

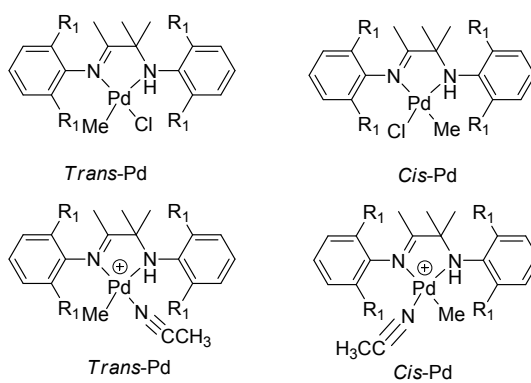
# Supporting Information

## **Amine-imine palladium catalysts for living polymerization of ethylene and copolymerization of ethylene with methyl acrylate: Incorporation of acrylate units into main chain and branch end**

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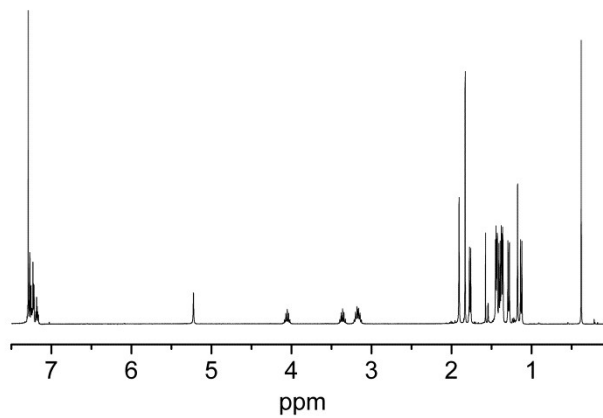
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**Scheme S1.** *Cis-* and *trans-*isomers of amine-imine palladium complexes

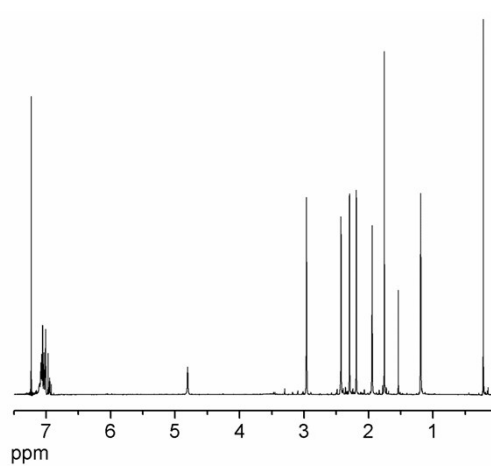


**Table S1.** Crystal data and structure refinement for palladium complexes

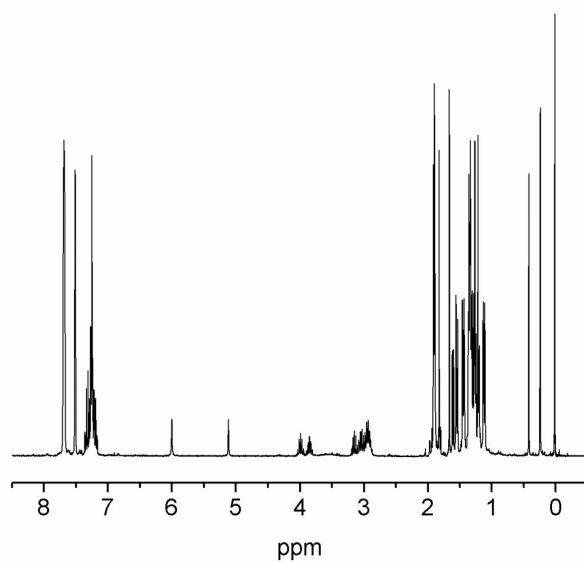
	<b>1</b>	<b>C1·0.5H<sub>2</sub>O</b>
Empirical formula	C <sub>30</sub> H <sub>47</sub> ClN <sub>2</sub> Pd	C <sub>64</sub> H <sub>62</sub> BF <sub>24</sub> N <sub>3</sub> O <sub>0.5</sub> Pd
Formula weight	577.55	1454.38
Crystal system	Monoclinic	Triclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> -1
a (Å)	15.919(2)	12.1356(2)
b (Å)	11.3592(16)	13.0597(2)
c (Å)	17.894(3)	22.3007(3)
α (deg)	90	103.2350(10)
β (deg)	114.701(2)	98.4960(10)
γ (deg)	90	101.5750(10)
Volume (Å <sup>3</sup> )	2939.7(7)	3300.29(9)
Z	4	2
D(calc.) (g/cm <sup>3</sup> )	1.305	1.464
F(000)	1216	1476
θ range (deg)	2.19 to 27.05	1.65 to 24.67
Index ranges	-20 ≤ <i>h</i> ≤ 16 -14 ≤ <i>k</i> ≤ 12 -22 ≤ <i>l</i> ≤ 15	-14 ≤ <i>h</i> ≤ 14 -15 ≤ <i>k</i> ≤ 15 -26 ≤ <i>l</i> ≤ 26
Reflections collected/unique	14657/6309 ( <i>R</i> <sub>int</sub> = 0.0261)	48203/10990 ( <i>R</i> <sub>int</sub> = 0.0572)
Data completeness	97.6 %	97.8%
Data/restraints/parameters	6309/0/339	10990/35/909
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.021	1.069
Final R indices [ <i>I</i> > 2σ( <i>I</i> )]	<i>R</i> <sub>1</sub> = 0.0308 <i>wR</i> <sub>2</sub> = 0.0716	<i>R</i> <sub>1</sub> = 0.0706 <i>wR</i> <sub>2</sub> = 0.1780
R indices (all data)	<i>R</i> <sub>1</sub> = 0.0506 <i>wR</i> <sub>2</sub> = 0.0807	<i>R</i> <sub>1</sub> = 0.0722 <i>wR</i> <sub>2</sub> = 0.1794
Largest diff. peak and hole (eÅ <sup>-3</sup> )	0.498/-0.425	2.202/-1.329



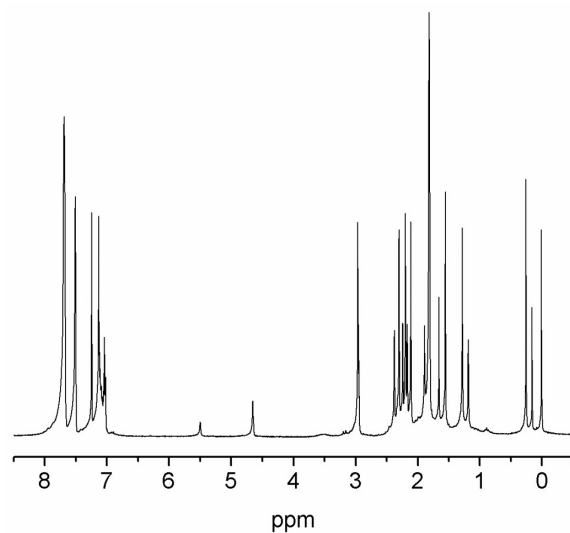
**Figure S1.** <sup>1</sup>H NMR spectrum of palladium complex 1



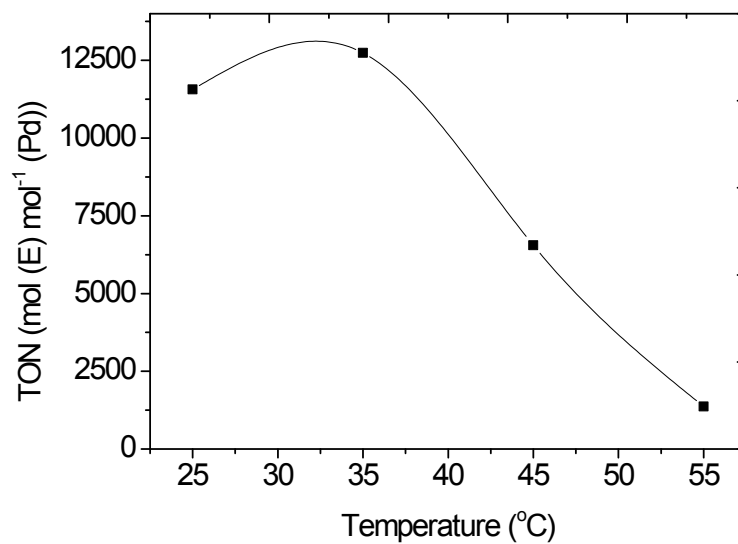
**Figure S2.** <sup>1</sup>H NMR spectrum of palladium complex 2



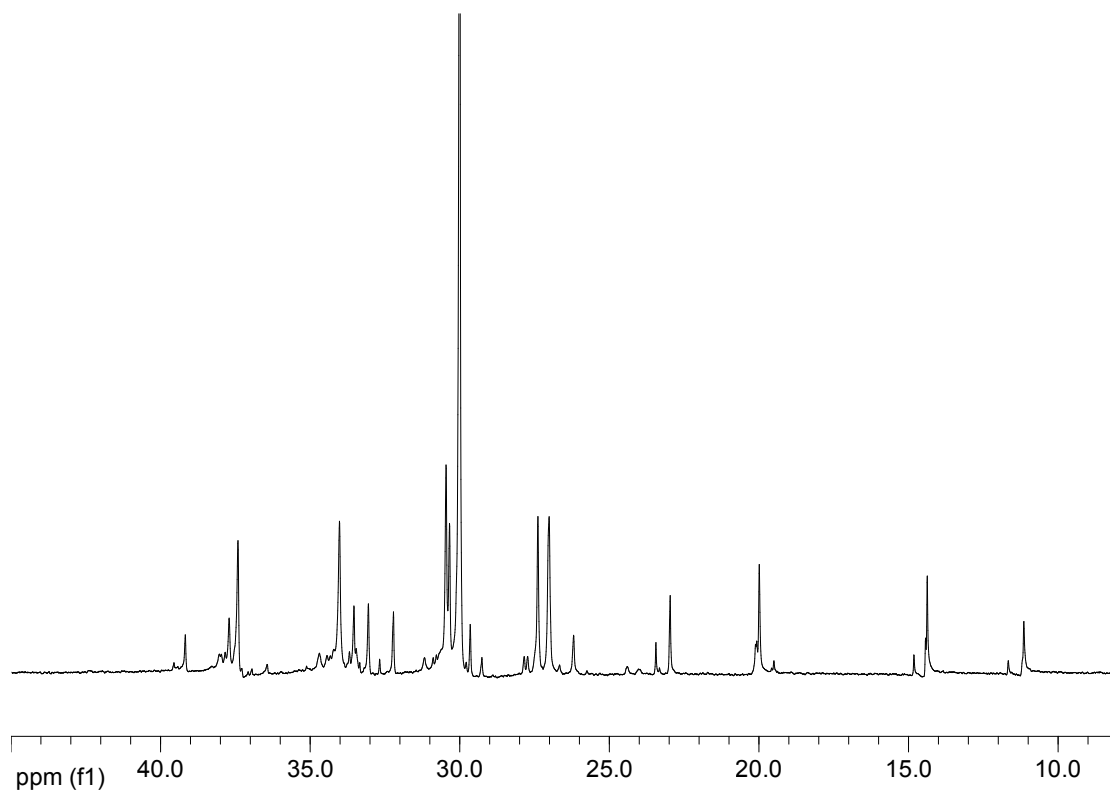
**Figure S3.** <sup>1</sup>H NMR spectrum of palladium complex C1



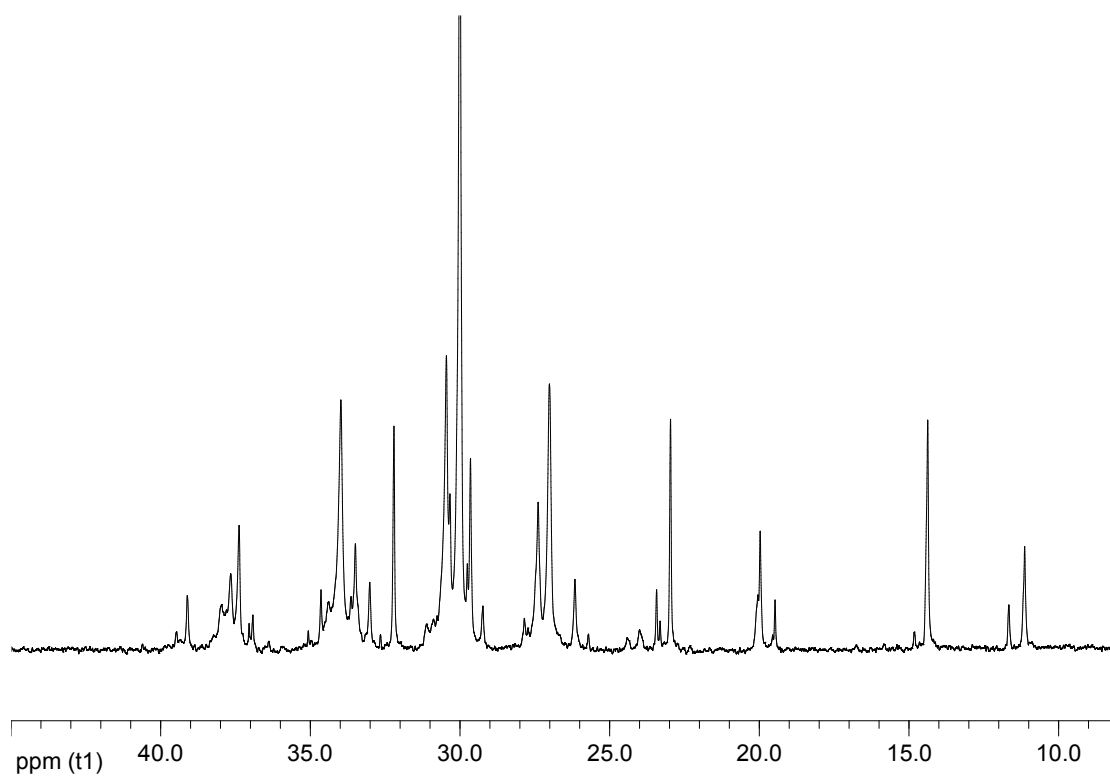
**Figure S4.**  $^1\text{H}$  NMR spectrum of palladium complex **C2**



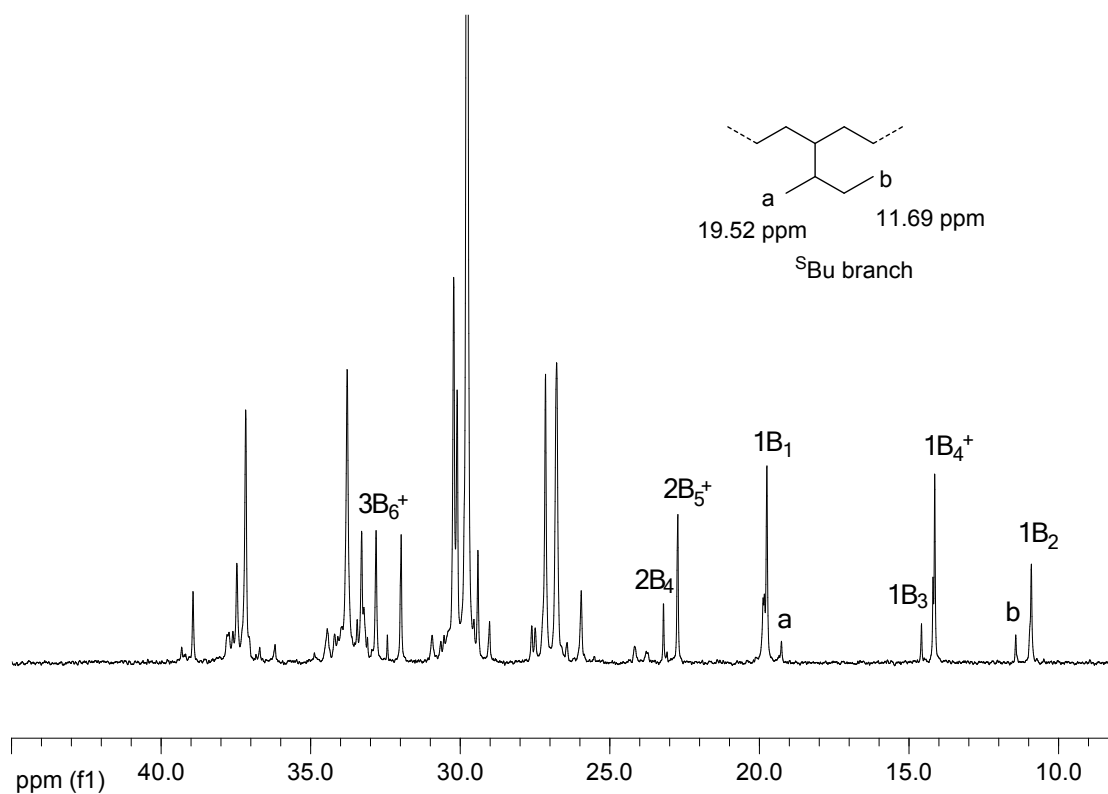
**Figure S5.** Influence of reaction temperature on ethylene polymerization activity with  $\alpha$ -diimine palladium **C3**. (Conditions: 10  $\mu\text{mol}$  Pd catalyst, 20 atm ethylene pressure 58 mL toluene and 2 mL  $\text{CH}_2\text{Cl}_2$ , 4 h.)



**Figure S6.** <sup>13</sup>C NMR spectrum of the PE obtained by **C1** (entry 2 in Table 1)



**Figure S7.** <sup>13</sup>C NMR spectrum of the PE obtained by **C2** (entry 5 in Table 1)

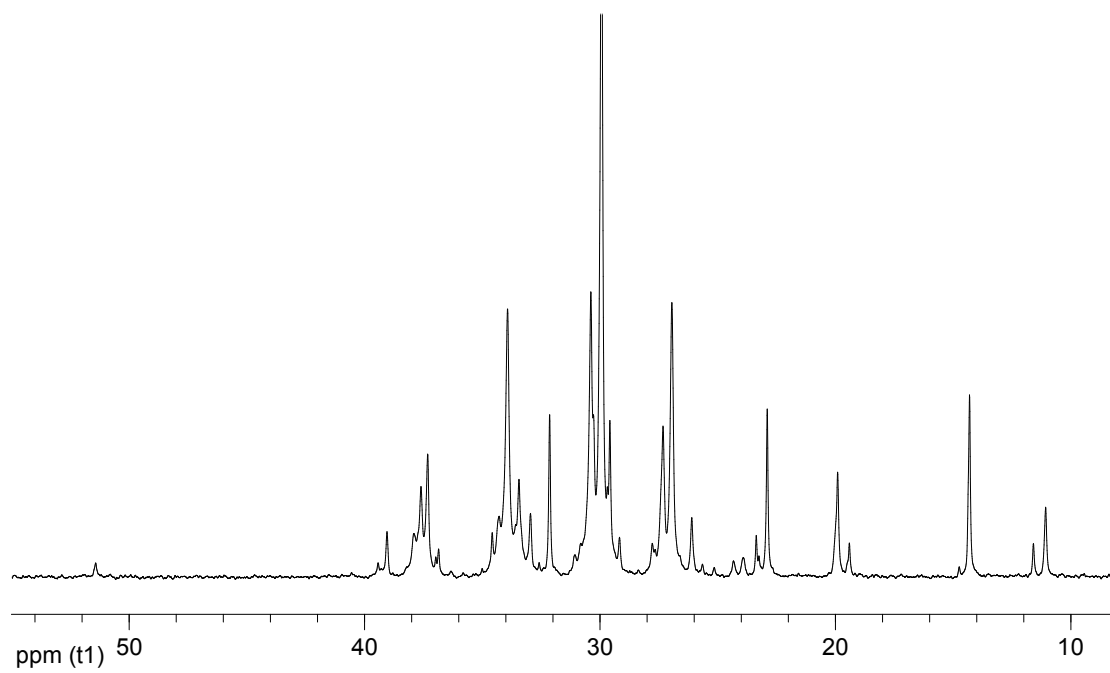


**Figure S8.**  $^{13}\text{C}$  NMR spectrum of the PE obtained by **C3** (entry 12 in Table 1)

**Table S2.** Branching distribution of PE samples obtained by different palladium catalysts

Entry	Cat.	Branching distribution (/1000C)							BD (/1000C)
		Me	Et	Pr	Bu	Am	Lg	$^{\text{s}}\text{Bu}$	
2	<b>C1</b>	53.9	14.6	3.7	8.8	2.4	16.1	2.7	102.2
5	<b>C2</b>	53.1	17.8	4.2	12.0	6.6	20.1	8.2	122.0
12	<b>C3</b>	54.2	13.8	4.0	9.7	5.0	18.4	5.5	110.6

Branching density is determined by  $^{13}\text{C}$  NMR spectroscopy in number of branches per 1000C according to previous reports (*Macromolecules*, **1999**, 32, 1620, *Science* **1999**, 283, 2059, *ACS Catal.* **2015**, 5, 456).

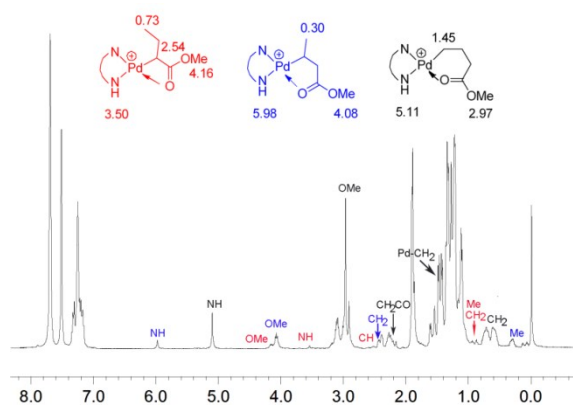


**Figure S9.**  $^{13}\text{C}$  NMR spectrum of the E-MA copolymer obtained by **C3**.



## Synthesis of cationic MA chelate palladium complexes

To a solution of complex **1** (0.44 g, 0.76 mmol) in dry  $\text{CH}_2\text{Cl}_2$  (20 mL) was added NaBARF (0.70 g, 0.79 mmol) and MA (2 mL) under nitrogen atmosphere, and the reaction mixture was stirred for 24 h at room temperature. Sodium chloride was removed from the reaction mixture via filtration, yielding a clear solution. The  $\text{CH}_2\text{Cl}_2$  was removed in vacuum, and the product was precipitated by 30 mL hexane. The resulting solid was filtered through Celite, washed with  $3 \times 10$  mL hexane and dried in vacuum.



**Figure S10.**  $^1\text{H}$  NMR spectrum of MA chelate amine-imine palladium complexes (N $\cap$ NH is amine-imine ligand).