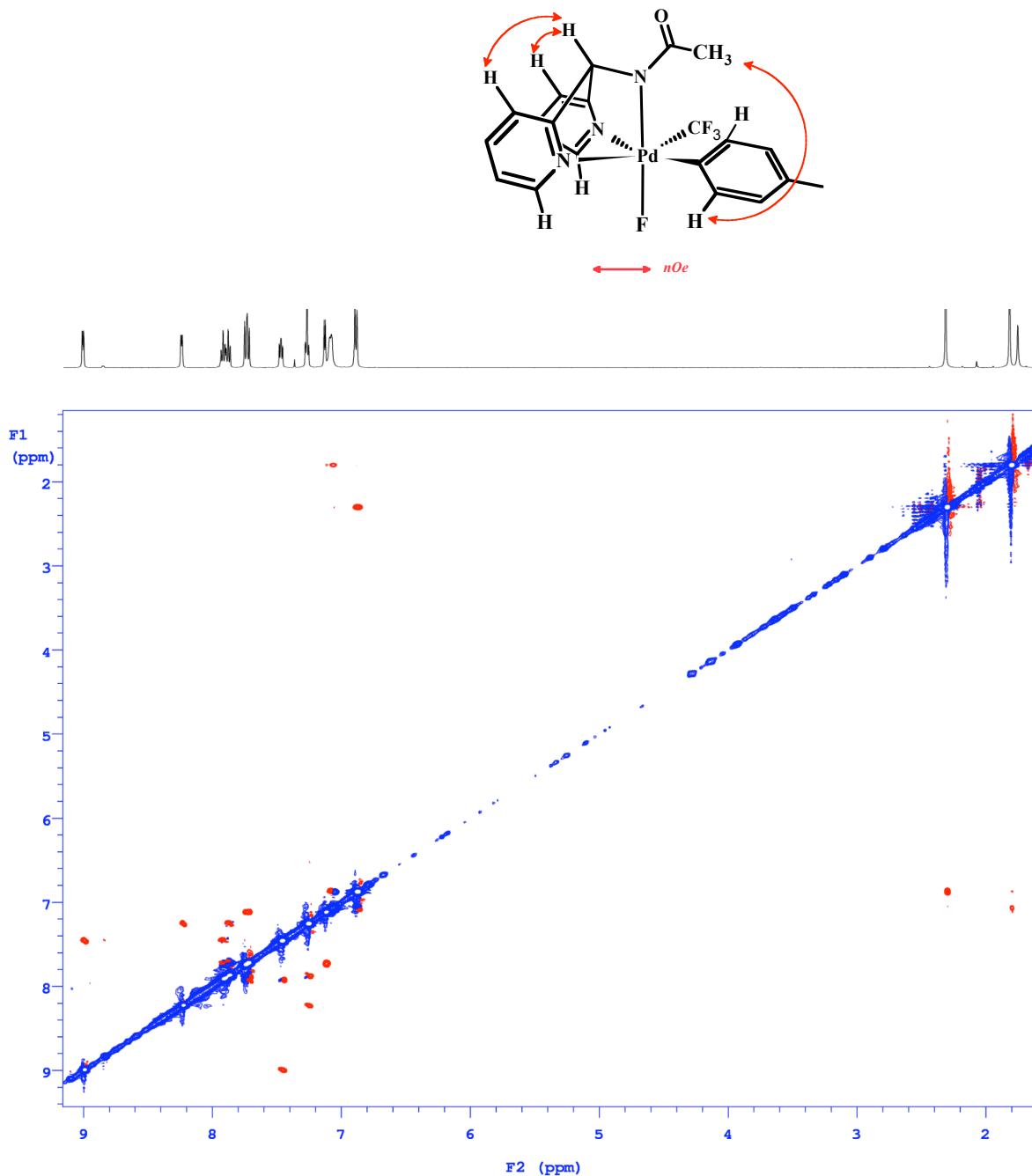
**150**

**155**

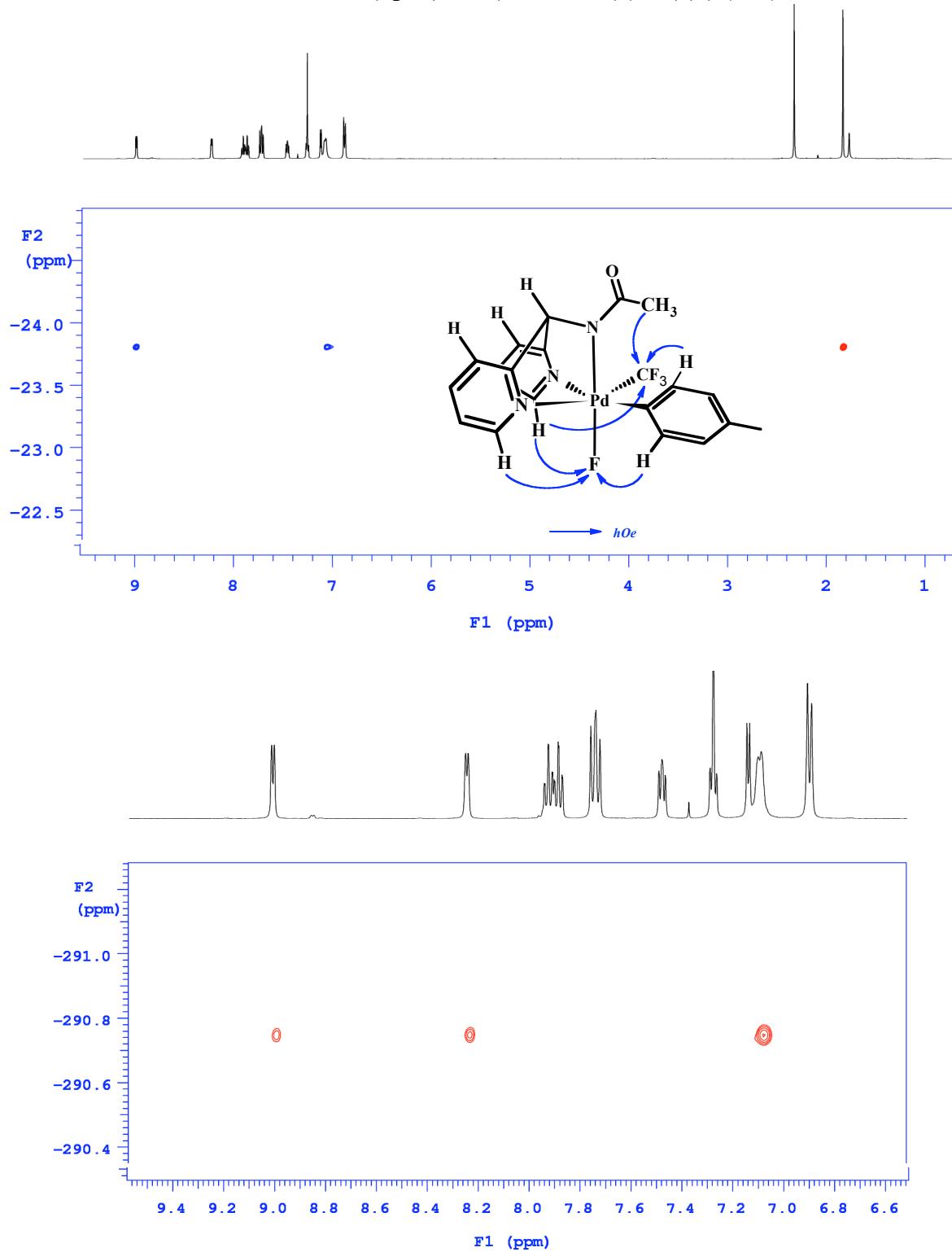
-21.5 -22.0 -22.5 -23.0 -23.5 -24.0 -24.5 -25.0 -25.5 -26.0

**F2 (ppm)**

<sup>1</sup>H/<sup>1</sup>H ROESY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13a)



<sup>19</sup>F/<sup>1</sup>H HOSY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13a)



<sup>1</sup>H NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)

STANDARD PROTON PARAMETERS  
Atropine

Sample Name:

Data Collected on:  
Yb-vnmrs700  
Archive directory:

Sample directory:

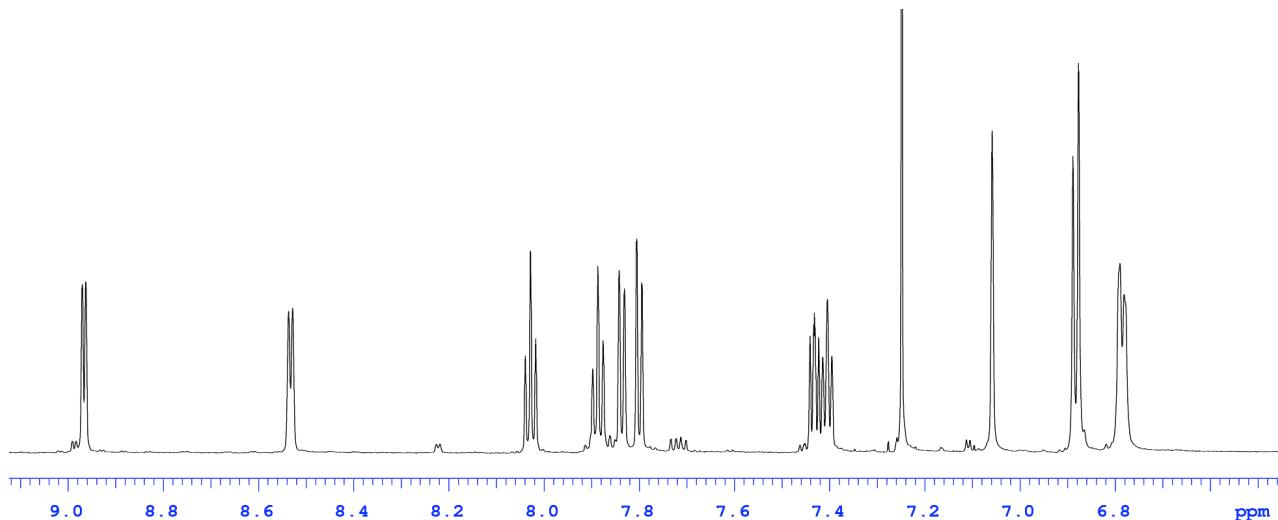
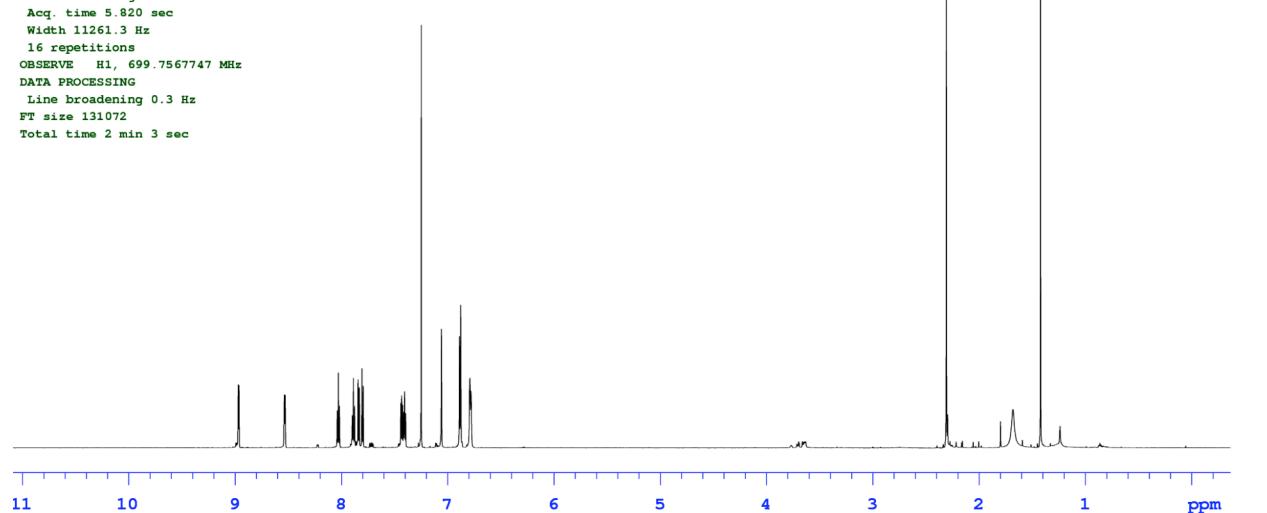
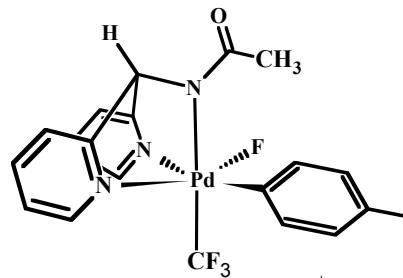
FidFile: AM3-38-F2

Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: May 15 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

Relax. delay 1.000 sec  
Pulse 45.0 degrees  
Acq. time 5.820 sec  
Width 11261.3 Hz  
16 repetitions  
OBSERVE H1, 699.7567747 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 131072  
Total time 2 min 3 sec

VARIAN 



$^{13}\text{C}\{\text{H}\}$  NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)

STANDARD PROTON PARAMETERS  
Atropine

Sample Name:

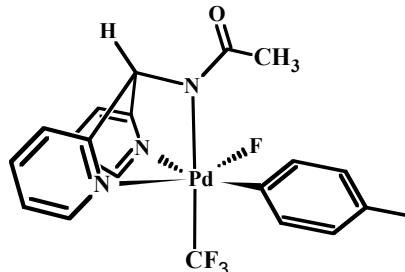
Data Collected on:  
Yb-vnmrs700  
Archive directory:

Sample directory:

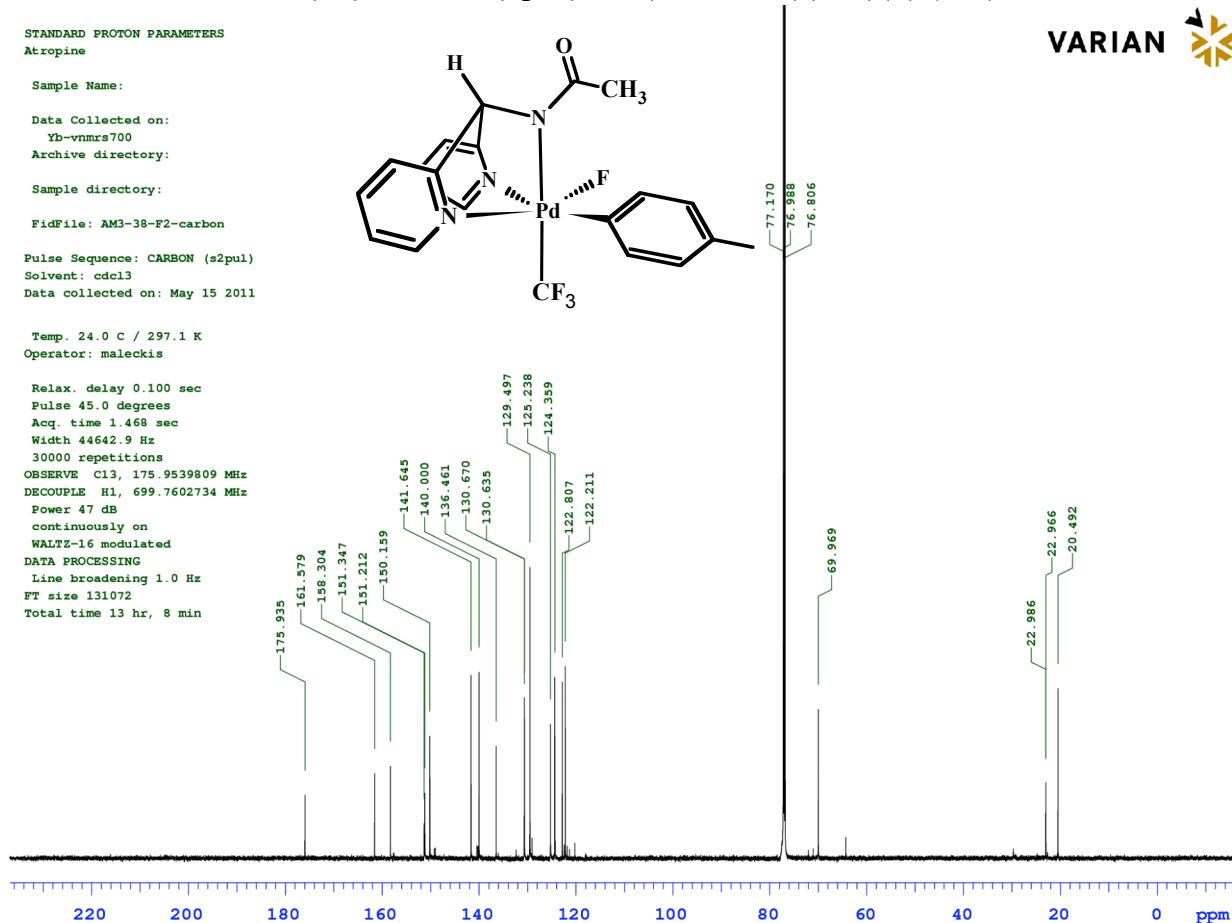
FidFile: AM3-38-F2-carbon  
Pulse Sequence: CARBON (s2pul)  
Solvent: cdc13  
Data collected on: May 15 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

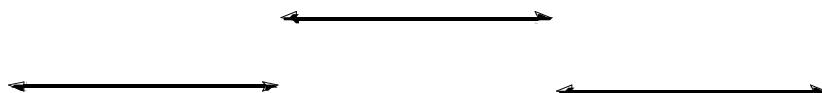
Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 1.468 sec  
Width 44642.9 Hz  
30000 repetitions  
OBSERVE C13, 175.9539809 MHz  
DECOUPLE H1, 699.7602734 MHz  
Power 47 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 13 hr, 8 min



VARIAN



$$J = 384 \text{ Hz}$$



**<sup>19</sup>F NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)**

STANDARD FLUORINE PARAMETERS

Sample Name:

Data Collected on:  
Te.Chem.LSA.UMich.edu-vnmrs500  
Archive directory:

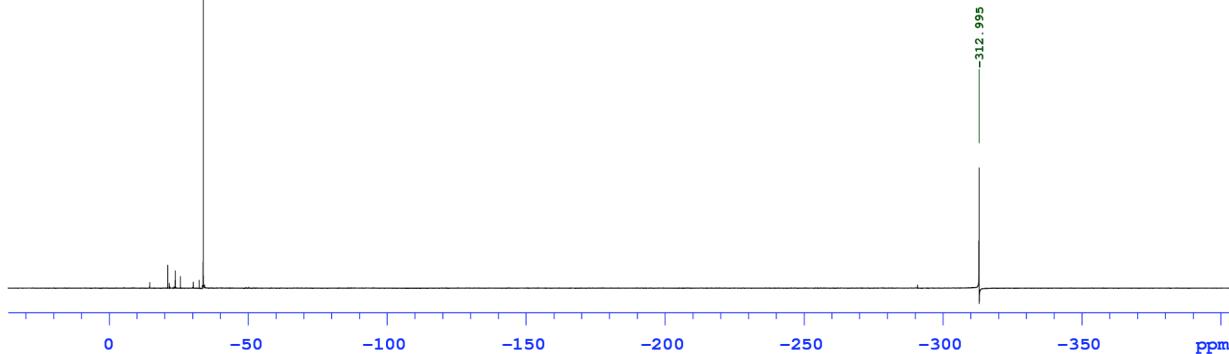
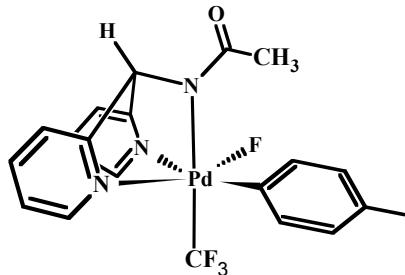
Sample directory:

FidFile: AM3-38-F2-fluorine  
Pulse Sequence: FLUORINE (s2pul)  
Solvent: cdcl3  
Data collected on: May 3 2011

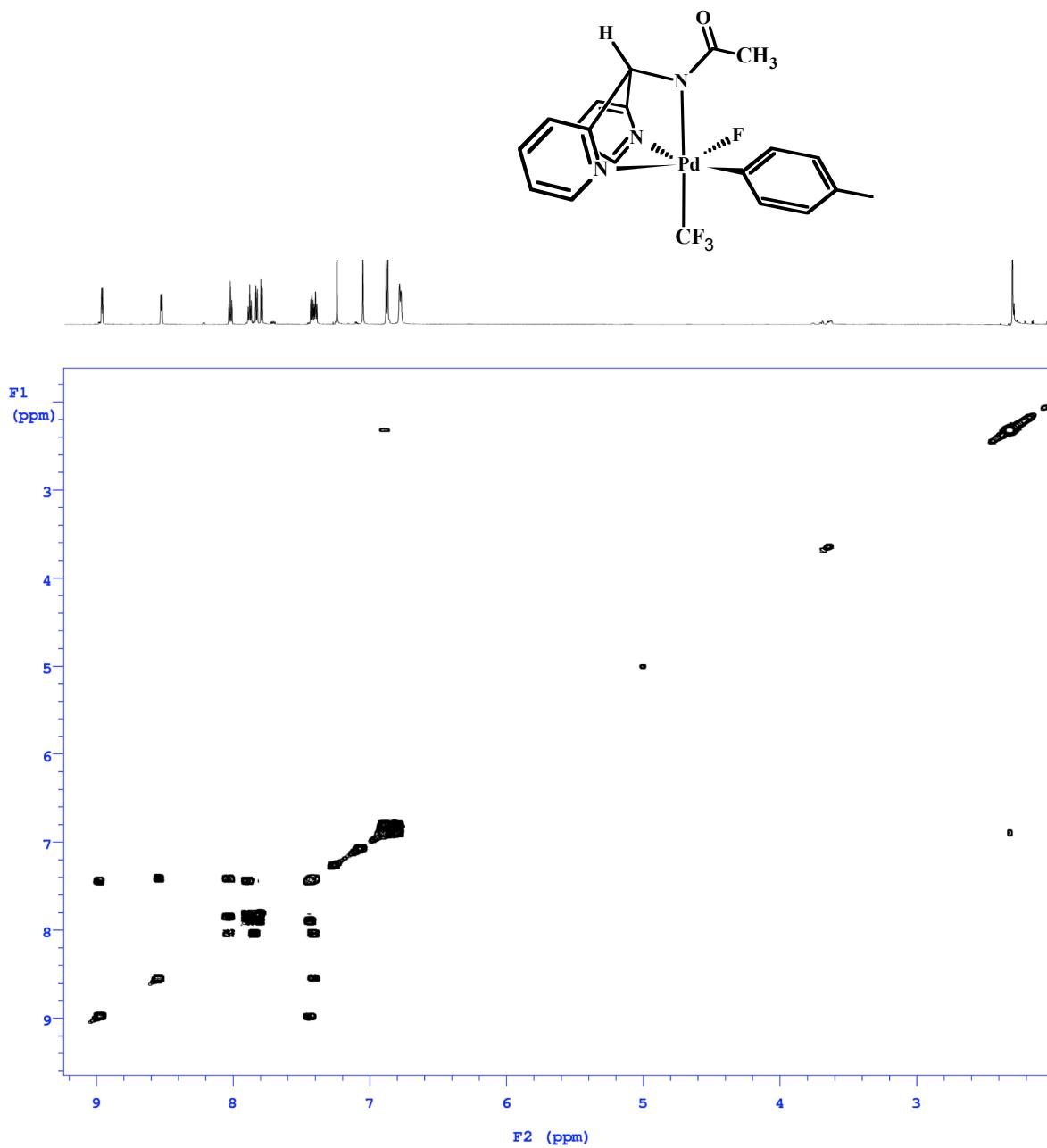
Temp. 28.0 C / 301.1 K  
Operator: maleckis

Relax. delay 1.000 sec  
Pulse 30.0 degrees  
Acc. time 0.629 sec  
Width 208.3 kHz  
16 repetitions  
OBSERVE F19, 470.5577223 MHz  
DATA PROCESSING  
Line broadening 1.5 Hz  
FT size 262144  
Total time 0 min 29 sec

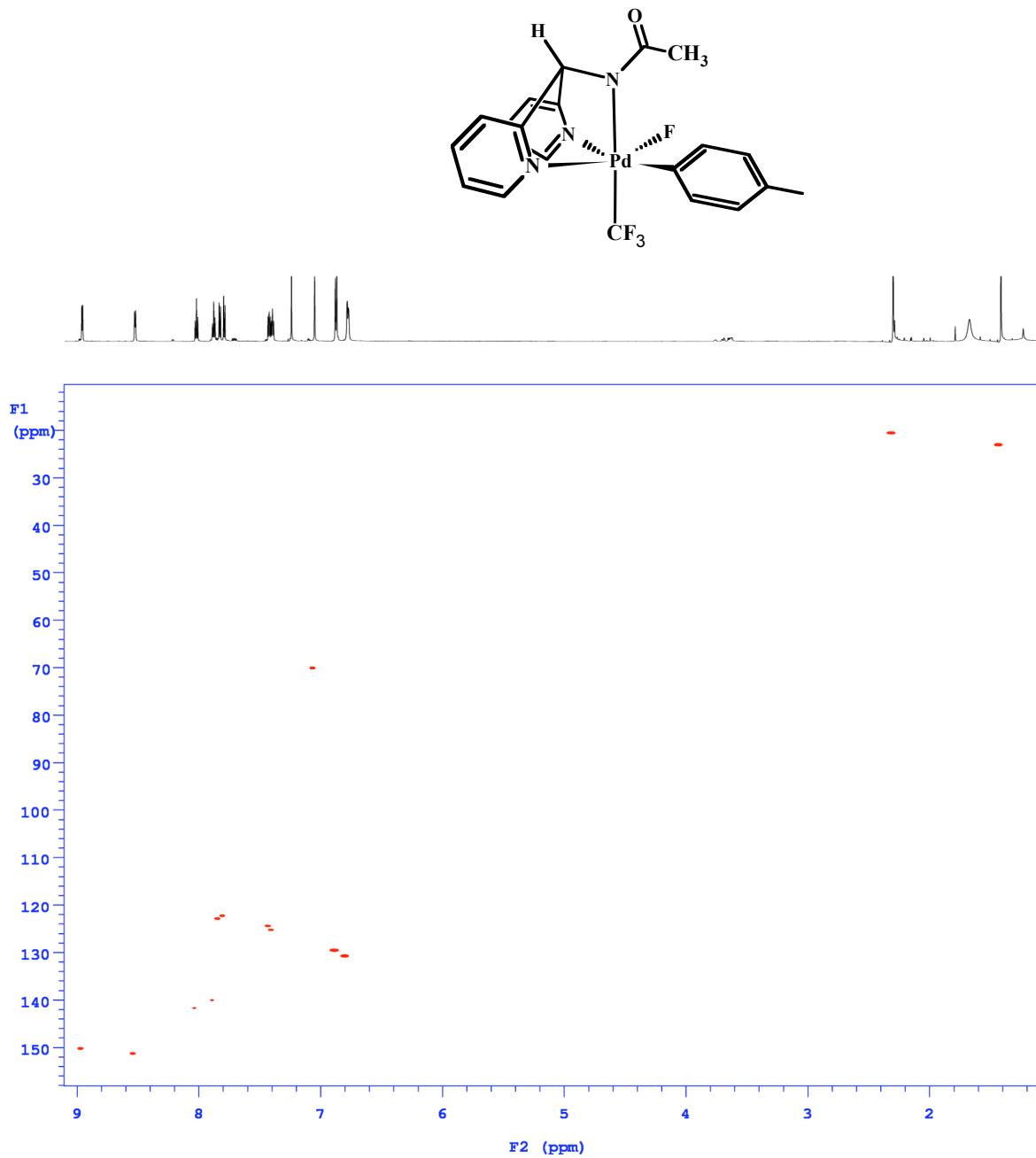
VARIAN 



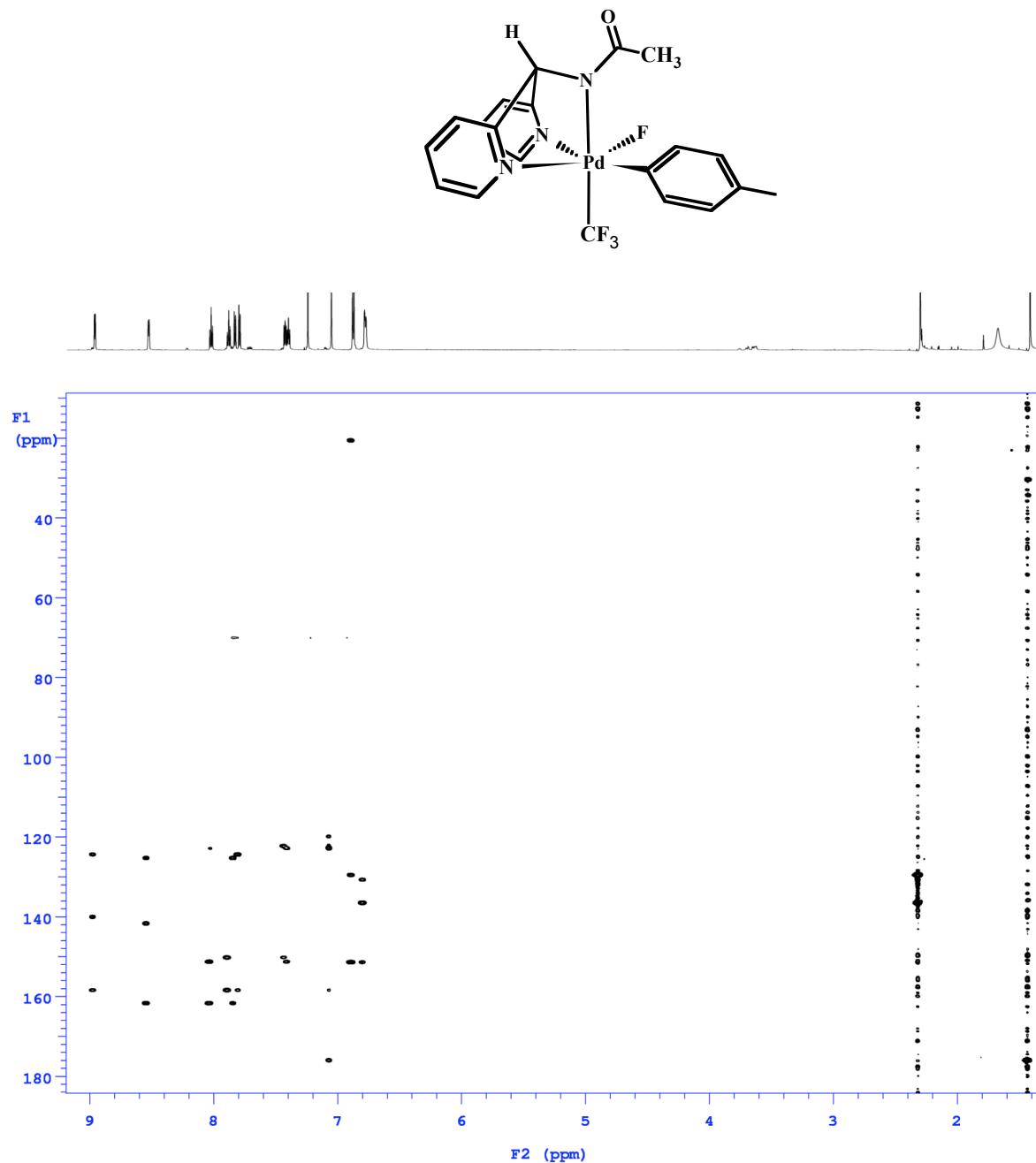
$^1\text{H}/^1\text{H}$  COSY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)



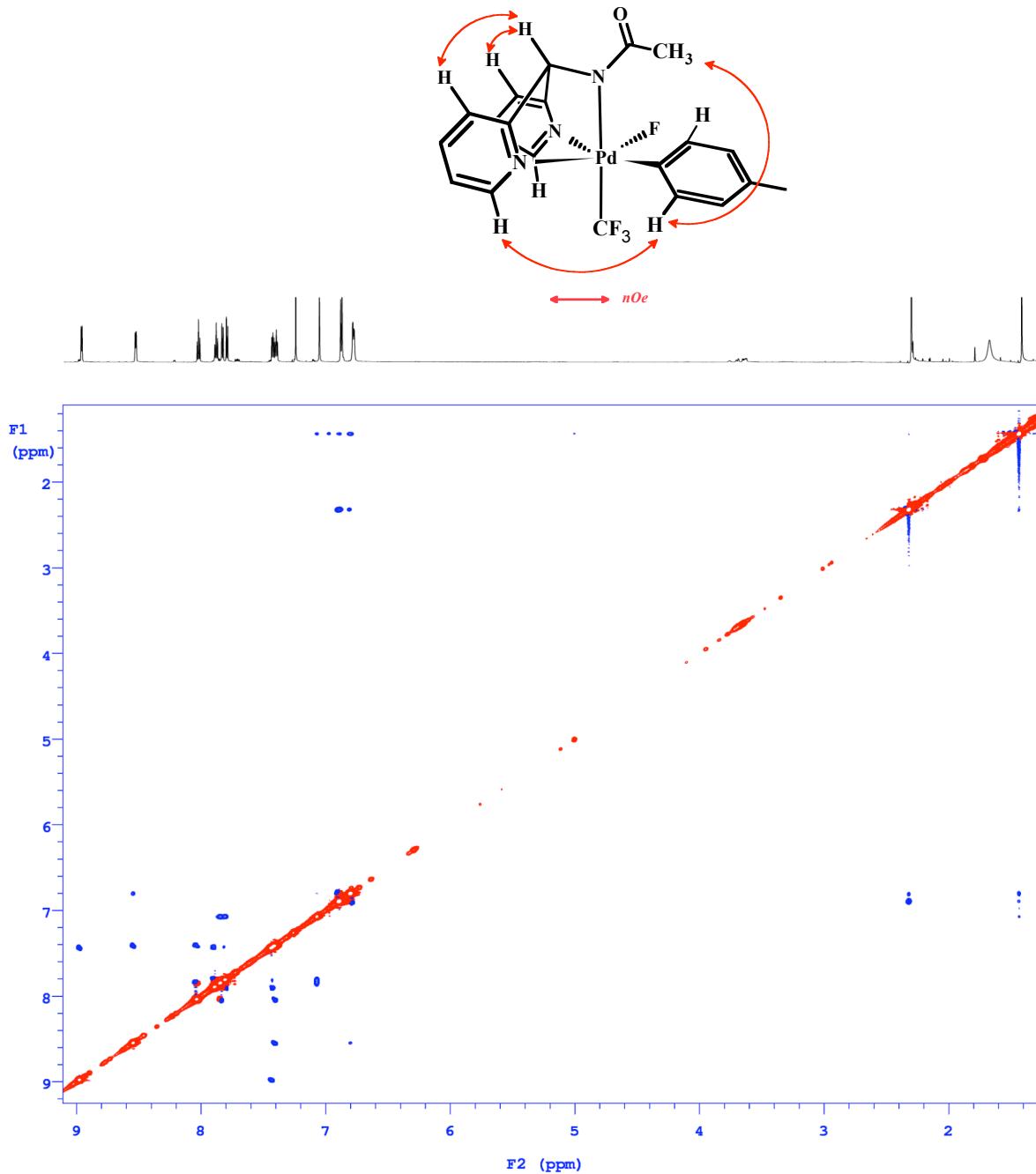
<sup>1</sup>H/<sup>13</sup>C ASAPHMQC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)



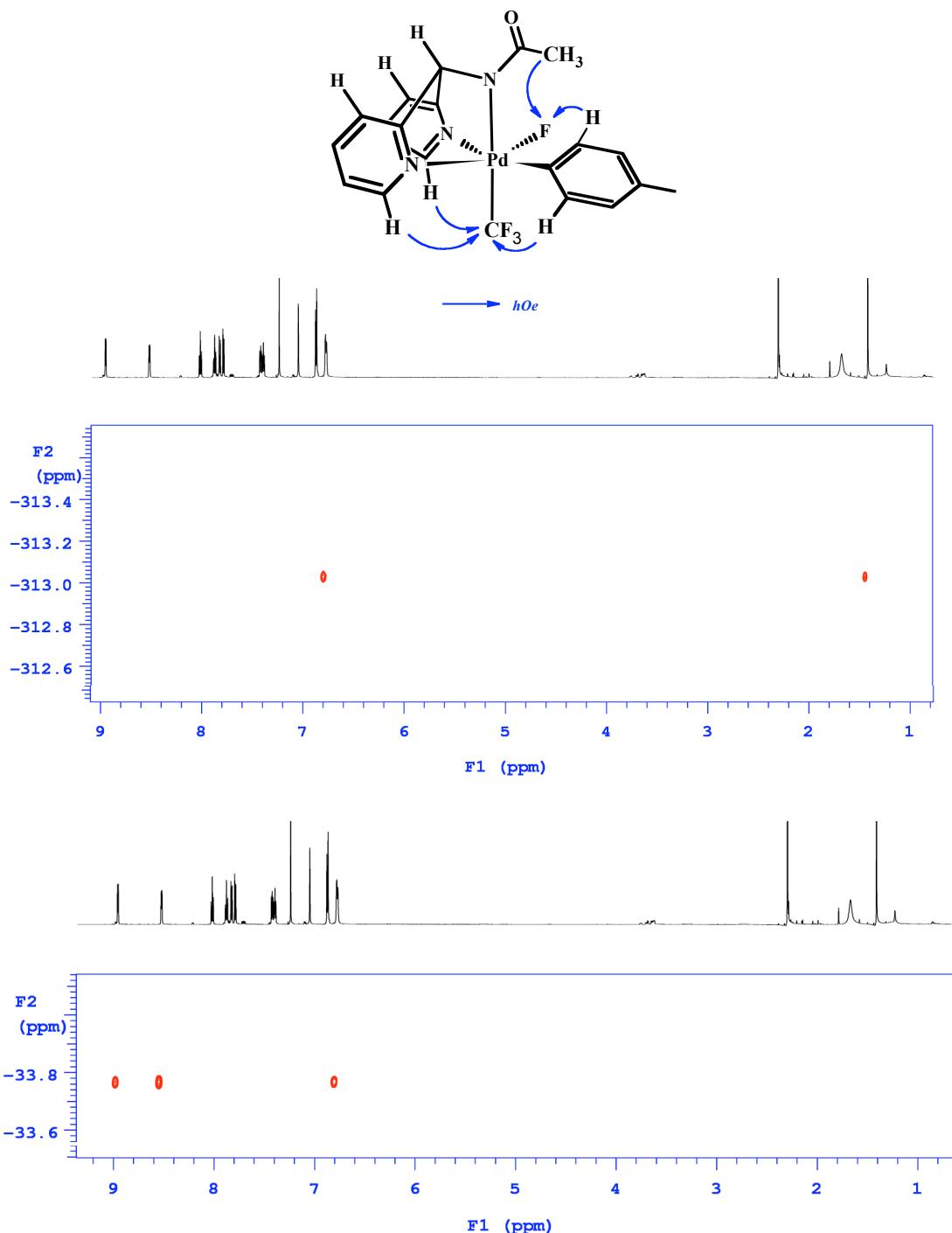
$^1\text{H}/^{13}\text{C}$  HMBC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)



<sup>1</sup>H/<sup>1</sup>H ROESY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)



<sup>19</sup>F/<sup>1</sup>H HOSY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (13b)



<sup>1</sup>H NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN 

Sample Name:

Data Collected on:  
Yb-vnmrs700

Archive directory:

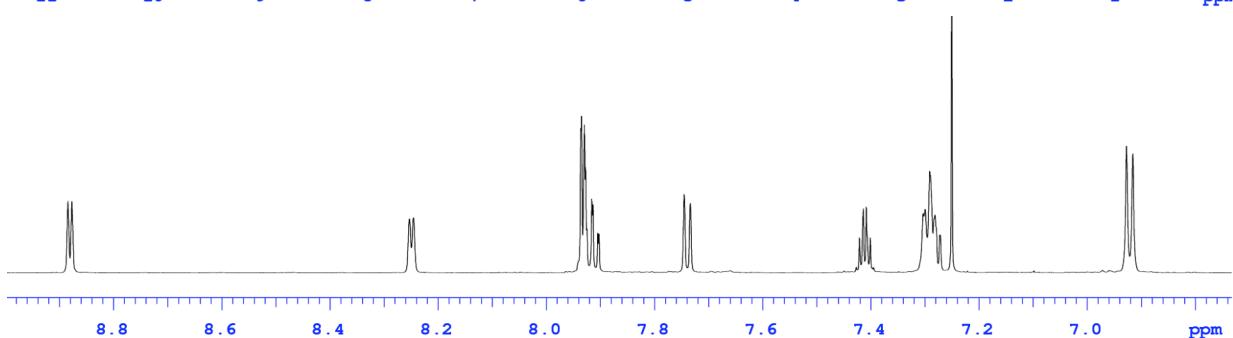
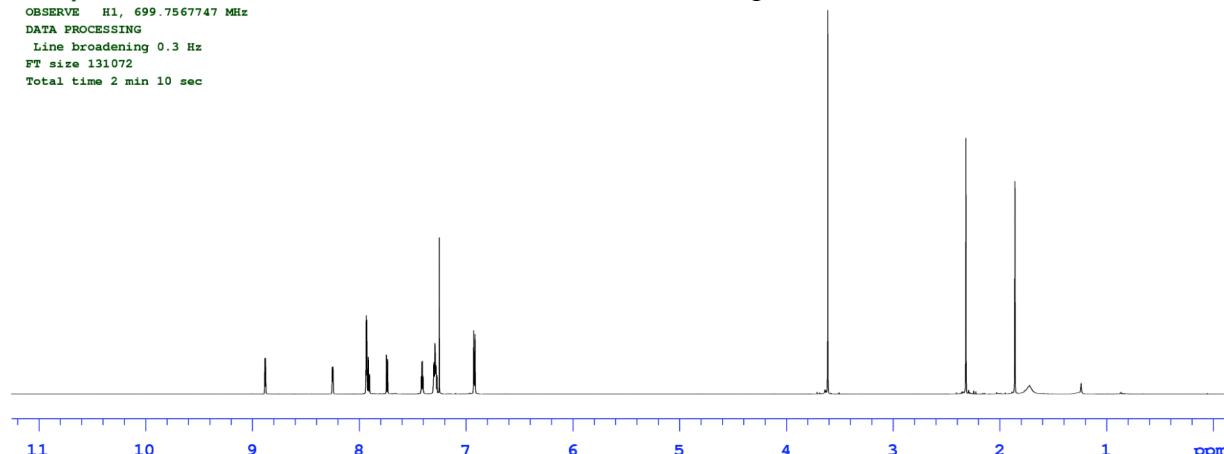
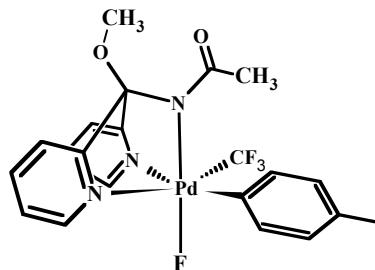
Sample directory:

FidFile: AM3-61-minor-pure

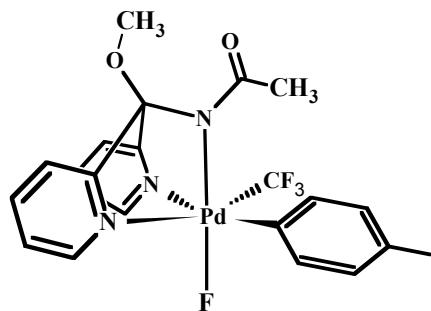
Pulse Sequence: PROTON (s2pul)  
Solvent: cdcl3  
Data collected on: May 18 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 5.190 sec  
Width 12626.3 Hz  
16 repetitions  
OBSERVE H1, 699.7567747 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 131072  
Total time 2 min 10 sec



$^{13}\text{C}\{^1\text{H}\}$  NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)



STANDARD PROTON PARAMETERS  
Atropine

VARIAN

Sample Name:

Data Collected on:  
Yb-vnmrs700

Archive directory:

Sample directory:

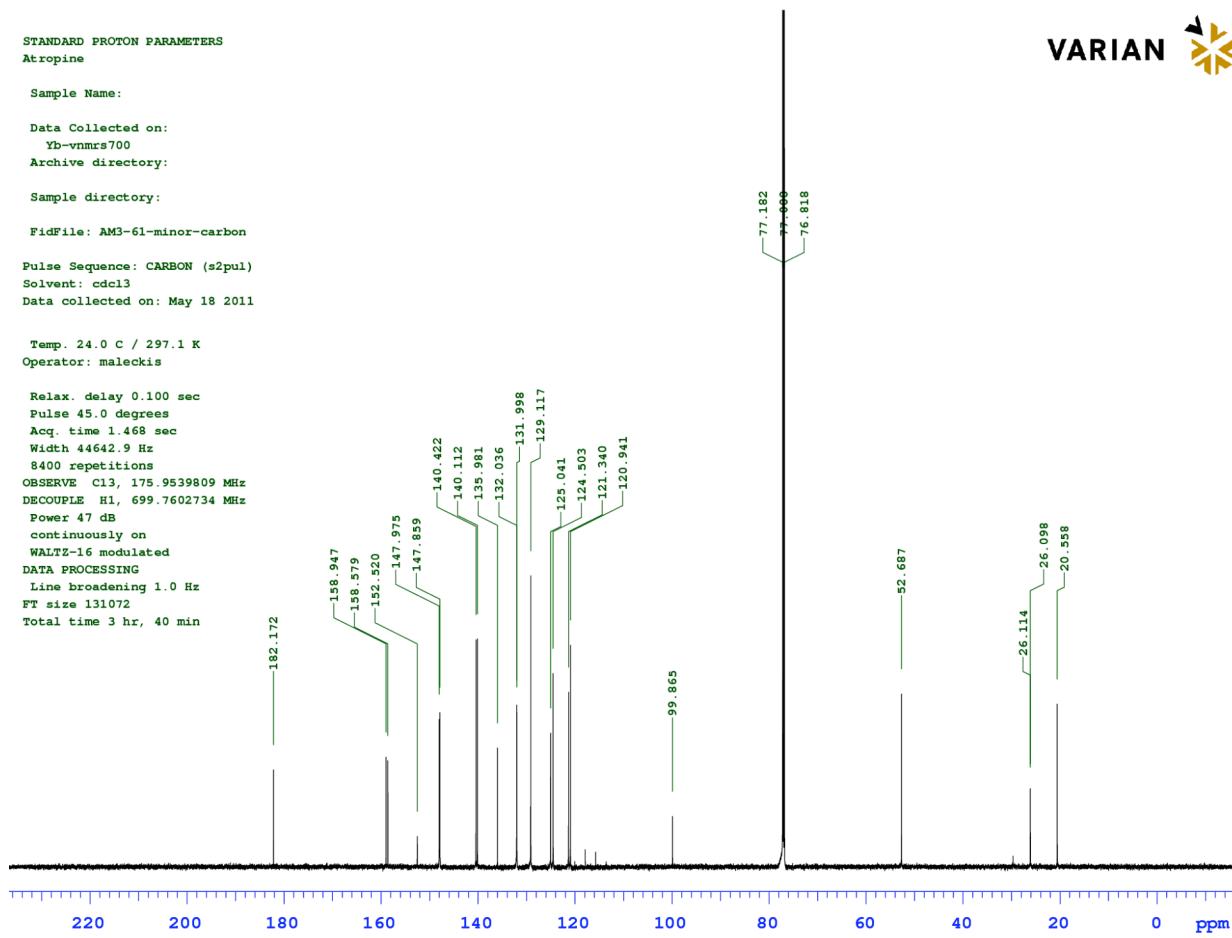
FidFile: AM3-61-minor-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3

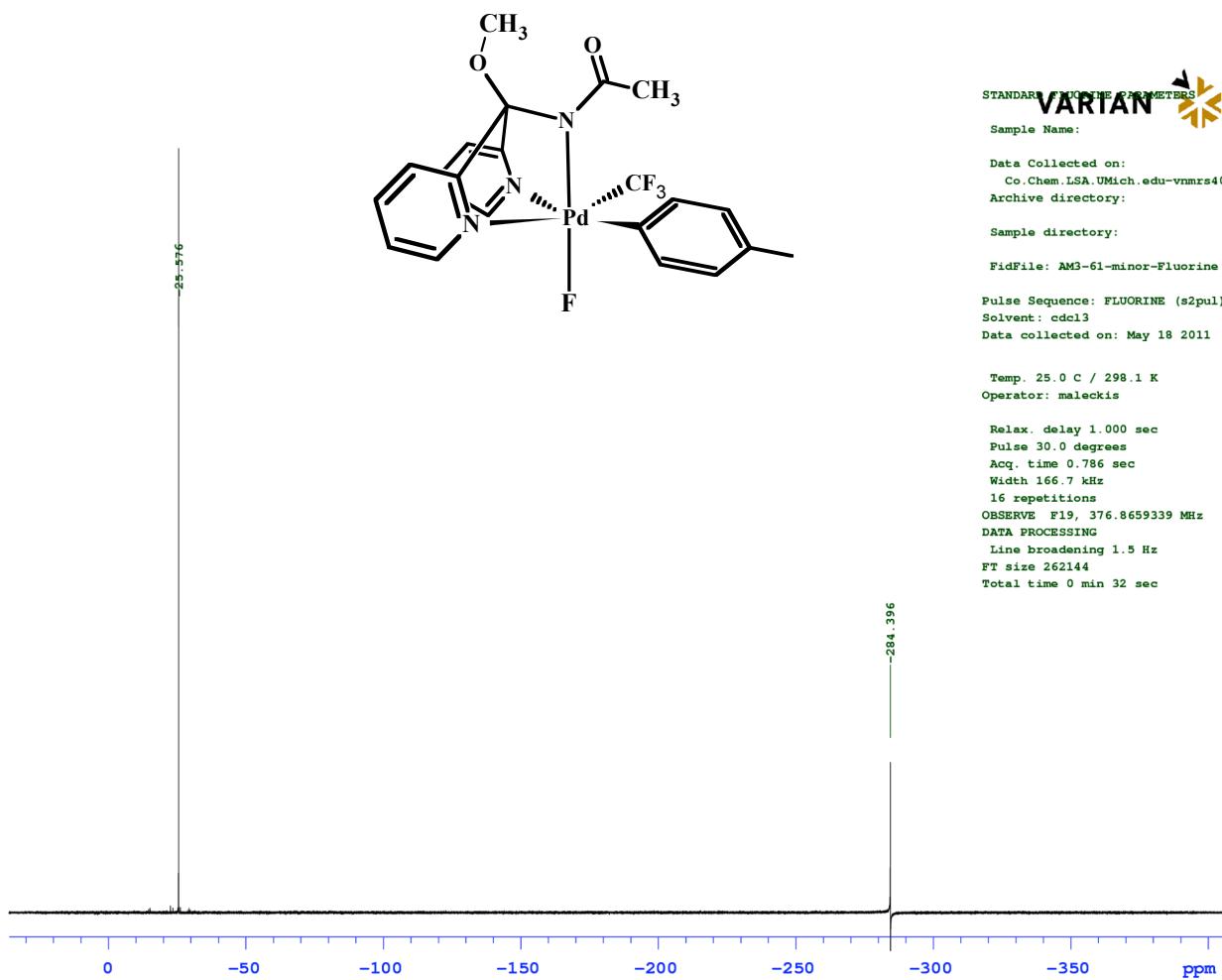
Data collected on: May 18 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

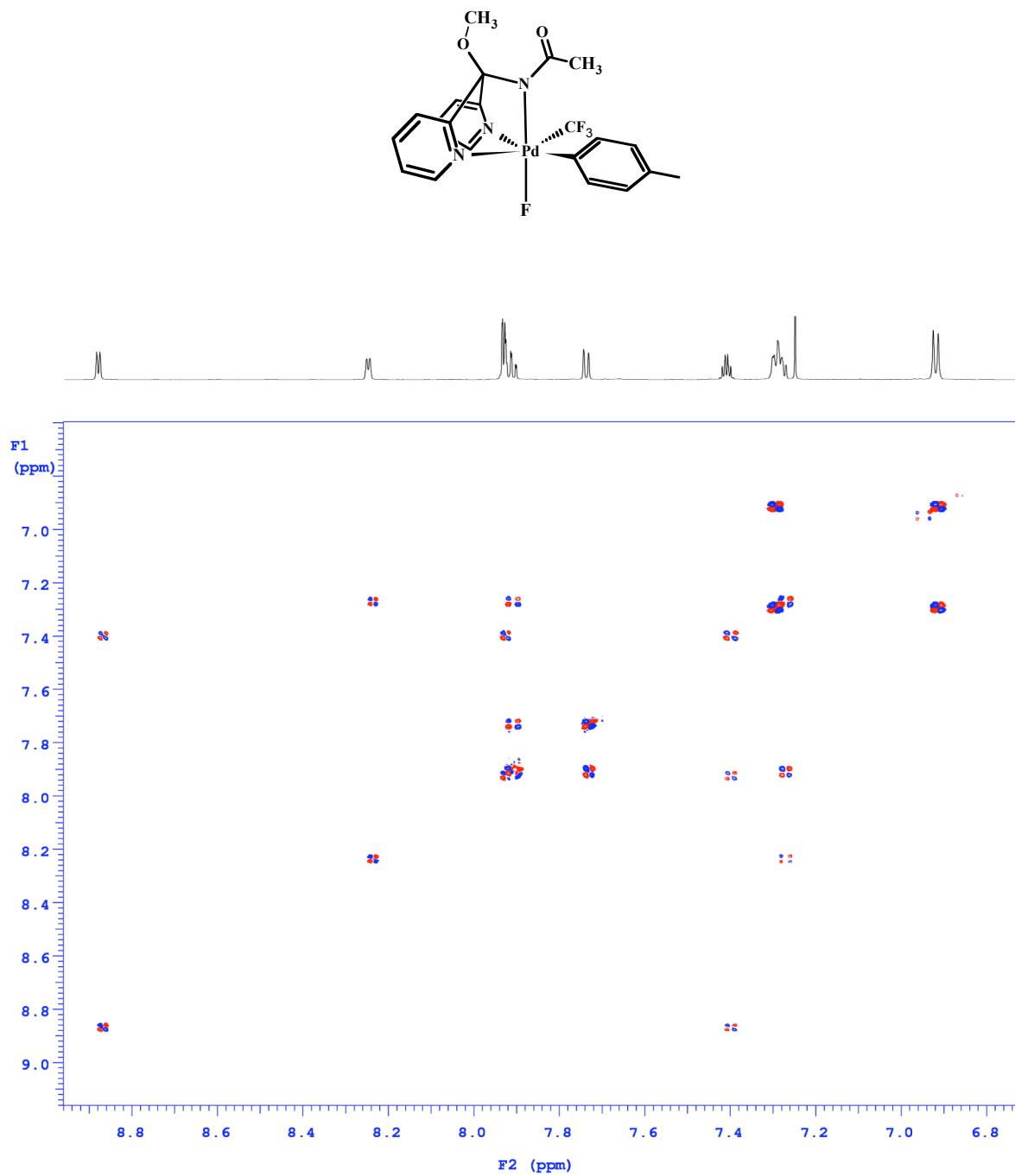
Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 1.468 sec  
Width 44642.9 Hz  
8400 repetitions  
OBSERVE C13, 175.9539809 MHz  
DECOUPLE H1, 699.7602734 MHz  
Power 47 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 3 hr, 40 min



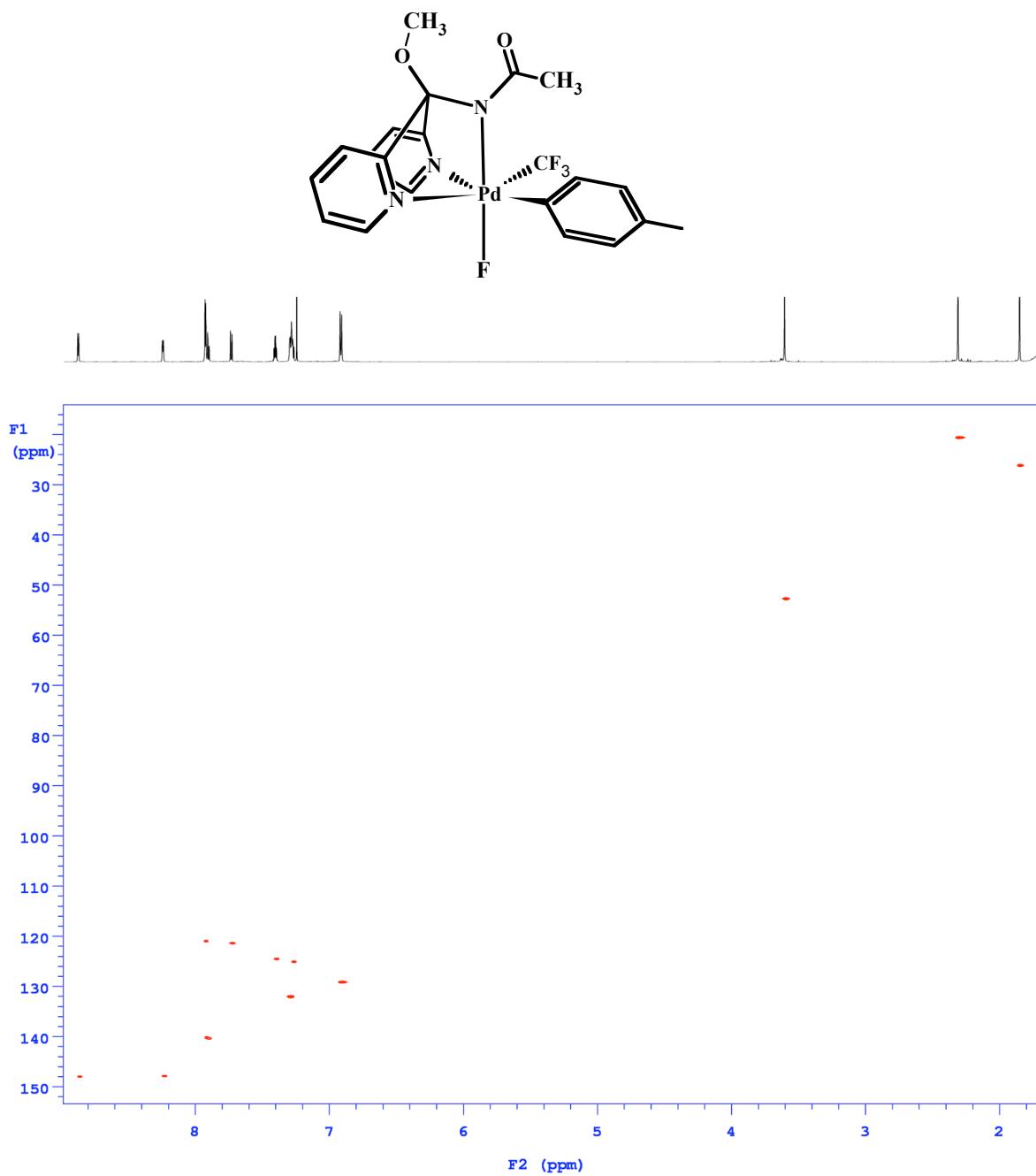
<sup>19</sup>F NMR of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)



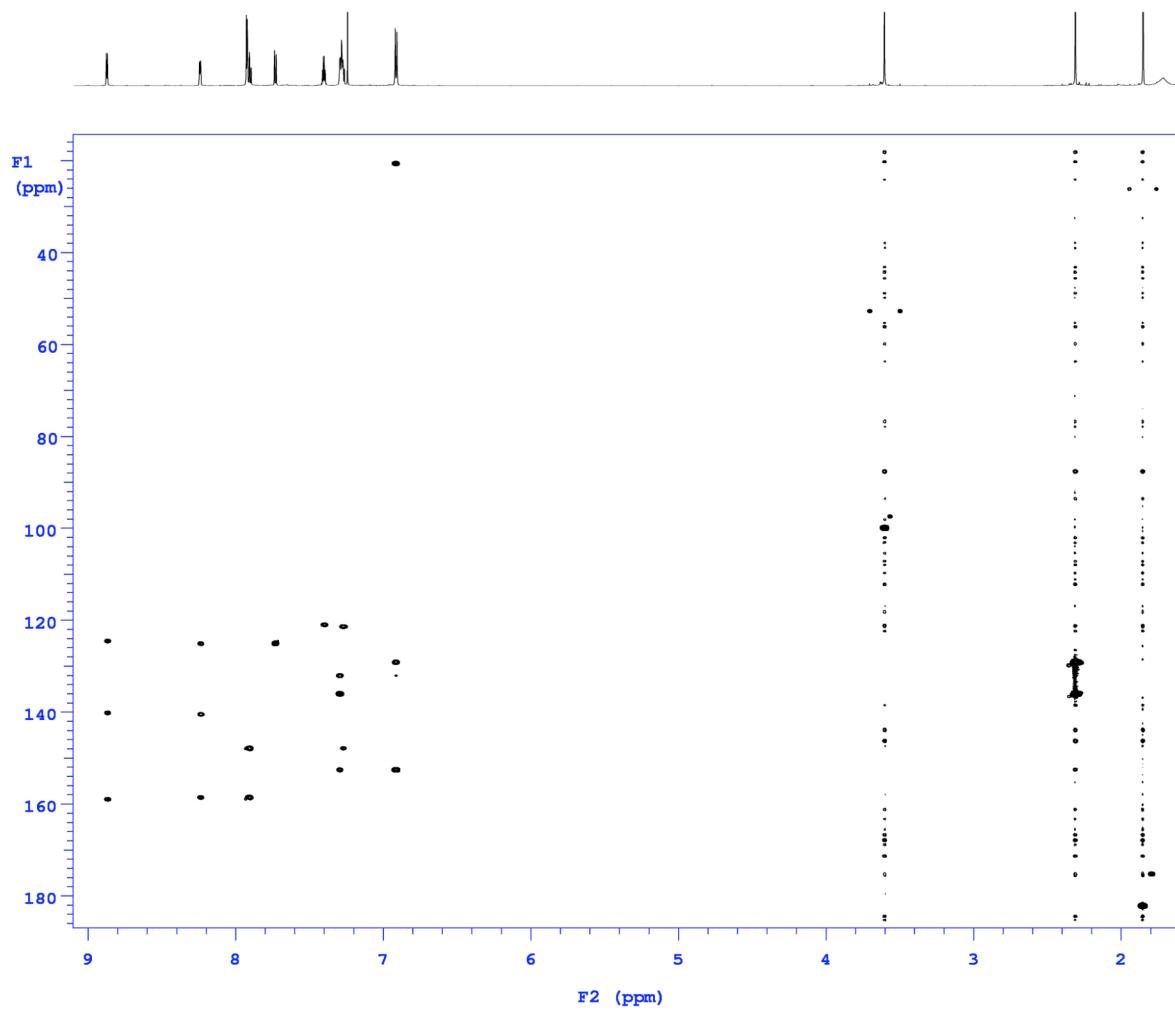
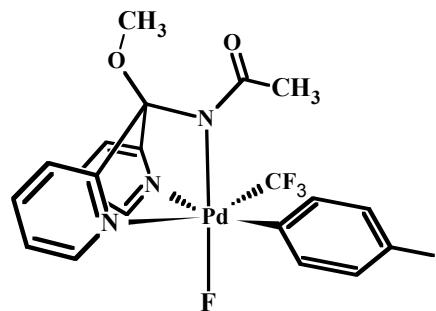
<sup>1</sup>H/<sup>1</sup>H gDQCOSY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)



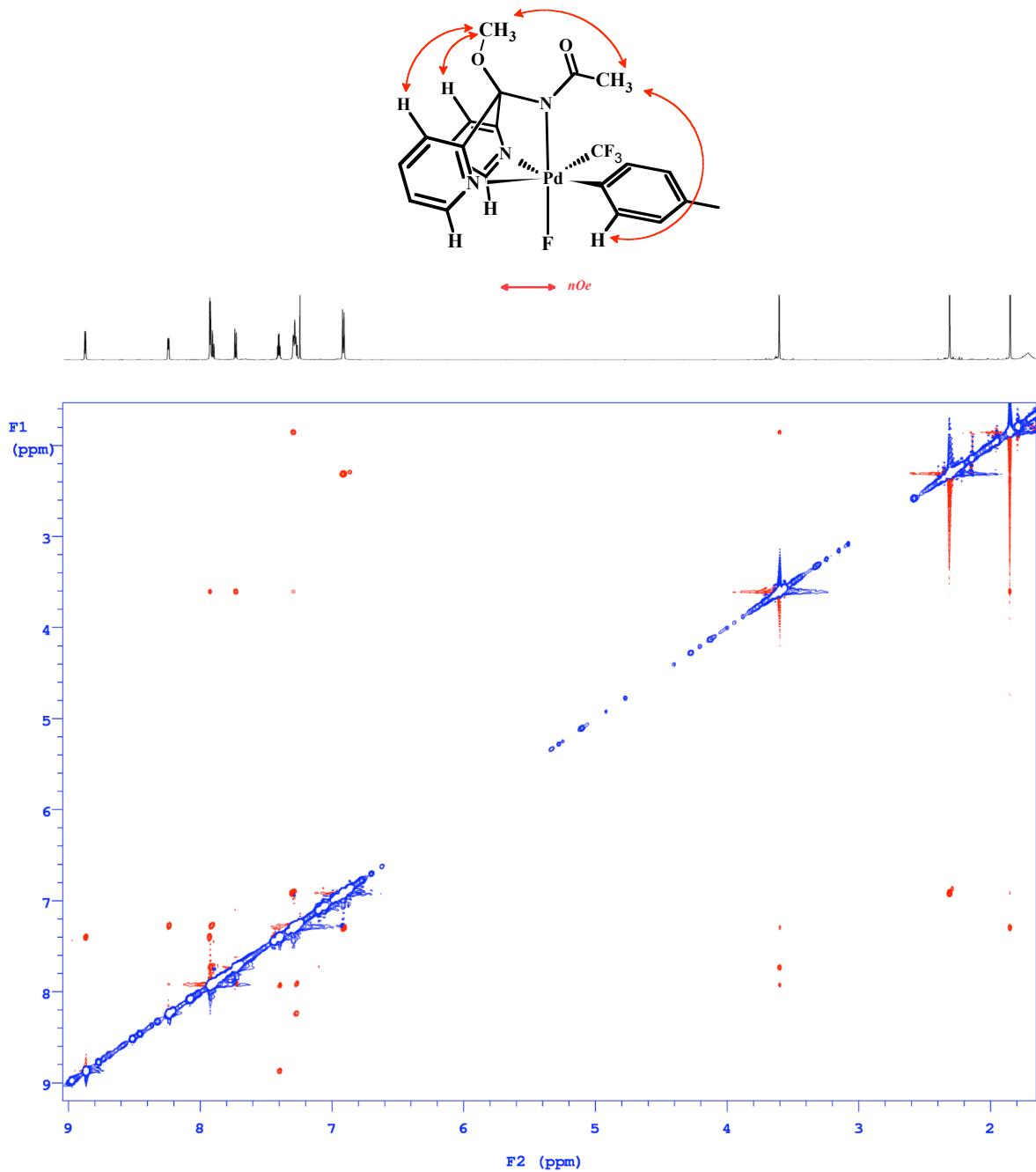
$^1\text{H}/^{13}\text{C}$  ASAPHMQC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)



$^1\text{H}/^{13}\text{C}$  HMBC of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)



<sup>1</sup>H/<sup>13</sup>C NOESY of (dpaa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (S1)



<sup>1</sup>H NMR of 1,1-di(2-pyridyl)phenylethane (dpph) (14)

STANDARD 1H OBSERVE - profile

Sample Name:

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

Sample directory:

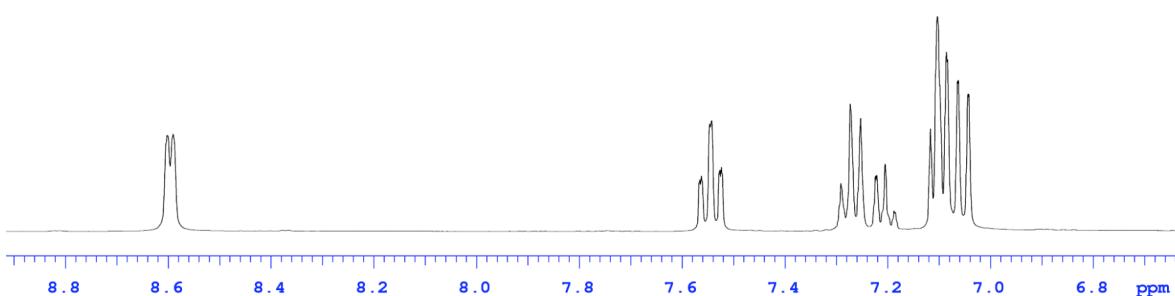
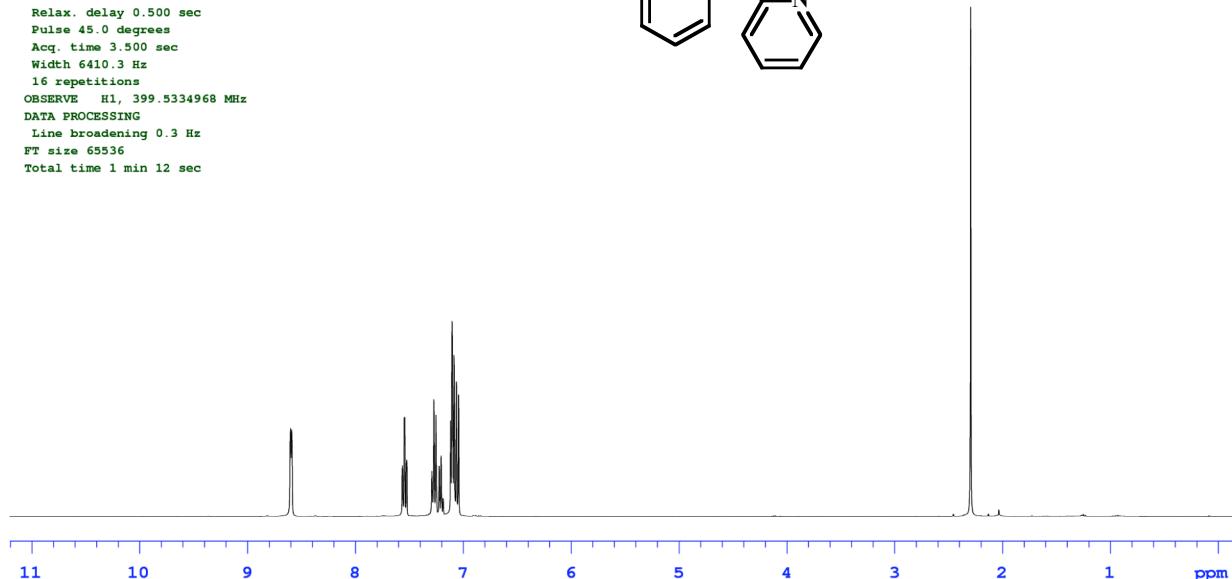
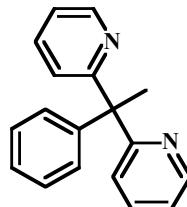
FidFile: AM3-29

Pulse Sequence: PROTON (s2pul)  
Solvent: cdc13  
Data collected on: Apr 29 2011

Operator: maleckis

Relax. delay 0.500 sec  
Pulse 45.0 degrees  
Acq. time 3.500 sec  
Width 6410.3 Hz  
16 repetitions  
OBSERVE H1, 399.5334968 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 65536  
Total time 1 min 12 sec

VARIAN 



<sup>13</sup>C{<sup>1</sup>H} NMR of 1,1-di(2-pyridyl)phenylethane (dpph) (14)

STANDARD 1H OBSERVE - profile

Sample Name:

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

Sample directory:

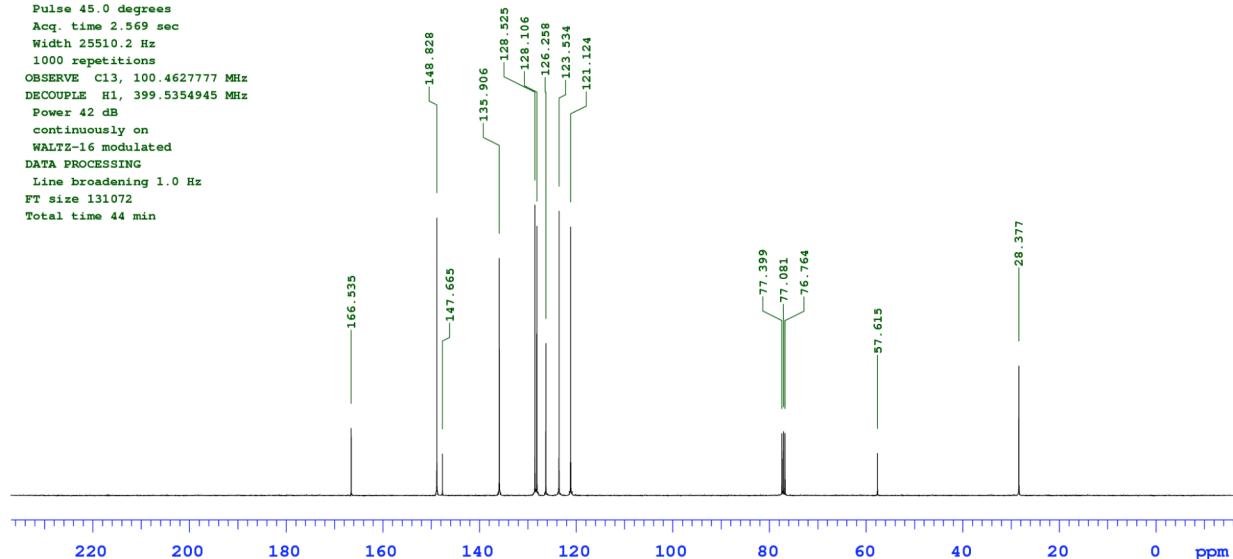
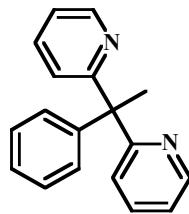
FidFile: AM3-29-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Apr 29 2011

Operator: maleckis

Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 2.569 sec  
Width 25510.2 Hz  
1000 repetitions  
OBSERVE C13, 100.4627777 MHz  
DECOUPLE H1, 399.5354945 MHz  
Power 42 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 44 min

VARIAN 



# <sup>1</sup>H NMR of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN 

Sample Name:

Data Collected on:

YB-vnmrs700

Archive directory:

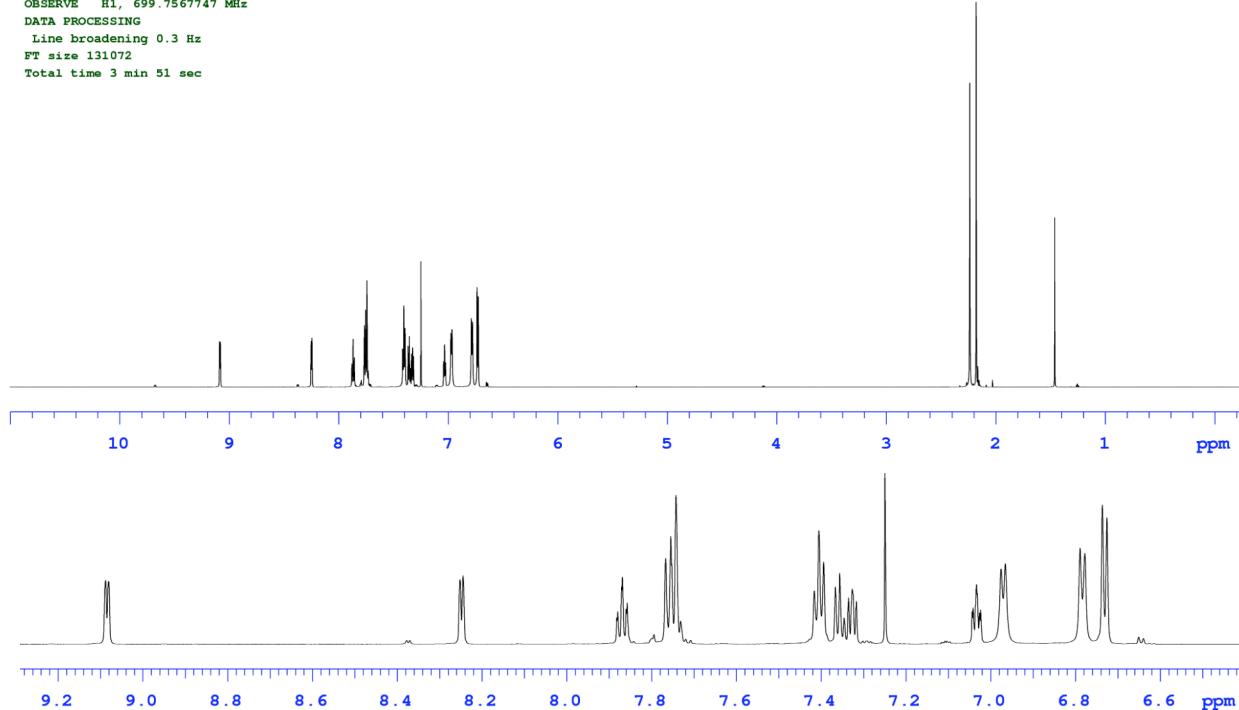
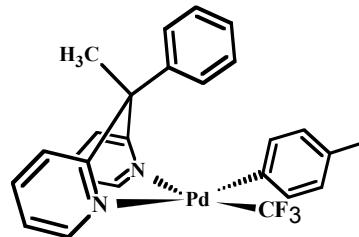
Sample directory:

FidFile: AM-all-C850

Pulse Sequence: PROTON (s2pul)  
Solvent: ccdcl3  
Data collected on: May 24 2011

Temp. 50.0 C / 323.1 K  
Operator: maleckis

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 3.500 sec  
Width 11261.3 Hz  
40 repetitions  
OBSERVE H1, 699.7567747 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 131072  
Total time 3 min 51 sec



$^{13}\text{C}\{^1\text{H}\}$  NMR of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)

STANDARD PROTON PARAMETERS  
Atropine

VARIAN

Sample Name:

Data Collected on:  
Yb-vnmrs700  
Archive directory:

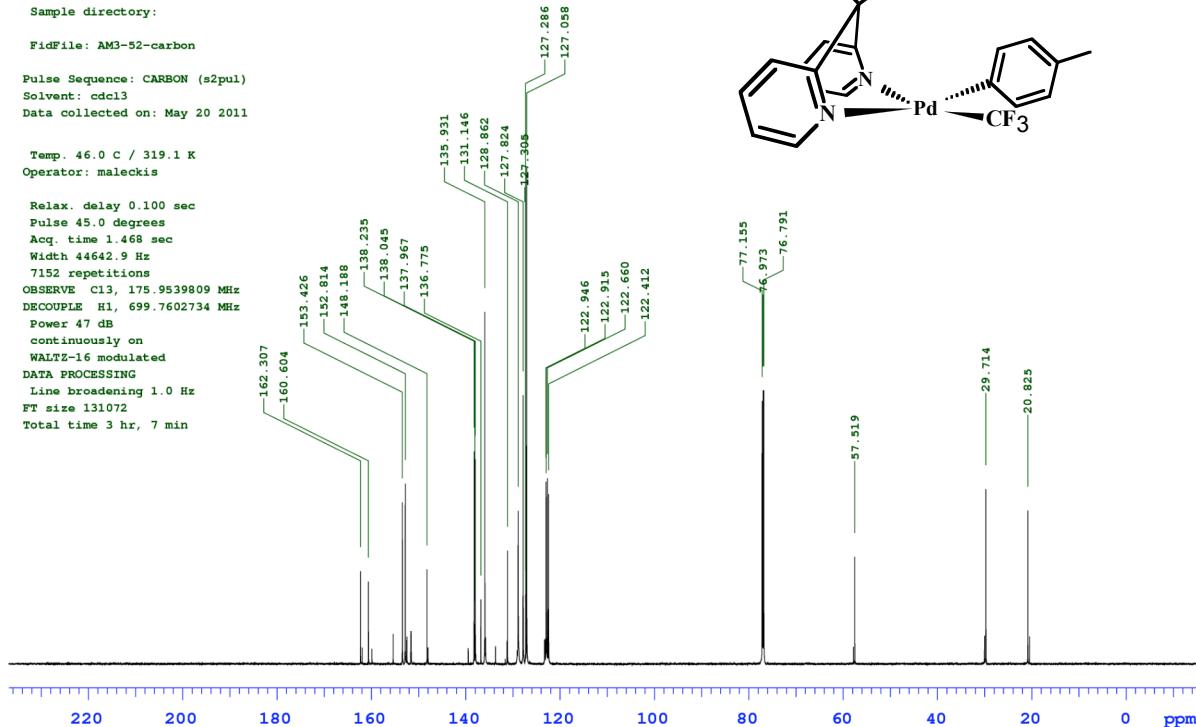
Sample directory:

FidFile: AM3-52-carbon

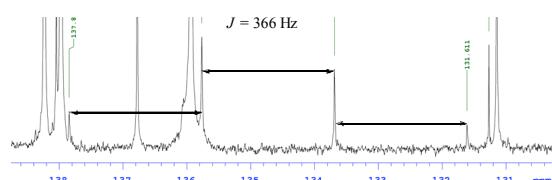
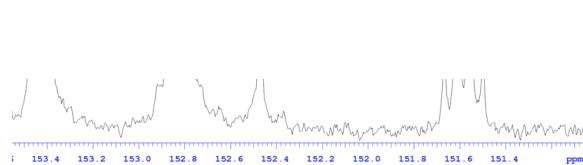
Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: May 20 2011

Temp. 46.0 C / 319.1 K  
Operator: maleckis

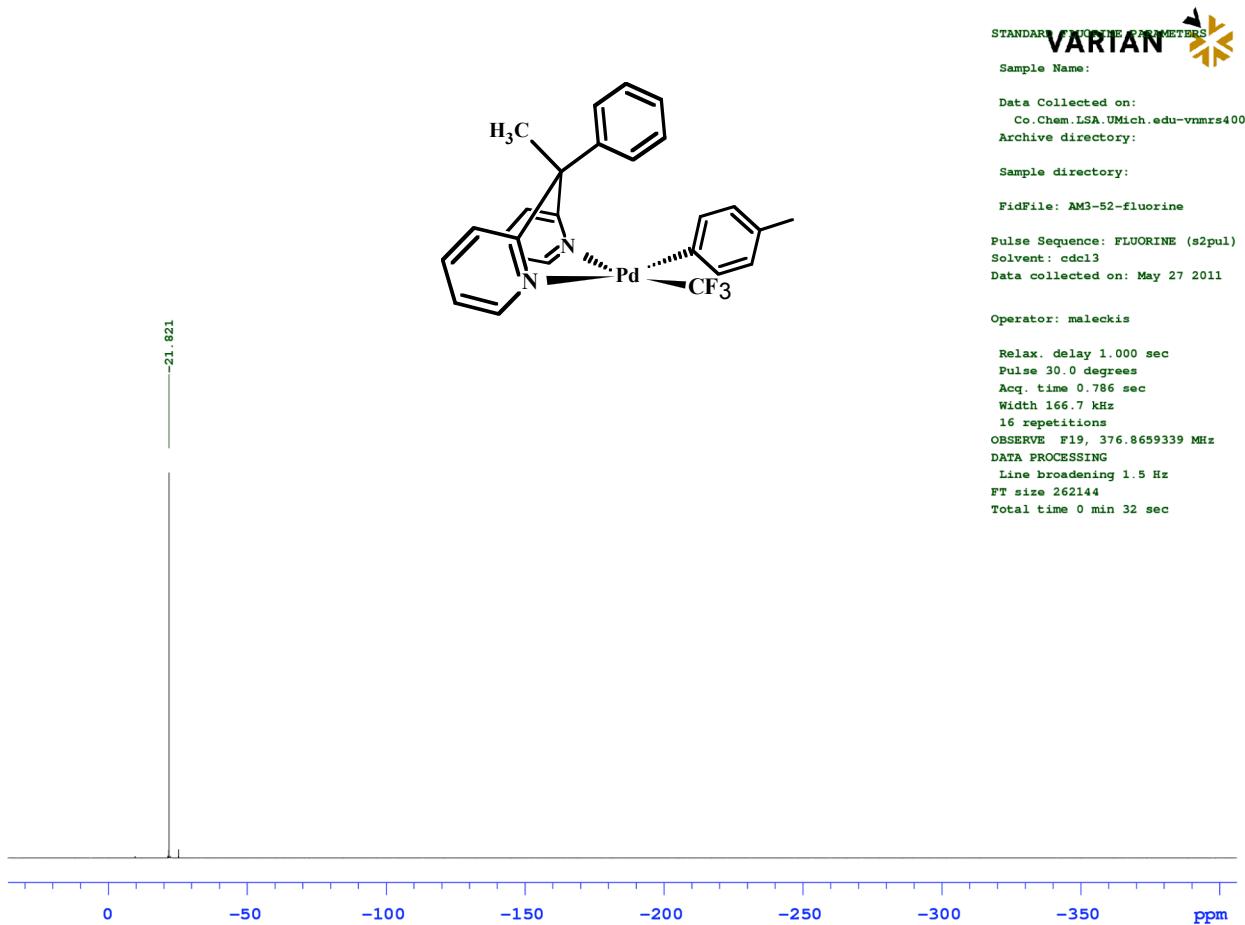
Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 1.468 sec  
Width 44642.9 Hz  
7152 repetitions  
OBSERVE C13, 175.9539809 MHz  
DECOUPLE H1, 699.7602734 MHz  
Power 47 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 3 hr, 7 min



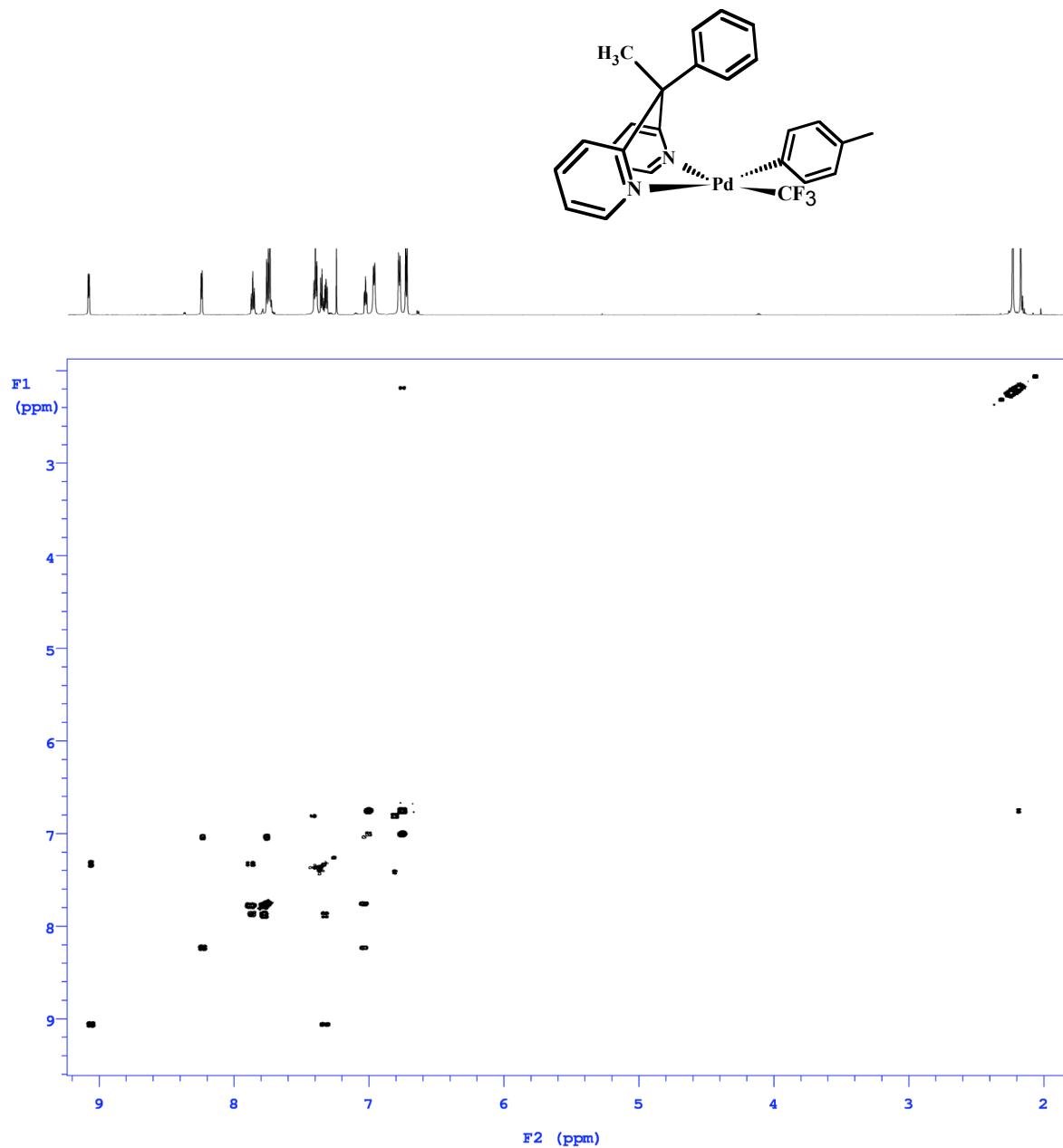
$J = 9.8 \text{ Hz}$



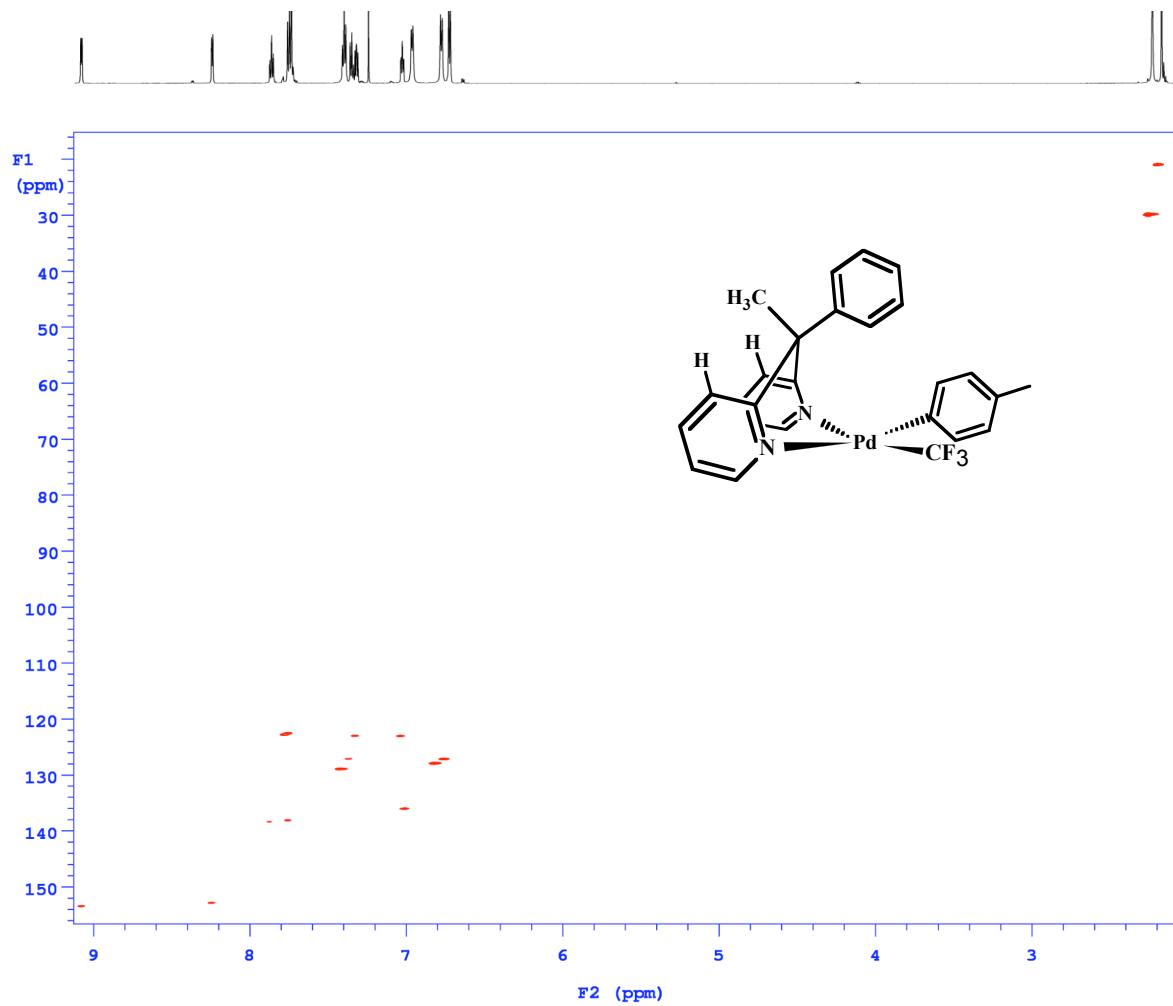
<sup>19</sup>F NMR of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)



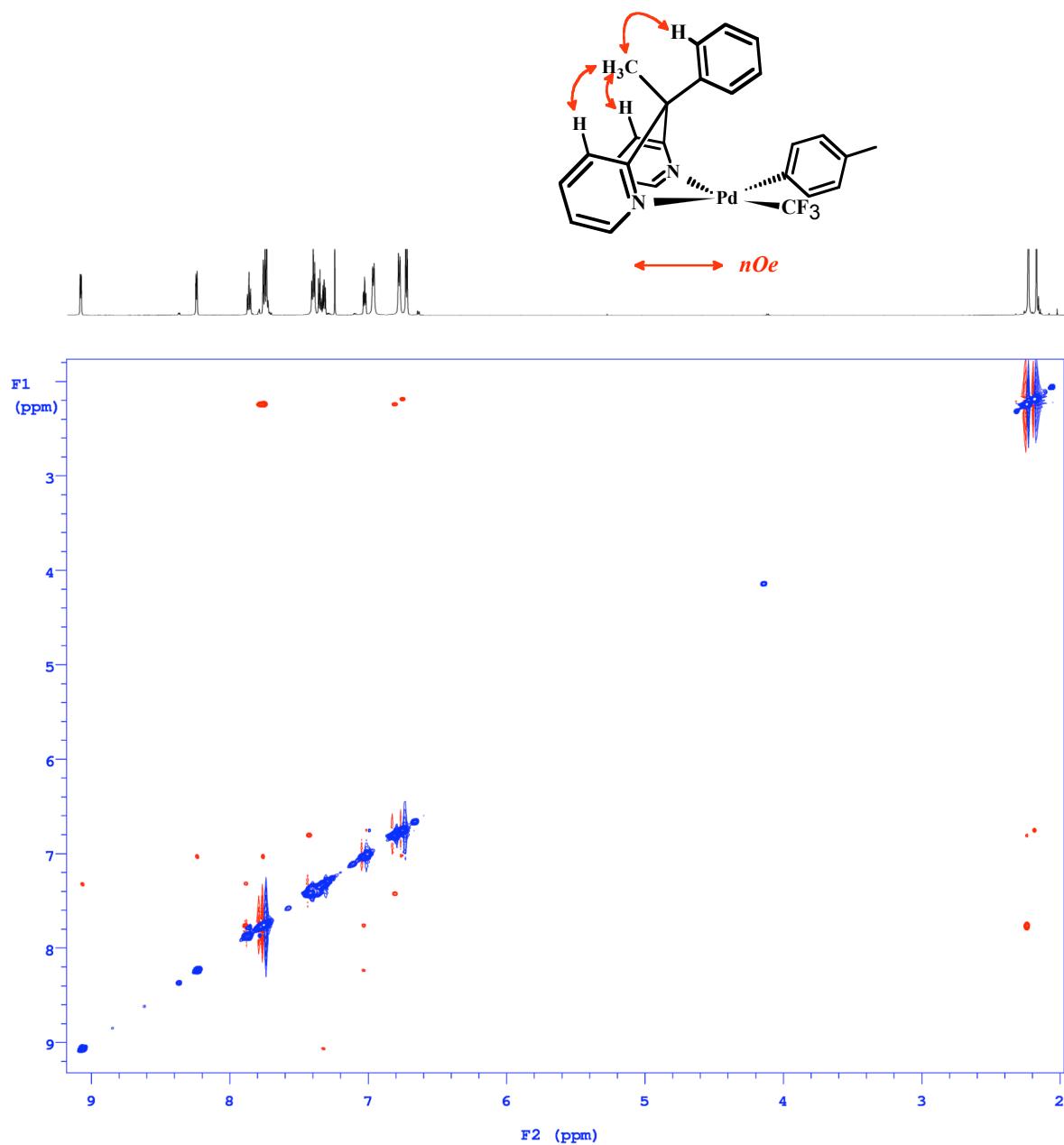
<sup>1</sup>H/<sup>1</sup>H COSY of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)



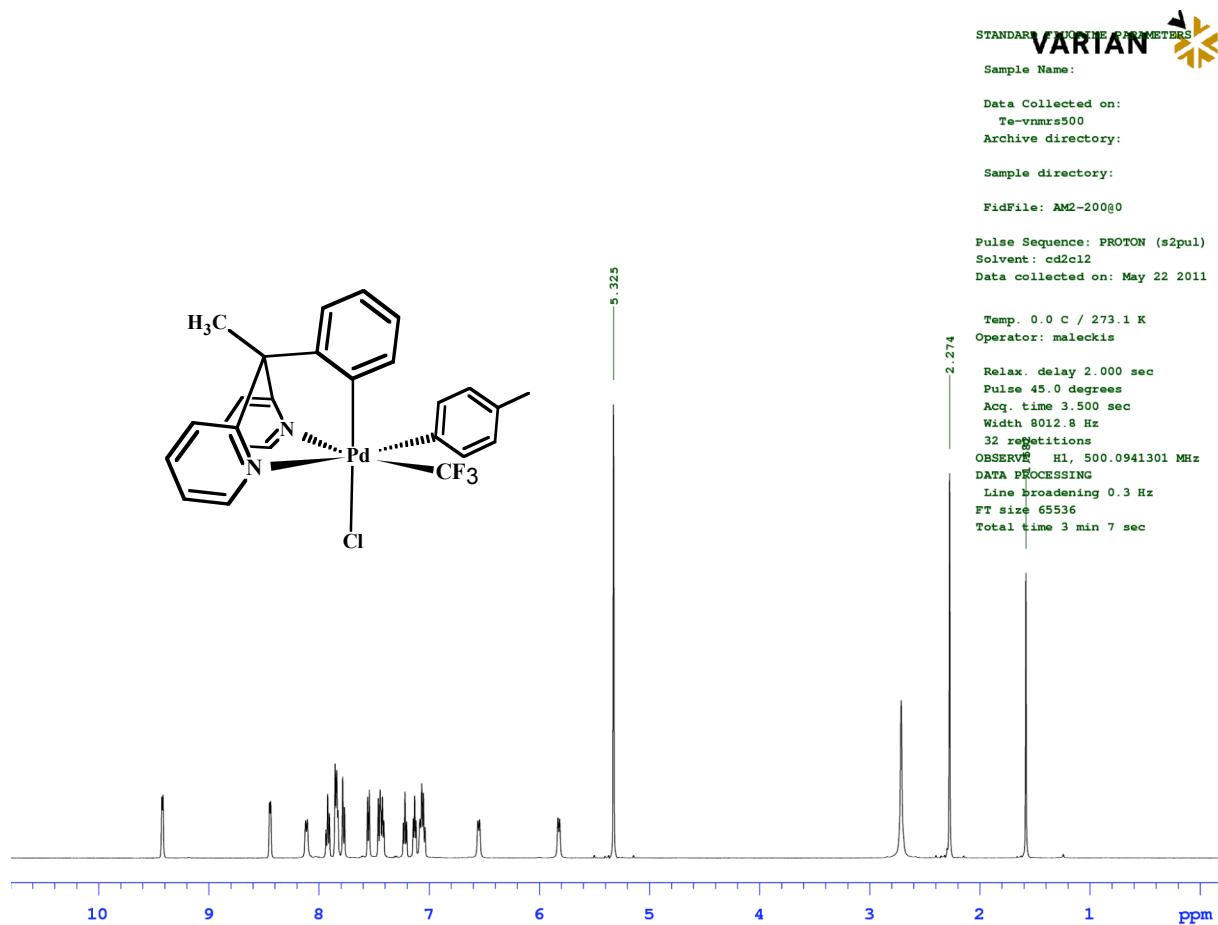
$^1\text{H}/^{13}\text{C}$  ASAPHMQC of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)



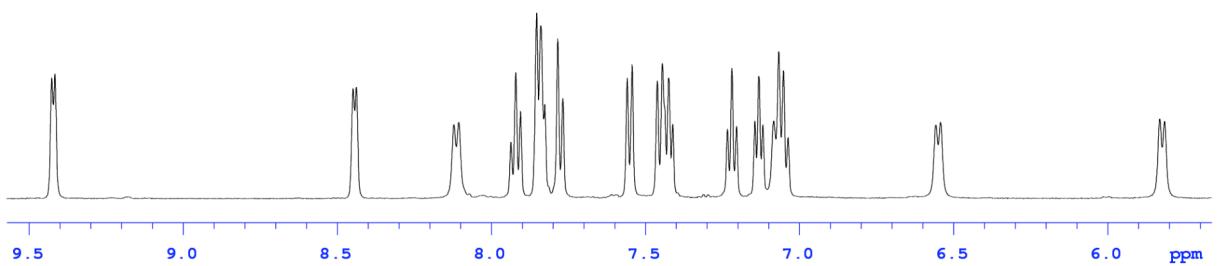
$^1\text{H}/^1\text{H}$  ROESY of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)



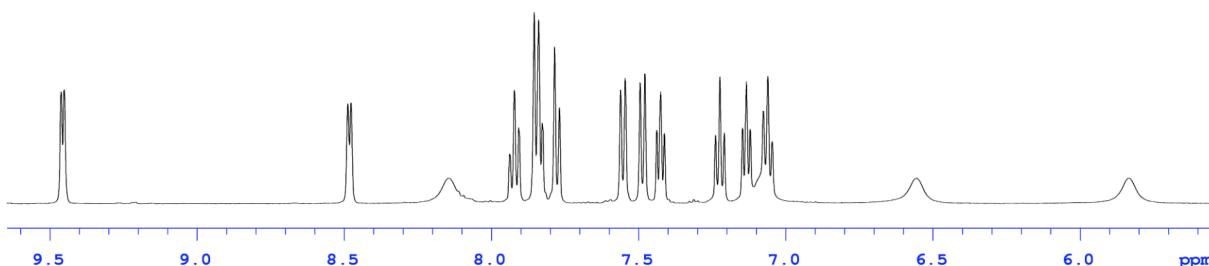
<sup>1</sup>H NMR of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at 0°C)



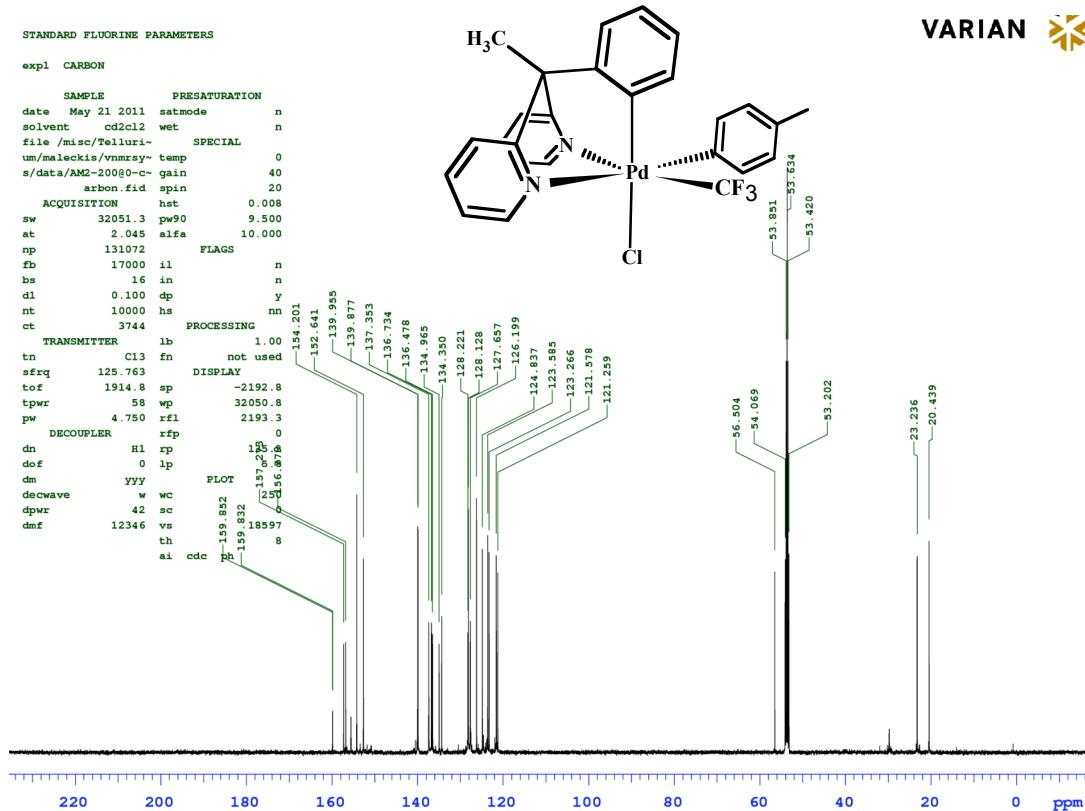
<sup>1</sup>H NMR of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at 0°C)



<sup>1</sup>H NMR of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at 20°C)



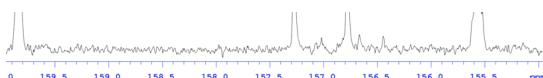
$^{13}\text{C}\{\text{H}\}$  NMR of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at 0°C)



VARIAN \*

$J = 3.9 \text{ Hz}$

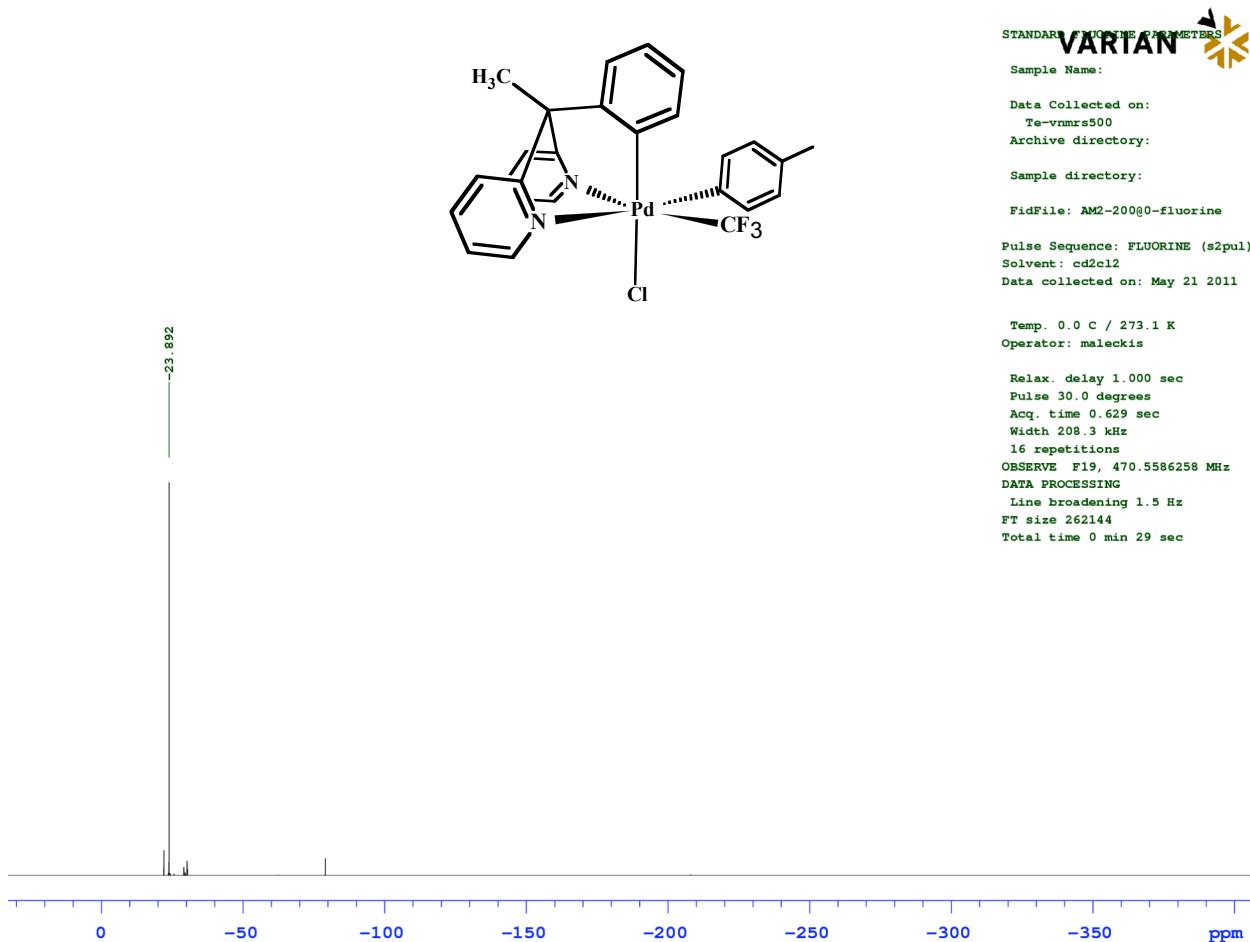
$J = 2.4 \text{ Hz}$



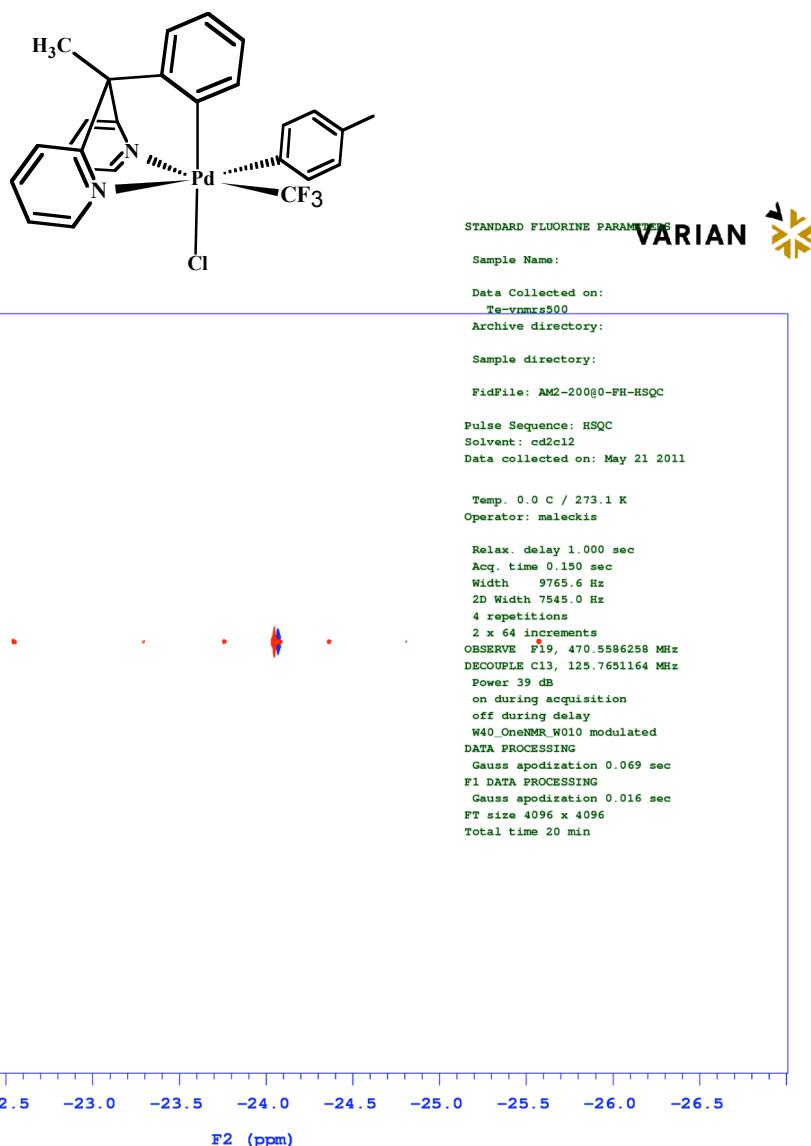
$J = 369 \text{ Hz}$



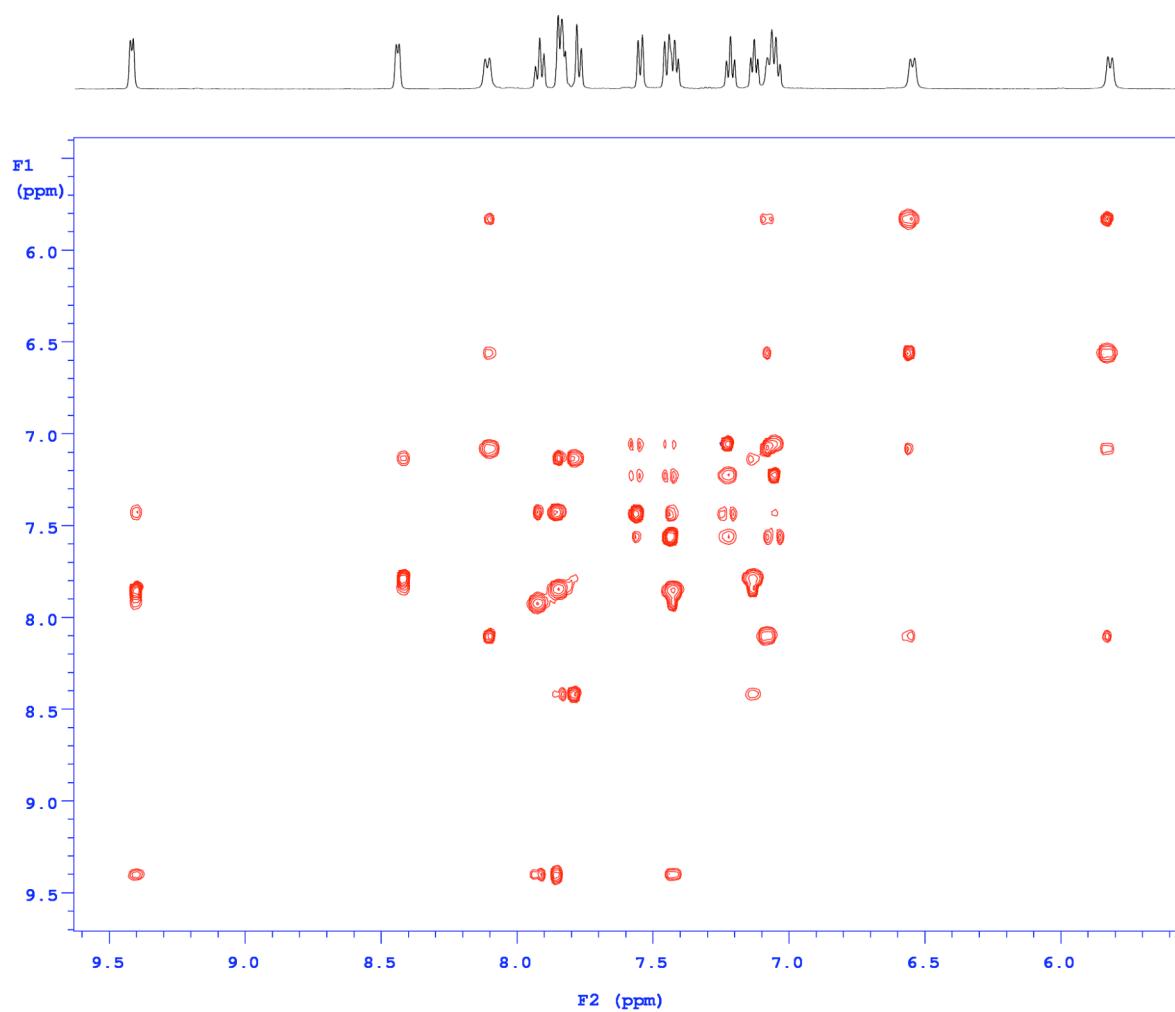
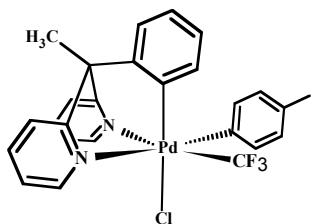
**<sup>19</sup>F NMR of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at 0°C)**



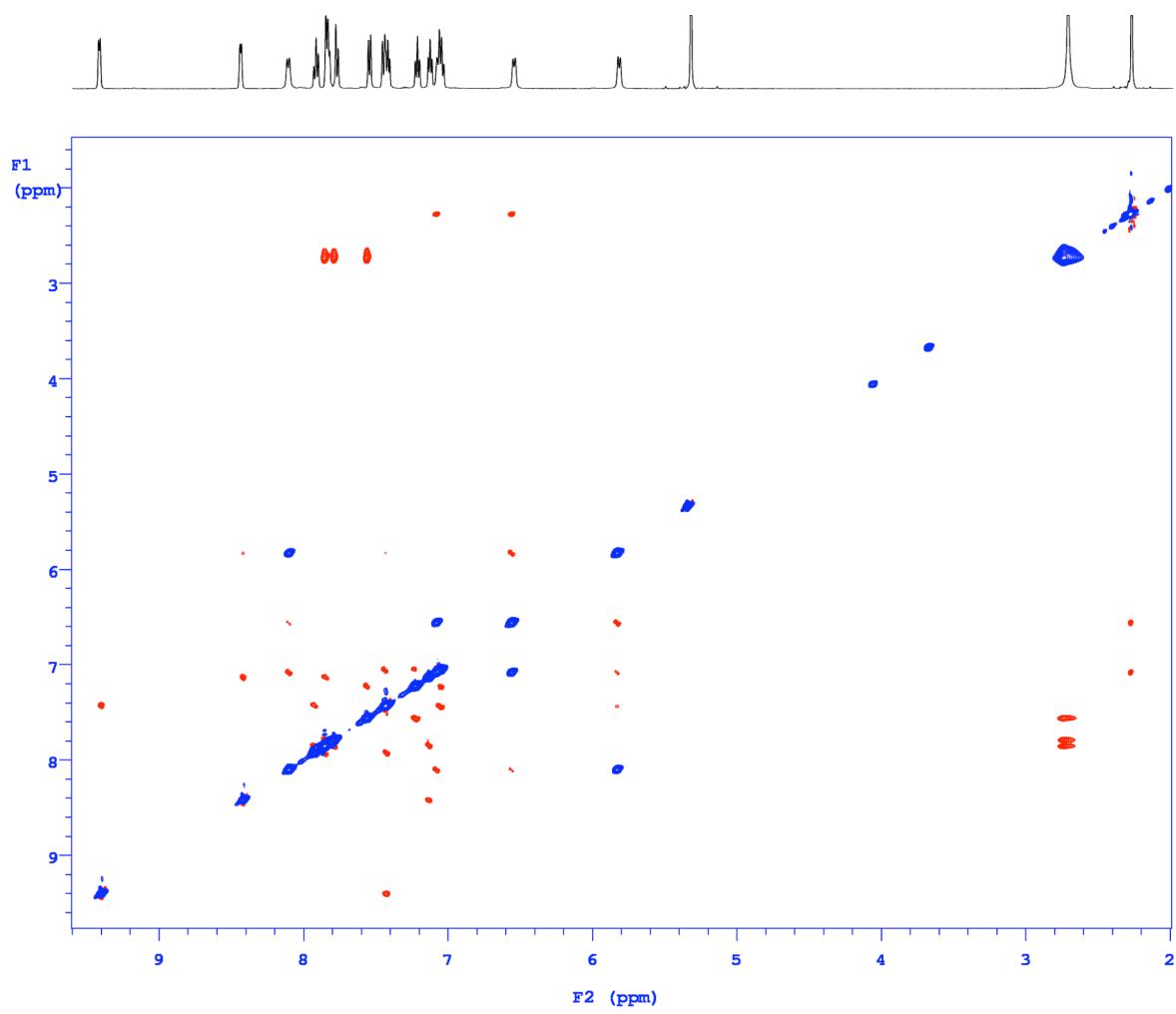
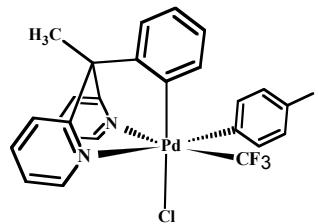
<sup>19</sup>F/<sup>13</sup>C HSQC of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at 0°C)



<sup>1</sup>H/<sup>1</sup>H TOCSY of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at -20°C)



<sup>1</sup>H/<sup>1</sup>H ROESY of (dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (**18**) (at -20°C)



<sup>1</sup>H NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19) (at 0°C)

STANDARD FLUORINE PARAMETERS

Sample Name:

Data Collected on:  
Te-vnmrs500

Archive directory:

Sample directory:

FidFile: AM3-77@0

Pulse Sequence: PROTON (s2pul)

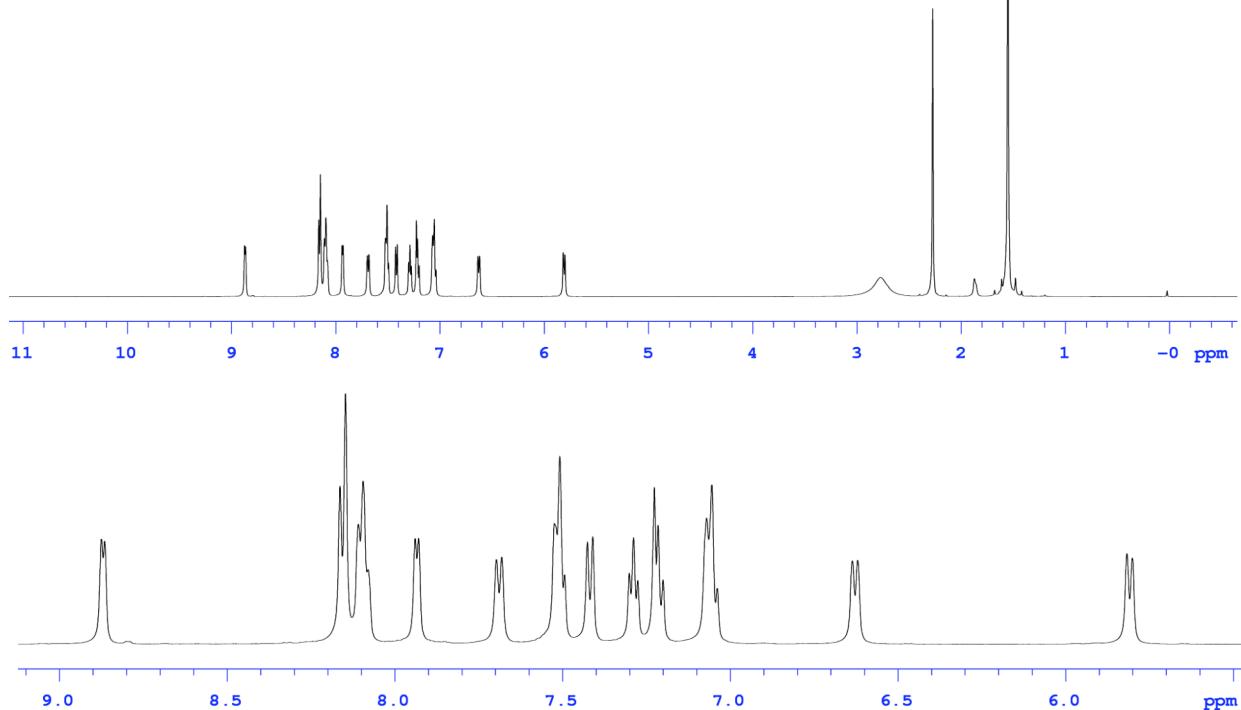
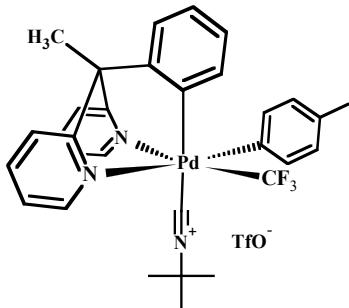
Solvent: ccd13

Data collected on: May 24 2011

Temp. 0.0 C / 273.1 K  
Operator: maleckis

Relax. delay 5.000 sec  
Pulse 45.0 degrees  
Acq. time 3.500 sec  
Width 8012.8 Hz  
24 repetitions  
OBSERVE H1, 500.0931699 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 65536  
Total time 3 min 41 sec

VARIAN



**$^{13}\text{C}\{^1\text{H}\}$  NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19) (at 0°C)**

STANDARD FLUORINE PARAMETERS

VARIAN

Sample Name:

Data Collected on:

Te-vnmrs500

Archive directory:

Sample directory:

FidFile: AM3-77@0-carbon

Pulse Sequence: CARBON (s2pul)

Solvent: ccdl3

Data collected on: May 24 2011

Temp. 0.0 C / 273.1 K

Operator: maleckis

Relax. delay 0.100 sec

Pulse 45.0 degrees

Acq. time 2.045 sec

Width 32051.3 Hz

2896 repetitions

OBSERVE C13, 125.7485276 MHz

DECOPPLE H1, 500.0956704 MHz

Power 42 dB

continuously on

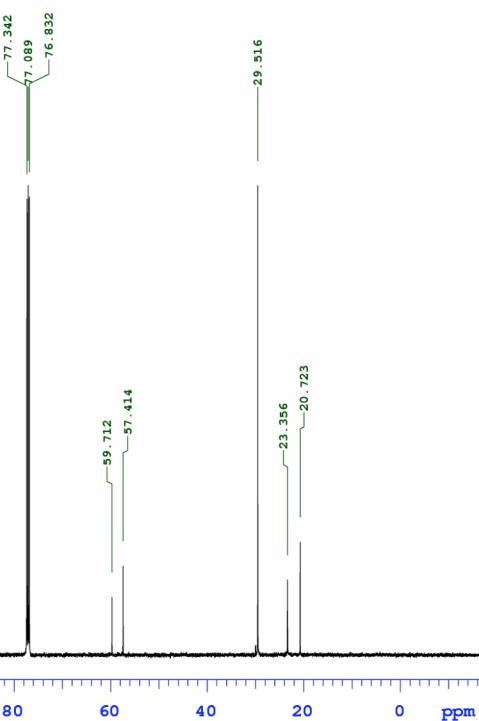
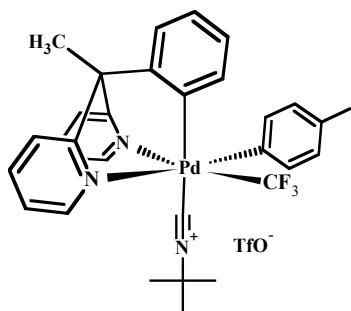
WALTZ-16 modulated

DATA PROCESSING

Line broadening 1.0 Hz

FT size 131072

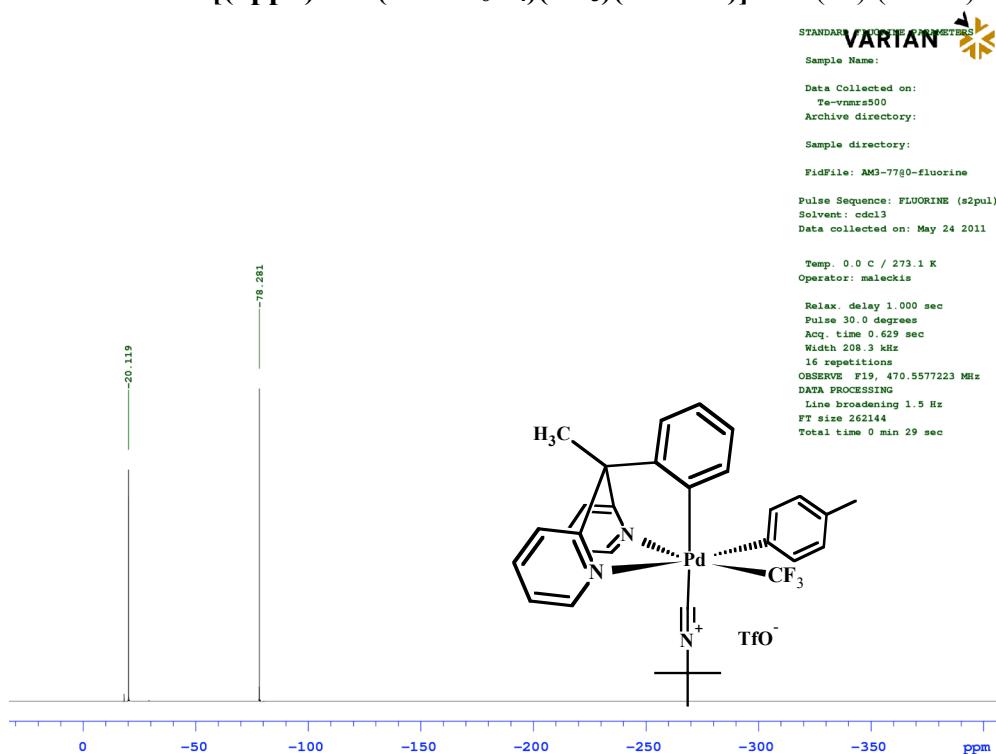
Total time 1 hr, 43 min



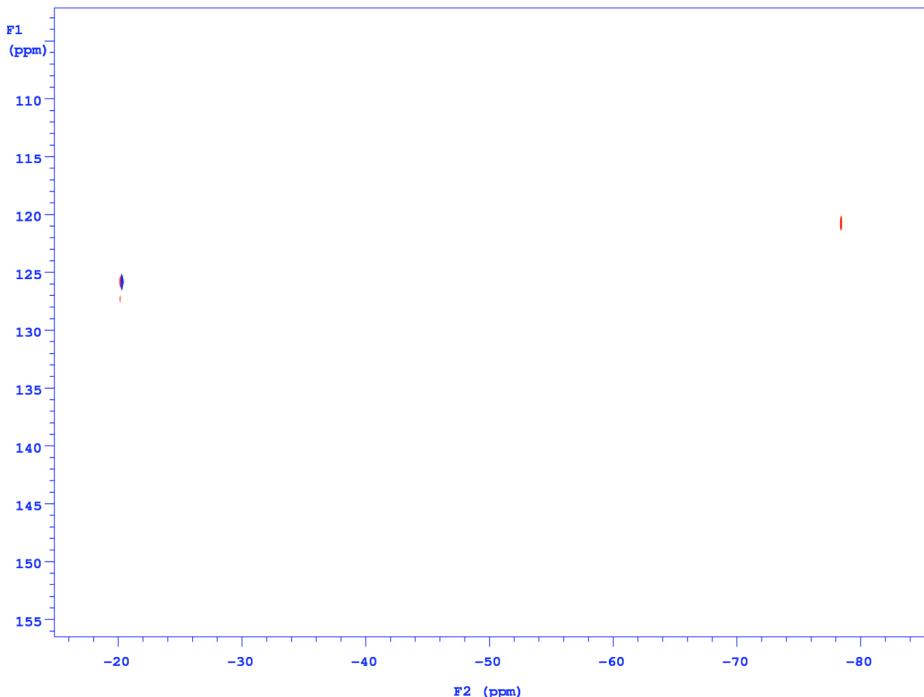
$$J = 321 \text{ Hz}$$



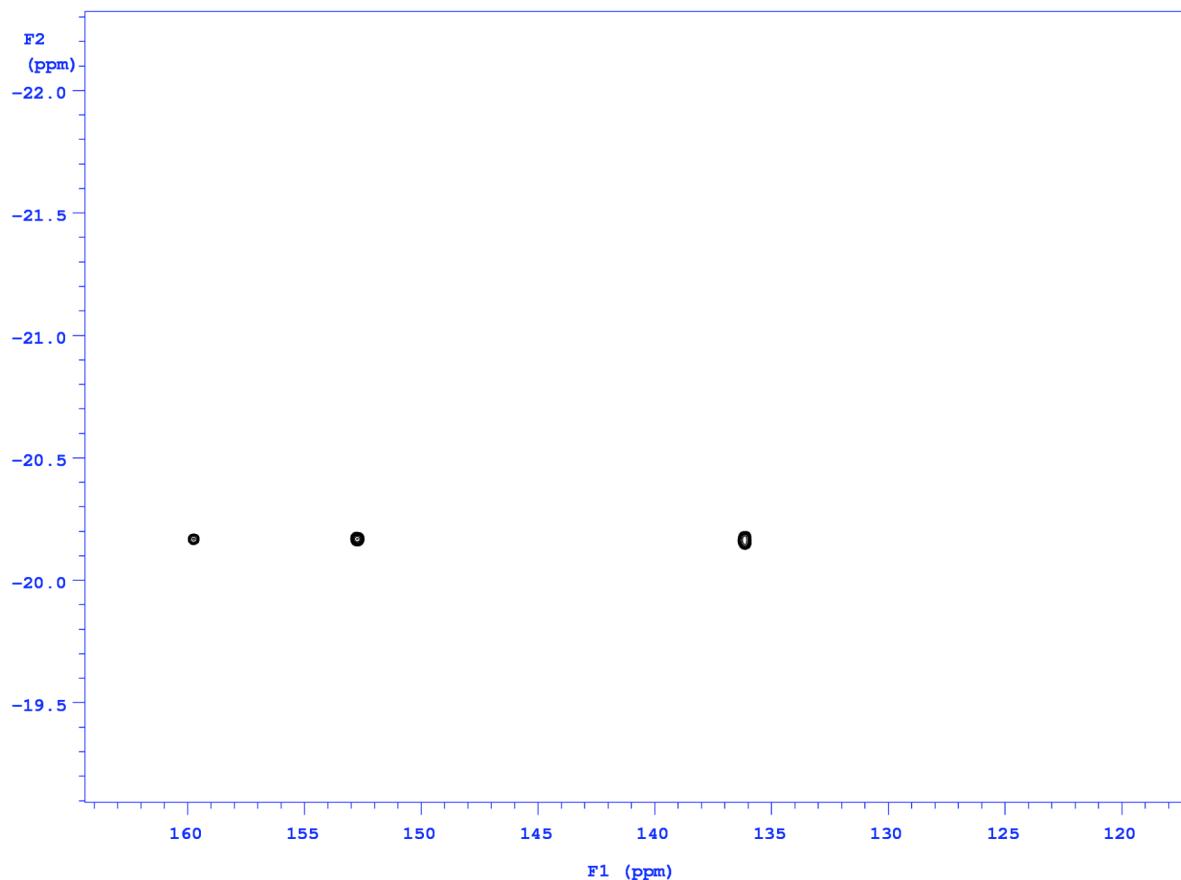
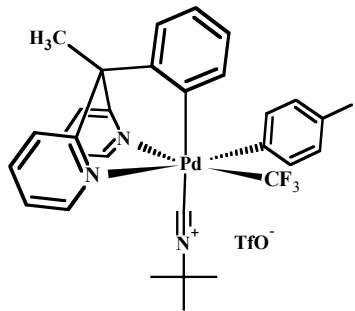
**<sup>19</sup>F NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19) (at 0°C)**



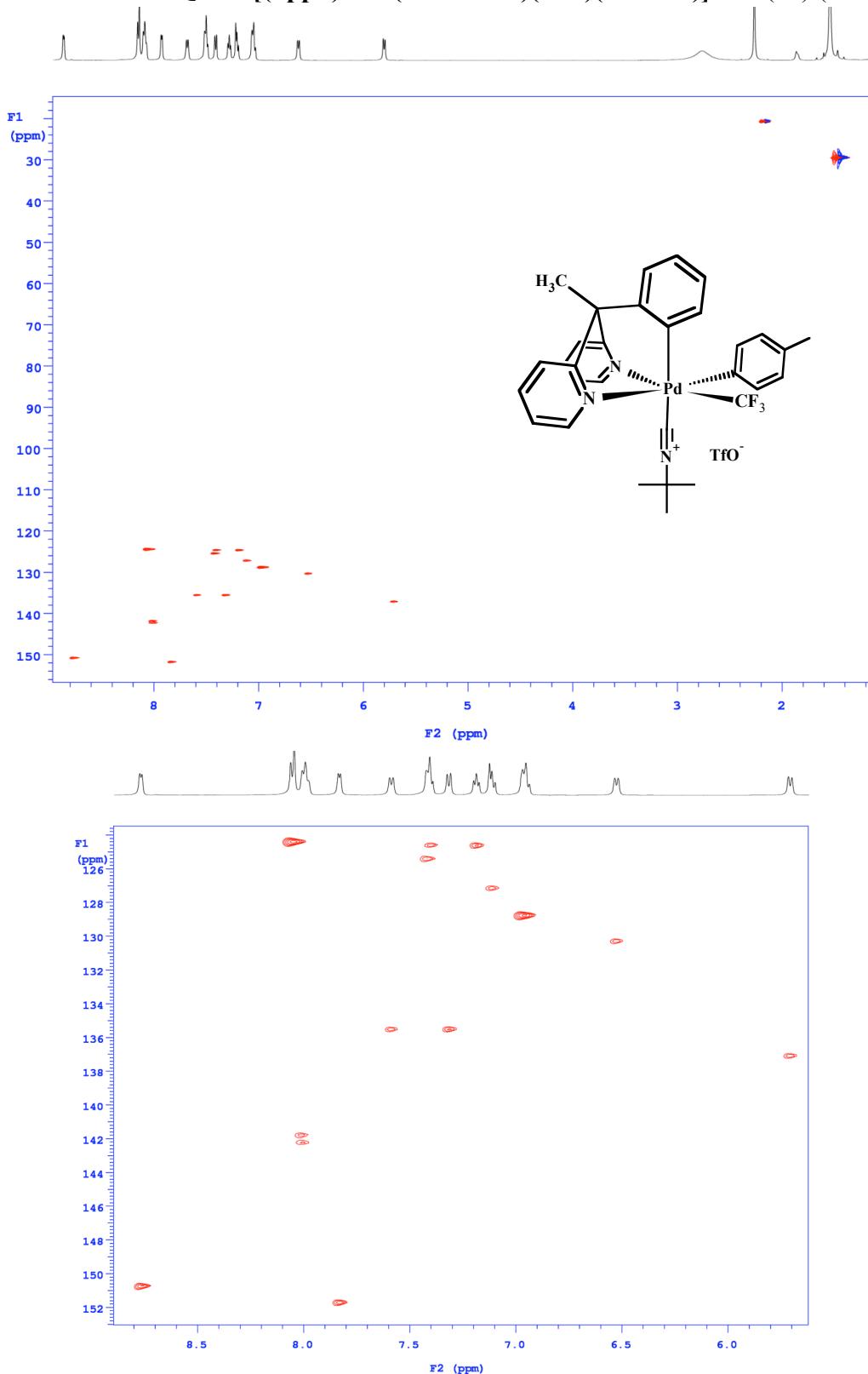
**<sup>19</sup>F/<sup>13</sup>C HSQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19) (at 0°C)**



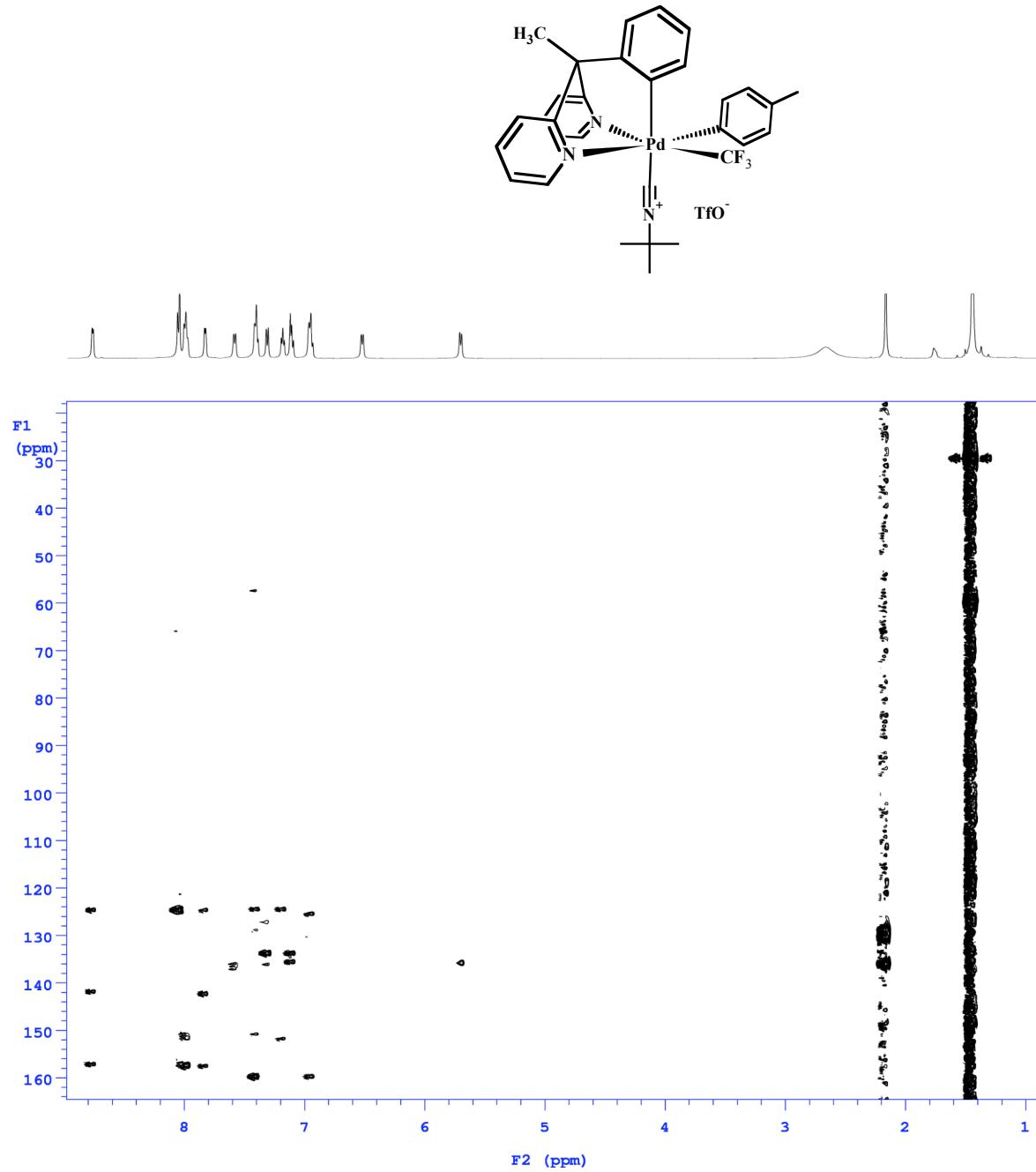
**$^{19}\text{F}/^{13}\text{C}$  HMBC of  $[(\text{dpph})\text{Pd}^{\text{IV}}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)(t\text{-BuNC})]\text{OTf}$  (**19**) (at 0°C)**



<sup>1</sup>H/<sup>13</sup>C ASAPHMQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19) (at 0°C)



<sup>1</sup>H/<sup>13</sup>C HMBC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19) (at 0°C)



**$^1\text{H}$  NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)**

STANDARD PROTON PARAMETERS

Sample Name:

Data Collected on:  
Yb-vnmrs700  
Archive directory:

Sample directory:

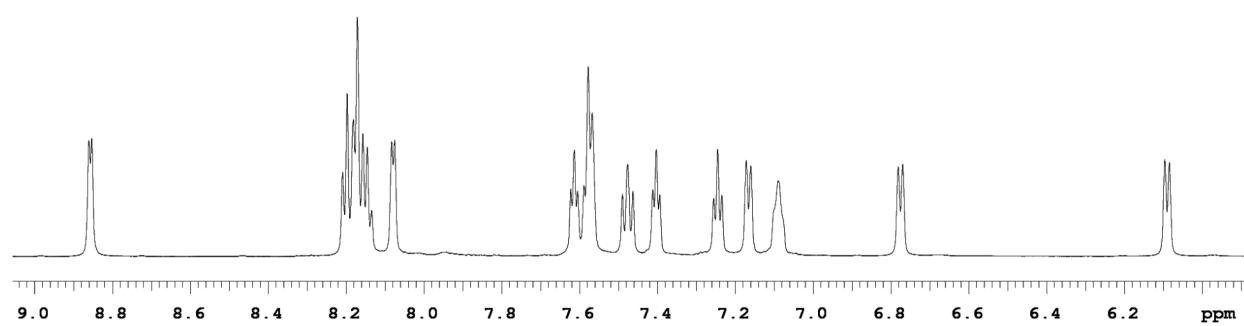
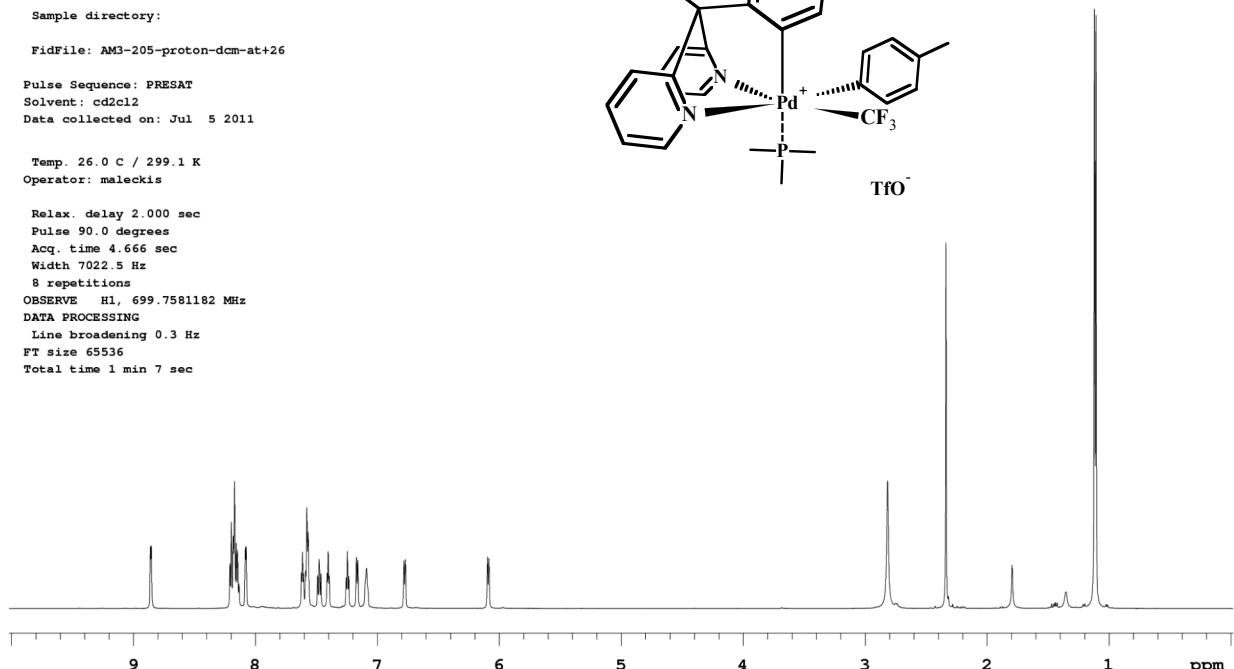
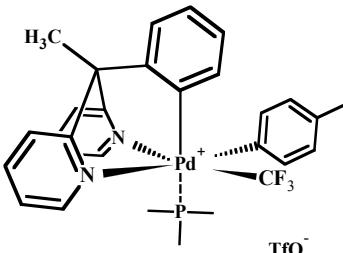
FidFile: AM3-205-proton-dcm-at+26

Pulse Sequence: PRESAT  
Solvent: cdcl<sub>2</sub>  
Data collected on: Jul 5 2011

Temp. 26.0 C / 299.1 K  
Operator: maleckis

Relax. delay 2.000 sec  
Pulse 90.0 degrees  
Acq. time 4.666 sec  
Width 7022.5 Hz  
8 repetitions  
OBSERVE H1, 699.7581182 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 65536  
Total time 1 min 7 sec

Agilent Technologies



### $^{13}\text{C}\{\text{H}\}$ NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)

STANDARD CARBON PARAMETERS



Sample Name:

Data Collected on:

Yb-vnmr700

Archive directory:

Sample directory:

FidFile: AM3-205-carbon-dcm-at+26

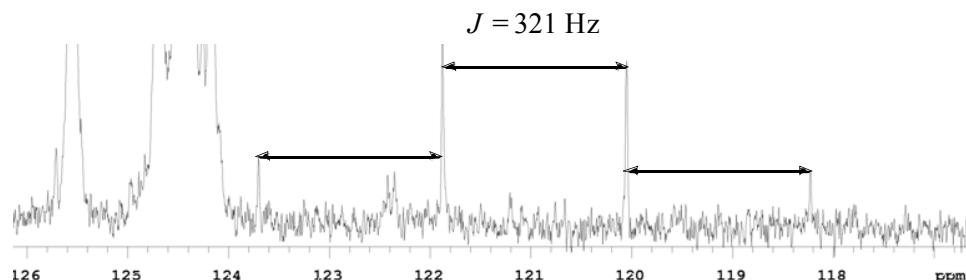
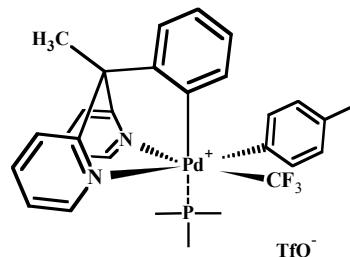
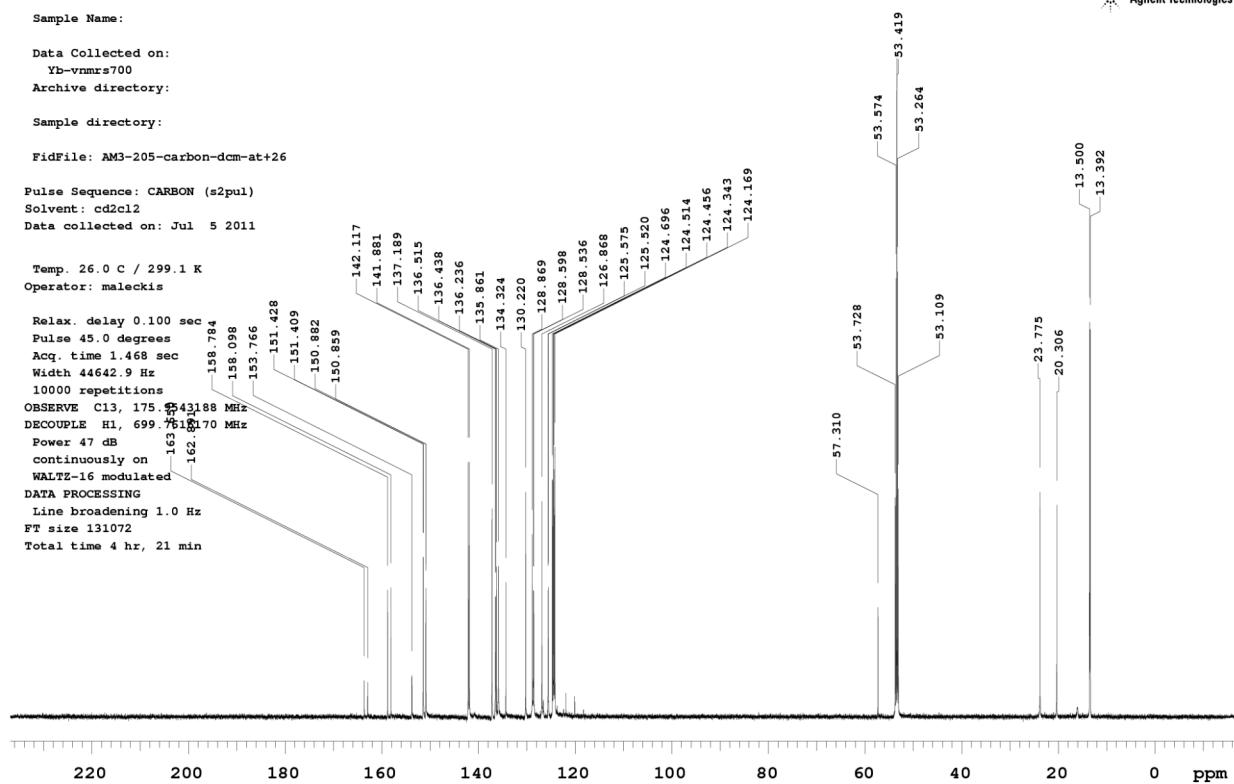
Pulse Sequence: CARBON (s2pul)

Solvent: cd2cl2

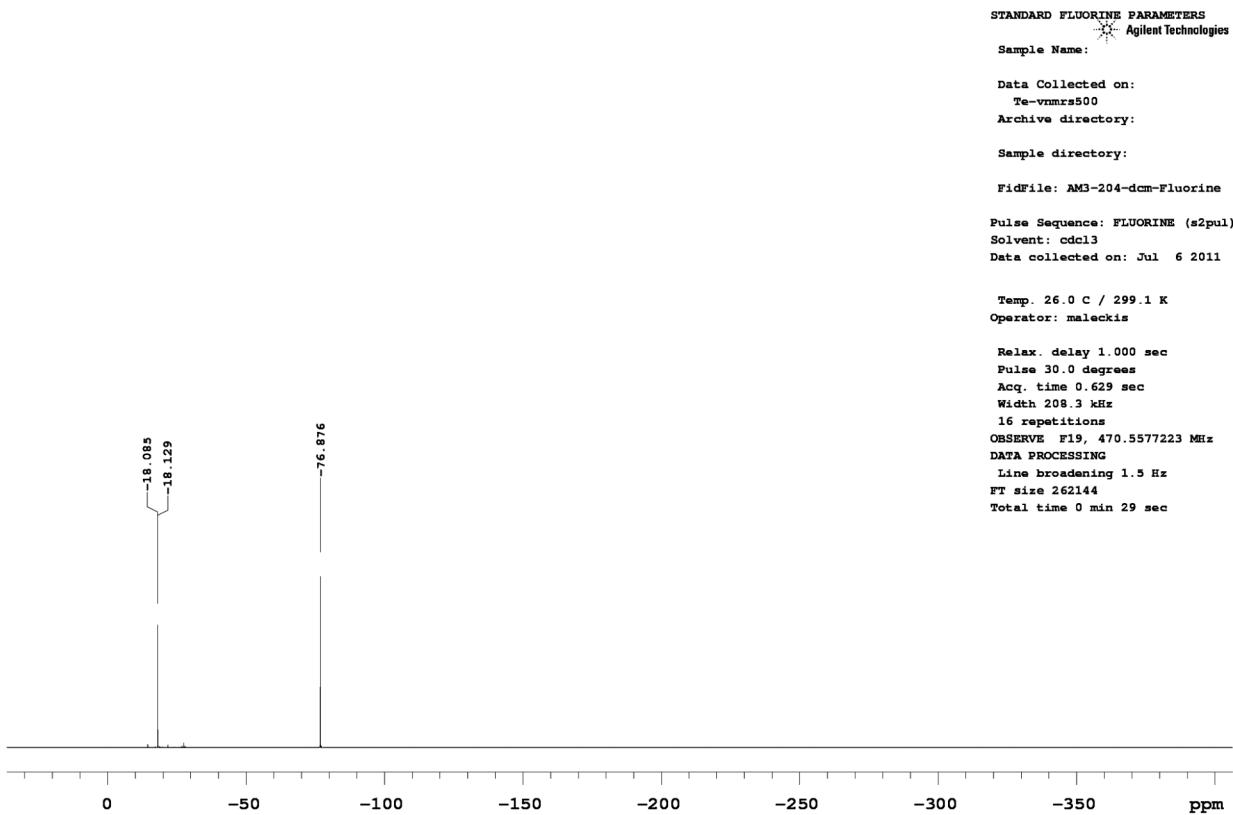
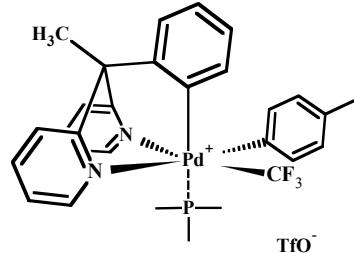
Data collected on: Jul 5 2011

Temp. 26.0 C / 299.1 K  
Operator: maleckis

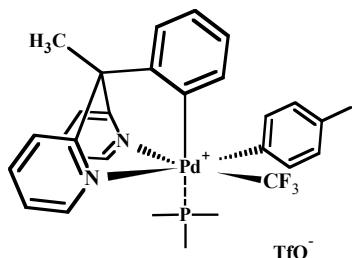
Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 1.468 sec  
Width 44642.9 Hz  
10000 repetitions  
OBSERVE C13, 175.43188 MHz  
DECOUPLE H1, 699.75170 MHz  
Power 47 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 4 hr, 21 min



**<sup>19</sup>F NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)**



<sup>31</sup>P{<sup>1</sup>H} NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)



STANDARD PHOSPHOROUS PARAMETERS

Sample Name:

Agilent Technologies

Data Collected on:

Te-vnmrs500

Archive directory:

Sample directory:

PidFile: AM3-204-dcm-P31

Pulse Sequence: PHOSPHORUS (s2pul)

Solvent: cdcl3

Data collected on: Jul 6 2011

Temp. 26.0 C / 299.1 K

Operator: maleckis

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 1.783 sec

Width 73529.4 Hz

64 repetitions

OBSERVE P31, 202.4414259 MHz

DECOUPLE H1, 500.0956704 MHz

Power 42 dB

on during acquisition

off during delay

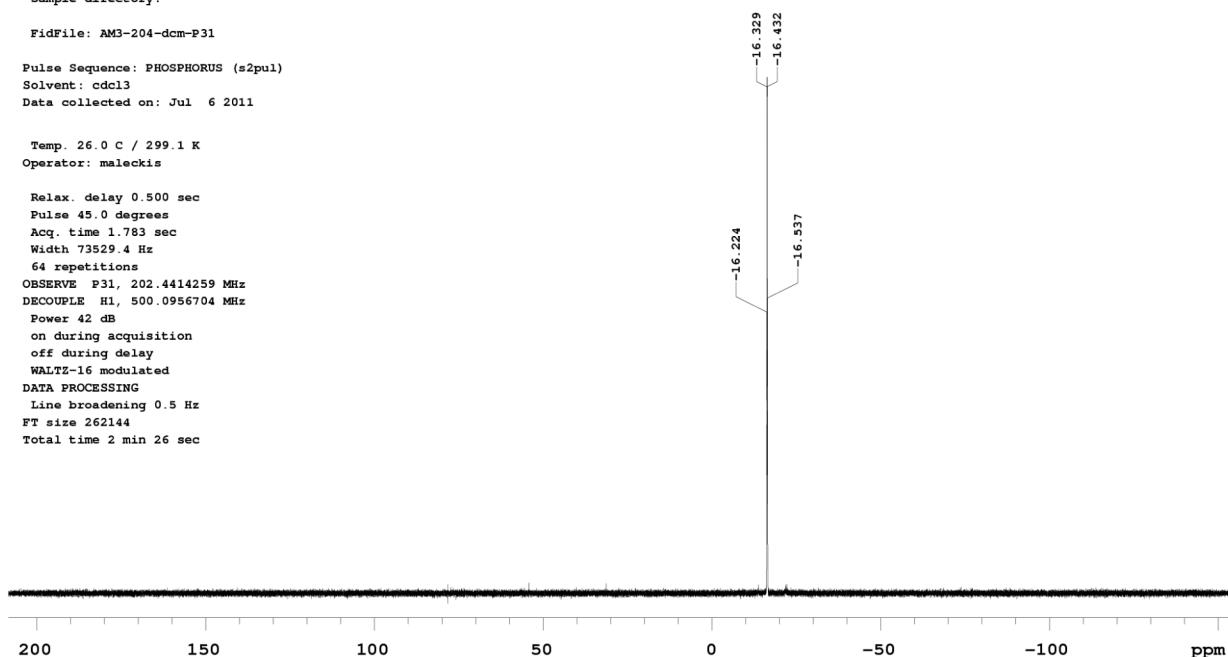
WALTZ-16 modulated

DATA PROCESSING

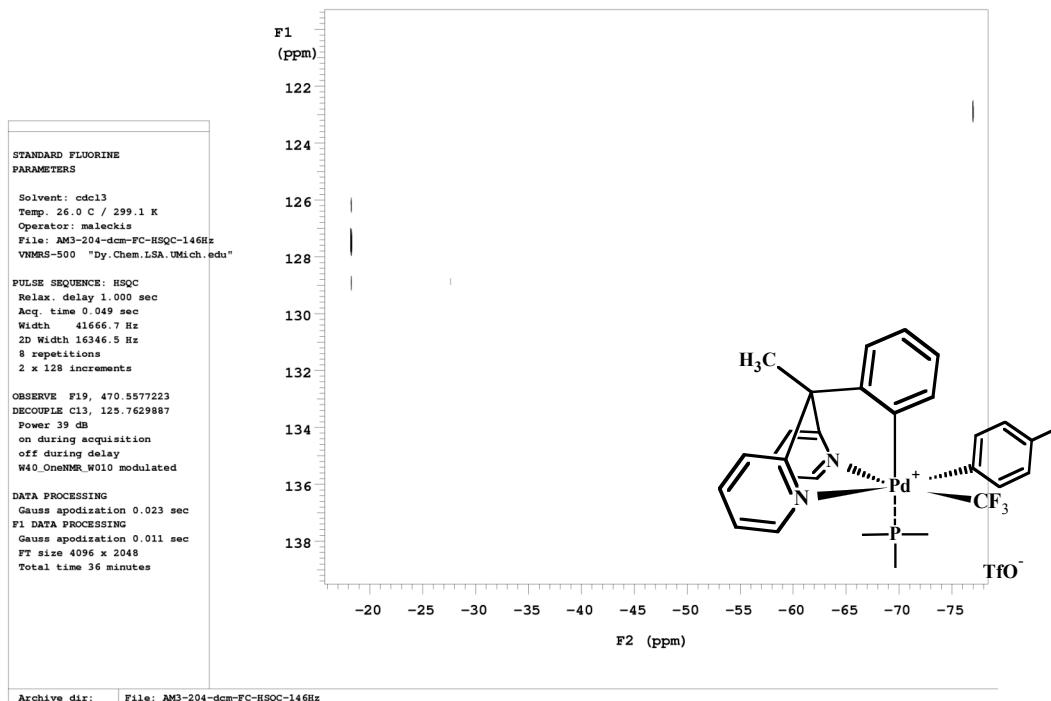
Line broadening 0.5 Hz

FT size 262144

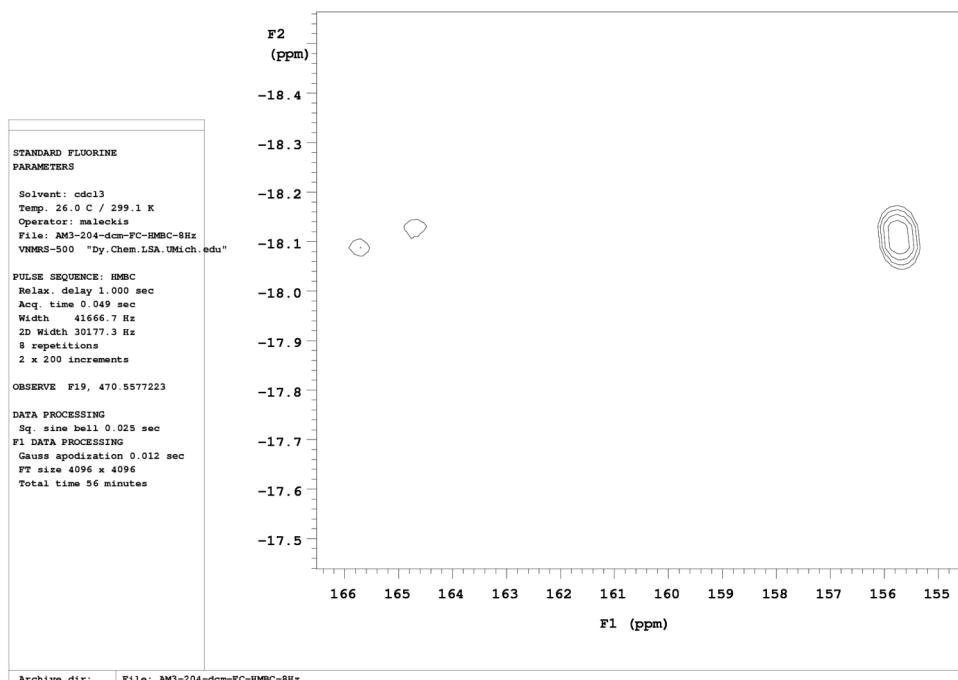
Total time 2 min 26 sec



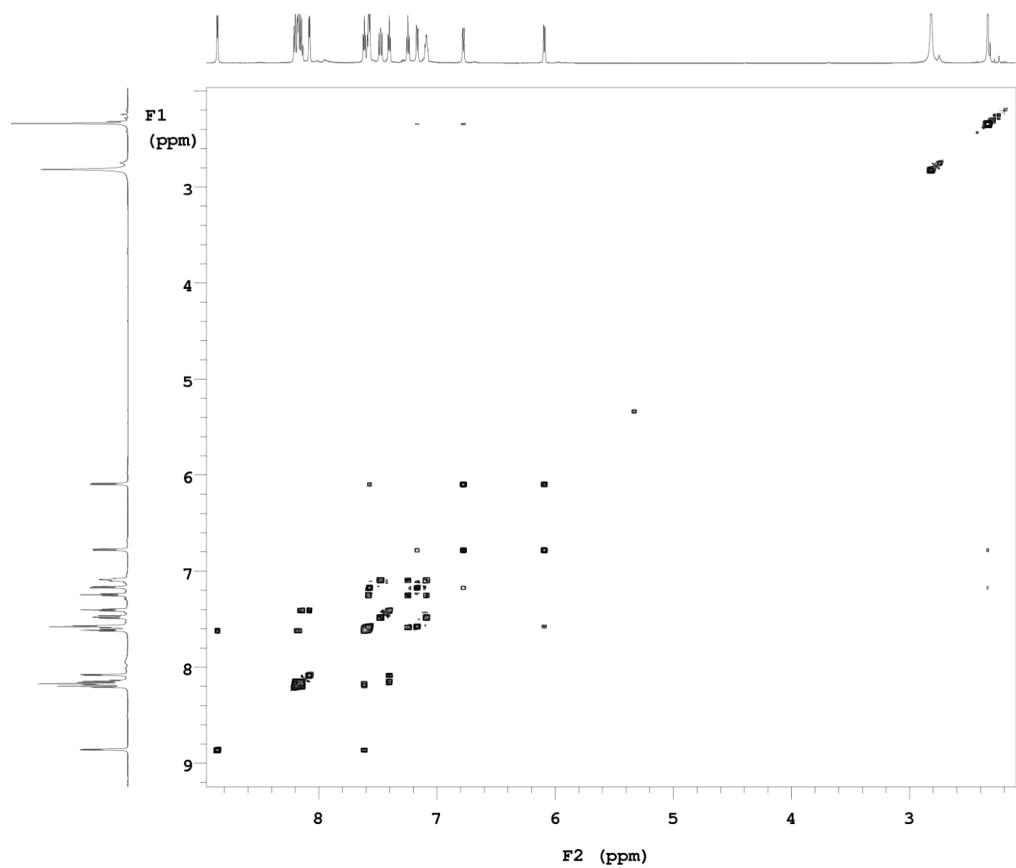
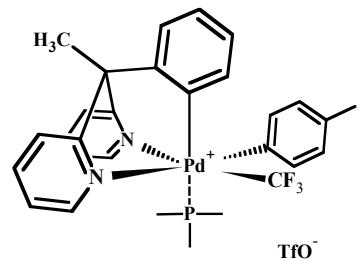
**<sup>19</sup>F/<sup>13</sup>C HSQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)**



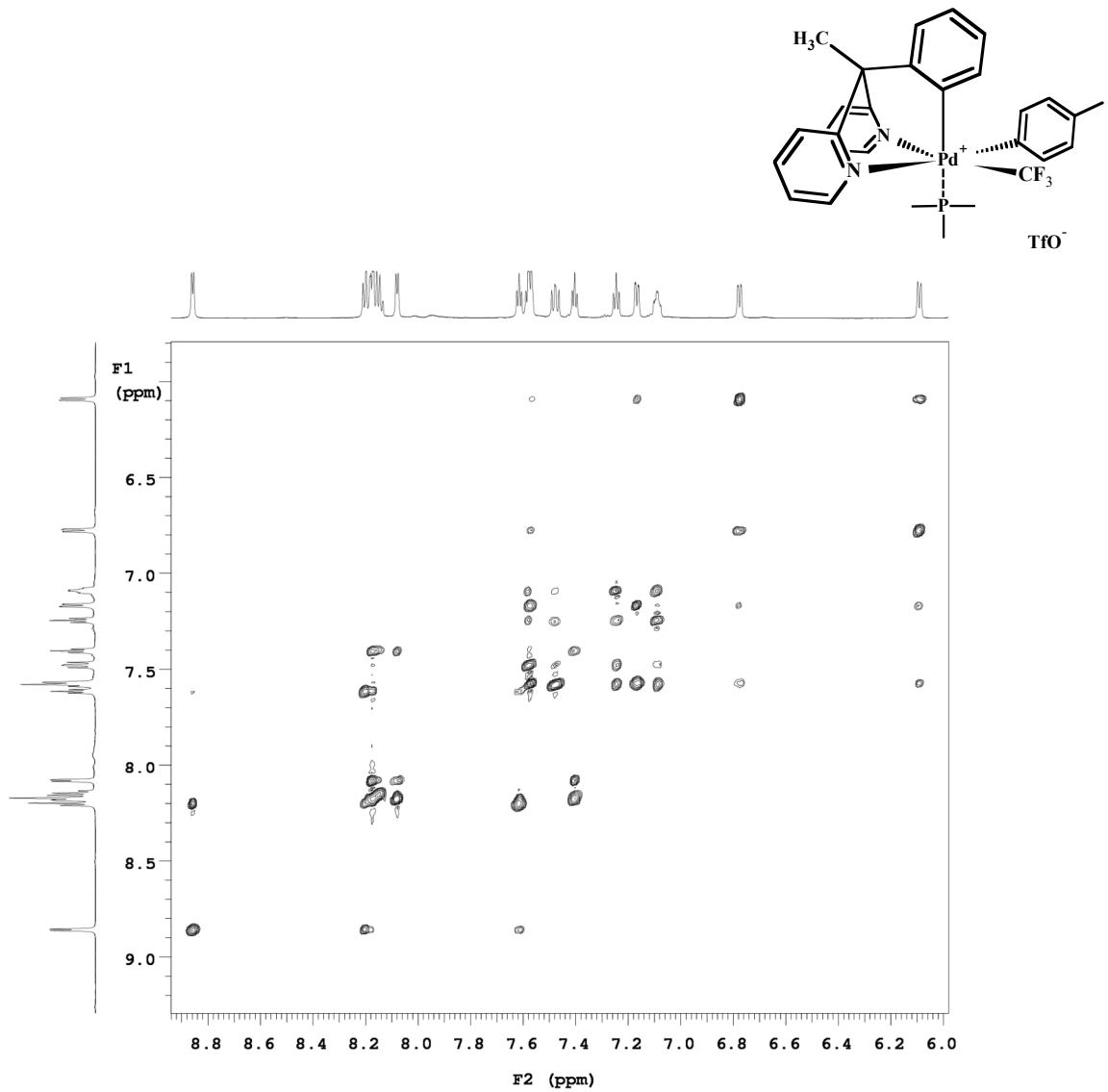
**<sup>19</sup>F/<sup>13</sup>C HMBC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)**



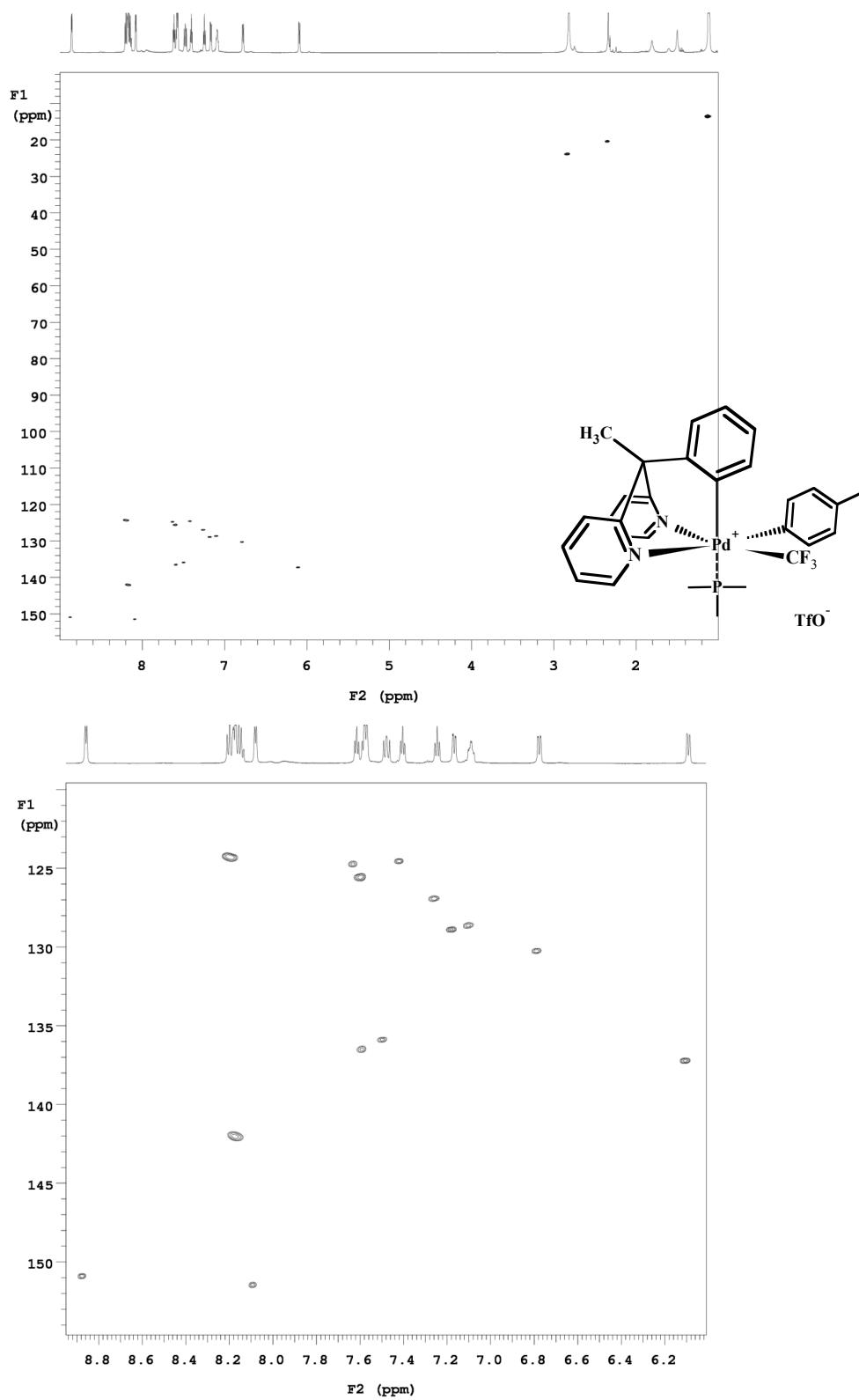
<sup>1</sup>H/<sup>1</sup>H gCOSY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)



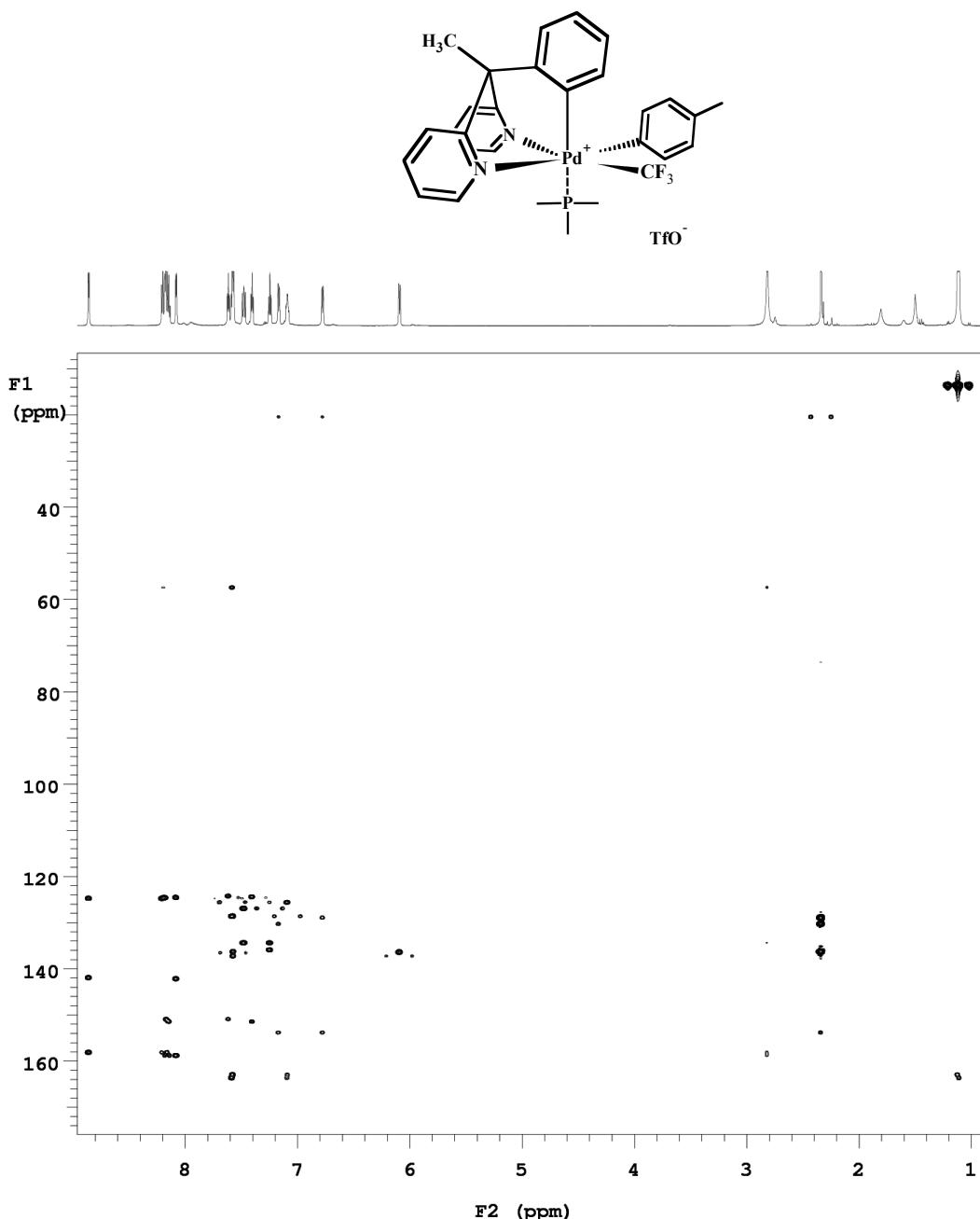
<sup>1</sup>H/<sup>1</sup>H TOCSY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)



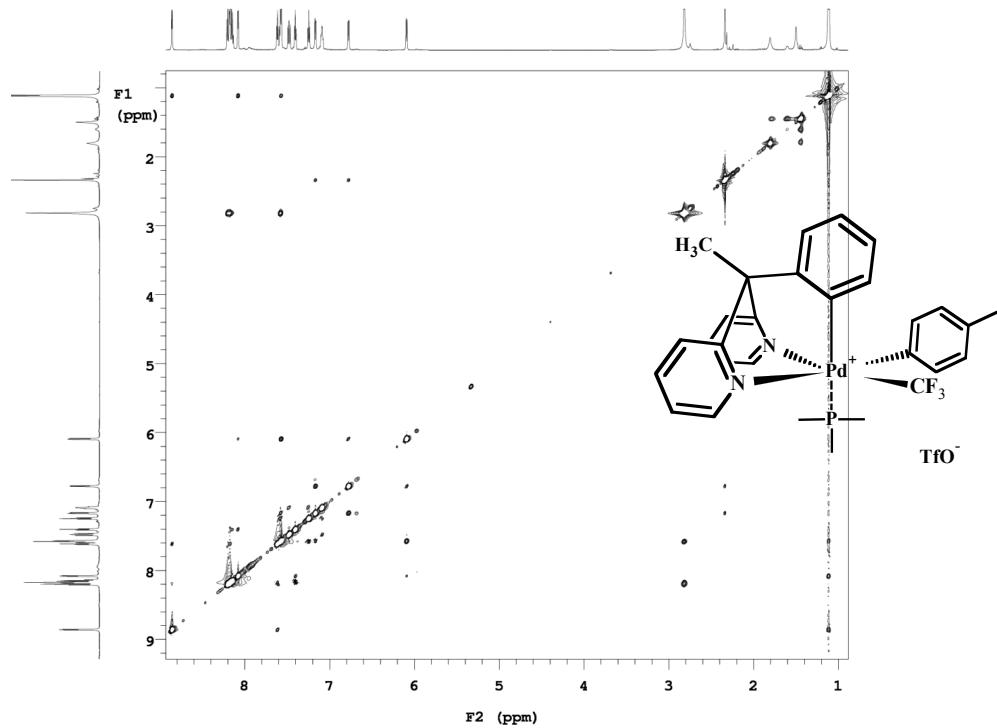
$^1\text{H}/^{13}\text{C}$  ASAPHMQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(PMe<sub>3</sub>)]OTf (20)



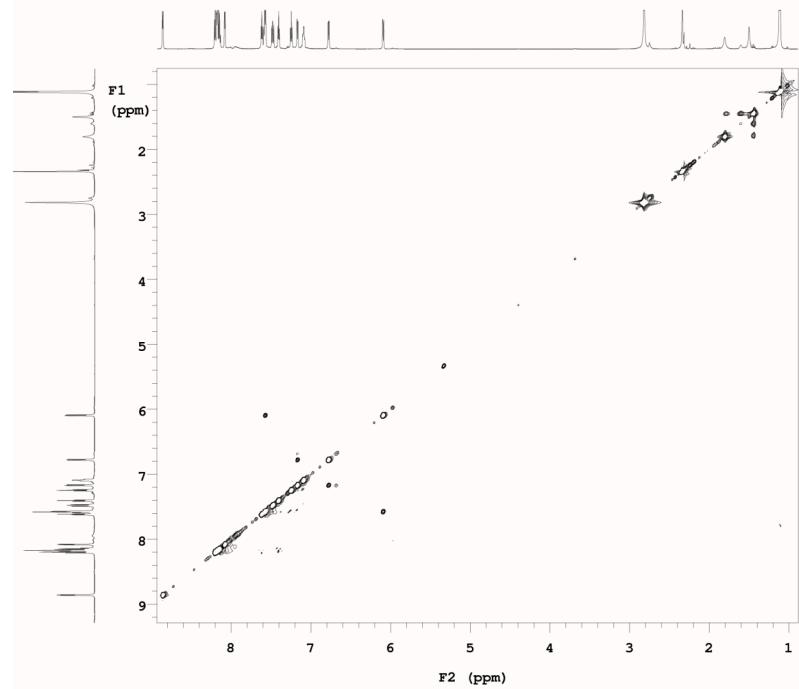
$^1\text{H}/^{13}\text{C}$  gHMBCAD of  $[(\text{dpph})\text{Pd}^{\text{IV}}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)(\text{PMe}_3)]\text{OTf}$  (**20**)



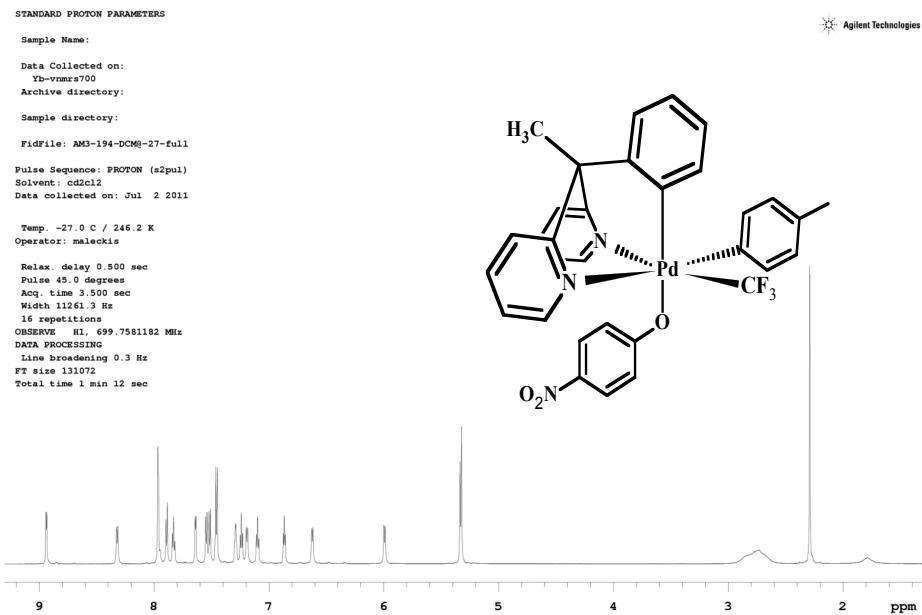
**$^1\text{H}/^1\text{H}$  NOESY of  $[(\text{dpph})\text{Pd}^{\text{IV}}(4\text{-MeC}_6\text{H}_4)(\text{CF}_3)(\text{PMe}_3)]\text{OTf}$  (**20**) (positive and negative contours)**



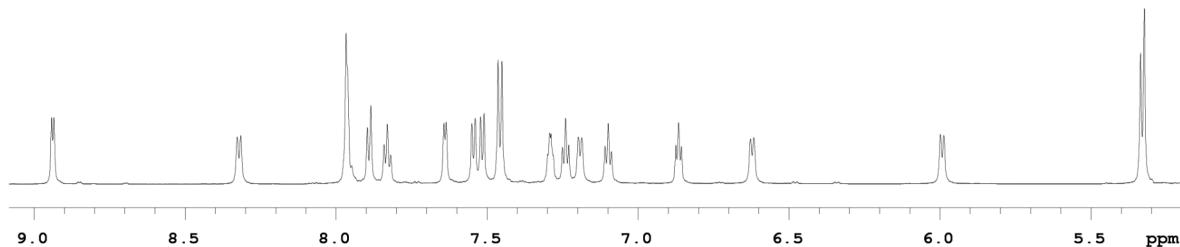
**$^1\text{H}/^1\text{H}$  NOESY of  $[(\text{dpph})\text{Pd}^{\text{IV}}(4\text{-MeC}_6\text{H}_4)(\text{CF}_3)(\text{PMe}_3)]\text{OTf}$  (**20**) (negative contours)**



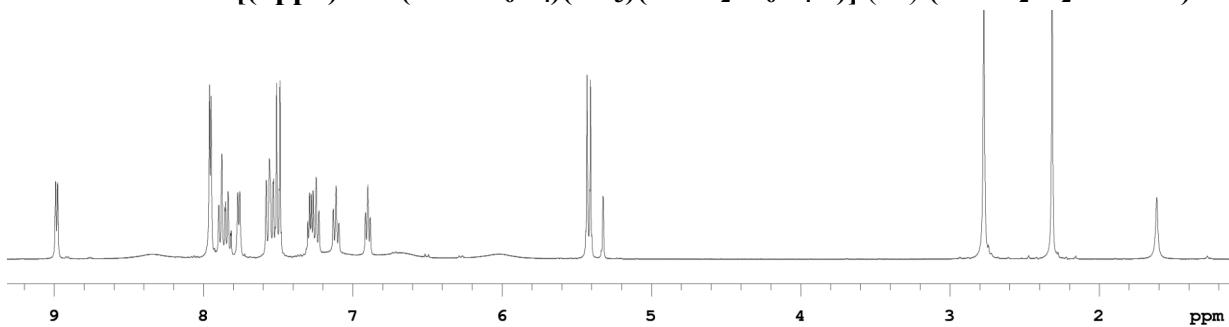
**$^1\text{H}$  NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -27°C)**



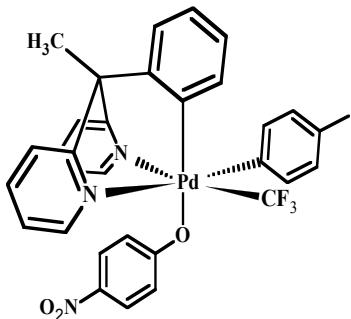
**$^1\text{H}$  NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -27°C)  
5-9ppm**



**$^1\text{H}$  NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at 24°C)**



<sup>13</sup>C{<sup>1</sup>H} NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -21°C)



STANDARD PROTON PARAMETERS

Sample Name:

Agilent Technologies

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

Archive directory:

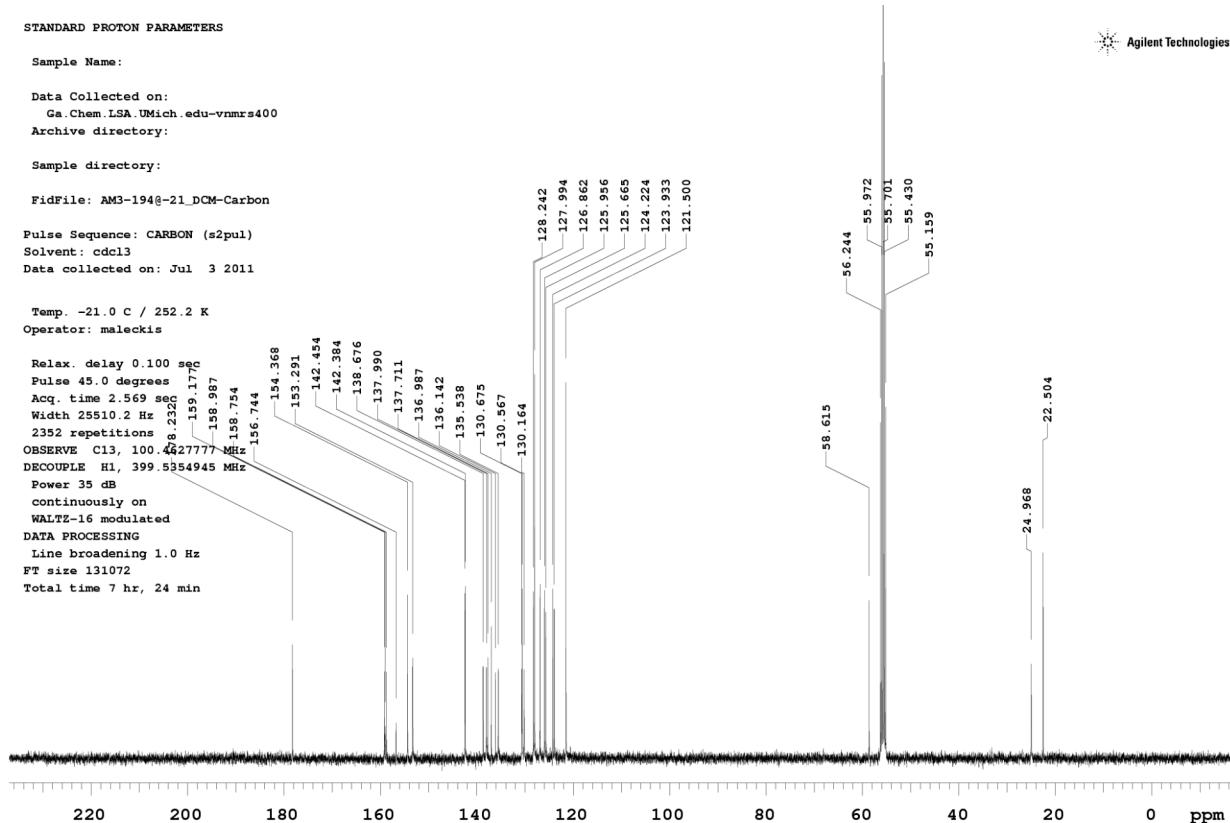
Sample directory:

FidFile: AM3-1948-21\_DCM-Carbon

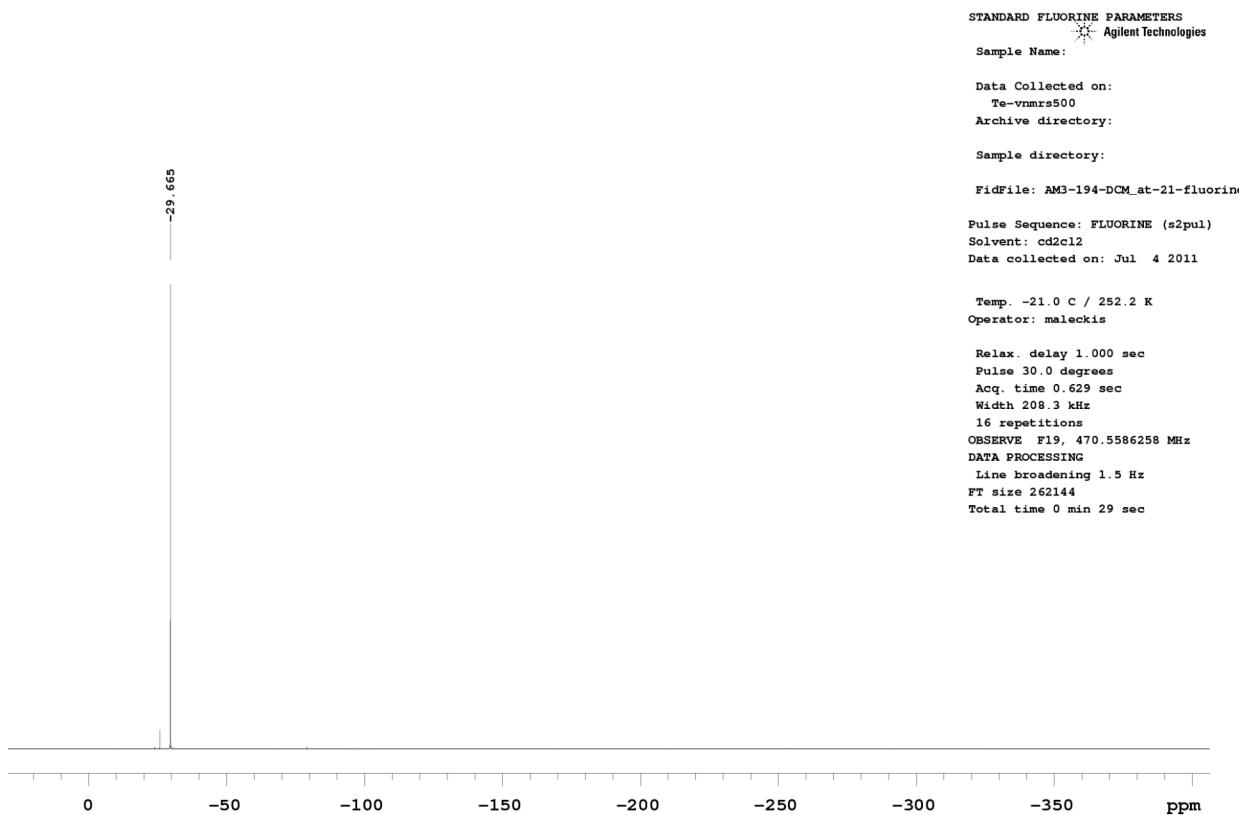
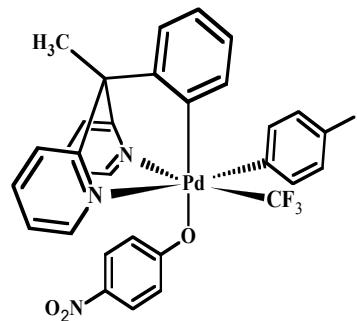
Pulse Sequence: CARBON (s2pul)  
Solvent: cdcl3  
Data collected on: Jul 3 2011

Temp. -21.0 C / 252.2 K  
Operator: maleckis

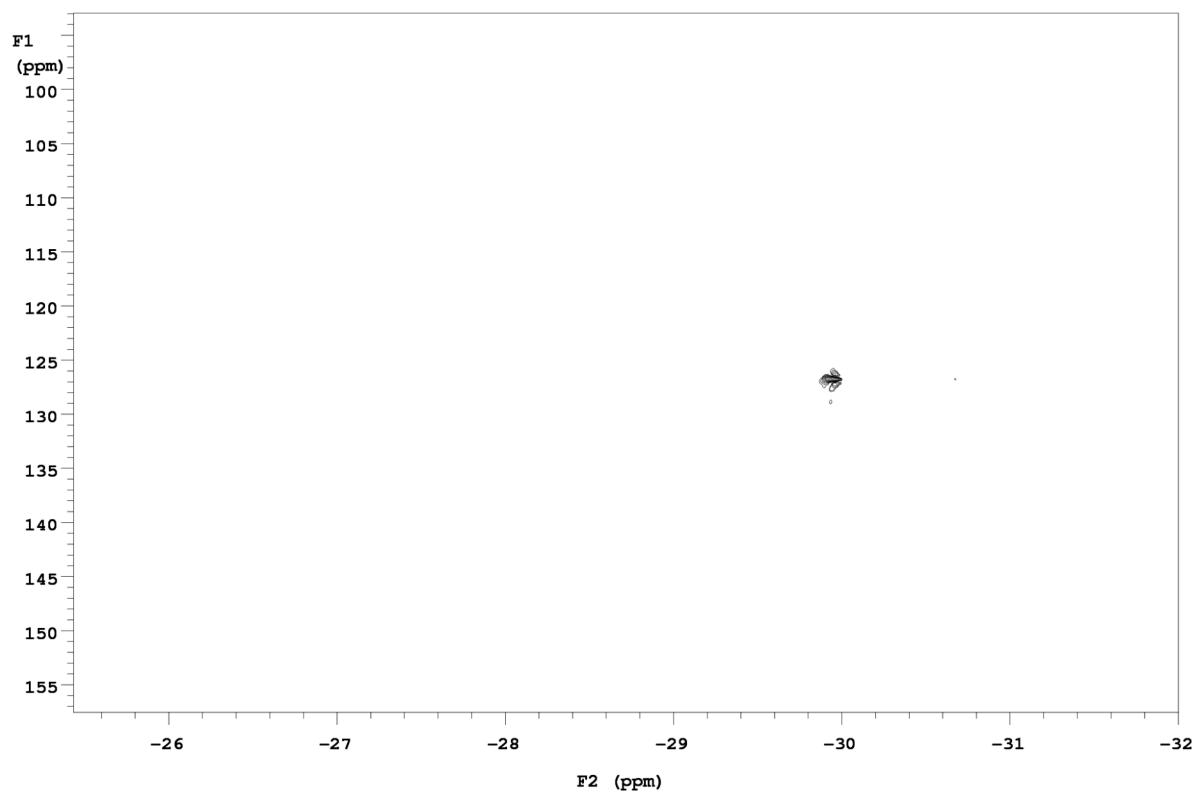
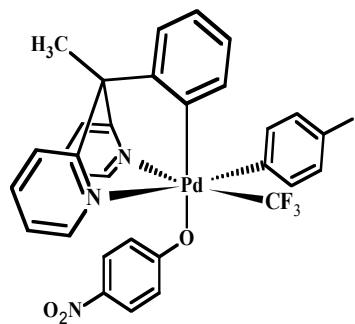
Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 2.569 sec  
Width 25510.2 Hz  
2352 repetitions  
OBSERVE C13, 100.46277777 MHz  
DECOUPLE H1, 399.5354945 MHz  
Power 35 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 7 hr, 24 min



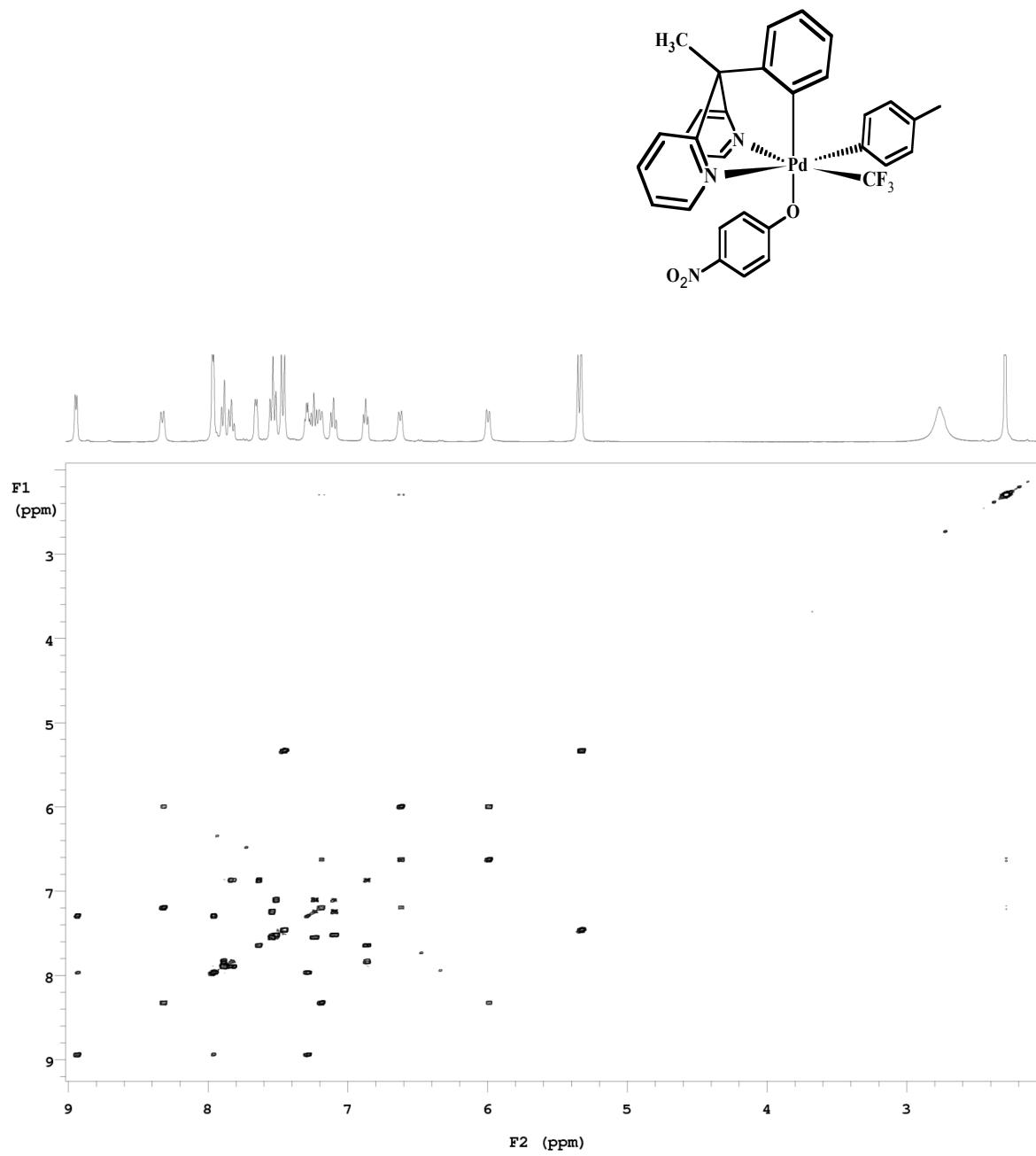
**<sup>19</sup>F NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -21°C)**



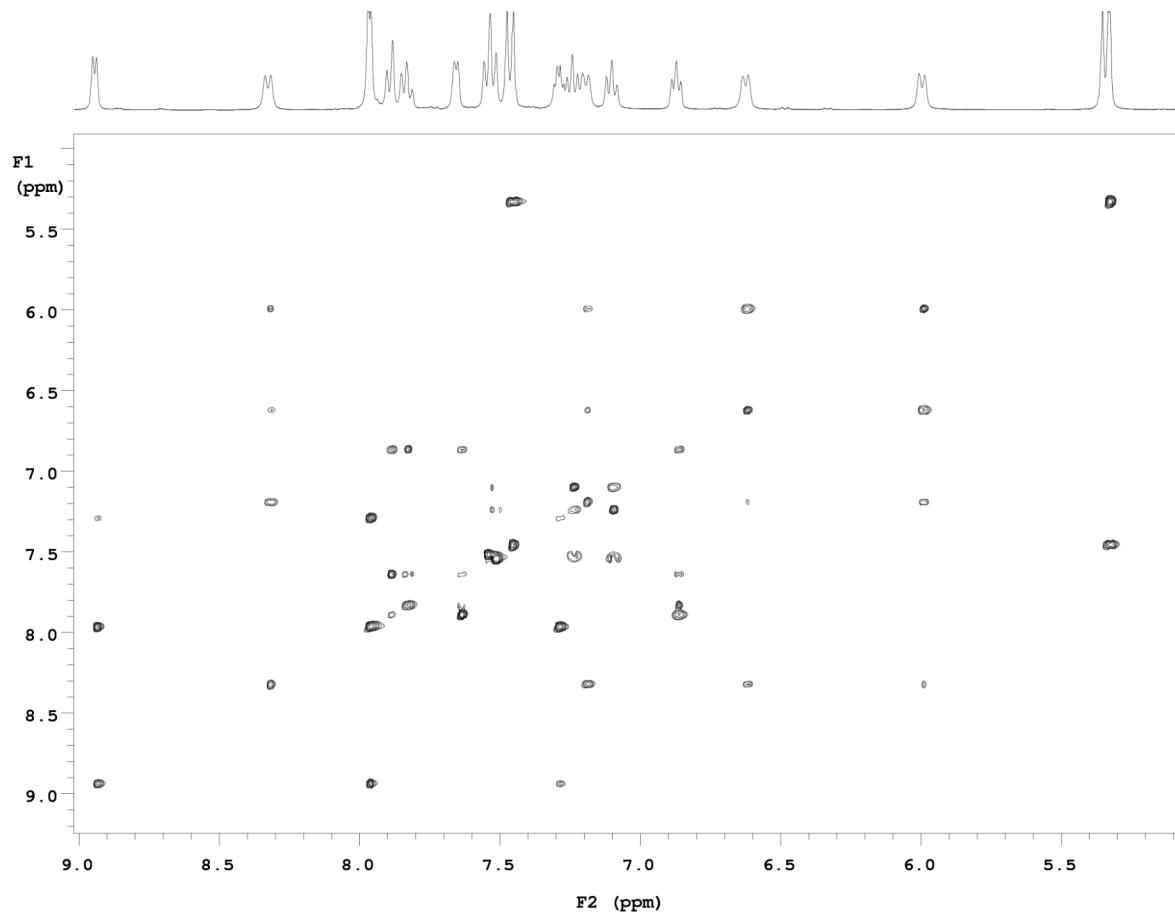
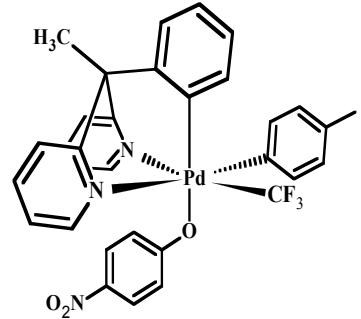
**$^{19}\text{F}/^{13}\text{C}$  ASAPHMQC of  $[(\text{dpph})\text{Pd}^{\text{IV}}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)(\text{4-NO}_2\text{-C}_6\text{H}_4\text{O})]$  (21)**  
**(in  $\text{CD}_2\text{Cl}_2$  at  $-21^\circ\text{C}$ )**



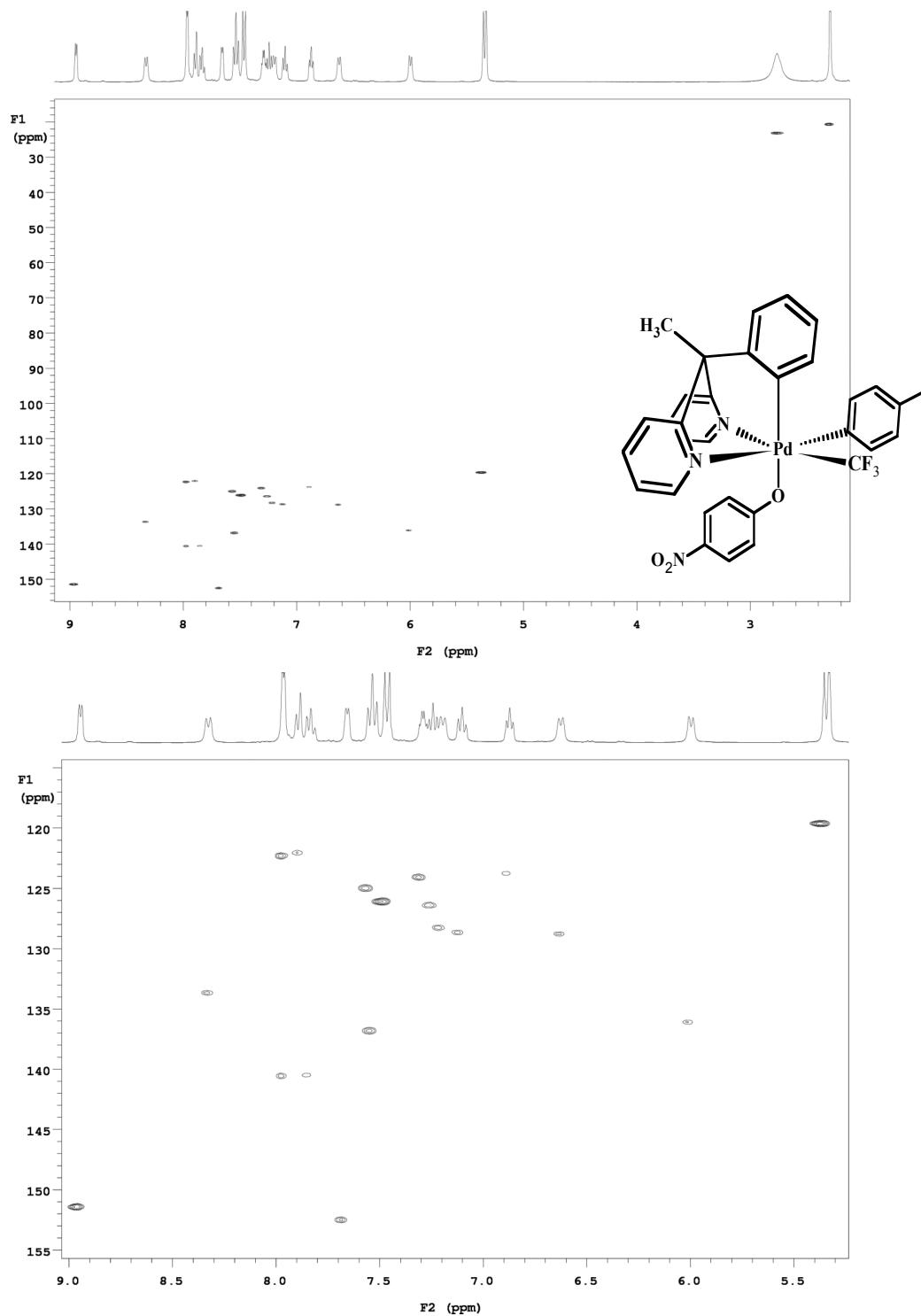
$^1\text{H}/^1\text{H}$  COSY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -27°C)



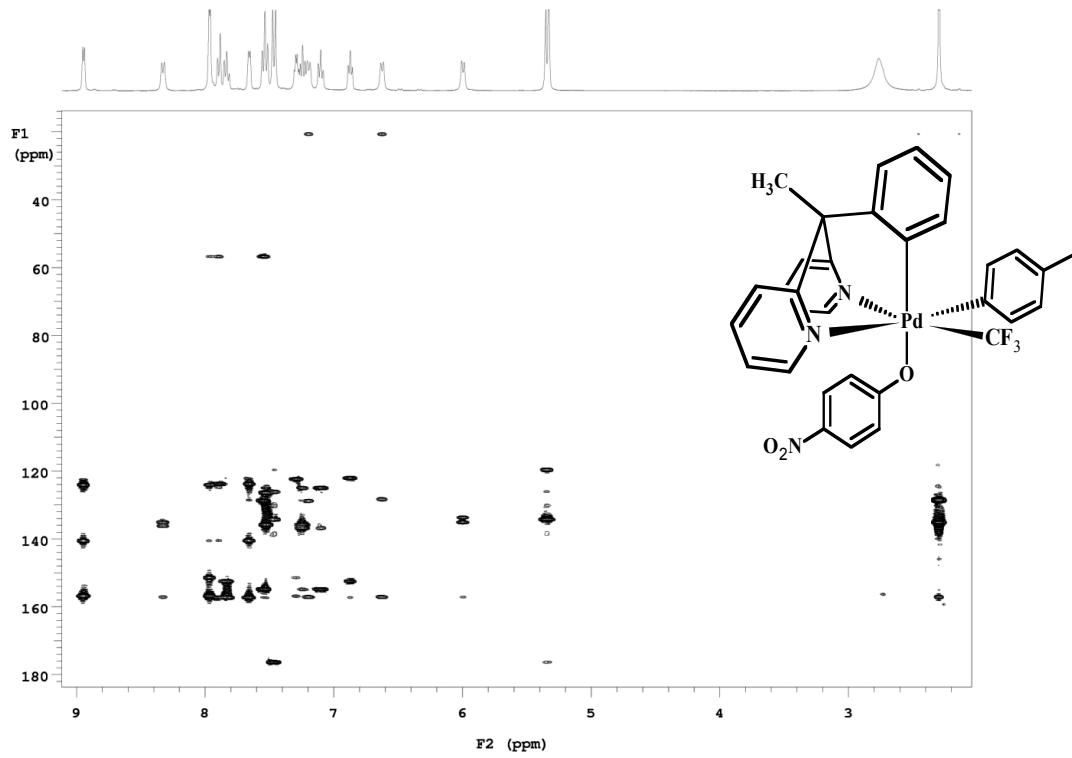
<sup>1</sup>H/<sup>1</sup>H TOCSY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -27°C)



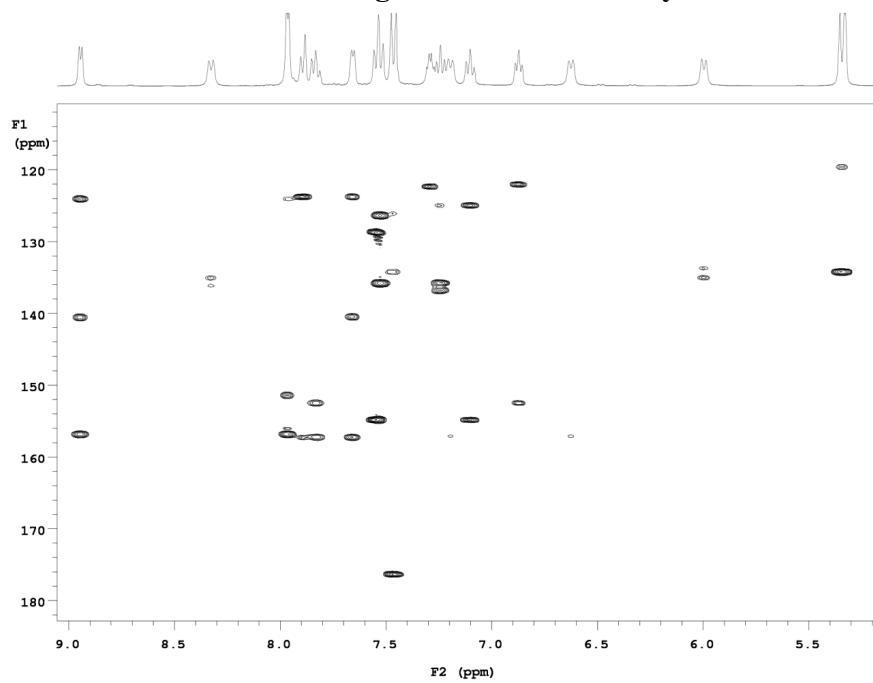
**$^1\text{H}/^{13}\text{C}$  ASAPHMQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21)  
(in CD<sub>2</sub>Cl<sub>2</sub> at -21°C)**



**$^1\text{H}/^{13}\text{C}$  gHMBCAD of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21)**  
**(in CD<sub>2</sub>Cl<sub>2</sub> at -21°C)**

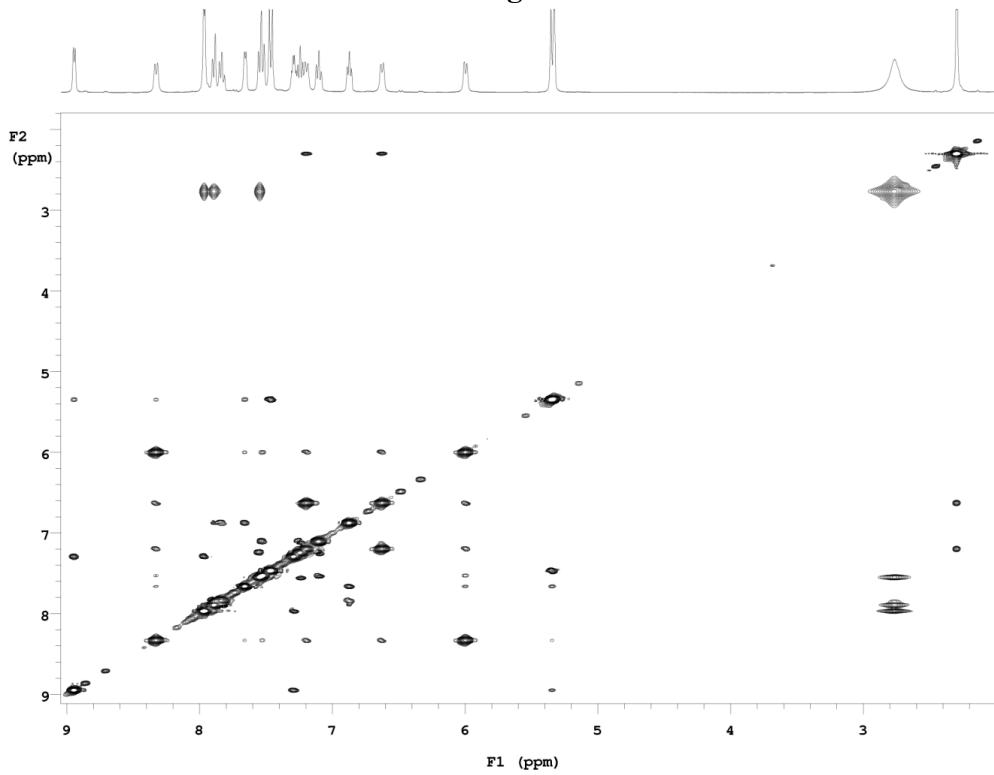


**Aromatic region at lower intensity**



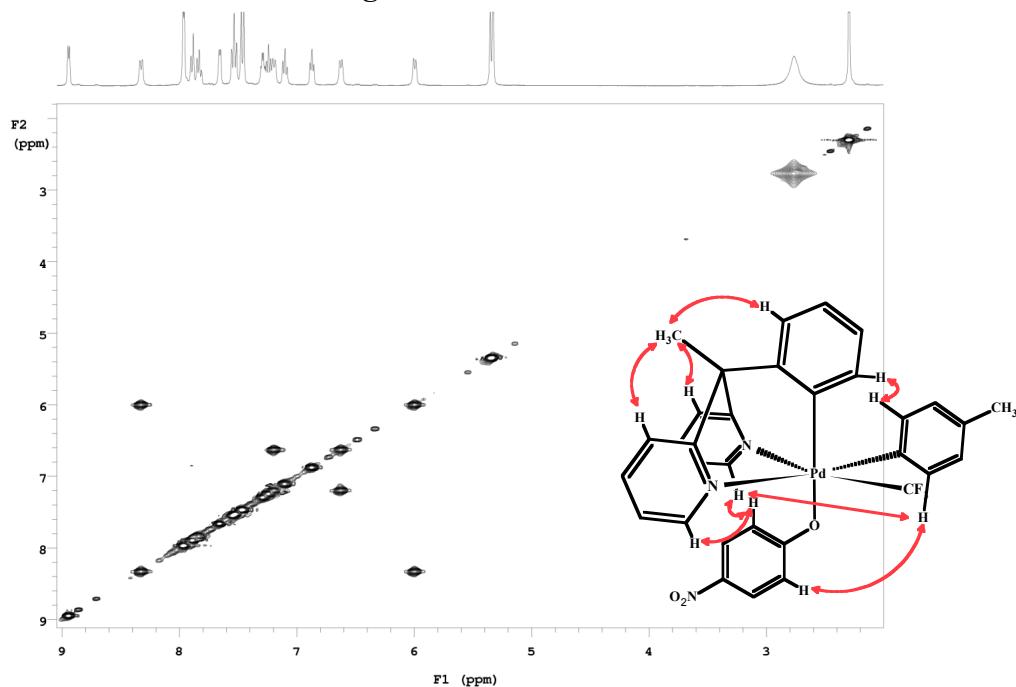
<sup>1</sup>H/<sup>1</sup>H ROESY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -21°C)

Positive and negative contours



<sup>1</sup>H/<sup>1</sup>H ROESY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(4-NO<sub>2</sub>-C<sub>6</sub>H<sub>4</sub>O)] (21) (in CD<sub>2</sub>Cl<sub>2</sub> at -21°C)

Negative contours



**$^1\text{H}$  NMR of  $[(\text{dpph})\text{Pd}^{\text{IV}}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)(\text{NPhth})] (22)$  (in  $\text{CDCl}_3$  at  $-51^\circ\text{C}$ )**

STANDARD FLUORINE PARAMETERS

Sample Name:

Agilent Technologies

Data Collected on:

Te-vnmrs500

Archive directory:

Sample directory:

FidFile: AM3-201-proton-at-51

Pulse Sequence: PROTON (s2pul)

Solvent: cdcl3

Data collected on: Jul 4 2011

Temp.  $-51.0^\circ\text{C}$  / 222.2 K

Operator: malekis

Relax. delay 0.500 sec

Pulse 45.0 degrees

Acq. time 3.500 sec

Width 8012.8 Hz

16 repetitions

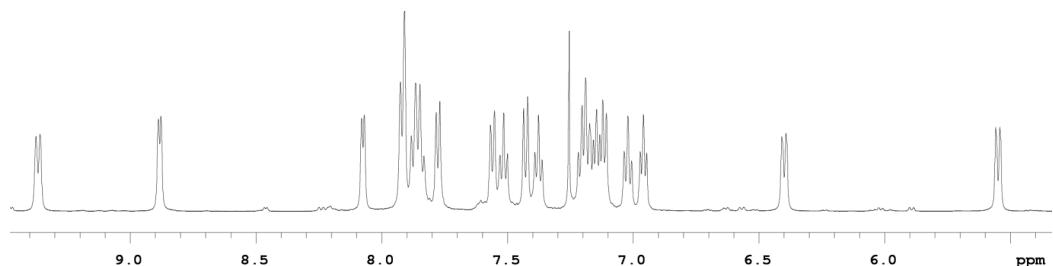
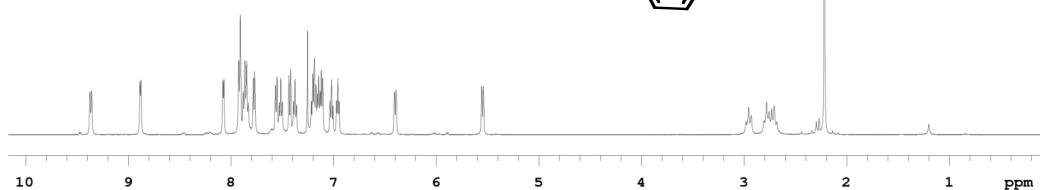
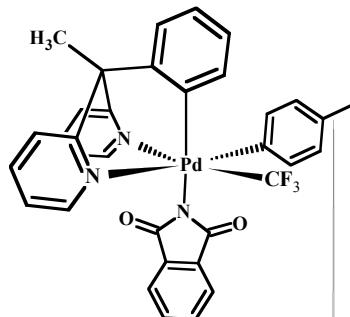
OBSERVE H1, 500.0931699 MHz

DATA PROCESSING

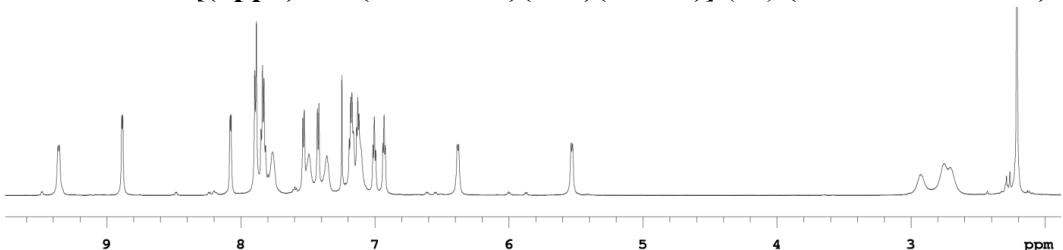
Line broadening 0.3 Hz

FT size 65536

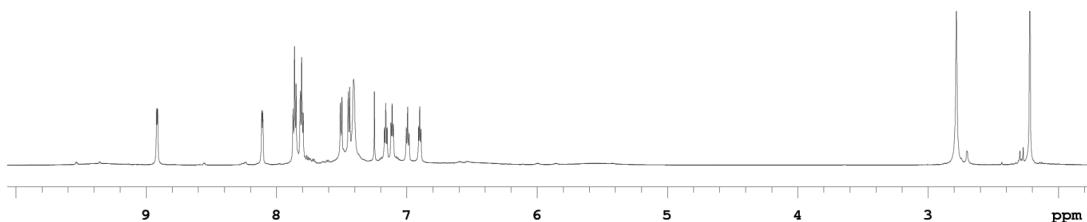
Total time 1 min 12 sec



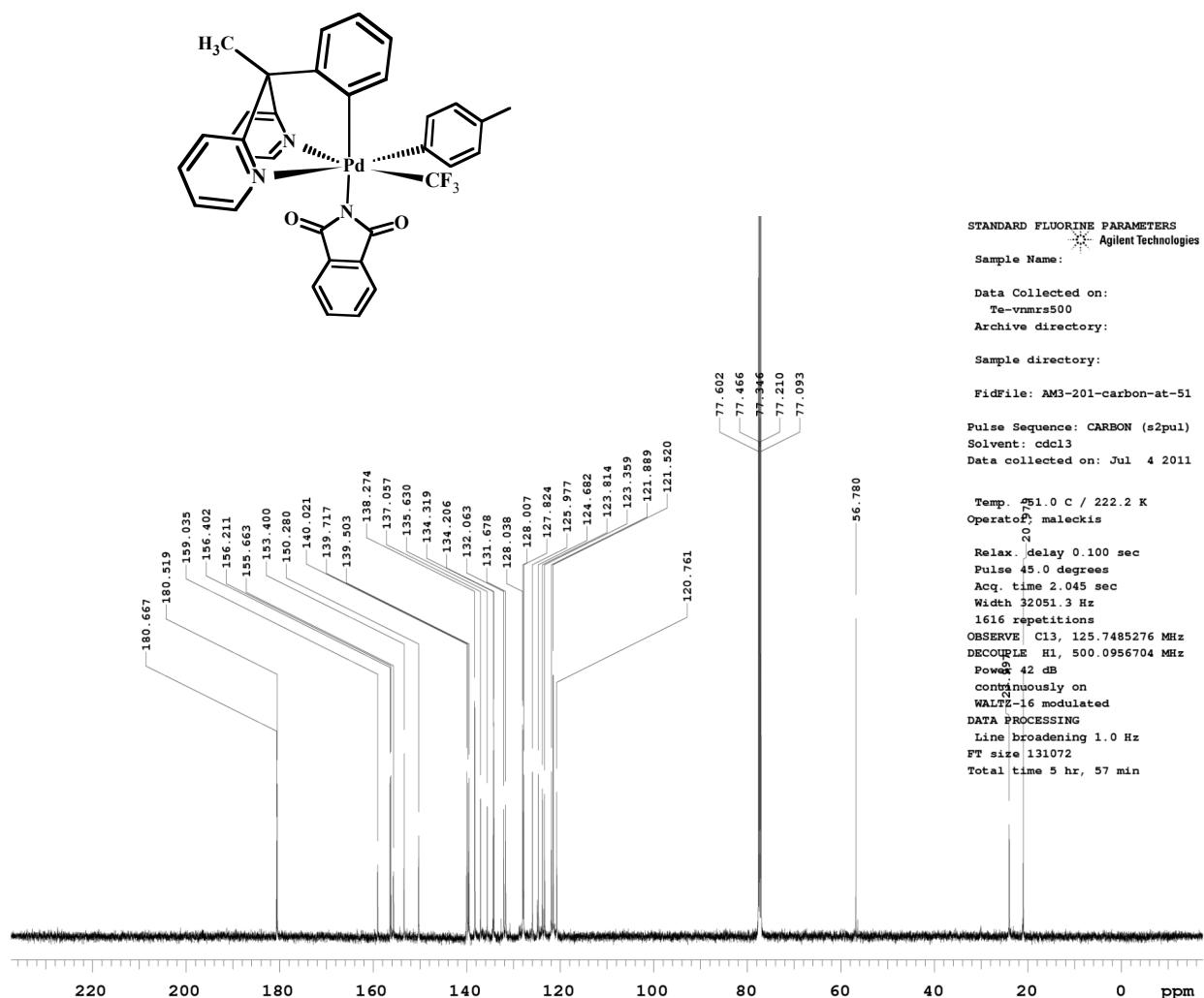
**$^1\text{H}$  NMR of  $[(\text{dpph})\text{Pd}^{\text{IV}}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)(\text{NPhth})] (22)$  (in  $\text{CDCl}_3$  at  $-33^\circ\text{C}$ )**



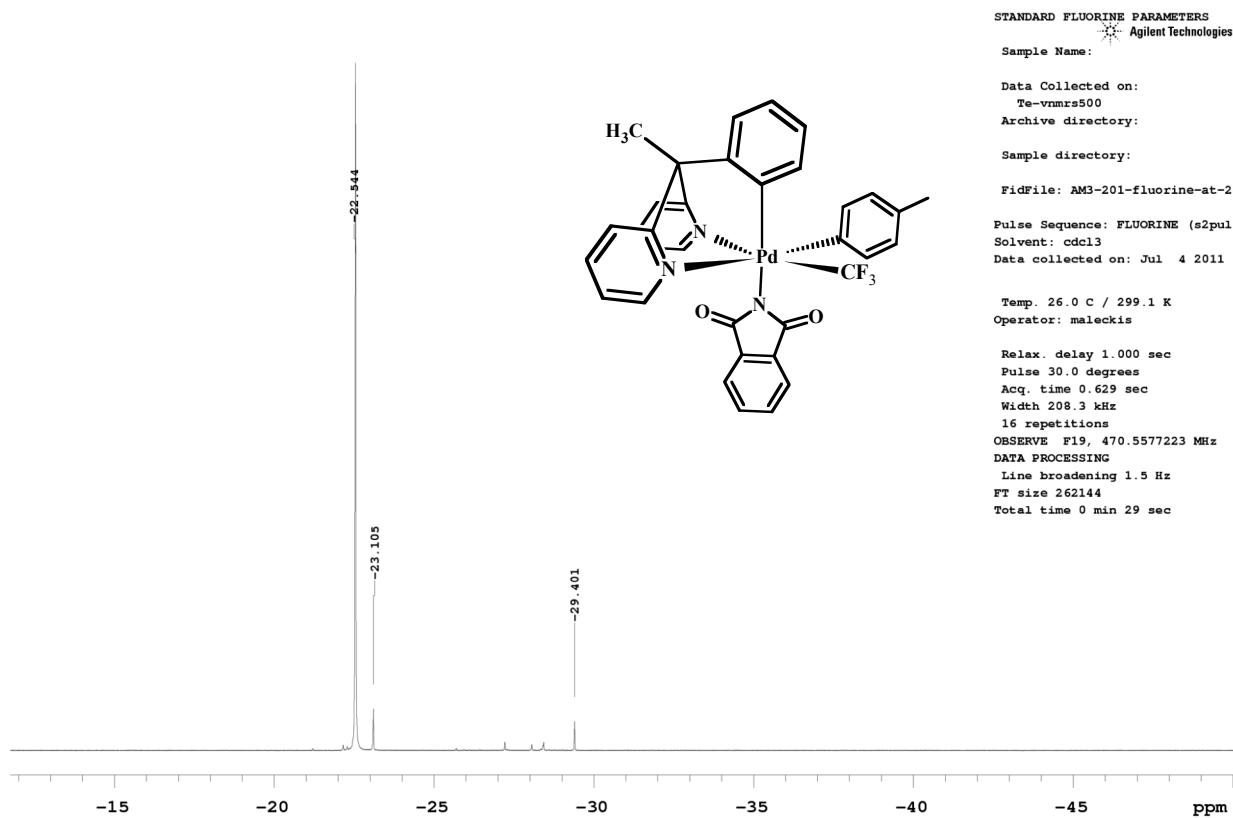
**$^1\text{H}$  NMR of  $[(\text{dpph})\text{Pd}^{\text{IV}}(\text{4-MeC}_6\text{H}_4)(\text{CF}_3)(\text{NPhth})] (22)$  (in  $\text{CDCl}_3$  at  $20^\circ\text{C}$ )**



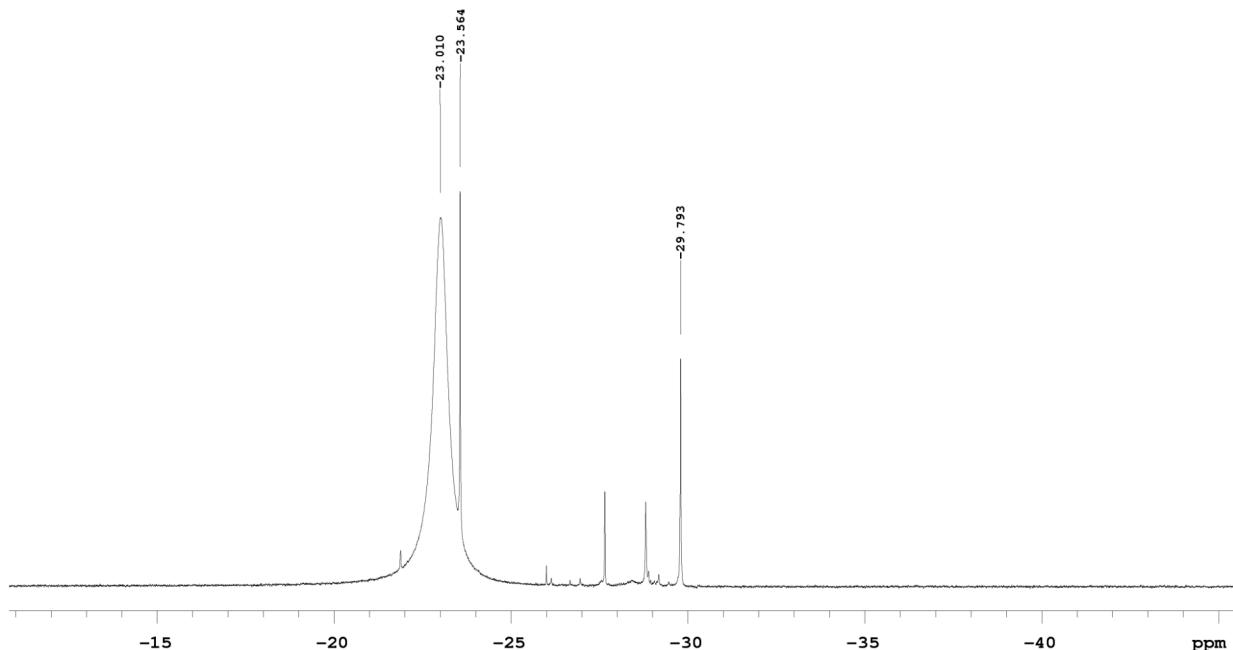
$^{13}\text{C}\{\text{H}\}$  NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)



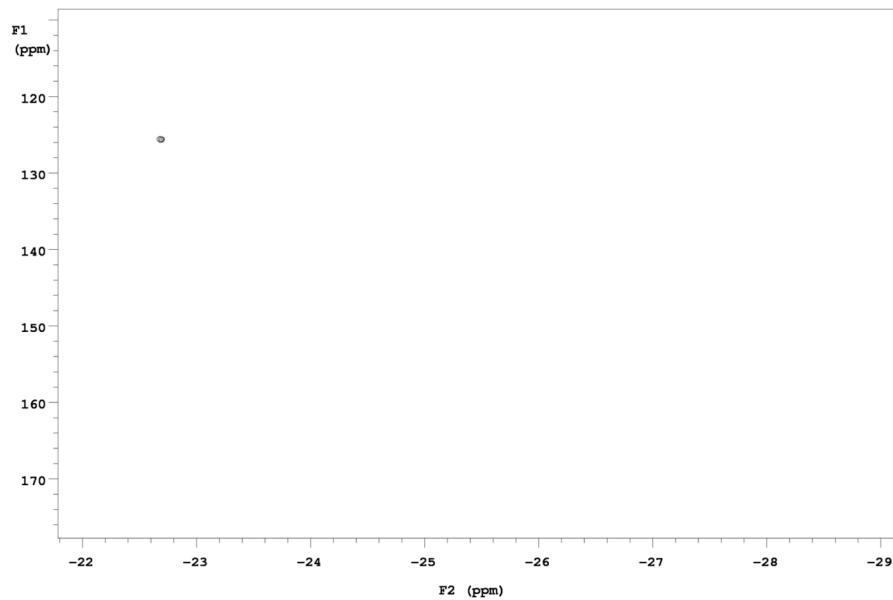
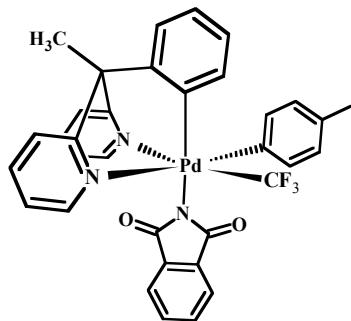
**<sup>19</sup>F NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)**



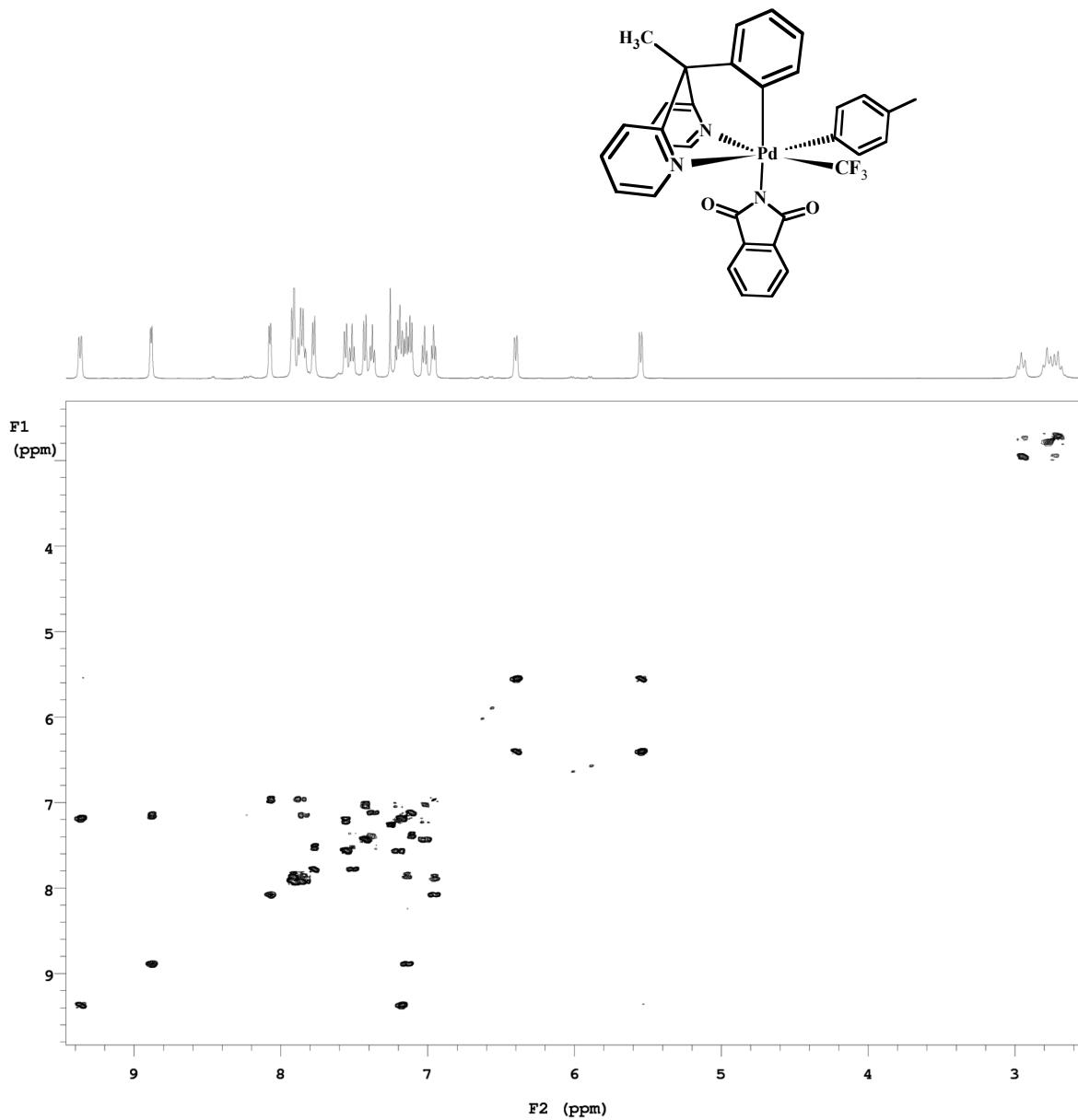
**<sup>19</sup>F NMR of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)**



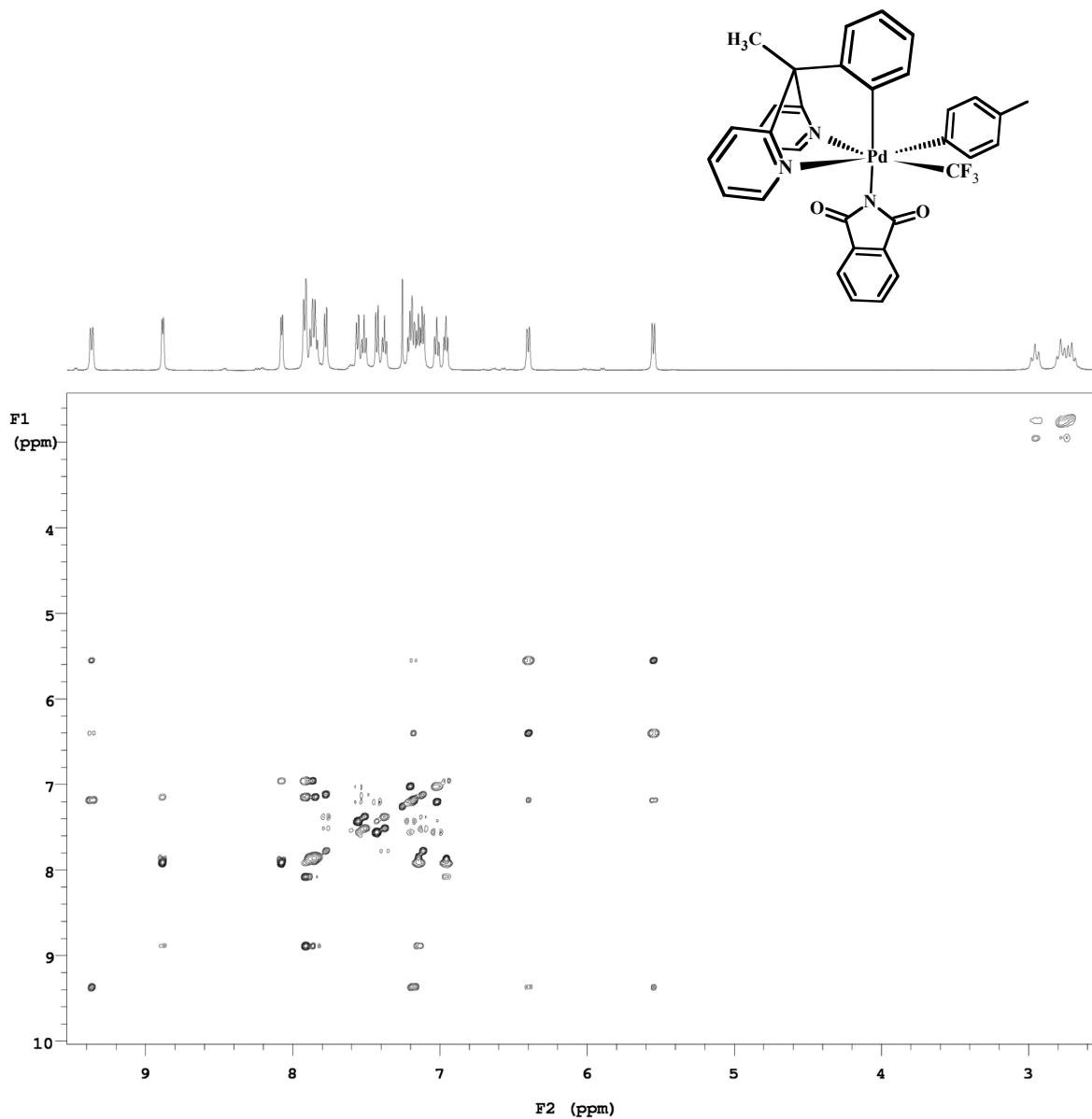
<sup>19</sup>F/<sup>13</sup>C ASAPHMQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at 24°C)



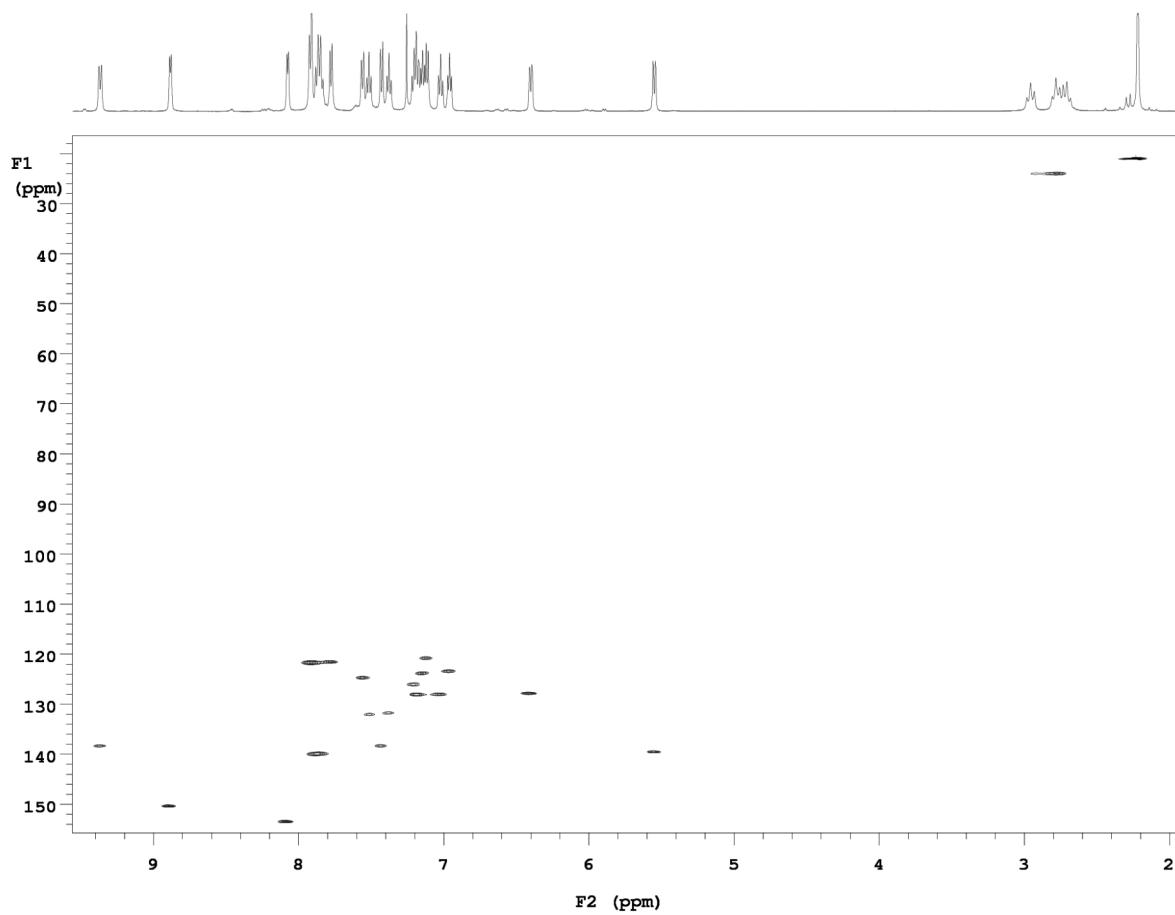
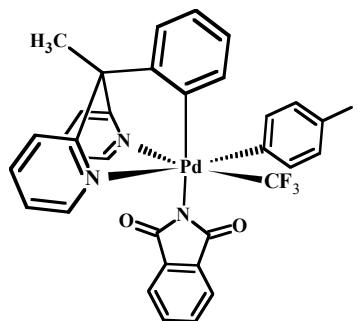
$^1\text{H}/^1\text{H}$  gCOSY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)



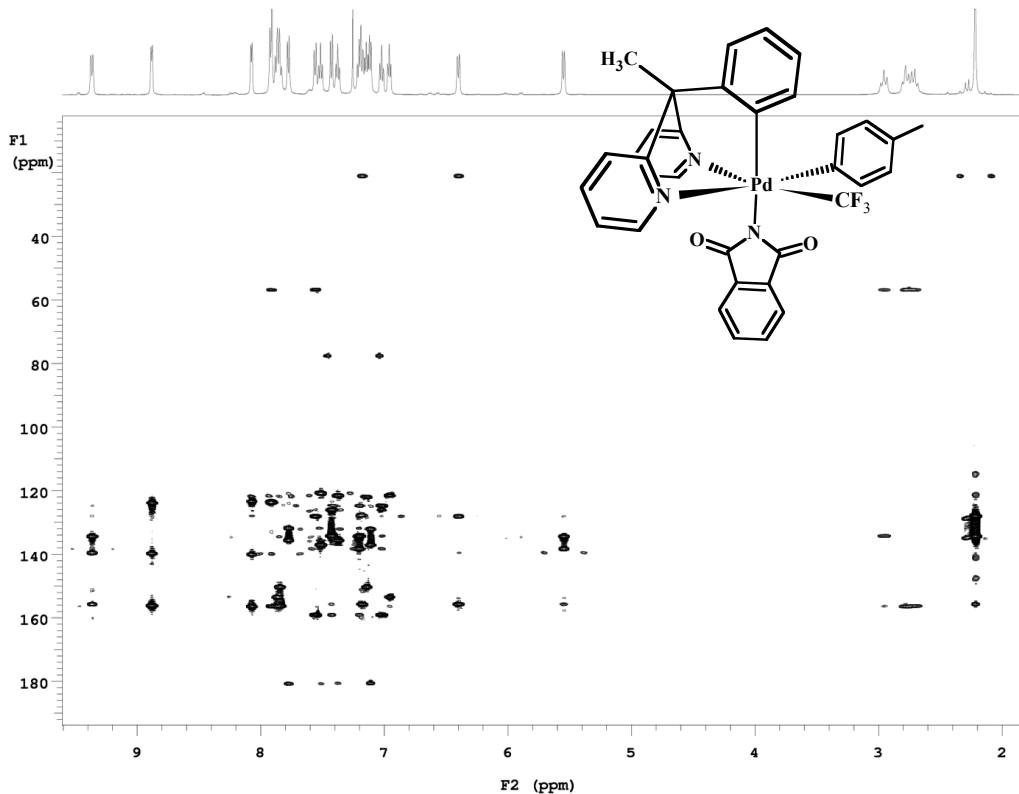
<sup>1</sup>H/<sup>1</sup>H TOCSY of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)



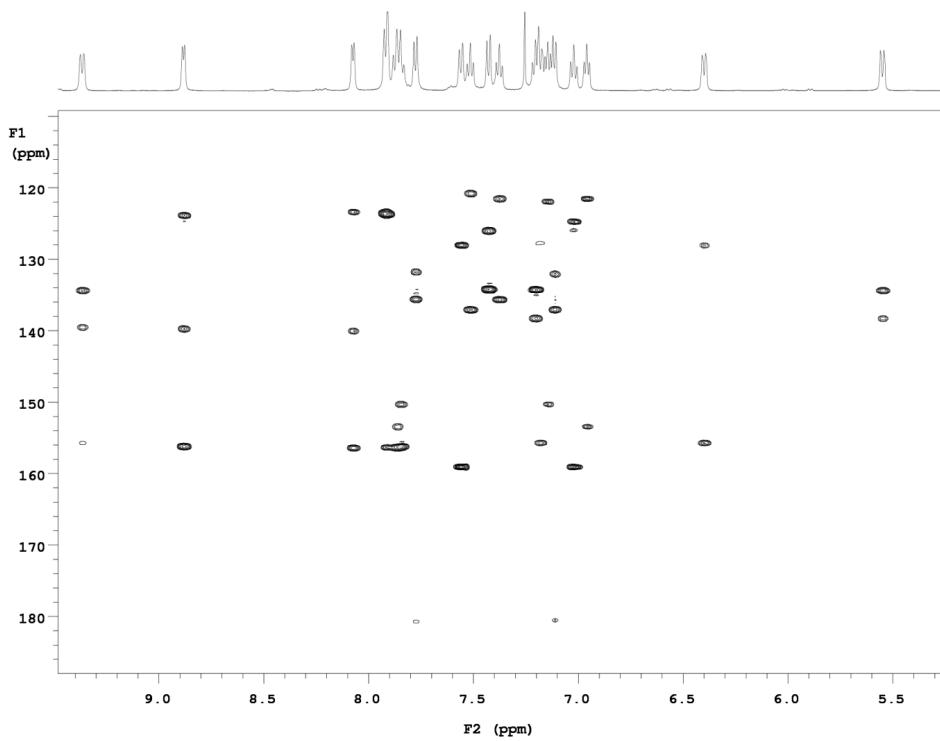
$^1\text{H}/^{13}\text{C}$  ASAPHMQC of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)



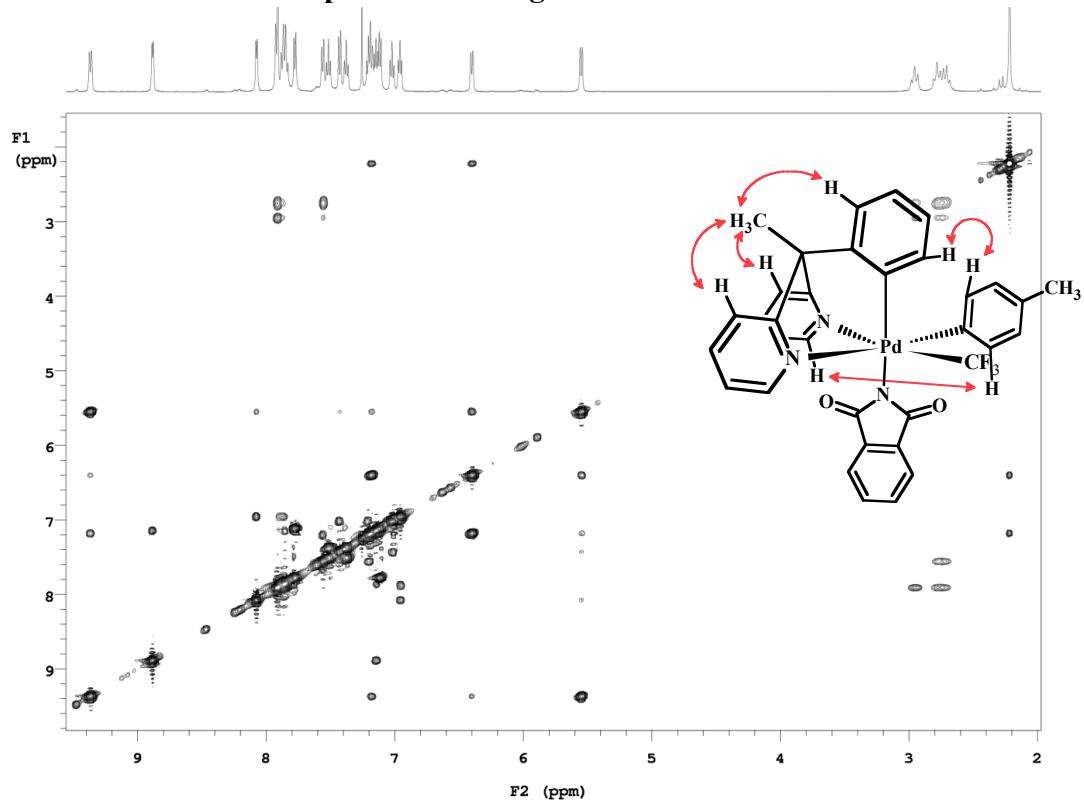
$^1\text{H}/^{13}\text{C}$  gHMBCAD of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)



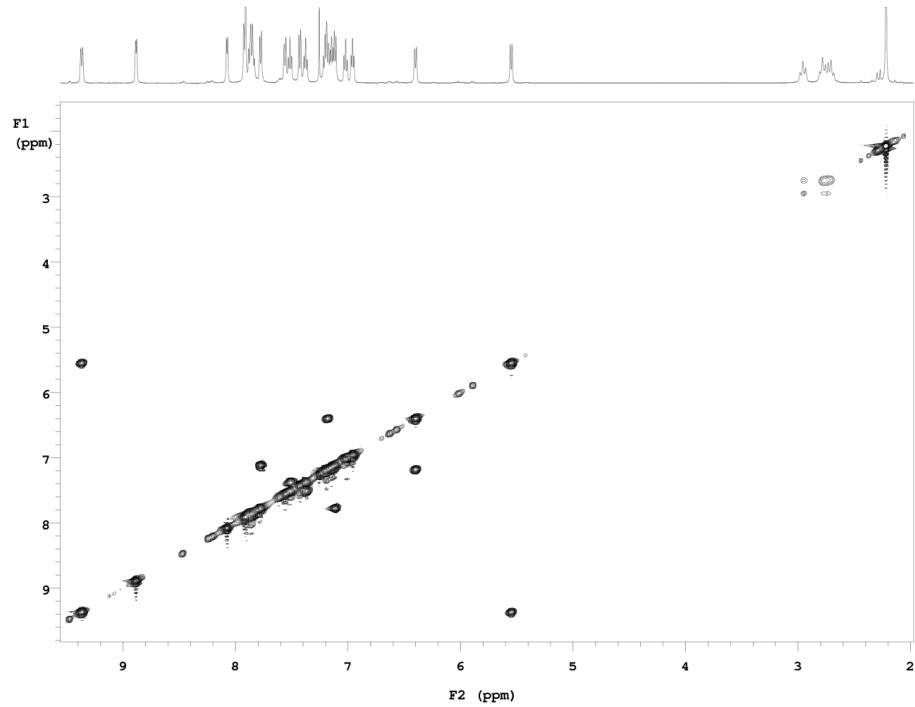
$^1\text{H}/^{13}\text{C}$  gHMBCAD of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22) (in CDCl<sub>3</sub> at -51°C)  
Aromatic region at lower intensity



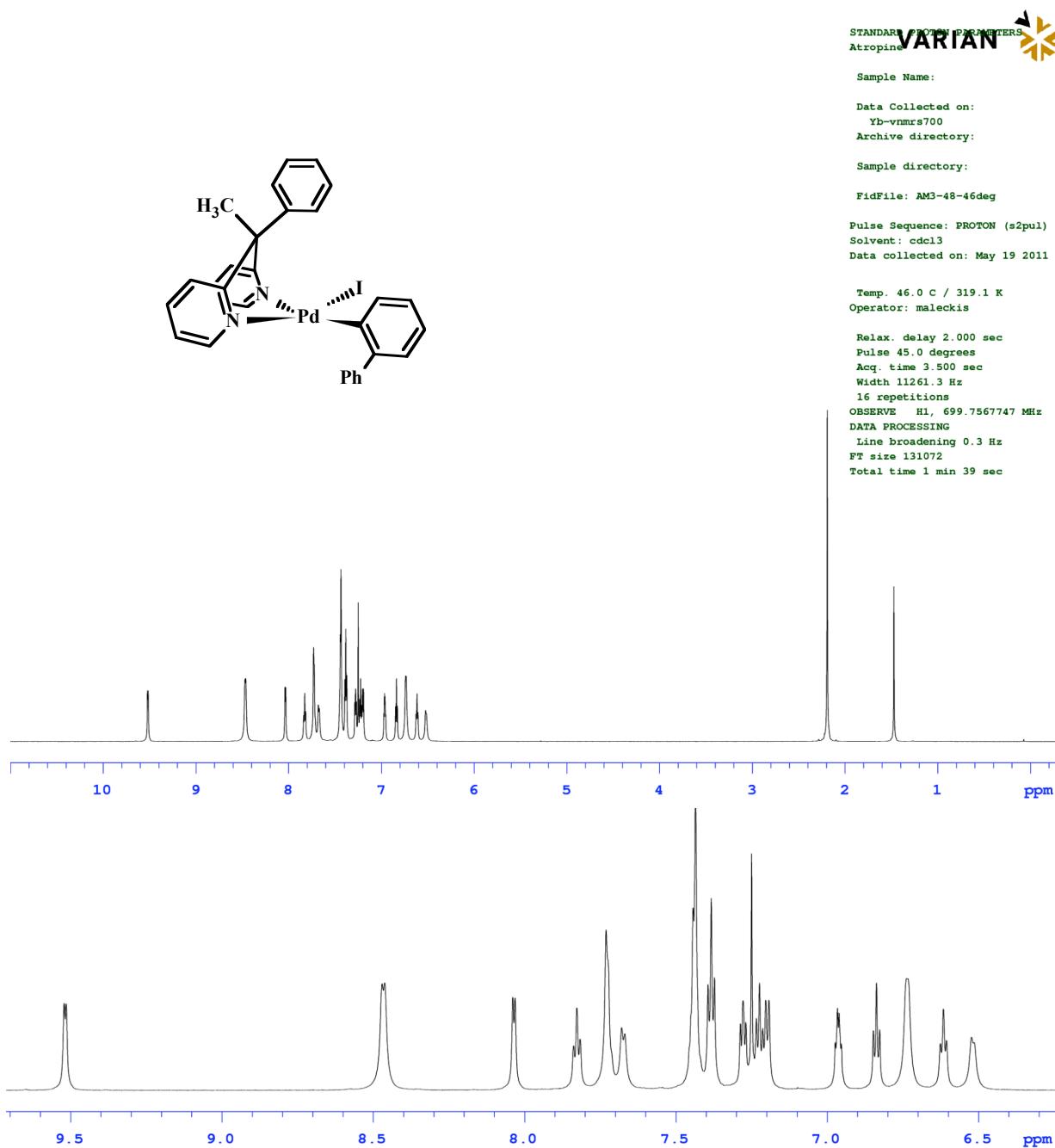
**$^1\text{H}/^1\text{H}$  ROESY of  $[(\text{dpph})\text{Pd}^{\text{IV}}(4\text{-MeC}_6\text{H}_4)(\text{CF}_3)(\text{NPhth})] (22)$  (in  $\text{CDCl}_3$  at  $-51^\circ\text{C}$ )  
positive and negative contours**



**$^1\text{H}/^1\text{H}$  ROESY of  $[(\text{dpph})\text{Pd}^{\text{IV}}(4\text{-MeC}_6\text{H}_4)(\text{CF}_3)(\text{NPhth})] (22)$  (in  $\text{CDCl}_3$  at  $-51^\circ\text{C}$ )  
negative contours**



<sup>1</sup>H NMR of (dpph)Pd<sup>II</sup>(2-PhC<sub>6</sub>H<sub>4</sub>)(I) (23) (at 46°C)



$^{13}\text{C}\{\text{H}\}$  NMR of (dpph)Pd<sup>II</sup>(2-PhC<sub>6</sub>H<sub>4</sub>)(I) (**23**) (at 46°C)

STANDARD PROTON PARAMETERS  
Atropine

Sample Name:

Data Collected on:  
Yb-vnmrs700

Archive directory:

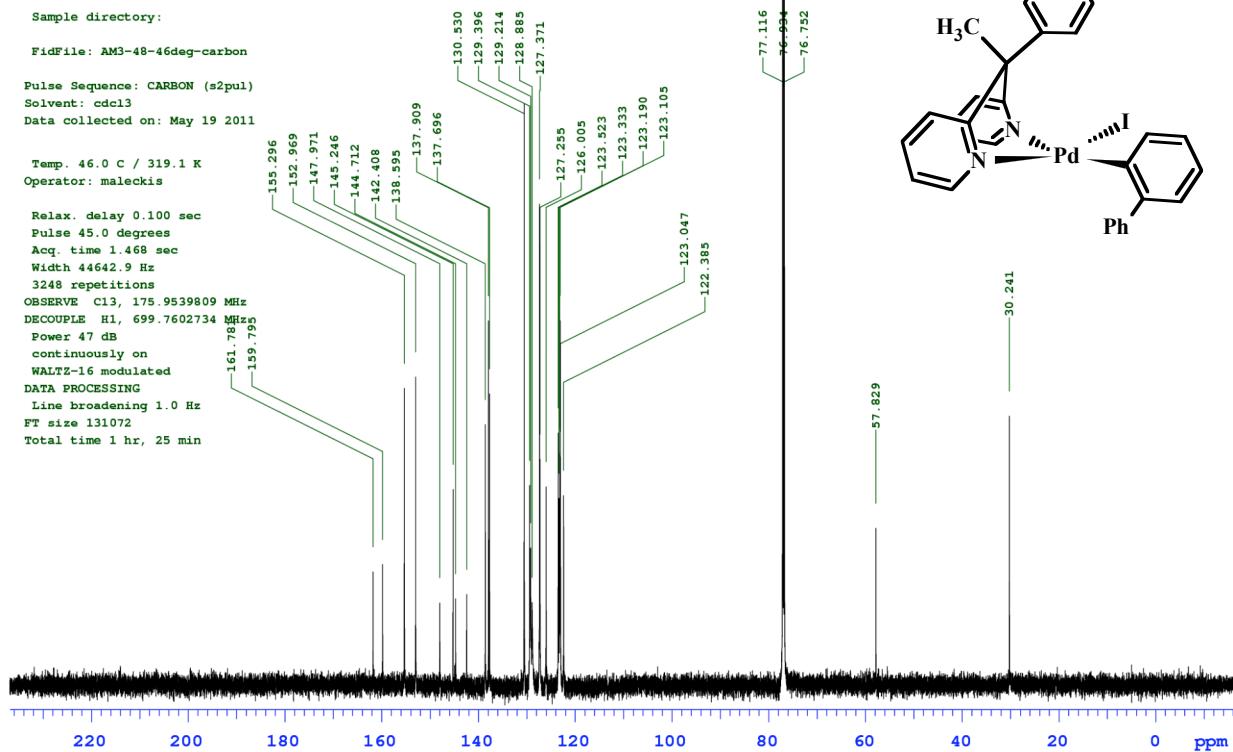
Sample directory:

FidFile: AM3-48-46deg-carbon

Pulse Sequence: CARBON (s2pul)  
Solvent: cdc13  
Data collected on: May 19 2011

Temp. 46.0 C / 319.1 K  
Operator: maleckis

Relax. delay 0.100 sec  
Pulse 45.0 degrees  
Acq. time 1.468 sec  
Width 44642.9 Hz  
3248 repetitions  
OBSERVE C13, 175.9539809 MHz  
DECOUPLE H1, 699.7602734 MHz  
Power 47 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 1 hr, 25 min



VARIAN

**<sup>1</sup>H NMR of (dpph)Pd<sup>IV</sup>(biphe)(Cl) (24) (CD<sub>2</sub>Cl<sub>2</sub> solvent)**

STANDARD PROTON PARAMETERS  
Atropine

VARIAN 

Sample Name:

Data Collected on:

Xb-vnmrs700

Archive directory:

Sample directory:

FidFile: AM3-78-dcm

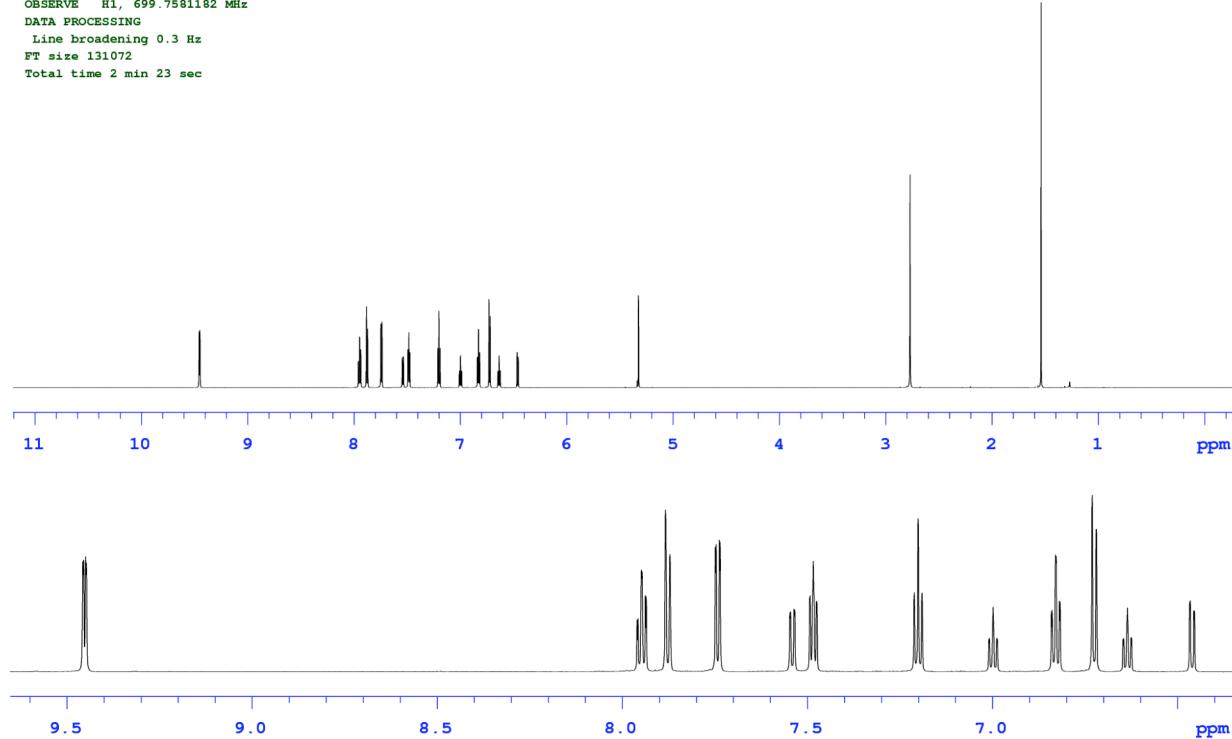
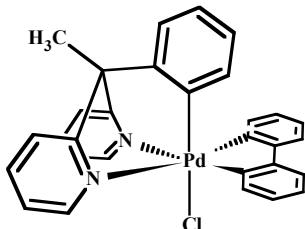
Pulse Sequence: PROTON (s2pul)

Solvent: cd2cl2

Data collected on: May 24 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

Relax. delay 2.000 sec  
Pulse 45.0 degrees  
Acq. time 3.500 sec  
Width 11261.3 Hz  
24 repetitions  
OBSERVE H1, 699.7581182 MHz  
DATA PROCESSING  
Line broadening 0.3 Hz  
FT size 131072  
Total time 2 min 23 sec



$^{13}\text{C}\{\text{H}\}$  NMR of (dpph)Pd<sup>IV</sup>(biphe)(Cl) (24) (CD<sub>2</sub>Cl<sub>2</sub> solvent)

STANDARD PROTON PARAMETERS  
Atropine

Sample Name:

Data Collected on:

Yb-vnmrs700

Archive directory:

Sample directory:

FidFile: AM3-78-dcm-carbon

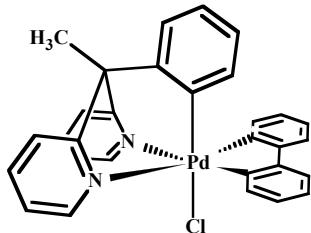
Pulse Sequence: CARBON (s2pul)

Solvent: cd2cl2

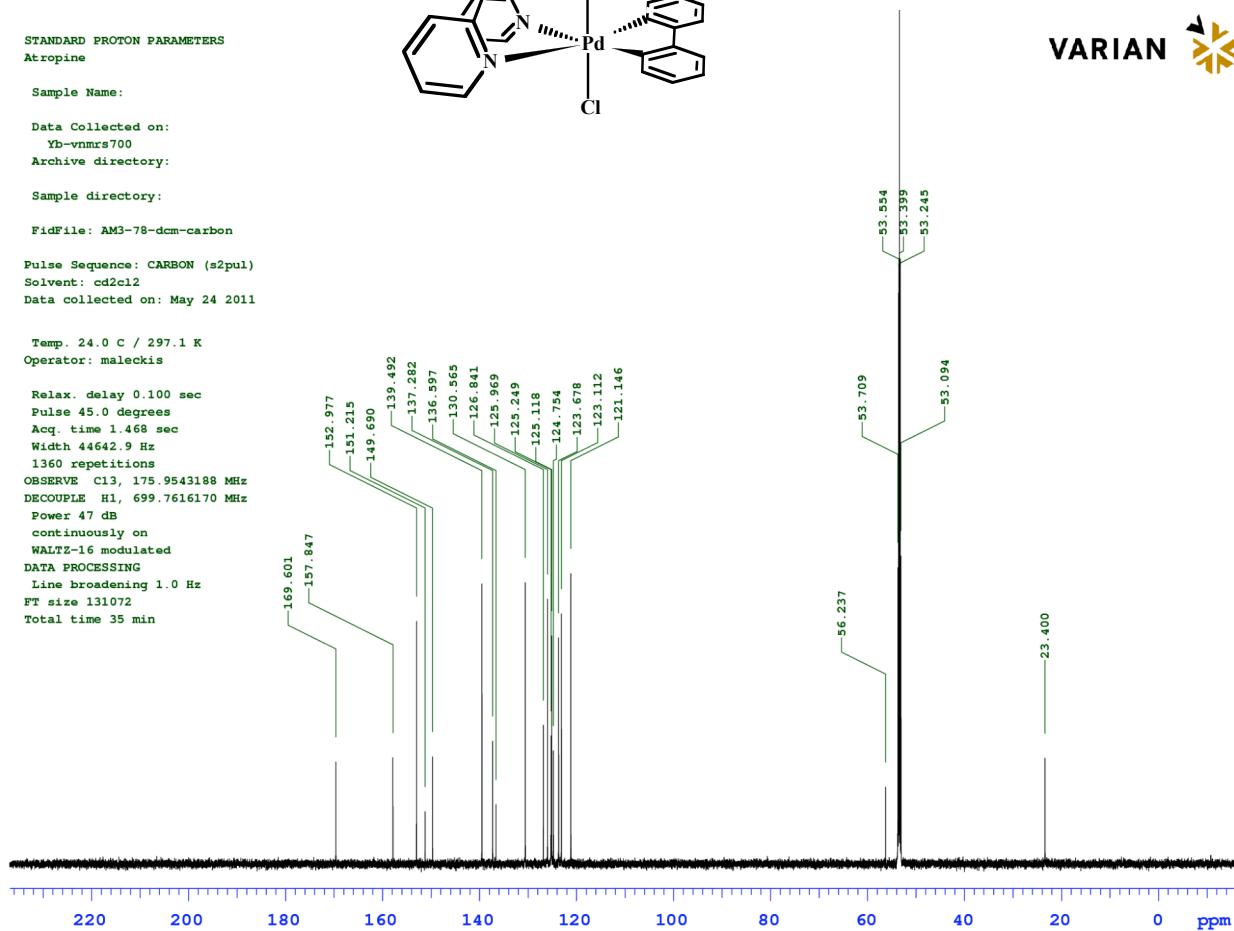
Data collected on: May 24 2011

Temp. 24.0 C / 297.1 K  
Operator: maleckis

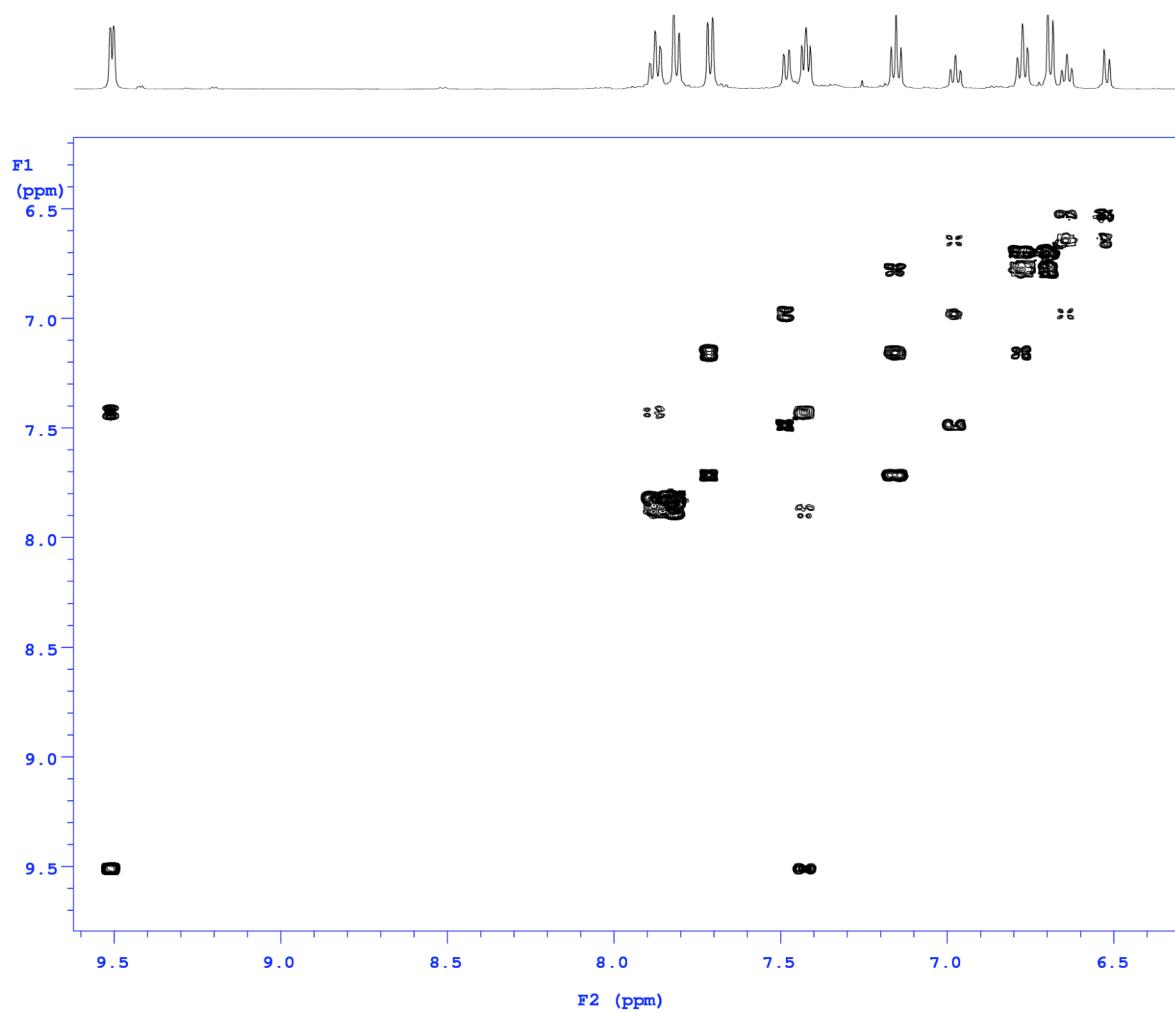
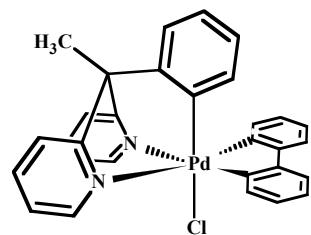
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Pulse 45.0 degrees  
Acq. time 1.468 sec  
Width 44642.9 Hz  
1360 repetitions  
OBSERVE C13, 175.9543188 MHz  
DECOUPLE H1, 699.7616170 MHz  
Power 47 dB  
continuously on  
WALTZ-16 modulated  
DATA PROCESSING  
Line broadening 1.0 Hz  
FT size 131072  
Total time 35 min



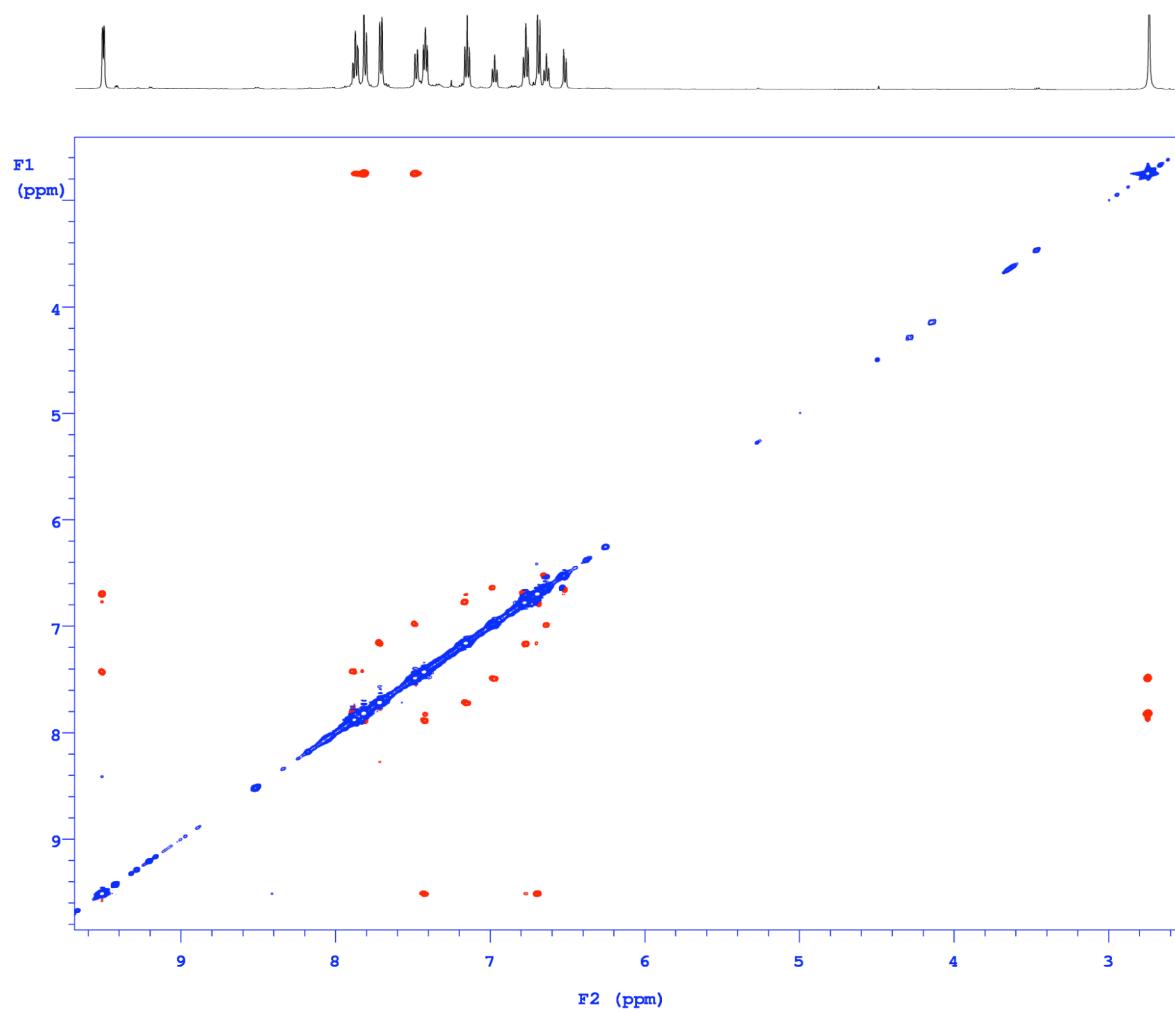
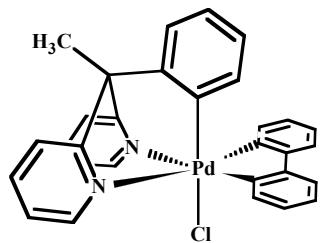
VARIAN



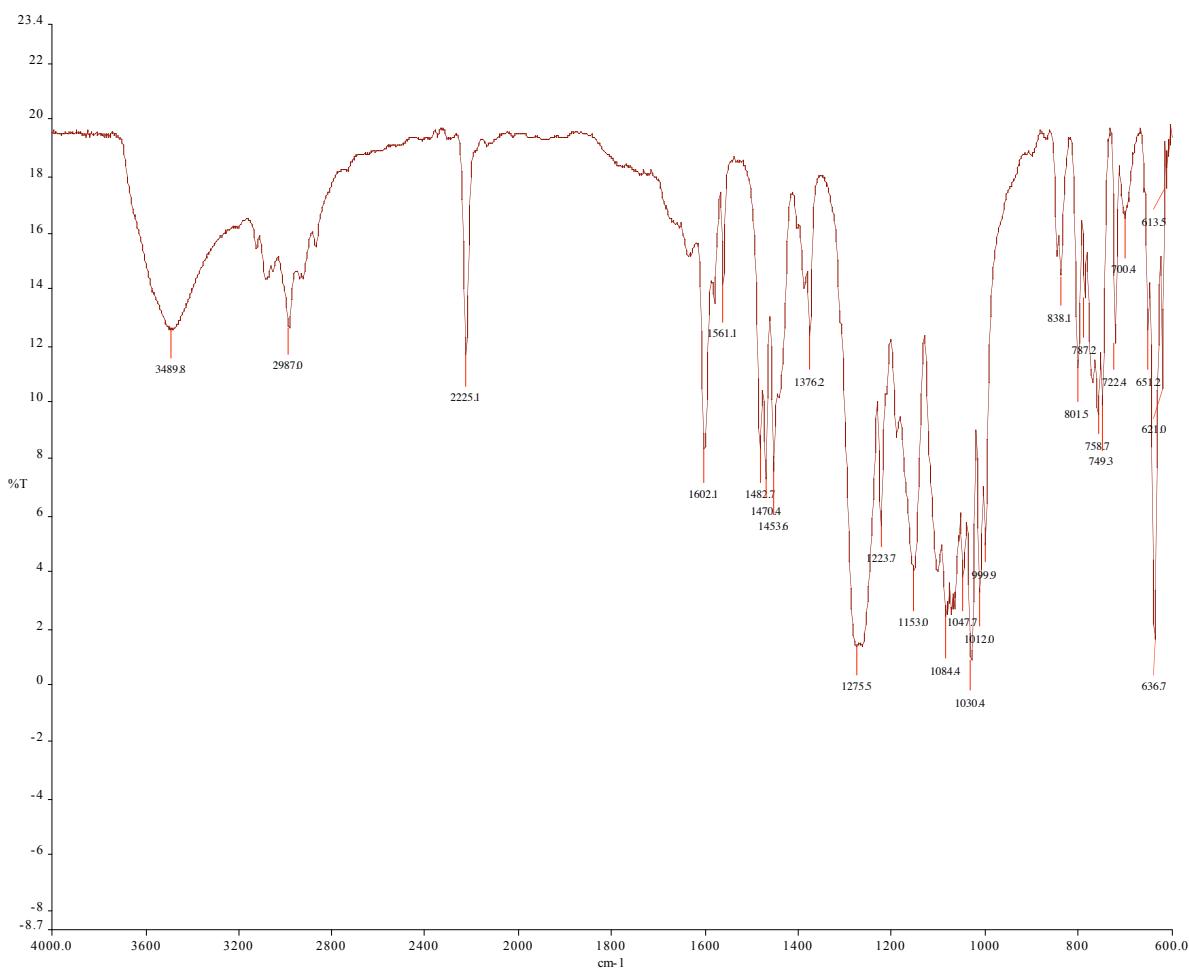
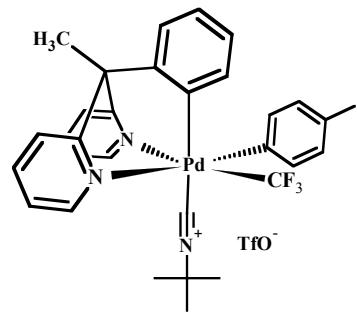
$^1\text{H}/^1\text{H}$  COSY of (dpph)Pd<sup>IV</sup>(biphe)(Cl) (**24**) (CDCl<sub>3</sub> solvent)



<sup>1</sup>H/<sup>1</sup>H ROESY of (dpph)Pd<sup>IV</sup>(biphe)(Cl) (**24**) (CDCl<sub>3</sub> solvent)



**IR spectrum of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(t-BuNC)]OTf (19)**



## X-ray crystallographic data of (**dpsa**)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(Cl) (11)

### Structure Determination.

Yellow, block-like crystals of **am341** were grown from an acetonitrile/methyl t-butyl ether solution at 23 deg. C. A crystal of dimensions 0.15 x 0.13 x 0.12 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ( $\lambda = 1.54187 \text{ \AA}$ ) operated at 0.2 kW power (20 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 1506 images were collected with an oscillation width of 2.0° in  $\omega$ . The exposure time was 10 sec. per image for low angle and 30 seconds for high angle images. The integration of the data yielded a total of 34052 reflections to a maximum 2θ value of 136.44° of which 5929 were independent and 5842 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 18798 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P1bar with Z = 2 for the formula C<sub>29</sub>H<sub>35</sub>ClF<sub>3</sub>N<sub>5</sub>O<sub>2</sub>PdS, 2(C<sub>2</sub>H<sub>3</sub>N). Full matrix least-squares refinement based on F<sup>2</sup> converged at R1 = 0.0297 and wR2 = 0.0729 [based on I > 2sigma(I)], R1 = 0.0304 and wR2 = 0.0734 for all data. The acetonitrile solvates and the t-butylphenylsulfonamido ligand are disordered. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r5, Rigaku Americas and Rigaku Corporation (2010), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table 1. Crystal data and structure refinement for am341.

Identification code	am341
Empirical formula	C33 H35 Cl F3 N5 O2 Pd S
Formula weight	764.57
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions 67.070(5) deg. 78.111(5) deg. 73.844(5) deg.	a = 9.9337(2) Å alpha = b = 13.4448(3) Å beta = c = 14.1447(10) Å gamma =
Volume	1660.93(13) Å^3
Z, Calculated density	2, 1.529 Mg/m^3
Absorption coefficient	6.306 mm^-1
F(000)	780
Crystal size	0.15 x 0.13 x 0.12 mm
Theta range for data collection	3.41 to 68.22 deg.
Limiting indices	-11<=h<=11, -16<=k<=16, -17<=l<=17
Reflections collected / unique	34052 / 5929 [R(int) = 0.0485]
Completeness to theta = 68.22	97.6 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.474 and 0.416
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5929 / 183 / 560
Goodness-of-fit on F^2	1.056
Final R indices [I>2sigma(I)]	R1 = 0.0270, wR2 = 0.0694
R indices (all data)	R1 = 0.0273, wR2 = 0.0696
Largest diff. peak and hole	0.472 and -0.599 e.Å^-3

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for am341.  
 U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
S(1)	2806(1)	1439(1)	3965(1)	23(1)
Pd(1)	4004(1)	2579(1)	1436(1)	14(1)
Cl(1)	4659(1)	3494(1)	-277(1)	28(1)
F(1)	1478(1)	3814(1)	2163(1)	43(1)
F(2)	2453(2)	4834(1)	774(1)	49(1)
F(3)	3350(1)	4303(1)	2192(1)	42(1)
O(1)	1414(1)	1705(1)	3672(1)	33(1)
O(2)	3273(1)	362(1)	4725(1)	27(1)
N(1)	5352(2)	1056(1)	1368(1)	15(1)
N(2)	5860(2)	2751(1)	1917(1)	18(1)
N(3)	3908(2)	1560(1)	2954(1)	16(1)
C(1)	5718(2)	689(2)	580(1)	22(1)
C(2)	6599(2)	-335(2)	680(2)	32(1)
C(3)	7126(2)	-982(2)	1615(2)	31(1)
C(4)	6761(2)	-598(2)	2429(2)	24(1)
C(5)	5856(2)	425(1)	2283(1)	16(1)
C(6)	5402(2)	998(1)	3066(1)	16(1)
C(7)	6300(2)	1857(1)	2733(1)	17(1)
C(8)	7515(2)	1716(2)	3148(1)	21(1)
C(9)	8305(2)	2524(2)	2693(2)	24(1)
C(10)	7839(2)	3447(2)	1855(2)	28(1)
C(11)	6600(2)	3541(2)	1491(2)	24(1)
C(12)	2914(5)	2488(4)	4440(3)	20(1)
C(13)	1882(4)	3498(3)	4323(3)	21(1)
C(14)	1888(4)	4209(3)	4815(3)	22(1)
C(15)	2910(4)	3984(3)	5458(3)	19(1)
C(16)	3910(5)	3037(4)	5561(4)	19(1)
C(17)	3986(5)	2293(4)	5066(3)	16(1)
C(18)	2748(4)	4730(3)	6082(3)	17(1)
C(19)	4049(5)	4509(4)	6600(4)	29(1)
C(20)	1543(5)	4447(4)	6948(4)	27(1)
C(21)	2352(6)	5973(4)	5409(4)	26(1)
C(12A)	2773(6)	2318(4)	4612(3)	24(1)
C(13A)	1494(4)	2957(3)	4779(3)	23(1)
C(14A)	1455(4)	3644(3)	5310(3)	26(1)
C(15A)	2650(5)	3681(3)	5654(3)	18(1)
C(16A)	3980(7)	3000(5)	5419(4)	25(1)
C(17A)	3989(6)	2318(5)	4891(4)	24(1)
C(18A)	2526(5)	4457(4)	6246(4)	20(1)
C(19A)	3811(5)	4083(4)	6869(4)	31(1)
C(20A)	1182(6)	4495(5)	6987(4)	19(1)
C(21A)	2565(6)	5622(4)	5453(4)	23(1)
C(22)	2337(2)	2251(2)	1059(1)	18(1)

C (23)	2057 (2)	1210 (2)	1580 (1)	18 (1)
C (24)	944 (2)	953 (2)	1322 (1)	21 (1)
C (25)	127 (2)	1709 (2)	552 (1)	24 (1)
C (26)	445 (2)	2746 (2)	32 (2)	27 (1)
C (27)	1554 (2)	3021 (2)	277 (2)	26 (1)
C (28)	-1077 (2)	1420 (2)	288 (2)	33 (1)
C (29)	2736 (2)	3958 (2)	1644 (2)	31 (1)
N (4)	3174 (4)	8335 (3)	3452 (4)	53 (1)
C (30)	2120 (5)	8741 (3)	3769 (3)	33 (1)
C (31)	725 (6)	9325 (4)	4106 (4)	33 (1)
N (6)	-232 (4)	8106 (4)	3241 (4)	48 (1)
C (34)	266 (5)	8481 (4)	3667 (4)	36 (1)
C (31A)	941 (7)	8930 (4)	4198 (4)	35 (1)
N (5)	183 (4)	8098 (3)	2542 (3)	38 (1)
C (32)	1184 (4)	7462 (3)	2492 (3)	24 (1)
C (33)	2550 (3)	6687 (2)	2334 (2)	41 (1)
N (7)	3496 (4)	8367 (3)	2271 (3)	40 (1)
C (35)	3107 (5)	7639 (3)	2259 (3)	32 (1)
C (33A)	2550 (3)	6687 (2)	2334 (2)	41 (1)

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## X-ray crystallographic data of (dpsa)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(F) (12)

### Structure Determination.

Yellow plates of **am355** were grown from an acetonitrile/methyl t-butyl ether solution at 23 deg. C. A crystal of dimensions 0.20 x 0.10 x 0.06 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ( $\lambda = 1.54187 \text{ \AA}$ ) operated at 0.25 kW power (25 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 3147 images were collected with an oscillation width of 1.0° in  $\omega$ . The exposure time was 10 sec. per image for low angle and 40 seconds for high angle images. The integration of the data yielded a total of 67691 reflections to a maximum 2θ value of 136.46° of which 5932 were independent and 5725 were greater than  $2\sigma(I)$ . The final cell constants (Table 1) were based on the xyz centroids of 67691 reflections above  $10\sigma(I)$ . Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group C2/c with Z = 8 for the formula C<sub>29</sub>H<sub>29</sub>F<sub>4</sub>N<sub>3</sub>O<sub>2</sub>PdS, (C<sub>2</sub>H<sub>3</sub>N), (C<sub>5</sub>H<sub>12</sub>O)<sub>0.5</sub>. Full matrix least-squares refinement based on F<sup>2</sup> converged at R1 = 0.0470 and wR2 = 0.1170 [based on I > 2sigma(I)], R1 = 0.0482 and wR2 = 0.1181 for all data. The acetonitrile and methyl t-butyl ether solvates are disordered. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r5, Rigaku Americas and Rigaku Corporation (2010), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table 1. Crystal data and structure refinement for am355.

Identification code	am355
Empirical formula	C33.50 H38 F4 N4 O2.50 Pd S
Formula weight	751.14
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, C2/c
Unit cell dimensions	a = 17.4944(3) Å alpha = 90 deg. b = 22.1204(4) Å beta = 114.778(8) deg.
	c = 18.4391(13) Å gamma = 90 deg.
Volume	6478.7(5) Å^3
Z, Calculated density	8, 1.540 Mg/m^3
Absorption coefficient	5.760 mm^-1
F(000)	3080
Crystal size	0.20 x 0.10 x 0.06 mm
Theta range for data collection	3.43 to 68.23 deg.
Limiting indices	-21<=h<=21, -26<=k<=26, -22<=l<=22
Reflections collected / unique	67911 / 5932 [R(int) = 0.0499]
Completeness to theta = 68.23	100.0 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.712 and 0.544
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5932 / 75 / 479
Goodness-of-fit on F^2	1.069
Final R indices [I>2sigma(I)]	R1 = 0.0470, wR2 = 0.1170
R indices (all data)	R1 = 0.0482, wR2 = 0.1181
Largest diff. peak and hole	1.075 and -1.361 e.Å^-3

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{Å}^2 \times 10^3$ ) for am355.  
 $U(\text{eq})$  is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	$U(\text{eq})$
S(1)	4127(1)	2737(1)	5379(1)	31(1)
Pd(1)	4866(1)	1952(1)	4238(1)	34(1)
F(1)	5390(1)	1590(1)	3595(1)	47(1)
F(2)	5830(2)	2740(1)	3773(2)	63(1)
F(3)	4736(1)	3162(1)	3793(2)	53(1)
F(4)	5833(1)	3024(1)	4877(1)	47(1)
O(1)	4985(1)	2844(1)	5926(1)	37(1)
O(2)	3537(1)	2567(1)	5705(1)	35(1)
N(1)	3678(2)	2088(1)	3193(2)	31(1)
N(2)	4261(2)	1128(1)	4285(2)	43(1)
N(3)	4124(2)	2215(1)	4776(2)	35(1)
C(1)	3534(2)	2129(1)	2425(2)	34(1)
C(2)	2717(2)	2160(1)	1840(2)	34(1)
C(3)	2054(2)	2159(1)	2052(2)	34(1)
C(4)	2210(2)	2109(2)	2854(2)	35(1)
C(5)	3035(2)	2066(1)	3410(2)	31(1)
C(6)	3322(2)	1903(1)	4291(2)	36(1)
C(7)	3523(2)	1234(2)	4321(2)	41(1)
C(8)	2992(3)	766(2)	4302(2)	49(1)
C(9)	3245(3)	178(2)	4226(2)	59(1)
C(10)	3982(3)	78(2)	4183(2)	60(1)
C(11)	4509(3)	568(2)	4220(2)	53(1)
C(12)	3728(2)	3426(1)	4866(2)	32(1)
C(13)	2875(2)	3496(1)	4389(2)	33(1)
C(14)	2574(2)	4052(2)	4047(2)	37(1)
C(15)	3120(3)	4551(2)	4176(2)	42(1)
C(16)	3958(3)	4461(2)	4640(3)	55(1)
C(17)	4273(3)	3907(2)	4993(3)	50(1)
C(18)	2759(3)	5173(2)	3818(2)	47(1)
C(19)	2199(4)	5398(2)	4185(3)	74(2)
C(20)	2309(3)	5137(2)	2918(2)	49(1)
C(21)	3482(4)	5646(2)	4025(4)	93(2)
C(22)	5916(2)	1734(2)	5224(2)	40(1)
C(23)	5864(2)	1579(2)	5924(2)	40(1)
C(24)	6601(2)	1401(2)	6588(2)	43(1)
C(25)	7374(2)	1374(2)	6545(2)	42(1)
C(26)	7397(2)	1515(2)	5818(2)	44(1)
C(27)	6672(2)	1698(2)	5156(2)	44(1)
C(28)	8168(2)	1214(2)	7262(2)	48(1)
C(29)	5364(2)	2767(2)	4179(2)	39(1)
N(4)	5405(5)	9481(4)	3613(5)	65(2)
C(30)	5247(6)	9883(4)	3180(5)	57(2)
C(31)	5079(10)	10418(4)	2646(8)	69(3)
N(5)	5372(5)	9061(4)	3373(6)	76(2)
C(32)	5176(5)	8636(4)	2984(5)	58(2)
C(33)	4888(5)	8078(4)	2522(7)	53(3)
O(3)	4718(4)	4896(3)	8126(3)	50(1)

C (34)	5197 (6)	5432 (4)	8427 (5)	54 (2)
C (35)	5020 (20)	4554 (3)	7500 (30)	72 (3)
C (36)	4321 (6)	4006 (4)	7395 (6)	56 (2)
C (37)	4621 (6)	4914 (4)	6777 (5)	59 (2)
C (38)	5798 (5)	4350 (5)	7897 (6)	56 (2)

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## X-ray crystallographic data of (dpph)Pd<sup>II</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>) (15)

### Structure Determination.

Colorless needles of **am352** were grown from an ethyl acetate solution of the compound at 23 deg. C. A crystal of dimensions 0.14 x 0.10 x 0.09 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ( $\lambda = 1.54187 \text{ \AA}$ ) operated at 0.2 kW power (20 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 1561 images were collected with an oscillation width of 2.0° in  $\omega$ . The exposure time was 20 sec. for the low angle images, 45 sec. for high angle. The integration of the data yielded a total of 23642 reflections to a maximum 2θ value of 136.46° of which 3880 were independent and 3814 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 22979 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P1bar with Z = 2 for the formula C<sub>26</sub>H<sub>23</sub>N<sub>2</sub>F<sub>3</sub>Pd, 2(C<sub>24</sub>H<sub>20</sub>B). Full matrix least-squares refinement based on F<sup>2</sup> converged at R1 = 0.0173 and wR2 = 0.0425 [based on I > 2sigma(I)], R1 = 0.0176 and wR2 = 0.0427 for all data. There is a minor substitutional site disorder of the –CF<sub>3</sub> group bonded to palladium which was refined as the contribution of 6.0% iodide. Additional details are presented in Table 1 and are given as Supporting Information in a CIF file. Acknowledgement is made for funding from NSF grant CHE-0840456 for X-ray instrumentation.

Sheldrick, G.M. SHELXTL, v. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r5, Rigaku Americas and Rigaku Corporation (2010), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

Table 1. Crystal data and structure refinement for am352.

Identification code	am352
Empirical formula	C25.94 H23 F2.82 I0.06 N2 Pd
Formula weight	529.95
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Triclinic, P -1
Unit cell dimensions 73.482(5) deg. deg.	a = 9.6736(2) Å alpha = b = 11.0702(2) Å beta = 75.138(5) c = 11.2344(8) Å gamma = 73.681(5) deg.
Volume	1086.38(8) Å^3
Z, Calculated density	2, 1.620 Mg/m^3
Absorption coefficient	7.850 mm^-1
F(000)	533.1
Crystal size	0.14 x 0.10 x 0.09 mm
Theta range for data collection	4.18 to 68.23 deg.
Limiting indices	-11<=h<=11, -13<=k<=13, -13<=l<=13
Reflections collected / unique	23642 / 3880 [R(int) = 0.0297]
Completeness to theta = 68.23	97.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.521 and 0.411
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	3880 / 0 / 301
Goodness-of-fit on F^2	1.034
Final R indices [I>2sigma(I)]	R1 = 0.0173, wR2 = 0.0425
R indices (all data)	R1 = 0.0176, wR2 = 0.0427
Largest diff. peak and hole	0.299 and -0.381 e.Å^-3

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for am352.  
 U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Pd(1)	3046(1)	3185(1)	7036(1)	9(1)
F(1)	5380(1)	1940(1)	8416(1)	17(1)
F(2)	5321(1)	881(1)	7105(1)	20(1)
F(3)	6249(1)	2565(1)	6435(1)	23(1)
N(1)	2260(1)	1721(1)	6654(1)	11(1)
N(2)	896(2)	4288(1)	6870(1)	12(1)
C(1)	3019(2)	1070(2)	5759(2)	14(1)
C(2)	2533(2)	143(2)	5477(2)	18(1)
C(3)	1236(2)	-162(2)	6186(2)	22(1)
C(4)	433(2)	510(2)	7109(2)	20(1)
C(5)	952(2)	1476(2)	7306(2)	13(1)
C(6)	42(2)	2351(2)	8214(2)	13(1)
C(7)	-268(2)	3745(2)	7403(2)	13(1)
C(8)	-1670(2)	4427(2)	7211(2)	18(1)
C(9)	-1873(2)	5678(2)	6468(2)	20(1)
C(10)	-678(2)	6222(2)	5928(2)	18(1)
C(11)	693(2)	5499(2)	6148(2)	14(1)
C(12)	821(2)	2288(2)	9276(2)	13(1)
C(13)	2013(2)	1302(2)	9605(2)	14(1)
C(14)	2554(2)	1208(2)	10672(2)	17(1)
C(15)	1902(2)	2094(2)	11423(2)	18(1)
C(16)	722(2)	3086(2)	11097(2)	20(1)
C(17)	191(2)	3184(2)	10032(2)	16(1)
C(18)	-1394(2)	1923(2)	8894(2)	20(1)
C(19)	3626(2)	4623(2)	7395(2)	12(1)
C(20)	3963(2)	5673(2)	6427(2)	14(1)
C(21)	4180(2)	6754(2)	6695(2)	16(1)
C(22)	4111(2)	6816(2)	7928(2)	15(1)
C(23)	3827(2)	5749(2)	8890(2)	15(1)
C(24)	3585(2)	4674(2)	8631(2)	14(1)
C(25)	4309(2)	8007(2)	8211(2)	22(1)
C(26)	5072(3)	2136(2)	7254(2)	14(1)
I(1)	5682(3)	1962(2)	6990(2)	15(1)

## X-ray crystallographic data of [(dpph)Pd<sup>IV</sup>(4-MeC<sub>6</sub>H<sub>4</sub>)(CF<sub>3</sub>)(NPhth)] (22)

### Structure Determination.

Colorless needles of **am3201** were grown from a chloroform solution at 23 deg. C. A crystal of dimensions 0.14 x 0.12 x 0.08 mm was mounted on a Rigaku AFC10K Saturn 944+ CCD-based X-ray diffractometer equipped with a low temperature device and Micromax-007HF Cu-target micro-focus rotating anode ( $\lambda = 1.54187 \text{ \AA}$ ) operated at 0.3 kW power (30 kV, 10 mA). The X-ray intensities were measured at 85(1) K with the detector placed at a distance 42.00 mm from the crystal. A total of 1239 images were collected with an oscillation width of 1.5° in  $\omega$ . The exposure time was 15 sec. per image for low angle and 35 seconds for high angle images. The integration of the data yielded a total of 53247 reflections to a maximum 2θ value of 136.48° of which 7380 were independent and 6784 were greater than 2σ(I). The final cell constants (Table 1) were based on the xyz centroids of 41264 reflections above 10σ(I). Analysis of the data showed negligible decay during data collection; the data were processed with CrystalClear 2.0 and corrected for absorption. The structure was solved and refined with the Bruker SHELXTL (version 2008/4) software package, using the space group P2(1)/n with Z = 4 for the formula C<sub>34</sub>H<sub>26</sub>F<sub>3</sub>N<sub>3</sub>O<sub>2</sub>Pd, 3(CHCl<sub>3</sub>). All non-hydrogen atoms were refined anisotropically with the hydrogen atoms placed in idealized positions. The dichloromethane solvate molecules are disordered and were modeled as diffuse scattering by use of the SQUEEZE subroutine of the PLATON program suite. Full matrix least-squares refinement based on F<sup>2</sup> converged at R1 = 0.0504 and wR2 = 0.1316 [based on I > 2sigma(I)], R1 = 0.0556 and wR2 = 0.1331 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. 2008/4; Bruker Analytical X-ray, Madison, WI, 2008.

CrystalClear Expert 2.0 r5, Rigaku Americas and Rigaku Corporation (2010), Rigaku Americas, 9009, TX, USA 77381-5209, Rigaku Tokyo, 196-8666, Japan.

A.L. Spek. (2008) PLATON, v. 180108, A Multi-purpose Crystallographic Tool, Utrecht University, Utrecht, The Netherlands.

Table 5. Crystal data and structure refinement for am3201.

Identification code	am3201
Empirical formula	C37 H29 Cl9 F3 N3 O2 Pd
Formula weight	1030.08
Temperature	85(2) K
Wavelength	1.54178 Å
Crystal system, space group	Monoclinic, P 1 21/n 1
Unit cell dimensions	a = 9.8196(2) Å alpha = 90 deg. b = 19.3578(4) Å beta = 98.596(7) deg.
	c = 21.4850(15) Å gamma = 90 deg.
Volume	4038.1(3) Å^3
Z, Calculated density	4, 1.694 Mg/m^3
Absorption coefficient	9.641 mm^-1
F(000)	2056
Crystal size	0.14 x 0.12 x 0.08 mm
Theta range for data collection	3.09 to 68.24 deg.
Limiting indices	-11<=h<=11, -23<=k<=22, -25<=l<=25
Reflections collected / unique	53247 / 7380 [R(int) = 0.0644]
Completeness to theta = 68.24	99.8 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.726 and 0.423
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	7380 / 0 / 391
Goodness-of-fit on F^2	1.097
Final R indices [I>2sigma(I)]	R1 = 0.0524, wR2 = 0.1316
R indices (all data)	R1 = 0.0556, wR2 = 0.1331
Largest diff. peak and hole	0.850 and -1.138 e.Å^-3

Table 6. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic displacement parameters ( $\text{\AA}^2 \times 10^3$ ) for am3201.  
 U(eq) is defined as one third of the trace of the orthogonalized  $U_{ij}$  tensor.

	x	y	z	U(eq)
Pd(1)	5488(1)	1266(1)	1998(1)	16(1)
F(1)	3657(2)	2041(2)	1109(1)	34(1)
F(2)	2718(3)	1101(2)	1404(1)	33(1)
F(3)	2874(3)	2003(2)	1996(1)	33(1)
O(1)	6875(3)	-184(2)	1484(2)	34(1)
O(2)	2914(4)	18(2)	2364(2)	43(1)
N(1)	7505(3)	959(2)	2347(2)	17(1)
N(2)	6042(3)	1181(2)	1072(2)	17(1)
N(3)	4951(3)	154(2)	1931(2)	22(1)
C(1)	7724(4)	491(2)	2812(2)	22(1)
C(2)	9024(4)	248(2)	3044(2)	25(1)
C(3)	10112(5)	482(3)	2748(2)	35(1)
C(4)	9893(4)	955(2)	2280(2)	28(1)
C(5)	8571(4)	1201(2)	2066(2)	20(1)
C(6)	8224(4)	1730(2)	1544(2)	17(1)
C(7)	7305(4)	1407(2)	976(2)	21(1)
C(8)	7706(5)	1349(2)	389(2)	30(1)
C(9)	6781(5)	1072(2)	-119(2)	28(1)
C(10)	5505(5)	848(2)	-12(2)	30(1)
C(11)	5179(5)	907(2)	588(2)	26(1)
C(12)	9585(4)	1989(2)	1336(2)	26(1)
C(13)	7452(4)	2345(2)	1797(2)	19(1)
C(14)	8009(5)	3005(2)	1820(2)	31(1)
C(15)	7340(5)	3557(2)	2072(3)	36(1)
C(16)	6131(6)	3457(2)	2283(3)	37(1)
C(17)	5544(5)	2797(2)	2259(2)	31(1)
C(18)	6220(4)	2250(2)	2027(2)	22(1)
C(19)	5115(5)	1427(2)	2915(2)	24(1)
C(20)	6158(6)	1682(3)	3353(2)	40(1)
C(21)	5928(7)	1784(3)	3982(3)	50(2)
C(22)	4667(8)	1655(3)	4156(3)	59(2)
C(23)	3577(8)	1389(3)	3704(3)	54(2)
C(24)	3844(6)	1277(3)	3093(2)	38(1)
C(25)	4351(11)	1798(4)	4817(4)	86(3)
C(26)	5797(4)	-308(2)	1684(2)	22(1)
C(27)	5238(5)	-1019(2)	1704(2)	31(1)
C(28)	5672(6)	-1660(3)	1513(2)	43(1)
C(29)	4883(7)	-2236(3)	1612(3)	51(2)
C(30)	3705(8)	-2169(4)	1890(3)	60(2)
C(31)	3244(7)	-1539(3)	2084(3)	50(2)
C(32)	4031(5)	-975(3)	1974(2)	34(1)
C(33)	3883(5)	-203(3)	2128(2)	28(1)
C(34)	3601(4)	1627(2)	1614(2)	25(1)