Supporting information

Mono- and binuclear palladacycles via regioselective C–H bond activation: syntheses, mechanistic insights and catalytic activity in direct arylation of azoles

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Contents

1. Kinetic measurements for palladation reactions

Rate order determination: The rate order of palladation reaction for each base was determined by the initial rate method. The data of the concentration of the product *vs* time (min) plot was fitted linear with OriginPro 8. The slope of the linear fitting represents the reaction rate. The order of the reaction was then determined by plotting the log(rate) *vs* log(conc. of base), wherein the slope indicates the order of reaction.

Rate order determination for K_3PO_4 (Fig S1): To determine the order of the palladation reaction on K_3PO_4, the initial rates at different initial concentrations (1 equiv, 3 equiv, 10 equiv) of K_3PO_4 were recorded. The final data was obtained by averaging the results of two independent measurements.

Experiment	Amount of K_3PO_4 [equiv]	Initial rate [$Mmin^{-1}$] x 10^{-3}
1	0.371 mmol [1.0]	0.466
2	1.113 mmol [3.0]	0.302
3	3.71 mmol [10.0]	0.360

Procedure: To a 25 mL round-bottom flask equipped with magnetic stir bar was introduced $Pd(COD)Cl_2$ (0.106 g, 0.371 mmol) and **1c** (0.120 g, 0.371 mmol), and 1,4-dioxane (5.0 mL) was added into it inside the glove-box, which makes 0.0742 M concentration of the reaction mixture. The reaction mixture was then stirred at room temperature for 1 h and 0.5 mL of the reaction mixture was drawn to a NMR tube. The ^{31}P NMR measurement of the reaction mixture indicated the formation of the species **6c**. To the reaction mixture in the flask, appropriate amount K_3PO_4 (as shown in table above) was added and the reaction mixture was heated in an oil bath at 70 ^oC. At regular intervals (5, 10, 15, 20 and 30 min), 0.5 mL of the reaction mixture was drawn to the NMR tube and ^{31}P NMR analyses were carried out for each sample. The concentration of the product **2c** obtained in each sample was determined from the peak integral percentage of the product with respect to the starting compound **6c**.

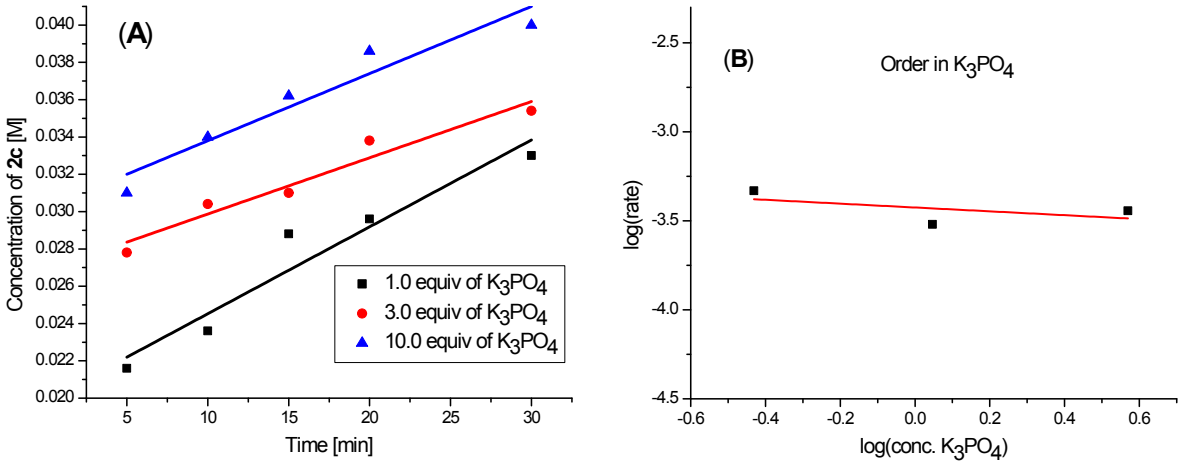


Fig. S1 (A) Time-dependent yields of the palladacycle **2c** at different initial loading of K_3PO_4. (B) Plot of log(rate) *vs* log(conc. K_3PO_4). The rates are average of two independent measurements.

Rate order determination for Et_3N (Fig S2): To determine the order of the palladation reaction on Et_3N, the initial rates at different initial concentrations (0.074, 0.222, 0.444 and 0.742 [M]) of Et_3N were recorded. The final data was obtained by averaging the results of two independent measurements.

Experiment	Conc. of Et_3N [M]	Initial rate [$Mmin^{-1}$] x 10^{-3}
1	0.074	1.14
2	0.222	1.69
3	0.444	0.80
4	0.742	0.702

Procedure: To a 25 mL round-bottom flask equipped with magnetic stir bar was introduced $Pd(COD)Cl_2$ (0.106 g, 0.371 mmol) and **1c** (0.120 g, 0.371 mmol), and 1,4-dioxane (5.0 mL) was added into it inside the glove-box, which makes 0.0742 M concentration of the reaction mixture. To the above reaction mixture appropriate amount Et_3N (as shown in table above) was added and the reaction mixture was stirred at room temperature for 1 h. About 0.5 mL of the reaction mixture was drawn to a NMR tube, whose ^{31}P NMR measurement indicated the

formation of the species **7c**. The reaction mixture on the flask was then heated in an oil bath at 70 ^{o}C. At regular intervals (5, 10, 15 and 20 min), 0.5 mL of the reaction mixture was drawn to the NMR tube and ^{31}P NMR analyses were carried out for each sample. The concentration of the product **4c** obtained in each sample was determined from the peak integral percentage of the product with respect to the starting compound **7c**.

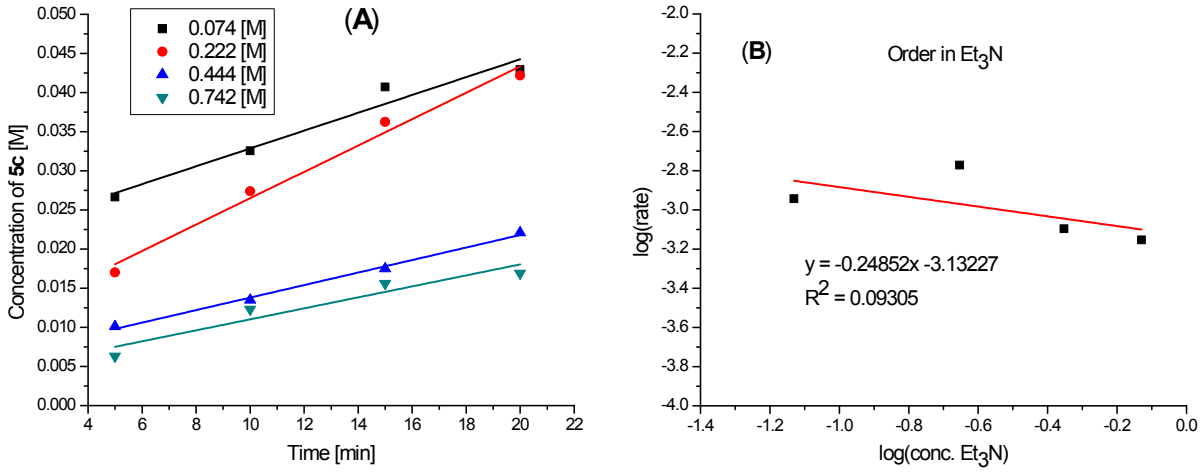


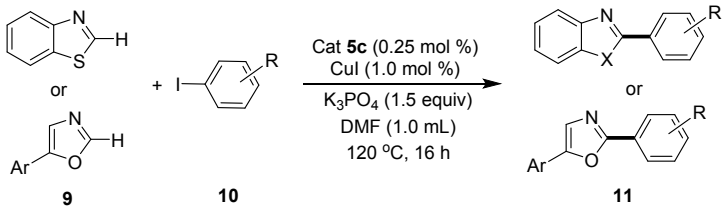
Fig. S2 (A) Time-dependent yields of the palladacycle **4c** at different initial concentration of Et_3N. (B) Plot of log(rate) *vs* log(conc. Et_3N). The rates are average of two independent measurements.

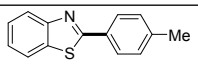
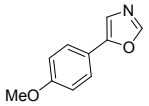
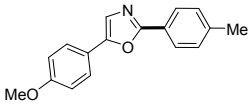
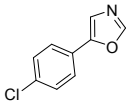
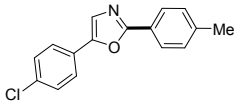
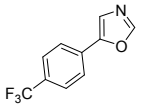
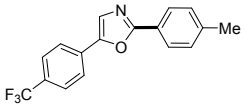
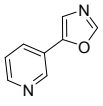
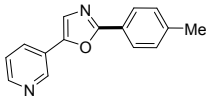
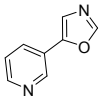
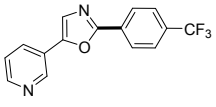
Rate order determination for pyridine: To determine the order of the palladation reaction on pyridine, the initial rates at different initial concentrations (0.074, 0.222, 0.444 and 0.742 [M]) of pyridine were recorded. The final data was obtained by averaging the results of two independent measurements.

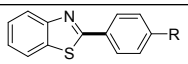
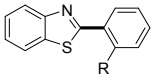
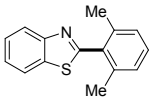
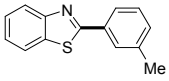
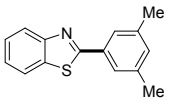
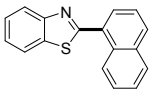
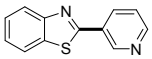
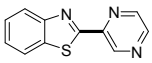
Experiment	Conc. of pyridine [M]	Initial rate [Mmin^{-1}] x 10^{-3}
1	0.074	0.296
2	0.222	0.280
3	0.444	0.135
4	0.742	0.134

Procedure: To a 25 mL round-bottom flask equipped with magnetic stir bar was introduced $Pd(COD)Cl_2$ (0.106 g, 0.371 mmol) and **1c** (0.120 g, 0.371 mmol), and 1,4-dioxane (5.0 mL) was added into it inside the glove-box, which makes 0.0742 M concentration of the reaction mixture. To the above reaction mixture appropriate amount pyridine (as shown in table above) was added and the reaction mixture was stirred at room temperature for 1 h. About 0.5 mL of the reaction mixture was drawn to a NMR tube, whose ^{31}P NMR measurement indicated the formation of the species **8c**. The reaction mixture on the flask was then heated in an oil bath at 70 ^{o}C. At regular intervals (5, 10, 15, 20, 30 and 45 min), 0.5 mL of the reaction mixture was drawn to the NMR tube and ^{31}P NMR analyses were carried out for each sample. The concentration of the product **2c** obtained in each sample was determined from the peak integral percentage of the product with respect to the starting compound **8c**.

2. Table S1 Scope for the arylation of azoles catalyzed by **4c**[a]



Entry	Azoles (**9**)	Product (**10**)		Yield (%)[b]
1			(**11aa**)	93
2			(**11ba**)	64
3			(**11ca**)	67
4			(**11da**)	75
5			(**11ea**)	87
6			(**11ee**)	81

					
7			R = OMe	(**11ab**)	96
8			R = F	(**11ac**)	76
9			R = Cl	(**11ad**)	79
10			R = CF_3	(**11ae**)	90
11			R = CN	(**11af**)	86
12			R = NO_2	(**11ag**)	26
13			R = COOMe	(**11ah**)	37
					
14			R = Me	(**11ai**)	91
15			R = OMe	(**11aj**)	72
16			R = Cl	(**11ak**)	79
17				(**11al**)	40
18				(**11am**)	75
19				(**11an**)	65
20				(**11ao**)	97
21				(**11ap**)	54
22				(**11aq**)	68

[a]Reaction conditions: Azole (0.3 mmol), aryl iodide (0.45 mmol), K_3PO_4 (0.096 g. 0.45 mmol), catalyst **4c** (0.0007 g, 0.25 mol %), CuI (0.0006 g, 1.0 mol %), DMF (1.0 mL), 120 ^oC, 16 h. [b]Yields of isolated compounds.

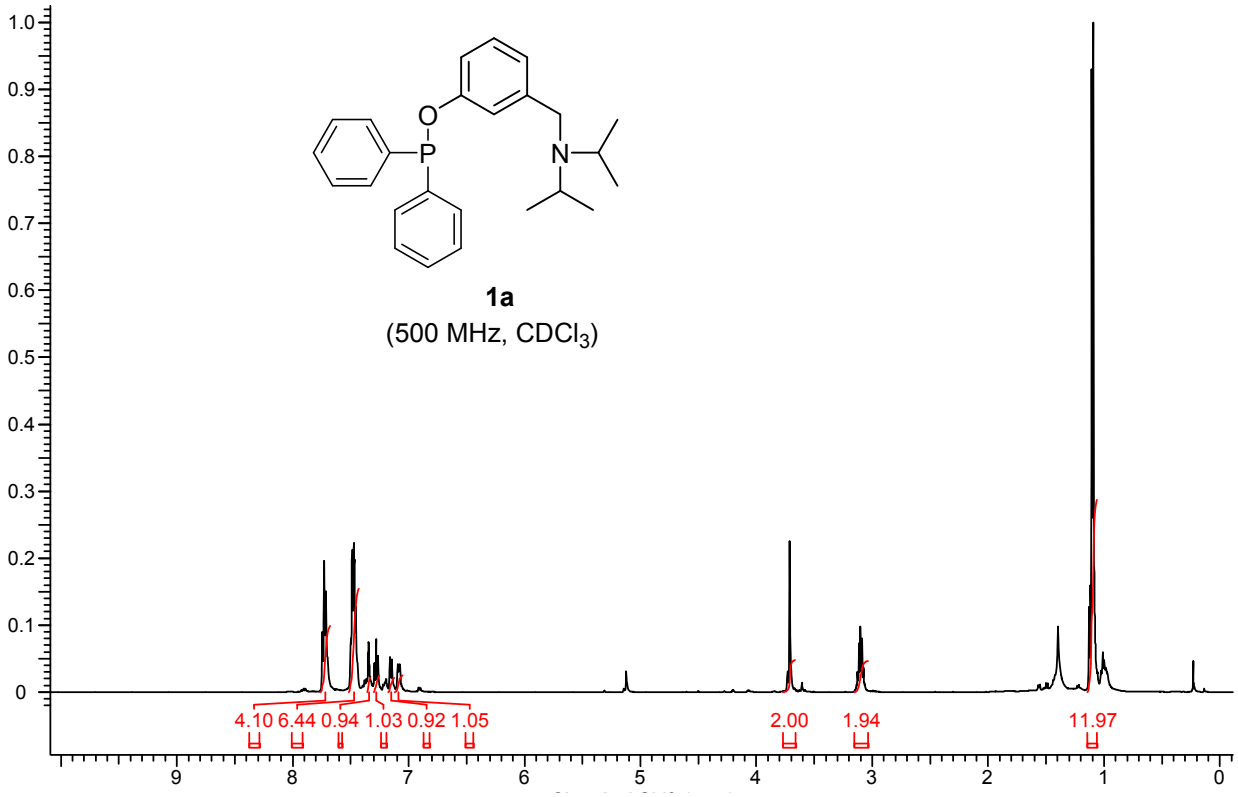
3. Table S2 Crystal data and structure refinement for complexes **2a**, **2b** and **3a**

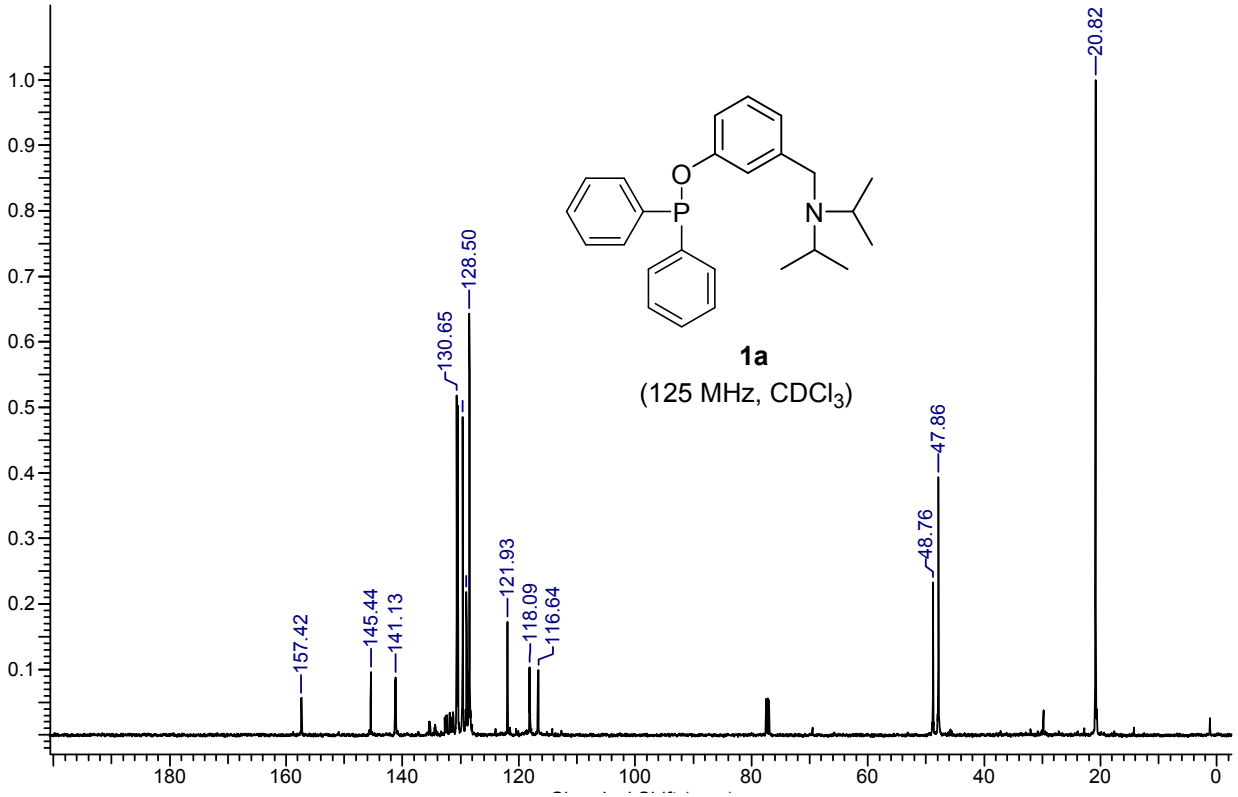
	2a	**2b**	**3a**
Empirical formula	$C_{25}H_{29}ClNOPPd$	$C_{21}H_{39}ClN_3OPPd$	$C_{27}H_{32}NO_3PPd$
Formula weight	532.31	522.37	555.91
Temperature (K)	150(2)	296(2)	200(2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a/Å	16.5228(14)	7.9316(3)	10.7002(3)
b/Å	10.2622(9)	13.8355(5)	15.0417(4)
c/Å	14.7716(13)	22.8534(8)	15.7925(4)
α/°	90	90	90
β/°	110.312(3)	98.291(2)	99.1280(10)
γ/°	90	90	90
V (Å^3)	2348.9(4)	2481.67(16)	2509.60(12)
Z	4	4	4
ρ_{calc}, (Mg/m^3)	1.505	1.398	1.471
ε (mm^{-1})	0.989	0.936	0.832
F (000)	1088	1088	1144
Crystal size (mm)	0.65 x 0.58 x 0.52	0.67 x 0.22 x 0.16	0.41 x 0.37 x 0.22
θ (min, max) (°)	2.38 to 25.00	1.73 to 25.00	1.88 to 25.00
R(int)	0.0227	0.0376	0.0265
Independent reflections	4137	4372	4410
Completeness to θ	99.9 %	100.0 %	100.0 %
Max. and min. transmission	0.6274, 0.5658	0.8647, 0.5729	0.8382, 0.7267
Data / restraints / parameters	4137 / 0 / 275	4372 / 0 / 261	4410 / 0 / 303
GOF (F^2)	1.093	1.155	1.027
R1, wR2 ($I>2\sigma(I)$)	0.0167, 0.0428	0.0241, 0.0600	0.0294, 0.0648
R1, wR2 (all data)	0.0170, 0.0430	0.0256, 0.0613	0.0317, 0.0660

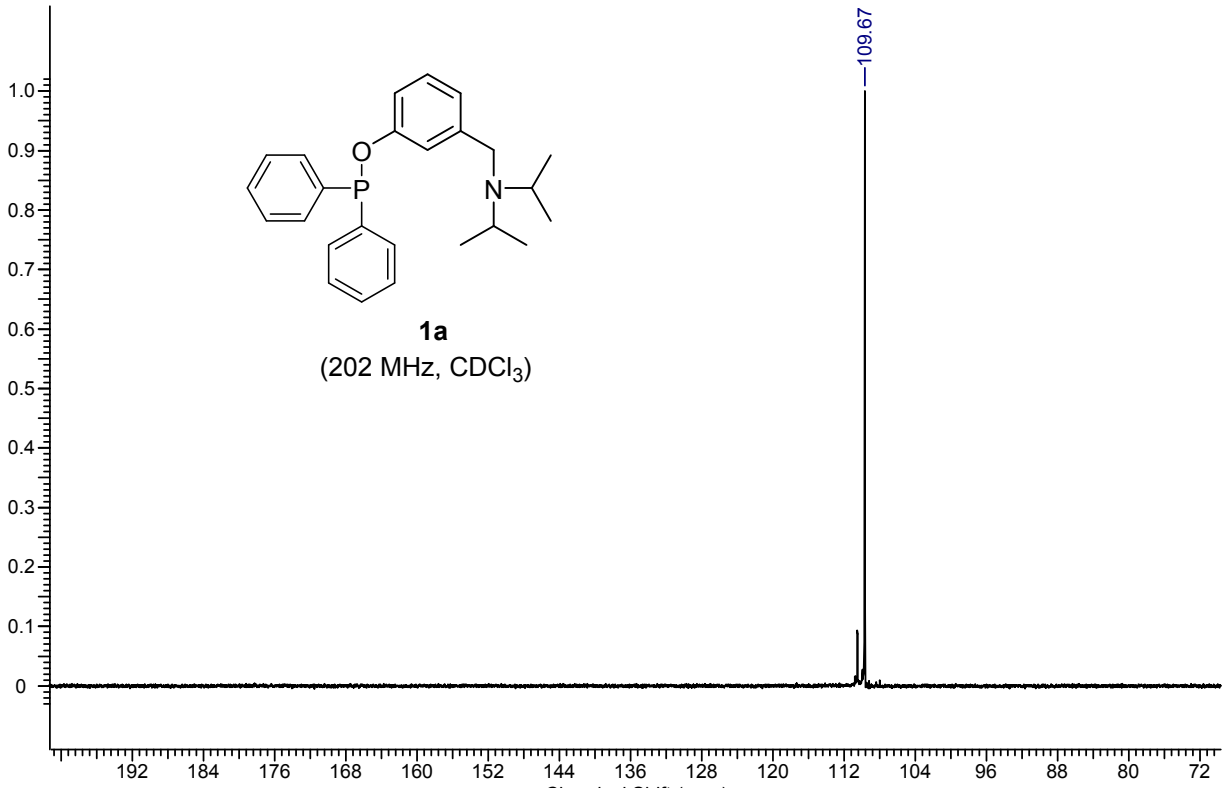
Table S3 Crystal data and structure refinement for complexes **3b** and **5a**

	3b	**5a**
Empirical formula	$C_{23}H_{42}N_3O_3PPd$	$C_{54}H_{64}N_2O_6P_2Pd_2$
Formula weight	545.97	1111.81
Temperature (K)	200(2)	200(2)
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
a/Å	11.5217(7)	11.1190(2)
b/Å	12.4022(8)	11.0743(3)
c/Å	18.4419(12)	21.2441(5)
α/°	90	90
β/°	101.270(2)	99.9410(10)
γ/°	90	90
V (Å^3)	2584.4(3)	2576.62(10)
Z	4	2
ρ_{calc}, (Mg/m^3)	1.403	1.433
ε (mm^{-1})	0.807	0.810
F (000)	1144	1144
Crystal size (mm)	0.39 x 0.32 x 0.21	0.42 x 0.31 x 0.21
θ (min, max) (°)	1.80 to 25.00	1.84 to 25.00
R(int)	0.0202	0.0289
Independent reflections	4553	4483
Completeness to θ	100.0 %	98.3 %
Max. and min. transmission	0.8487, 0.7436	0.8483, 0.7272
Data / restraints / parameters	4553 / 0 / 289	4483 / 0 / 303
GOF (F^2)	1.160	1.000
R1, wR2 ($I>2\sigma(I)$)	0.0204, 0.0541	0.0452, 0.0744
R1, wR2 (all data)	0.0220, 0.0558	0.0620, 0.0805

4. NMR spectra of ligands **1a** and **1b**

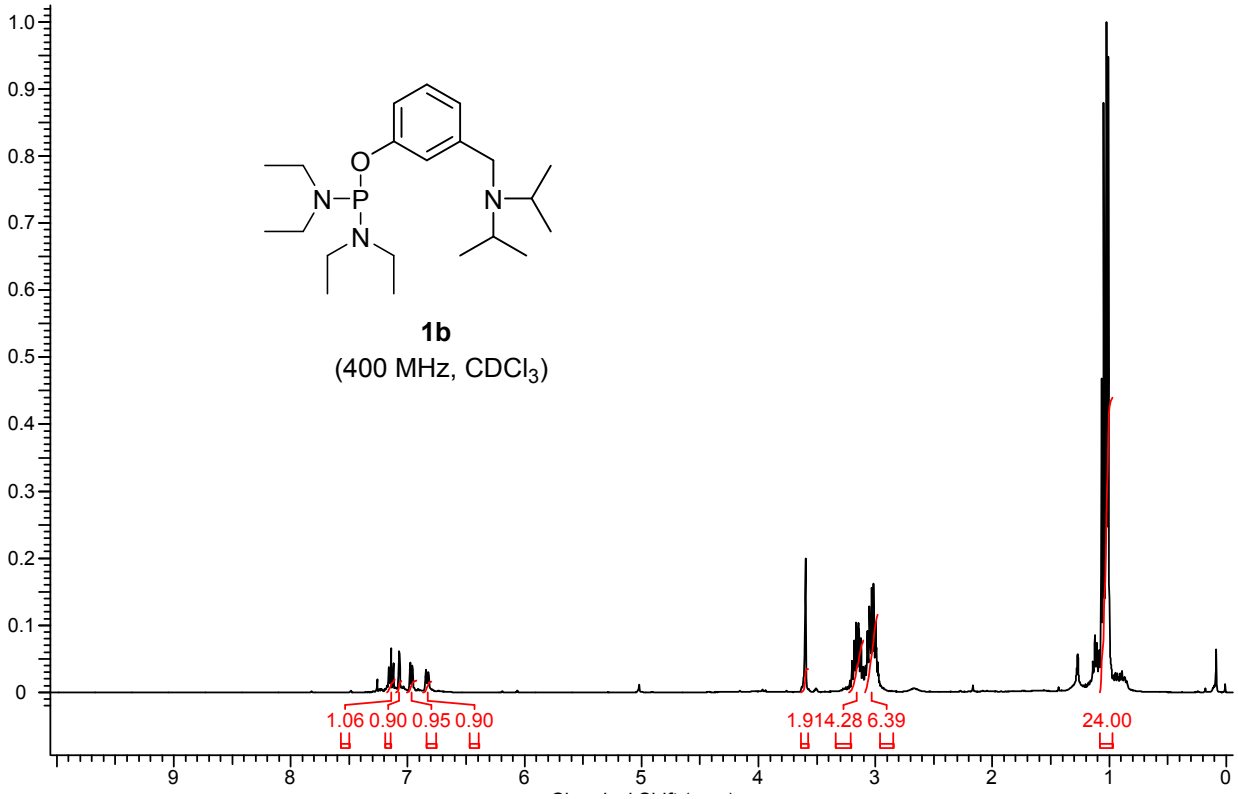






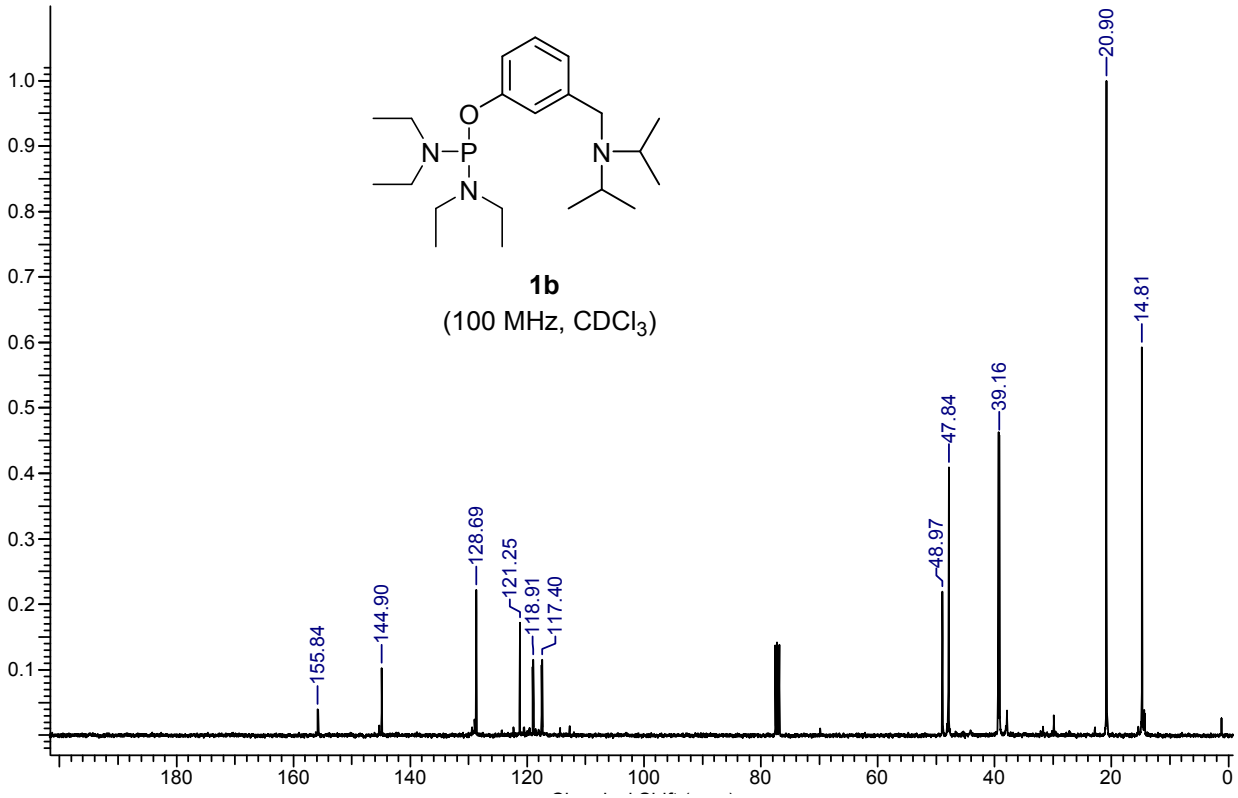
1a

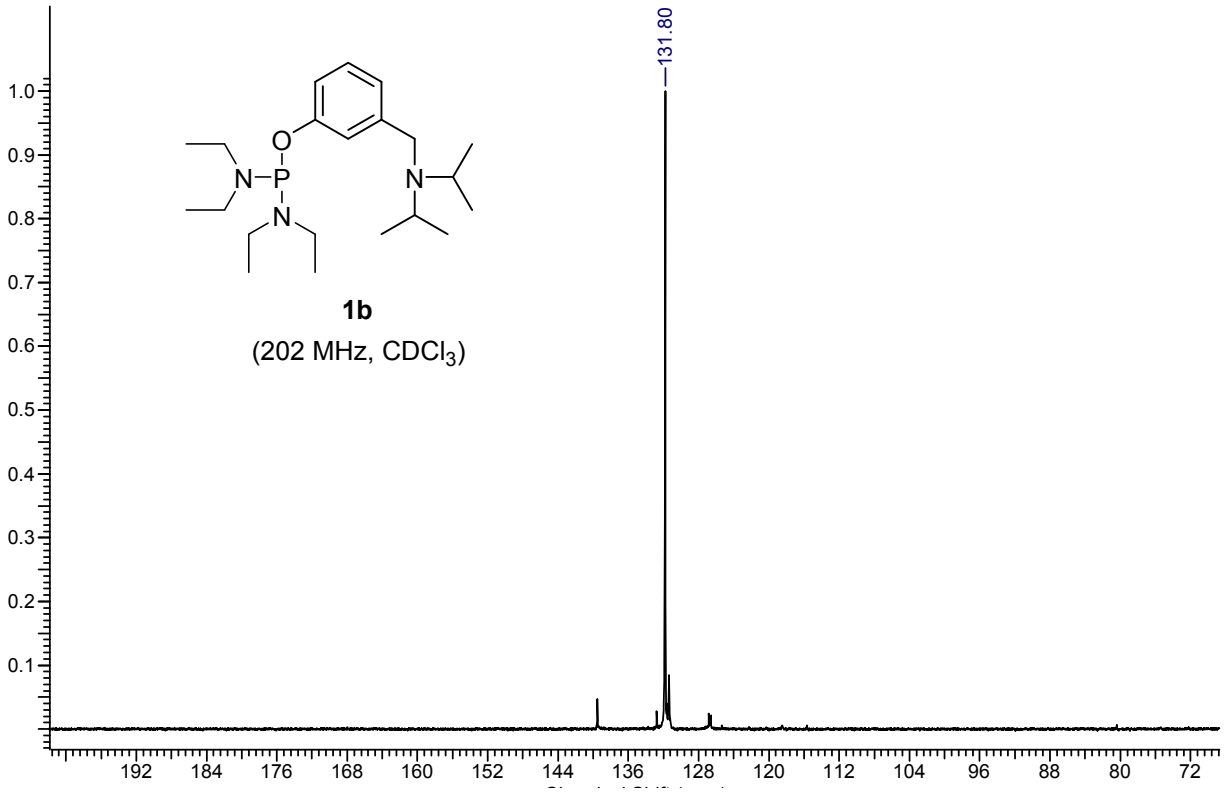
(202 MHz, $CDCl_3$)



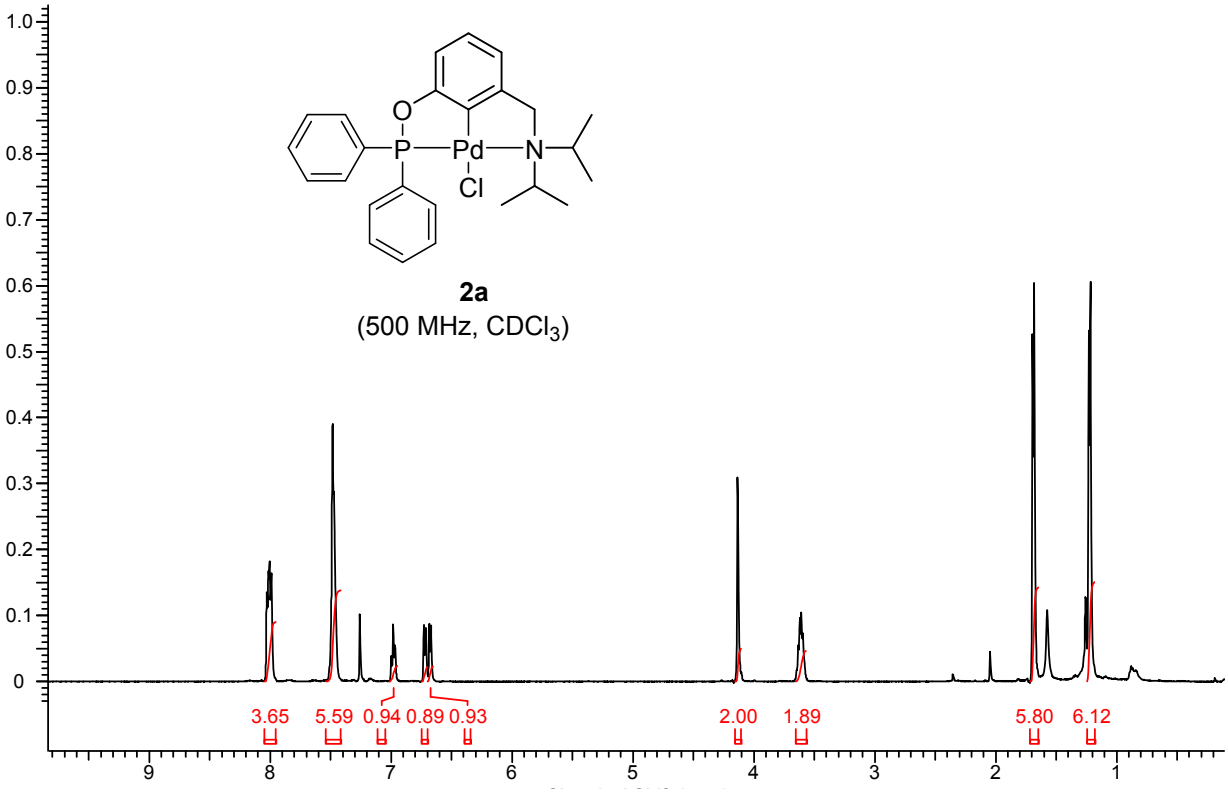
1b

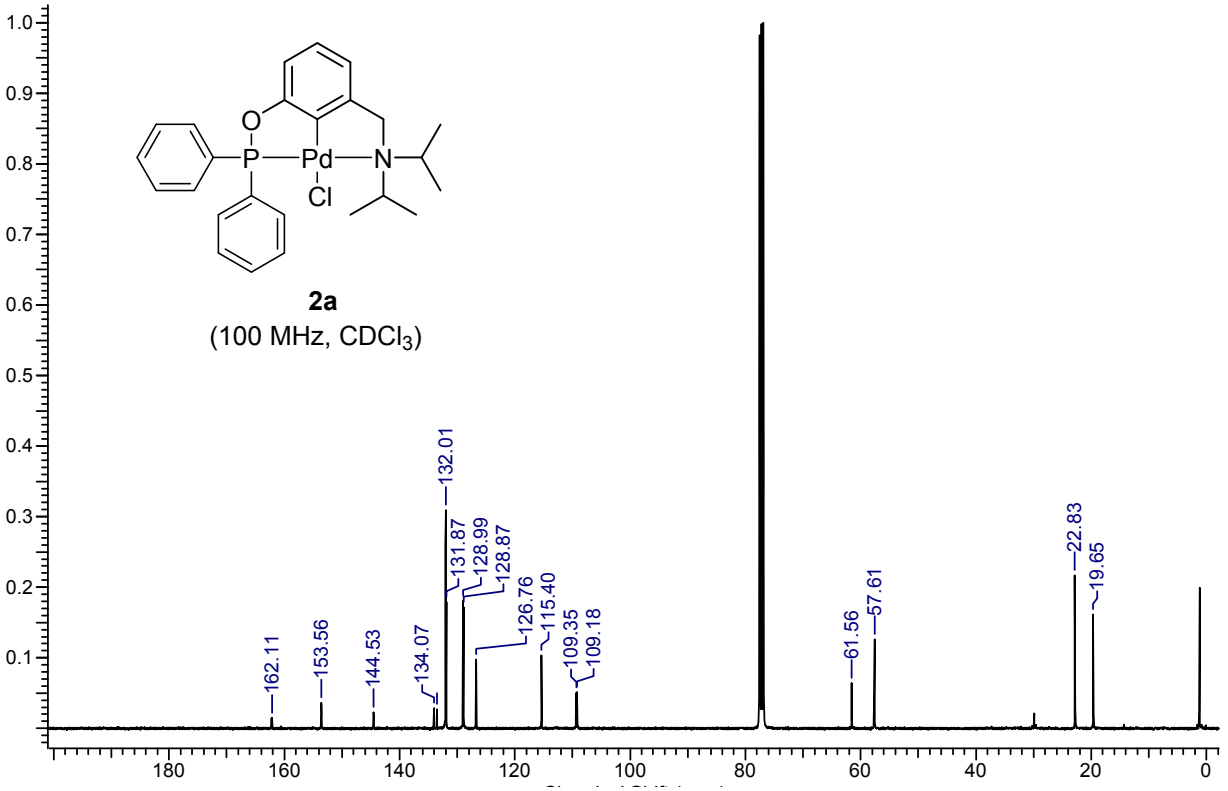
(400 MHz, $CDCl_3$)

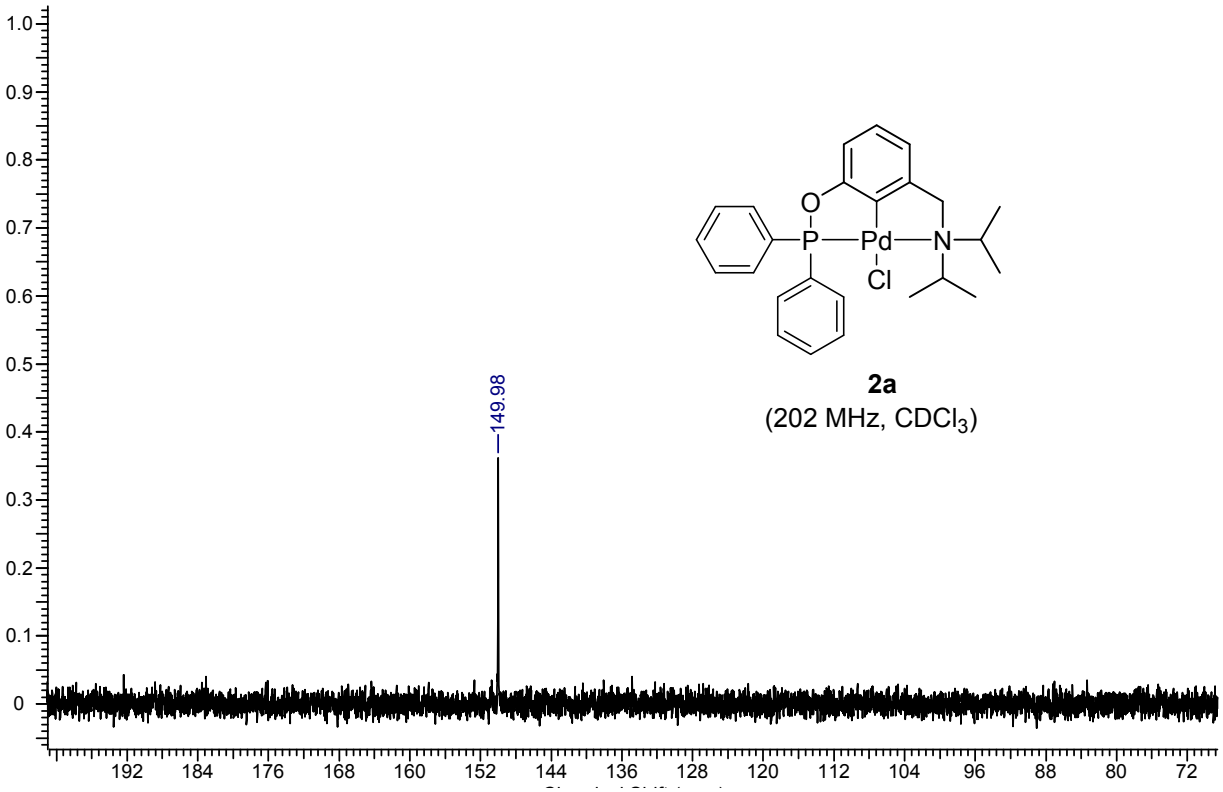

1b
(100 MHz, CDCl3)
155.84
144.90
128.69
121.25
118.91
117.40
48.97
47.84
39.16
20.90
14.81


1b
(202 MHz, CDCl3)
131.80

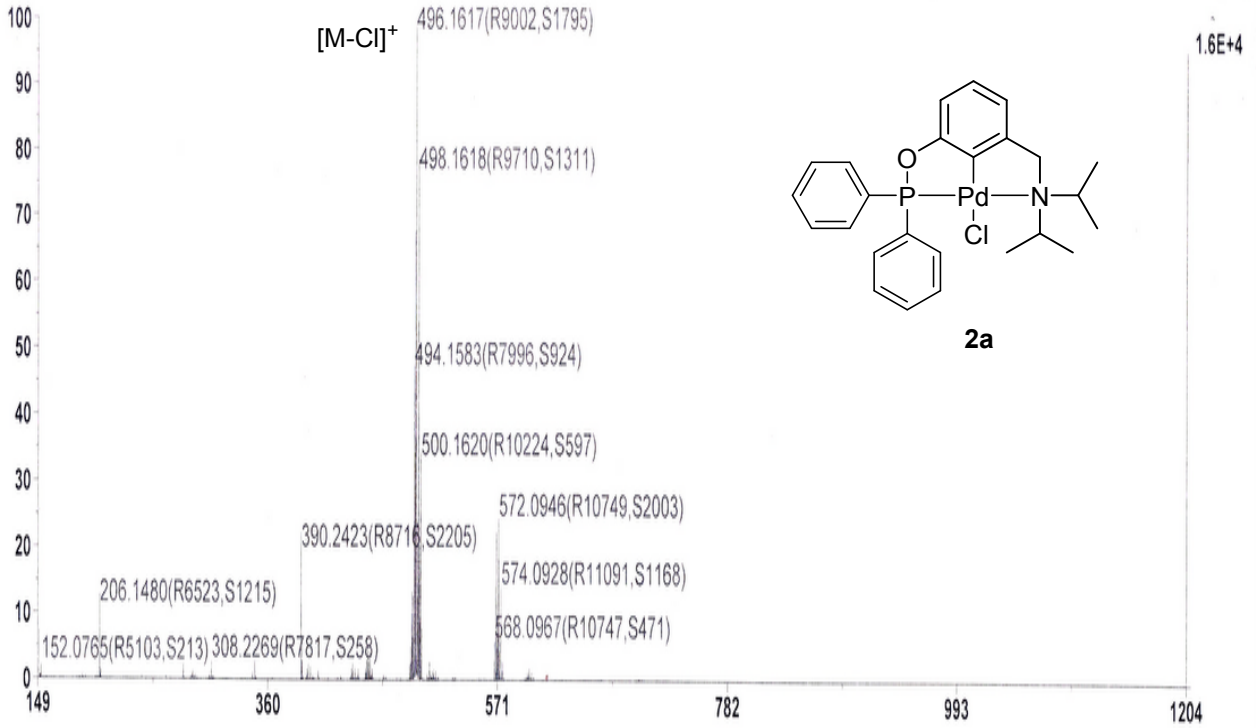
5. NMR and mass spectra of complexes



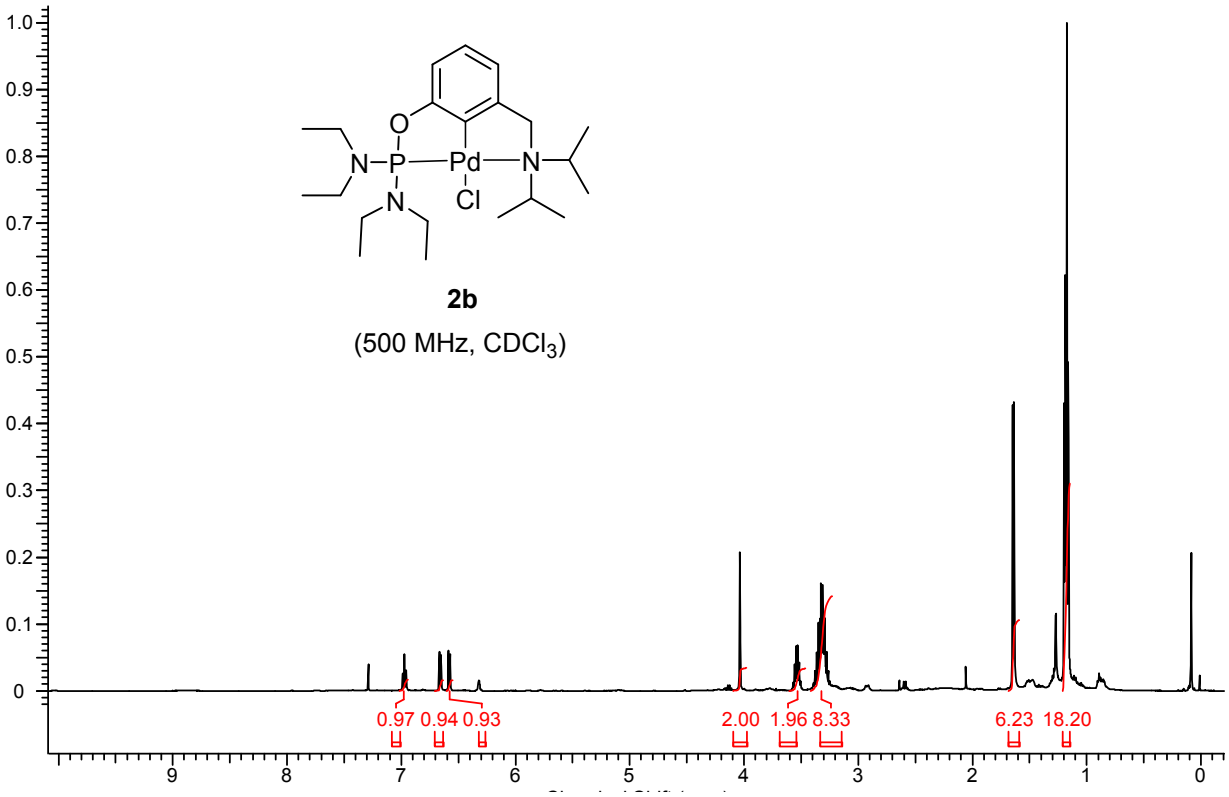




2a
(202 MHz, $CDCl_3$)

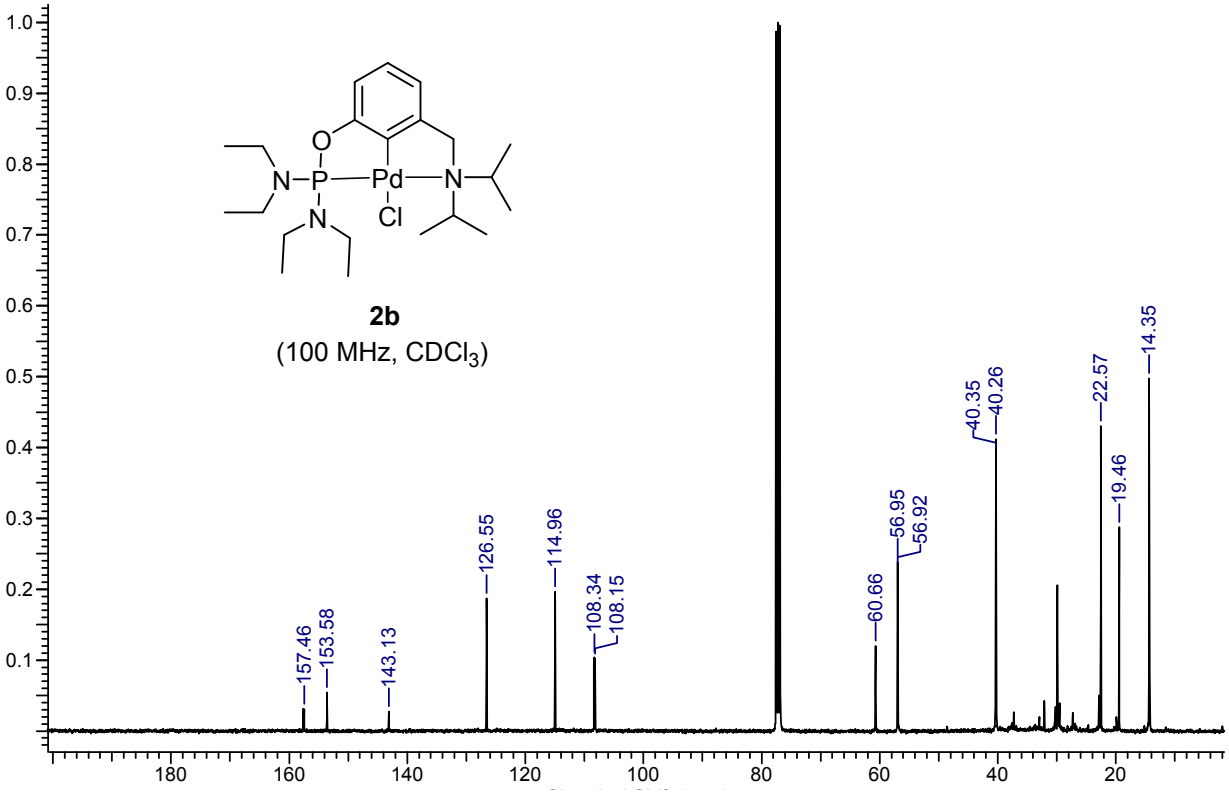


2a



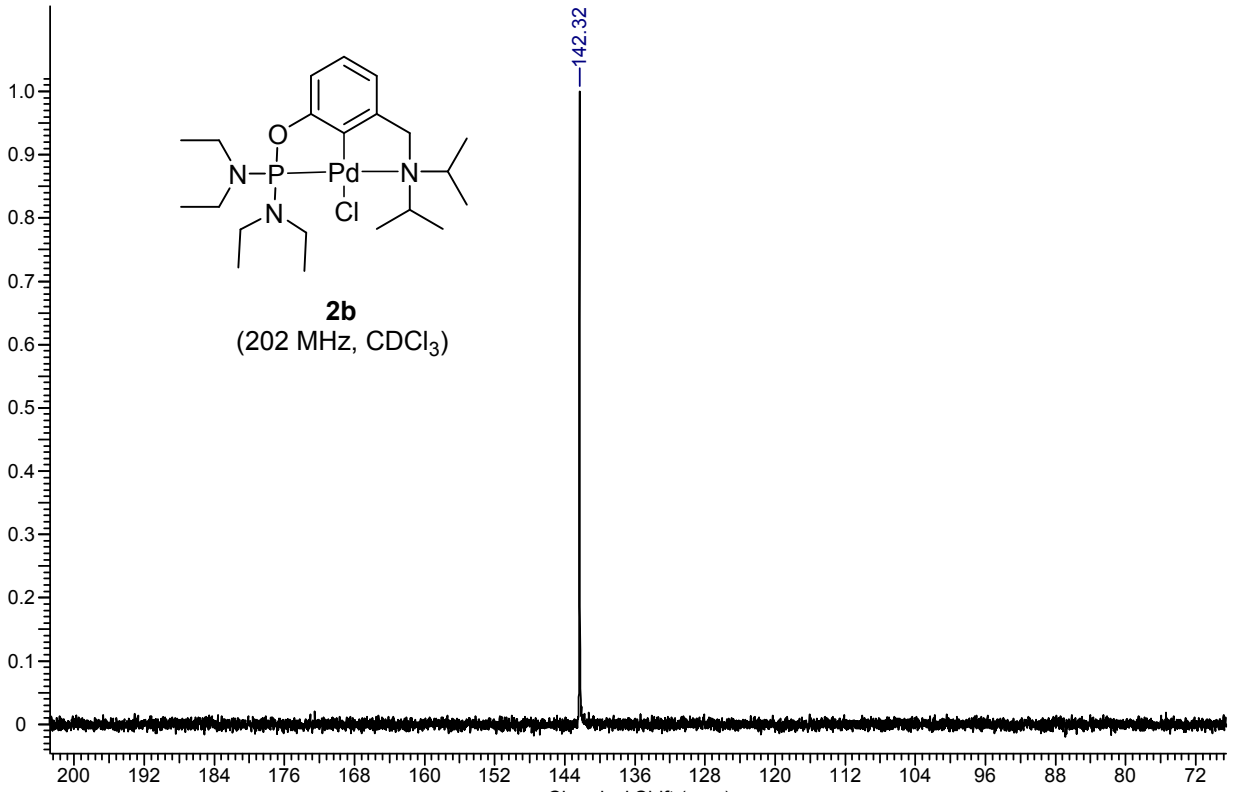
2b

(500 MHz, $CDCl_3$)

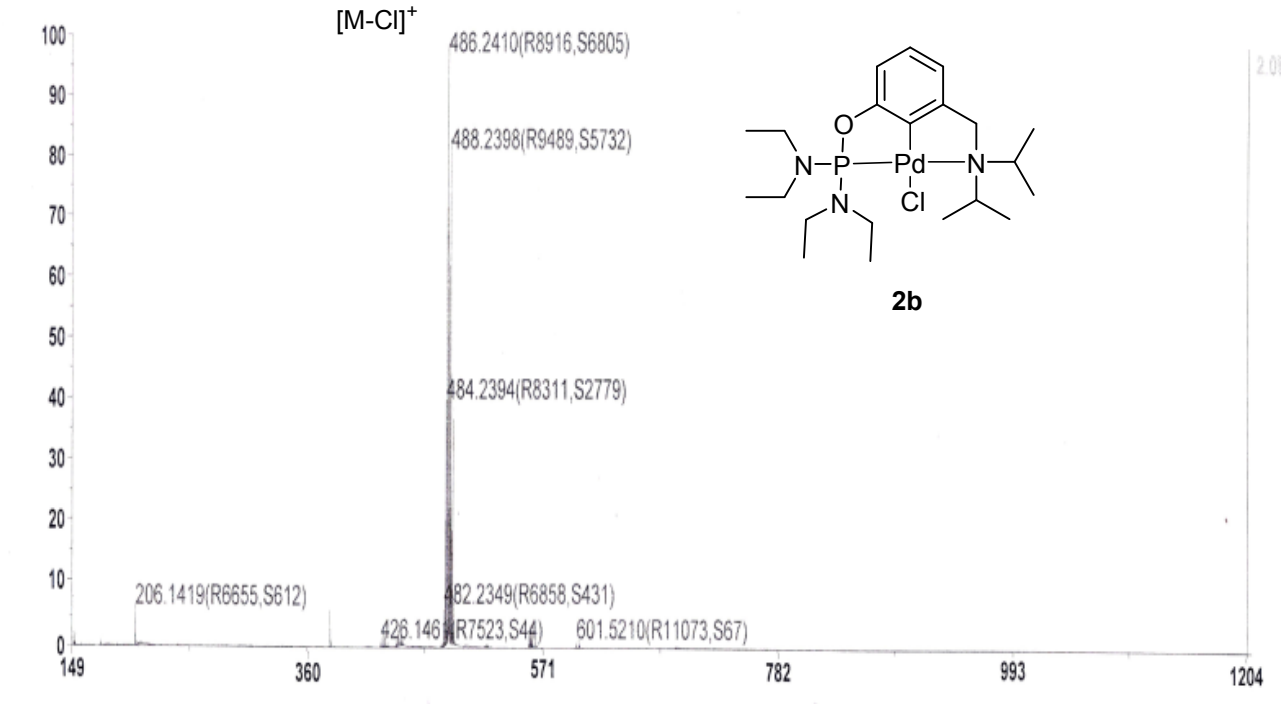


2b

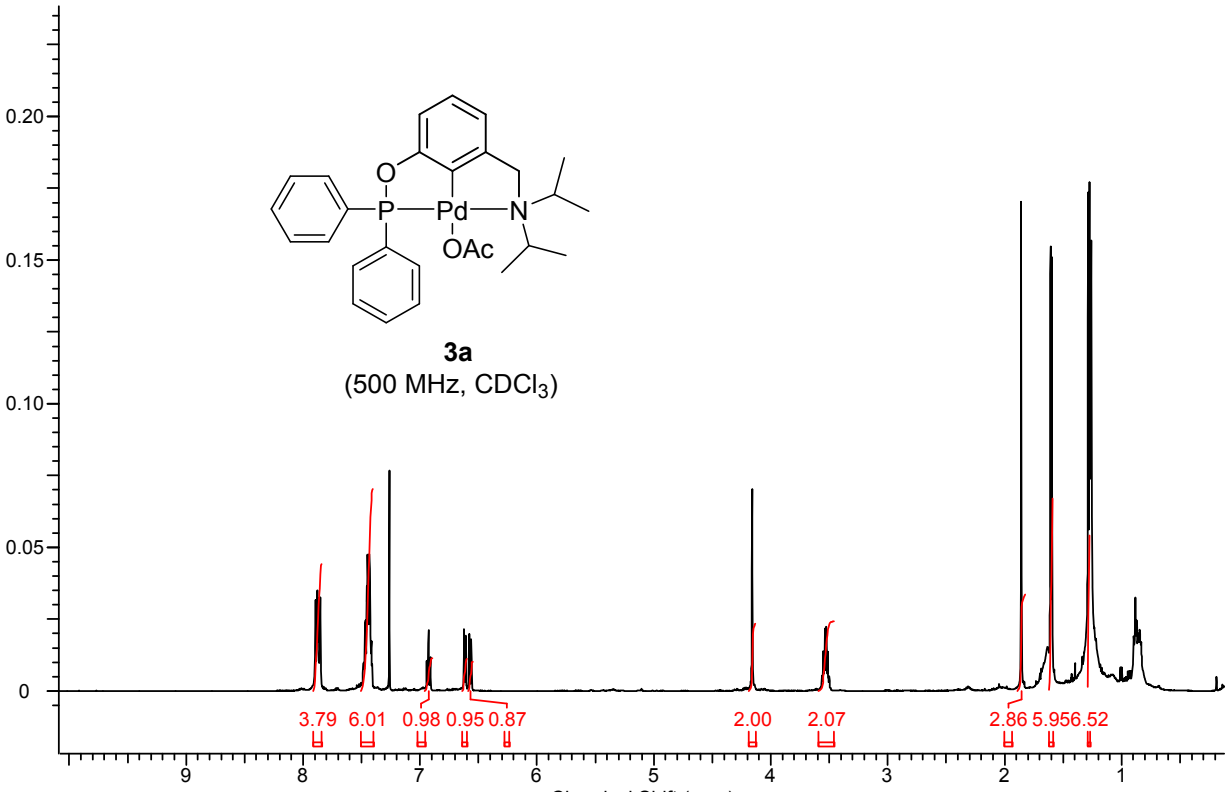
(100 MHz, $CDCl_3$)

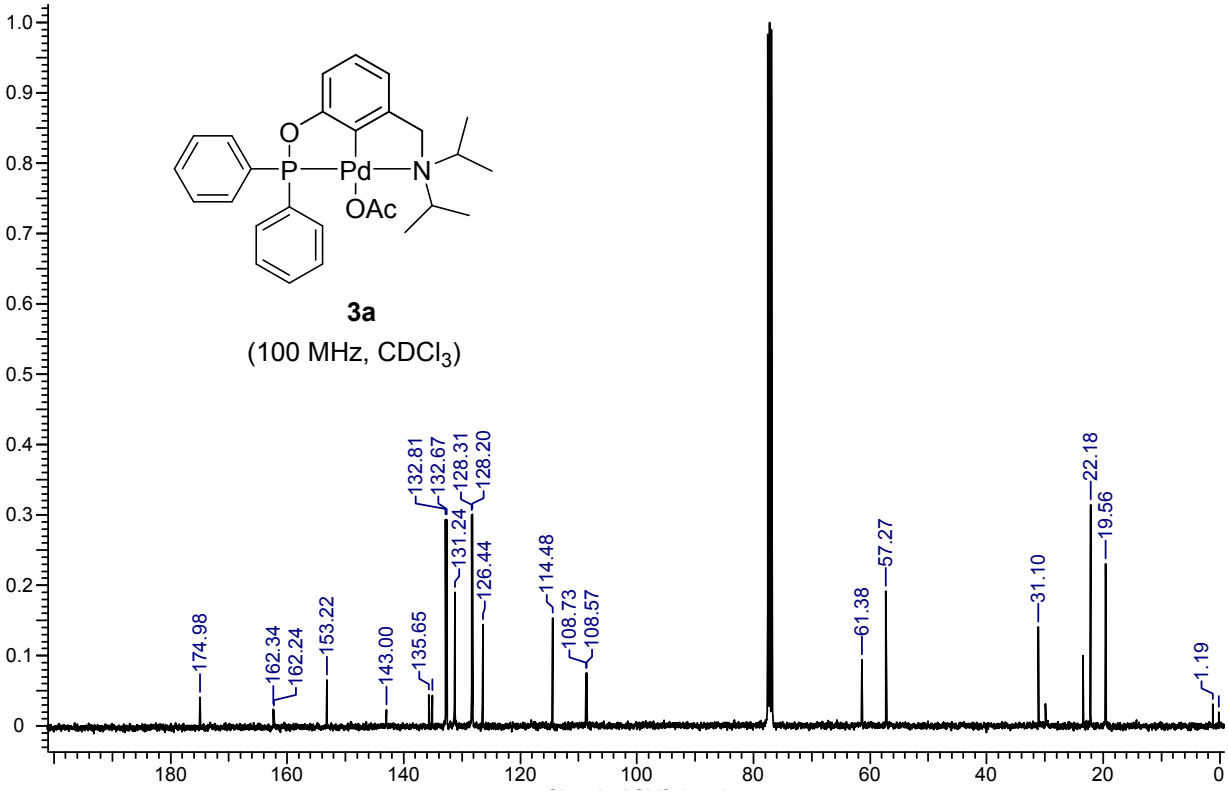


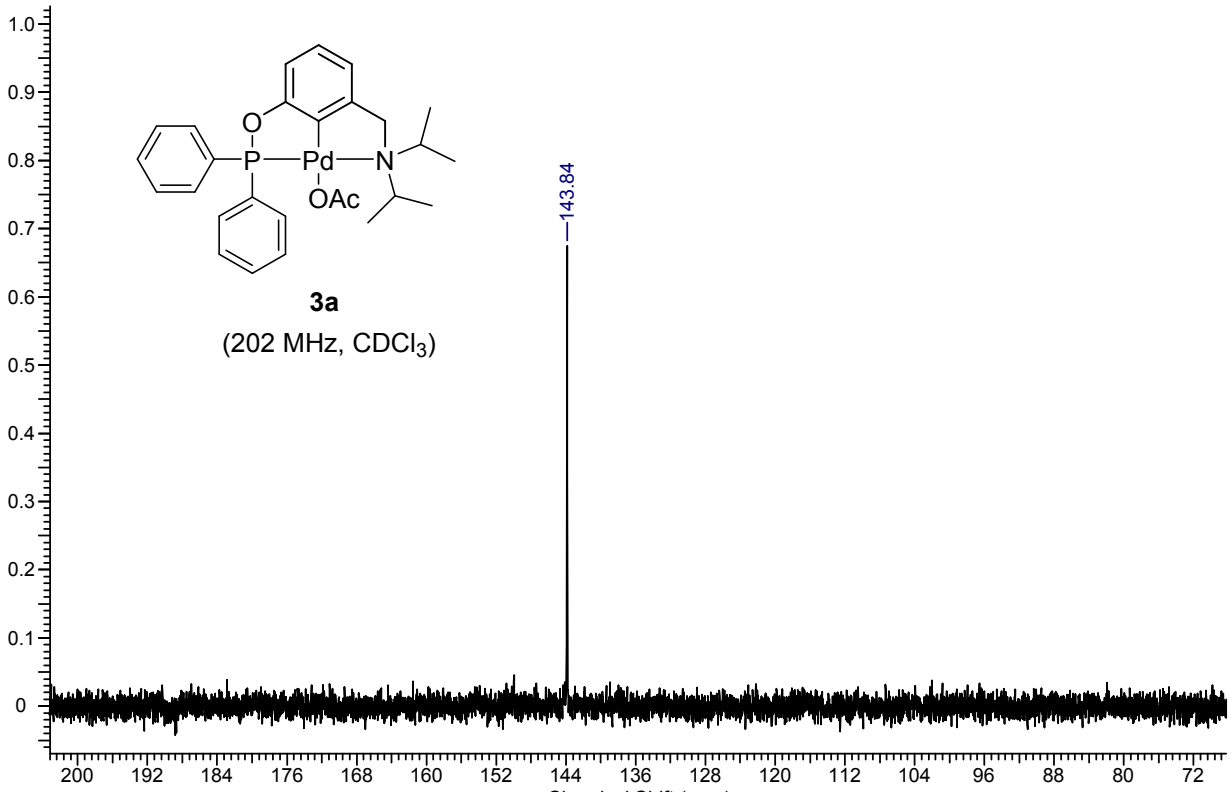
2b
(202 MHz, $CDCl_3$)



2b


O
P
Pd
N
OAc
3a
(500 MHz, CDCl3)
3.79 6.01 0.98 0.95 0.87
2.00
2.07
2.86 5.95 6.52

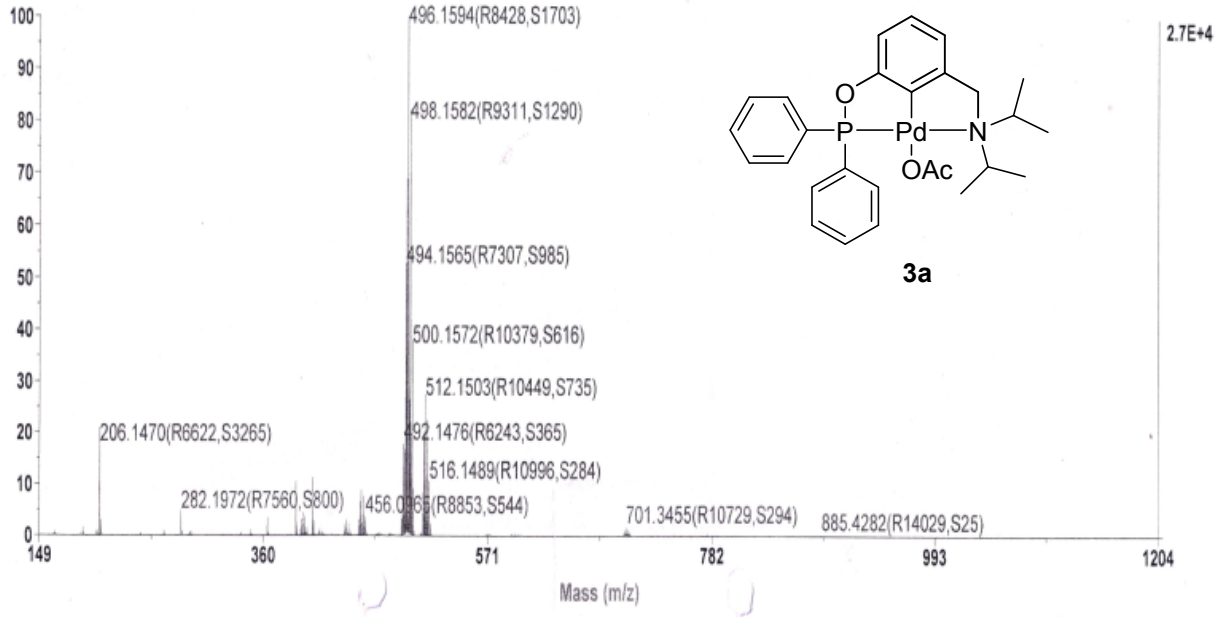

O
P
Pd
N
OAc
3a
(100 MHz, CDCl3)
174.98
162.34
162.24
153.22
143.00
135.65
132.81
132.67
131.24
128.31
128.20
126.44
114.48
108.73
108.57
61.38
57.27
31.10
22.18
19.56
1.19



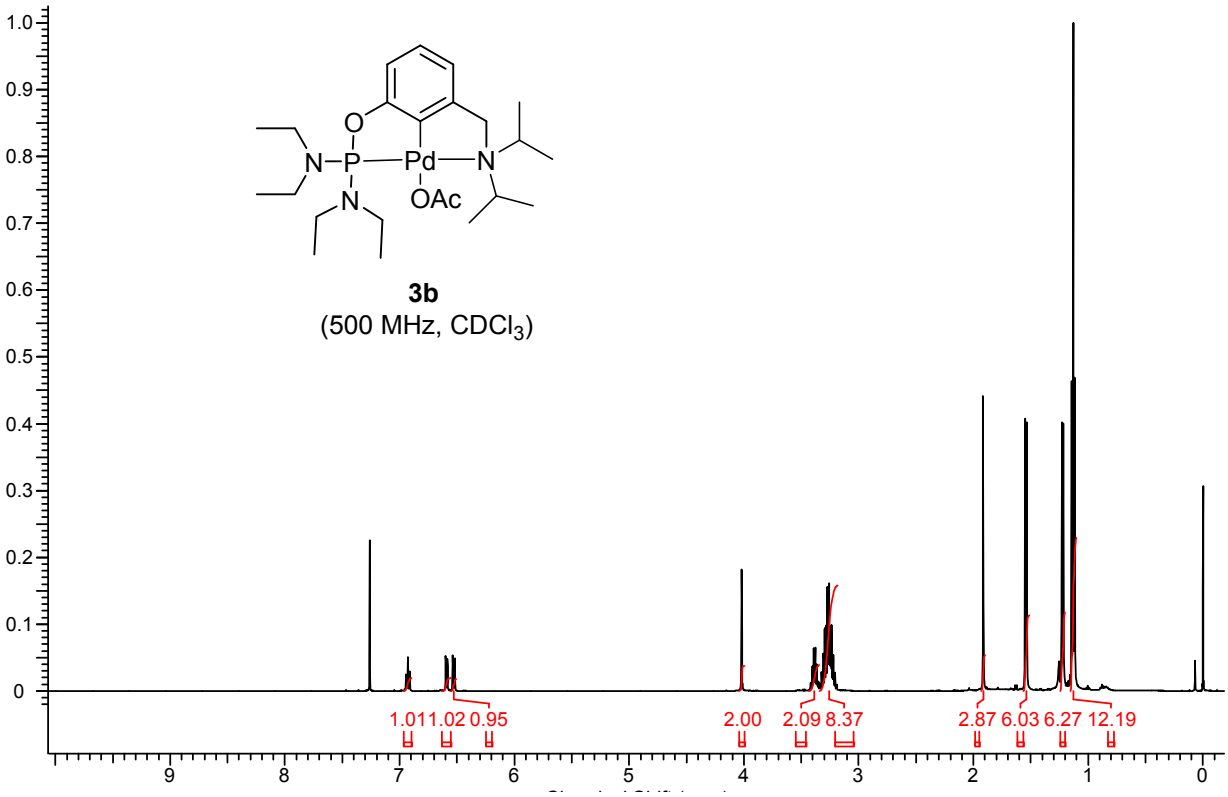
3a

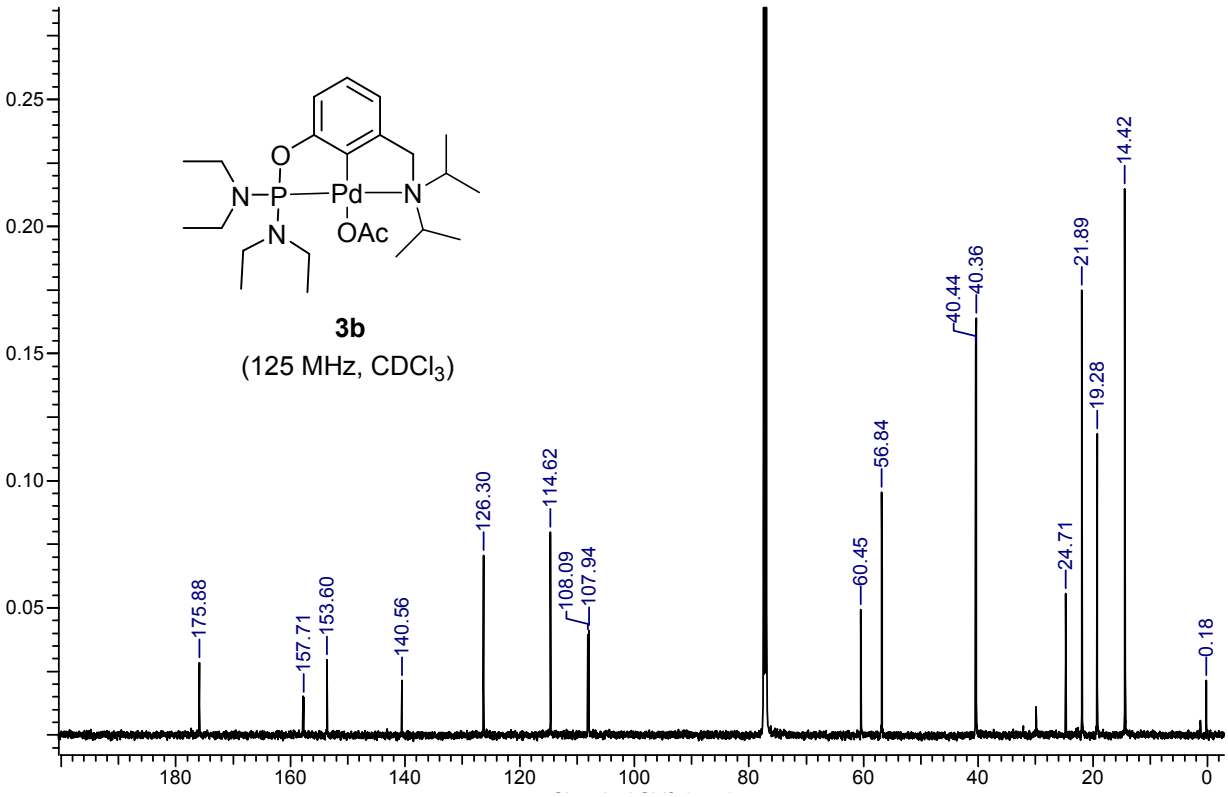
(202 MHz, $CDCl_3$)

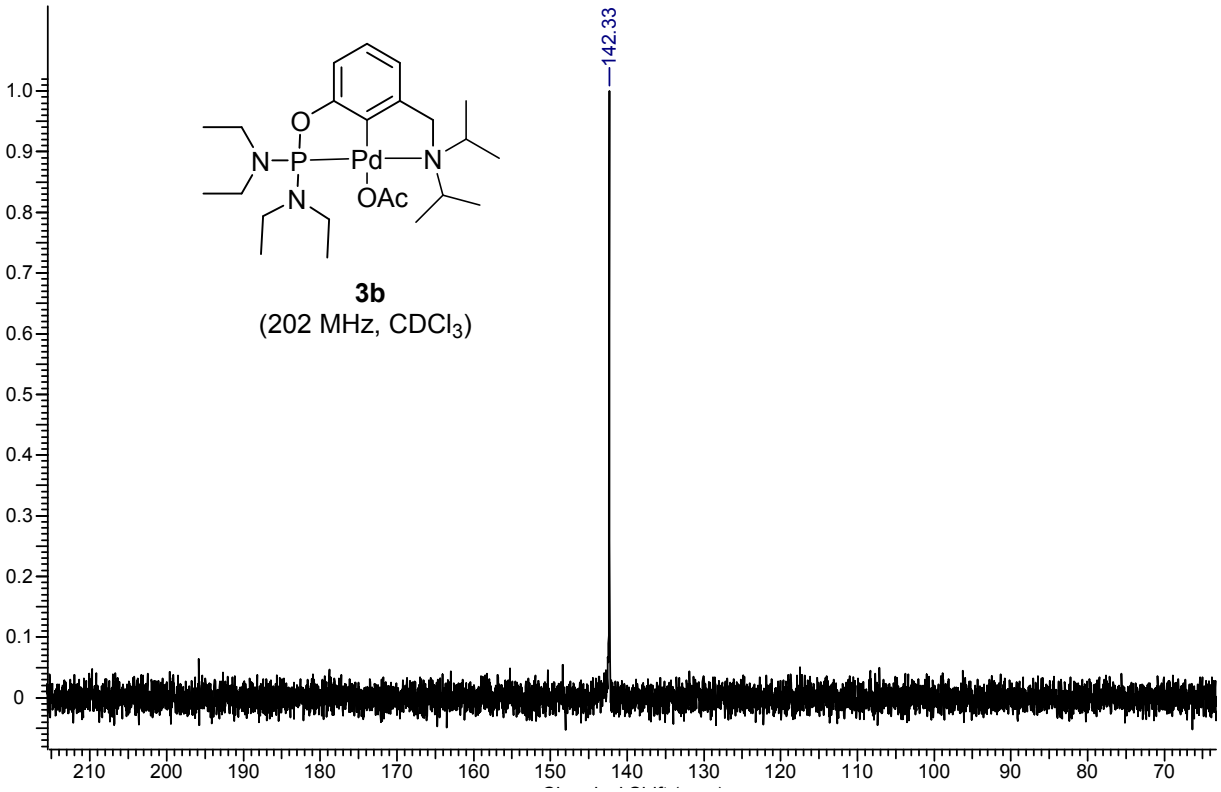
$[M\text{-}OAc]^+$



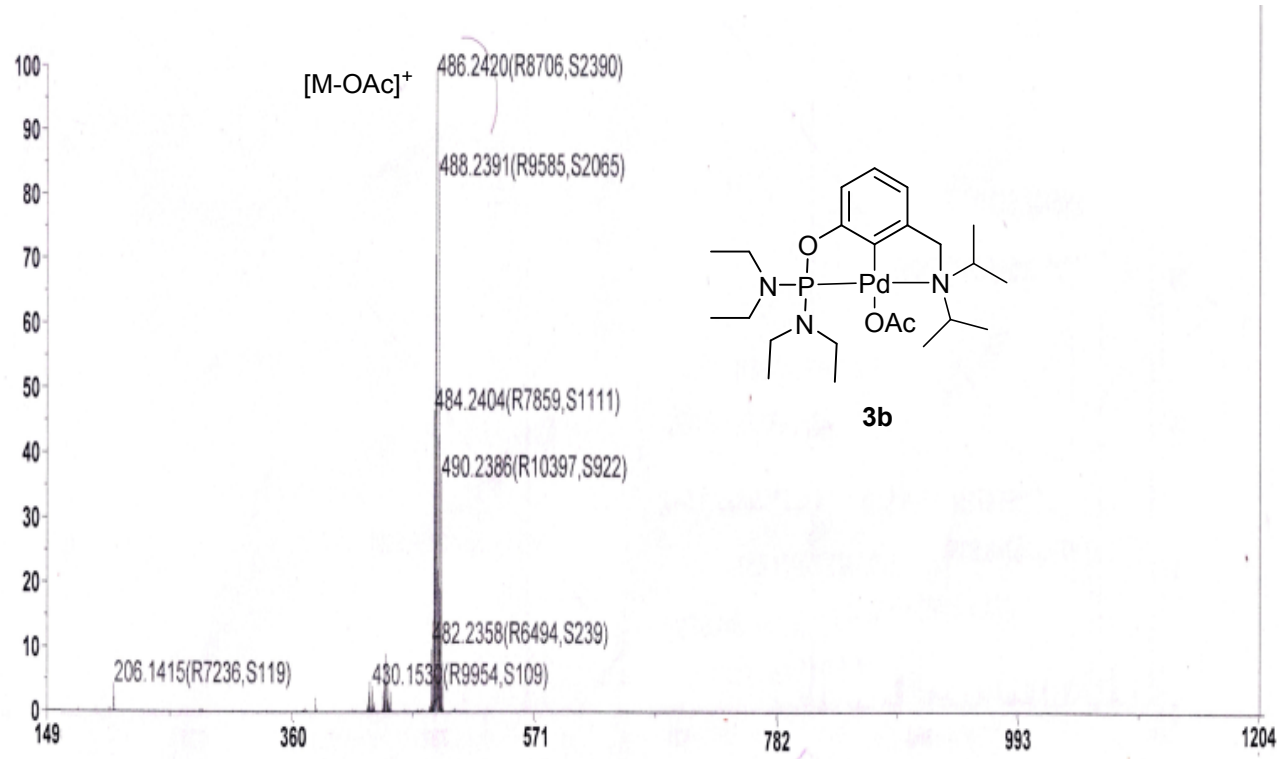
3a


O
N
P
Pd
N
N
OAc
3b
(500 MHz, CDCl3)
1.01 1.02 0.95
2.00
2.09 8.37
2.87 6.03 6.27 12.19

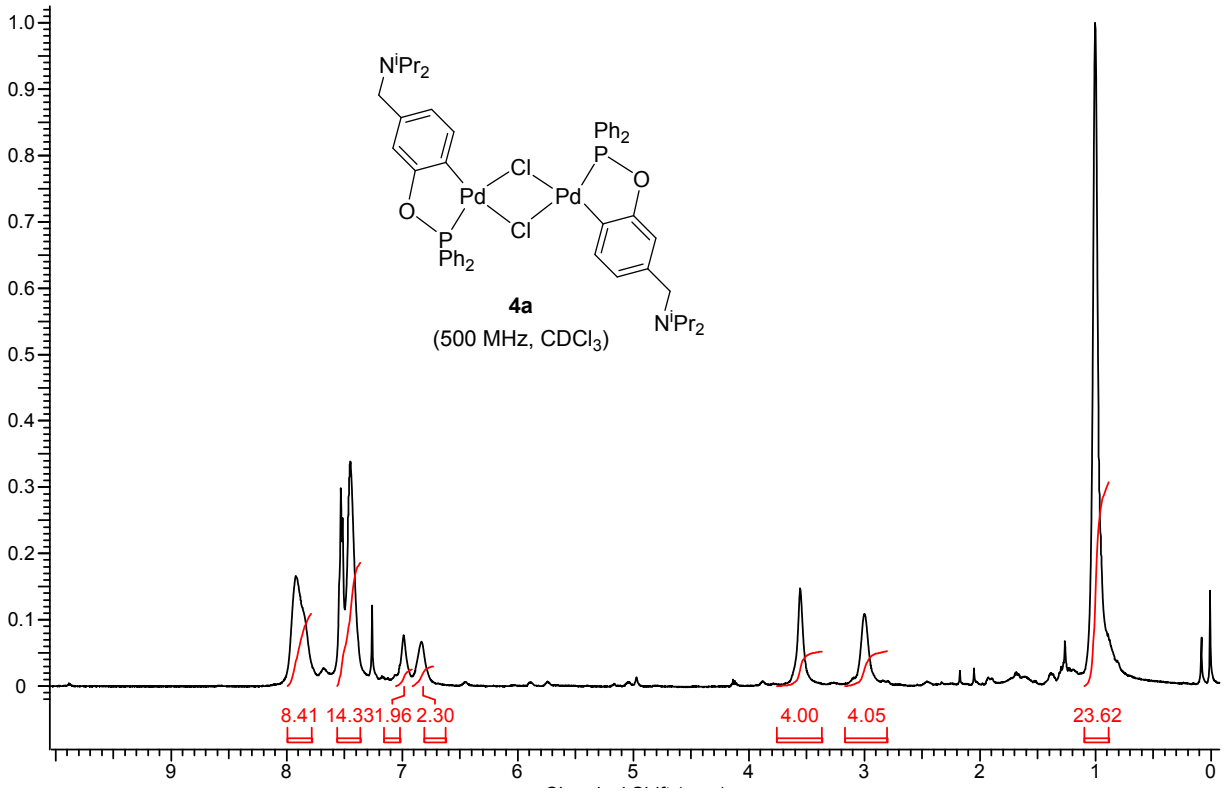

O
N
P
Pd
N
N
OAc
3b
(125 MHz, CDCl3)
175.88
157.71
153.60
140.56
126.30
114.62
108.09
107.94
60.45
56.84
40.44
40.36
24.71
21.89
19.28
14.42
0.18



3b
(202 MHz, $CDCl_3$)

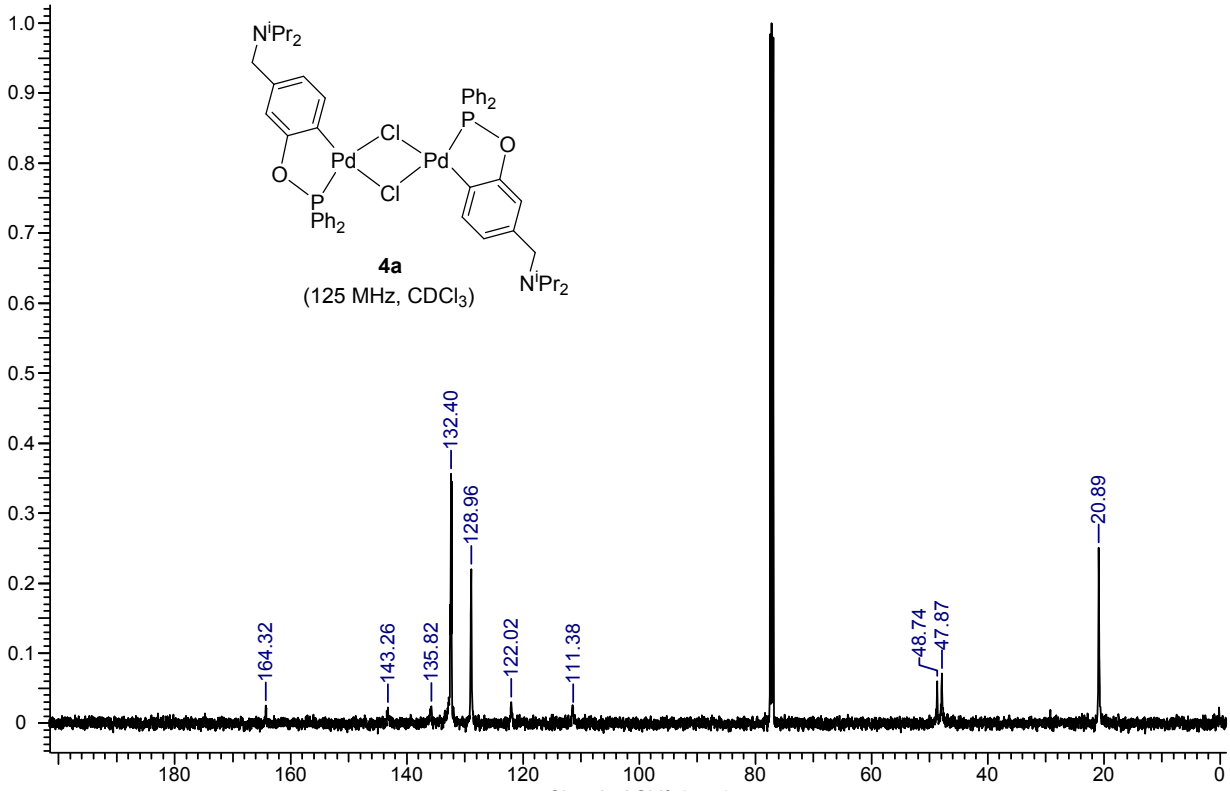


3b



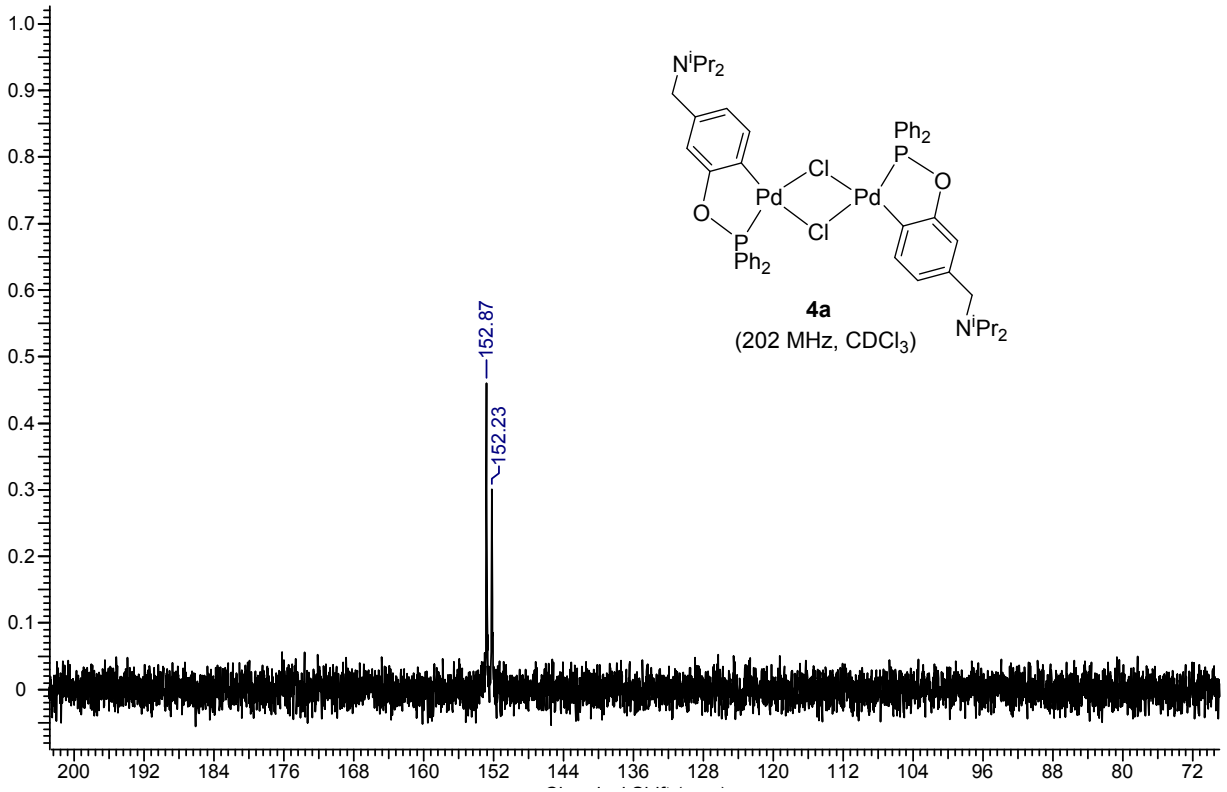
4a

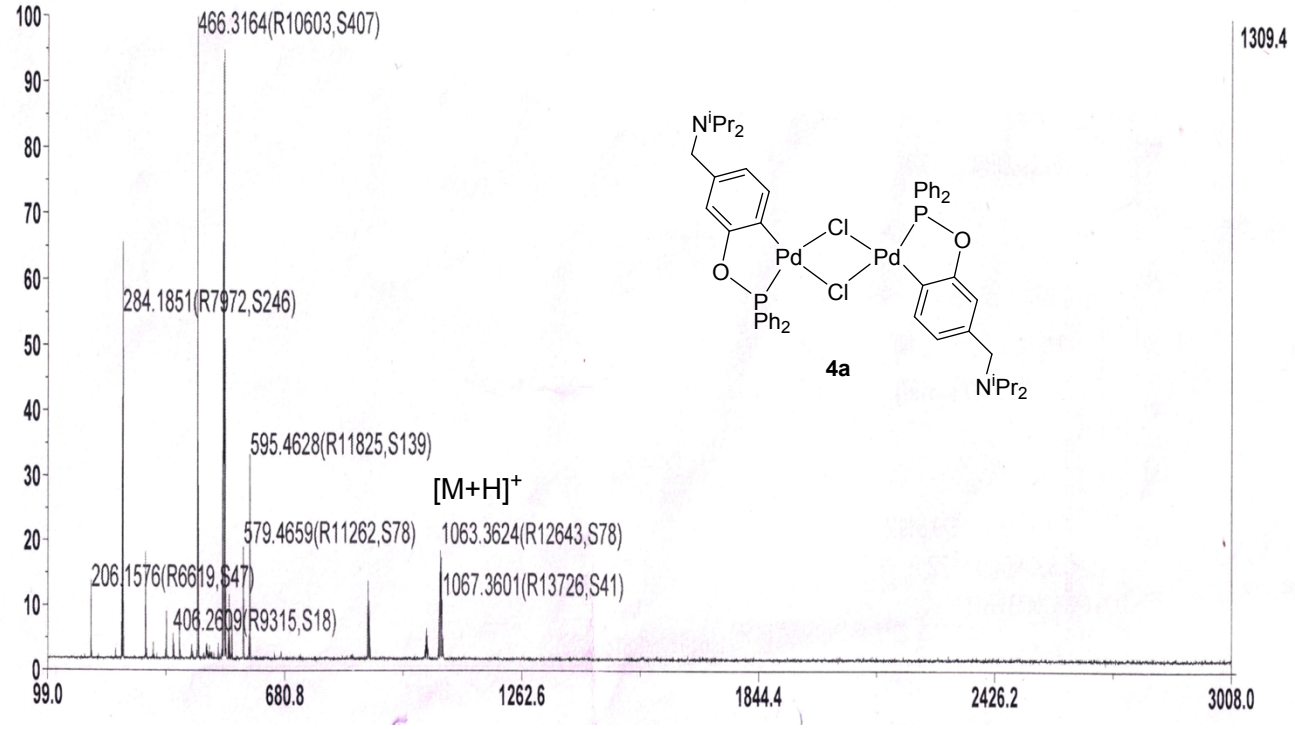
(500 MHz, $CDCl_3$)

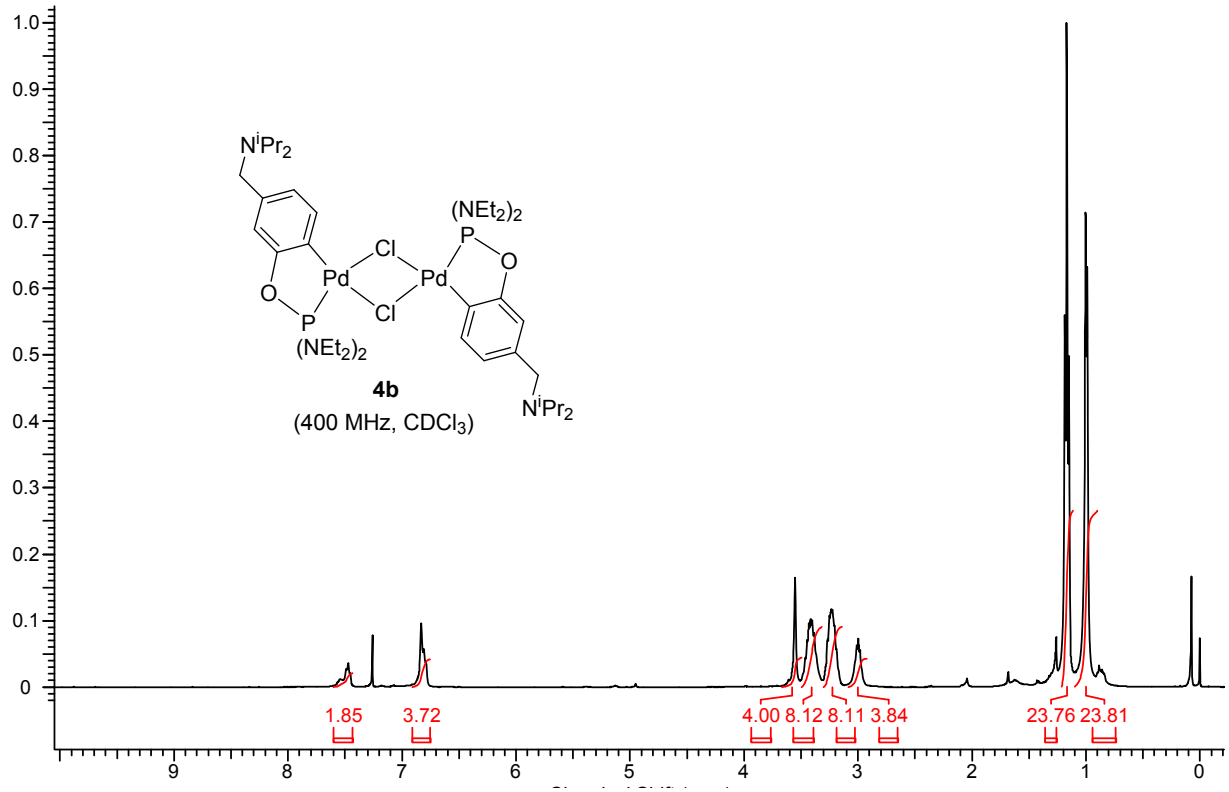


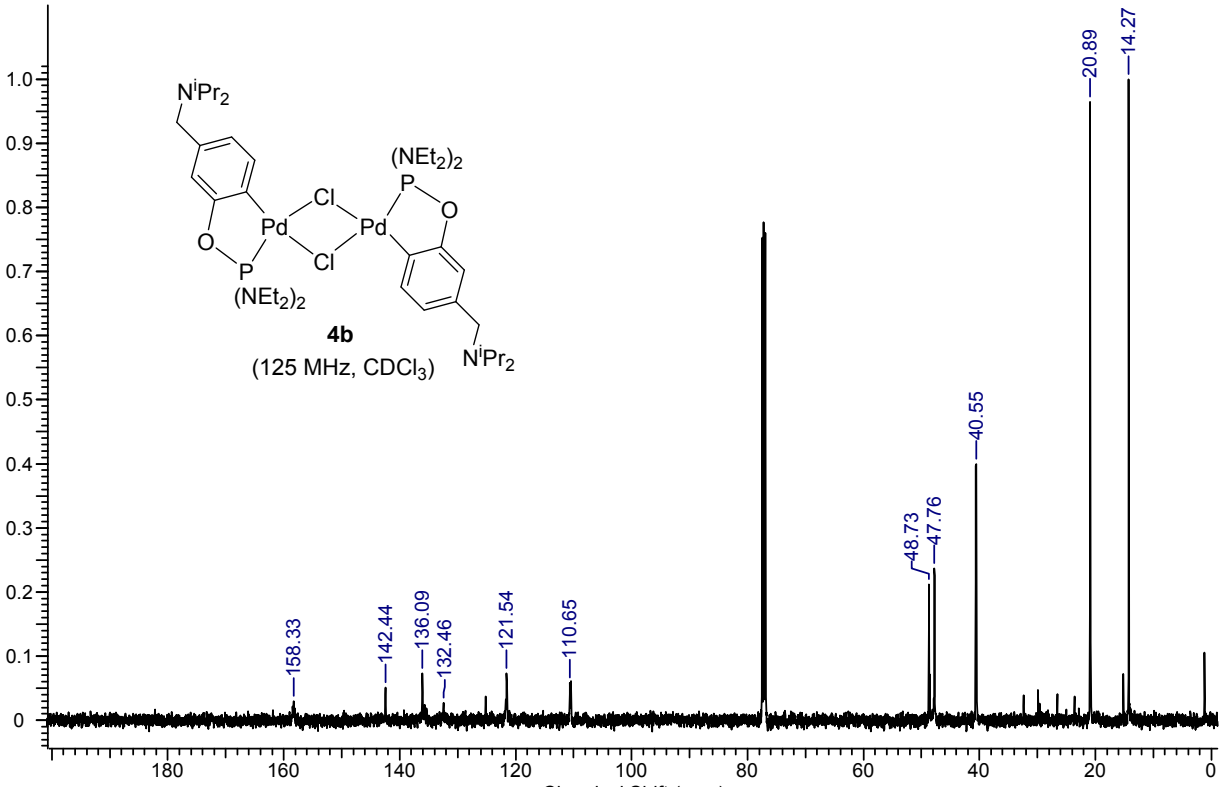
4a

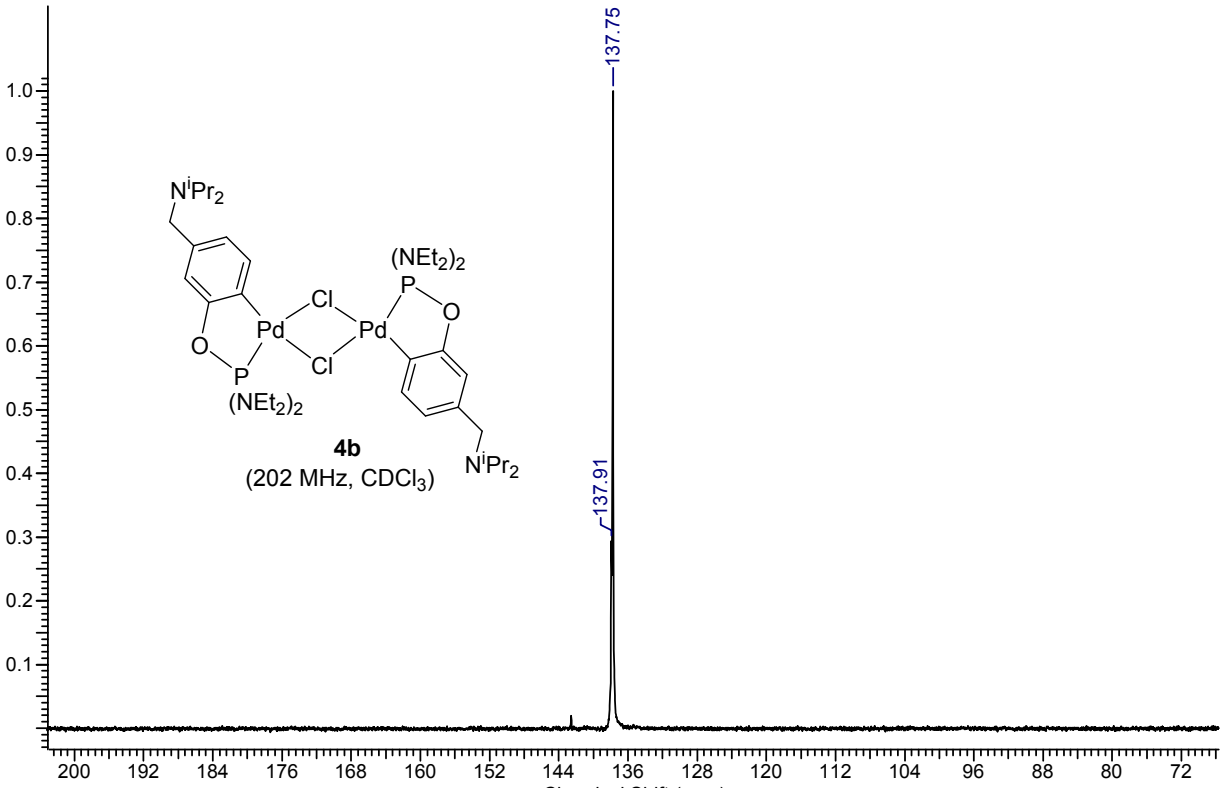
(125 MHz, $CDCl_3$)

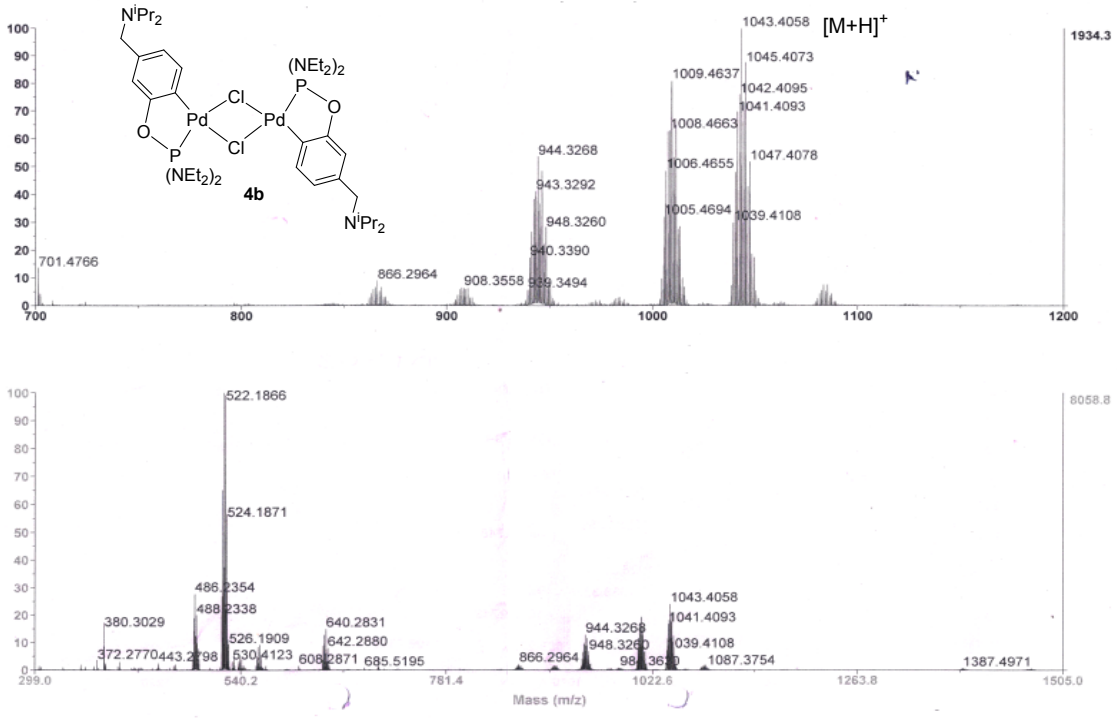

152.87
152.23
4a
(202 MHz, CDCl3)

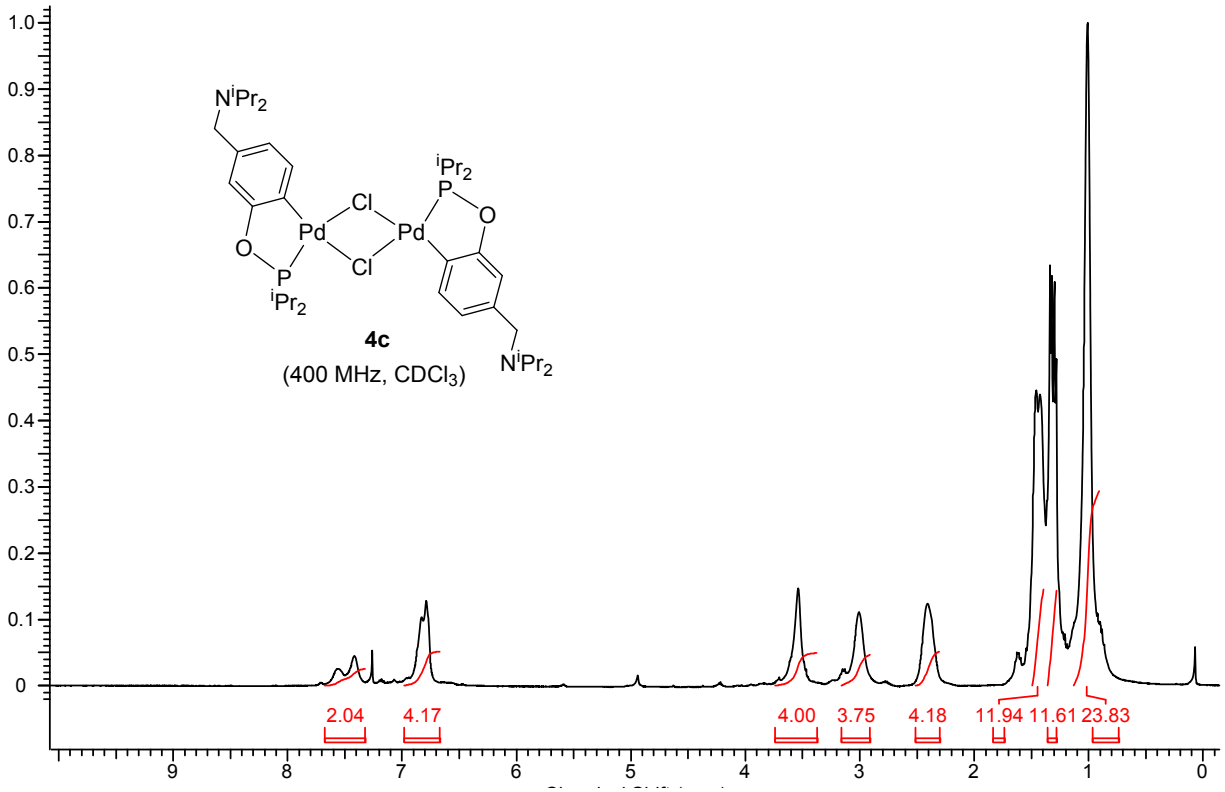

466.3164(R10603,S407)
284.1851(R7972,S246)
595.4628(R11825,S139)
[M+H]+
579.4659(R11262,S78)
1063.3624(R12643,S78)
206.1576(R6619,S47)
1067.3601(R13726,S41)
406.2609(R9315,S18)
1309.4
4a

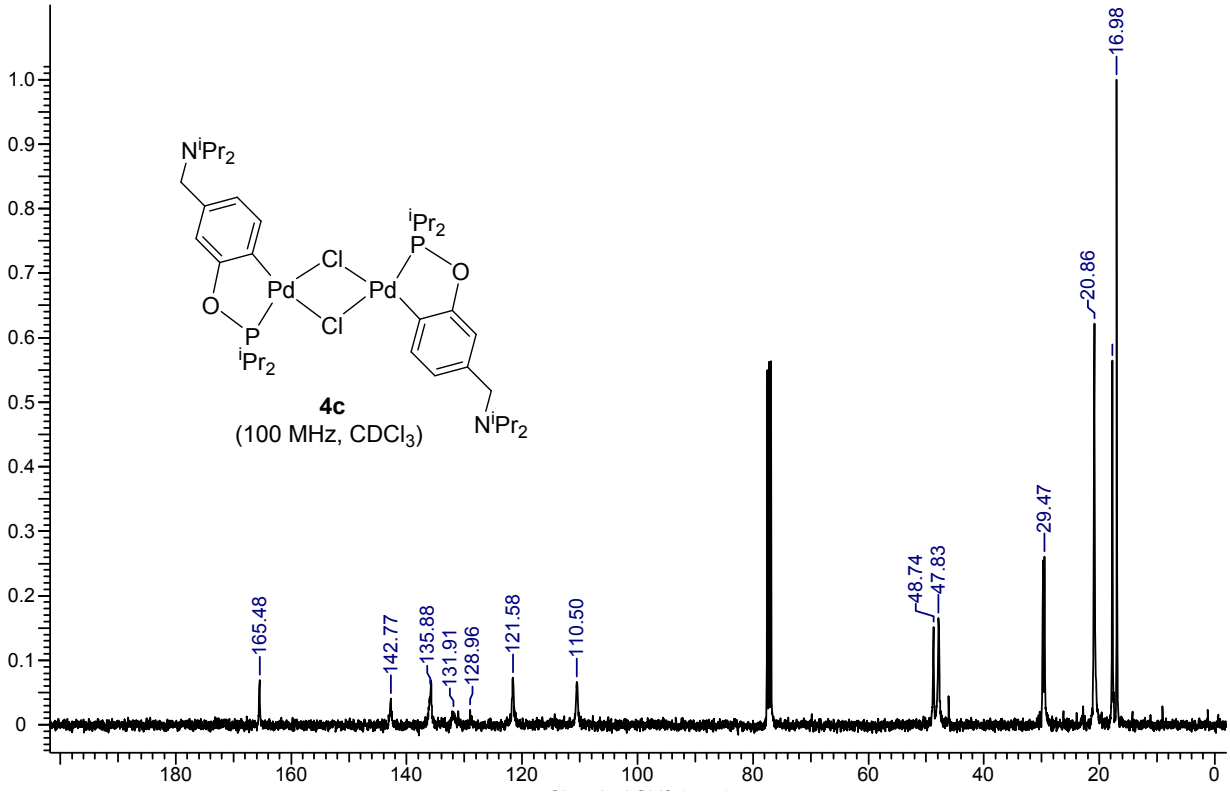

NiPr2
(NEt2)2
P
O
Cl
Pd
Pd
Cl
O
P
(NEt2)2
NiPr2
4b
(400 MHz, CDCl3)
1.85
3.72
4.00
8.12
8.11
3.84
23.76
23.81

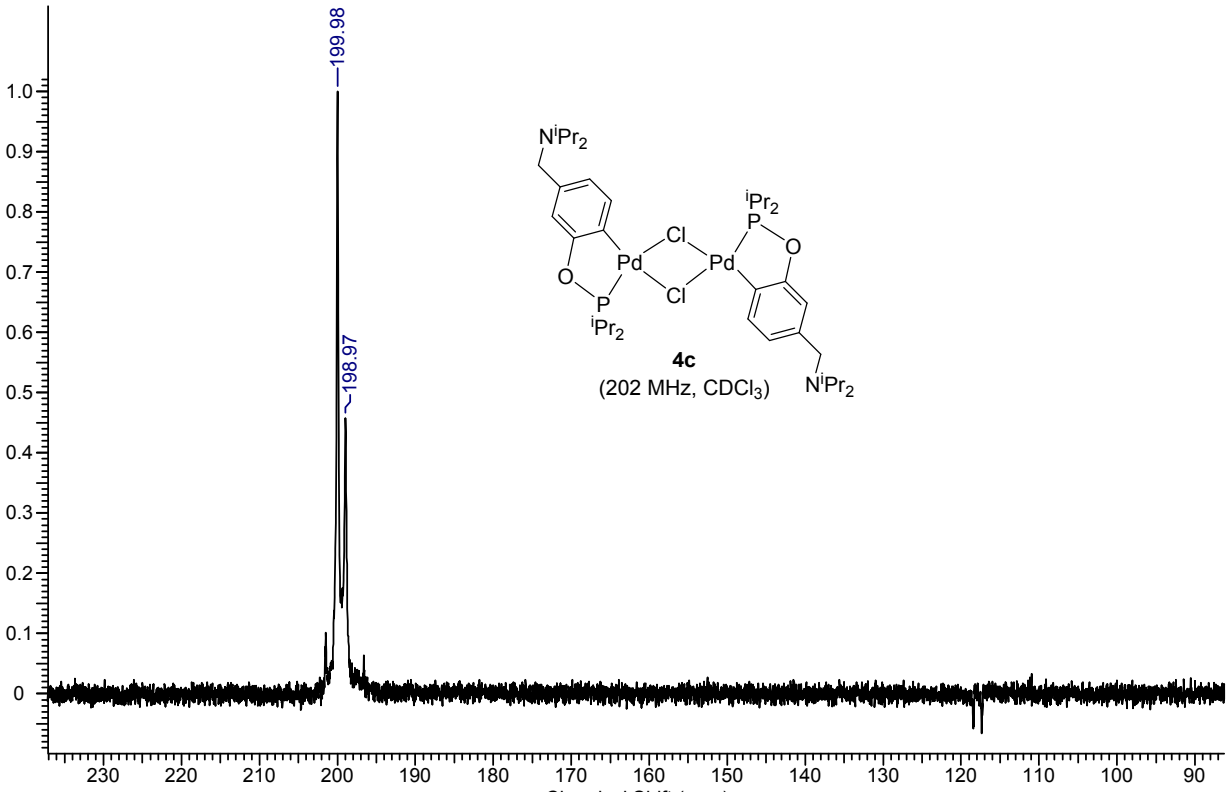

NiPr2
(NEt2)2
P
O
Cl
Pd
Pd
Cl
O
P
(NEt2)2
NiPr2
4b
(125 MHz, CDCl3)
20.89
14.27
40.55
48.73
47.76
158.33
142.44
136.09
132.46
121.54
110.65

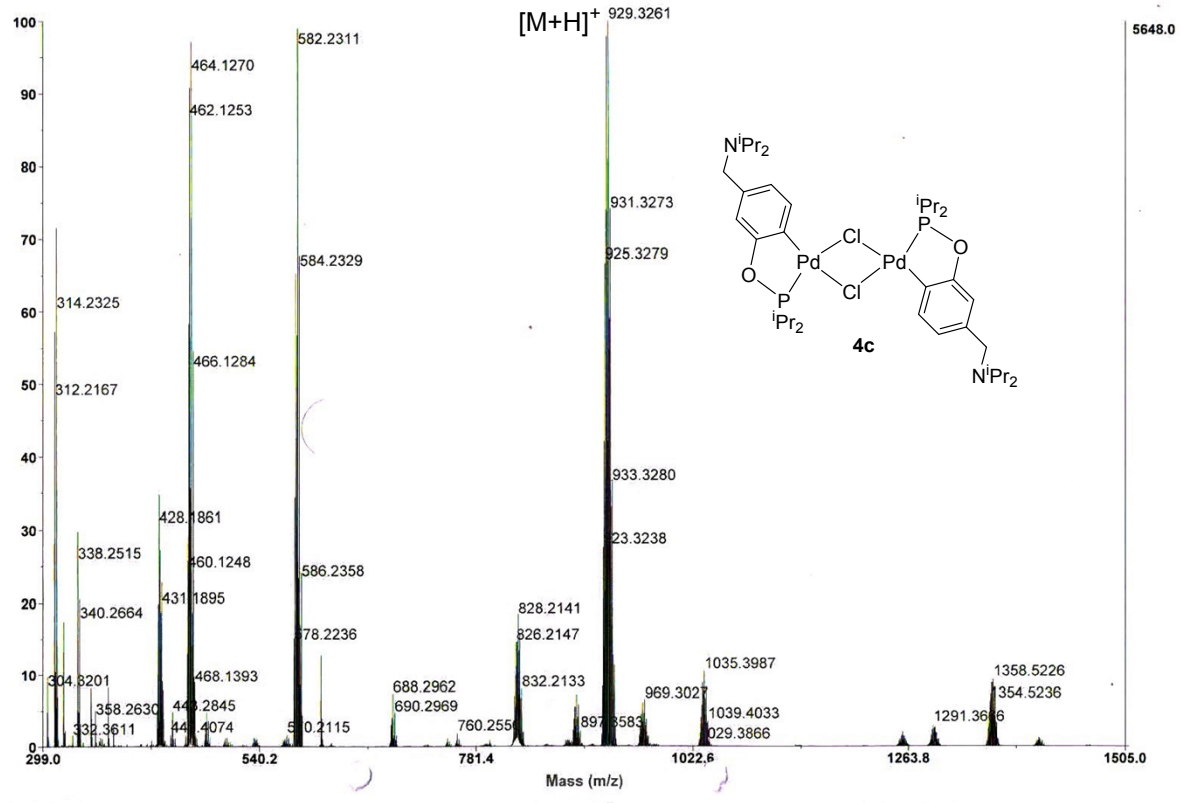

137.75
137.91
4b
(202 MHz, CDCl3)

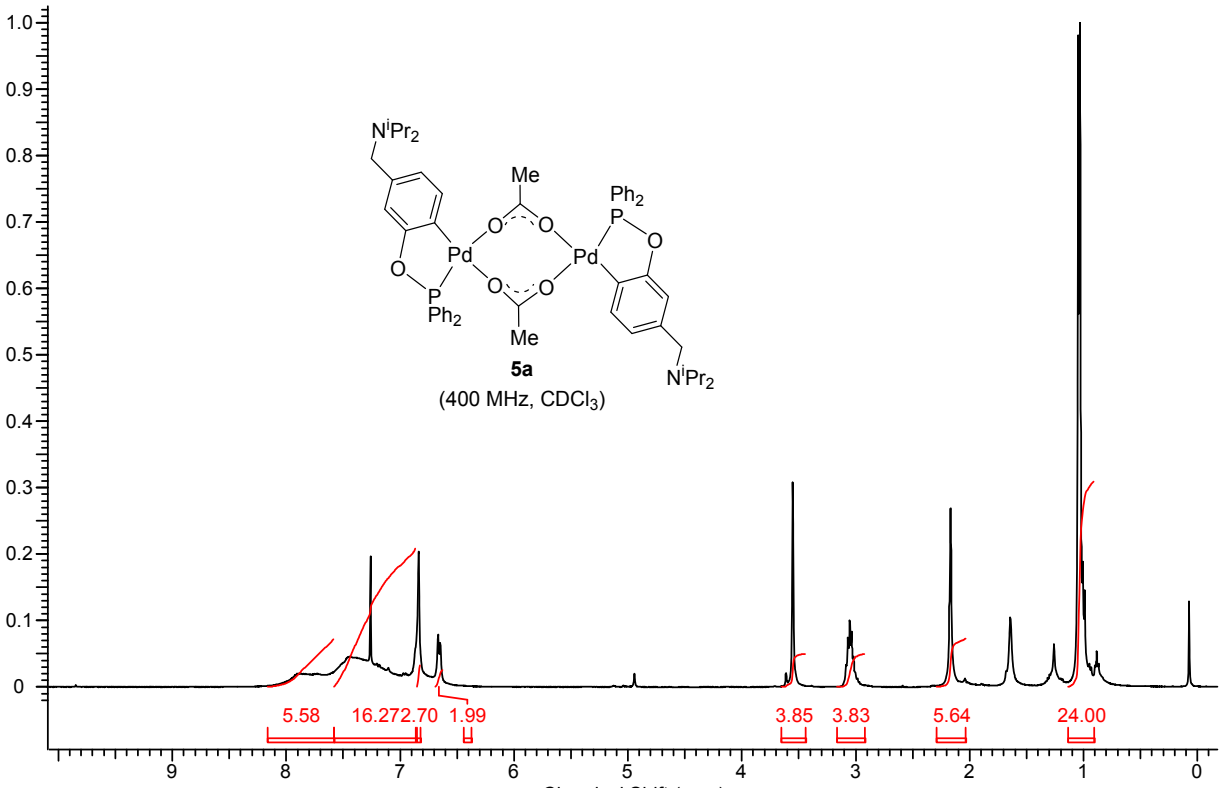

4b
[M+H]+
1043.4058
1045.4073
1009.4637
1042.4095
1041.4093
1008.4663
1047.4078
1006.4655
944.3268
943.3292
948.3260
1005.4694
1039.4108
940.3390
701.4766
866.2964
908.3558
939.3494
1934.3
522.1866
524.1871
486.2354
488.2338
380.3029
640.2831
642.2880
526.1909
372.2770
530.4123
685.5195
866.2964
1087.3754
1387.4971
8058.8
Mass (m/z)

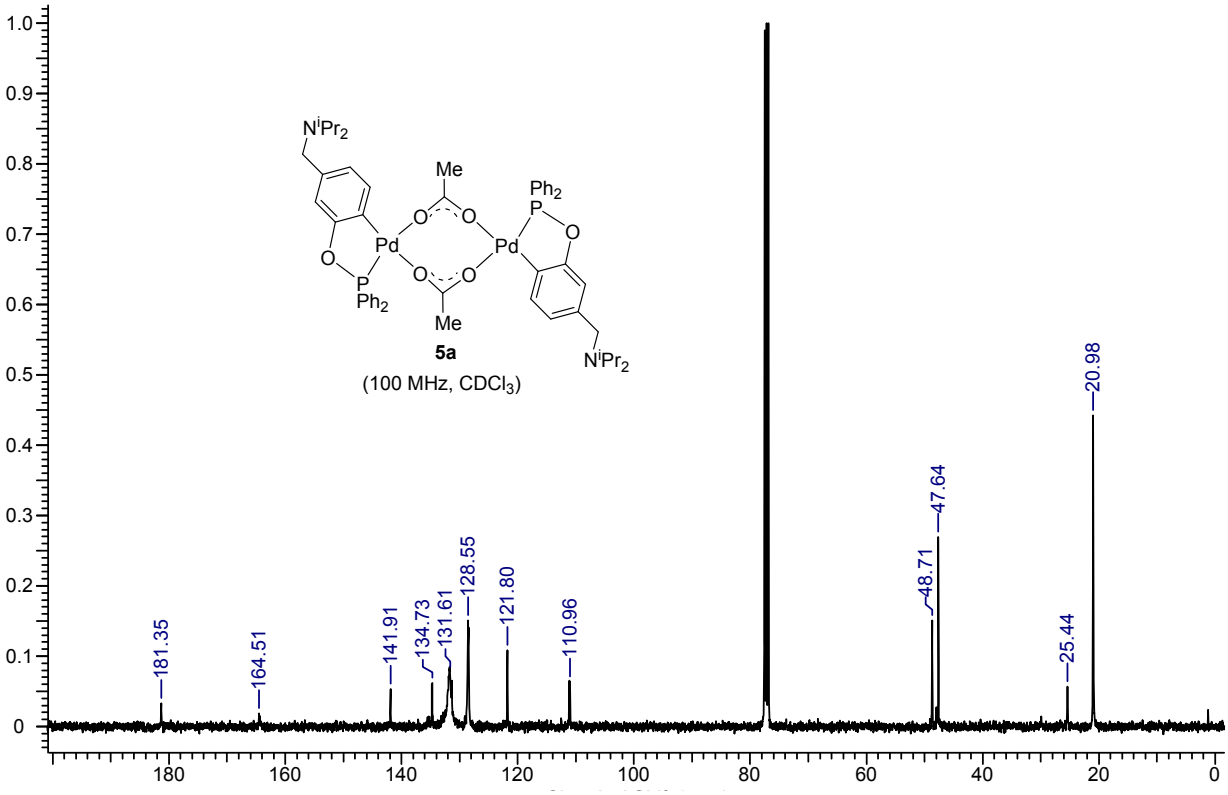

N^{i}Pr$_2$
^{i}Pr$_2$
P
O
Cl
Pd
Pd
Cl
O
P
^{i}Pr$_2$
N^{i}Pr$_2$
4c
(400 MHz, CDCl$_3$)
2.04
4.17
4.00
3.75
4.18
11.94
11.61
23.83

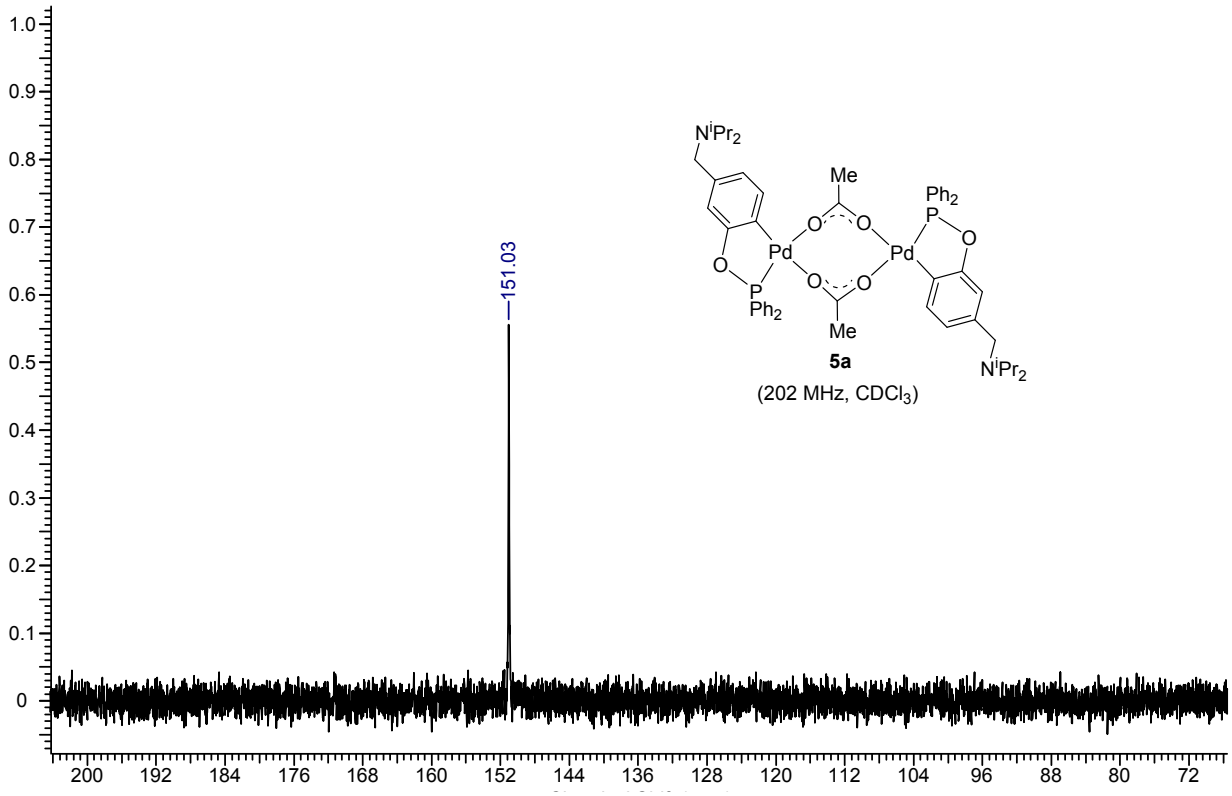

N^{i}Pr$_2$
^{i}Pr$_2$
P
O
Cl
Pd
Pd
Cl
O
P
^{i}Pr$_2$
N^{i}Pr$_2$
4c
(100 MHz, CDCl$_3$)
16.98
20.86
29.47
48.74
47.83
165.48
142.77
135.88
131.91
128.96
121.58
110.50

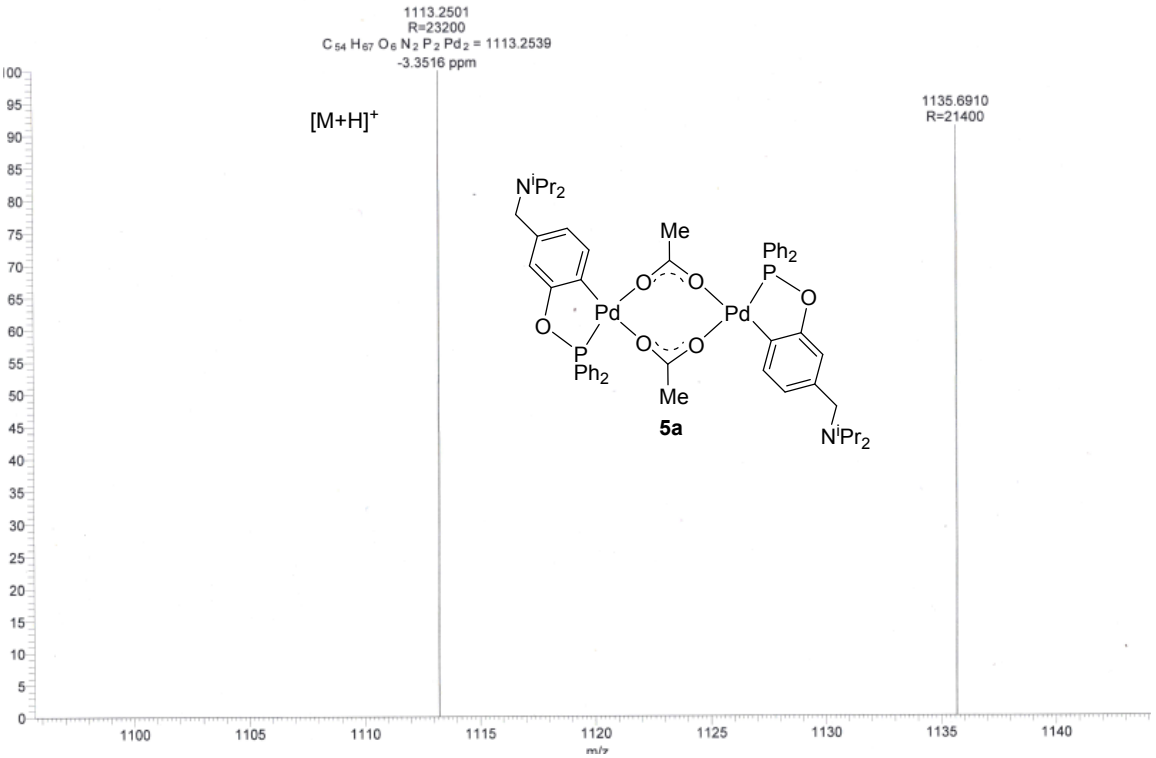

199.98
198.97
4c
(202 MHz, CDCl3)


[M+H]+
929.3261
582.2311
464.1270
462.1253
931.3273
584.2329
925.3279
314.2325
466.1284
312.2167
933.3280
428.1861
460.1248
586.2358
338.2515
340.2664
828.2141
826.2147
688.2962
690.2969
832.2133
1035.3987
969.3027
1039.4033
1358.5226
354.5236
4c
Mass (m/z)

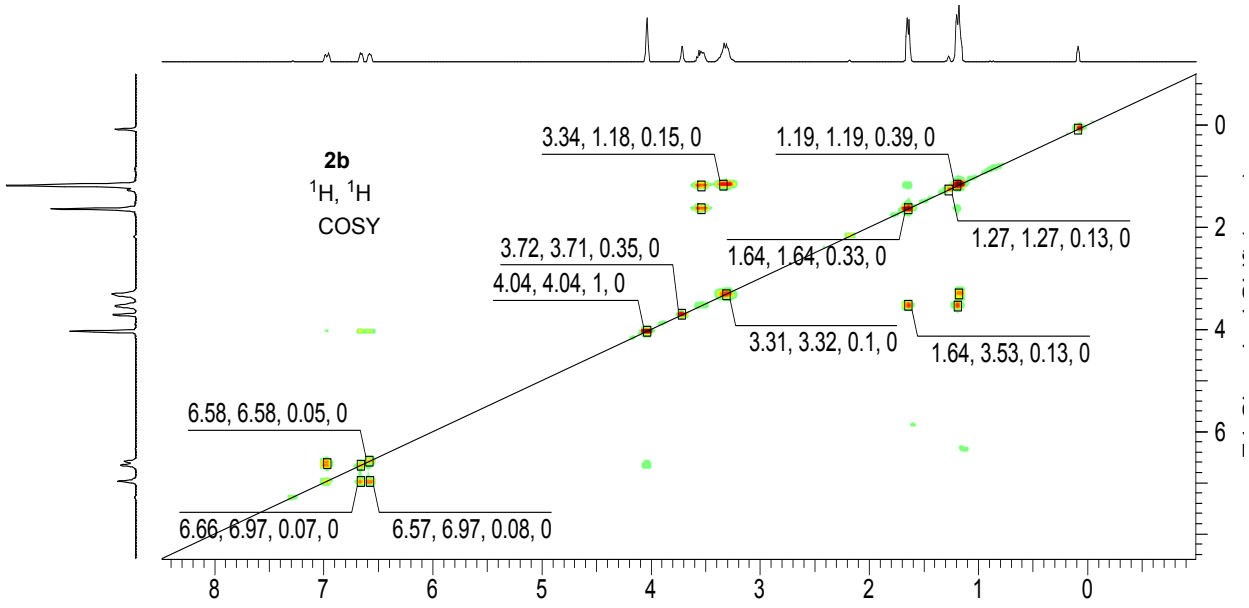

NiPr2
Me
Ph2
P
O
Pd
Pd
O
O
O
O
P
Ph2
Me
NiPr2
5a
(400 MHz, CDCl3)
5.58
16.272.70
1.99
3.85
3.83
5.64
24.00

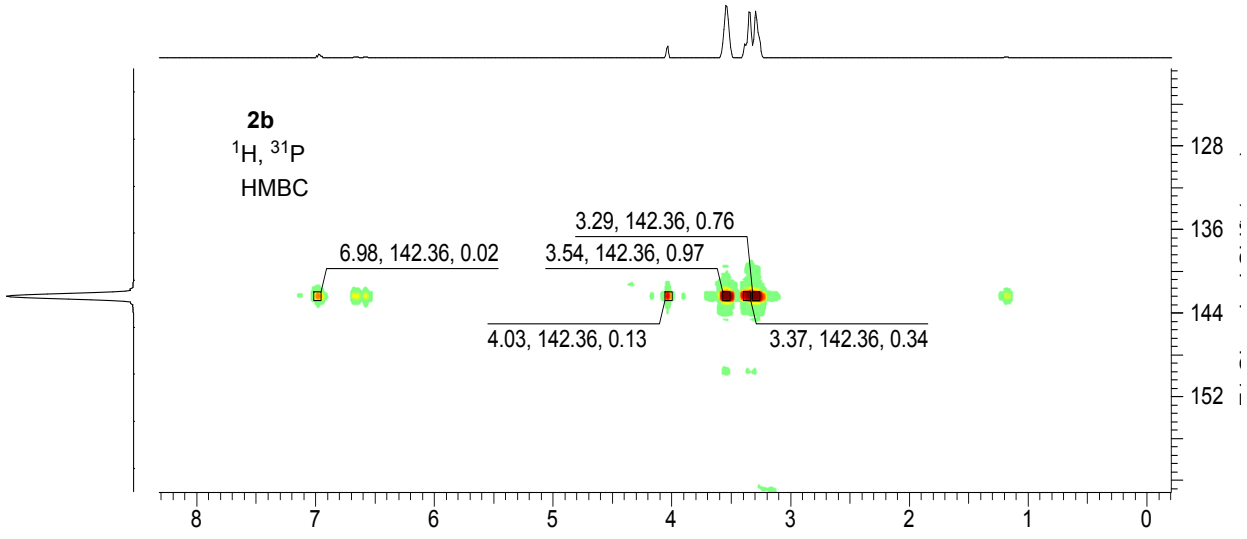

NiPr2
Me
Ph2
P
O
Pd
Pd
O
O
O
O
P
Ph2
Me
NiPr2
5a
(100 MHz, CDCl3)
181.35
164.51
141.91
134.73
131.61
128.55
121.80
110.96
48.71
47.64
25.44
20.98

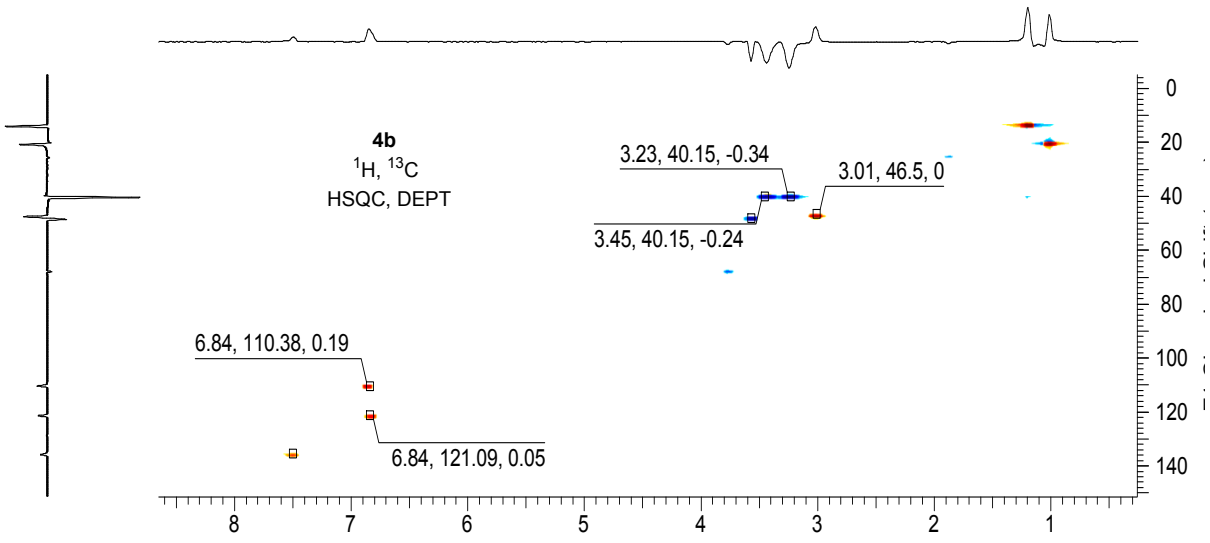

151.03
N^{i}Pr$_2$
Me
Ph$_2$
P
O
Pd
Pd
O
P
Ph$_2$
Me
N^{i}Pr$_2$
5a
(202 MHz, CDCl$_3$)

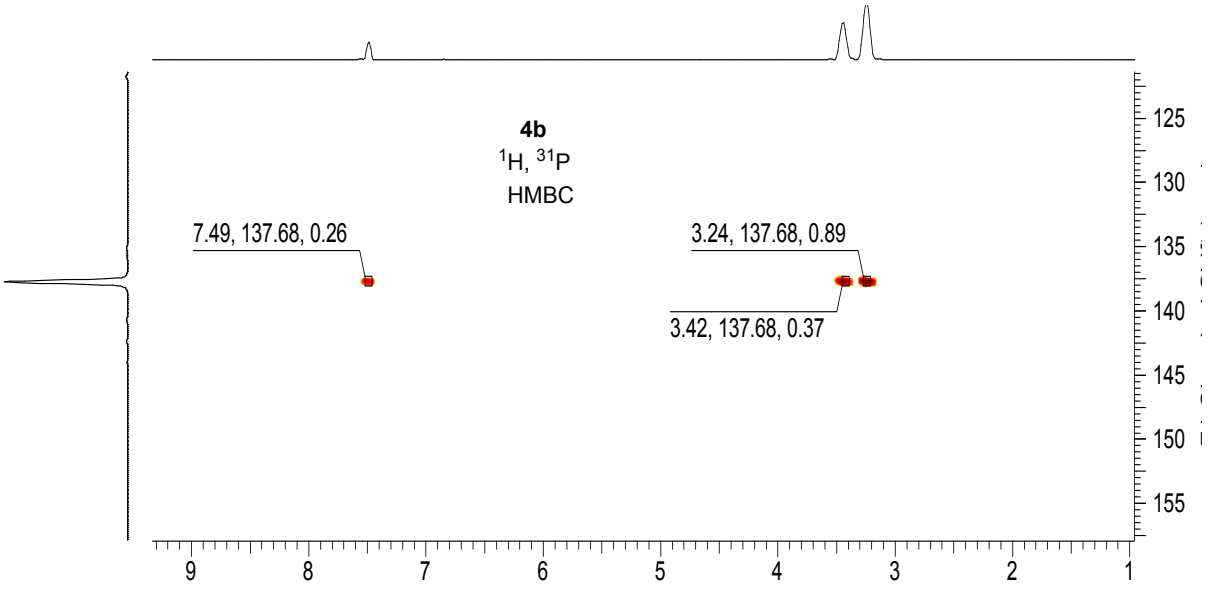

1113.2501
R=23200
C$_{54}$ H$_{67}$ O$_6$ N$_2$ P$_2$ Pd$_2$ = 1113.2539
-3.3516 ppm
[M+H]$^+$
1135.6910
R=21400
N^{i}Pr$_2$
Me
Ph$_2$
P
O
Pd
Pd
O
P
Ph$_2$
Me
N^{i}Pr$_2$
5a

6. 2D NMR spectra of **2b** and **4b**

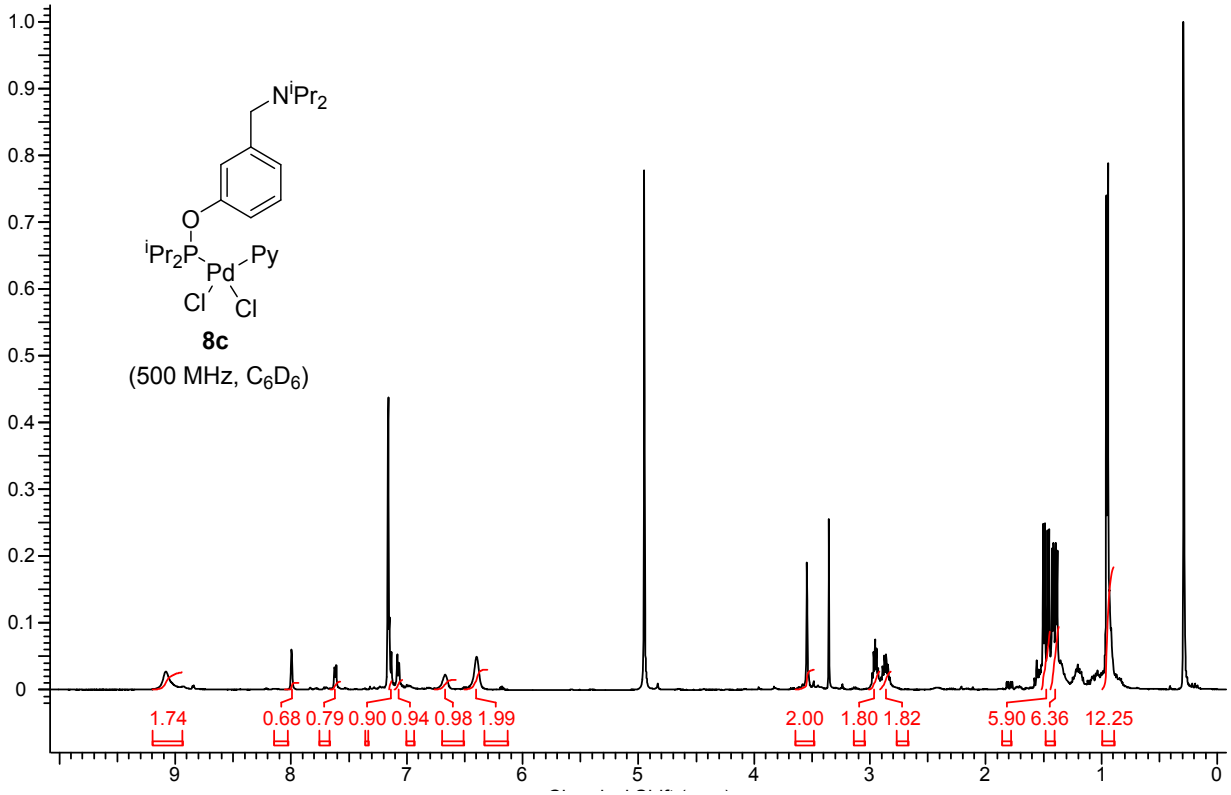


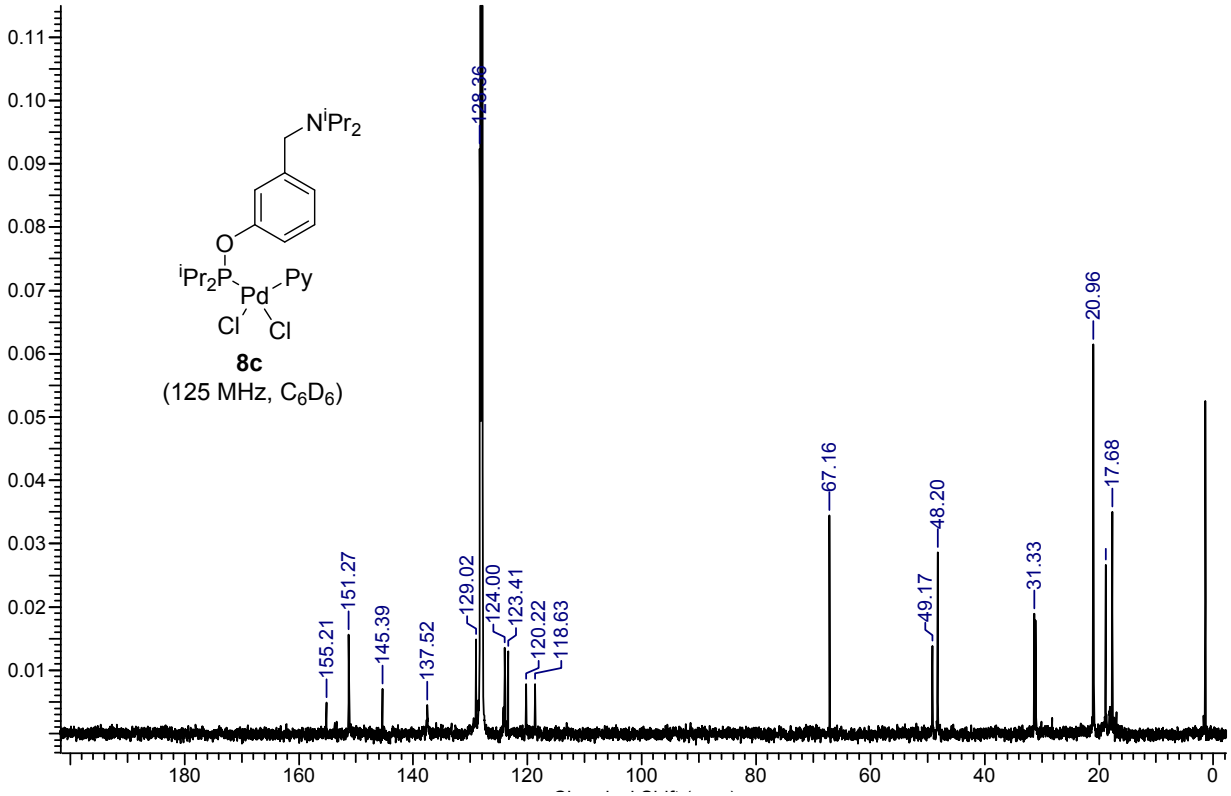


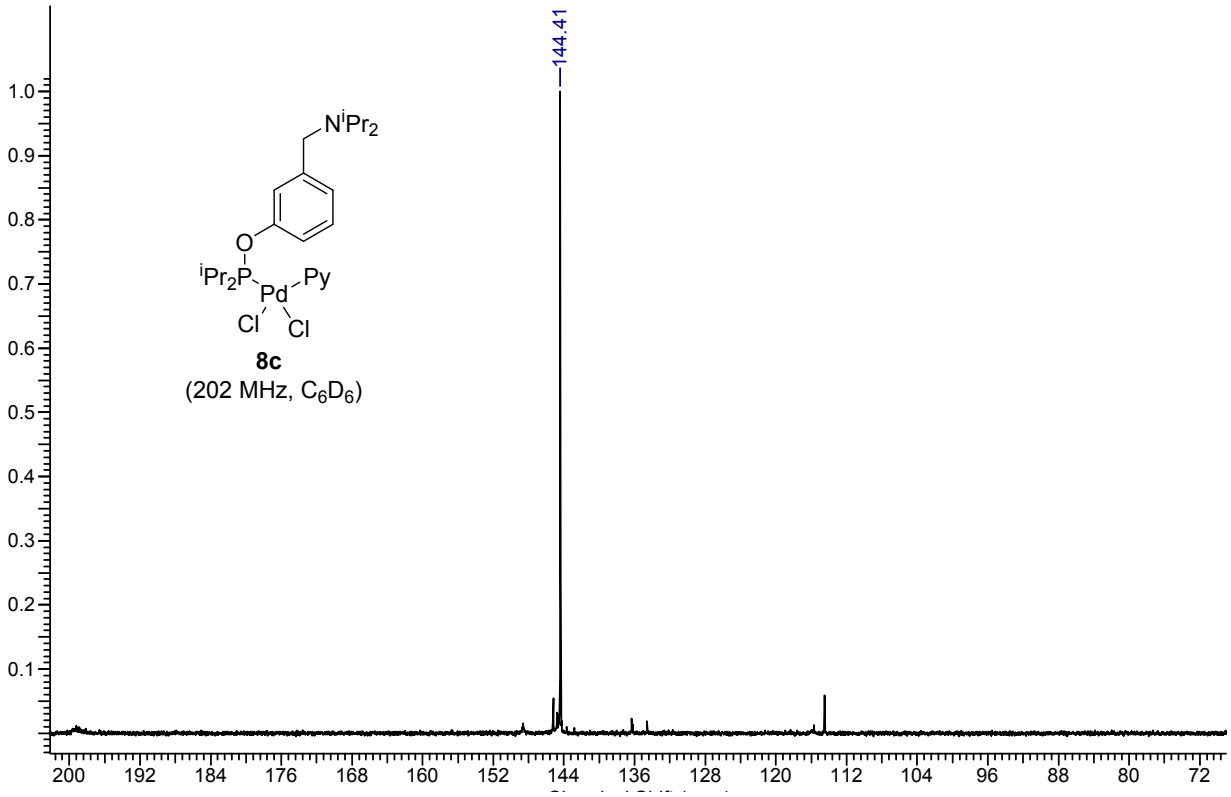

4b
^{1}H, ^{13}C
HSQC, DEPT
3.23, 40.15, -0.34
3.01, 46.5, 0
3.45, 40.15, -0.24
6.84, 110.38, 0.19
6.84, 121.09, 0.05

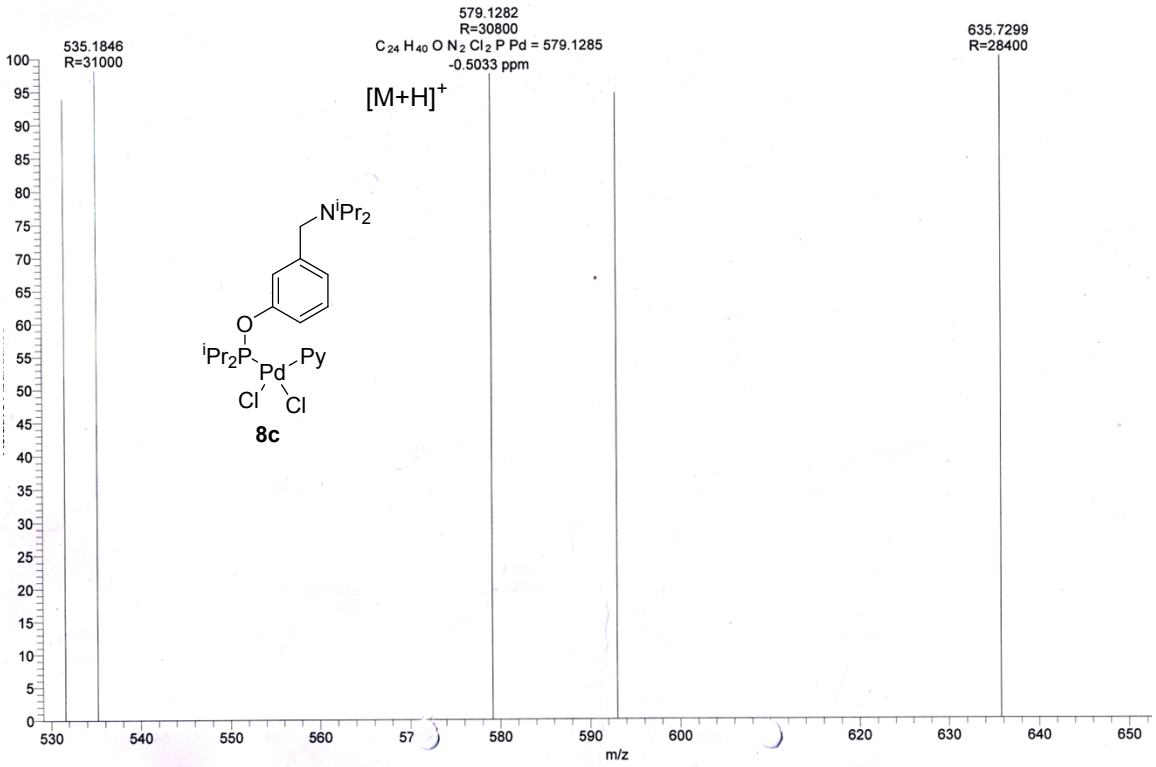

4b
^{1}H, ^{31}P
HMBC
7.49, 137.68, 0.26
3.24, 137.68, 0.89
3.42, 137.68, 0.37

7. NMR and mass spectra of **8c**






144.41
N^{i}Pr$_2$
O
^{i}Pr$_2$P
Pd
Py
Cl
Cl
8c
(202 MHz, C$_6$D$_6$)


535.1846
R=31000
579.1282
R=30800
C 24 H 40 O N 2 Cl 2 P Pd = 579.1285
-0.5033 ppm
[M+H]+
635.7299
R=28400
N^{i}Pr$_2$
O
^{i}Pr$_2$P
Pd
Py
Cl
Cl
8c
m/z

8. Bond lengths [Å] and bond angles [°] of the complexes

Bond lengths [Å] and bond angles [°] for **2a**

Pd(1)-C(1)	1.9514(16)	C(11)-C(13)	1.519(3)
Pd(1)-P(1)	2.1885(4)	C(11)-H(11)	0.9800
Pd(1)-N(1)	2.2032(13)	C(12)-H(12A)	0.9600
Pd(1)-Cl(1)	2.3848(4)	C(12)-H(12B)	0.9600
P(1)-O(1)	1.6498(11)	C(12)-H(12C)	0.9600
P(1)-C(20)	1.8053(17)	C(13)-H(13A)	0.9600
P(1)-C(14)	1.8125(16)	C(13)-H(13B)	0.9600
O(1)-C(2)	1.396(2)	C(13)-H(13C)	0.9600
N(1)-C(7)	1.508(2)	C(14)-C(19)	1.391(2)
N(1)-C(8)	1.516(2)	C(14)-C(15)	1.394(2)
N(1)-C(11)	1.525(2)	C(15)-C(16)	1.386(3)
C(1)-C(2)	1.386(2)	C(15)-H(15)	0.9300
C(1)-C(6)	1.392(2)	C(16)-C(17)	1.382(3)
C(2)-C(3)	1.382(2)	C(16)-H(16)	0.9300
C(3)-C(4)	1.390(3)	C(17)-C(18)	1.386(3)
C(3)-H(3)	0.9300	C(17)-H(17)	0.9300
C(4)-C(5)	1.389(3)	C(18)-C(19)	1.388(3)
C(4)-H(4)	0.9300	C(18)-H(18)	0.9300
C(5)-C(6)	1.395(2)	C(19)-H(19)	0.9300
C(5)-H(5)	0.9300	C(20)-C(25)	1.389(2)
C(6)-C(7)	1.497(2)	C(20)-C(21)	1.390(2)
C(7)-H(7A)	0.9700	C(21)-C(22)	1.391(3)
C(7)-H(7B)	0.9700	C(21)-H(21)	0.9300
C(8)-C(10)	1.524(3)	C(22)-C(23)	1.377(3)
C(8)-C(9)	1.529(3)	C(22)-H(22)	0.9300
C(8)-H(8)	0.9800	C(23)-C(24)	1.385(3)
C(9)-H(9A)	0.9600	C(23)-H(23)	0.9300
C(9)-H(9B)	0.9600	C(24)-C(25)	1.391(2)
C(9)-H(9C)	0.9600	C(24)-H(24)	0.9300
C(10)-H(10A)	0.9600	C(25)-H(25)	0.9300
C(10)-H(10B)	0.9600		
C(10)-H(10C)	0.9600		
C(11)-C(12)	1.513(2)		

C(1)-Pd(1)-P(1)	80.52(5)	C(1)-C(6)-C(7)	116.98(15)
C(1)-Pd(1)-N(1)	81.72(6)	C(5)-C(6)-C(7)	123.57(15)
P(1)-Pd(1)-N(1)	161.10(4)	C(6)-C(7)-N(1)	112.08(13)
C(1)-Pd(1)-Cl(1)	176.08(5)	C(6)-C(7)-H(7A)	109.2
P(1)-Pd(1)-Cl(1)	98.672(16)	N(1)-C(7)-H(7A)	109.2
N(1)-Pd(1)-Cl(1)	99.48(4)	C(6)-C(7)-H(7B)	109.2
O(1)-P(1)-C(20)	102.66(7)	N(1)-C(7)-H(7B)	109.2
O(1)-P(1)-C(14)	101.65(7)	H(7A)-C(7)-H(7B)	107.9
C(20)-P(1)-C(14)	105.67(7)	N(1)-C(8)-C(10)	111.60(15)
O(1)-P(1)-Pd(1)	107.18(4)	N(1)-C(8)-C(9)	113.64(15)
C(20)-P(1)-Pd(1)	117.03(5)	C(10)-C(8)-C(9)	111.03(17)
C(14)-P(1)-Pd(1)	120.19(5)	N(1)-C(8)-H(8)	106.7
C(2)-O(1)-P(1)	112.28(10)	C(10)-C(8)-H(8)	106.7
C(7)-N(1)-C(8)	110.36(13)	C(9)-C(8)-H(8)	106.7
C(7)-N(1)-C(11)	107.79(12)	C(8)-C(9)-H(9A)	109.5
C(8)-N(1)-C(11)	112.02(13)	C(8)-C(9)-H(9B)	109.5
C(7)-N(1)-Pd(1)	107.65(10)	H(9A)-C(9)-H(9B)	109.5
C(8)-N(1)-Pd(1)	109.14(10)	C(8)-C(9)-H(9C)	109.5
C(11)-N(1)-Pd(1)	109.77(10)	H(9A)-C(9)-H(9C)	109.5
C(2)-C(1)-C(6)	119.31(15)	H(9B)-C(9)-H(9C)	109.5
C(2)-C(1)-Pd(1)	122.34(12)	C(8)-C(10)-H(10A)	109.5
C(6)-C(1)-Pd(1)	118.35(12)	C(8)-C(10)-H(10B)	109.5
C(3)-C(2)-C(1)	122.31(15)	H(10A)-C(10)-H(10B)	109.5
C(3)-C(2)-O(1)	120.04(15)	C(8)-C(10)-H(10C)	109.5
C(1)-C(2)-O(1)	117.65(14)	H(10A)-C(10)-H(10C)	109.5
C(2)-C(3)-C(4)	117.75(16)	H(10B)-C(10)-H(10C)	109.5
C(2)-C(3)-H(3)	121.1	C(12)-C(11)-C(13)	109.60(16)
C(4)-C(3)-H(3)	121.1	C(12)-C(11)-N(1)	112.68(14)
C(5)-C(4)-C(3)	121.33(16)	C(13)-C(11)-N(1)	111.60(14)
C(5)-C(4)-H(4)	119.3	C(12)-C(11)-H(11)	107.6
C(3)-C(4)-H(4)	119.3	C(13)-C(11)-H(11)	107.6
C(4)-C(5)-C(6)	119.89(16)	N(1)-C(11)-H(11)	107.6
C(4)-C(5)-H(5)	120.1	C(11)-C(12)-H(12A)	109.5
C(6)-C(5)-H(5)	120.1	C(11)-C(12)-H(12B)	109.5
C(1)-C(6)-C(5)	119.41(16)	H(12A)-C(12)-H(12B)	109.5

C(11)-C(12)-H(12C)	109.5	C(21)-C(22)-H(22)	119.8
H(12A)-C(12)-H(12C)	109.5	C(22)-C(23)-C(24)	120.04(16)
H(12B)-C(12)-H(12C)	109.5	C(22)-C(23)-H(23)	120.0
C(11)-C(13)-H(13A)	109.5	C(24)-C(23)-H(23)	120.0
C(11)-C(13)-H(13B)	109.5	C(23)-C(24)-C(25)	120.16(17)
H(13A)-C(13)-H(13B)	109.5	C(23)-C(24)-H(24)	119.9
C(11)-C(13)-H(13C)	109.5	C(25)-C(24)-H(24)	119.9
H(13A)-C(13)-H(13C)	109.5	C(20)-C(25)-C(24)	119.83(16)
H(13B)-C(13)-H(13C)	109.5	C(20)-C(25)-H(25)	120.1
C(19)-C(14)-C(15)	119.16(16)	C(24)-C(25)-H(25)	120.1
C(19)-C(14)-P(1)	122.24(13)		
C(15)-C(14)-P(1)	118.53(12)		
C(16)-C(15)-C(14)	120.36(16)		
C(16)-C(15)-H(15)	119.8		
C(14)-C(15)-H(15)	119.8		
C(17)-C(16)-C(15)	120.29(17)		
C(17)-C(16)-H(16)	119.9		
C(15)-C(16)-H(16)	119.9		
C(16)-C(17)-C(18)	119.68(17)		
C(16)-C(17)-H(17)	120.2		
C(18)-C(17)-H(17)	120.2		
C(17)-C(18)-C(19)	120.38(17)		
C(17)-C(18)-H(18)	119.8		
C(19)-C(18)-H(18)	119.8		
C(18)-C(19)-C(14)	120.10(16)		
C(18)-C(19)-H(19)	119.9		
C(14)-C(19)-H(19)	119.9		
C(25)-C(20)-C(21)	119.81(16)		
C(25)-C(20)-P(1)	118.29(12)		
C(21)-C(20)-P(1)	121.88(13)		
C(20)-C(21)-C(22)	119.85(16)		
C(20)-C(21)-H(21)	120.1		
C(22)-C(21)-H(21)	120.1		
C(23)-C(22)-C(21)	120.31(16)		
C(23)-C(22)-H(22)	119.8		

Bond lengths [Å] and bond angles [°] for **2b**

Pd(1)-C(1)	1.960(2)	C(10)-H(10B)	0.9600
Pd(1)-P(1)	2.1951(6)	C(10)-H(10C)	0.9600
Pd(1)-N(1)	2.2361(16)	C(11)-C(12)	1.524(3)
Pd(1)-Cl(1)	2.4082(6)	C(11)-C(13)	1.527(3)
P(1)-N(3)	1.637(2)	C(11)-H(11)	0.9800
P(1)-O(1)	1.6524(16)	C(12)-H(12A)	0.9600
P(1)-N(2)	1.658(2)	C(12)-H(12B)	0.9600
O(1)-C(2)	1.393(3)	C(12)-H(12C)	0.9600
N(1)-C(11)	1.511(3)	C(13)-H(13A)	0.9600
N(1)-C(7)	1.509(3)	C(13)-H(13B)	0.9600
N(1)-C(8)	1.510(3)	C(13)-H(13C)	0.9600
N(2)-C(16)	1.458(3)	C(14)-C(15)	1.507(4)
N(2)-C(14)	1.472(3)	C(14)-H(14A)	0.9700
N(3)-C(20)	1.470(3)	C(14)-H(14B)	0.9700
N(3)-C(18)	1.468(3)	C(15)-H(15A)	0.9600
C(1)-C(2)	1.381(3)	C(15)-H(15B)	0.9600
C(1)-C(6)	1.388(3)	C(15)-H(15C)	0.9600
C(2)-C(3)	1.384(3)	C(16)-C(17)	1.497(5)
C(3)-C(4)	1.387(4)	C(16)-H(16A)	0.9700
C(3)-H(3)	0.9300	C(16)-H(16B)	0.9700
C(4)-C(5)	1.383(4)	C(17)-H(17A)	0.9600
C(4)-H(4)	0.9300	C(17)-H(17B)	0.9600
C(5)-C(6)	1.398(3)	C(17)-H(17C)	0.9600
C(5)-H(5)	0.9300	C(18)-C(19)	1.509(4)
C(6)-C(7)	1.499(3)	C(18)-H(18A)	0.9700
C(7)-H(7A)	0.9700	C(18)-H(18B)	0.9700
C(7)-H(7B)	0.9700	C(19)-H(19A)	0.9600
C(8)-C(9)	1.521(4)	C(19)-H(19B)	0.9600
C(8)-C(10)	1.521(3)	C(19)-H(19C)	0.9600
C(8)-H(8)	0.9800	C(20)-C(21)	1.503(4)
C(9)-H(9A)	0.9600	C(20)-H(20A)	0.9700
C(9)-H(9B)	0.9600	C(20)-H(20B)	0.9700
C(9)-H(9C)	0.9600	C(21)-H(21A)	0.9600
C(10)-H(10A)	0.9600	C(21)-H(21B)	0.9600
C(21)-H(21C)	0.9600		

C(1)-Pd(1)-P(1)	80.26(6)	C(5)-C(4)-H(4)	119.3
C(1)-Pd(1)-N(1)	81.09(8)	C(3)-C(4)-H(4)	119.3
P(1)-Pd(1)-N(1)	161.30(5)	C(4)-C(5)-C(6)	120.2(2)
C(1)-Pd(1)-Cl(1)	176.84(6)	C(4)-C(5)-H(5)	119.9
P(1)-Pd(1)-Cl(1)	97.42(2)	C(6)-C(5)-H(5)	119.9
N(1)-Pd(1)-Cl(1)	101.27(5)	C(1)-C(6)-C(5)	118.8(2)
N(3)-P(1)-O(1)	105.48(9)	C(1)-C(6)-C(7)	117.27(19)
N(3)-P(1)-N(2)	105.96(10)	C(5)-C(6)-C(7)	123.9(2)
O(1)-P(1)-N(2)	97.93(10)	C(6)-C(7)-N(1)	111.96(17)
N(3)-P(1)-Pd(1)	115.53(8)	C(6)-C(7)-H(7A)	109.2
O(1)-P(1)-Pd(1)	105.99(6)	N(1)-C(7)-H(7A)	109.2
N(2)-P(1)-Pd(1)	123.19(7)	C(6)-C(7)-H(7B)	109.2
C(2)-O(1)-P(1)	111.76(13)	N(1)-C(7)-H(7B)	109.2
C(11)-N(1)-C(7)	110.19(17)	H(7A)-C(7)-H(7B)	107.9
C(11)-N(1)-C(8)	110.63(17)	N(1)-C(8)-C(9)	111.93(19)
C(7)-N(1)-C(8)	109.08(17)	N(1)-C(8)-C(10)	112.35(19)
C(11)-N(1)-Pd(1)	109.60(12)	C(9)-C(8)-C(10)	109.1(2)
C(7)-N(1)-Pd(1)	106.46(12)	N(1)-C(8)-H(8)	107.8
C(8)-N(1)-Pd(1)	110.80(13)	C(9)-C(8)-H(8)	107.8
C(16)-N(2)-C(14)	115.6(2)	C(10)-C(8)-H(8)	107.8
C(16)-N(2)-P(1)	120.44(19)	C(8)-C(9)-H(9A)	109.5
C(14)-N(2)-P(1)	117.77(17)	C(8)-C(9)-H(9B)	109.5
C(20)-N(3)-C(18)	116.7(2)	H(9A)-C(9)-H(9B)	109.5
C(20)-N(3)-P(1)	122.64(16)	C(8)-C(9)-H(9C)	109.5
C(18)-N(3)-P(1)	119.76(18)	H(9A)-C(9)-H(9C)	109.5
C(2)-C(1)-C(6)	119.85(19)	H(9B)-C(9)-H(9C)	109.5
C(2)-C(1)-Pd(1)	121.77(15)	C(8)-C(10)-H(10A)	109.5
C(6)-C(1)-Pd(1)	118.37(16)	C(8)-C(10)-H(10B)	109.5
C(1)-C(2)-C(3)	122.2(2)	H(10A)-C(10)-H(10B)	109.5
C(1)-C(2)-O(1)	117.64(18)	C(8)-C(10)-H(10C)	109.5
C(3)-C(2)-O(1)	120.2(2)	H(10A)-C(10)-H(10C)	109.5
C(2)-C(3)-C(4)	117.6(2)	H(10B)-C(10)-H(10C)	109.5
C(2)-C(3)-H(3)	121.2	N(1)-C(11)-C(12)	111.38(19)
C(4)-C(3)-H(3)	121.2	N(1)-C(11)-C(13)	113.8(2)
C(5)-C(4)-C(3)	121.4(2)	C(12)-C(11)-C(13)	110.8(2)

N(1)-C(11)-H(11)	106.8	H(17A)-C(17)-H(17B)	109.5
C(12)-C(11)-H(11)	106.8	C(16)-C(17)-H(17C)	109.5
C(13)-C(11)-H(11)	106.8	H(17A)-C(17)-H(17C)	109.5
C(11)-C(12)-H(12A)	109.5	H(17B)-C(17)-H(17C)	109.5
C(11)-C(12)-H(12B)	109.5	N(3)-C(18)-C(19)	113.7(2)
H(12A)-C(12)-H(12B)	109.5	N(3)-C(18)-H(18A)	108.8
C(11)-C(12)-H(12C)	109.5	C(19)-C(18)-H(18A)	108.8
H(12A)-C(12)-H(12C)	109.5	N(3)-C(18)-H(18B)	108.8
H(12B)-C(12)-H(12C)	109.5	C(19)-C(18)-H(18B)	108.8
C(11)-C(13)-H(13A)	109.5	H(18A)-C(18)-H(18B)	107.7
C(11)-C(13)-H(13B)	109.5	C(18)-C(19)-H(19A)	109.5
H(13A)-C(13)-H(13B)	109.5	C(18)-C(19)-H(19B)	109.5
C(11)-C(13)-H(13C)	109.5	H(19A)-C(19)-H(19B)	109.5
H(13A)-C(13)-H(13C)	109.5	C(18)-C(19)-H(19C)	109.5
H(13B)-C(13)-H(13C)	109.5	H(19A)-C(19)-H(19C)	109.5
N(2)-C(14)-C(15)	115.2(3)	H(19B)-C(19)-H(19C)	109.5
N(2)-C(14)-H(14A)	108.5	N(3)-C(20)-C(21)	113.6(3)
C(15)-C(14)-H(14A)	108.5	N(3)-C(20)-H(20A)	108.8
N(2)-C(14)-H(14B)	108.5	C(21)-C(20)-H(20A)	108.8
C(15)-C(14)-H(14B)	108.5	N(3)-C(20)-H(20B)	108.8
H(14A)-C(14)-H(14B)	107.5	C(21)-C(20)-H(20B)	108.8
C(14)-C(15)-H(15A)	109.5	H(20A)-C(20)-H(20B)	107.7
C(14)-C(15)-H(15B)	109.5	C(20)-C(21)-H(21A)	109.5
H(15A)-C(15)-H(15B)	109.5	C(20)-C(21)-H(21B)	109.5
C(14)-C(15)-H(15C)	109.5	H(21A)-C(21)-H(21B)	109.5
H(15A)-C(15)-H(15C)	109.5	C(20)-C(21)-H(21C)	109.5
H(15B)-C(15)-H(15C)	109.5	H(21A)-C(21)-H(21C)	109.5
N(2)-C(16)-C(17)	112.9(3)	H(21B)-C(21)-H(21C)	109.5
N(2)-C(16)-H(16A)	109.0		
C(17)-C(16)-H(16A)	109.0		
N(2)-C(16)-H(16B)	109.0		
C(17)-C(16)-H(16B)	109.0		
H(16A)-C(16)-H(16B)	107.8		
C(16)-C(17)-H(17A)	109.5		
C(16)-C(17)-H(17B)	109.5		

Bond lengths [Å] and bond angles [°] for **3a**

Pd(1)-C(1)	1.952(3)	C(11)-C(12)	1.514(5)
Pd(1)-O(2)	2.084(2)	C(11)-C(13)	1.525(4)
Pd(1)-N(1)	2.207(2)	C(11)-H(11)	0.9800
Pd(1)-P(1)	2.2136(8)	C(12)-H(12A)	0.9600
P(1)-O(1)	1.696(2)	C(12)-H(12B)	0.9600
P(1)-C(14)	1.811(3)	C(12)-H(12C)	0.9600
P(1)-C(20)	1.822(3)	C(13)-H(13A)	0.9600
O(1)-C(2)	1.379(3)	C(13)-H(13B)	0.9600
O(2)-C(26)	1.276(4)	C(13)-H(13C)	0.9600
O(3)-C(26)	1.243(4)	C(14)-C(19)	1.375(4)
N(1)-C(11)	1.501(4)	C(14)-C(15)	1.381(4)
N(1)-C(8)	1.508(4)	C(15)-C(16)	1.383(5)
N(1)-C(7)	1.523(4)	C(15)-H(15)	0.9300
C(1)-C(2)	1.383(4)	C(16)-C(17)	1.368(5)
C(1)-C(6)	1.383(4)	C(16)-H(16)	0.9300
C(2)-C(3)	1.386(4)	C(17)-C(18)	1.372(5)
C(3)-C(4)	1.372(4)	C(17)-H(17)	0.9300
C(3)-H(3)	0.9300	C(18)-C(19)	1.381(5)
C(4)-C(5)	1.385(5)	C(18)-H(18)	0.9300
C(4)-H(4)	0.9300	C(19)-H(19)	0.9300
C(5)-C(6)	1.395(4)	C(20)-C(21)	1.379(4)
C(5)-H(5)	0.9300	C(20)-C(25)	1.384(4)
C(6)-C(7)	1.506(4)	C(21)-C(22)	1.374(5)
C(7)-H(7A)	0.9700	C(21)-H(21)	0.9300
C(7)-H(7B)	0.9700	C(22)-C(23)	1.358(5)
C(8)-C(9)	1.513(5)	C(22)-H(22)	0.9300
C(8)-C(10)	1.525(5)	C(23)-C(24)	1.376(5)
C(8)-H(8)	0.9800	C(23)-H(23)	0.9300
C(9)-H(9A)	0.9600	C(24)-C(25)	1.377(5)
C(9)-H(9B)	0.9600	C(24)-H(24)	0.9300
C(9)-H(9C)	0.9600	C(25)-H(25)	0.9300
C(10)-H(10A)	0.9600	C(26)-C(27)	1.511(4)
C(10)-H(10B)	0.9600	C(27)-H(27A)	0.9600
C(10)-H(10C)	0.9600	C(27)-H(27B)	0.9600
C(27)-H(27C)	0.9600		

C(1)-Pd(1)-O(2)	175.64(10)	C(1)-C(6)-C(5)	118.8(3)
C(1)-Pd(1)-N(1)	82.44(10)	C(1)-C(6)-C(7)	117.8(3)
O(2)-Pd(1)-N(1)	93.34(9)	C(5)-C(6)-C(7)	123.3(3)
C(1)-Pd(1)-P(1)	81.21(8)	C(6)-C(7)-N(1)	111.9(2)
O(2)-Pd(1)-P(1)	102.90(6)	C(6)-C(7)-H(7A)	109.2
N(1)-Pd(1)-P(1)	162.89(6)	N(1)-C(7)-H(7A)	109.2
O(1)-P(1)-C(14)	98.16(12)	C(6)-C(7)-H(7B)	109.2
O(1)-P(1)-C(20)	98.45(12)	N(1)-C(7)-H(7B)	109.2
C(14)-P(1)-C(20)	106.47(13)	H(7A)-C(7)-H(7B)	107.9
O(1)-P(1)-Pd(1)	103.56(7)	N(1)-C(8)-C(9)	111.0(3)
C(14)-P(1)-Pd(1)	127.00(10)	N(1)-C(8)-C(10)	111.4(3)
C(20)-P(1)-Pd(1)	117.06(10)	C(9)-C(8)-C(10)	109.9(3)
C(2)-O(1)-P(1)	112.65(16)	N(1)-C(8)-H(8)	108.1
C(26)-O(2)-Pd(1)	119.61(19)	C(9)-C(8)-H(8)	108.1
C(11)-N(1)-C(8)	112.9(2)	C(10)-C(8)-H(8)	108.1
C(11)-N(1)-C(7)	109.7(2)	C(8)-C(9)-H(9A)	109.5
C(8)-N(1)-C(7)	107.2(2)	C(8)-C(9)-H(9B)	109.5
C(11)-N(1)-Pd(1)	106.88(18)	H(9A)-C(9)-H(9B)	109.5
C(8)-N(1)-Pd(1)	112.90(17)	C(8)-C(9)-H(9C)	109.5
C(7)-N(1)-Pd(1)	107.12(16)	H(9A)-C(9)-H(9C)	109.5
C(2)-C(1)-C(6)	120.1(3)	H(9B)-C(9)-H(9C)	109.5
C(2)-C(1)-Pd(1)	121.9(2)	C(8)-C(10)-H(10A)	109.5
C(6)-C(1)-Pd(1)	118.0(2)	C(8)-C(10)-H(10B)	109.5
C(1)-C(2)-O(1)	117.8(2)	H(10A)-C(10)-H(10B)	109.5
C(1)-C(2)-C(3)	121.6(3)	C(8)-C(10)-H(10C)	109.5
O(1)-C(2)-C(3)	120.6(3)	H(10A)-C(10)-H(10C)	109.5
C(4)-C(3)-C(2)	117.8(3)	H(10B)-C(10)-H(10C)	109.5
C(4)-C(3)-H(3)	121.1	N(1)-C(11)-C(12)	112.1(3)
C(2)-C(3)-H(3)	121.1	N(1)-C(11)-C(13)	114.1(3)
C(3)-C(4)-C(5)	121.9(3)	C(12)-C(11)-C(13)	110.5(3)
C(3)-C(4)-H(4)	119.1	N(1)-C(11)-H(11)	106.5
C(5)-C(4)-H(4)	119.1	C(12)-C(11)-H(11)	106.5
C(4)-C(5)-C(6)	119.8(3)	C(13)-C(11)-H(11)	106.5
C(4)-C(5)-H(5)	120.1	C(11)-C(12)-H(12A)	109.5
C(6)-C(5)-H(5)	120.1	C(11)-C(12)-H(12B)	109.5

H(12A)-C(12)-H(12B)	109.5	C(23)-C(22)-H(22)	119.9
C(11)-C(12)-H(12C)	109.5	C(21)-C(22)-H(22)	119.9
H(12A)-C(12)-H(12C)	109.5	C(22)-C(23)-C(24)	119.9(3)
H(12B)-C(12)-H(12C)	109.5	C(22)-C(23)-H(23)	120.1
C(11)-C(13)-H(13A)	109.5	C(24)-C(23)-H(23)	120.1
C(11)-C(13)-H(13B)	109.5	C(25)-C(24)-C(23)	120.3(3)
H(13A)-C(13)-H(13B)	109.5	C(25)-C(24)-H(24)	119.8
C(11)-C(13)-H(13C)	109.5	C(23)-C(24)-H(24)	119.8
H(13A)-C(13)-H(13C)	109.5	C(24)-C(25)-C(20)	120.1(3)
H(13B)-C(13)-H(13C)	109.5	C(24)-C(25)-H(25)	120.0
C(19)-C(14)-C(15)	119.4(3)	C(20)-C(25)-H(25)	120.0
C(19)-C(14)-P(1)	121.4(2)	O(3)-C(26)-O(2)	125.0(3)
C(15)-C(14)-P(1)	119.0(2)	O(3)-C(26)-C(27)	120.6(3)
C(16)-C(15)-C(14)	120.3(3)	O(2)-C(26)-C(27)	114.3(3)
C(16)-C(15)-H(15)	119.8	C(26)-C(27)-H(27A)	109.5
C(14)-C(15)-H(15)	119.8	C(26)-C(27)-H(27B)	109.5
C(17)-C(16)-C(15)	119.9(3)	H(27A)-C(27)-H(27B)	109.5
C(17)-C(16)-H(16)	120.1	C(26)-C(27)-H(27C)	109.5
C(15)-C(16)-H(16)	120.1	H(27A)-C(27)-H(27C)	109.5
C(18)-C(17)-C(16)	120.0(3)	H(27B)-C(27)-H(27C)	109.5
C(18)-C(17)-H(17)	120.0		
C(16)-C(17)-H(17)	120.0		
C(17)-C(18)-C(19)	120.3(3)		
C(17)-C(18)-H(18)	119.8		
C(19)-C(18)-H(18)	119.8		
C(14)-C(19)-C(18)	120.0(3)		
C(14)-C(19)-H(19)	120.0		
C(18)-C(19)-H(19)	120.0		
C(21)-C(20)-C(25)	118.6(3)		
C(21)-C(20)-P(1)	117.0(2)		
C(25)-C(20)-P(1)	124.4(2)		
C(22)-C(21)-C(20)	121.0(3)		
C(22)-C(21)-H(21)	119.5		
C(20)-C(21)-H(21)	119.5		
C(23)-C(22)-C(21)	120.1(3)		

Bond lengths [Å] and bond angles [°] for **3b**

Pd(1)-C(1)	1.9510(17)	C(9)-H(9C)	0.9600
Pd(1)-O(2)	2.1247(12)	C(10)-H(10A)	0.9600
Pd(1)-P(1)	2.2140(5)	C(10)-H(10B)	0.9600
Pd(1)-N(1)	2.2295(14)	C(10)-H(10C)	0.9600
P(1)-N(3)	1.6387(14)	C(11)-C(13)	1.523(3)
P(1)-O(1)	1.6613(12)	C(11)-C(12)	1.529(3)
P(1)-N(2)	1.6691(14)	C(11)-H(11)	0.9800
O(1)-C(6)	1.395(2)	C(12)-H(12A)	0.9600
O(2)-C(22)	1.263(2)	C(12)-H(12B)	0.9600
O(3)-C(22)	1.238(2)	C(12)-H(12C)	0.9600
N(1)-C(7)	1.511(2)	C(13)-H(13A)	0.9600
N(1)-C(8)	1.518(2)	C(13)-H(13B)	0.9600
N(1)-C(11)	1.517(2)	C(13)-H(13C)	0.9600
N(2)-C(16)	1.474(2)	C(14)-C(15)	1.516(3)
N(2)-C(14)	1.475(2)	C(14)-H(14A)	0.9700
N(3)-C(18)	1.475(2)	C(14)-H(14B)	0.9700
N(3)-C(20)	1.474(2)	C(15)-H(15A)	0.9600
C(1)-C(6)	1.390(3)	C(15)-H(15B)	0.9600
C(1)-C(2)	1.391(3)	C(15)-H(15C)	0.9600
C(2)-C(3)	1.397(3)	C(16)-C(17)	1.512(3)
C(2)-C(7)	1.503(3)	C(16)-H(16A)	0.9700
C(3)-C(4)	1.388(3)	C(16)-H(16B)	0.9700
C(3)-H(3)	0.9300	C(17)-H(17A)	0.9600
C(4)-C(5)	1.395(3)	C(17)-H(17B)	0.9600
C(4)-H(4)	0.9300	C(17)-H(17C)	0.9600
C(5)-C(6)	1.384(3)	C(18)-C(19)	1.520(3)
C(5)-H(5)	0.9300	C(18)-H(18A)	0.9700
C(7)-H(7A)	0.9700	C(18)-H(18B)	0.9700
C(7)-H(7B)	0.9700	C(19)-H(19A)	0.9600
C(8)-C(9)	1.522(3)	C(19)-H(19B)	0.9600
C(8)-C(10)	1.521(3)	C(19)-H(19C)	0.9600
C(8)-H(8)	0.9800	C(20)-C(21)	1.510(3)
C(9)-H(9A)	0.9600	C(20)-H(20A)	0.9700
C(9)-H(9B)	0.9600	C(20)-H(20B)	0.9700
C(21)-H(21A)	0.9600	C(23)-H(23A)	0.9600

C(21)-H(21B)	0.9600	C(23)-H(23B)	0.9600
C(21)-H(21C)	0.9600	C(23)-H(23C)	0.9600
C(22)-C(23)	1.513(3)		

C(1)-Pd(1)-O(2)	170.84(6)	C(1)-C(2)-C(3)	119.68(17)
C(1)-Pd(1)-P(1)	80.77(6)	C(1)-C(2)-C(7)	117.33(15)
O(2)-Pd(1)-P(1)	102.48(4)	C(3)-C(2)-C(7)	122.87(16)
C(1)-Pd(1)-N(1)	81.97(7)	C(4)-C(3)-C(2)	119.97(17)
O(2)-Pd(1)-N(1)	95.14(5)	C(4)-C(3)-H(3)	120.0
P(1)-Pd(1)-N(1)	162.35(4)	C(2)-C(3)-H(3)	120.0
N(3)-P(1)-O(1)	107.60(7)	C(3)-C(4)-C(5)	121.10(17)
N(3)-P(1)-N(2)	103.51(8)	C(3)-C(4)-H(4)	119.4
O(1)-P(1)-N(2)	97.84(7)	C(5)-C(4)-H(4)	119.4
N(3)-P(1)-Pd(1)	115.69(5)	C(6)-C(5)-C(4)	117.84(17)
O(1)-P(1)-Pd(1)	105.89(5)	C(6)-C(5)-H(5)	121.1
N(2)-P(1)-Pd(1)	124.03(6)	C(4)-C(5)-H(5)	121.1
C(6)-O(1)-P(1)	113.07(11)	C(5)-C(6)-C(1)	122.29(17)
C(22)-O(2)-Pd(1)	117.78(12)	C(5)-C(6)-O(1)	120.23(16)
C(7)-N(1)-C(8)	108.40(13)	C(1)-C(6)-O(1)	117.48(15)
C(7)-N(1)-C(11)	110.12(13)	C(2)-C(7)-N(1)	112.61(14)
C(8)-N(1)-C(11)	111.48(13)	C(2)-C(7)-H(7A)	109.1
C(7)-N(1)-Pd(1)	106.61(10)	N(1)-C(7)-H(7A)	109.1
C(8)-N(1)-Pd(1)	110.85(10)	C(2)-C(7)-H(7B)	109.1
C(11)-N(1)-Pd(1)	109.26(10)	N(1)-C(7)-H(7B)	109.1
C(16)-N(2)-C(14)	114.83(14)	H(7A)-C(7)-H(7B)	107.8
C(16)-N(2)-P(1)	118.32(11)	C(9)-C(8)-N(1)	110.83(15)
C(14)-N(2)-P(1)	118.76(12)	C(9)-C(8)-C(10)	109.52(17)
C(18)-N(3)-C(20)	116.10(14)	N(1)-C(8)-C(10)	113.49(15)
C(18)-N(3)-P(1)	121.72(12)	C(9)-C(8)-H(8)	107.6
C(20)-N(3)-P(1)	119.80(11)	N(1)-C(8)-H(8)	107.6
C(6)-C(1)-C(2)	119.11(16)	C(10)-C(8)-H(8)	107.6
C(6)-C(1)-Pd(1)	122.56(13)	C(8)-C(9)-H(9A)	109.5
C(2)-C(1)-Pd(1)	118.28(13)	C(8)-C(9)-H(9B)	109.5

H(9A)-C(9)-H(9B)	109.5	C(14)-C(15)-H(15B)	109.5
C(8)-C(9)-H(9C)	109.5	H(15A)-C(15)-H(15B)	109.5
H(9A)-C(9)-H(9C)	109.5	C(14)-C(15)-H(15C)	109.5
H(9B)-C(9)-H(9C)	109.5	H(15A)-C(15)-H(15C)	109.5
C(8)-C(10)-H(10A)	109.5	H(15B)-C(15)-H(15C)	109.5
C(8)-C(10)-H(10B)	109.5	N(2)-C(16)-C(17)	112.45(16)
H(10A)-C(10)-H(10B)	109.5	N(2)-C(16)-H(16A)	109.1
C(8)-C(10)-H(10C)	109.5	C(17)-C(16)-H(16A)	109.1
H(10A)-C(10)-H(10C)	109.5	N(2)-C(16)-H(16B)	109.1
H(10B)-C(10)-H(10C)	109.5	C(17)-C(16)-H(16B)	109.1
N(1)-C(11)-C(13)	111.39(14)	H(16A)-C(16)-H(16B)	107.8
N(1)-C(11)-C(12)	113.96(15)	C(16)-C(17)-H(17A)	109.5
C(13)-C(11)-C(12)	110.44(16)	C(16)-C(17)-H(17B)	109.5
N(1)-C(11)-H(11)	106.9	H(17A)-C(17)-H(17B)	109.5
C(13)-C(11)-H(11)	106.9	C(16)-C(17)-H(17C)	109.5
C(12)-C(11)-H(11)	106.9	H(17A)-C(17)-H(17C)	109.5
C(11)-C(12)-H(12A)	109.5	H(17B)-C(17)-H(17C)	109.5
C(11)-C(12)-H(12B)	109.5	N(3)-C(18)-C(19)	113.26(17)
H(12A)-C(12)-H(12B)	109.5	N(3)-C(18)-H(18A)	108.9
C(11)-C(12)-H(12C)	109.5	C(19)-C(18)-H(18A)	108.9
H(12A)-C(12)-H(12C)	109.5	N(3)-C(18)-H(18B)	108.9
H(12B)-C(12)-H(12C)	109.5	C(19)-C(18)-H(18B)	108.9
C(11)-C(13)-H(13A)	109.5	H(18A)-C(18)-H(18B)	107.7
C(11)-C(13)-H(13B)	109.5	C(18)-C(19)-H(19A)	109.5
H(13A)-C(13)-H(13B)	109.5	C(18)-C(19)-H(19B)	109.5
C(11)-C(13)-H(13C)	109.5	H(19A)-C(19)-H(19B)	109.5
H(13A)-C(13)-H(13C)	109.5	C(18)-C(19)-H(19C)	109.5
H(13B)-C(13)-H(13C)	109.5	H(19A)-C(19)-H(19C)	109.5
N(2)-C(14)-C(15)	115.21(17)	H(19B)-C(19)-H(19C)	109.5
N(2)-C(14)-H(14A)	108.5	N(3)-C(20)-C(21)	113.76(16)
C(15)-C(14)-H(14A)	108.5	N(3)-C(20)-H(20A)	108.8
N(2)-C(14)-H(14B)	108.5	C(21)-C(20)-H(20A)	108.8
C(15)-C(14)-H(14B)	108.5	N(3)-C(20)-H(20B)	108.8
H(14A)-C(14)-H(14B)	107.5	C(21)-C(20)-H(20B)	108.8
C(14)-C(15)-H(15A)	109.5	H(20A)-C(20)-H(20B)	107.7
C(20)-C(21)-H(21A)	109.5	O(2)-C(22)-C(23)	116.41(18)

C(20)-C(21)-H(21B)	109.5	C(22)-C(23)-H(23A)	109.5
H(21A)-C(21)-H(21B)	109.5	C(22)-C(23)-H(23B)	109.5
C(20)-C(21)-H(21C)	109.5	H(23A)-C(23)-H(23B)	109.5
H(21A)-C(21)-H(21C)	109.5	C(22)-C(23)-H(23C)	109.5
H(21B)-C(21)-H(21C)	109.5	H(23A)-C(23)-H(23C)	109.5
O(3)-C(22)-O(2)	124.74(18)	H(23B)-C(23)-H(23C)	109.5
O(3)-C(22)-C(23)	118.80(18)		

Symmetry transformations used to generate equivalent atoms:

Bond lengths [Å] and bond angles [°] for **5a**

Pd(1)-C(1)	2.002(4)	C(9)-H(9C)	0.9600
Pd(1)-O(2)	2.093(3)	C(10)-H(10A)	0.9600
Pd(1)-O(3)	2.139(3)	C(10)-H(10B)	0.9600
Pd(1)-P(1)	2.1730(12)	C(10)-H(10C)	0.9600
P(1)-O(1)	1.620(3)	C(11)-C(12)	1.490(12)
P(1)-C(14)	1.790(5)	C(11)-C(13)	1.549(12)
P(1)-C(20)	1.803(5)	C(11)-H(11)	0.9800
O(1)-C(6)	1.414(5)	C(12)-H(12A)	0.9600
O(2)-C(26)	1.253(5)	C(12)-H(12B)	0.9600
O(3)-C(26)#1	1.249(5)	C(12)-H(12C)	0.9600
N(1)-C(7)	1.456(6)	C(13)-H(13A)	0.9600
N(1)-C(11)	1.456(7)	C(13)-H(13B)	0.9600
N(1)-C(8)	1.464(6)	C(13)-H(13C)	0.9600
C(1)-C(6)	1.394(6)	C(14)-C(19)	1.342(7)
C(1)-C(2)	1.388(6)	C(14)-C(15)	1.366(6)
C(2)-C(3)	1.392(6)	C(15)-C(16)	1.382(7)
C(2)-H(2)	0.9300	C(15)-H(15)	0.9300
C(3)-C(4)	1.376(6)	C(16)-C(17)	1.332(7)
C(3)-H(3)	0.9300	C(16)-H(16)	0.9300
C(4)-C(5)	1.387(6)	C(17)-C(18)	1.335(7)
C(4)-C(7)	1.509(6)	C(17)-H(17)	0.9300
C(5)-C(6)	1.375(6)	C(18)-C(19)	1.386(8)
C(5)-H(5)	0.9300	C(18)-H(18)	0.9300
C(7)-H(7A)	0.9700	C(19)-H(19)	0.9300
C(7)-H(7B)	0.9700	C(20)-C(21)	1.361(7)
C(8)-C(10)	1.515(9)	C(20)-C(25)	1.364(7)
C(8)-C(9)	1.522(8)	C(21)-C(22)	1.379(7)
C(8)-H(8)	0.9800	C(21)-H(21)	0.9300
C(9)-H(9A)	0.9600	C(22)-C(23)	1.354(10)
C(9)-H(9B)	0.9600	C(22)-H(22)	0.9300
C(23)-C(24)	1.330(10)	C(26)-O(3)#1	1.249(5)
C(23)-H(23)	0.9300	C(26)-C(27)	1.518(6)
C(24)-C(25)	1.387(8)	C(27)-H(27A)	0.9600
C(24)-H(24)	0.9300	C(27)-H(27B)	0.9600
C(25)-H(25)	0.9300	C(27)-H(27C)	0.9600

C(1)-Pd(1)-O(2)	92.23(15)	C(3)-C(4)-C(5)	118.3(4)
C(1)-Pd(1)-O(3)	171.83(14)	C(3)-C(4)-C(7)	120.8(4)
O(2)-Pd(1)-O(3)	90.06(11)	C(5)-C(4)-C(7)	120.8(5)
C(1)-Pd(1)-P(1)	79.51(12)	C(6)-C(5)-C(4)	118.9(4)
O(2)-Pd(1)-P(1)	169.83(9)	C(6)-C(5)-H(5)	120.6
O(3)-Pd(1)-P(1)	97.33(9)	C(4)-C(5)-H(5)	120.6
O(1)-P(1)-C(14)	102.34(19)	C(5)-C(6)-C(1)	124.6(4)
O(1)-P(1)-C(20)	103.4(2)	C(5)-C(6)-O(1)	117.8(4)
C(14)-P(1)-C(20)	105.6(2)	C(1)-C(6)-O(1)	117.6(4)
O(1)-P(1)-Pd(1)	108.63(11)	N(1)-C(7)-C(4)	113.5(4)
C(14)-P(1)-Pd(1)	119.96(15)	N(1)-C(7)-H(7A)	108.9
C(20)-P(1)-Pd(1)	115.02(16)	C(4)-C(7)-H(7A)	108.9
C(6)-O(1)-P(1)	110.8(3)	N(1)-C(7)-H(7B)	108.9
C(26)-O(2)-Pd(1)	128.2(3)	C(4)-C(7)-H(7B)	108.9
C(26)#1-O(3)-Pd(1)	127.1(3)	H(7A)-C(7)-H(7B)	107.7
C(7)-N(1)-C(11)	114.7(4)	N(1)-C(8)-C(10)	116.9(6)
C(7)-N(1)-C(8)	113.4(5)	N(1)-C(8)-C(9)	110.8(5)
C(11)-N(1)-C(8)	115.7(5)	C(10)-C(8)-C(9)	110.7(6)
C(6)-C(1)-C(2)	115.2(4)	N(1)-C(8)-H(8)	105.8
C(6)-C(1)-Pd(1)	120.3(3)	C(10)-C(8)-H(8)	105.8
C(2)-C(1)-Pd(1)	124.4(3)	C(9)-C(8)-H(8)	105.8
C(1)-C(2)-C(3)	121.1(4)	C(8)-C(9)-H(9A)	109.5
C(1)-C(2)-H(2)	119.4	C(8)-C(9)-H(9B)	109.5
C(3)-C(2)-H(2)	119.4	H(9A)-C(9)-H(9B)	109.5
C(4)-C(3)-C(2)	121.9(4)	C(8)-C(9)-H(9C)	109.5
C(4)-C(3)-H(3)	119.1	H(9A)-C(9)-H(9C)	109.5
C(2)-C(3)-H(3)	119.1	H(9B)-C(9)-H(9C)	109.5
C(8)-C(10)-H(10A)	109.5	C(18)-C(17)-H(17)	120.6
C(8)-C(10)-H(10B)	109.5	C(17)-C(18)-C(19)	120.9(6)
H(10A)-C(10)-H(10B)	109.5	C(17)-C(18)-H(18)	119.6
C(8)-C(10)-H(10C)	109.5	C(19)-C(18)-H(18)	119.6
H(10A)-C(10)-H(10C)	109.5	C(14)-C(19)-C(18)	121.4(5)
H(10B)-C(10)-H(10C)	109.5	C(14)-C(19)-H(19)	119.3
N(1)-C(11)-C(12)	109.5(7)	C(18)-C(19)-H(19)	119.3
N(1)-C(11)-C(13)	113.4(7)	C(21)-C(20)-C(25)	117.9(5)
C(12)-C(11)-C(13)	113.1(7)	C(21)-C(20)-P(1)	119.4(4)

N(1)-C(11)-H(11)	106.8	C(25)-C(20)-P(1)	122.7(4)
C(12)-C(11)-H(11)	106.8	C(20)-C(21)-C(22)	120.7(6)
C(13)-C(11)-H(11)	106.8	C(20)-C(21)-H(21)	119.7
C(11)-C(12)-H(12A)	109.5	C(22)-C(21)-H(21)	119.7
C(11)-C(12)-H(12B)	109.5	C(23)-C(22)-C(21)	119.7(7)
H(12A)-C(12)-H(12B)	109.5	C(23)-C(22)-H(22)	120.1
C(11)-C(12)-H(12C)	109.5	C(21)-C(22)-H(22)	120.1
H(12A)-C(12)-H(12C)	109.5	C(24)-C(23)-C(22)	121.1(7)
H(12B)-C(12)-H(12C)	109.5	C(24)-C(23)-H(23)	119.5
C(11)-C(13)-H(13A)	109.5	C(22)-C(23)-H(23)	119.5
C(11)-C(13)-H(13B)	109.5	C(23)-C(24)-C(25)	119.2(7)
H(13A)-C(13)-H(13B)	109.5	C(23)-C(24)-H(24)	120.4
C(11)-C(13)-H(13C)	109.5	C(25)-C(24)-H(24)	120.4
H(13A)-C(13)-H(13C)	109.5	C(20)-C(25)-C(24)	121.4(6)
H(13B)-C(13)-H(13C)	109.5	C(20)-C(25)-H(25)	119.3
C(19)-C(14)-C(15)	116.9(5)	C(24)-C(25)-H(25)	119.3
C(19)-C(14)-P(1)	120.2(4)	O(2)-C(26)-O(3)#1	126.7(4)
C(15)-C(14)-P(1)	123.0(4)	O(2)-C(26)-C(27)	115.4(4)
C(14)-C(15)-C(16)	121.2(5)	O(3)#1-C(26)-C(27)	117.8(4)
C(14)-C(15)-H(15)	119.4	C(26)-C(27)-H(27A)	109.5
C(16)-C(15)-H(15)	119.4	C(26)-C(27)-H(27B)	109.5
C(17)-C(16)-C(15)	120.9(5)	H(27A)-C(27)-H(27B)	109.5
C(17)-C(16)-H(16)	119.6	C(26)-C(27)-H(27C)	109.5
C(15)-C(16)-H(16)	119.6	H(27A)-C(27)-H(27C)	109.5
C(16)-C(17)-C(18)	118.8(6)	H(27B)-C(27)-H(27C)	109.5
C(16)-C(17)-H(17)	120.6		