Electronic Supplementary Material (ESI) for Polymer Chemistry.

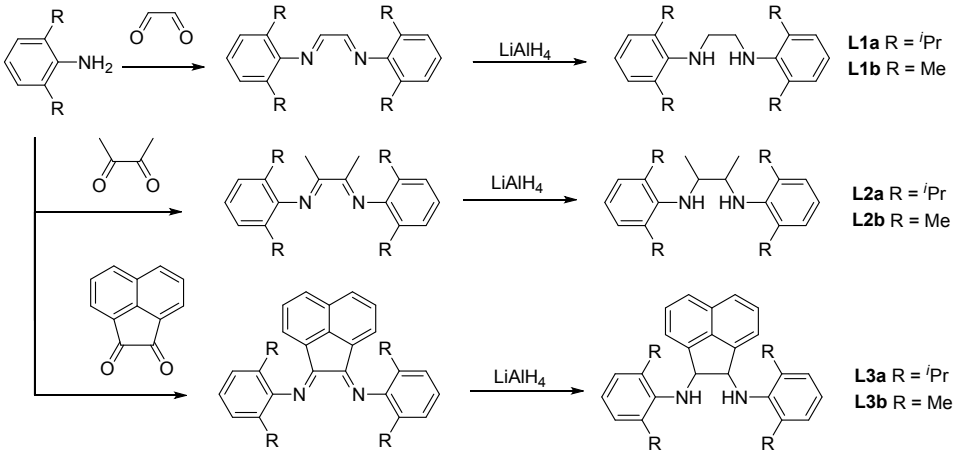
Supporting Information

Synthesis and Characterization of *α*-Diamine Palladium Complexes and Insight into Hybridization Effects of Nitrogen Donor Atoms on Norbornene (Co)polymerizations

Ting Zheng,[a] Heng Liao,[a] Jie Gao,[a] Liu Zhong,[a] Haiyang Gao*[a] and Qing Wu[a]

[a] School of Materials Science and Engineering, PCFM Lab, Sun Yat-sen University, Guangzhou 510275, China.

* Corresponding author. Fax: +86-20-84114033. Tel.: +86-20-84113250. E-mail: Gao H.: gaohy@mail.sysu.edu.cn



Scheme S1. Synthetic routes of α-diamine ligands

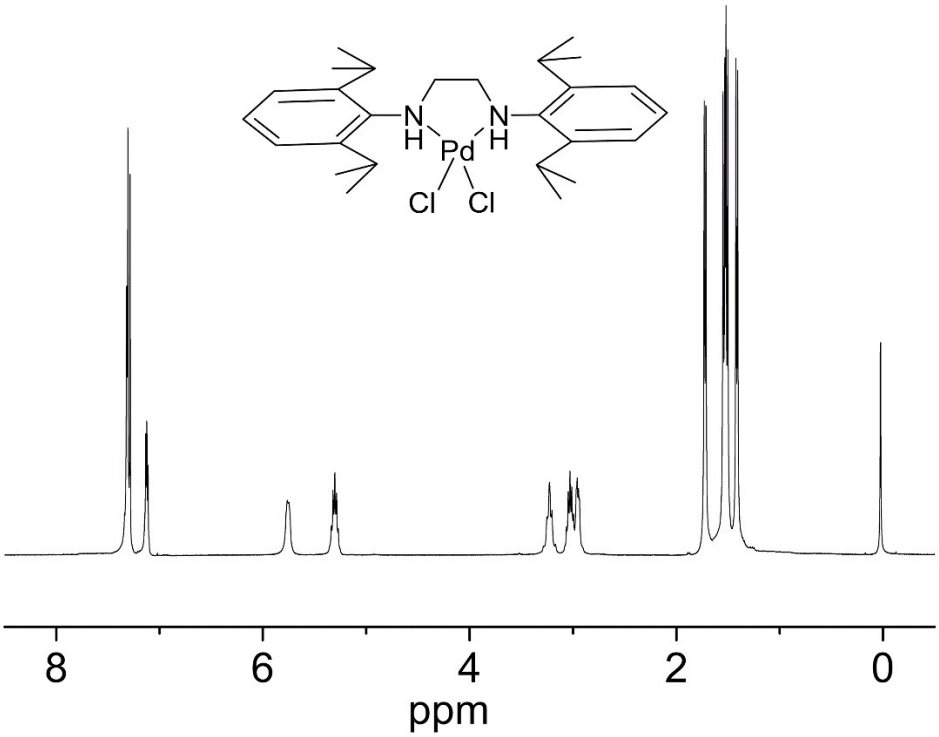


Figure S1. ^{1}H NMR spectrum of palladium complex **1a** in $CDCl_3$**.**

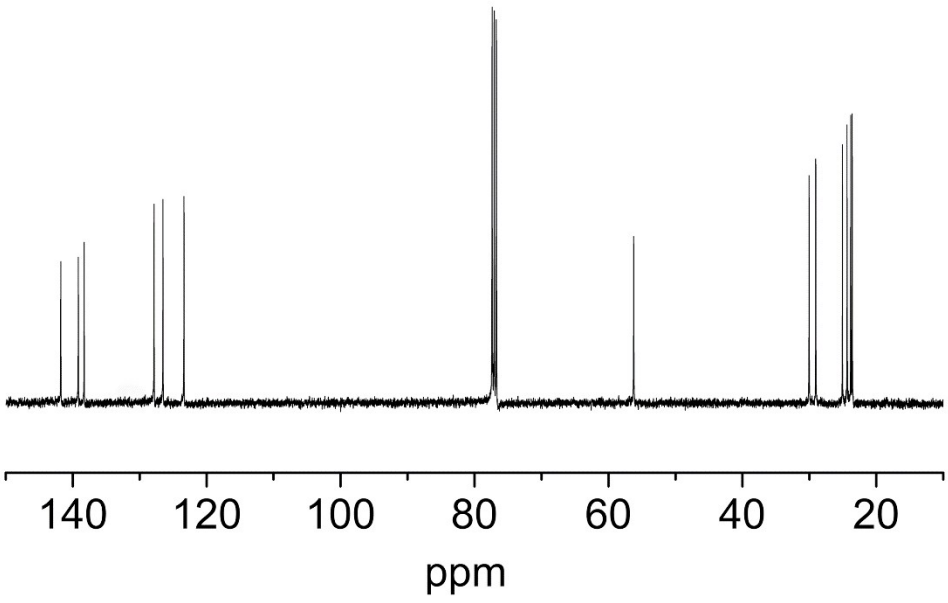


Figure S2. ^{13}C NMR spectrum of palladium complex **1a** in $CDCl_3$**.**

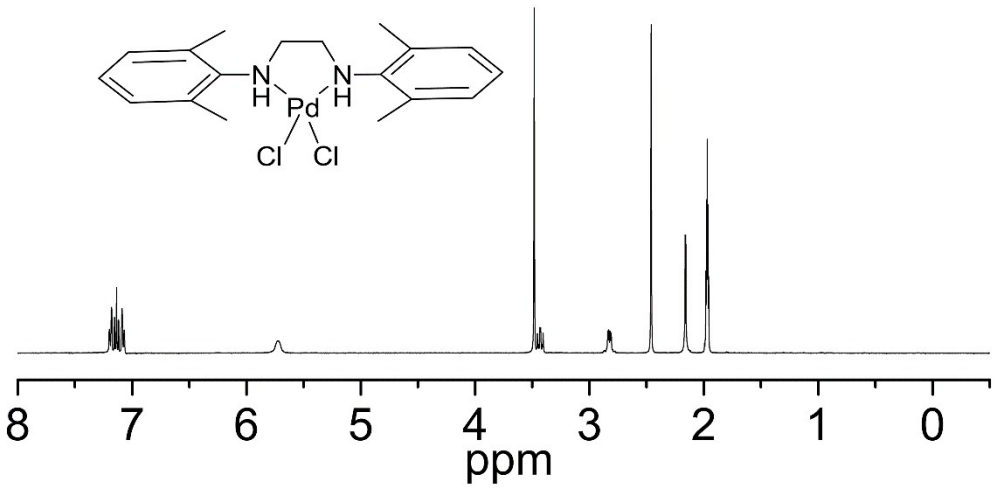


Figure S3. ^{1}H NMR spectrum of palladium complex **1b** in CD_3CN**.**

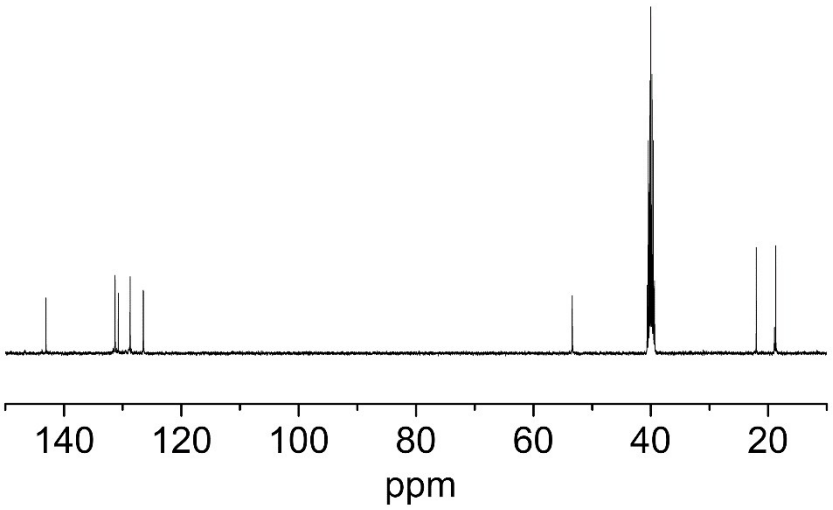


Figure S4. ^{13}C NMR spectrum of palladium complex **1b** in ***d*-**DMSO**.**

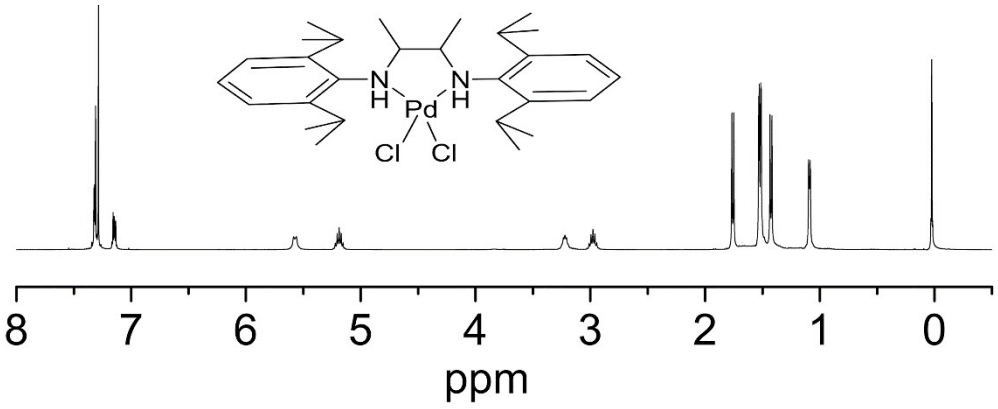


Figure S5. ^{1}H NMR spectrum of palladium complex **2a** in $CDCl_3$**.**

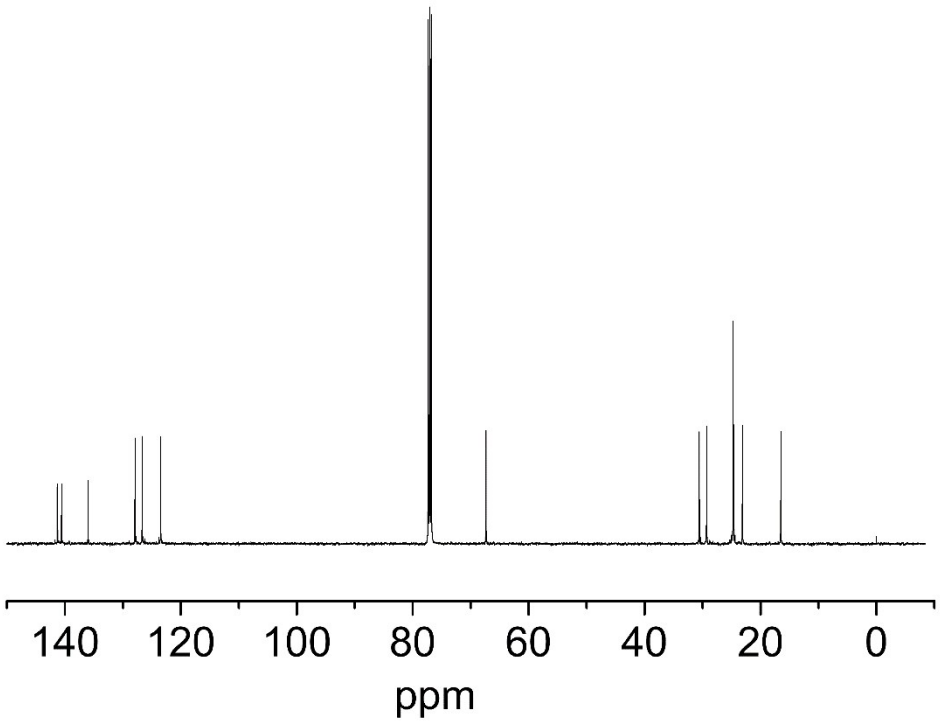


Figure S6. ^{13}C NMR spectrum of palladium complex **2a** in $CDCl_3$**.**

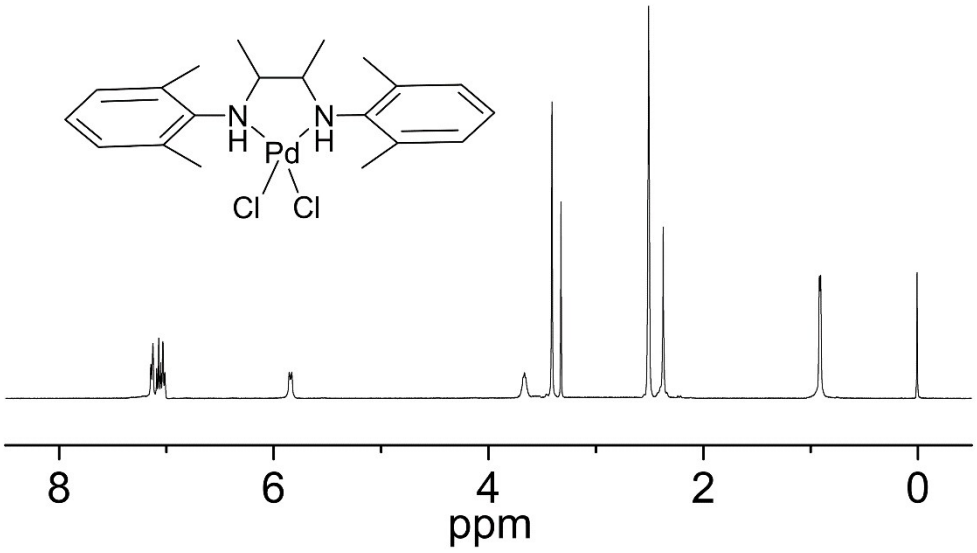


Figure S7. ^{1}H NMR spectrum of palladium complex **2b** in ***d***-DMSO**.**

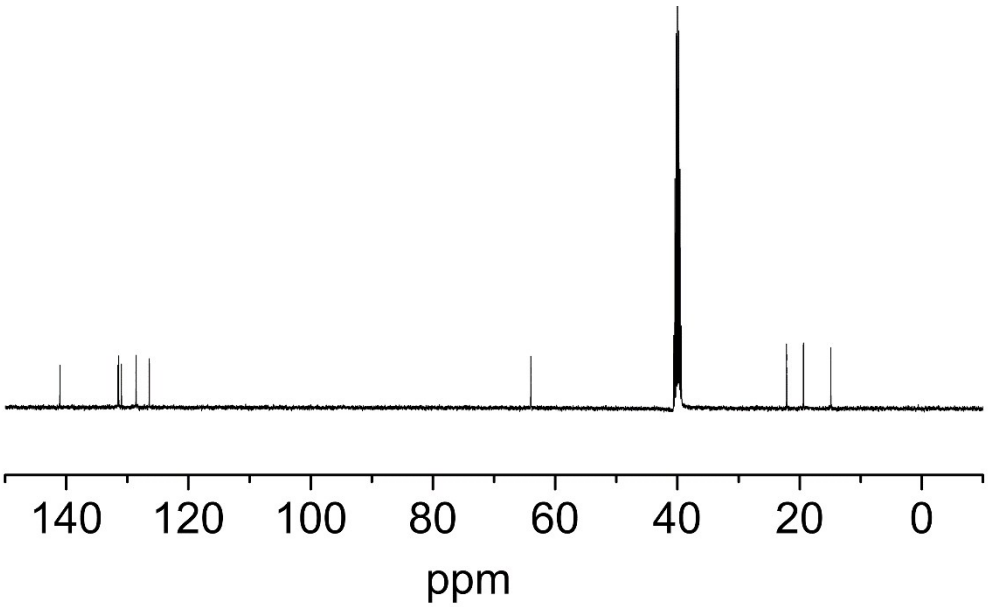


Figure S8. ^{13}C NMR spectrum of palladium complex **2b** in ***d***-DMSO.

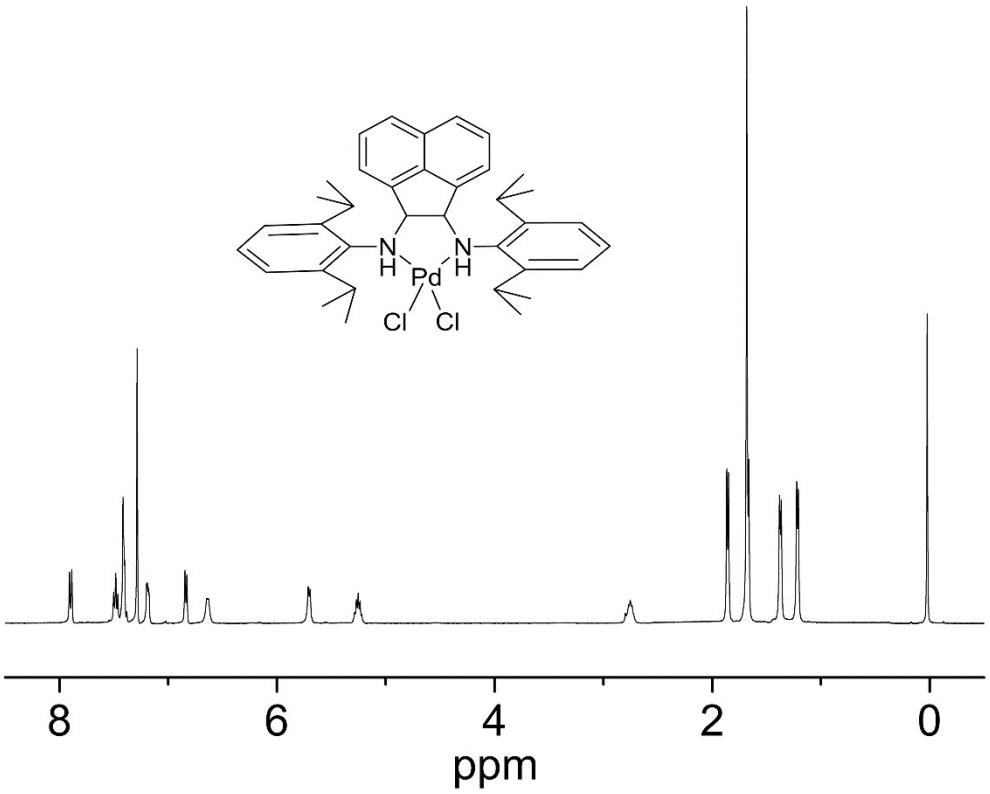


Figure S9. ^{1}H NMR spectrum of palladium complex **3a** in $CDCl_3$**.**

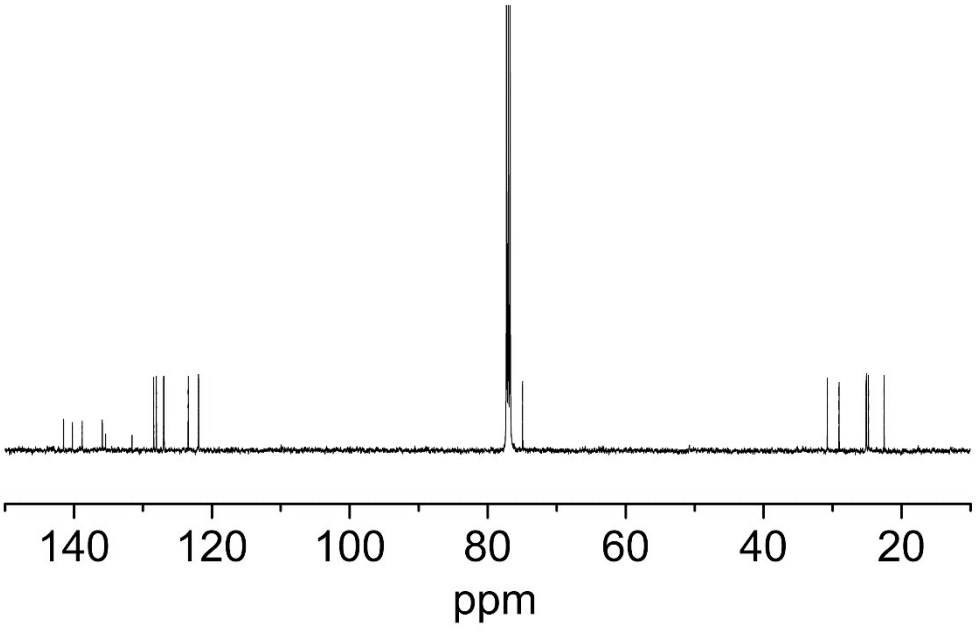


Figure S10. ^{13}C NMR spectrum of palladium complex **3a** in $CDCl_3$.

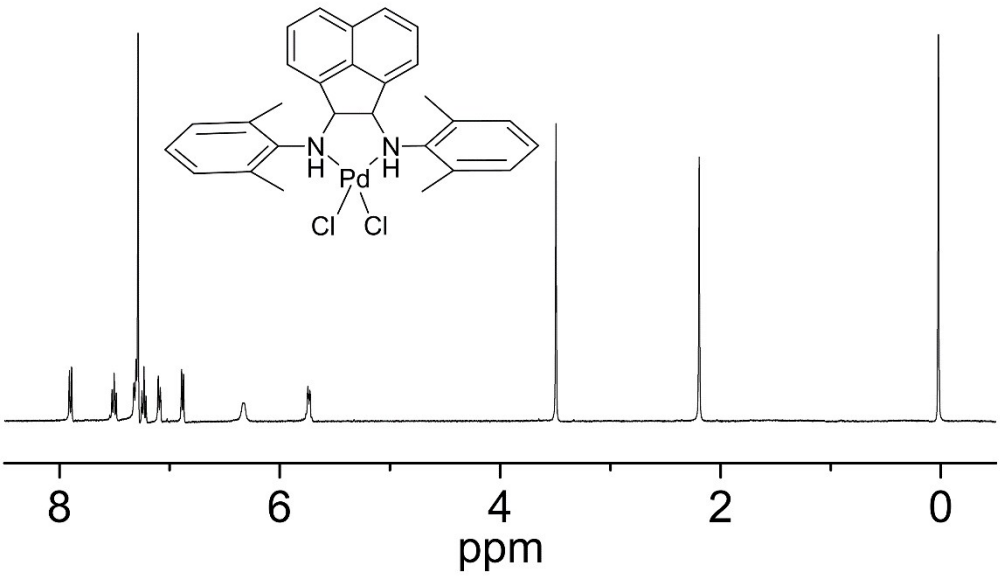


Figure S11. ^{1}H NMR spectrum of palladium complex **3b** in $CDCl_3$**.**

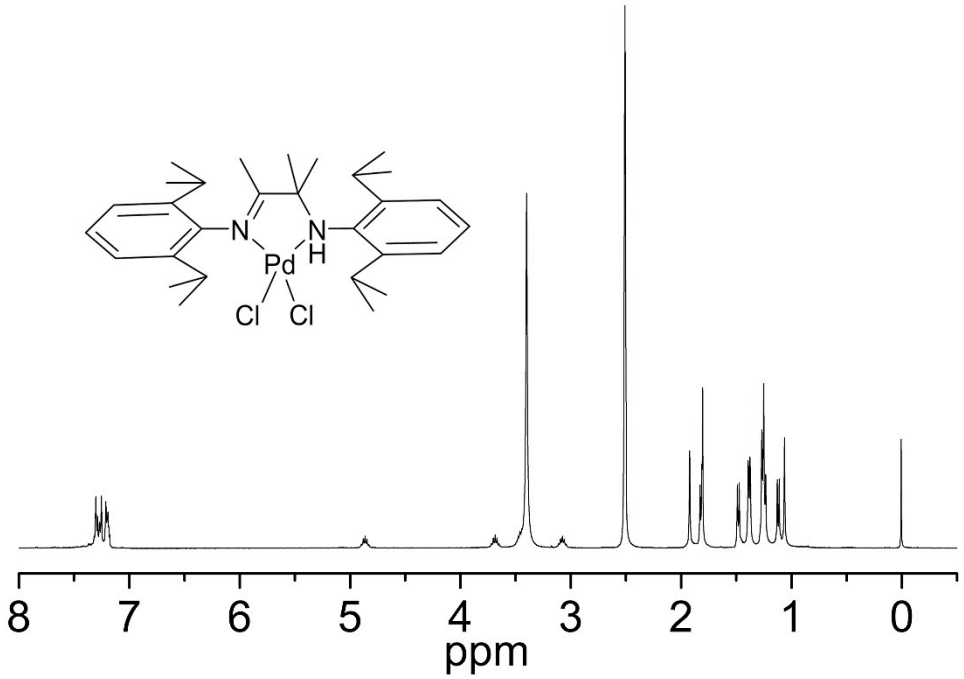


Figure S12. ^{1}H NMR spectrum of amine-imine palladium complex **4a** in ***d*-**DMSO**.**

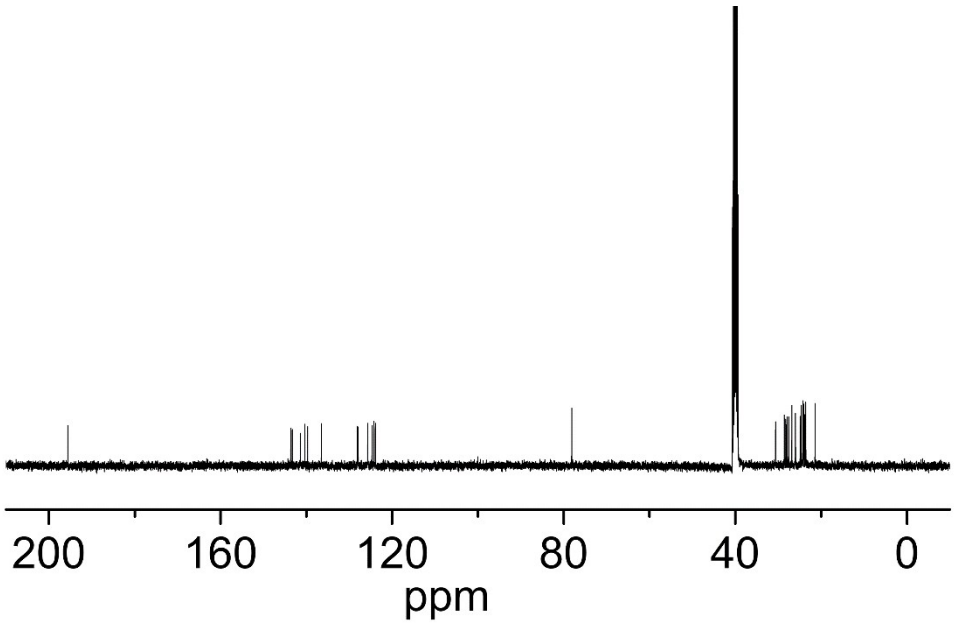


Figure S13. ^{13}C NMR spectrum of amine-imine palladium complex **4a** in ***d*-**DMSO**.**

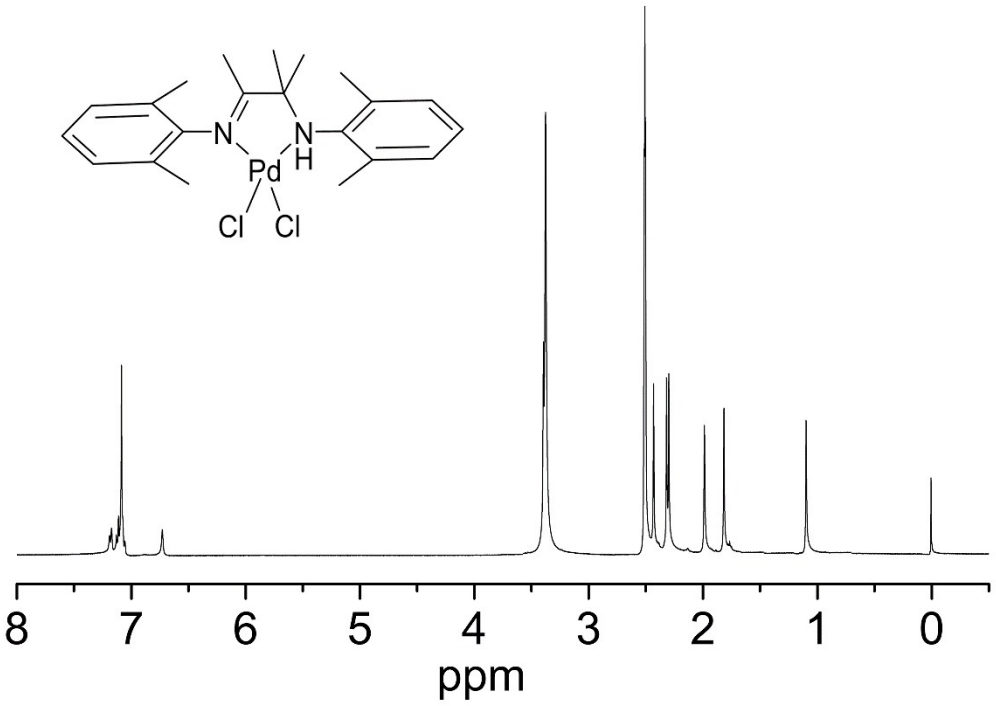


Figure S14. ^{1}H NMR spectrum of amine-imine palladium complex **4b** in ***d*-**DMSO**.**

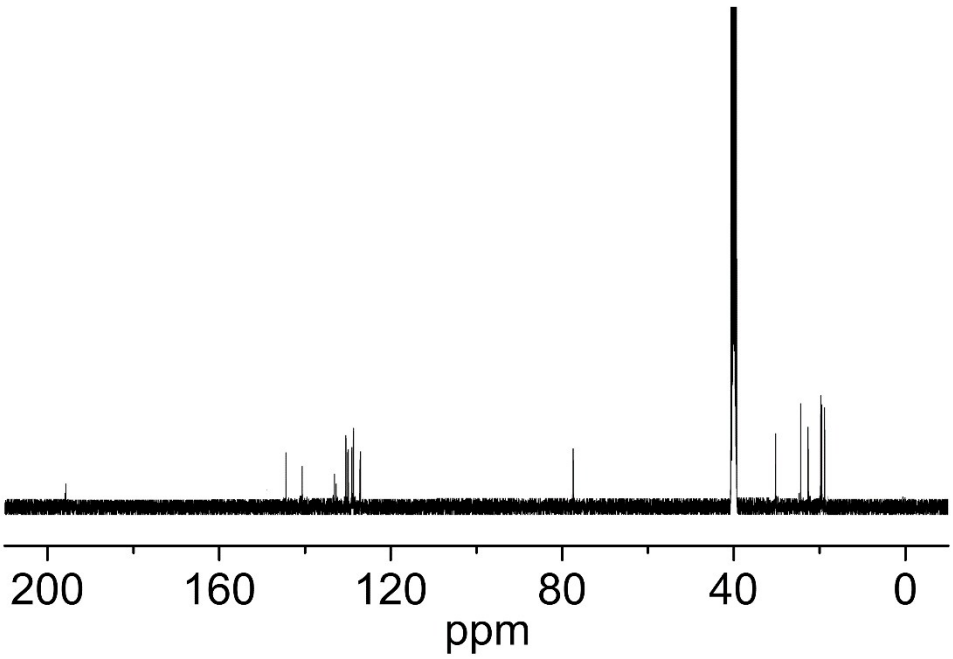


Figure S15. ^{13}C NMR spectrum of amine-imine palladium complex **4b** in ***d*-**DMSO**.**

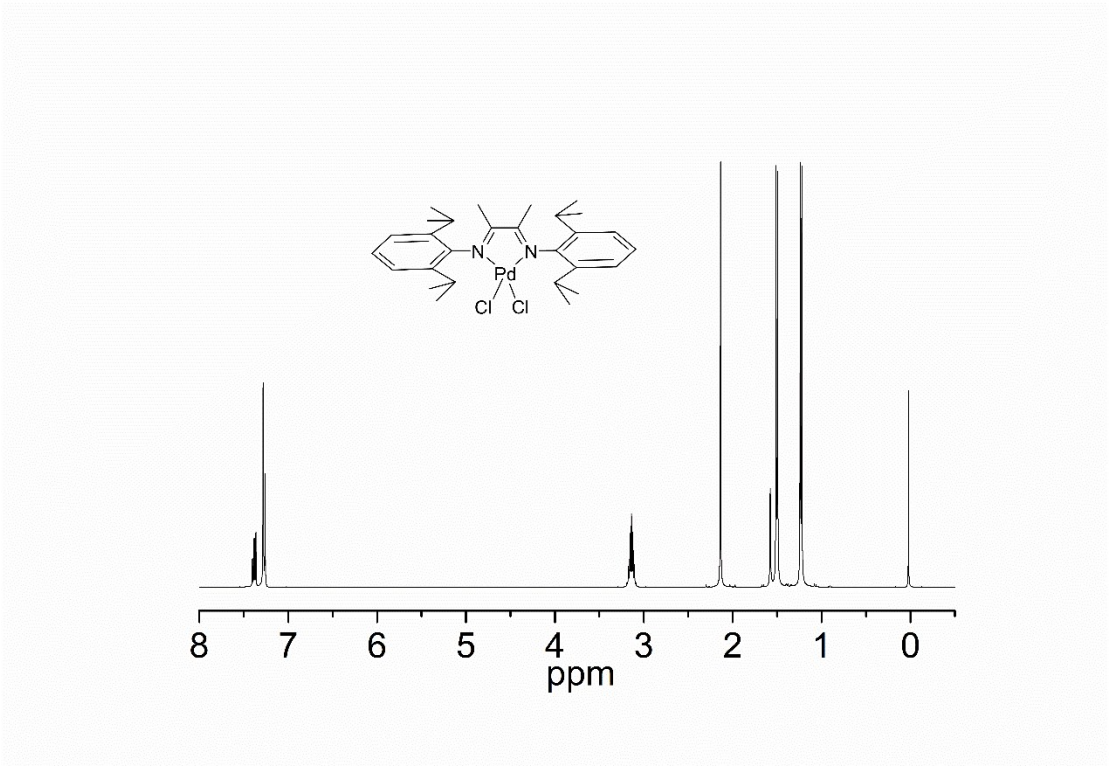


Figure S16.[1]H NMR spectrum of α-diimine palladium complex **5a** in $CDCl_3$**.**

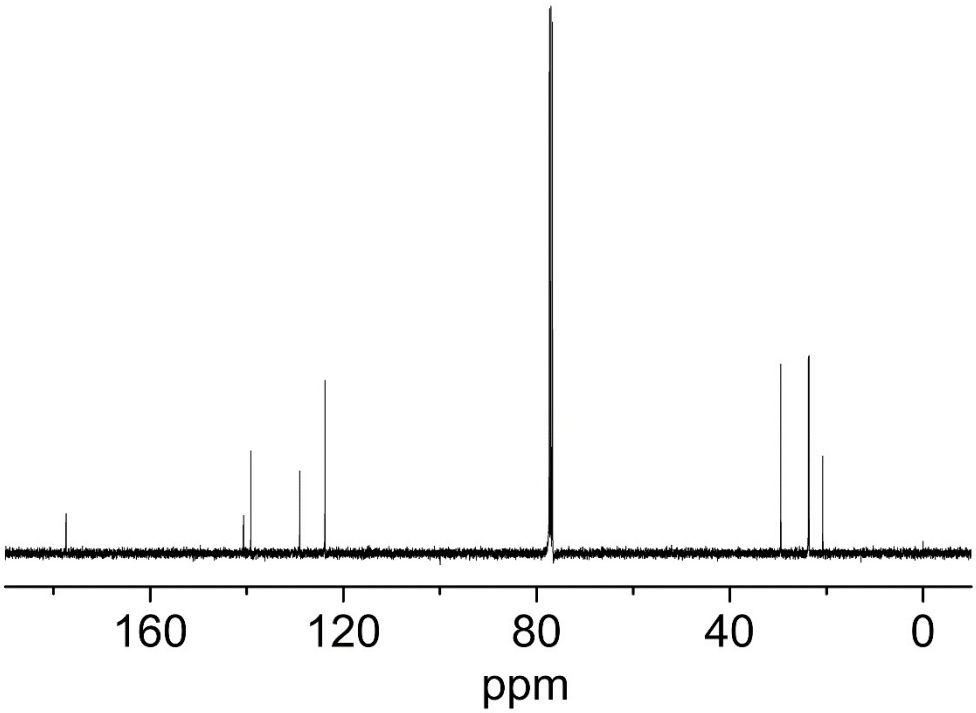


Figure S17.[13]C NMR spectrum of α-diimine palladium complex **5a** in $CDCl_3$**.**

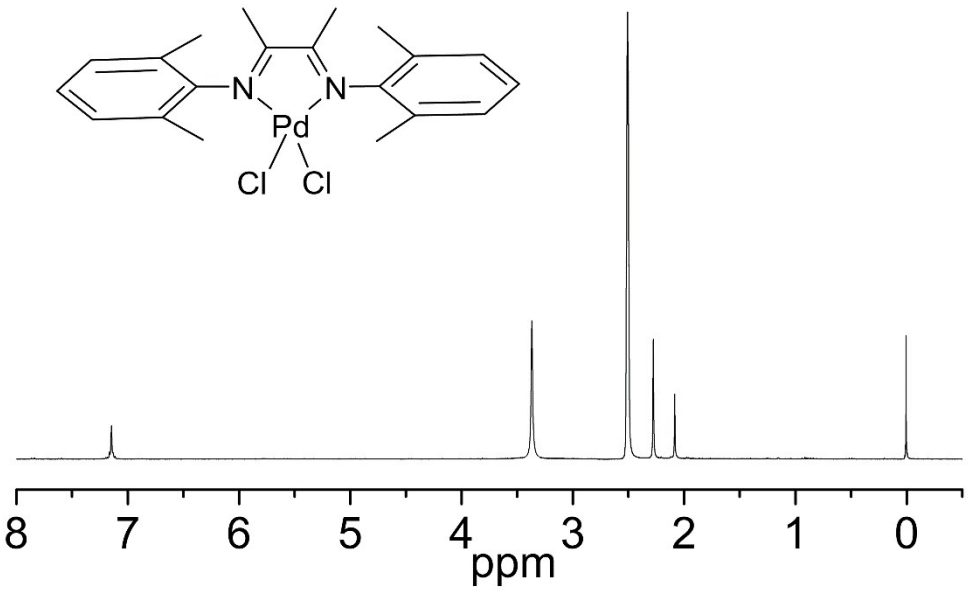


Figure S18.[1]H NMR spectrum of α-diimine palladium complex **5b** in ***d***-DMSO**.**

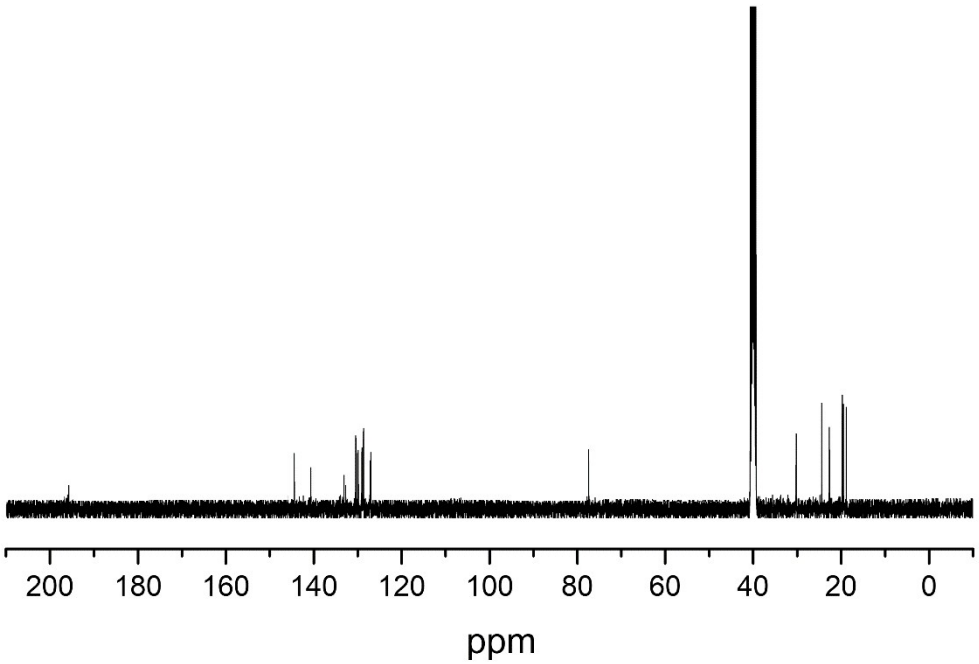


Figure S19.[13]C NMR spectrum of α-diimine palladium complex **5b** in ***d***-DMSO**.**

Table S1. Crystallographic data for the palladium complexes

	1a	**2b**
Empirical formula	$C_{27}H_{42}Cl_4N_2Pd$	$C_{40}H_{56}Cl_4N_4Pd_2$
Formula weight	642.83	947.48
Crystal system	Tetragonal	Orthorhombic
space group	$I4_1/a$	Pbca
a (Å)	27.4219(2)	13.5058(3)
b (Å)	27.4219(2)	13.9638(3)
c (Å)	15.9884(2)	21.6147(8)
α (deg)	90	90
β (deg)	90	90
γ (deg)	90	90
Volume($Å^3$)	12022.65(19)	4076.4(2)
Z	16	4
Calculated density (g/cm^3)	1.421	1.544
F(000)	5312	1936
Crystal size (mm)	0.35 × 0.20 × 0.08	0.2 × 0.2 × 0.2
Theta range for data collection (deg)	4.54 to 66.00	3.417 to 26.995
Limiting indices	-32 ≤ h ≤ 31	-17 ≤ h ≤ 15
	-32 ≤ k ≤ 21	-17 ≤ k ≤ 17
	-18 ≤ l ≤ 12	-18 ≤ l ≤ 27
Reflections collected / unique	11280 / 5234	16975 / 4414
	[R(int) = 0.0262]	[R(int) = 0.0321]
Data / restraints / parameters	5234 / 55 / 343	4414 / 0 / 232
Goodness-of-fit on F^2	1.122	1.030
Final R indices [I>2sigma(I)]	R1 = 0.0543, *w*R2 = 0.1536	R1 = 0.0286, *w*R2 = 0.0584
R indices (all data)	R1 = 0.0558, *w*R2 = 0.1554	R1 = 0.0407, *w*R2 = 0.0626
Largest diff. peak and hole ($e/Å^3$)	1.662 and -2.199	0.856 and -0.395

Table S2. Crystallographic data for the palladium complexes

	3a	**3b**
Empirical formula	$C_{36}H_{46}Cl_2N_2OPd$	$C_{28}H_{30}Cl_2N_2OPd$
Formula weight	700.05	587.84
Crystal system	Orthorhombic	Monoclinic
space group	Pnma	$P2_1/n$
a (Å)	11.5645(10)	14.0031(4)
b (Å)	21.3415(3)	17.0473(4)
c (Å)	13.8095(2)	21.8047(7)
α (deg)	90	90
β (deg)	90	102.678(3)
γ (deg)	90	90
Volume($Å^3$)	3408.24(7)	5078.2(3)
Z	4	8
Calculated density (g/cm^3)	1.364	1.538
F(000)	1456	2400
Crystal size (mm)	0.15 × 0.12 × 0.12	0.4 × 0.3 × 0.08
Theta range for data collection (deg)	3.437 to 29.567	3.389 to 26.373
Limiting indices	$-15 \le h \le 15$	$-16 \le h \le 17$
	$-28 \le k \le 29$	$-21 \le k \le 21$
	$-18 \le l \le 19$	$-27 \le l \le 27$
Reflections collected / unique	27858 / 4515	28792 / 10370
	[R(int) = 0.0286]	[R(int) = 0.0335]
Data / restraints / parameters	4515 / 0 / 200	10370 / 0 / 621
Goodness-of-fit on F^2	1.058	1.044
Final R indices [I>2sigma(I)]	R1 = 0.0256, *w*R2 = 0.0612	R1 = 0.0326, *w*R2 = 0.0705
R indices (all data)	R1 = 0.0311, *w*R2 = 0.0638	R1 = 0.0432, *w*R2 = 0.0769
Largest diff. peak and hole ($e/Å^3$)	0.615 and -0.560	0.468 and -0.477

Table S3 Influence of [Al]/[Pd] mole ratio on norbornene polymerization [a]

Entry	Al(MAO)/Pd	Yield (mg)	Conversion (%)	Activity [b]
1	1000	131	10.9	0.786
2	3000	504	42.0	3.02
3	6000	761	63.4	4.57
4	9000	945	78.8	5.67
5	12000	982	81.9	5.89

[a] Polymerization conditions: palladium complex **2a**: 1 μmol; T = 50 °C, t = 1 min; norbornene monomer, 1.2 g; total volume, 20 mL; solvent, toluene. [b] In units of 10^7 g of PNBE/(mol Pd·h).