Supporting Information

Room Temperature Asymmetric Pd-Catalyzed Methoxycarbonylation of Norbornene. Highly Selective Catalysis and HP-NMR Studies

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Contents

SI. 1 Experimental Section

General Methods

All reactions were carried out under an argon atmosphere using Standard Schlenk techniques. All solvents were carefully purified by appropriate procedures. $PdCl_2$ was purchased from Johnson Matthey Inc. and used without further purification. All other reagents were used as received from commercial suppliers. CD_2Cl_2, THF-d_8, $CDCl_3$ were stored over molecular sieves under nitrogen. Air sensitive compounds were stored under argon.

NMR data

^{1}H, $^{13}C\{^{1}H\}$, $^{31}P\{^{1}H\}$ spectra were recorded on a Varian Mercury 400 spectrometer (400.14, 100.63, and 161.98 MHz respectively). Chemical shifts were reported relative to tetramethylsilane for ^{1}H and $^{13}C\{^{1}H\}$ as internal standard. ^{31}P chemical shifts were referenced to an external 85% H_3PO_4 sample.

SI. 2 Caracterization of Palladium Complexes

Figure 1. ^{1}H NMR spectrum of complex $[PdCl_2(1)_2]$ 1a (CD_2Cl_2, 298K)

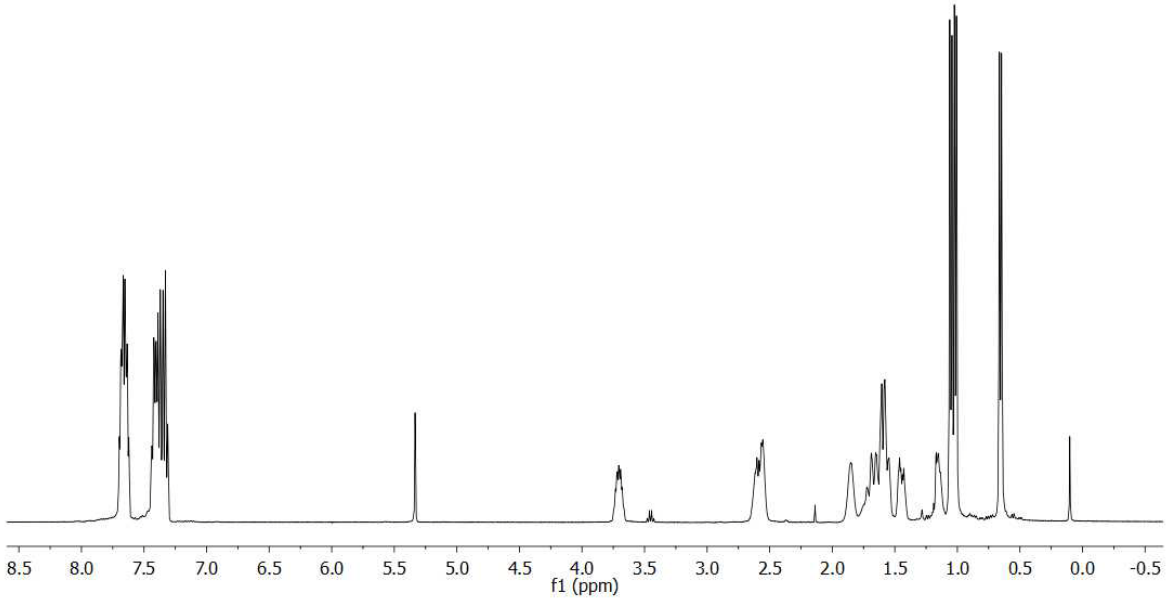


Figure 2. $^{31}P\{^{1}H\}$ NMR spectrum of complex 1a (CD_2Cl_2, 298K)

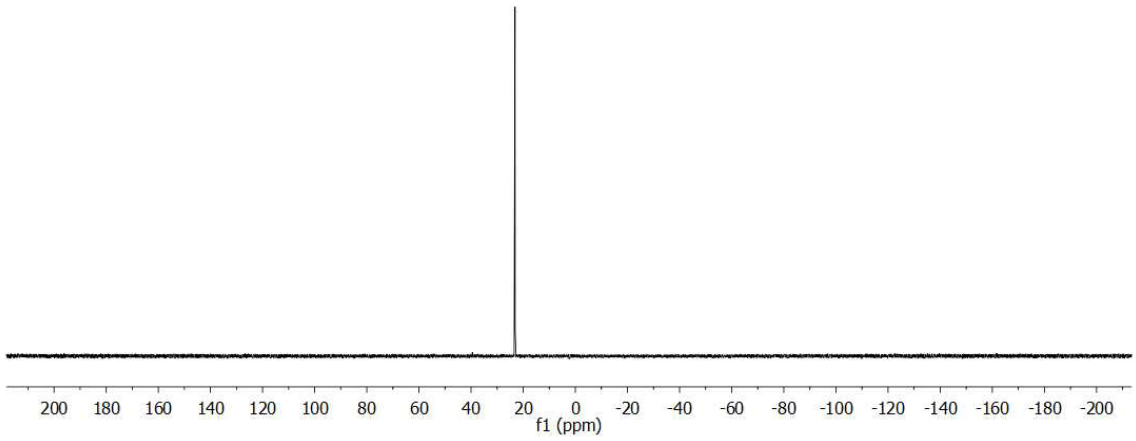


Figure 3. ^{1}H NMR spectrum of [$PdCl_2$(4)] 4a (CD_2Cl_2, 298K)

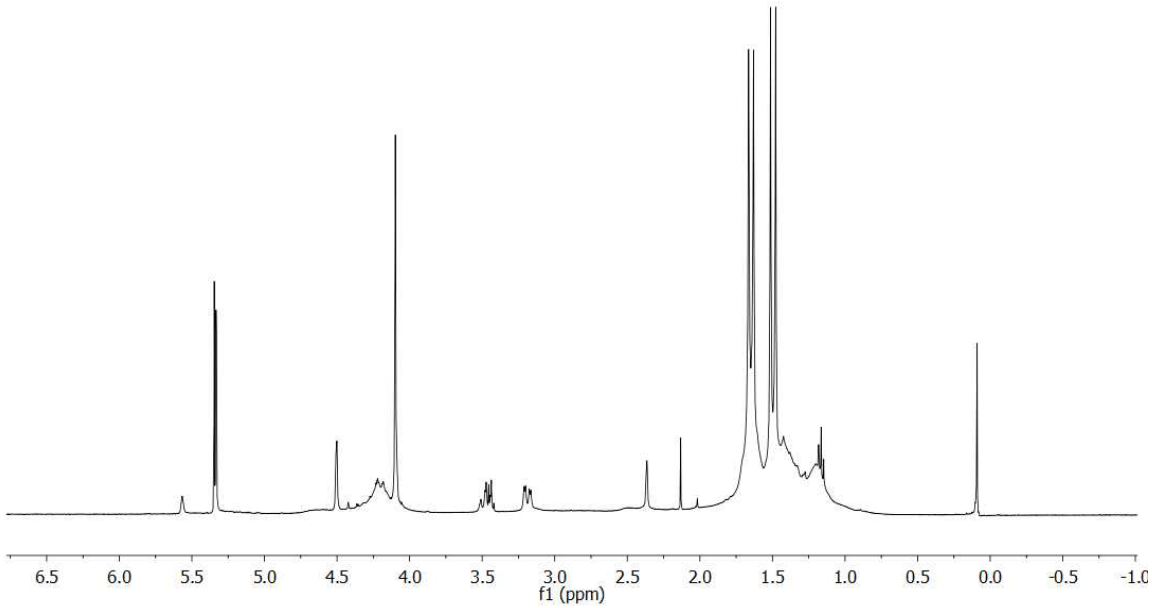


Figure 4. ^{31}P{^{1}H}NMR spectrum of [$PdCl_2$(4)] 4a (CD_2Cl_2, 298K)

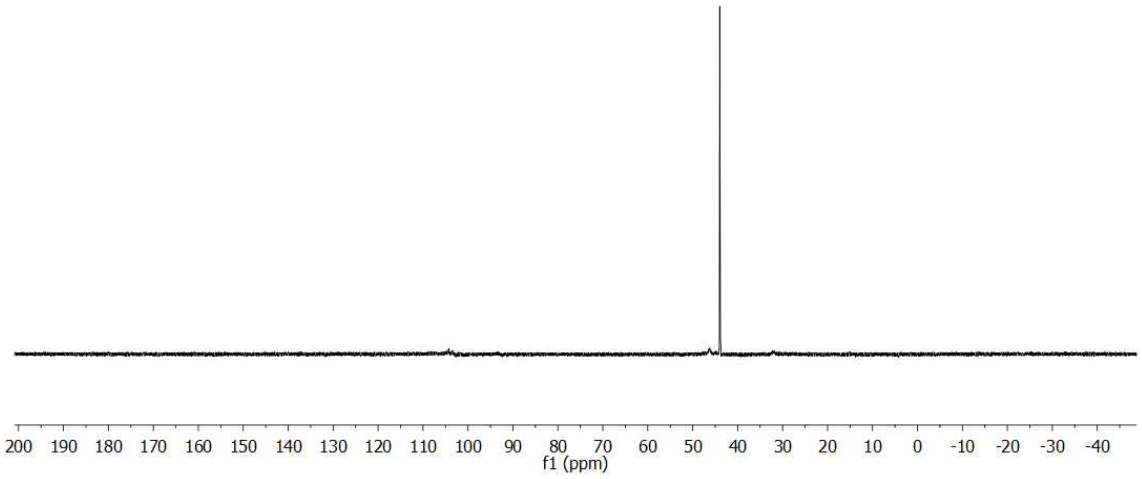


Figure 5. ^{1}H NMR spectrum of 4-$(H^{+})_2$ (THF-d_8, 298K)

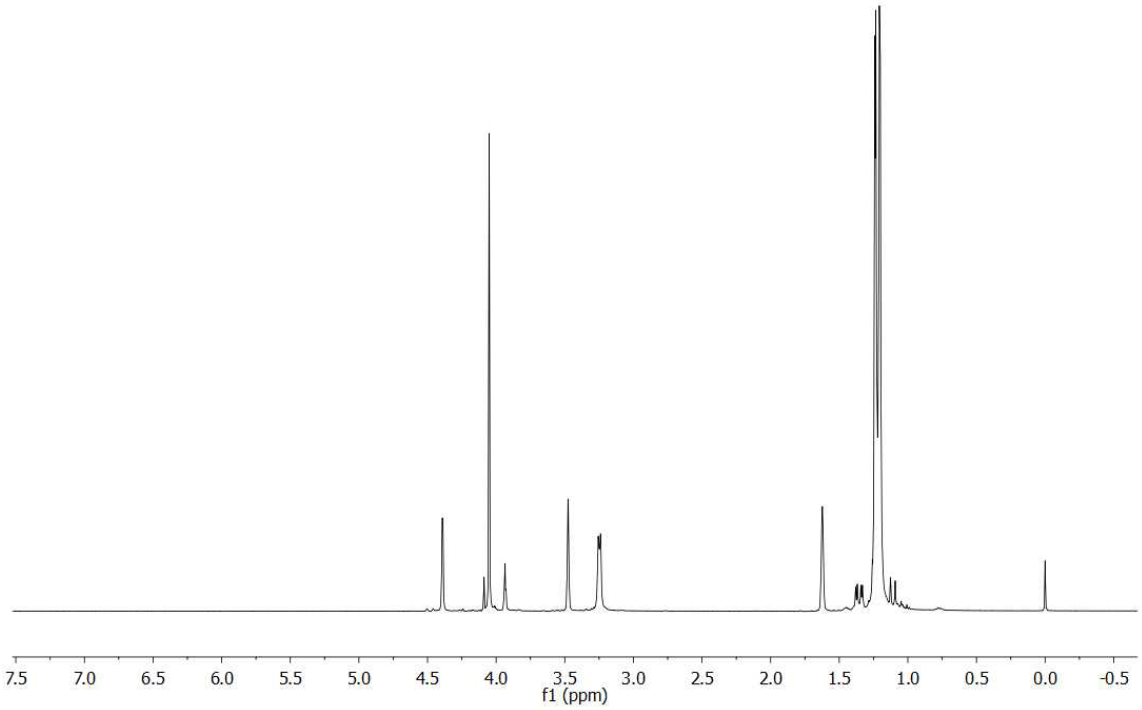


Figure 6. ^{31}P{^{1}H}NMR spectrum of 4-$(H^{+})_2$ (THF-d_8, 298K)

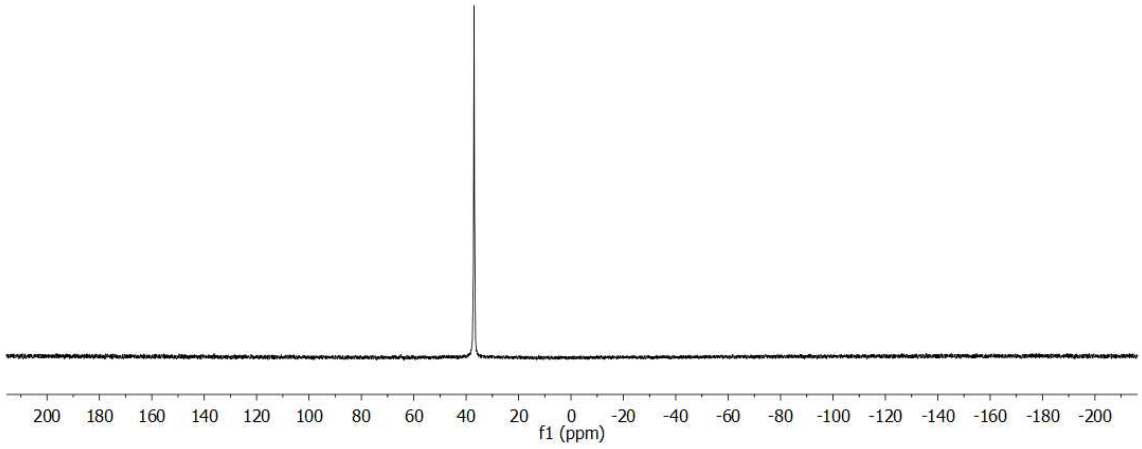


Figure 7. ^{1}H NMR spectrum of [PdBr(7)] 7a (CD_2Cl_2 298K)

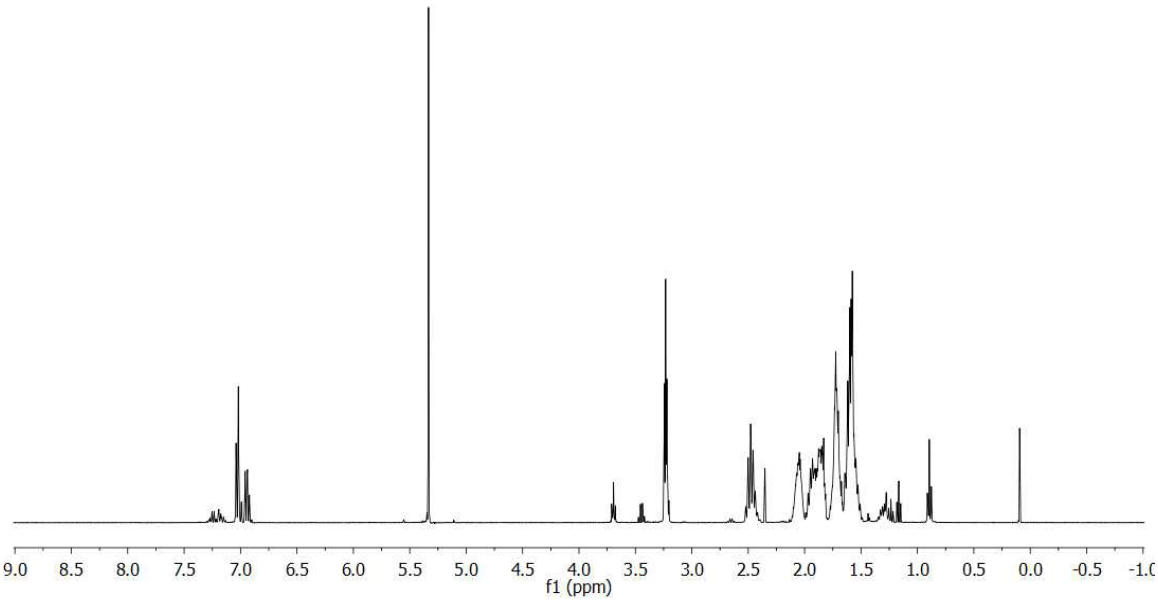
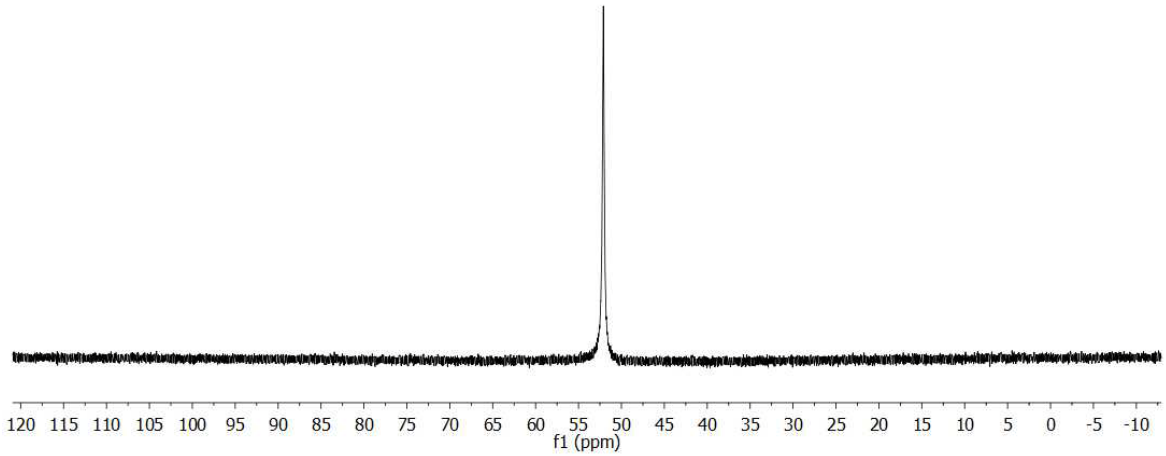


Figure 8. $^{31}P\{^{1}H\}$NMR spectrum of [PdBr(7)] 7a (CD_2Cl_2 298K)



SI. 3 X-ray data

Table 1. Crystal data for structures **4a** and **7a**

	4a	**7a**
Empirical Formula	$C_{28}H_{48}Cl_2FeP_2Pd.\ C_4H_8O$	$C_{28}H_{43}BrP_2Pd$
M	751.86	627.87
T/K	293(2)	
λ/Å	0.71073	
Crystal system	Monoclinic	Othorhombic
Space group	*P* 2_1/n	*P* bca
a/Å	11.558(3)	15.151(3)
b/Å	14.646(3)	17.180(4)
c/Å	20.721(4)	21.361(4)
β/°	94.29(3)	90.0
Unit cell volume/Å^3	3497.8(13)	5560(2)
D_{calcd}/g cm^{-3}	1.428	1.500
Z	4	8
μ(Mo Kα)/mm^{-1}	1.196	2.234
F(000)	1568	2576
Theta range for data collection	1.70 - 25.02	2.62 - 27.10
Absorption correction	refdelf	
Refinement method	Full-matrix least squares on F^2	
Data/parameter	6015/352	5864/289
Final R indices [I>2σ(I)]	R_1= 0.0510, wR_2= 0.1159	R_1= 0.0395, wR_2= 0.0959
R indices (all data)	R_1= 0.1008, wR_2= 0.1359	R_1= 0.852, wR_2= 0.1079
Goodness-of-fit on F^2	0.894	0.860
Largest diff peak and hole (e/Å^3)	0.668, -0.406	0.382, -0.697