Development of A Novel Chiral Palladacycle and its Application in Asymmetric Hydrophosphination Reaction

Jeanette See Leng Yap, Bin Bin Li, Jonathon Wong,, Yongxin Li, Sumod A. Pullarkat, Pak-Hing Leung*

Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, Singapore 637371, Singapore

*Corresponding author. Tel.: (+65) 6316 8905.

e-mail address: pakhing@ntu.edu.sg (P.-H. Leung).

SUPPORTING INFORMATION

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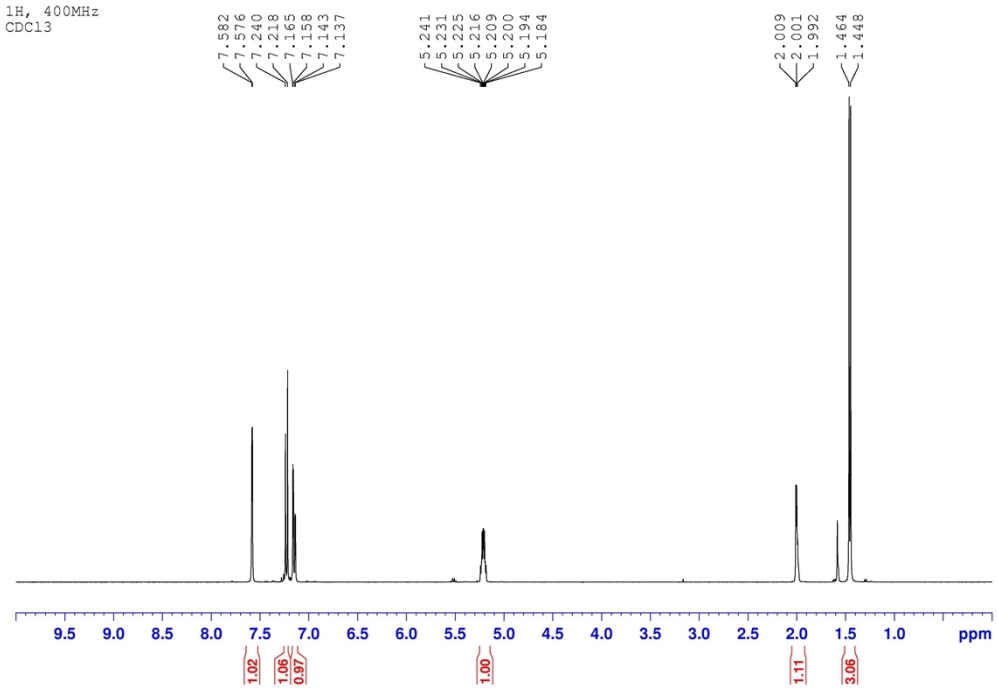
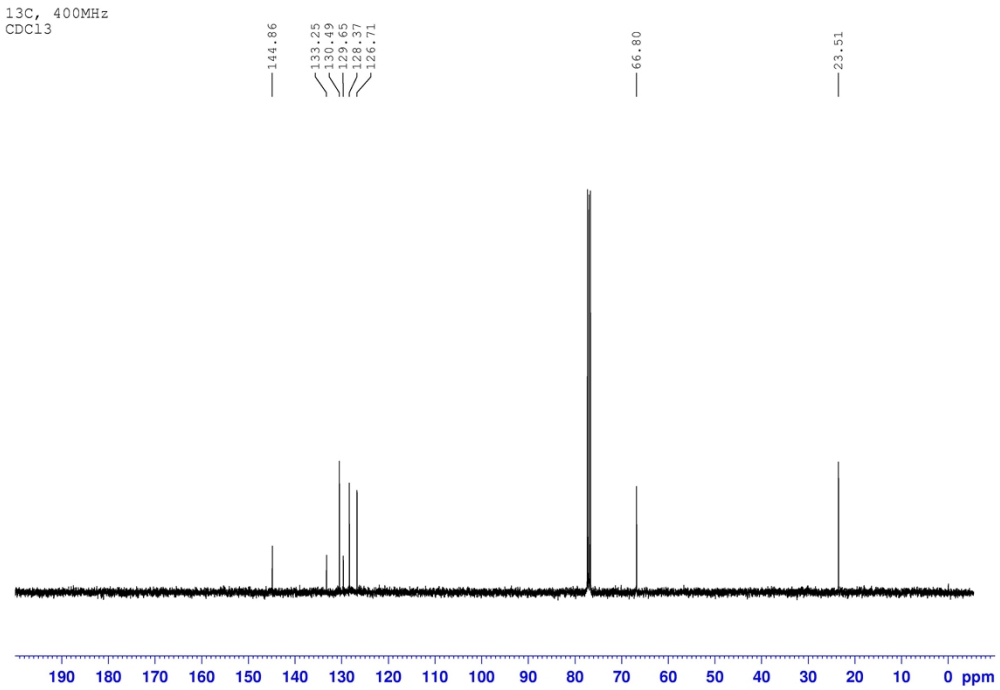
1-(2,5-dichlorophenyl)ethanol, (±)-**4**





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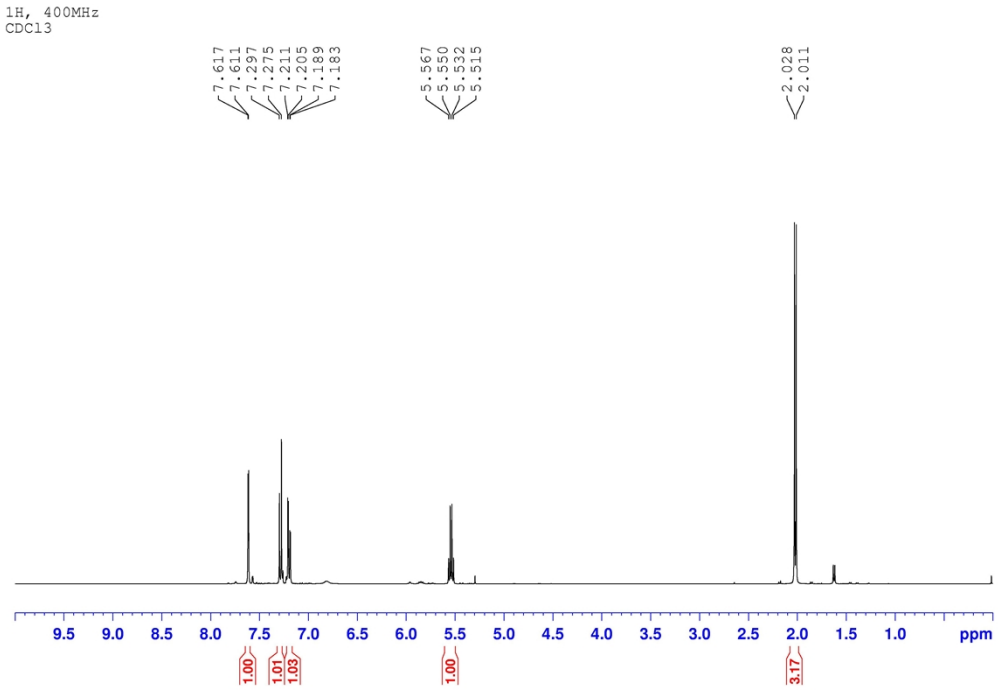
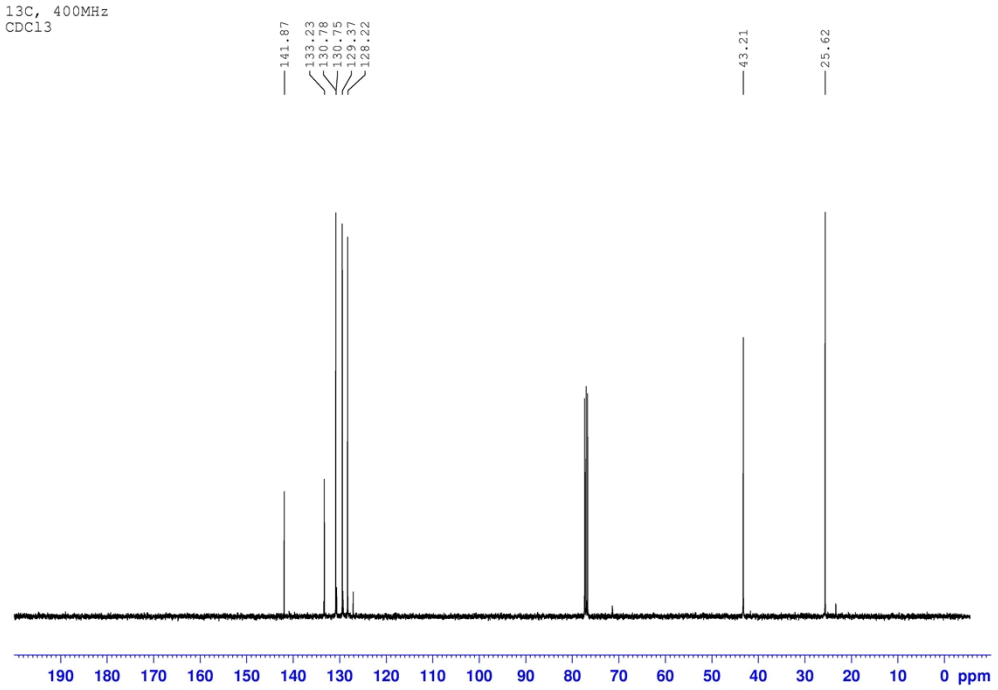
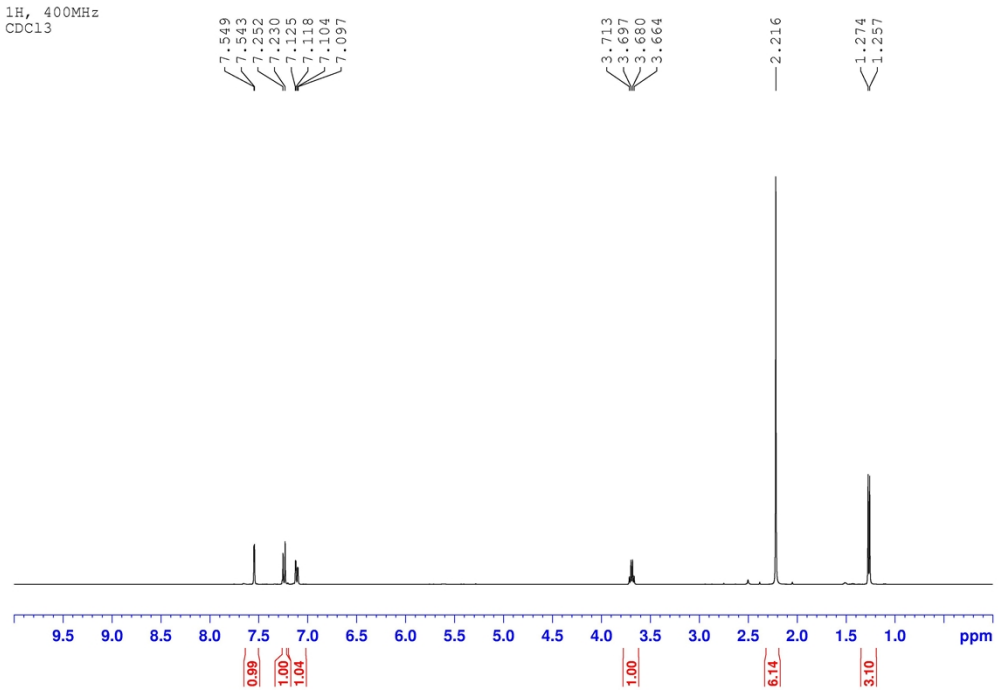
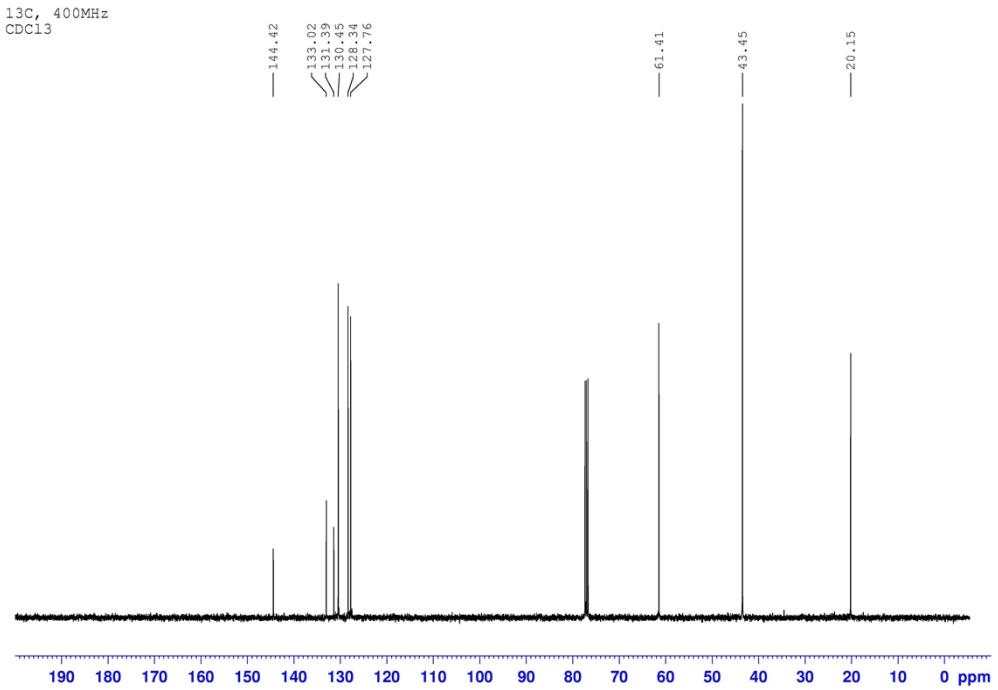


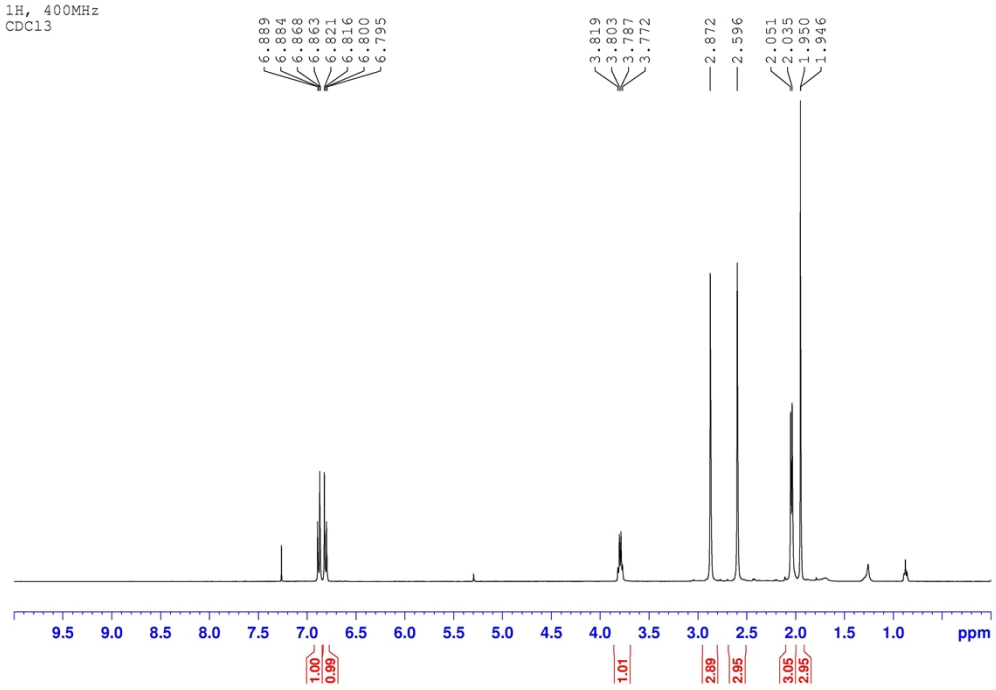


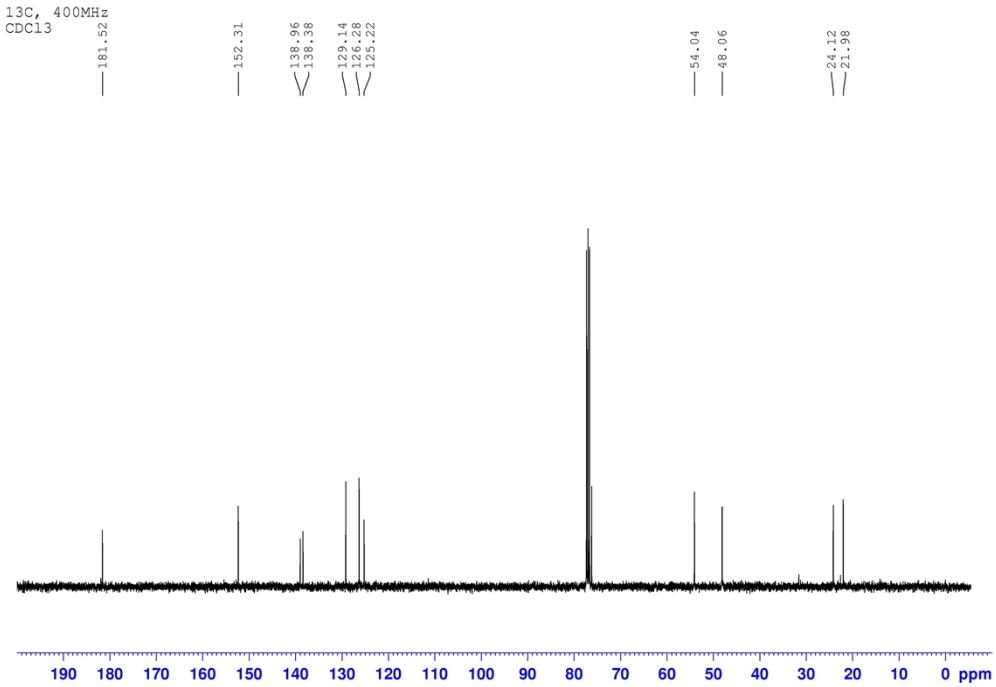
1-(2,5-dichlorophenyl)-N,N-dimethylethanamine, (±)-**6**



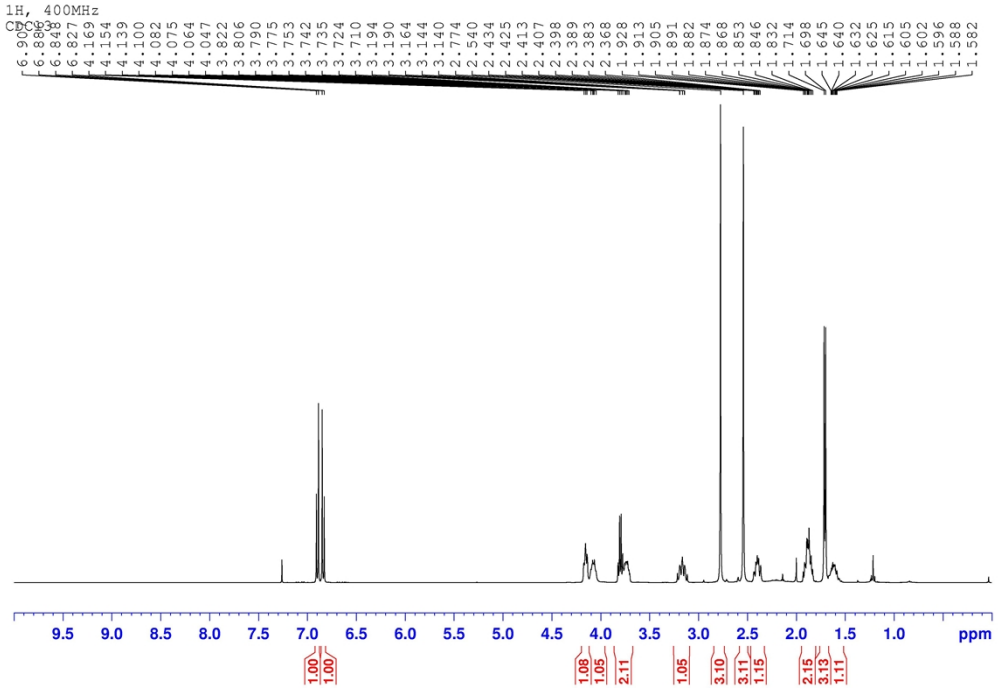


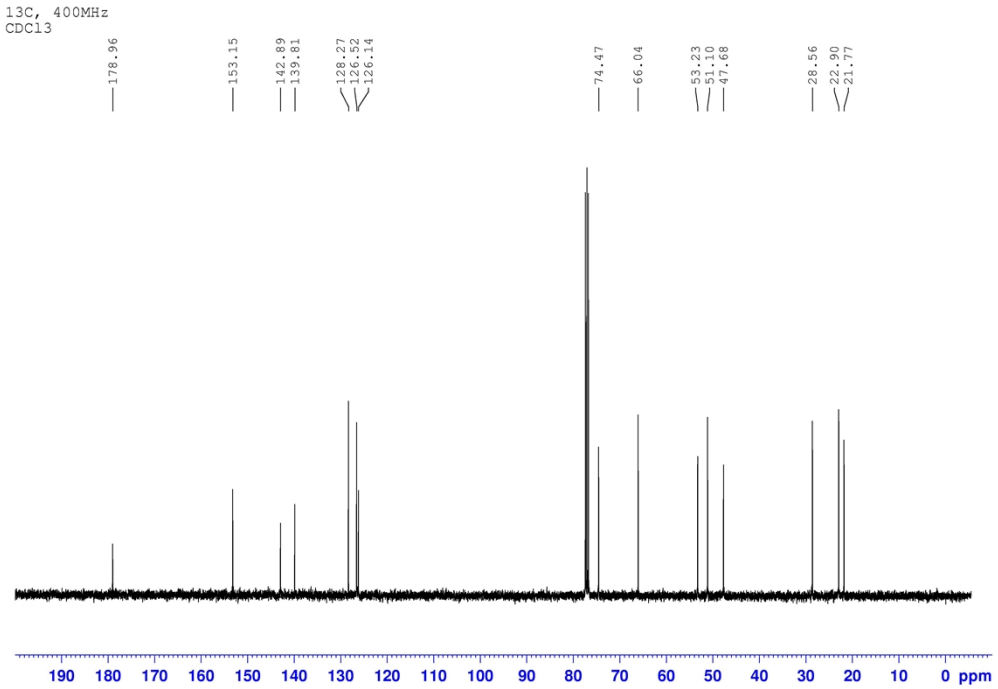
(±)-Di-μ-acetatobis-{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}dipalladium(II), (±)-**7**



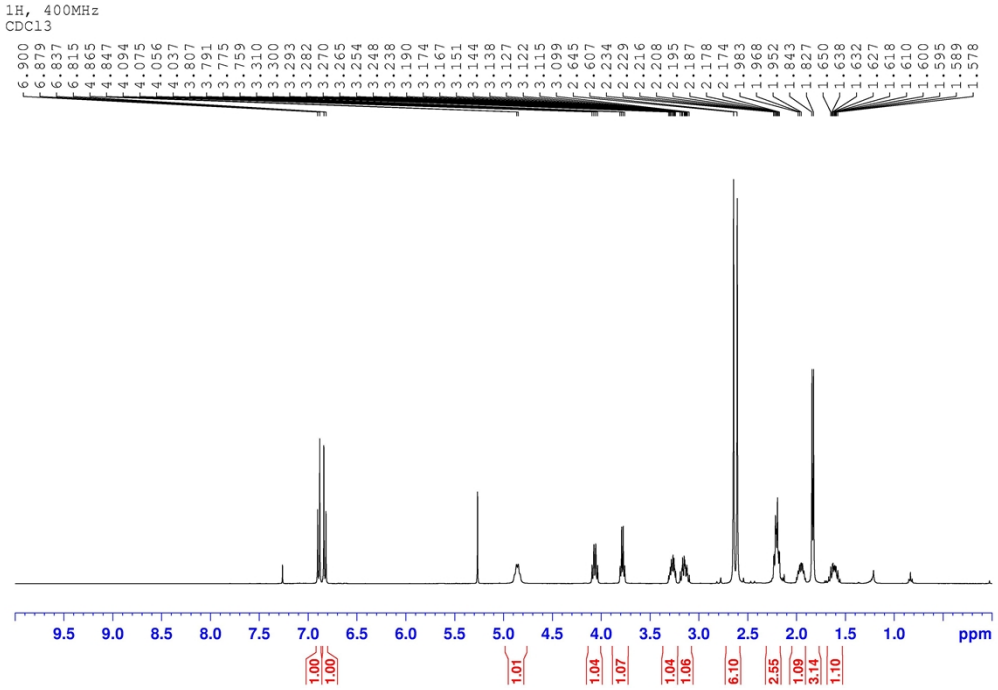


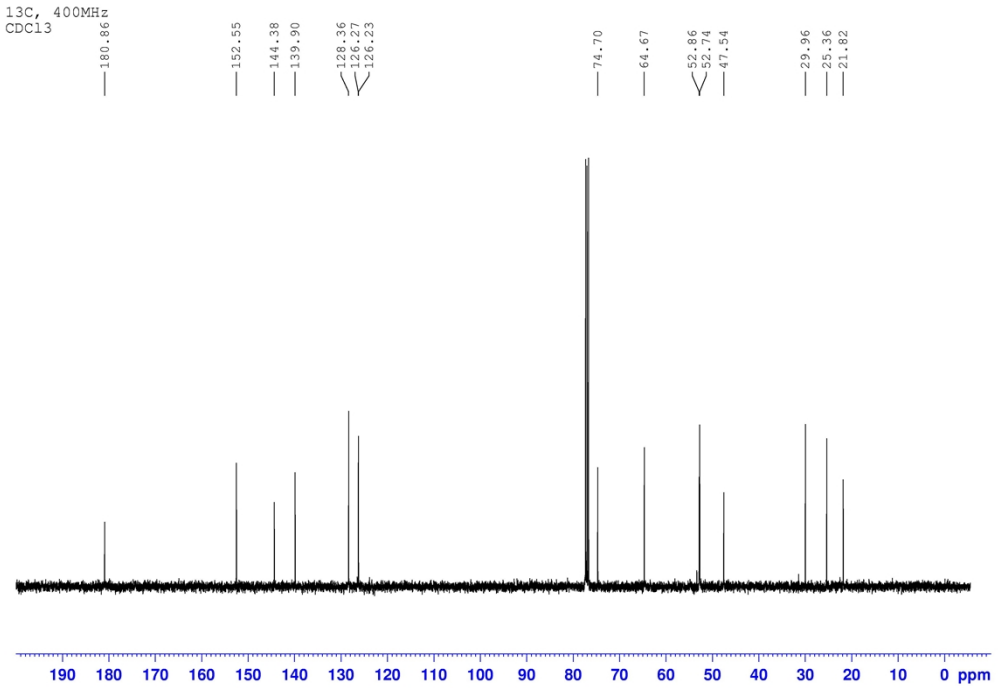
(R_C,$S_C$$S_N$)-{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}(prolinato-N,O)palladium(II), (R_C,$S_C$$S_N$)-**8**



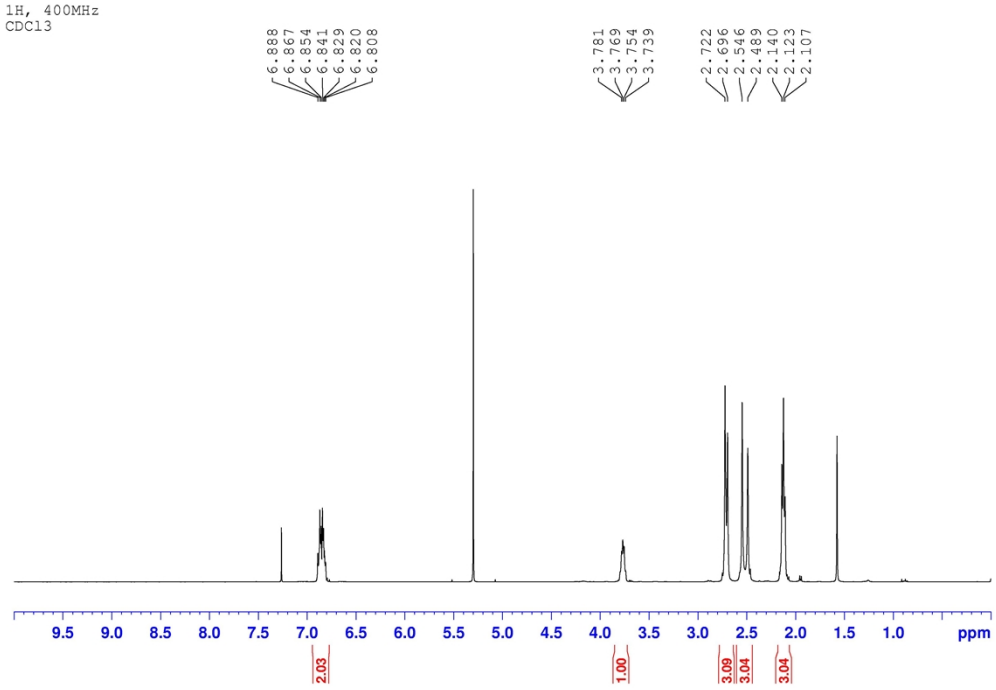


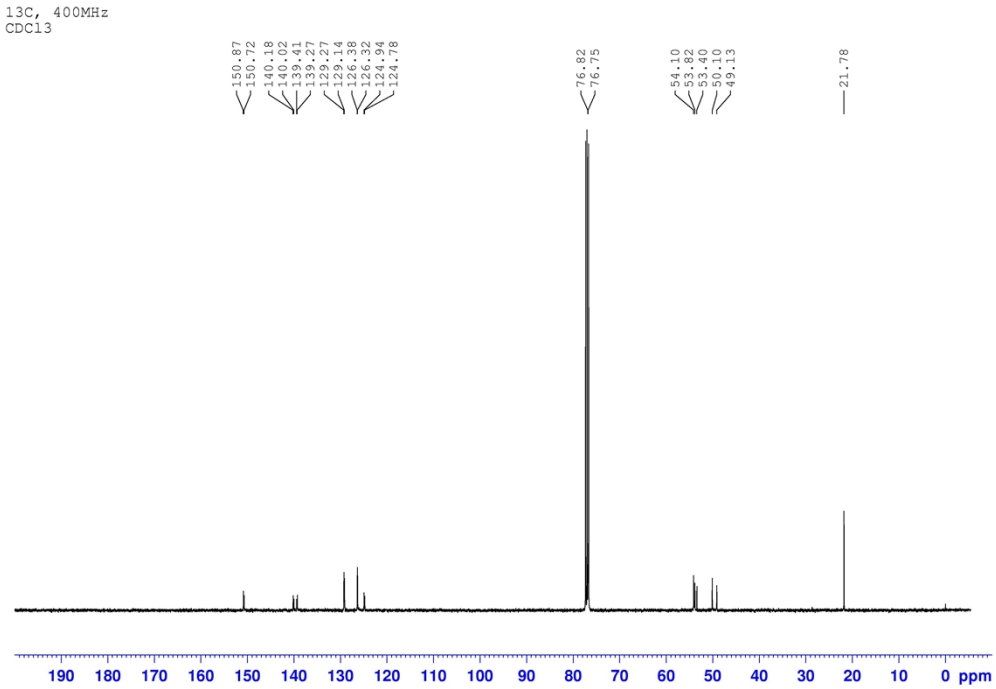
(S_C,$S_C$$S_N$)-{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}(prolinato-N,O)palladium(II), (S_C,$S_C$$S_N$)-**8**



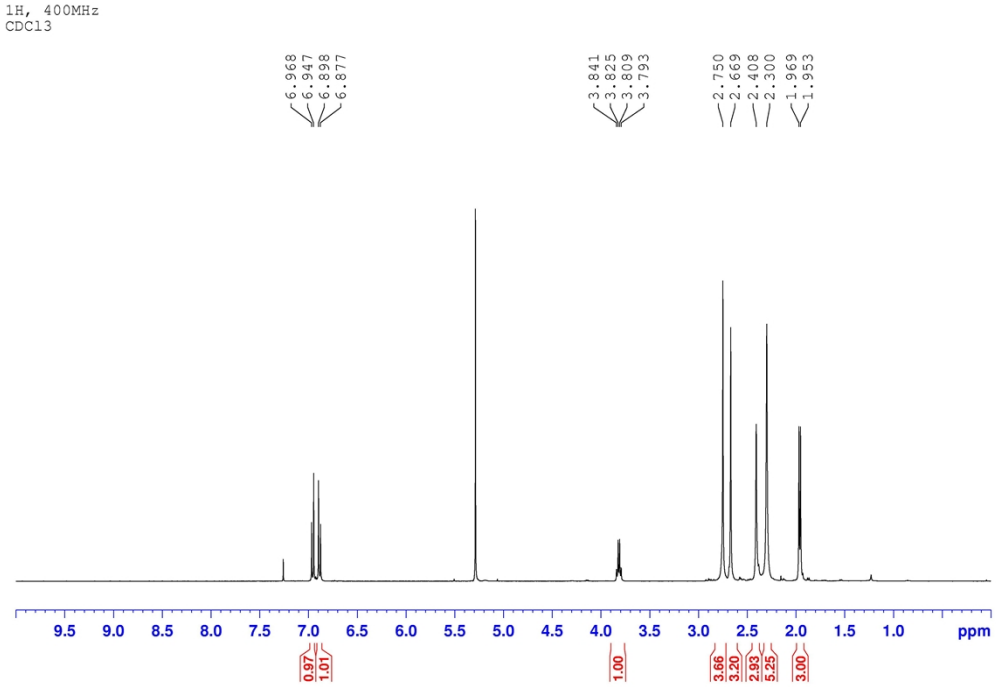


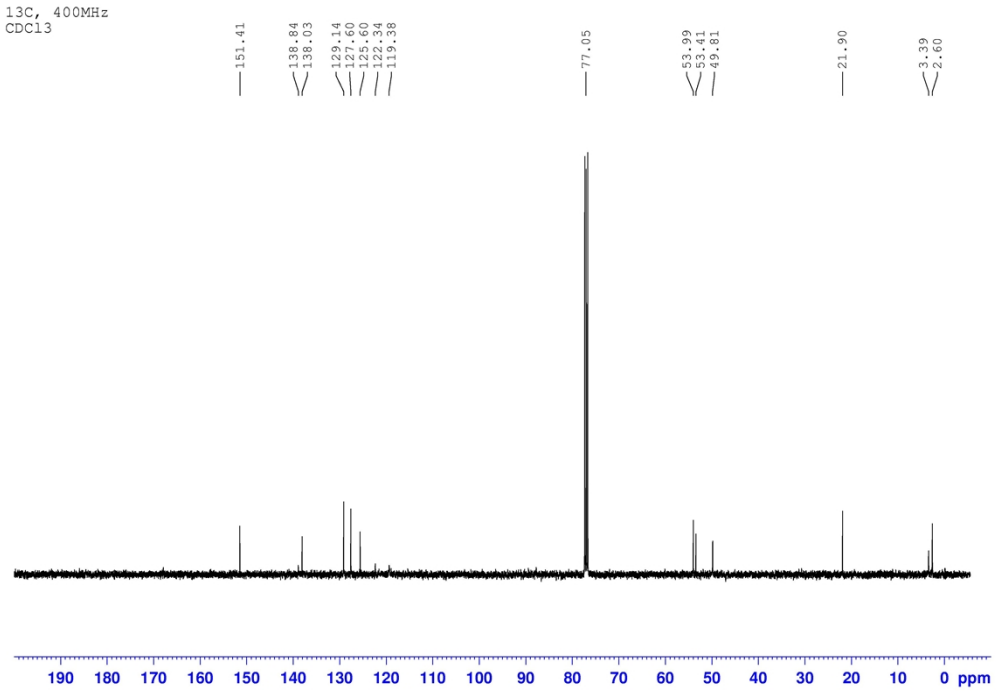
(S,S)-Di-μ-chlorobis{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}dipalladium(II), (*S,S*)-**2**



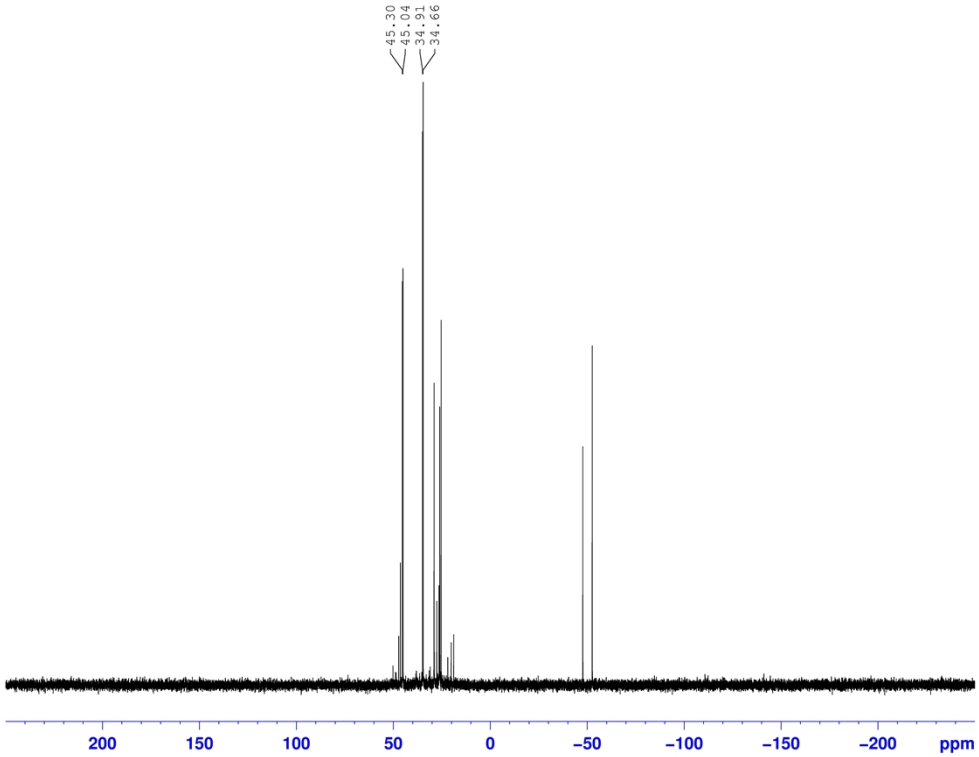


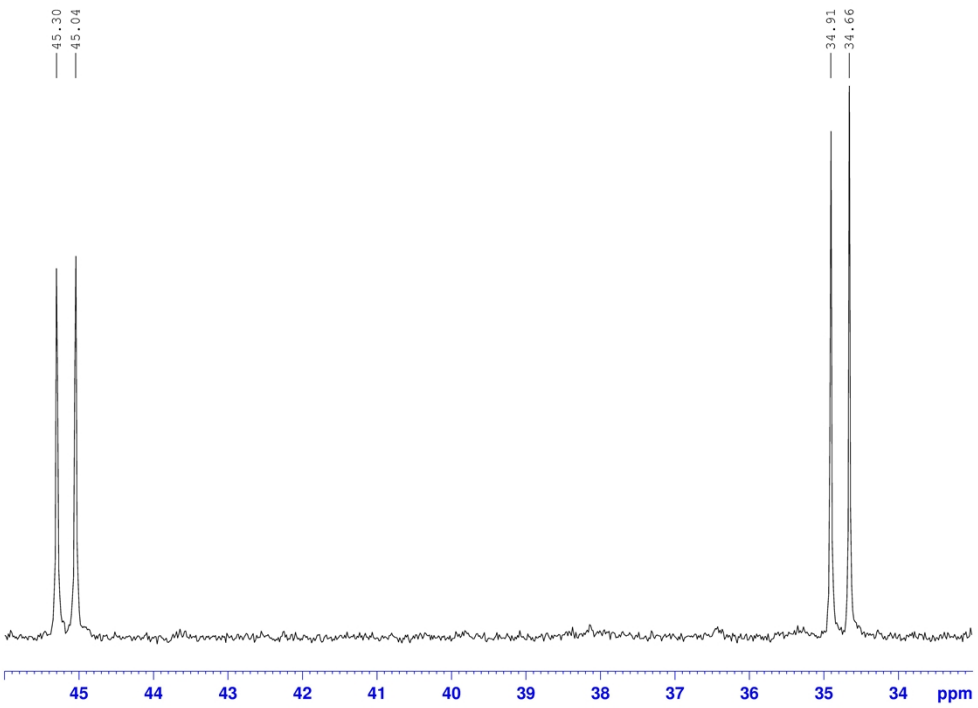
(*S*)-Bis(acetonitrile-N){6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}palladium(II) perchlorate, (*S*)-**10**





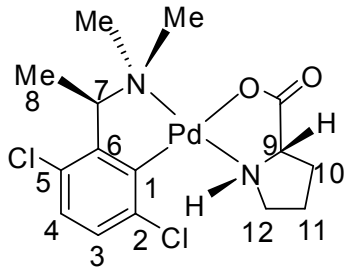
Crude $^{31}P\{^{1}H\}$ NMR for Chiral Palladacycle Promoted Asymmetric Hydrophosphination Reaction, (*S,RR*)**-11**

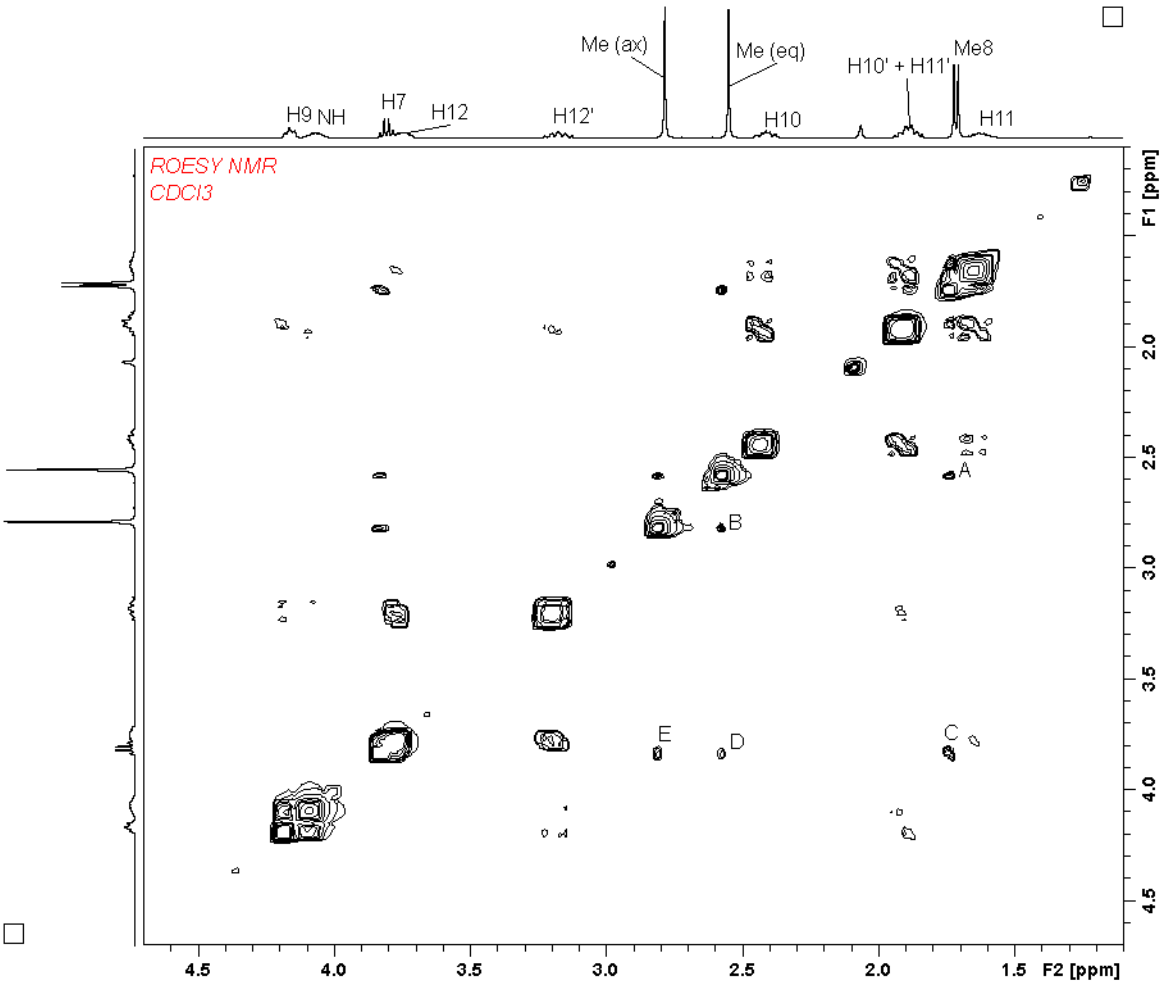




2D ^{1}H-^{1}H ROSEY Spectra

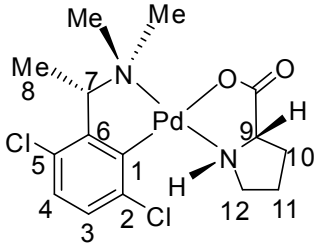
*2D ^{1}H-^{1}H ROESY NMR spectrum of the complex (R_C,S_CS_N)-**8** in $CDCl_3$*

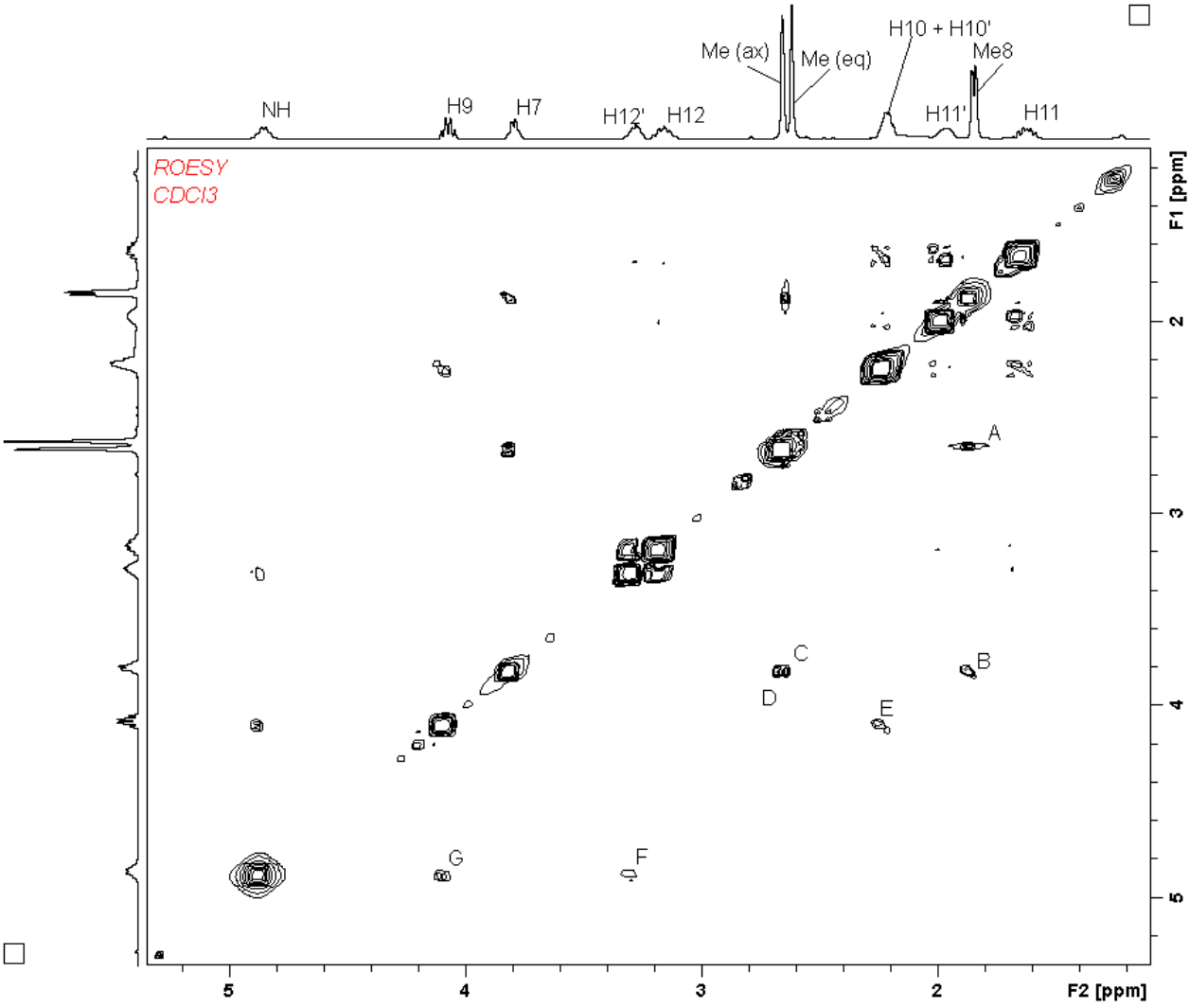




Selected ROESY Interactions: (A) Me8 - NMe(eq); (B) NMe(eq)–NMe(ax); (C) H7–Me8; (D) H7–NMe(eq); (E) H7–NMe(ax)

*2D ^{1}H-^{1}H ROESY NMR spectrum of the complex (S_C,$S_C$$S_N$)-**8** in $CDCl_3$*

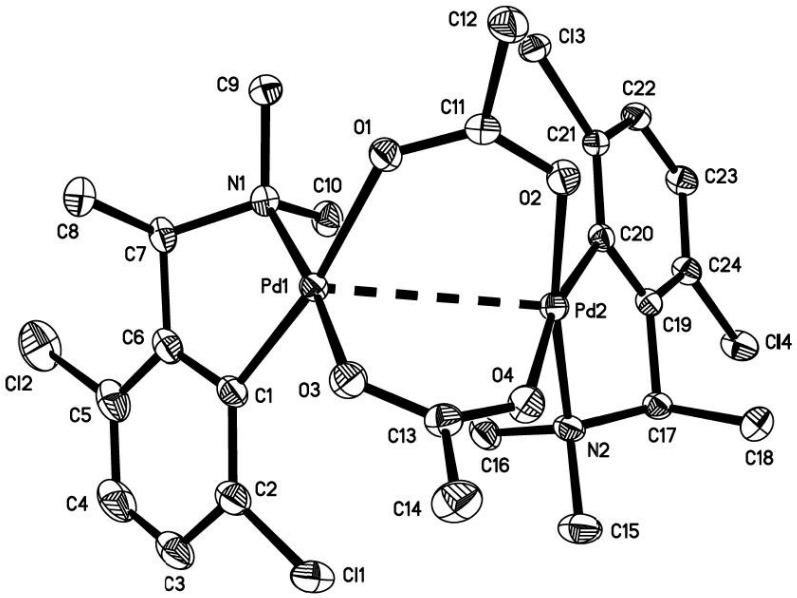




Selected ROESY Interactions: (A) Me8−NMe(eq); (B) H7–Me8; (C) H7–NMe(eq); (D) H7–NMe(ax); (E) H9−H10 and H10'; (F) NH−H12'; (G) NH−H9

Single Crystal X-Ray Crystallographic Data

(±)-Di-μ-acetatobis-{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}dipalladium(II), (±)-**7**



Empirical formula	$C_{25.5}H_{33.5}Cl_4N_2O_4Pd_2$	
Formula weight	786.64	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C2/c	
Unit cell dimensions	a = 16.5309(3) Å	a= 90°.
	b = 25.6674(4) Å	b= 94.7660(10)°.
	c = 15.1461(3) Å	g = 90°.
Volume	6404.3(2) $Å^3$	
Z	8	
Density (calculated)	1.632 Mg/m^3	
Absorption coefficient	1.488 mm^{-1}	

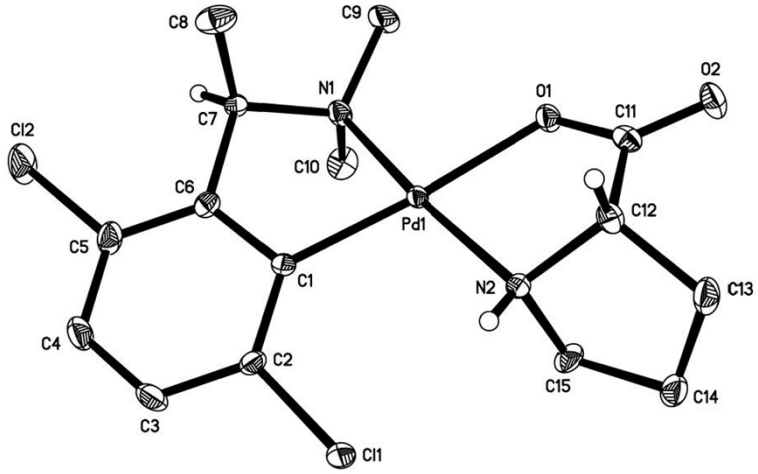
F(000)	3140
Crystal size	0.40 x 0.24 x 0.04 mm^3
Theta range for data collection	3.85 to 37.20°.
Index ranges	-28<=h<=28, -43<=k<=43, -25<=l<=9
Reflections collected	55693
Independent reflections	16434 [R(int) = 0.0448]
Completeness to theta = 37.20°	99.5 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.9429 and 0.5874
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	16434 / 77 / 388
Goodness-of-fit on F^2	1.024
Final R indices [I>2sigma(I)][ab]	R1 = 0.0347, wR2 = 0.0761
R indices (all data)[ab]	R1 = 0.0596, wR2 = 0.0875
Largest diff. peak and hole	0.912 and -1.181 e.$Å^{-3}$

Selected bond lengths (Å) and angles (°) for complex (±)-**7**

Pd(1)-C(1)	1.9888(19)	Pd(1)-N(1)	2.0468(17)
Pd(1)-O(1)	2.1110(14)	Pd(1)-O(3)	2.0260(15)
Pd(2)-C(20)	1.9933(18)	Pd(2)-N(2)	2.0656(16)
Pd(2)-O(2)	2.0341(14)	Pd(2)-O(4)	2.1010(15)
C(11)-O(1)	1.249(2)	C(11)-O(2)	1.265(2)
C(13)-O(3)	1.264(3)	C(13)-O(4)	1.253(2)
C(1)-Pd(1)-N(1)	81.84(8)	C(1)-Pd(1)-O(3)	96.66(8)

O(3)-Pd(1)-O(1)	87.91(6)	N(1)-Pd(1)-O(1)	92.69(6)
C(1)-Pd(1)-O(1)	171.41(7)	O(3)-Pd(1)-N(1)	172.52(6)
C(20)-Pd(2)-N(2)	82.05(7)	C(20)-Pd(2)-O(2)	95.92(7)
O(2)-Pd(2)-O(4)	88.13(6)	N(2)-Pd(2)-O(4)	92.40(6)
C(20)-Pd(2)-O(4)	169.23(7)	O(2)-Pd(2)-N(2)	170.95(6)
O(1)-C(11)-O(2)	126.79(18)	O(4)-C(13)-O(3)	126.42(19)
O(1)-C(11)-C(12)	117.48(17)	O(2)-C(11)-C(12)	115.72(17)
O(4)-C(13)-C(14)	117.37(19)	O(3)-C(13)-C(14)	116.20(18)

(R_C,$S_C$$S_N$)-{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}(prolinato-N,O)palladium(II), (R_C,$S_C$$S_N$)-**8**



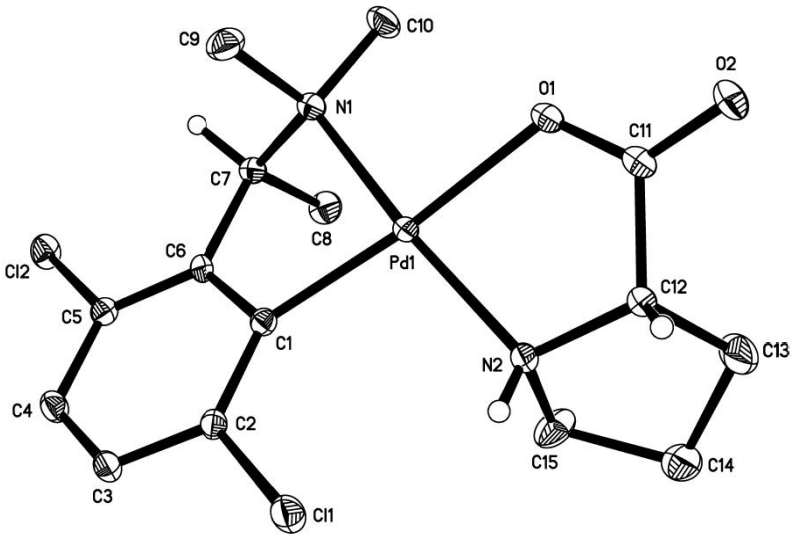
Empirical formula	$C_{15}H_{20}Cl_2N_2O_2Pd$	
Formula weight	437.63	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Tetragonal	
Space group	P4(1)	
Unit cell dimensions	a = 8.8546(3) Å	a= 90°.
	b = 8.8546(3) Å	b= 90°.
	c = 22.2760(9) Å	g = 90°.
Volume	1746.53(11) $Å^3$	
Z	4	
Density (calculated)	1.664 Mg/m^3	
Absorption coefficient	1.375 mm^{-1}	
F(000)	880	
Crystal size	0.40 x 0.20 x 0.14 mm^3	

Theta range for data collection	2.30 to 31.09°.
Index ranges	-12<=h<=11, -11<=k<=12, -27<=l<=32
Reflections collected	12460
Independent reflections	5319 [R(int) = 0.0389]
Completeness to theta = 31.09°	99.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8308 and 0.6092
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	5319 / 1 / 202
Goodness-of-fit on F^2	1.036
Final R indices [I>2sigma(I)][ab]	R1 = 0.0307, wR2 = 0.0593
R indices (all data)[ab]	R1 = 0.0343, wR2 = 0.0608
Absolute structure parameter	-0.04(2)
Largest diff. peak and hole	0.352 and -0.458 e.$Å^{-3}$

Selected bond lengths (Å) and angles (°) for (R_C,$S_C$$S_N$)-**8**

Pd(1)-C(1)	2.003(3)	Pd(1)-N(1)	2.054(2)
Pd(1)-N(2)	2.051(2)	Pd(1)-O(1)	2.0856(19)
C(11)-O(1)	1.291(3)	C(11)-O(2)	1.232(3)
C(1)-Pd(1)-N(1)	81.62(10)	C(1)-Pd(1)-N(2)	104.59(10)
N(1)-Pd(1)-O(1)	94.13(8)	N(2)-Pd(1)-O(1)	79.74(8)
C(1)-Pd(1)-O(1)	175.60(9)	N(2)-Pd(1)-N(1)	172.46(9)

(S_C,$S_C$$S_N$)-{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}(prolinato-N,O)palladium(II), (S_C,$S_C$$S_N$)-**8**



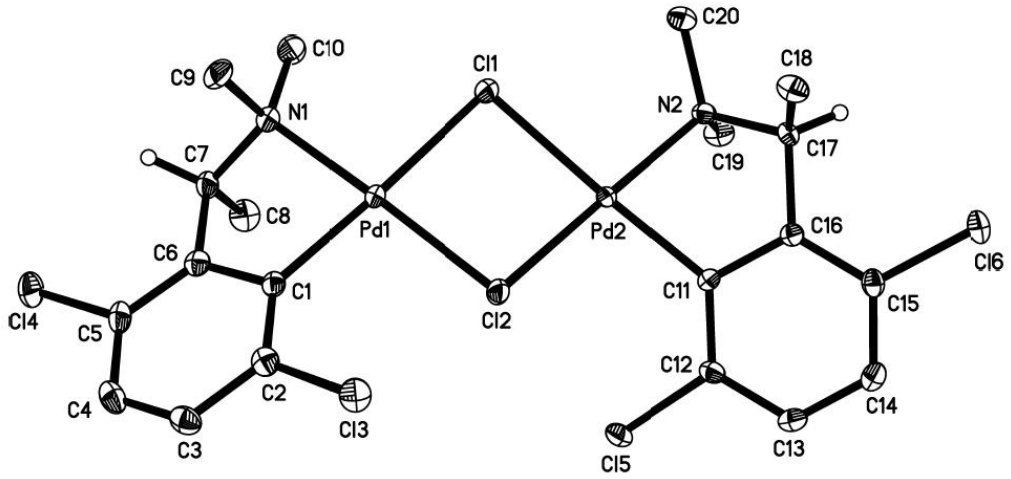
Empirical formula	$C_{15}H_{20}Cl_2N_2O_2Pd$	
Formula weight	437.63	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P2(1)	
Unit cell dimensions	a = 6.7161(2) Å	a= 90°.
	b = 8.8109(3) Å	b= 102.6990(10)°.
	c = 14.4813(5) Å	g = 90°.
Volume	835.97(5) $Å^3$	
Z	2	
Density (calculated)	1.739 Mg/m^3	
Absorption coefficient	1.437 mm^{-1}	
F(000)	440	
Crystal size	0.40 x 0.16 x 0.14 mm^3	

Theta range for data collection	1.44 to 33.14°.
Index ranges	-10<=h<=10, -13<=k<=5, -22<=l<=22
Reflections collected	10095
Independent reflections	4480 [R(int) = 0.0162]
Completeness to theta = 33.14°	99.9 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8242 and 0.5972
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	4480 / 1 / 206
Goodness-of-fit on F^2	1.106
Final R indices [I>2sigma(I)][ab]	R1 = 0.0181, wR2 = 0.0434
R indices (all data)[ab]	R1 = 0.0187, wR2 = 0.0479
Absolute structure parameter	0.002(18)
Largest diff. peak and hole	1.433 and -0.665 e.$Å^{-3}$

Selected bond lengths (Å) and angles (°) for (S_C,$S_C S_N$)**-8**

Pd(1)-C(1)	2.0034(19)	Pd(1)-N(1)	2.0700(18)
Pd(1)-N(2)	2.0544(18)	Pd(1)-O(1)	2.0687(15)
C(11)-O(1)	1.284(3)	C(11)-O(2)	1.238(2)
C(1)-Pd(1)-N(1)	81.53(7)	C(1)-Pd(1)-N(2)	102.40(7)
O(1)-Pd(1)-N(1)	94.14(6)	N(2)-Pd(1)-O(1)	82.36(6)
C(1)-Pd(1)-O(1)	174.68(8)	N(2)-Pd(1)-N(1)	170.48(7)

(S,S)-Di-μ-chlorobis{6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}dipalladium(II), (*S,S*)-**2**



Chemical formula	$C_{10.50}H_{13}Cl_4NPd$	
Formula weight	401.42	
Temperature	103(2) K	
Wavelength	0.71073 Å	
Crystal size	0.120 x 0.300 x 0.400 mm	
Crystal habit	yellow block	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 8.8571(2) Å	α = 90°
	b = 14.1867(3) Å	β = 95.0910(10)°
	c = 11.1258(3) Å	γ = 90°
Volume	1392.48(6) $Å^3$	
Z	4	
Density (calculated)	1.915 g/cm^3	
Absorption coefficient	2.074 mm^{-1}	
F(000)	788	

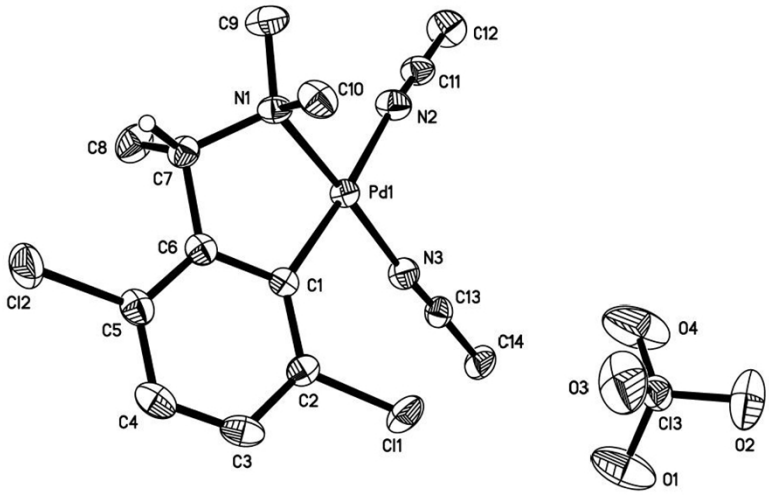
Theta range for data collection	2.82 to 30.53°
Index ranges	-12<=h<=12, -16<=k<=20, -15<=l<=15
Reflections collected	14642
Independent reflections	7623 [R(int) = 0.0255]
Coverage of independent reflections	99.0%
Absorption correction	multi-scan
Max. and min. transmission	0.7889 and 0.4909
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	7623 / 1 / 304
Goodness-of-fit on F^2	1.010
Δ/σ_{max}	0.001
Final R indices 7393 data; I>2σ(I)	R1 = 0.0226, wR2 = 0.0460
Final R indices all data	R1 = 0.0237, wR2 = 0.0466
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0115P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.480 and -0.730 eÅ^{-3}
R.M.S. deviation from mean	0.095 eÅ^{-3}

Selected bond lengths (Å) and angles (°) for complex (*S,S*)**-2**

Pd(1)-C(1)	2.002(3)	Pd(1)-N(1)	2.068(2)
Pd(1)-Cl(2)	2.3283(7)	Pd(1)-Cl(1)	2.4177(7)

Pd(2)-C(11)	1.984(2)	Pd(2)-N(2)	2.077(2)
Pd(2)-Cl(2)	2.3352(6)	Pd(2)-Cl(1)	2.4174(7)
C(1)-Pd(1)-N(1)	81.35(10)	C(1)-Pd(1)-Cl(2)	98.63(8)
N(1)-Pd(1)-Cl(2)	173.55(7)	C(1)-Pd(1)-Cl(1)	176.53(8)
N(1)-Pd(1)-Cl(1)	95.67(6)	Cl(2)-Pd(1)-Cl(1)	84.13(2)
C(11)-Pd(2)-N(2)	80.82(9)	C(11)-Pd(2)-Cl(2)	97.85(7)
N(2)-Pd(2)-Cl(2)	173.66(7)	C(11)-Pd(2)-Cl(1)	177.69(7)
N(2)-Pd(2)-Cl(1)	97.20(6)	Cl(2)-Pd(2)-Cl(1)	83.99(2)

(*S*)-bis(acetonitrile-N){6-(1'-dimethylaminoethyl)-2,5-dichlorophenyl-C,N}palladium(II) perchlorate, (*S*)-**10**



Chemical formula	$C_{14}H_{18}Cl_3N_3O_4Pd$	
Formula weight	505.06	
Temperature	153(2) K	
Wavelength	0.71073 Å	
Crystal size	0.080 x 0.120 x 0.400 mm	
Crystal habit	yellow needle	
Crystal system	monoclinic	
Space group	P 1 21 1	
Unit cell dimensions	a = 10.8357(8) Å	α = 90°
	b = 6.3586(4) Å	β = 108.798(2)°
	c = 14.7427(11) Å	γ = 90°
Volume	961.59(12) $Å^3$	
Z	2	
Density (calculated)	1.744 g/cm^3	
Absorption coefficient	1.405 mm^{-1}	
F(000)	504	
Theta range for data collection	1.46 to 35.66°	
Index ranges	-17<=h<=17, -10<=k<=10, -24<=l<=23	

Reflections collected	21041
Independent reflections	8531 [R(int) = 0.0396]
Coverage of independent reflections	99.7%
Absorption correction	multi-scan
Max. and min. transmission	0.8959 and 0.6034
Structure solution technique	direct methods
Structure solution program	SHELXS-97 (Sheldrick, 2008)
Refinement method	Full-matrix least-squares on F^2
Refinement program	SHELXL-97 (Sheldrick, 2008)
Function minimized	$\Sigma\, w(F_o^2 - F_c^2)^2$
Data / restraints / parameters	8531 / 1 / 231
Goodness-of-fit on F^2	1.095
Δ/σ_{max}	0.001
Final R indices 7247 data; I>2σ(I)	R1 = 0.0370, wR2 = 0.0805
Final R indices all data	R1 = 0.0505, wR2 = 0.1045
Weighting scheme	$w=1/[\sigma^2(F_o^2)+(0.0482P)^2+0.0000P]$ where $P=(F_o^2+2F_c^2)/3$
Absolute structure parameter	-0.0(0)
Largest diff. peak and hole	0.806 and -0.665 eÅ^{-3}
R.M.S. deviation from mean	0.165 eÅ^{-3}

Selected bond lengths (Å) and angles (°) for complex (*S*)-**10**

Pd(1)-C(1)	1.993(3)	Pd(1)-N(3)	2.005(3)
Pd(1)-N(1)	2.051(3)	Pd(1)-N(2)	2.108(3)

C(1)-Pd(1)-N(3)	96.16(12)	C(1)-Pd(1)-N(1)	80.89(11)
N(3)-Pd(1)-N(1)	176.92(11)	C(1)-Pd(1)-N(2)	174.49(13)
N(3)-Pd(1)-N(2)	85.23(12)	N(1)-Pd(1)-N(2)	97.62(11)