Electronic Supplementary Information (ESI)

Palladium(II) complexes with pentafluorophenyl ligands: Structures, C_6F_5 fluxionality by 2D NMR studies and pre-catalysts for the vinyl addition polymerization of norbornene

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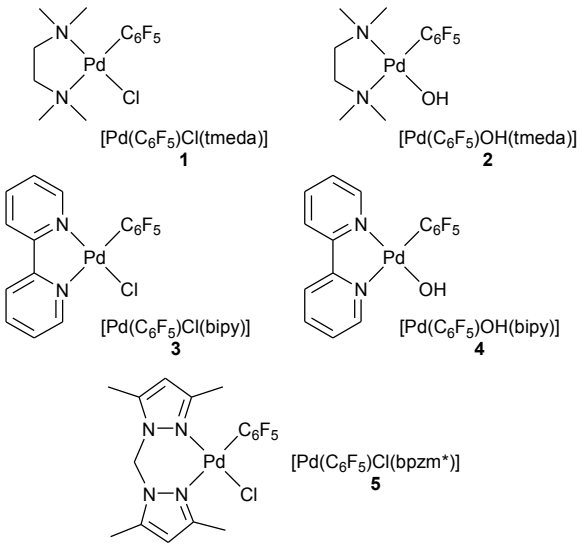
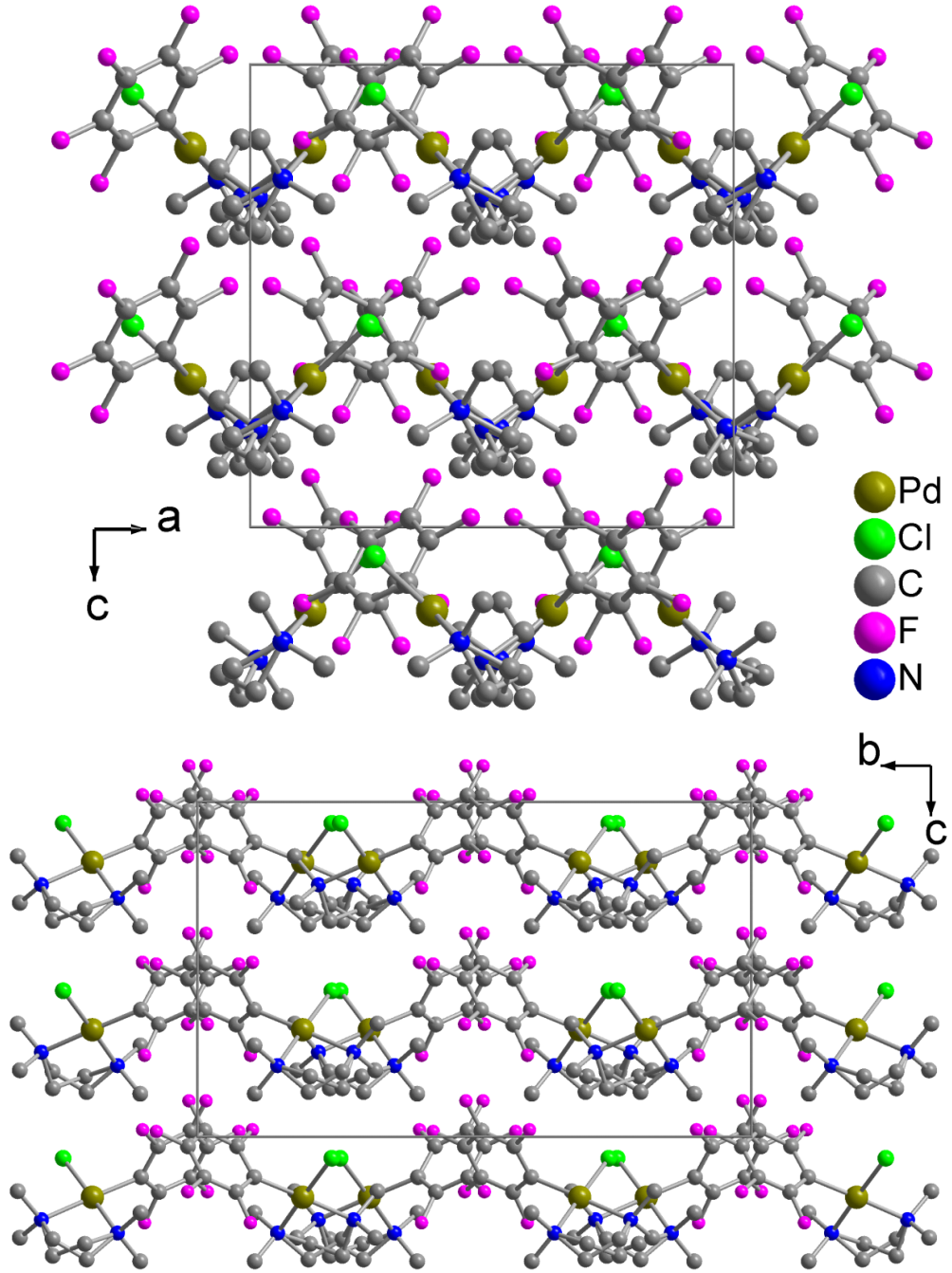


Scheme Palladium(II)-C_6F_5 complexes with their structural formula and number.

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==========================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
==========================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------

 1       1 C(7)  --H(7A)  ..F(5)   [  8565.01]       0.98       2.54   3.248(5)        129
 2       1 C(8)  --H(8B)  ..Cl     [  3655.01]       0.98       2.80   3.749(6)        164
 3       1 C(8)  --H(8C)  ..F(2)   [  5545.01]       0.98       2.55   3.458(5)        155
 4       1*C(9A) --H(9A)  ..F(1)   [  6765.01]       0.99       2.52   3.467(9)        159

:: No Classic Hydrogen Bonds Found

Translation of ARU-code to Equivalent Position Code
==================================================
   [  3655. ]  = 3/2-x,y,1/2+z
   [  8565. ]  = 1/2+x,3/2-y,z
   [  6765. ]  = 2-x,3/2-y,1/2+z
   [  5545. ]  = x,-1/2+y,1/2+z
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Figure S1 Packing diagram of **1** projected onto the *ac* and *bc* plane to show the identical molecule orientation along the *c* direction (H atoms not shown) and C-H...X analysis.

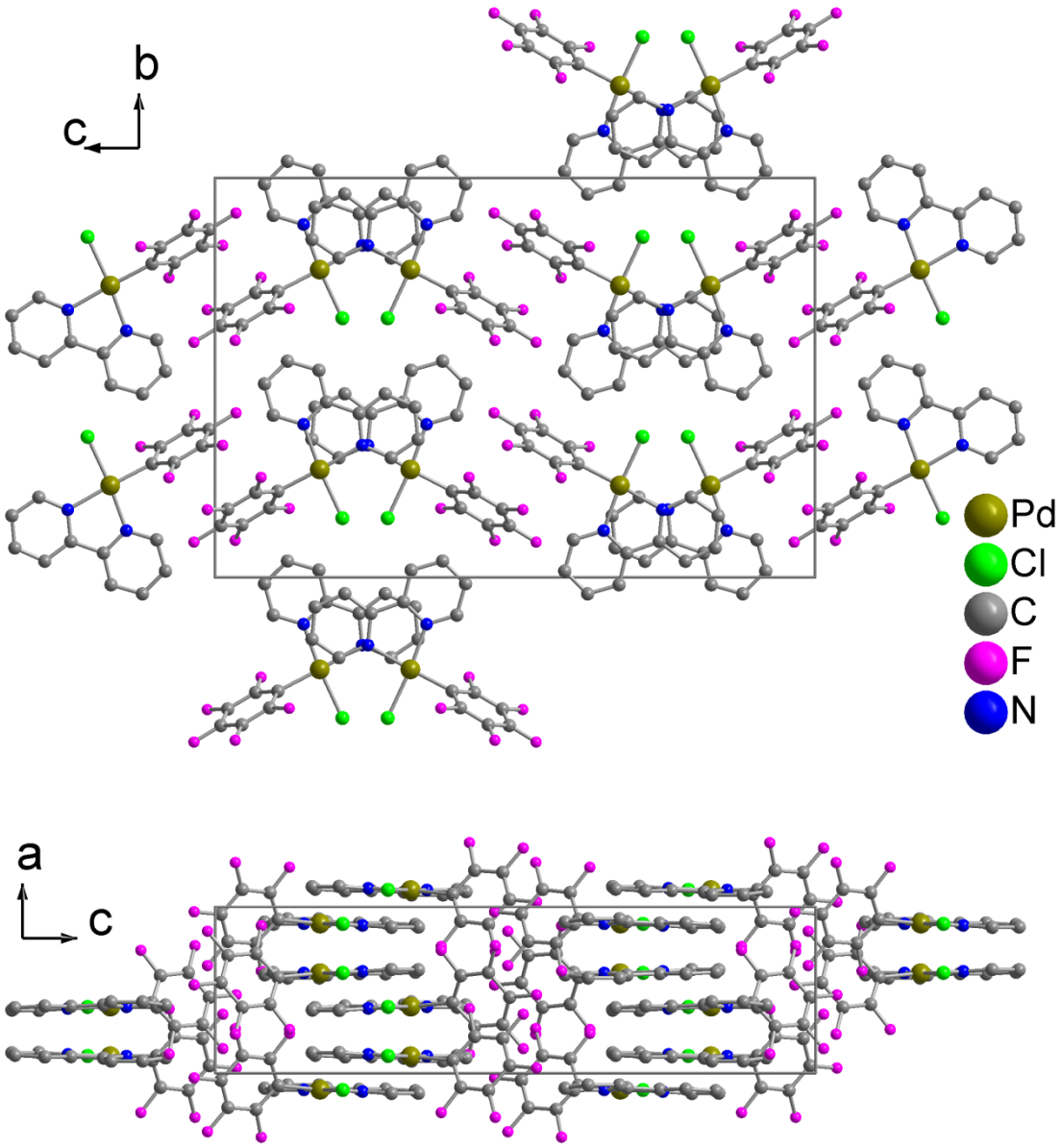

Figure S2 Packing diagrams of **3** (H atoms not shown).

Analysis of π-stacking interactions in **3** (highlighted in yellow):

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================================================================================================================================
Analysis of Short Ring-Interactions with Cg-Cg Distances <   6.0 Angstrom and Beta < 60.0 Deg.
================================================================================================================================
- Cg(I)     = Plane number I (= ring number in () above)
- Alpha     = Dihedral Angle between Planes I and J (Deg)
- Beta      = Angle Cg(I)-->Cg(J) or Cg(I)-->Me vector and normal to plane I (Deg)
- Gamma     = Angle Cg(I)-->Cg(J) vector and normal to plane J (Deg)
- Cg-Cg     = Distance between ring Centroids (Ang.)
- CgI_Perp  = Perpendicular distance of Cg(I) on ring J (Ang.)
- CgJ_Perp  = Perpendicular distance of Cg(J) on ring I (Ang.)
- Slippage  = Distance between Cg(I) and Perpendicular Projection of Cg(J) on Ring I (Ang).
- P,Q,R,S   = J-Plane Parameters for Carth. Coord. (Xo, Yo, Zo)

Cg(I) Res(I)    Cg(J)   [   ARU(J)]       Cg-Cg Transformed J-Plane P, Q, R, S     Alpha  Beta Gamma    CgI_Perp    CgJ_Perp  Slippage

Cg(1)  [ 1] -> Cg(1)  [  6455.01]  4.3839(11)  0.9993-0.0302 0.0218   0.8056         2 35.41 37.91   3.4588(7)  -3.5728(7)
Cg(1)  [ 1] -> Cg(1)  [  6555.01]  4.3838(11)  0.9993-0.0302 0.0218   7.8371         2 37.91 35.41  -3.5727(7)   3.4587(7)
Cg(1)  [ 1] -> Cg(2)  [  6455.01]  3.4734(11)  0.9973-0.0656 0.0334   0.8141   3.76(9)  6.43 10.05   3.4200(7)  -3.4514(8)
Cg(1)  [ 1] -> Cg(2)  [  6555.01]  3.6027(11)  0.9973-0.0656 0.0334   7.8315   3.76(9)  6.43  3.13  -3.5973(7)   3.5801(8)
Cg(1)  [ 1] -> Cg(3)  [  6455.01]  5.8009(12)  0.9958-0.0859-0.0301   0.2844   3.24(9) 51.09 51.94   3.5765(7)  -3.6437(8)
Cg(1)  [ 1] -> Cg(3)  [  6555.01]  5.6979(12)  0.9958-0.0859-0.0301   7.2916   3.24(9) 53.52 52.98  -3.4307(7)   3.3878(8)
Cg(2)  [ 1] -> Cg(1)  [  6455.01]  3.6027(11)  0.9993-0.0302 0.0218   0.8056   3.76(9)  3.13  6.43   3.5801(8)  -3.5973(7)
Cg(2)  [ 1] -> Cg(1)  [  6555.01]  3.4733(11)  0.9993-0.0302 0.0218   7.8371   3.76(9) 10.05  6.43  -3.4515(8)   3.4200(7)
Cg(2)  [ 1] -> Cg(2)  [  6455.01]  4.0409(12)  0.9973-0.0656 0.0334   0.8141         4 31.58 27.78   3.5750(8)  -3.4423(8)
Cg(2)  [ 1] -> Cg(2)  [  6555.01]  4.0409(12)  0.9973-0.0656 0.0334   7.8315         4 27.78 31.58  -3.4424(8)   3.5750(8)
Cg(2)  [ 1] -> Cg(3)  [  6455.01]  4.3867(12)  0.9958-0.0859-0.0301   0.2844  1.18(10) 34.16 35.09   3.5893(8)  -3.6297(8)
Cg(2)  [ 1] -> Cg(3)  [  6555.01]  4.1406(12)  0.9958-0.0859-0.0301   7.2916  1.18(10) 35.10 34.37  -3.4179(8)   3.3876(8)
Cg(3)  [ 1] -> Cg(1)  [  6455.01]  5.6978(12)  0.9993-0.0302 0.0218   0.8056   3.24(9) 52.98 53.52   3.3878(8)  -3.4308(7)
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Cg(3)  [ 1] -> Cg(1)  [  6555.01]  5.8008(12)  0.9993-0.0302 0.0218   7.8371   3.24(9) 51.94 51.09  -3.6437(8)   3.5764(7)
Cg(3)  [ 1] -> Cg(2)  [  6455.01]  4.1405(12)  0.9973-0.0656 0.0334   0.8141  1.18(10) 34.37 35.10   3.3876(8)  -3.4178(8)
Cg(3)  [ 1] -> Cg(2)  [  6555.01]  4.3868(12)  0.9973-0.0656 0.0334   7.8315  1.18(10) 35.09 34.16  -3.6298(8)   3.5894(8)
Cg(3)  [ 1] -> Cg(4)  [  7645.01]  4.7760(12) -0.3705 0.8103 0.4540  -4.1656 64.86(10) 55.37  9.51   4.7103(9)   2.7144(9)
Cg(4)  [ 1] -> Cg(3)  [  1555.01]  5.3013(13)  0.9958-0.0859 0.0301   4.1715 71.76(10) 55.49 82.56  -0.6861(9)  -3.0034(9)
Cg(4)  [ 1] -> Cg(3)  [  7655.01]  4.7759(12) -0.9958-0.0859 0.0301  -7.0677 64.86(10)  9.51 55.37   2.7143(9)   4.7103(9)
Cg(4)  [ 1] -> Cg(4)  [  3455.01]  5.2574(13)  0.3705-0.8103-0.4540  -1.5586        43 25.42 65.96  -2.1416(9)  -4.7485(9)
                                   ----------                                                      ----------------------------------------------
                             Min or Max  3.473                                    1.18  3.13 82.56      -3.644      -4.748

[  6455] = -1/2+X,Y,1/2-Z
[  6555] = 1/2+X,Y,1/2-Z
[  7645] = 3/2-X,-1/2+Y,Z
[  1555] = X,Y,Z
[  7655] = 3/2-X,1/2+Y,Z
[  3455] = -1/2+X,1/2-Y,-Z
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Ring systems in **3**:

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Nr  1        P             Q             R             S     Sigref  0.002     Sigpln  0.053     Chisq    1968.4    Pl.Hyp.    P<5
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Ring     0.9993(1)    -0.0302(6)    -0.0218(7)      4.044(4) #Pd     -0.035(1) #N(1)    0.035(1) #N(2)    0.045(1) #C(11)  -0.014(2)
A  5     7.0315(2)    -0.511(10)    -0.555(19)      4.044(4) #C(16)  -0.031(2)  Cl     -0.105(1)  F(3)   -0.510(1)  C(1)   -0.200(2)
                                                            C(2)   -1.351(2)  C(3)   -1.477(2)  C(4)   -0.412(2)  C(5)    0.751(2)
                                                            C(6)    0.831(2)  C(7)    0.071(2)  C(8)    0.058(2)  C(9)   -0.001(2)
                                                            C(10)  -0.024(2)  C(12)   0.103(2)  C(13)   0.060(2)  C(14)  -0.067(2)
                                                            C(15)  -0.108(2)
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Nr  2        P             Q             R             S     Sigref  0.002     Sigpln  0.005     Chisq      17.9    Pl.Hyp.    P<5
-------------------------------------------------------------------------------------------------------------------------------------------
Ring     0.9973(1)    -0.0656(9)    -0.0334(8)      3.898(7) #N(1)   -0.002(1) #C(7)    0.001(2) #C(8)    0.003(2) #C(9)   -0.006(2)
A  6     7.0173(5)    -1.112(15)      -0.85(2)      3.898(7) #C(10)   0.005(2) #C(11)  -0.001(2)  Pd     -0.087(1)  Cl     -0.242(1)
                                                            F(3)   -0.609(1)  N(2)    0.068(1)  C(1)   -0.264(2)  C(2)   -1.434(2)
                                                            C(4)   -0.499(2)  C(5)    0.683(2)  C(6)    0.774(2)  C(12)   0.155(2)
                                                            C(13)   0.164(2)  C(14)   0.060(2)  C(15)  -0.010(2)  C(16)   0.015(2)
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Nr  4        P             Q             R             S     Sigref  0.002     Sigpln  0.006     Chisq      27.6    Pl.Hyp.    P<5
-------------------------------------------------------------------------------------------------------------------------------------------
Ring     0.3705(9)     0.8103(5)     0.4540(8)      6.617(2) #C(1)    0.006(2) #C(2)   -0.002(2) #C(3)   -0.004(2) #C(4)    0.007(2)
A  6      2.607(6)     13.743(9)      11.56(2)      6.617(2) #C(5)   -0.003(2) #C(6)   -0.003(2)  Pd     0.130(1)  F(1)   -0.005(1)
                                                            F(2)   -0.021(2)  F(3)    0.018(1)  F(4)    0.005(2)  F(5)    0.011(1)
                                                            N(1)    0.141(2)  C(7)    1.158(2)  C(8)    1.039(2)  C(9)   -0.165(2)
                                                            C(10)  -1.222(2)  C(11)  -1.044(2)
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C-H...X analysis in **3**:

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===========================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
===========================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
===========================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
-------------------------------------------------------------------------------------------------------------------------------------------

 1 Intra 1 C(7)  --H(7)   ..Cl     [         ]       0.95       2.70   3.295(2)        121
 2       1 C(7)  --H(7)   ..F(1)   [  6555.01]       0.95       2.52   3.166(3)        125'       112'              358.00
 3       1 C(8)  --H(8)   ..F(5)   [  6455.01]       0.95       2.47   3.164(3)        130
 4       1 C(10) --H(10)  ..Cl     [  4645.01]       0.95       2.64   3.499(2)        150
 5       1 C(12) --H(12)  ..F(4)   [  3455.01]       0.95       2.43   3.058(3)        123

:: No Classic Hydrogen Bonds Found


Translation of ARU-code to Equivalent Position Code
===================================================
   [  6455. ]  = -1/2+x,y,1/2-z
   [  6555. ]  = 1/2+x,y,1/2-z
   [  3455. ]  = -1/2+x,1/2-y,-z
   [  4645. ]  = 1-x,-1/2+y,1/2-z
```

C-F...ring analysis in **3**:

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===========================================================================================================================================

Analysis of Y-X...Cg(Pi-Ring) Interactions (X..Cg < 4.0 Ang. - Gamma <  30.0 Deg)
===========================================================================================================================================

   Y--X(I)    Res(I)   Cg(J)  [   ARU(J)]       X..Cg  Transformed J-Plane P, Q, R, S  X-Perp Gamma      Y-X..Cg        Y..Cg Y-X,Pi

C(5)   -F(4)   [ 1] -> Cg(4)  [  3555.01]  3.2485(17)   0.3705-0.8103-0.4540   1.0483 -3.219   7.72   123.10(13)     4.140(2)  34.07
                                          ----------                                  ----------------------------------------------
                                    Min or Max  3.249                                  -3.219   7.72       123.10        4.140  34.07

[  3555] = 1/2+X,1/2-Y,-Z
```

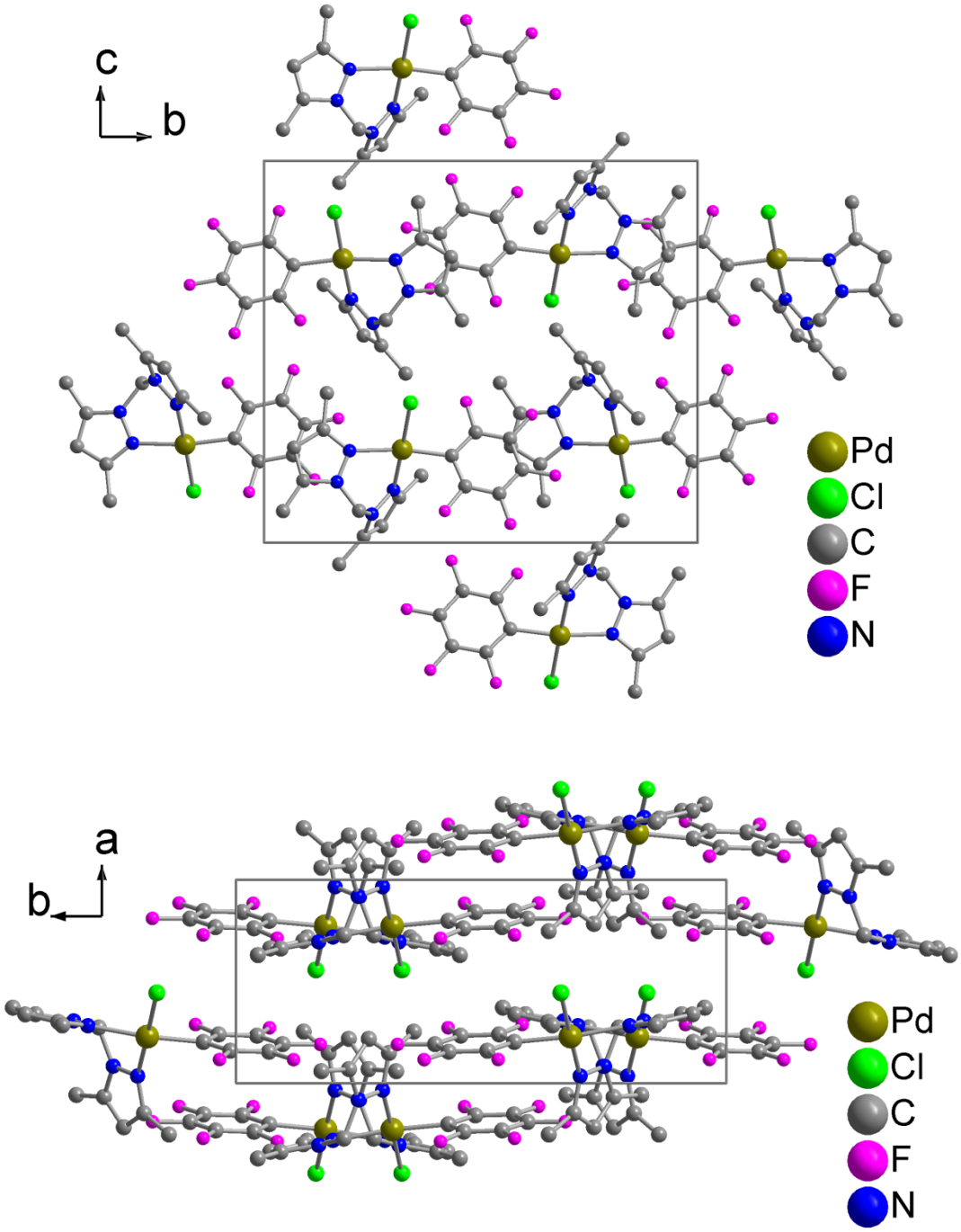

Figure S3 Packing diagrams of **5** (H atoms not shown).

C-H...X analysis in **5**:

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==========================================================================================================================================
Analysis of Potential Hydrogen Bonds and Schemes with d(D...A) < R(D)+R(A)+0.50, d(H...A) < R(H)+R(A)-0.12 Ang., D-H...A > 100.0 Deg
==========================================================================================================================================
Note: - ARU codes in [] are with reference to the Coordinates printed above (Possibly transformed, when MOVE .NE. 1.555)
==========================================================================================================================================

Nr Typ Res Donor --- H....Acceptor [    ARU  ]      D - H      H...A      D...A  D - H...A    A..H..A* A'..H..A" Sum(XY,YZ)  Sum(XZ)
------------------------------------------------------------------------------------------------------------------------------------------

 1 Intra 1 C(10) --H(10A) ..Cl     [         ]       0.98       2.83   3.550(3)        131
 2       1 C(17) --H(17A) ..F(1)   [  4554.01]       0.98       2.42   2.988(3)        117
 3       1 C(17) --H(17B) ..F(3)   [  3565.01]       0.98       2.48   3.295(3)        140

:: No Classic Hydrogen Bonds Found

Translation of ARU-code to Equivalent Position Code
==================================================
   [  3565. ]  = -x,1-y,-z
   [  4554. ]  = x,1/2-y,-1/2+z
```

C-F...ring analysis in **5**:

Analysis of Y-X...Cg(Pi-Ring) Interactions (X..Cg < 4.0 Ang. - Gamma < 30.0 Deg)

Y--X(I)	Res(I)	Cg(J)	[ARU(J)]	X..Cg	Transformed J-Plane P, Q, R, S	X-Perp	Gamma	Y-X..Cg	Y..Cg	Y-X,Pi
C(3) -F(2)	[1] ->	Cg(1)	[2555.01]	3.094(2)	-0.9685 0.1775-0.1748 3.8517	-3.067	7.63	98.26(16)	3.547(3)	15.86
C(3) -F(2)	[1] ->	Cg(2)	[2555.01]	3.0268(19)	-0.2679 0.7767 0.5701 14.0499	-2.970	11.12	157.97(16)	4.305(3)	78.77
C(4) -F(3)	[1] ->	Cg(1)	[2655.01]	3.785(2)	-0.9685 0.1775-0.1748 -3.0884	3.663	14.59	76.40(15)	3.706(3)	11.07
			Min or Max	3.027		-3.067	7.63	157.97	3.547	78.77

[2555] = -X,1/2+Y,1/2-Z
[2655] = 1-X,1/2+Y,1/2-Z

Ring systems in **5**:

Nr 1	P	Q	R	S	Sigref	0.003	Sigpln	0.005	Chisq	7.0	Pl.Hyp.	P<5
Ring	0.9685(4)	0.1775(14)	0.1748(14)	2.776(5)	#N(1)	0.002(2)	#N(2)	0.001(2)	#C(7)	-0.003(3)	#C(8)	0.004(3)
A 5	6.940(3)	3.06(2)	0.91(2)	2.776(5)	#C(9)	-0.004(3)	Pd	0.004(1)	F(1)	-0.215(1)	F(2)	0.211(2)
					F(3)	0.754(2)	F(4)	0.890(2)	F(5)	0.569(2)	N(3)	-1.372(2)
					N(4)	-1.497(2)	C(1)	0.156(3)	C(2)	0.080(3)	C(3)	0.272(3)
					C(4)	0.543(3)	C(5)	0.616(3)	C(6)	0.435(3)	C(10)	-0.011(3)
					C(11)	0.005(4)	C(12)	-0.133(3)				

Nr 2	P	Q	R	S	Sigref	0.002	Sigpln	0.009	Chisq	27.6	Pl.Hyp.	P<5
Ring	0.2679(13)	0.7767(8)	-0.5701(10)	2.807(5)	#N(3)	0.006(2)	#N(4)	-0.002(2)	#C(13)	-0.004(3)	#C(14)	0.007(3)
A 5	1.919(9)	13.378(14)	-9.107(16)	2.807(5)	#C(15)	-0.008(2)	Pd	-0.330(1)	Cl	-0.768(1)	F(1)	0.289(2)
					N(1)	-1.415(2)	C(1)	1.303(3)	C(2)	1.399(3)	C(12)	-0.104(3)
					C(16)	-0.038(3)	C(17)	-0.075(3)				

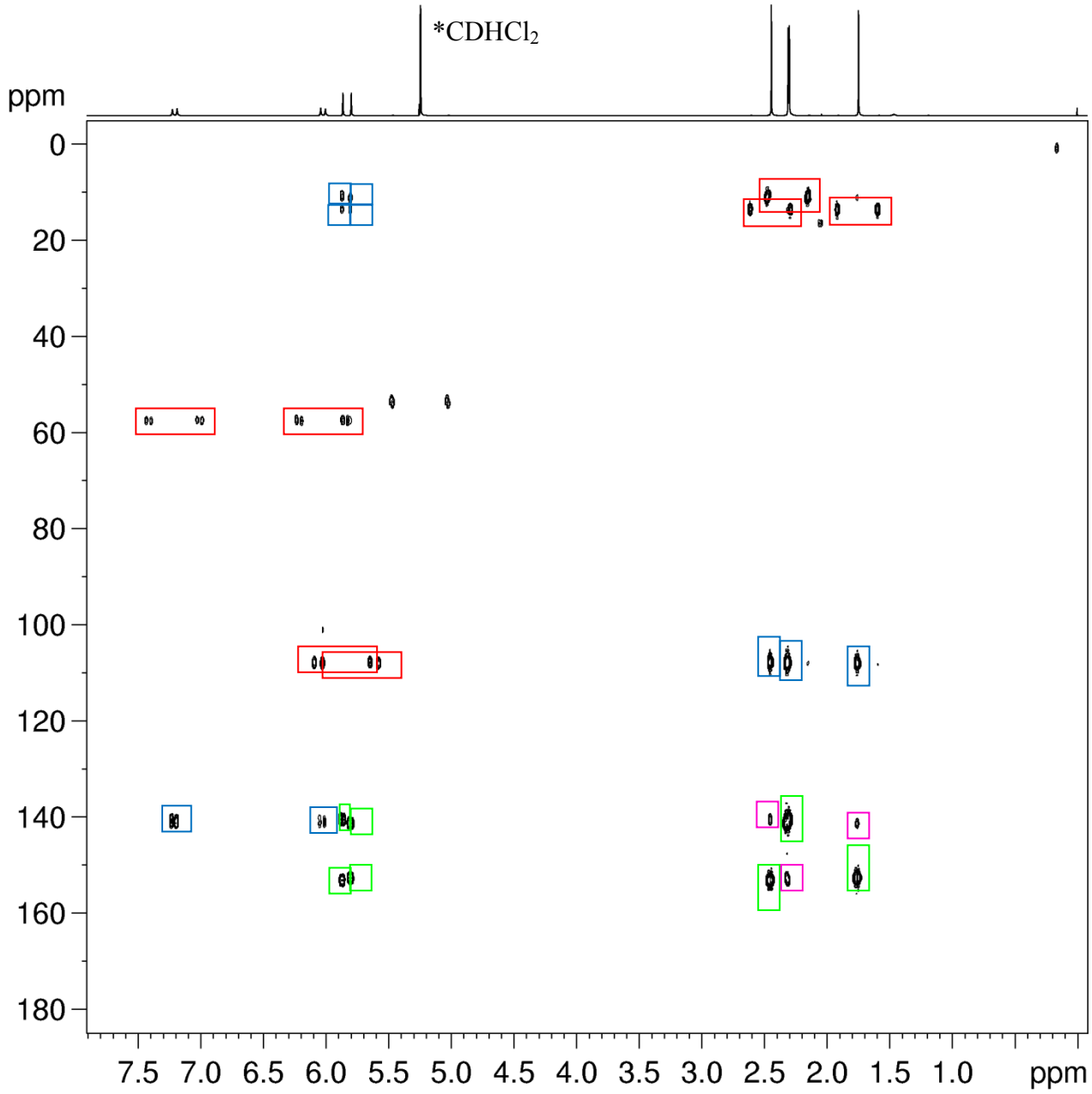

Figure S4 $^{13}C,^{1}H$-HMBC spectrum of complex **5** in CD_2Cl_2 (0.03 mol·l^{-1}) at room temperature.
The crosspeaks represent the coupling constants
$^{1}J(^{1}H,^{13}C)$ in red rectangles,
$^{2}J(^{1}H,^{13}C)$ in green rectangles,
$^{3}J(^{1}H,^{13}C)$ in blue rectangles and
$^{4}J(^{1}H,^{13}C)$ in violet rectangles.
Due to low sample concentration a good quality ^{13}C NMR spectrum could not be measured separately.

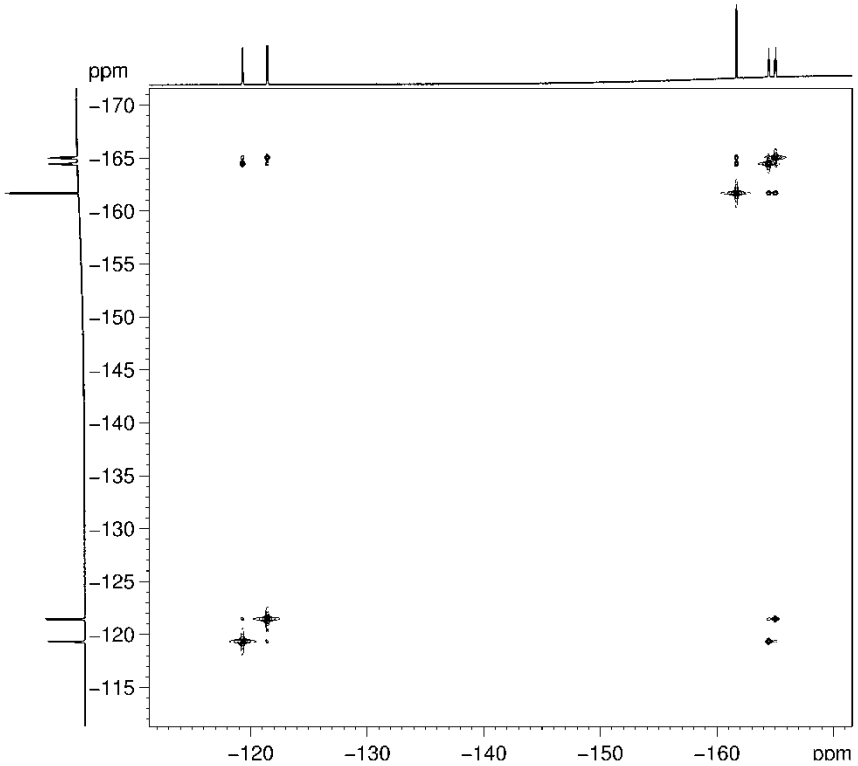

Figure S5 $^{19}F,^{19}F$-COSY spectrum of complex **5** in CD_2Cl_2 (0.03 mol·l^{-1}) at room temperature.

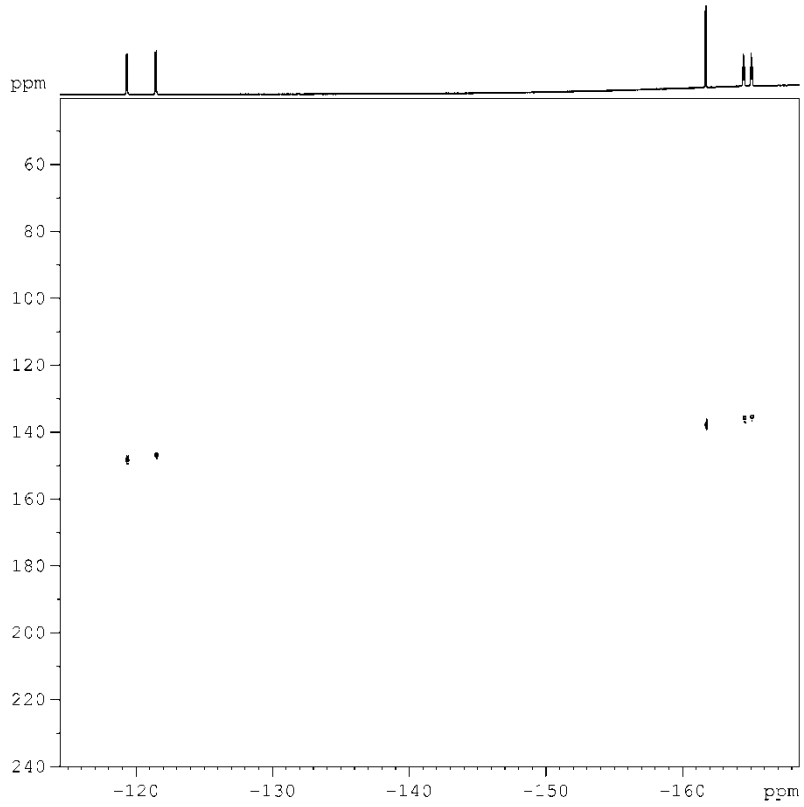

Figure S6 $^{19}F,^{13}C$-HSQC spectrum of complex **5** in CD_2Cl_2 (0.03 mol·l^{-1}) at room temperature. The Heteronuclear Single Quantum Coherence (HSQC[1]) is a 2D experiment, which correlates resonances of nuclei with the resonances of other nuclei by means of the one-bond coupling between them.

1 G. Bodenhausen and D. J. Ruben, *Chem. Phys. Lett.*, 1980, **69**, 185-189.

Table S1. $^{19}F,^{19}F$-coupling constants for the pentafluorophenyl, C_6F_5 ligand of complex **5**.

^{19}F resonance /ppm	–119.3	–121.4	–161.7	–164.5	–165.0
–119.3		^4J = 7.5 Hz	^4J = 1.2 Hz	^3J = 29.0 Hz	^5J = 8.6 Hz
–121.4	^4J = 7.5 Hz		^4J = 29.5 Hz	^5J = 9.0 Hz	^3J = 29.5 Hz
–161.7	^4J = 1.2 Hz	^4J = 1.2 Hz		^3J = 19.8 Hz	^3J = 19.7 Hz
–164.5	^3J = 29.0 Hz	^5J = 9.0 Hz	^3J = 19.8 Hz		^4J = 3.2 Hz
–165.0	^5J = 8.6 Hz	^3J = 29.5 Hz	^3J = 19.7 Hz	^4J = 3.2 Hz	

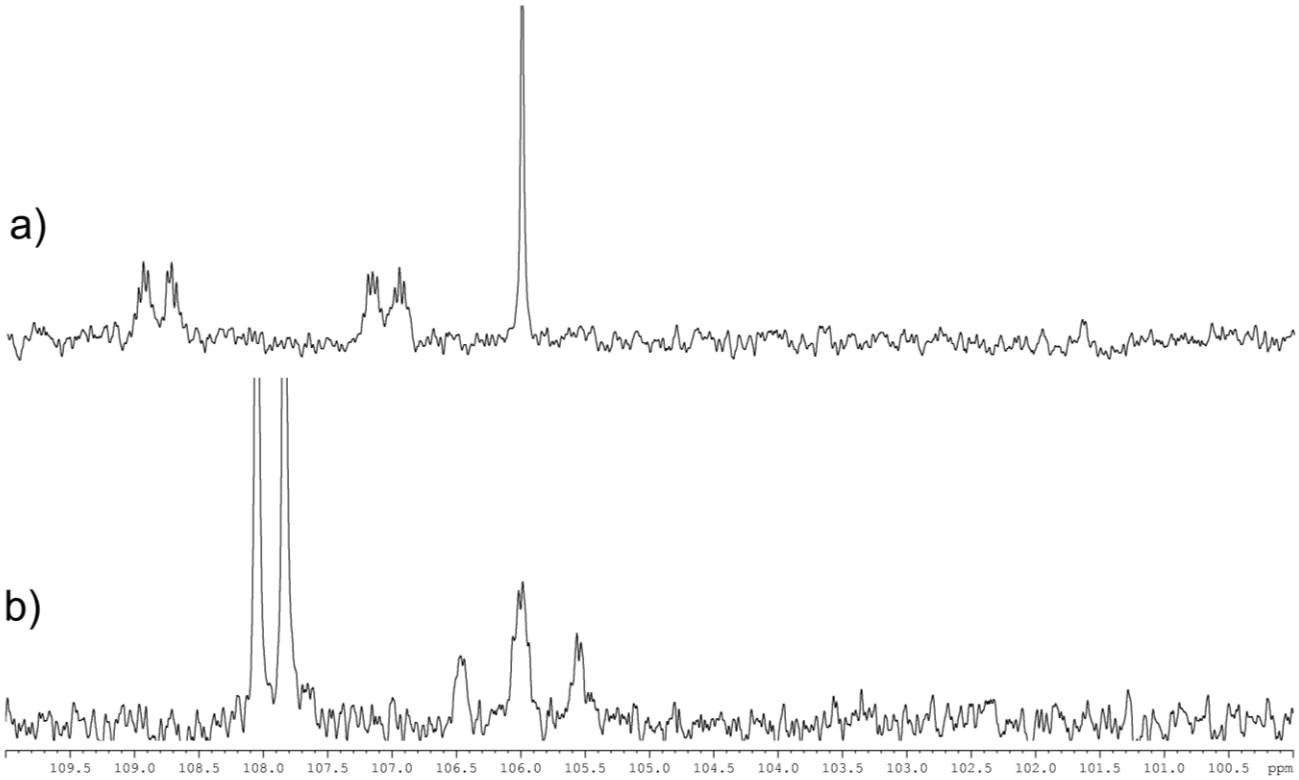

Figure S7 Section with the C_6F_5 ipso-C atom (106 ppm) and the two pyrazolyl-methine *C*H atoms (around 108 ppm, cf. Table 2 in publication) of the ^{13}C NMR spectrum of **5** (0.03 mol·l^{-1}) at room temperature;
a) ^{19}F-decoupled ^{13}C-NMR spectrum of complex **5** in CD_2Cl_2;
b) ^{1}H-decoupled ^{13}C-NMR spectrum of complex **5**.

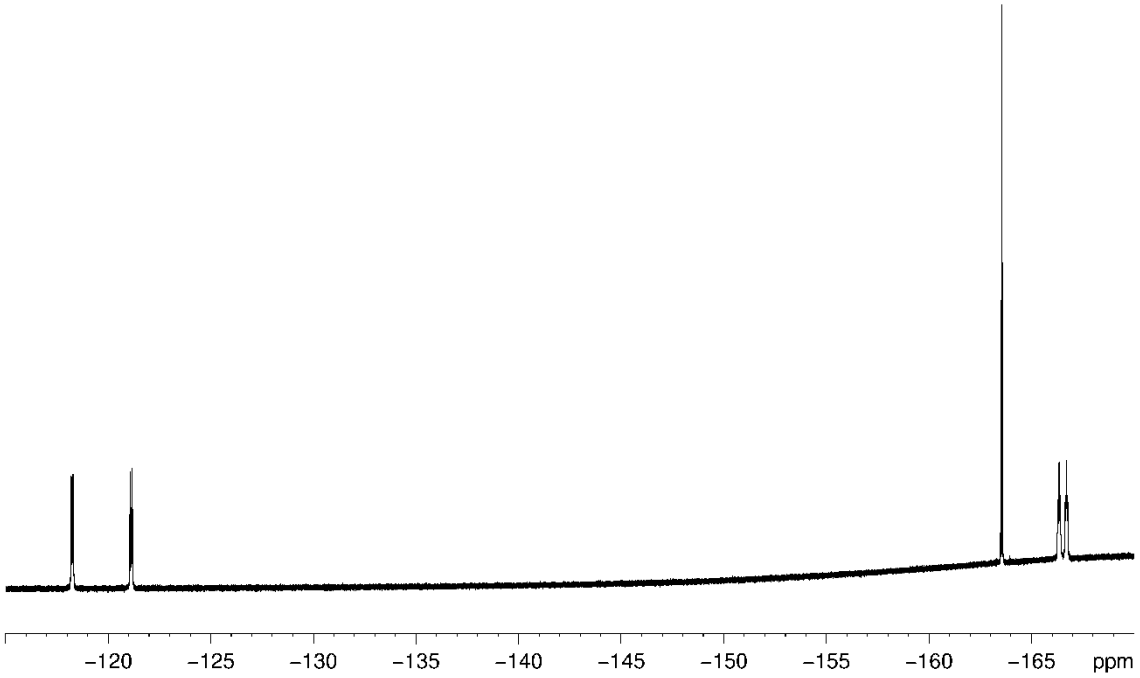

Figure S8 ^{19}F-NMR spectrum of complex **5** in acetone-d_6 (0.03 mol·l^{-1}) at room temperature.

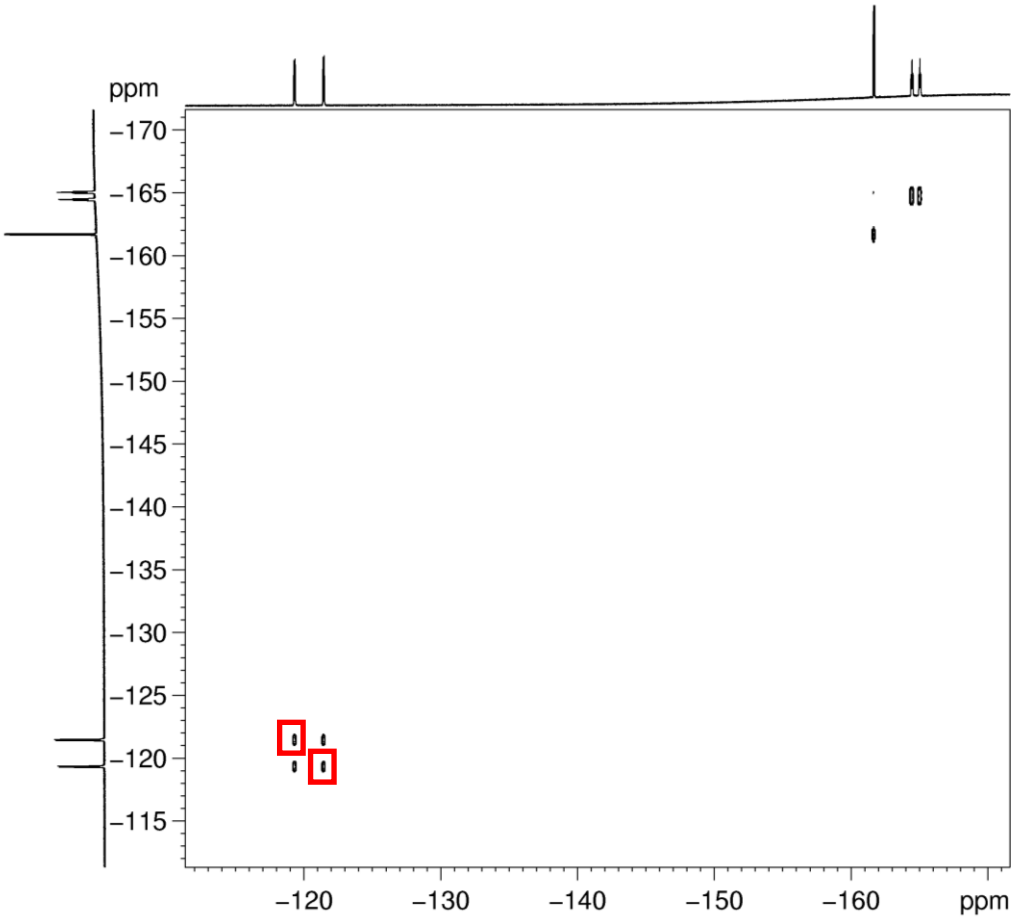

Figure S9 ^{19}F,^{19}F-EXSY spectrum of complex **5** (mixing time: 0.8 s) in CD_2Cl_2 (0.03 mol·l^{-1}) at room temperature, which displays crosspeaks between the two *ortho*-fluorine resonances and the *meta*-fluorine resonances, respectively.

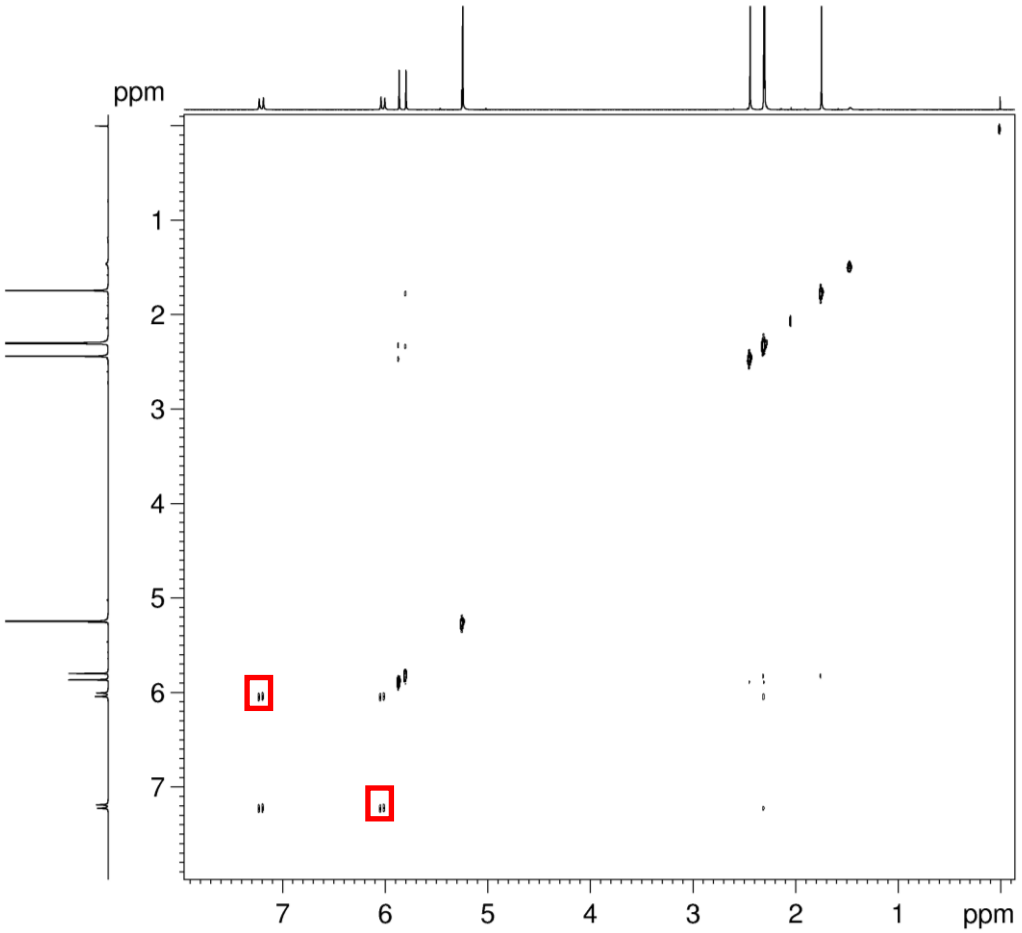

Figure S10 $^{1}H,^{1}H$-NOESY spectrum of **5** (mixing time: 1.5 s) in CD_2Cl_2 (0.03 $mol \cdot l^{-1}$) at room temperature, which displays crosspeaks between the resonances of the two methylene protons at δ = 6.02 and 7.21 ppm.

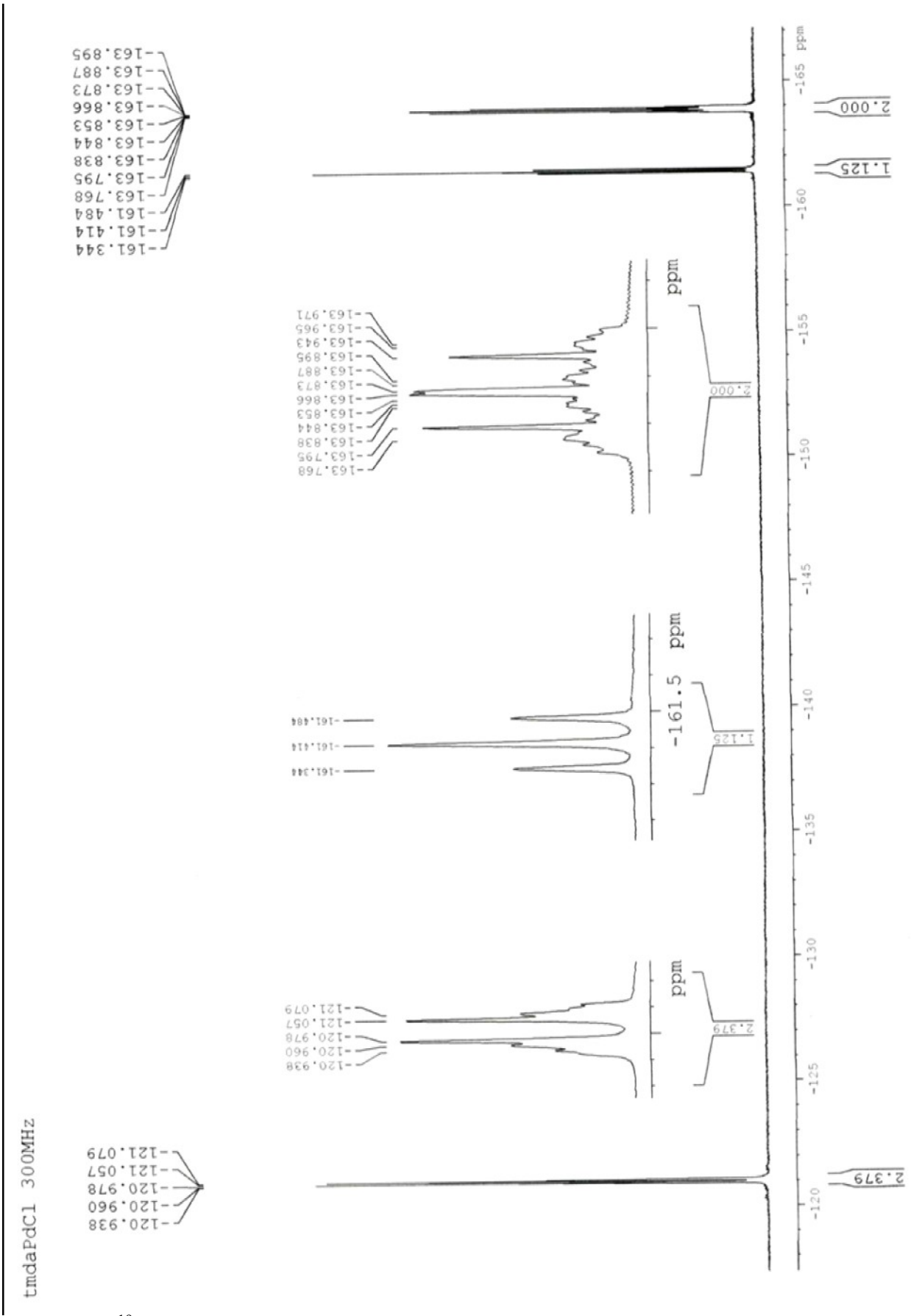

Figure S11 ^{19}F NMR of complex [Pd(C_6F_5)Cl(tmeda)], **1**; *ortho*-fluorine atoms at –121.0 ppm, *para*-fluorine atom δ = –161.4 ppm and the *meta*-fluorine atoms δ = –163.9 ppm.

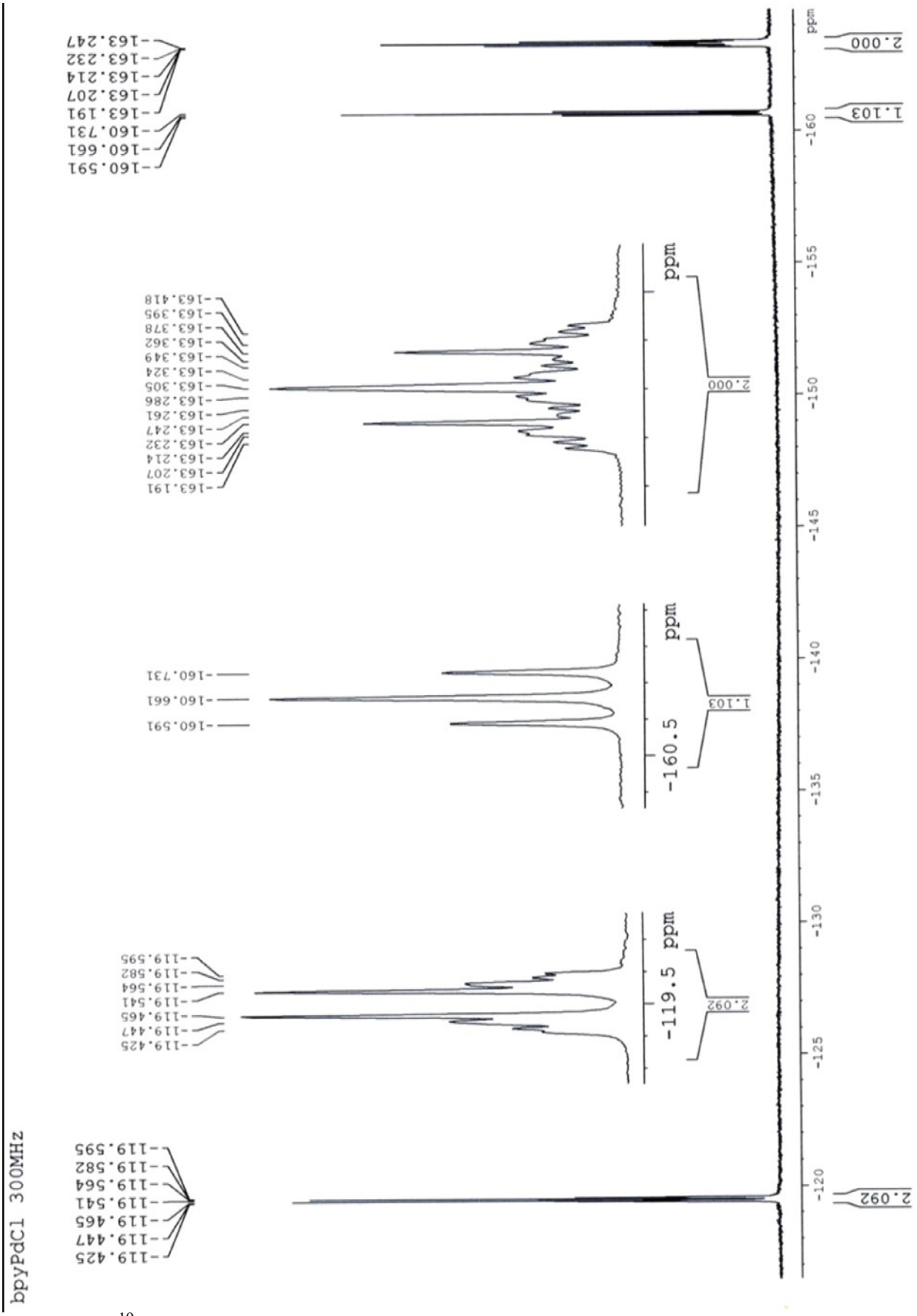

Figure S12 ^{19}F NMR of complex [Pd(C_6F_5)Cl(bipy)], **3**; *ortho*-fluorine atoms at –119.5 ppm, *para*-fluorine atom at –160.6 ppm and *meta*-fluorine atoms at δ = –163.3 ppm.

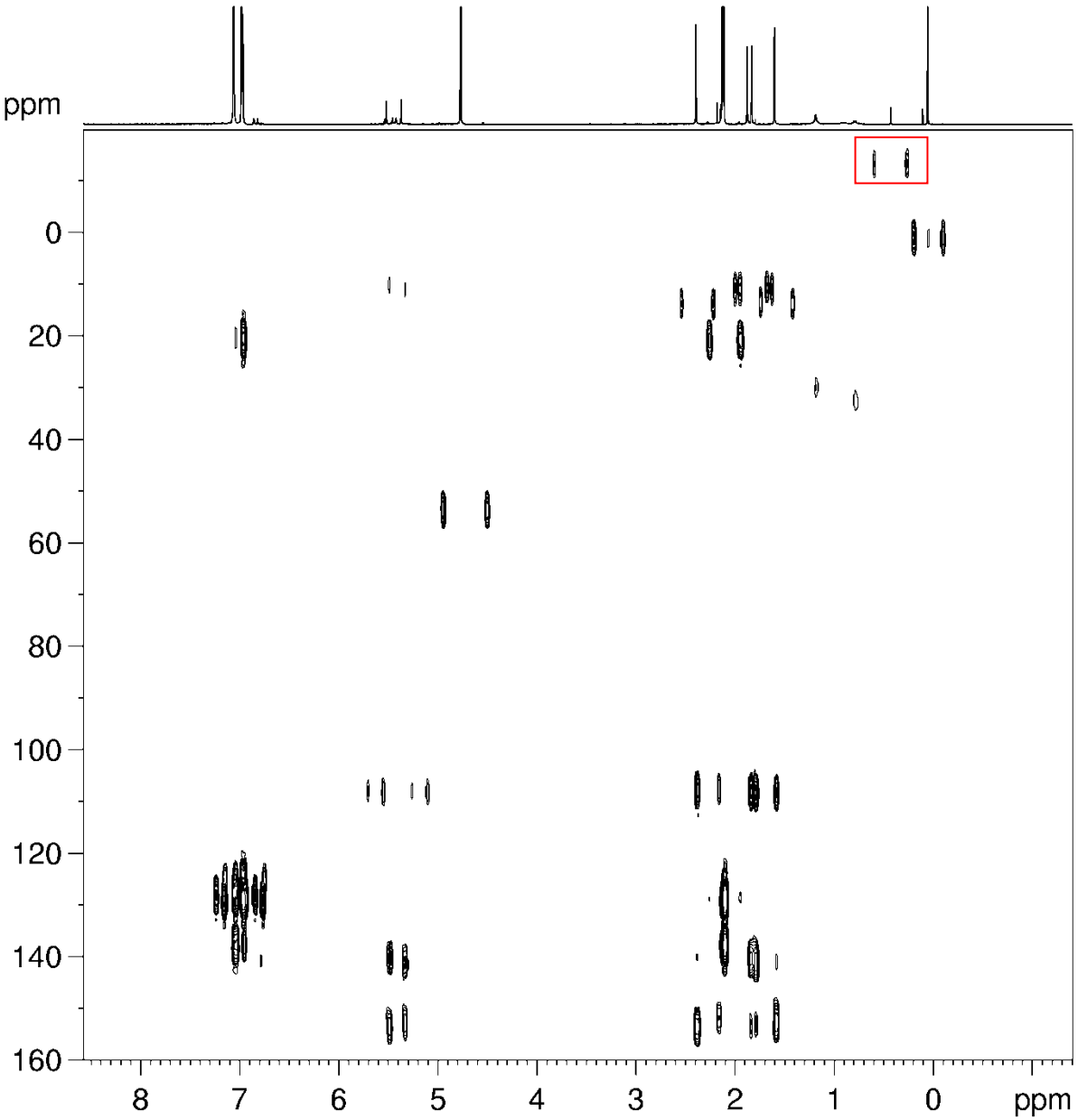

Figure S13 $^{13}C,^{1}H$-HMBC spectrum of **5**/MAO (Pd:Al = 1:10, 0.03 mol·l^{-1} in Pd, at room temperature). The crosspeaks represent the coupling constants $^{1}J(^{1}H,^{13}C)$, $^{2}J(^{1}H,^{13}C)$, $^{3}J(^{1}H,^{13}C)$ and $^{4}J(^{1}H,^{13}C)$.
The red rectangle highlights the crosspeaks from the $^{1}J(^{1}H,^{13}C)$ coupling constant for the new resonance at 0.43 ppm in the ^{1}H NMR for methylated **5**, i.e. [Pd(C_6F_5)CH_3(bpzm*)] from which the carbon resonance at –13 ppm was identified.
The spectrum was recorded in a 1:1 mixture of CD_2Cl_2 and toluene-d_8.

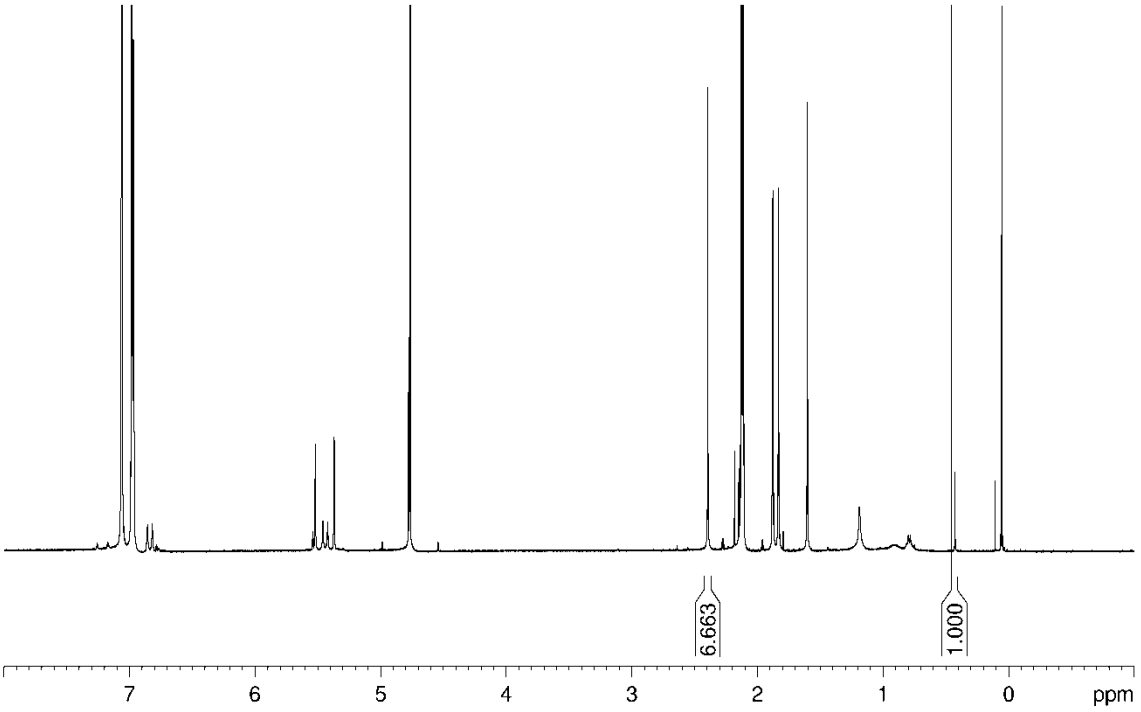

Figure S14 ^{1}H-NMR spectrum of the MAO activated complex **5** with a molecular Pd:Al ratio of 1:10 (in a 1:1 mixture of CD_2Cl_2 and toluene-d_8 as a 0.03 mol·l^{-1} solution in Pd, RT). The integral for **5** was chosen for the CH_3 group at 2.44 ppm with no underlying signal from **5**/MAO. The integrals show that only ~13% of **5** were methylated to [Pd(C_6F_5)CH_3(bpzm*)].

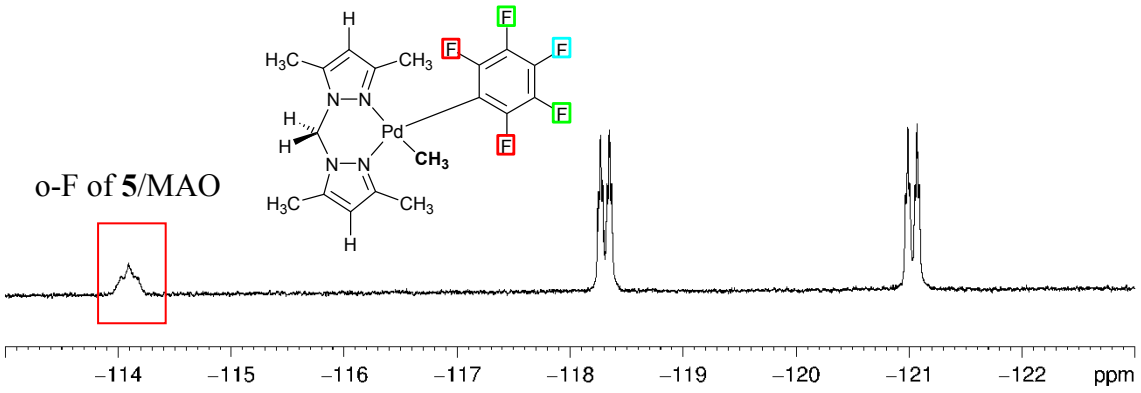

Figure S15a *o*-F region of the ^{19}F-NMR spectrum of the MAO activated complex **5** with a molecular Pd:Al ratio of 1:10, i.e., a mixture of [Pd(C_6F_5)Cl(bpzm*)] and the methyl derivative [Pd(C_6F_5)CH_3(bpzm*)] (in a 1:1 mixture of CD_2Cl_2 and toluene-d_8 as a 0.03 mol·l^{-1} solution in Pd, RT).

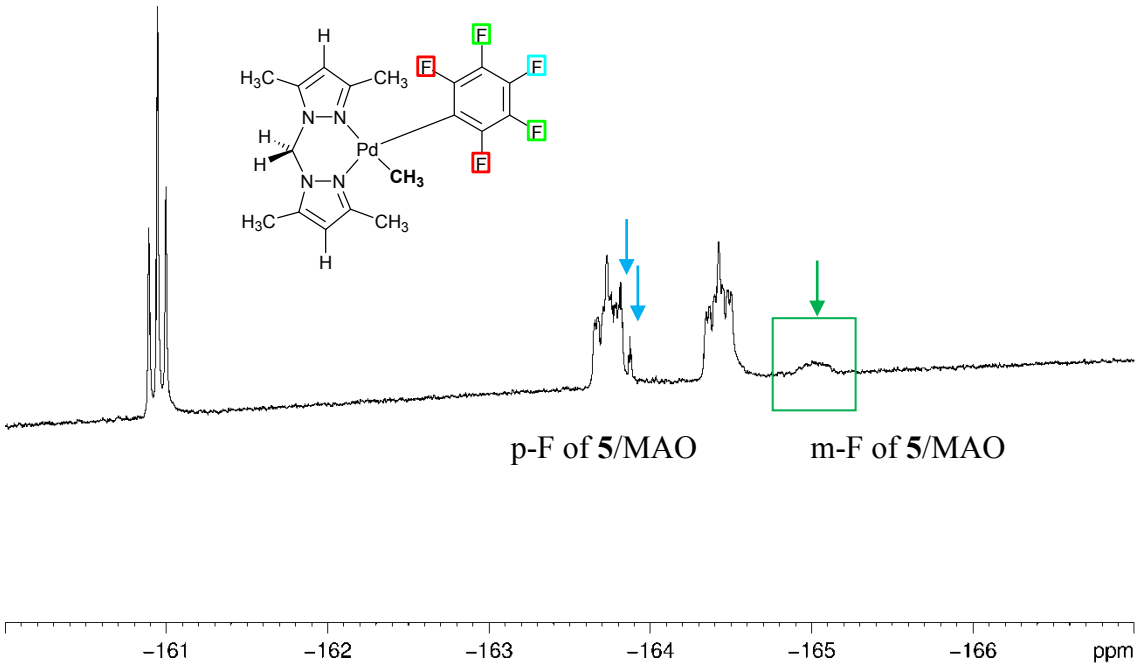

Figure S15b *p*-F and *m*-F region of the ^{19}F-NMR spectrum of the MAO activated complex **5** with a molecular Pd:Al ratio of 1:10, i.e., a mixture of [Pd(C_6F_5)Cl(bpzm*)] and the methyl derivative [Pd(C_6F_5)CH_3(bpzm*)] (in a 1:1 mixture of CD_2Cl_2 and toluene-d_8 as a 0.03 mol·l^{-1} solution in Pd, RT).

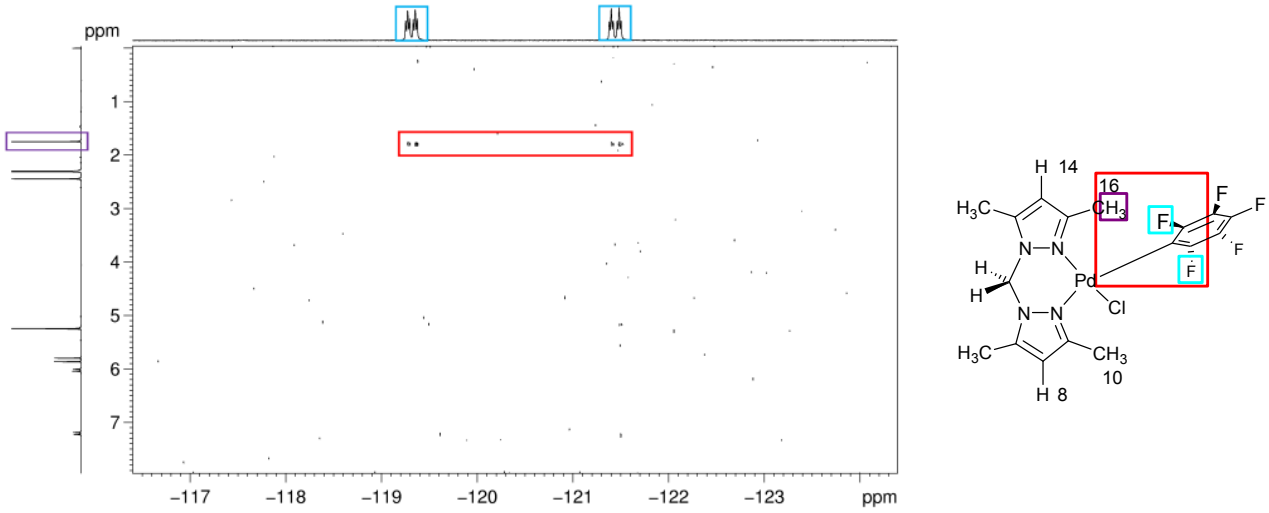

Figure S16 ^{1}H,^{19}F-HOESY spectrum of **5** (mixing time: 0.8 s) in CD_2Cl_2 (0.03 mol·l^{-1}) at room temperature. The crosspeaks (red rectangle) indicate a spatial proximity of the pyrazolyl methyl group at 1.75 ppm to the *o*-F atoms (cf. Fig. 10).