Supporting Information

Combined hydrogen bonding interactions with steric and electronic modifications for thermally robust *α*-diimine palladium catalysts toward ethylene (co)polymerizations

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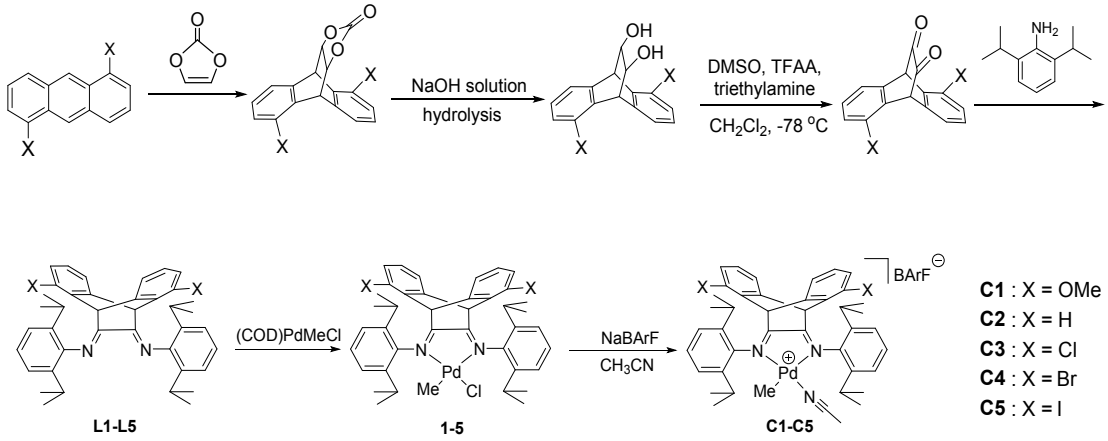
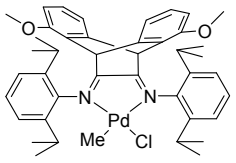
1 Synthetic routes and NMR spectroscopy of complexes



Scheme S1 Synthetic routes of α-diimine palladium complexes.



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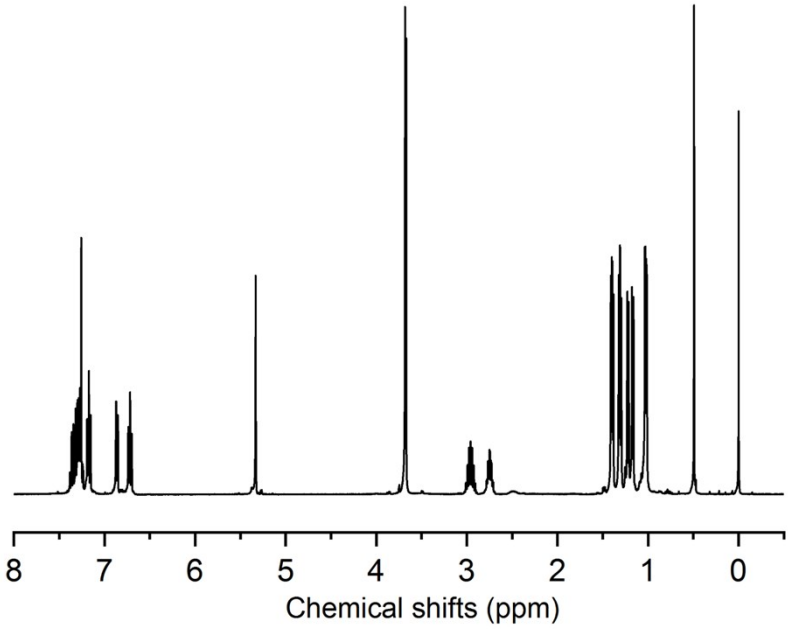


Fig. S1 ^{1}H NMR spectrum of palladium complex **1** in $CDCl_3$.

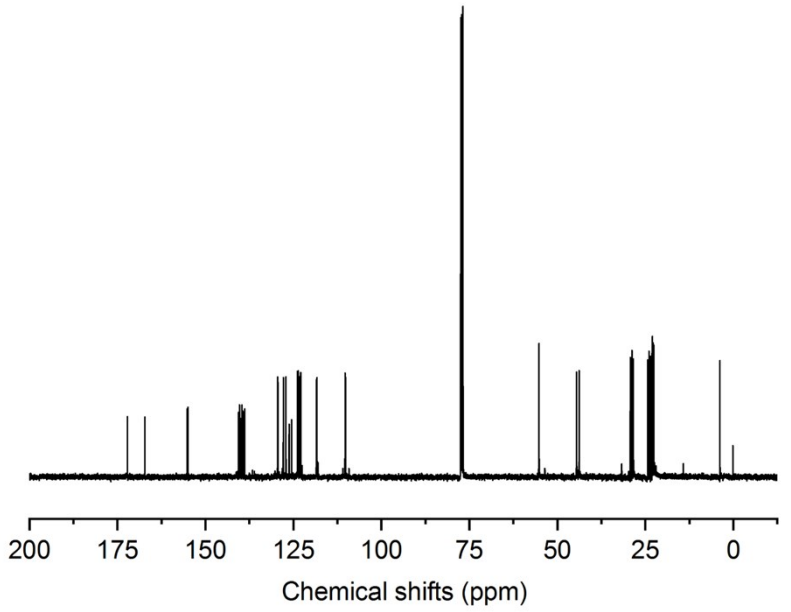
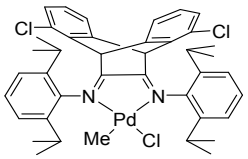


Fig. S2 ^{13}C NMR spectrum of palladium complex **1** in $CDCl_3$.



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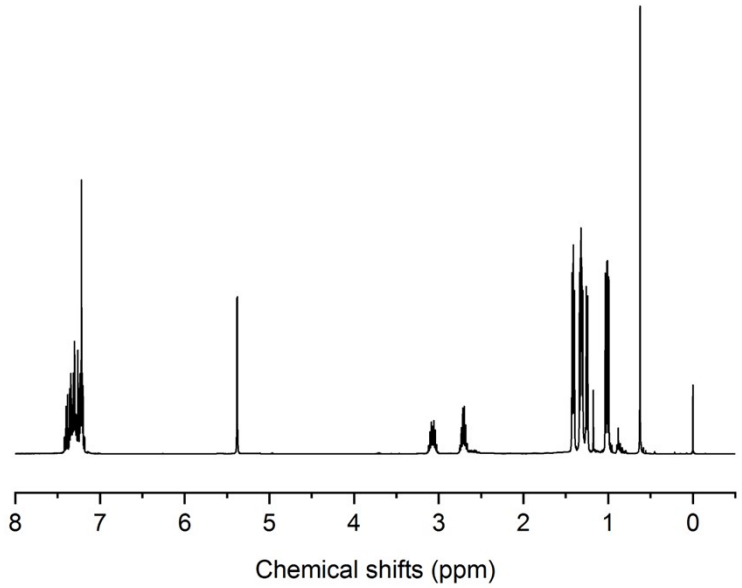


Fig. S3 ^{1}H NMR spectrum of palladium complex **3** in $CDCl_3$.

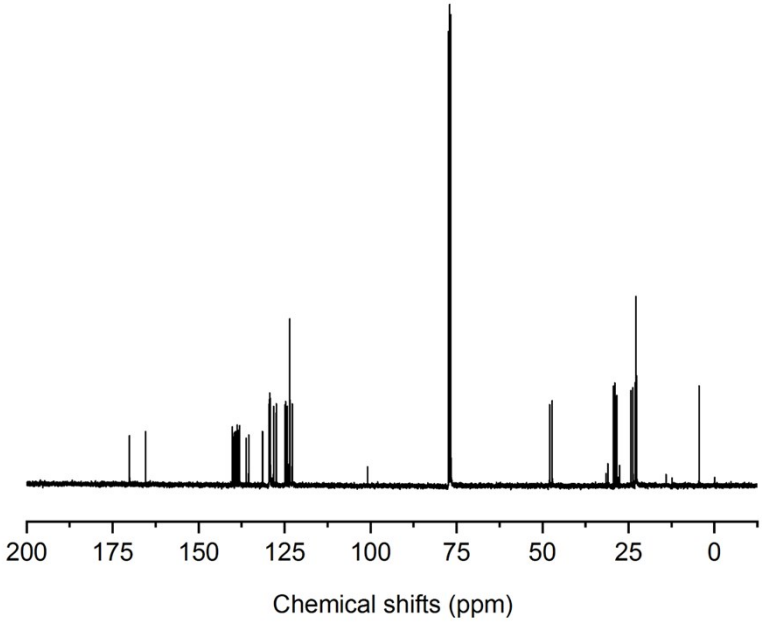
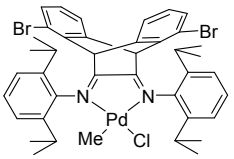


Fig. S4 ^{13}C NMR spectrum of palladium complex **3** in $CDCl_3$.



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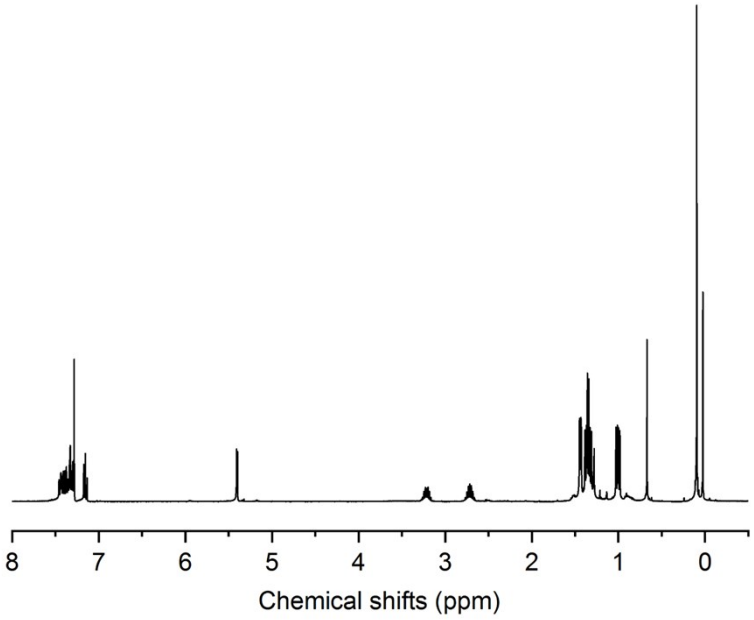


Fig. S5 ^{1}H NMR spectrum of palladium complex **4** in $CDCl_3$.

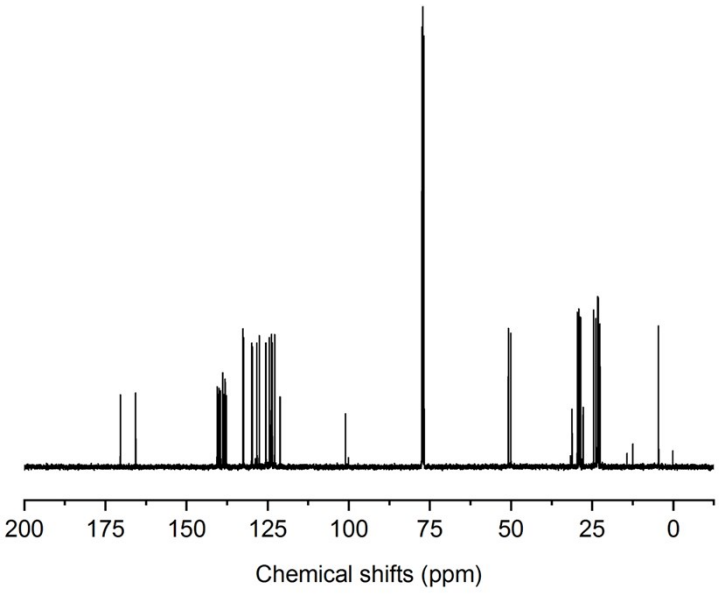
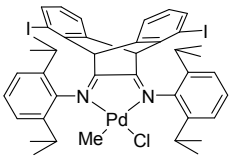


Fig. S6 ^{13}C NMR spectrum of palladium complex **4** in $CDCl_3$.



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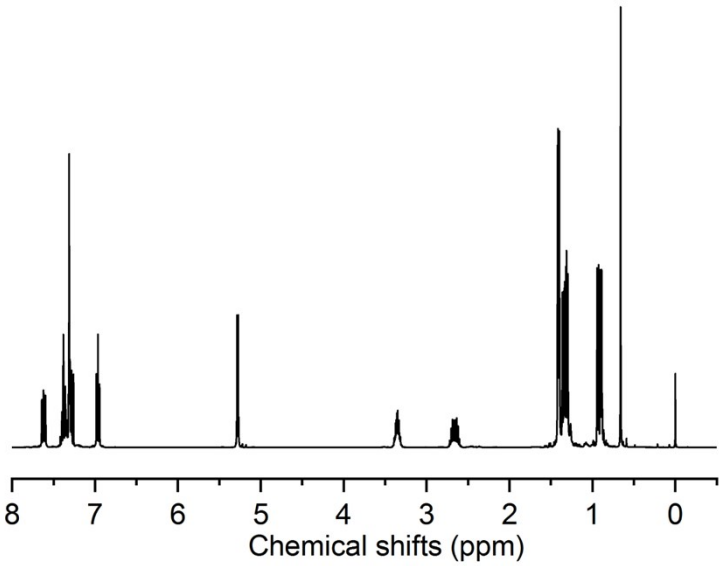


Fig. S7 ^{1}H NMR spectrum of palladium complex **5** in $CDCl_3$.

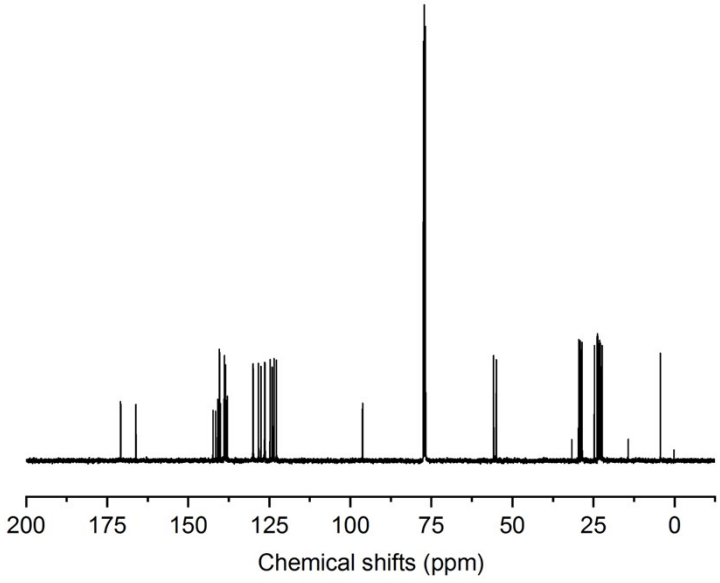
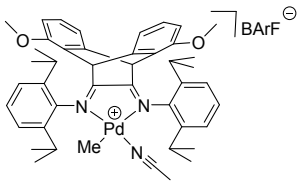


Fig. S8 ^{13}C NMR spectrum of palladium complex **5** in $CDCl_3$.



C1

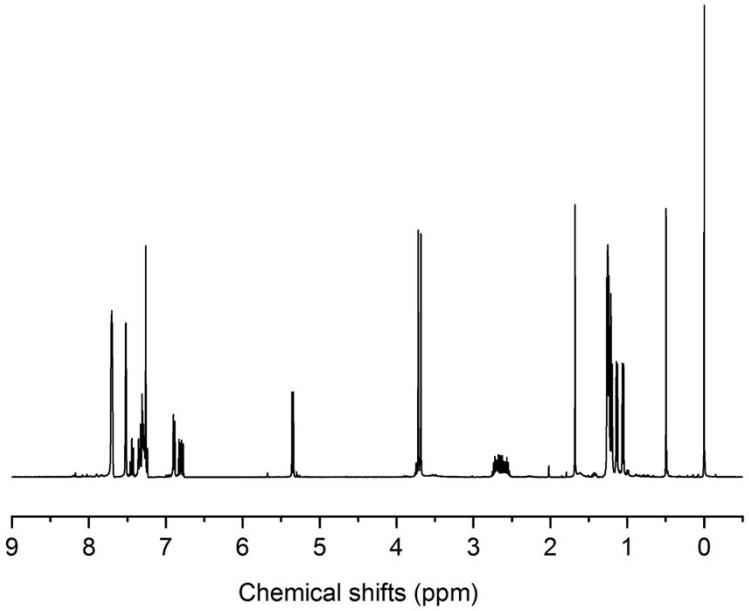


Fig. S9 ^{1}H NMR spectrum of palladium complex **C1** in $CDCl_3$.

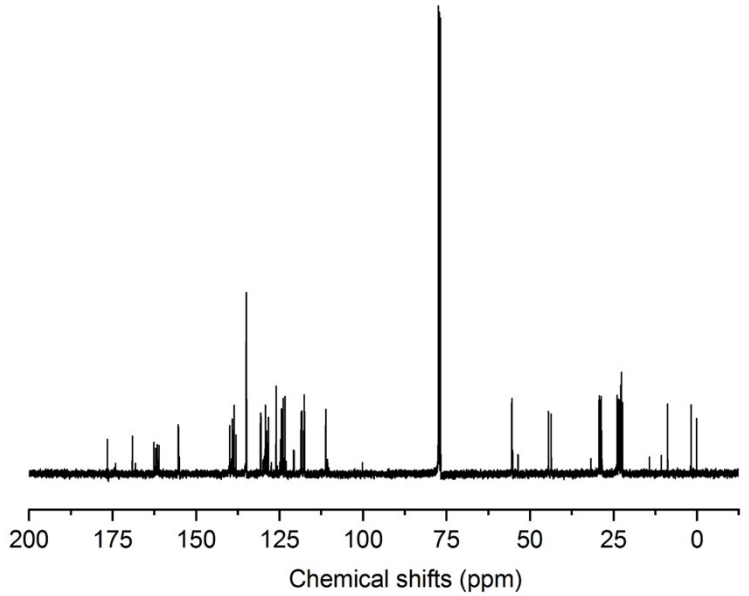
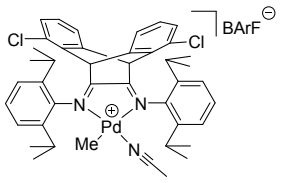


Fig. S10 ^{13}C NMR spectrum of palladium complex **C1** in $CDCl_3$.



C3

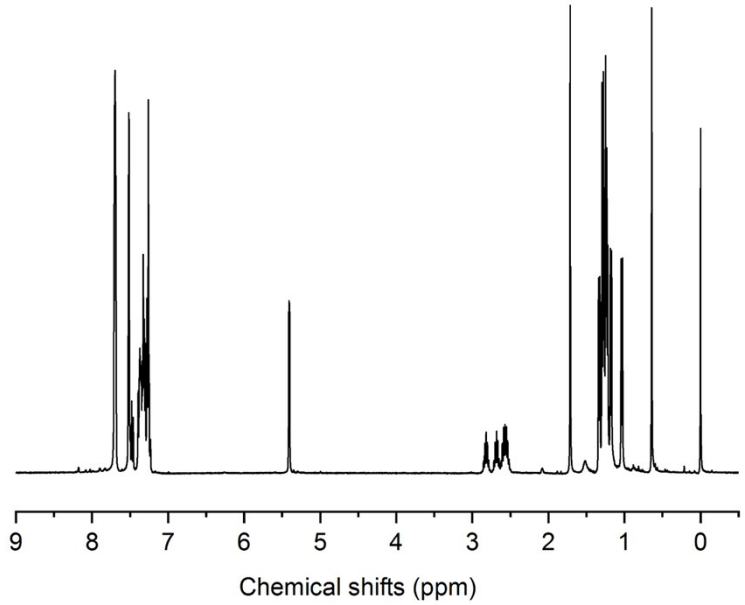


Fig. S11 ^{1}H NMR spectrum of palladium complex **C3** in $CDCl_3$.

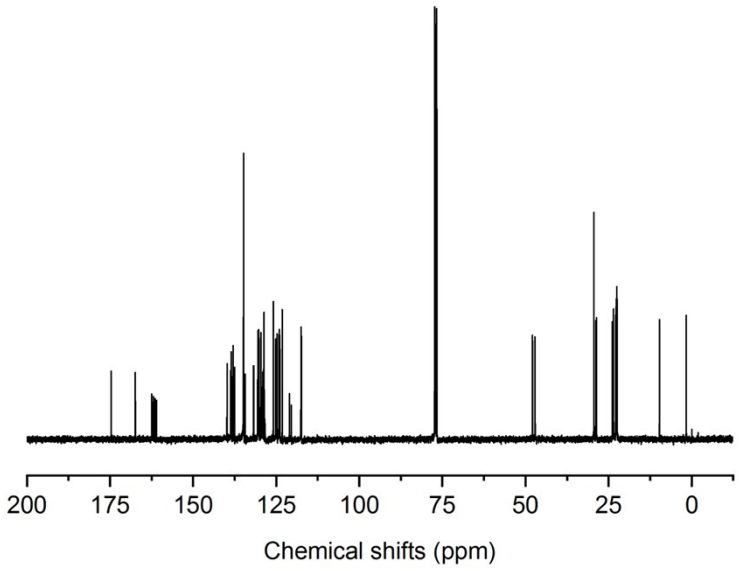
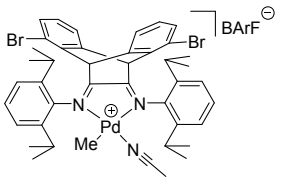


Fig. S12 ^{13}C NMR spectrum of palladium complex **C3** in $CDCl_3$.



C4

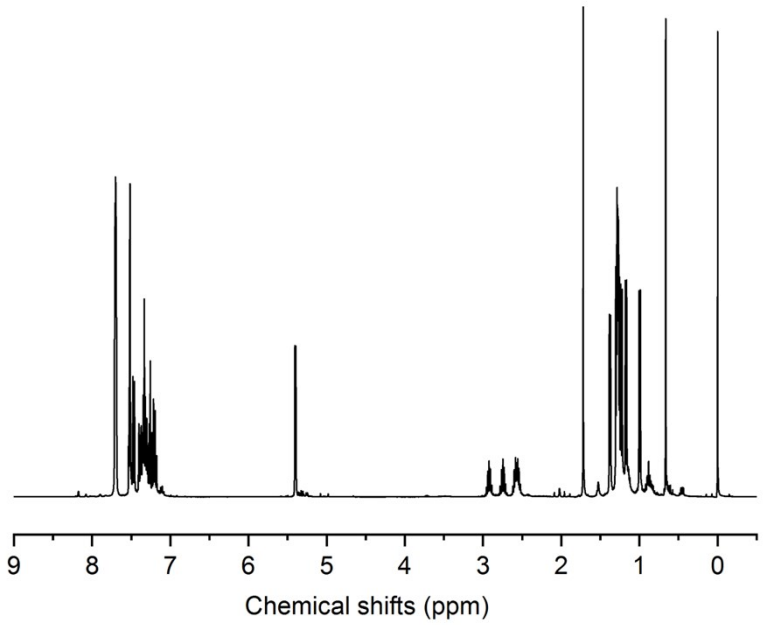


Fig. S13 ^{1}H NMR spectrum of palladium complex **C4** in $CDCl_3$.

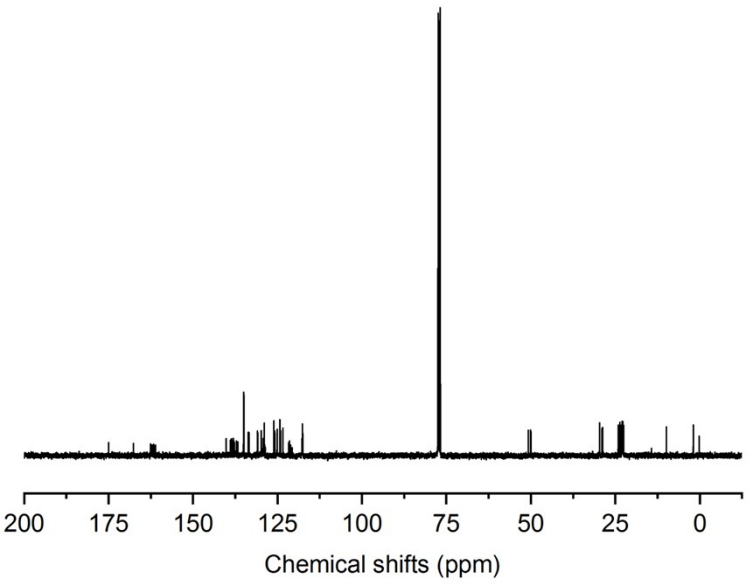
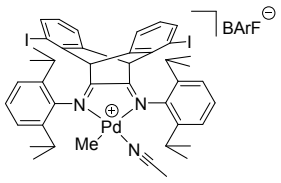


Fig. S14 ^{13}C NMR spectrum of palladium complex **C4** in $CDCl_3$.



C5

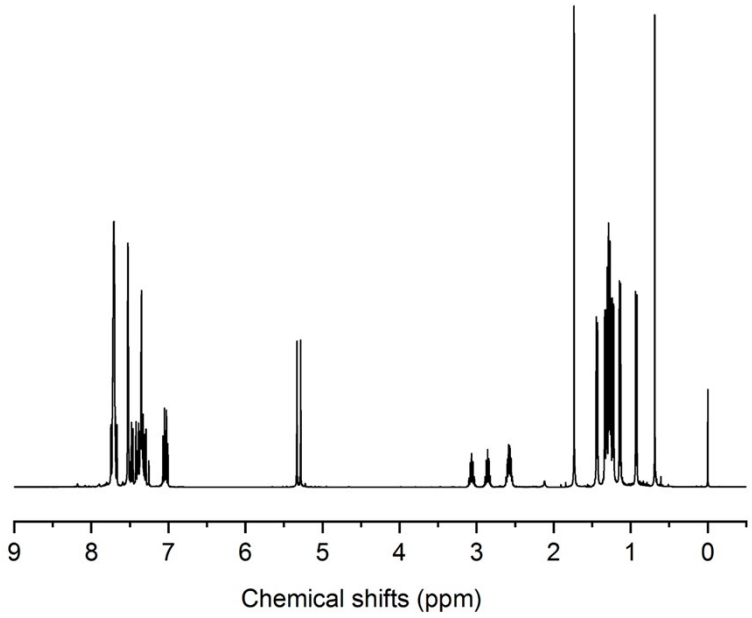


Fig. S15 ^{1}H NMR spectrum of palladium complex **C5** in $CDCl_3$.

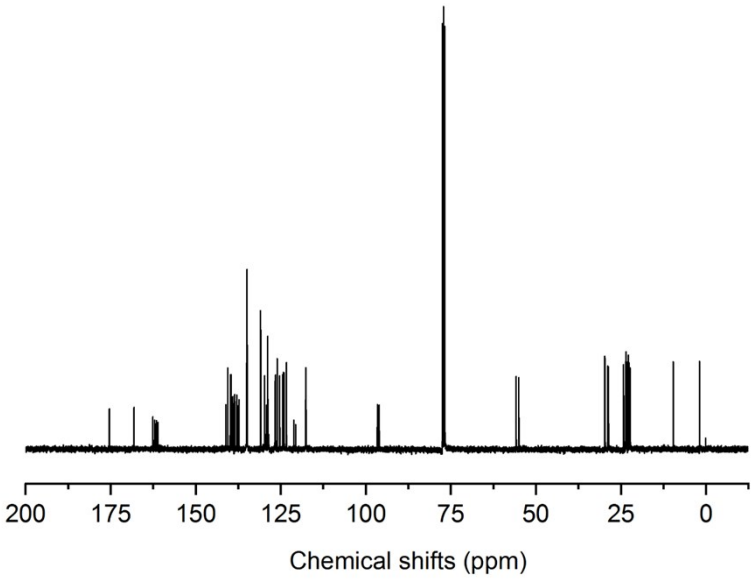


Fig. S16 ^{13}C NMR spectrum of palladium complex **C5** in $CDCl_3$.

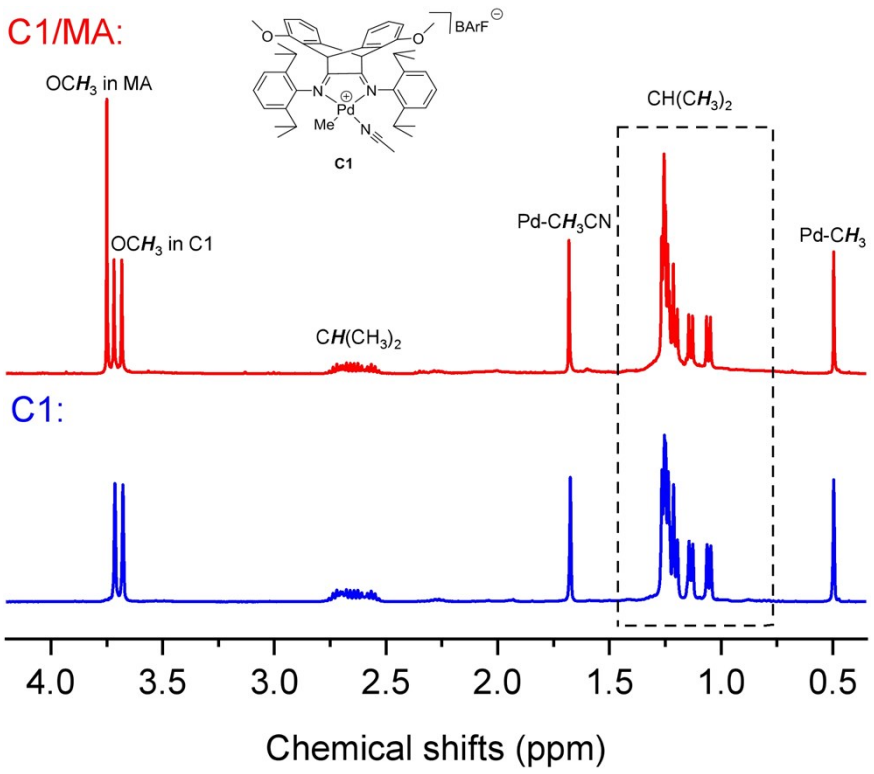


Fig. S17 ^{1}H NMR spectrum of palladium complex **C1** and **C1/MA** in $CDCl_3$.

2 Variable-temperature stacked ^{1}H NMR spectra of palladium complexes

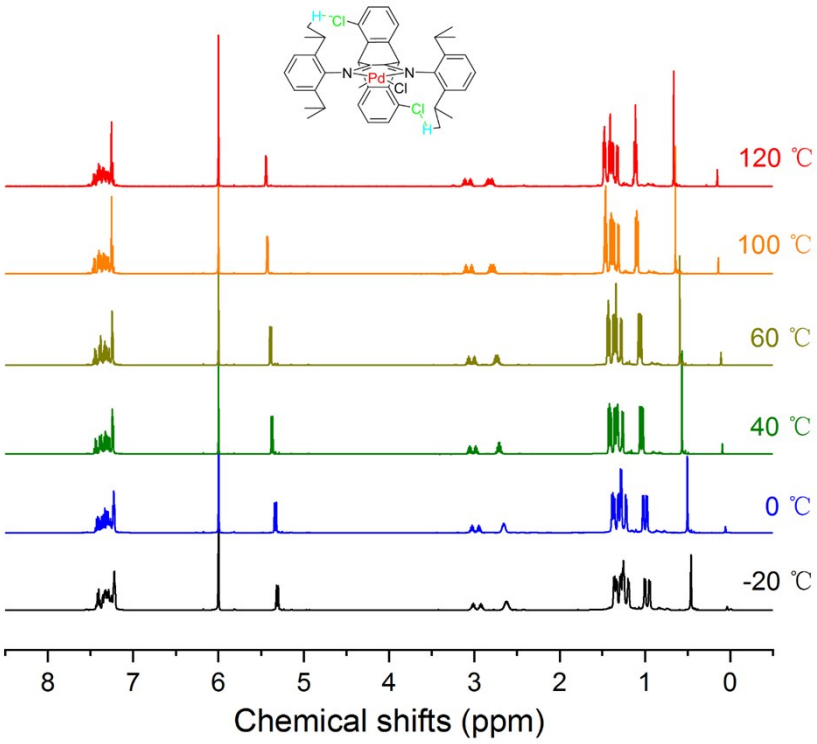


Fig. S18 Variable-temperature stacked ^{1}H NMR spectra of the palladium complex **3** in $C_2D_2Cl_4$.

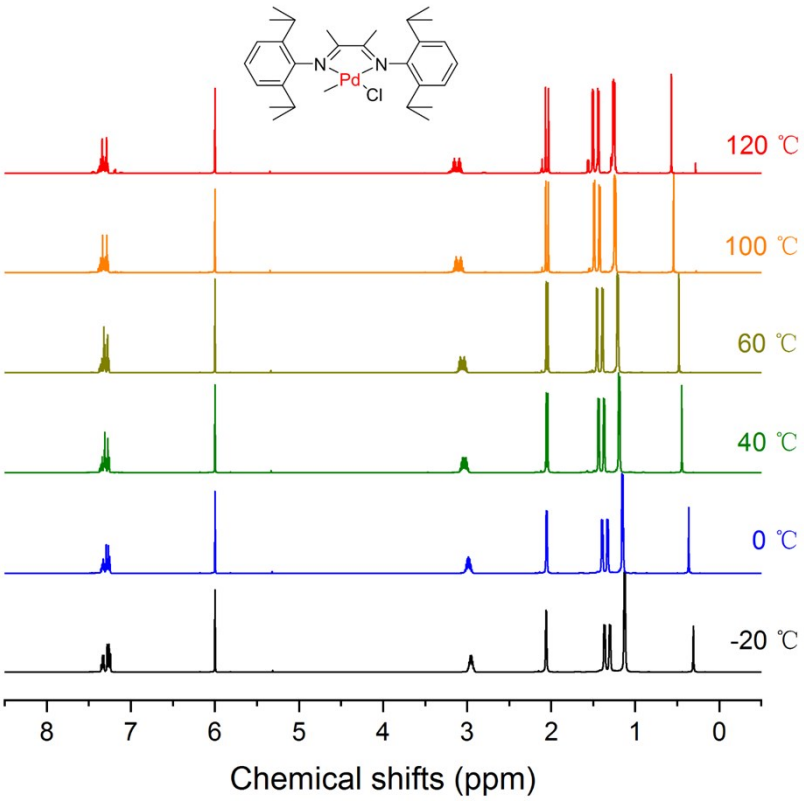


Fig. S19 Variable-temperature stacked ^{1}H NMR spectra of the palladium complex **7** in $C_2D_2Cl_4$.

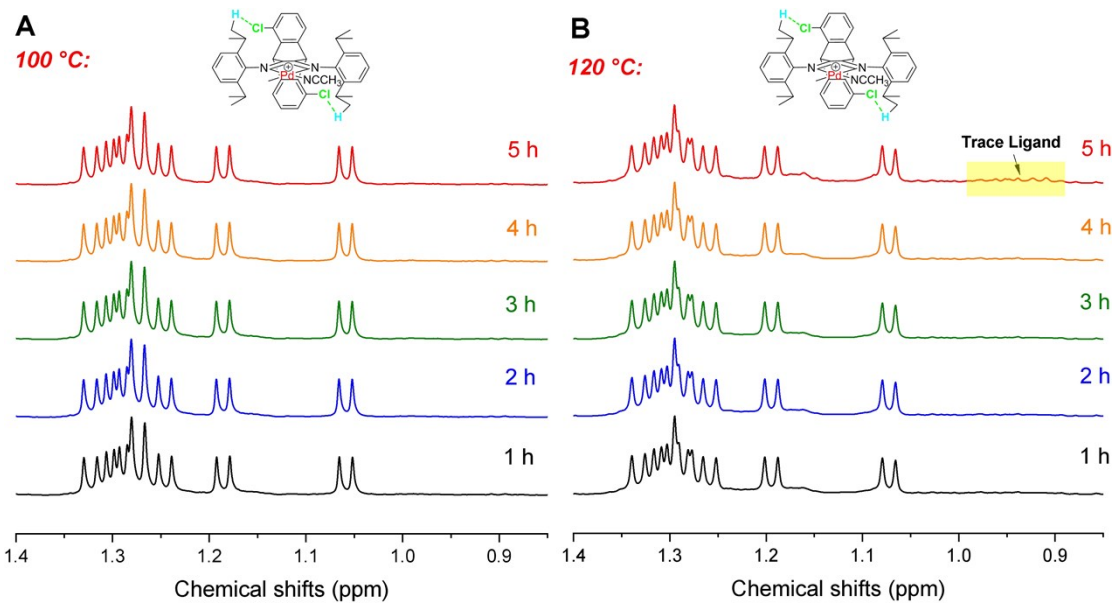


Fig. S20 The high temperature ^{1}H NMR spectra of cationic palladium complex **C3** at different times under 100 °C (A) and 120 °C (B).

3 Crystallographic data for palladium complexes

Table S1 Crystallographic data for the palladium complexes **1** and **3**.

Compounds	**1** (X = OMe)	**3** (X = Cl)
Empirical formula	$C_{43}H_{51}ClN_2O_2Pd\cdot CH_2Cl_2$	$C_{41}H_{45}Cl_3N_2Pd$
Formula weight	854.63	778.54
Crystal color	Light red	Red
Crystal system	Monoclinic	Triclinic
space group	$P2_1/n$	P-1
a (Å)	11.7251(4)	11.0716(4)
b (Å)	18.4561(6)	16.3730(6)
c (Å)	19.8210(6)	21.6279(7)
α (deg)	90	89.420(3)
β (deg)	101.805(3)	76.403(3)
γ (deg)	90	88.652(3)
Volume(Å^3)	4198.5(2)	3809.6(2)
Z	4	4
ρ_{calc} (g/cm^3)	1.352	1.357
μ (mm^{-1})	0.670	6.088
F(000)	1776.0	1608.0
Crystal size (mm^3)	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.1
2θ range for data collection (deg)	6.606 to 60.532	6.828 to 145.77
Index ranges	$-15 \le h \le 14$	$-13 \le h \le 11$
	$-25 \le k \le 17$	$-20 \le k \le 18$
	$-17 \le l \le 28$	$-26 \le l \le 26$
Reflections collected	19845	30181
Data/restraints/parameters	10461/0/480	14875/541/1053
Goodness-of-fit on F^2	1.117	1.108
Final R indices [I>2σ(I)]	R_1 = 0.0631, wR_2 = 0.1557	R_1 = 0.0688, wR_2 = 0.1742
R indices (all data)	R_1 = 0.0760, wR_2 = 0.1636	R_1 = 0.0800, wR_2 = 0.1820
Largest diff. peak and hole (e/Å^3)	2.49 and -1.49	1.37 and -1.36
CCDC number	2021215	2021211

Table S2 Crystallographic data for the palladium complexes **4** and **5**.

Compounds	**4** (X = Br)	**5** (X = I)
Empirical formula	$C_{41}H_{45}Br_2ClN_2Pd$	$C_{41}H_{45}ClI_2N_2Pd$
Formula weight	867.46	961.44
Crystal color	Colourless	Orange
Crystal system	Monoclinic	Monoclinic
space group	$P2_1/n$	$P2_1/c$
a (Å)	12.8172(2)	10.0308(2)
b (Å)	18.0795(3)	19.7307(4)
c (Å)	16.7528(3)	20.2309(4)
α (deg)	90	90
β (deg)	96.9770(10)	101.055(2)
γ (deg)	90	90
Volume(Å^3)	3853.36(11)	3929.69(14)
Z	4	4
ρ_{calc} (g/cm^3)	1.495	1.625
μ (mm^{-1})	7.173	2.141
F(000)	1752.0	1896.0
Crystal size (mm^3)	0.3 × 0.2 × 0.01	0.32 × 0.045 × 0.03
2θ range for data collection (deg)	7.222 to 150.79	6.362 to 55.932
Index ranges	$-16 \le h \le 15$	$-13 \le h \le 12$
	$-14 \le k \le 22$	$-24 \le k \le 25$
	$-20 \le l \le 20$	$-24 \le l \le 26$
Reflections collected	13144	68625
Data/restraints/parameters	7604/30/452	8763/24/440
Goodness-of-fit on F^2	1.036	1.056
Final R indices [I>2σ(I)]	R_1 = 0.0532, wR_2 = 0.1458	R_1 = 0.0447, wR_2 = 0.0927
R indices (all data)	R_1 = 0.0594, wR_2 = 0.1538	R_1 = 0.0638, wR_2 = 0.1004
Largest diff. peak and hole (e/Å^3)	1.59 and -1.43	2.03 and -1.57
CCDC number	2021212	2021210

Table S3 Crystallographic data for the palladium complexes **C1**, **C3**, and **C5**.

Compounds	**C1** (X = OMe)	**C3** (X = Cl)	**C5** (X = I)
Empirical formula	$C_{77}H_{66}BF_{24}N_3O_2Pd\cdot(CH_2Cl_2)_{1/4}$	$C_{75}H_{60}BCl_2F_{24}N_3Pd$	$C_{75}H_{60}BF_{24}I_2N_3Pd\cdot(C_6H_{14})_{1/2}$
Formula weight	1659.77	1647.37	1873.35
Crystal color	Light Orange	Yellow	Colourless
Crystal system	Triclinic	Triclinic	Triclinic
space group	P-1	P-1	P-1
a (Å)	14.4315(6)	12.48880(10)	13.0060(4)
b (Å)	16.2211(6)	16.9952(2)	16.8630(5)
c (Å)	18.6665(8)	19.3546(2)	19.2164(6)
α (deg)	109.704(4)	69.1710(10)	98.154(2)
β (deg)	107.844(4)	75.0500(10)	96.070(2)
γ (deg)	95.369(3)	81.7150(10)	99.498(2)
Volume(Å^3)	3820.3(3)	3703.33(7)	4078.6(2)
Z	2	2	2
ρ_{calc} (g/cm^3)	1.443	1.477	1.525
μ (mm^{-1})	3.059	3.617	8.639
F(000)	1685.0	1664.0	1856.0
Crystal size (mm^3)	0.1 × 0.1 × 0.1	0.5 × 0.4 × 0.3	0.3 × 0.1 × 0.05
2θ range for data collection (deg)	7.844 to 149.224	7.338 to 149.932	7.694 to 148.638
Index ranges	-16 ≤ h ≤ 17 -20 ≤ k ≤ 19 -22 ≤ l ≤ 23	-15 ≤ h ≤ 15 -21 ≤ k ≤ 21 -23 ≤ l ≤ 24	-16 ≤ h ≤ 14 -21 ≤ k ≤ 17 -23 ≤ l ≤ 23
Reflections collected	25386	62440	24442
Data/restraints/parameters	14830/51/1083	14901/50/1059	15742/20/1028
Goodness-of-fit on F^2	1.074	1.025	1.036
Final R indices [I>2σ(I)]	R_1 = 0.0767, wR_2 = 0.2011	R_1 = 0.0501, wR_2 = 0.1295	R_1 = 0.0635, wR_2 = 0.1706
R indices (all data)	R_1 = 0.0973, wR_2 = 0.2201	R_1 = 0.0508, wR_2 = 0.1302	R_1 = 0.0727, wR_2 = 0.1843
Largest diff. peak and hole (e/Å^3)	1.01 and -1.22	1.42 and -2.12	1.49 and -1.07
CCDC number	2021213	2021209	2021214

Table S4 Four-coordinate geometry indices τ_4 for palladium complexes and representative examples.

Pd complex	X	Geometry	τ_4
		Tetrahedral (T_d)	1.00
1	OMe	Dist. square planar	0.06
2	H	Dist. square planar	0.06
3	Cl	Dist. square planar	0.09
4	Br	Dist. square planar	0.08
5	I	Dist. square planar	0.08
C1	OMe	Dist. square planar	0.08
C2	H	Dist. square planar	0.06
C3	Cl	Dist. square planar	0.07
C5	I	Dist. square planar	0.08
		Square planar (D_{4h})	0.00

The distortion around the Pd metal centers were quantified by the τ4 parameter, τ4 is a simple formula that can be used to gauge the geometries of four-coordinate transition metal complexes and main group compounds.

4 Inductive parameters and resonance parameters of substituents

Table S5 Inductive and resonance parameters of substituents. [a]

X	σ_{para}	σ_I	σ_R
OMe	-0.268	+0.250	-0.518
H	0	0	0
Cl	+0.227	+0.470	-0.245
Br	+0.232	+0.450	-0.218
I	+0.276	+0.390	-0.114

[a] $\sigma = \sigma_I + \sigma_{R,}$ referenced by *J. Am. Chem. Soc.*, 1958, **80**, 2436–2443; *Prog. Phys. Org. Chem.*, 1981, **13**, 119–251.

5 Characterization of selected polymer samples

Table S6. Ethylene polymerization results using **C3** (X = Cl) at different times.[a]

entry	time (h)	yield (mg)	TOF[b]	M_n (kg/mol)[c]	PDI[c]	BD[d]
1	1	150	536	2.2	1.20	103
2	2	287	513	3.7	1.20	103
3	3	410	488	5.1	1.20	100
4	4	524	468	6.7	1.20	101
5	5	598	427	7.9	1.22	103

[a] Conditions: 10 μmol Pd, 100 °C, 0.2 atm ethylene pressure, 28 mL of toluene and 2 mL of CH_2Cl_2. [b] TOF in mol E/(mol Pd·h). [c] Determined by gel permeation chromatography (GPC) in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector. [d] Branching density determined by ^{1}H NMR spectroscopy in number of branches per 1000 carbon.

Table S7. Ethylene polymerization results using **C3** (X = Cl) at different ethylene pressures.[a]

entry	press. (atm)	yield (mg)	act.[b]	M_n[c] (kg/mol)	PDI[c]	BD[d]
1	0.2	287	14.4	3.7	1.20	103
2[e]	5	591	29.6	8.9	1.20	97
3[e]	10	693	34.7	10.0	1.21	95
4[e]	20	896	44.8	11.8	1.22	84

[a] Conditions: 10 μmol Pd, 100 °C, 2 h, 28 mL of toluene and 2 mL of CH_2Cl_2. [b] act.: kg PE/(mol Pd·h). [c] Determined by GPC in 1,2,4-trichlorobenzene at 150 °C using a light scattering detector. [d] Branching density determined by ^{1}H NMR in number of branches per 1000 carbons. [e] 58 mL of toluene and 2 mL of CH_2Cl_2.

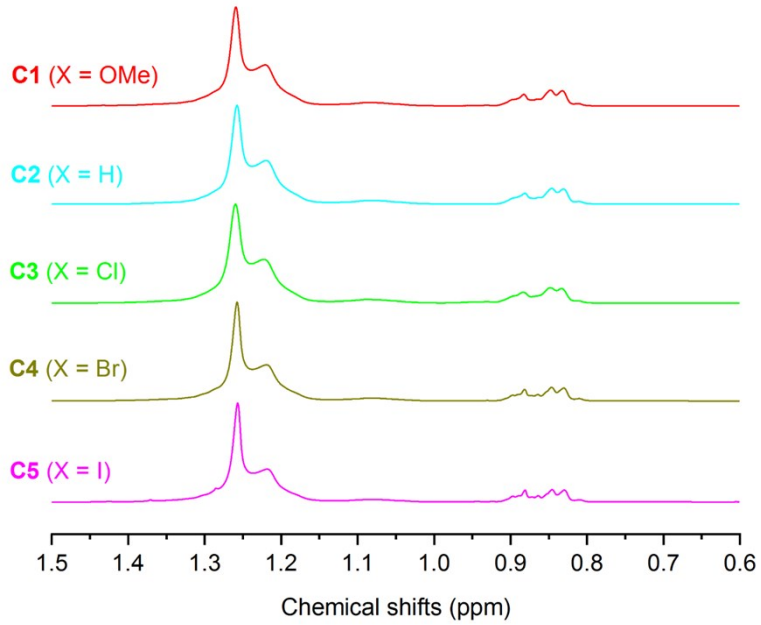


Fig. S21 ^{1}H NMR spectra of PEs produced by complexes **C1-C5** in $CDCl_3$ (entries 5, 12, 19, 26, and 33 in Table 2).

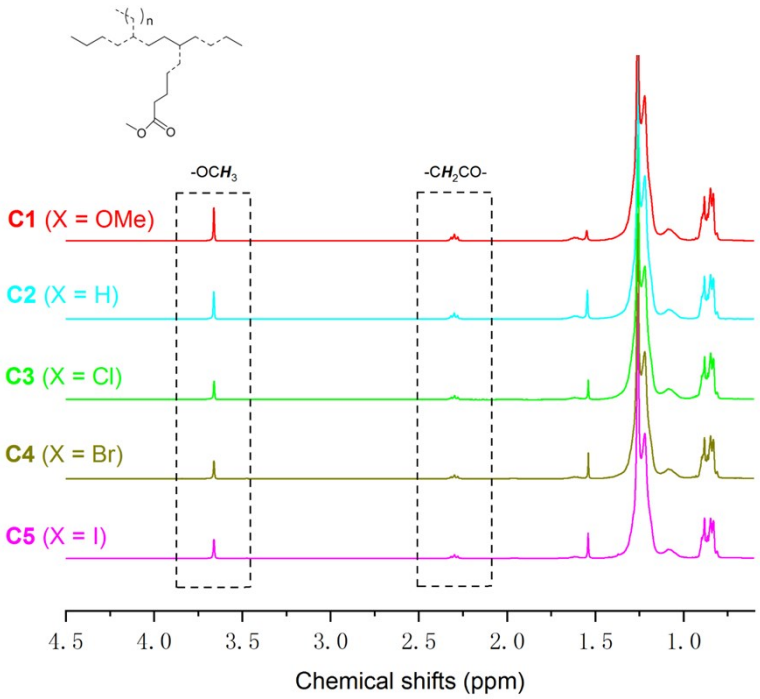


Fig. S22 ^{1}H NMR spectra of copolymers obtained by complexes **C1-C5** in $CDCl_3$ (entries 1, 7, 10, 13, and 14 in Table 3).

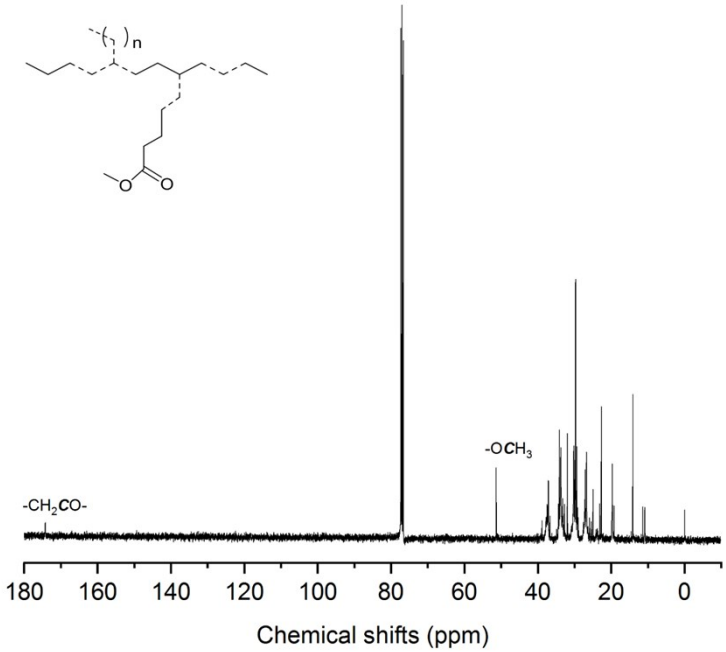


Fig. S23 ^{13}C NMR spectrum of copolymers obtained by palladium complex **C1** in $CDCl_3$ (entry 2 in Table 3).