Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Living (Co)polymerization of Ethylene and Bio-based Furfuryl Acrylate by Dibenzobarrelene Derived *α*-Diimine Palladium Catalysts

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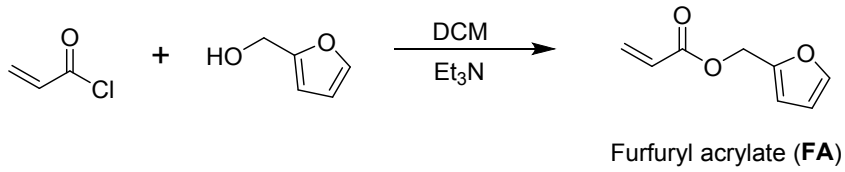
1. Synthesis and characterizations of furfuryl acrylate.



Furfuryl acrylate (**FA**)

Scheme S1. Synthetic route of Furfuryl acrylate (**FA**).

Furfuryl acrylate was synthesized according to the literature.[1] In a 250 mL Schlenk round-bottom flask, 15.01g (0.153 mol) furfuryl alcohol, 120 mL dry dichloromethane and 23.23 g (0.230 mol) triethylamine were mixed while stirring vigorously at 0°C for 10 min under a nitrogen atmosphere. Afterwards 4.16 g (0.046 mol) acryloyl chloride was added dropwise at 0°C. After the addition, the reaction mixture was stirred at room temperature overnight. The white triethylammonium chloride was removed by filtration and the yellow turbid solution was concentrated under vacuum. Finally, the crude product was purified by distillation under vacuum (100 °C). Yield: 10.64 g (45%). ^{1}H NMR (400MHz, $CDCl_3$), δ(ppm): 7.43(s,1H, Ar-**H**), 6.46-6.42 (m, 2H, Ar-**H**), 6.37(s, 1H, CO**CH**CH_2), 6.14(dd, 1H, COCH**CH_2**), 5.84(d, 1H, COCH**CH_2**), 5.14(s, 2H, CO**CH_2**).

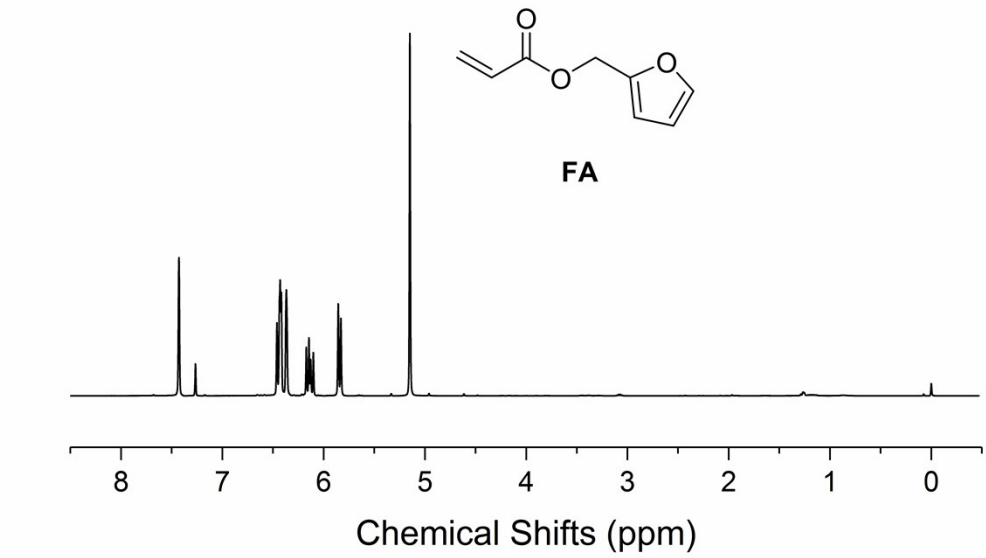
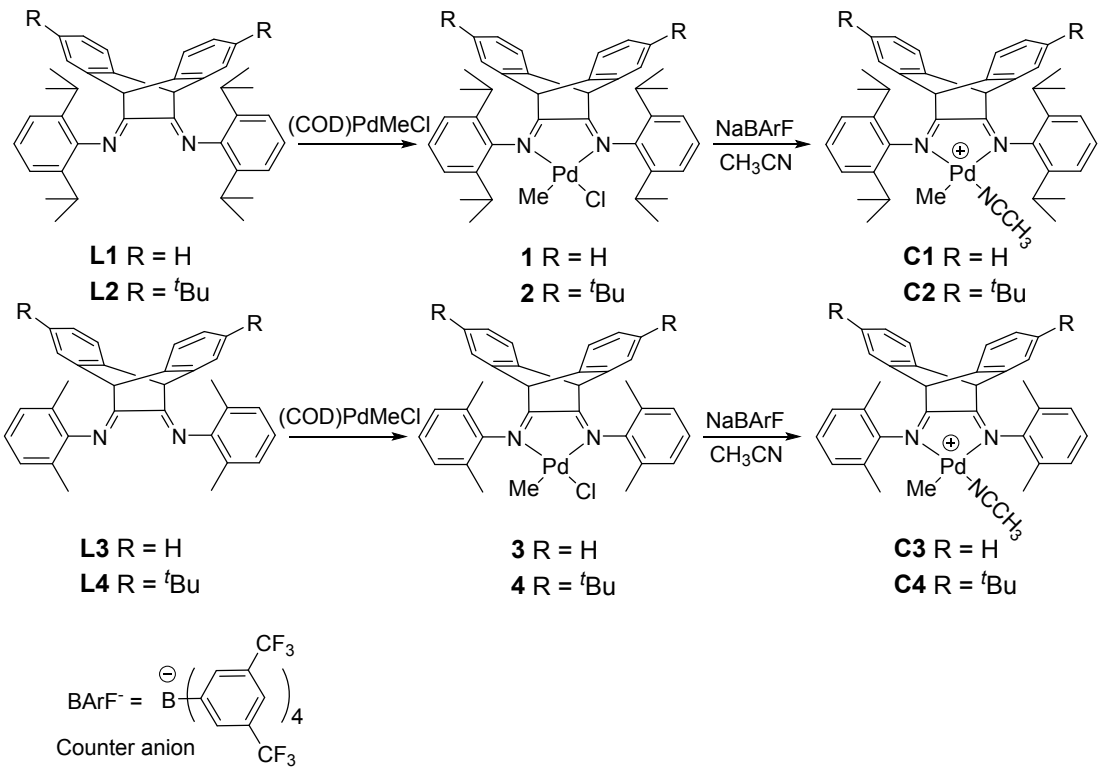


Figure S1. ^{1}H NMR spectrum of **FA**.

2. Synthesis and characterizations of α-diimine Pd complexes.



Scheme S2. Synthetic route of *α*-diimine Pd complexes.

α-Diimine ligands **L1**-**L4** were synthesized according to the literature.[2] **L1**-**L4** were fully confirmed by ^{1}H and ^{13}C NMR spectroscopies.

L1: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm): 7.25-7.05 (m, 14H, Ar-**H**), 4.98 (s, 2H, C**H**), 2.49 (m, 4H, C**H**$(CH_3)_2$), 1.15 (d, 12H, CH(C**H**$_3)_2$), 1.02 (d, 12H, CH(C**H**$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 158.45(2C, **C**=N), 145.56(2C, Ar-**C**-N), 138.57, 136.38, 127.27, 125.40, 124.12, 122.79(22C, Ar-**C**), 51.10(**C**H), 28.46(2C, **C**H$(CH_3)_2$), 23.29, 22.49(8C, CH(**C**H$_3)_2$). Anal. Calcd for $C_{40}H_{44}N_2$: C, 86.91; H, 8.02; N, 5.07. Found: C, 86.94; H, 7.95; N, 5.12.

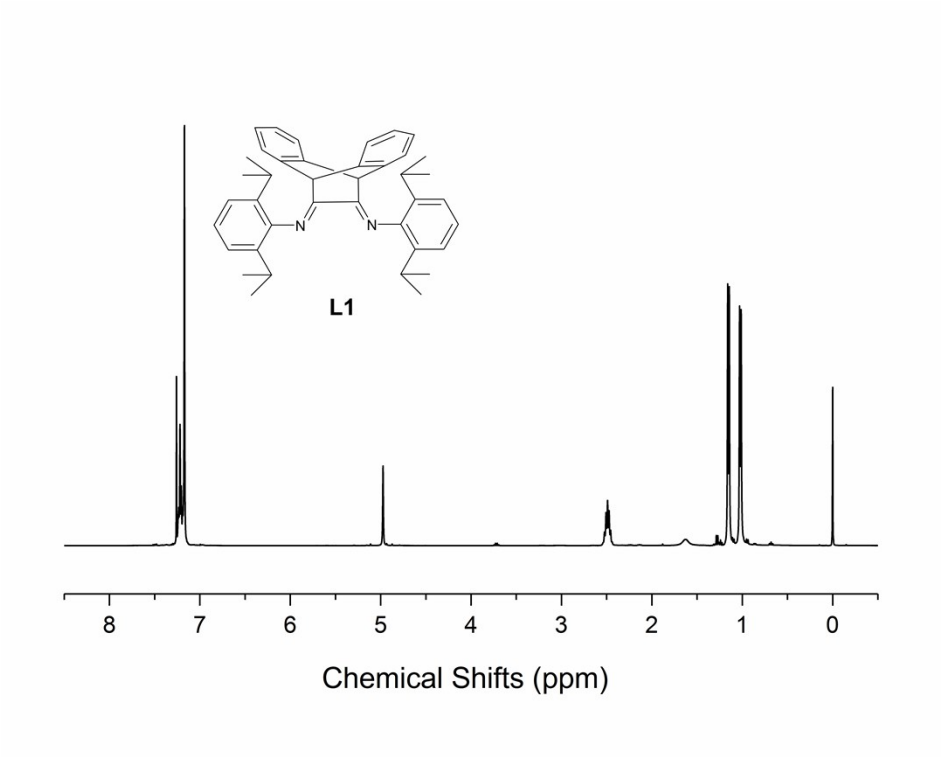


Figure S2. ^{1}H NMR spectrum of **L1**

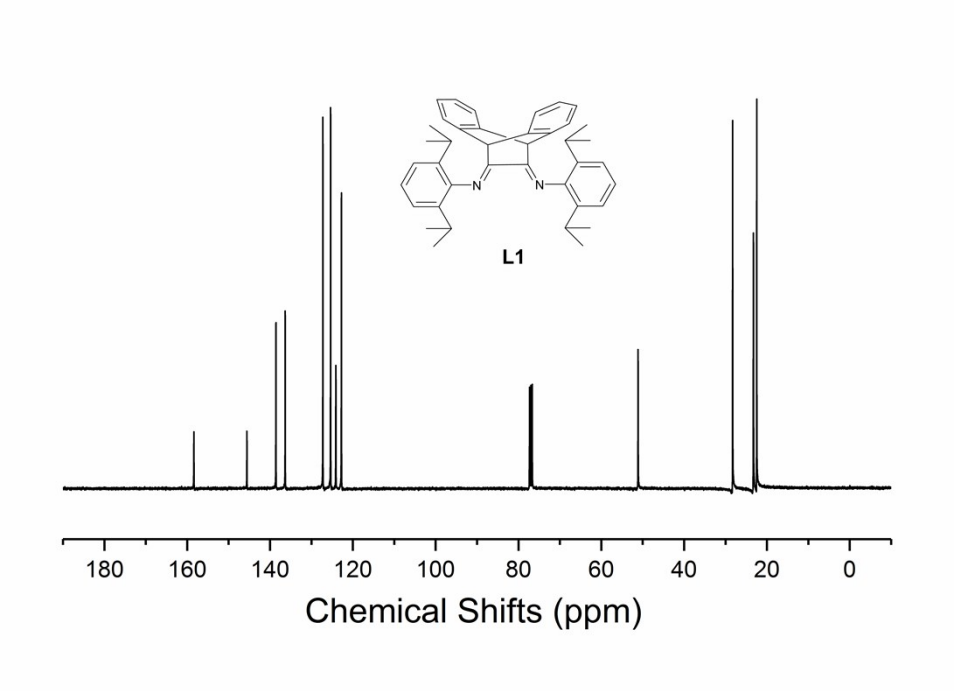


Figure S3. ^{13}C NMR spectrum of **L1**

L2: ^{1}H NMR (400 MHz, $CDCl_3$), δ (ppm) : 7.25-7.07 (m, 12H, Ar-**H**), 4.91 (s, 2H, C**H**), 2.53 (m, 4H, C**H**$(CH_3)_2$), 1.23 (s, 18H, C**H**$_3$ in ^{t}Bu), 1.15 (m, 12H, CH(C**H**$_3)_2$), 1.03 (m, 12H, CH(C**H**$_3)_2$). ^{13}C NMR (100 MHz, $CDCl_3$), δ (ppm): 158.91, 150.50, 145.77, 138.52, 136.65, 136.35, 135.79, 124.95, 124.11, 123.99, 122.77, 122.69, 122.47, 50.99, 34.77, 31.38, 28.39, 28.22, 23.39, 22.24, 23.17, 22.35. Anal. Calcd for $C_{48}H_{60}N_2$: C, 86.69; H, 9.09; N, 4.21. Found: C, 86.75; H, 9.11; N, 4.11.

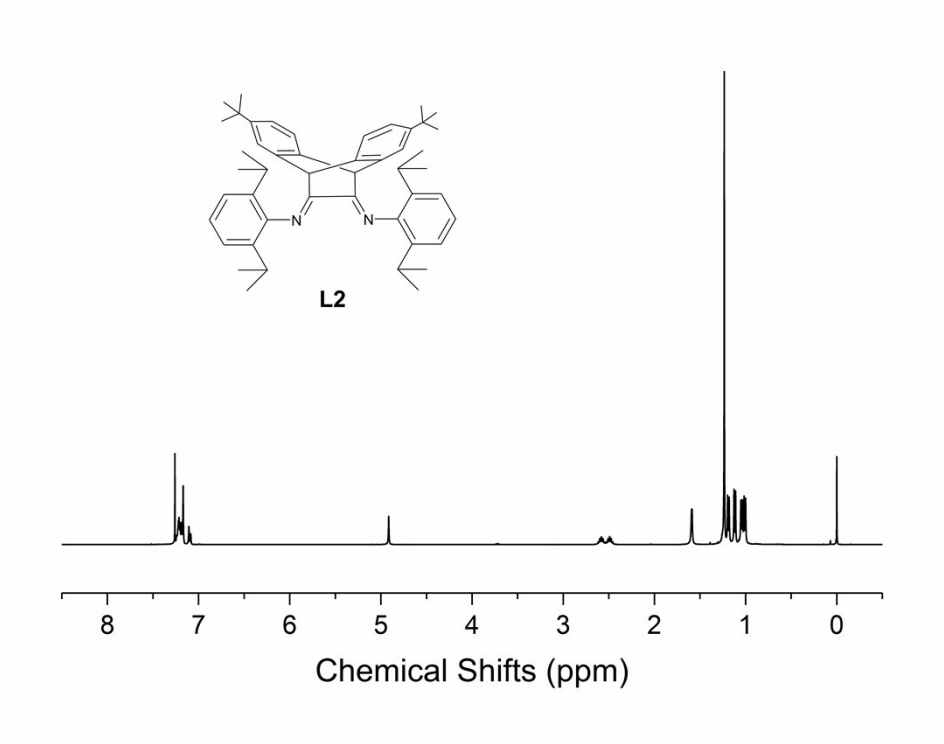


Figure S4. ^{1}H NMR spectrum of **L2**

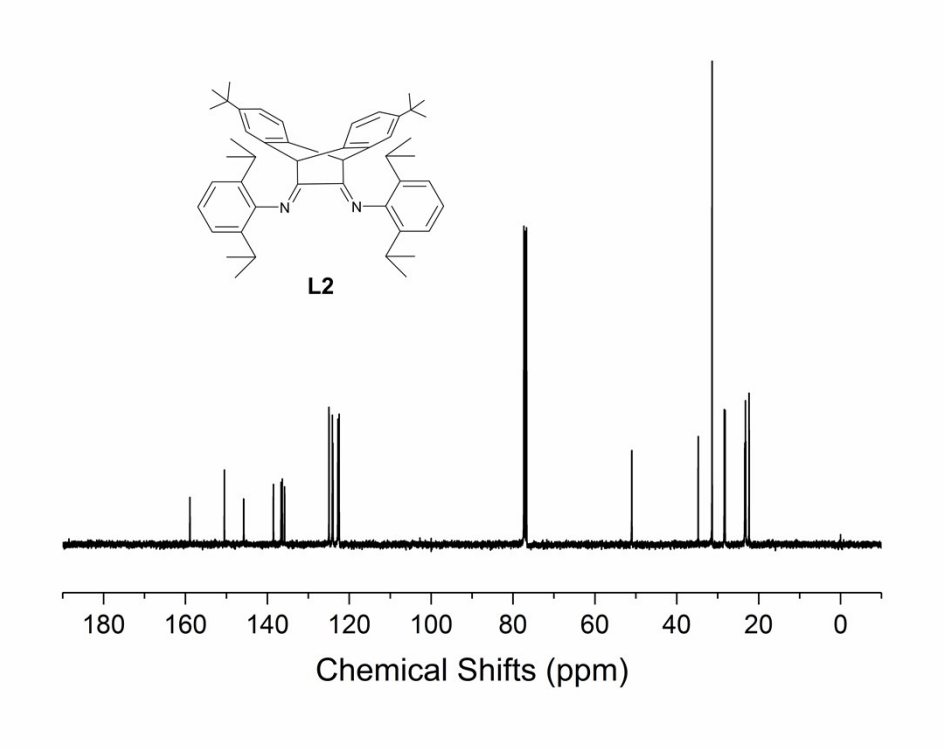


Figure S5. ^{13}C NMR spectrum of **L2**

L3: ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.25-7.04 (m, 14H, Ar-**H**), 4.86 (s, 2H, C**H**), 1.88 (s, 12H, C**H**$_3$). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 159.61, 147.92, 138.13, 128.44, 127.75, 126.11, 125.63, 123.56, 50.13, 17.82. Anal. Calcd for $C_{32}H_{28}N_2$: C, 87.24; H, 6.41; N, 6.36. Found: C, 87.31; H, 6.40; N, 6.29.

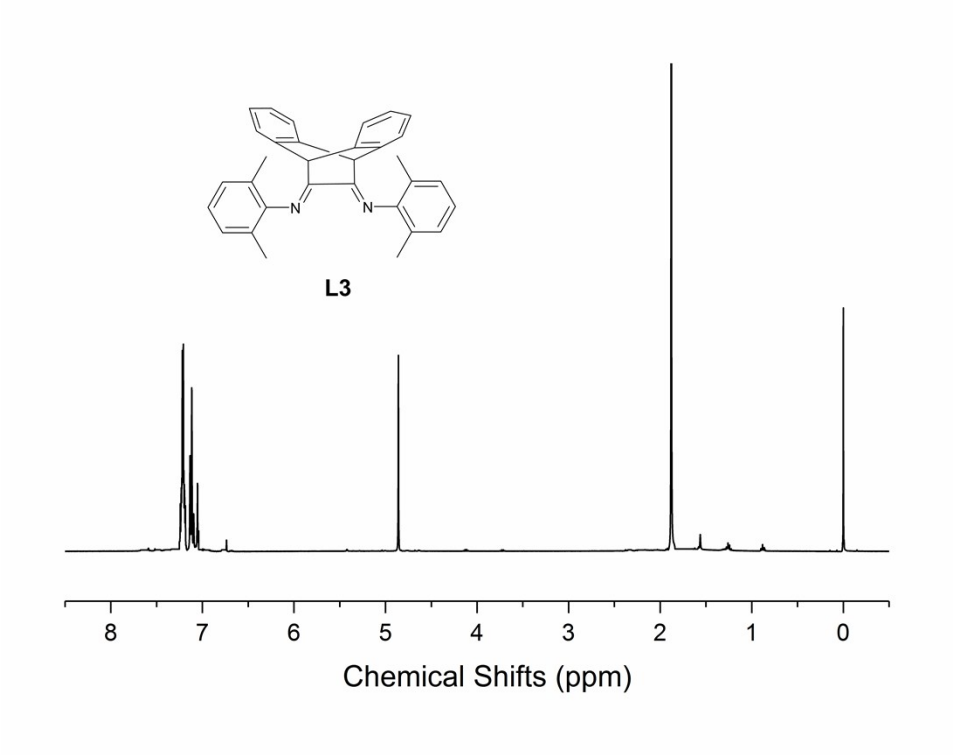


Figure S6. ^{1}H NMR spectrum of **L3**

L4: ^{1}H NMR ($CDCl_3$, 400 MHz), δ (ppm): 7.21-6.99 (m, 12H, Ar-**H**), 4.79 (s, 2H, C**H**), 1.91 (s, 6H, C**H**$_3$), 1.83 (s, 6H, C**H**$_3$), 1.23 (s, 18H, C**H**$_3$ in ^{t}Bu). ^{13}C NMR ($CDCl_3$, 100 MHz), δ (ppm): 160.21, 150.91, 148.05, 137.90, 134.89, 127.70, 125.73, 124.73, 124.25, 123.30, 122.56, 50.93, 31.35, 17.96, 17.60. Anal. Calcd for $C_{40}H_{44}N_2$: C, 86.91; H, 8.02; N, 5.07. Found: C, 86.95; H, 7.98; N, 5.03.

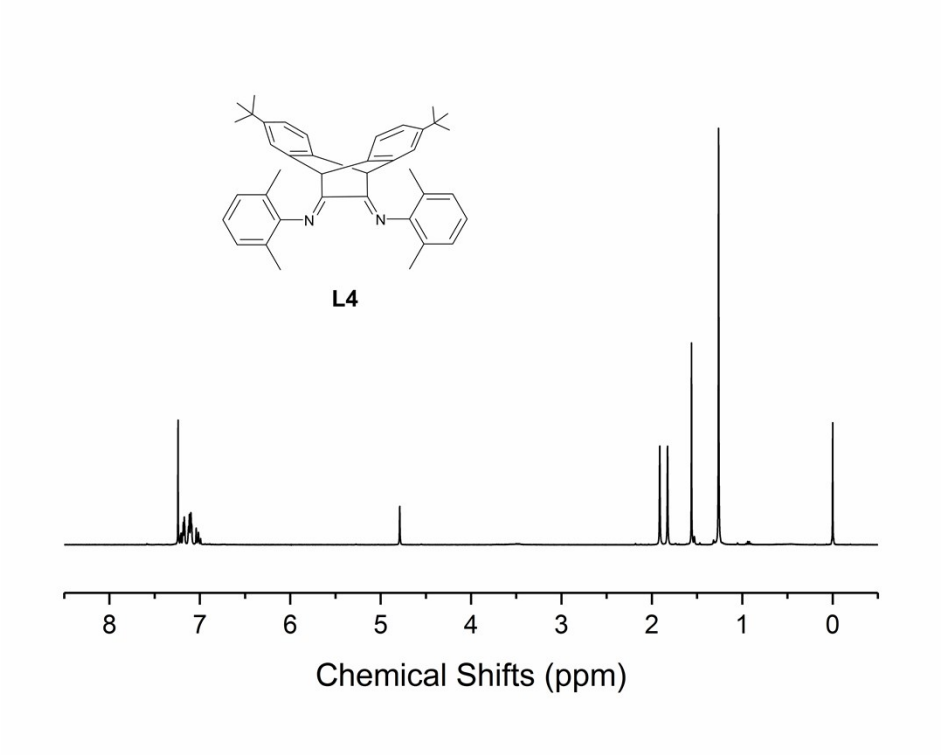


Figure S7. ^{1}H NMR spectrum of **L4**

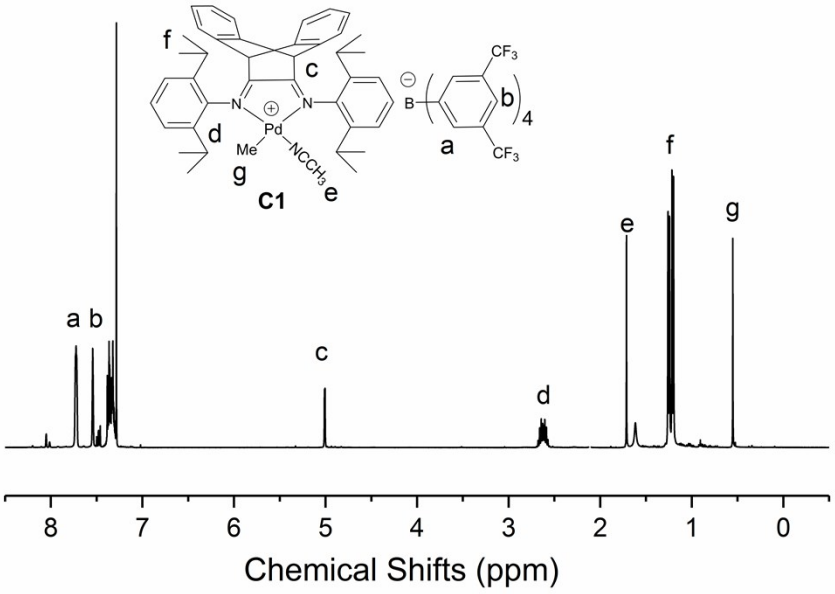


Figure S8. ^{1}H NMR spectrum of **C1**

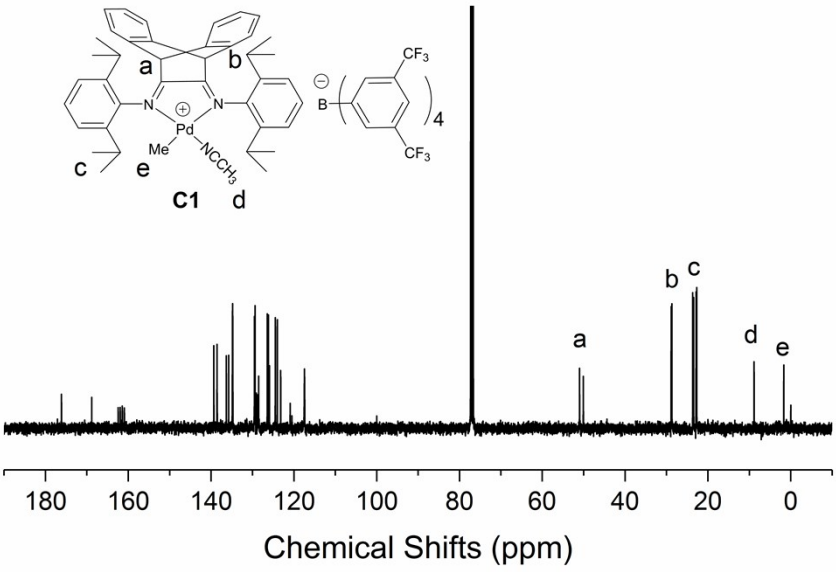


Figure S9. ^{13}C NMR spectrum of **C1**

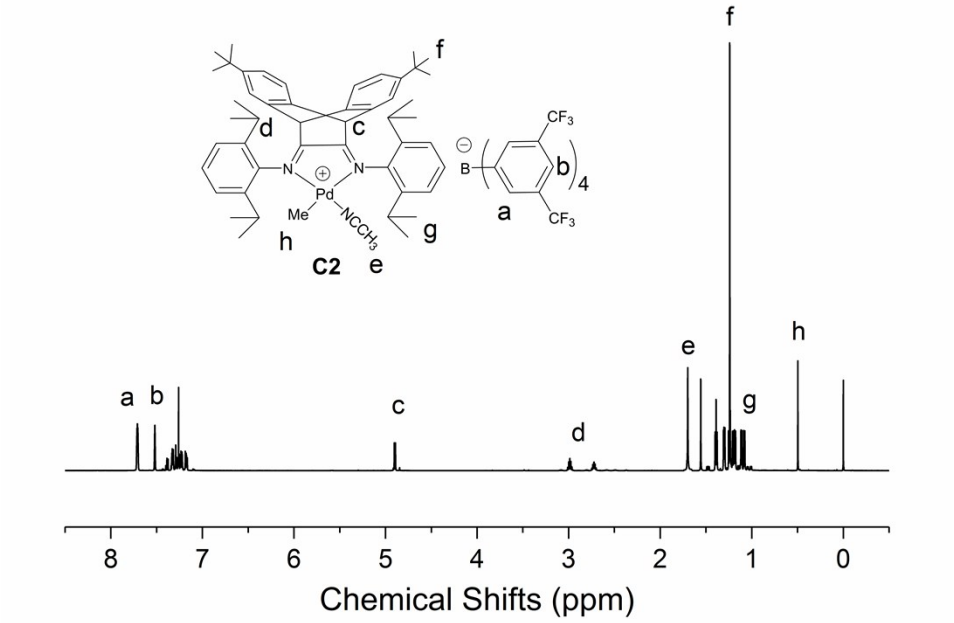


Figure S10. ^{1}H NMR spectrum of **C2**

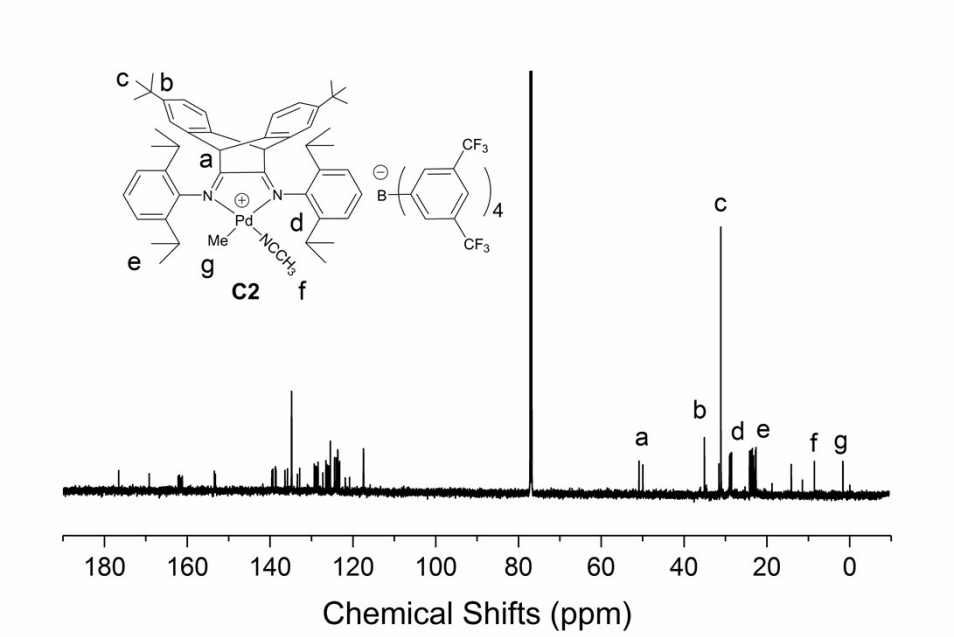


Figure S11. ^{13}C NMR spectrum of **C2**

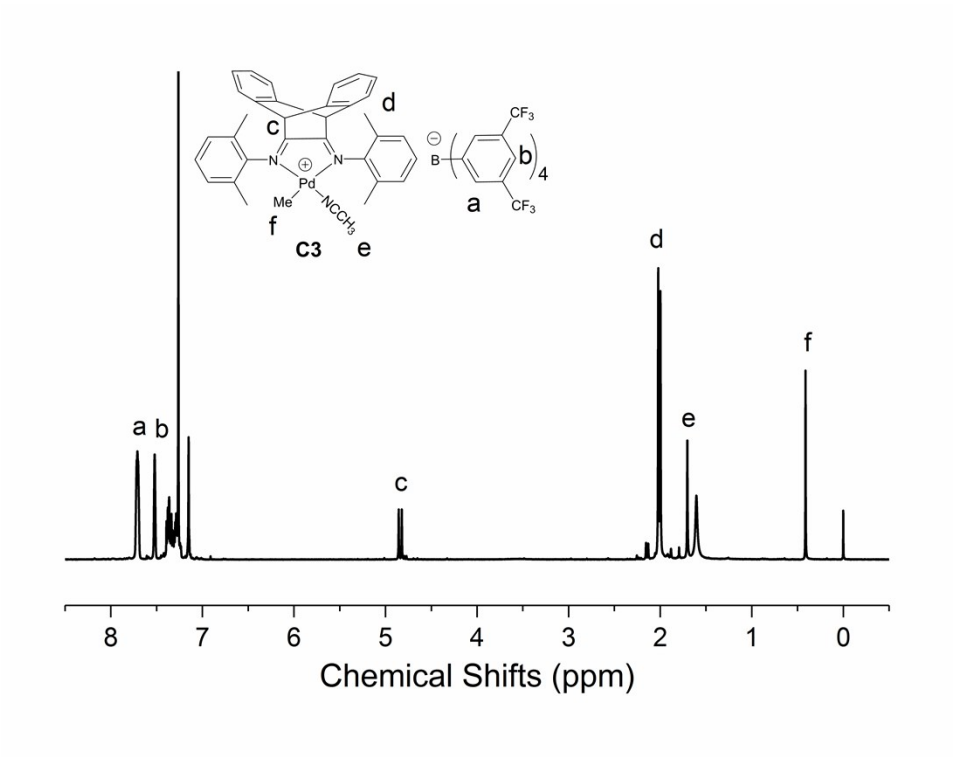


Figure S12. ^{1}H NMR spectrum of **C3**

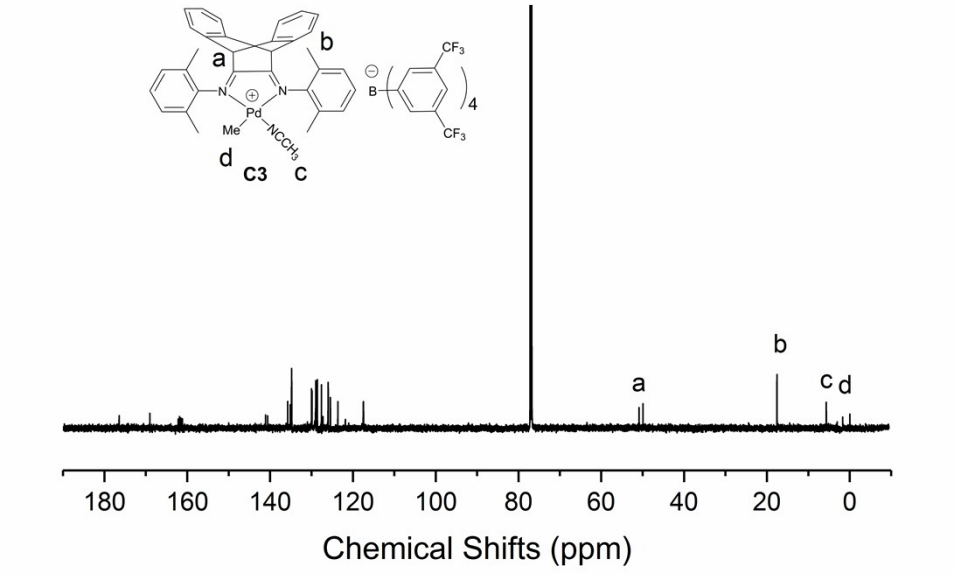


Figure S13. ^{13}C NMR spectrum of **C3**

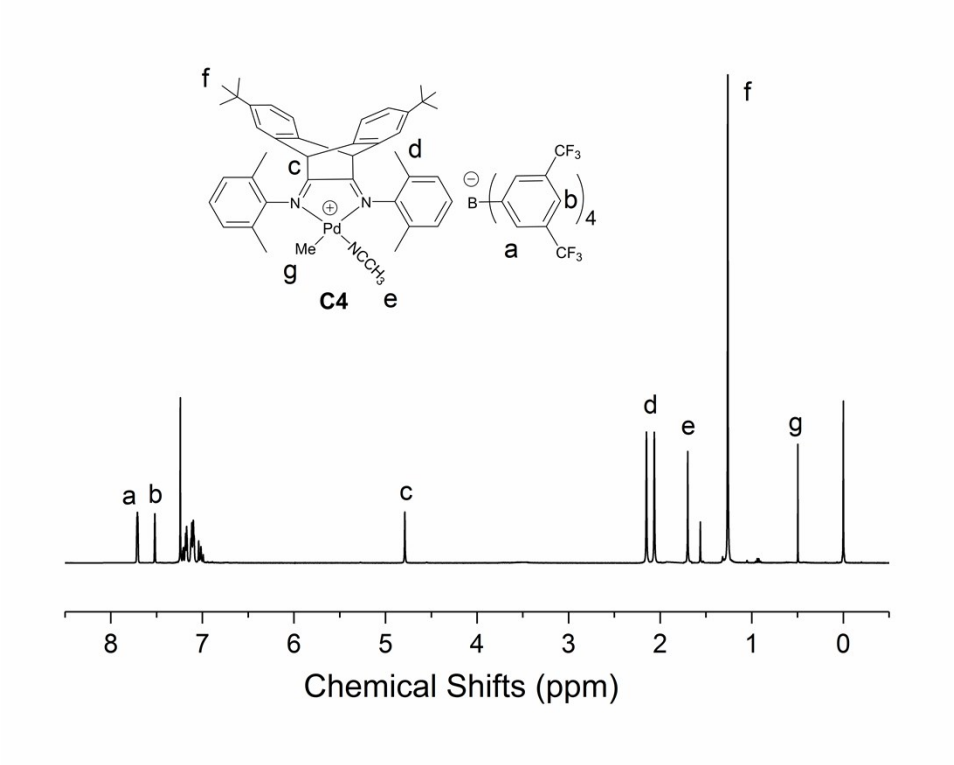


Figure S14. ^{1}H NMR spectrum of **C4**

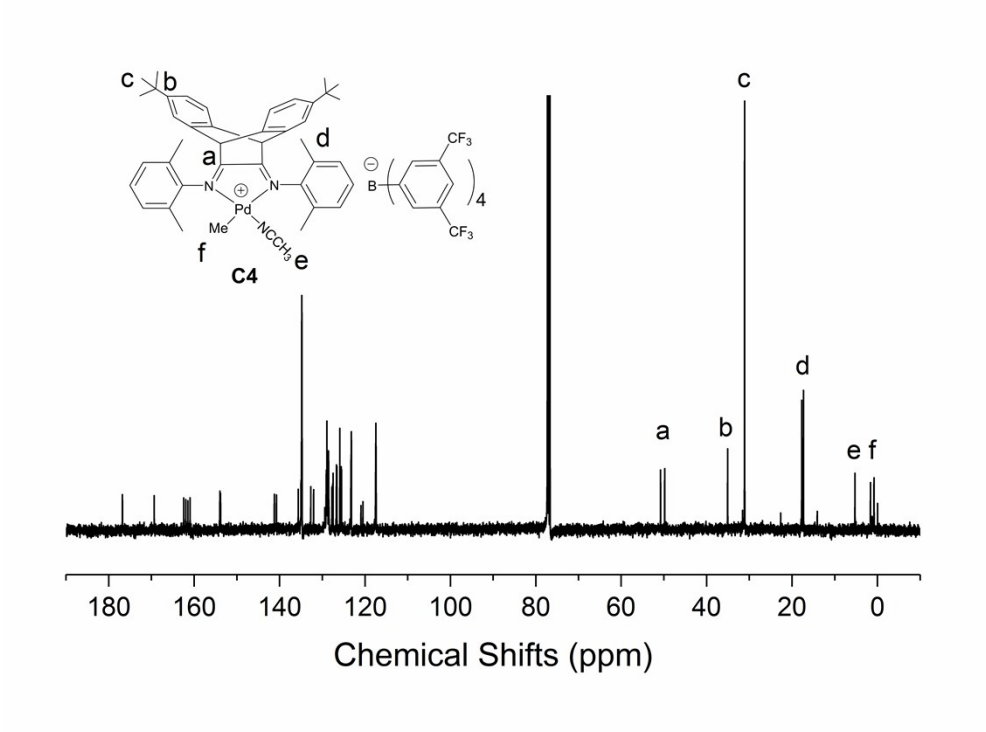


Figure S15. ^{13}C NMR spectrum of **C4**

3. Living copolymerization of ethylene and FA

Table S1. Living copolymerizations of ethylene and furfuryl acrylate using **C1**[a]

Entry	Time (h)	Yield (mg)	Act.[b]	Incorp.[c] (mol%)	M_n[d] (kg/mol)	PDI[d]	BD[c]
1	1	80	4.0	0.17	8.3	1.07	103
2	2	132	3.3	0.19	13.2	1.09	100
3	3	214	3.6	0.21	20.9	1.13	101
4	4	260	3.3	0.20	25.2	1.10	104

[a] Polymerization conditions: 20 μmol catalysts, 19 mL of toluene and 1 mL of CH_2Cl_2, 3 psig, 15°C, 0.51mL FA (0.2M). [b]Act.: kg CP/(mol Pd·h). [c]Incorp. and Branching density were determined by ^{1}H NMR spectroscopy. [d]M_n and PDI were measured by gel permeation chromatography (GPC) in THF.

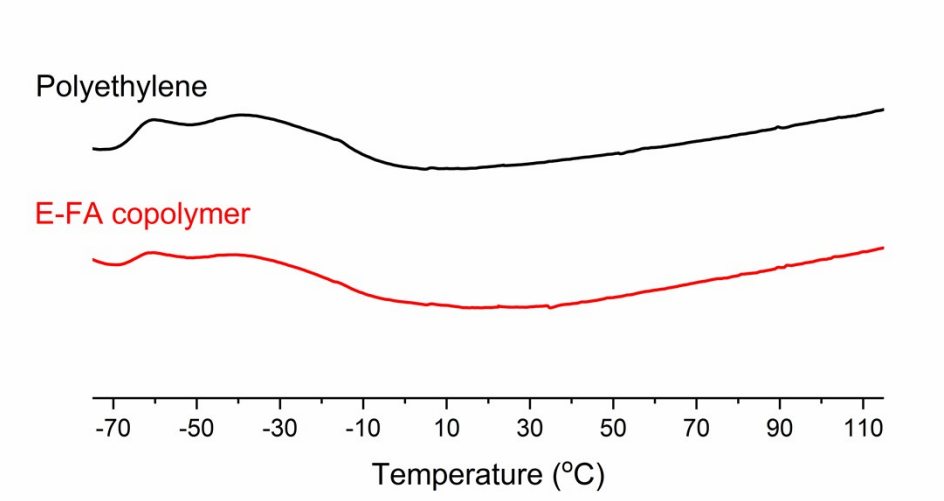


Figure S16. DSC curves of polyethylene (entry 11 in Table 1) and E-FA copolymer (entry 2 in Table 2).

4. Crystallographic data for palladium complexes 2 and FA-Pd

Table S2. Crystallographic date for the palladium complexes **2** and **FA-Pd**

	2	**FA-Pd**
Empirical formula	$C_{49}H_{63}ClN_2Pd$	$C_{80.75}H_{62.6}BF_{23.88}N_2O_{2.75}Pd$
Formula weight	821.86	1675.76
Crystal color	red	yellow
Crystal system	tetragonal	monoclinic
space group	$I4_1cd$	$P2_1/c$
a (Å)	24.7912(3)	27.646(2)
b (Å)	24.7912(3)	21.9906(11)
c (Å)	31.0121(6)	25.7467(16)
α (deg)	90.0	90
β (deg)	90.0	90.474(7)
γ (deg)	90.0	90
Volume($Å^3$)	19060.2(5)	15652.3(17)
Z	16	8
ρ_{calc} (g/cm^3)	1.146	1.422
μ (mm^{-1})	3.881	0.342
F(000)	6944.0	6792.0
Crystal size (mm^3)	0.55 × 0.2 × 0.15	0.22 × 0.2 × 0.16
Radiation	CuKα	MoKα
2θ range for data collection (°)	7.132 to 147.64	6.488 to 52
Index ranges	-17 ≤ h ≤ 30 -16 ≤ k ≤ 27 -26 ≤ l ≤ 37	-34 ≤ h ≤ 33 -27 ≤ k ≤ 21 -29 ≤ l ≤ 31
Reflections collected	18906	49391
Data/restraints/parameters	6411 / 378 / 626	28441/44/2151
Goodness-of-fit on F^2	1.067	1.012
Final R indices [I>2σ(I)]	R1 = 0.0410, wR2 = 0.1008	R1 = 0.0839, wR2 = 0.1984
R indices (all data)	R1 = 0.0470, wR2 = 0.1063	R1 = 0.1423, wR2 = 0.2428
Largest diff. peak/hole ($e/Å^3$)	0.34/-0.49	1.64/-0.97

References

(1) Engel, T.; Kickelbick, G. Self-healing nanocomposites from silica - polymer core - shell nanoparticles. *Polym. Int.* **2014**, 63 (5), 915-923

(2) Zhong, L.; Li, G. L.; Liang, G. D.; Gao, H. Y.; Wu, Q. Enhancing Thermal Stability and Living Fashion in α-Diimine-Nickel-Catalyzed (Co)polymerization of Ethylene and Polar Monomer by Increasing the Steric Bulk of Ligand Backbone. *Macromolecules* **2017**, 50 (7), 2675-2682