

Supplementary Information for

Initiating Ability of Diphosphine- and Diamine-ligated Pd Complexes/NaBPh₄ Systems for C1

Polymerization of Diazoacetates

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Experimental

Materials. Tetrahydrofuran (THF, Kanto Chemical, >99.5%, dehydrated Super Plus grade) was used after passage through solvent purification columns (Nikko Hansen & Co., Glass Contour MINI). Acetone (FUJIFILM Wako Pure Chemical, >99.5%, super dehydrated), diethyl ether (FUJIFILM Wako Pure Chemical, >99.5%, super dehydrated), 1,4-dioxane (FUJIFILM Wako Pure Chemical, >99.5%, super dehydrated), hexane (FUJIFILM Wako Pure Chemical, >96.0%, super dehydrated), chloroform (Junsei Chemical, 99%), methanol (Yoneyama Yakuhin Kogyo, 99%), triphenylphosphine (PPh₃, Nacalai Tesque, >98.0%), 1,1'-bis(diphenylphosphino)ferrocene (dppf, Kanto Chemical, >97.0%), 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene (xantphos, Tokyo Chemical Industry, > 98.0%), 2,3-dichloro-1,4-naphthoquinone (Cl₂-nq, dichlone, Tokyo Chemical Industry, > 95.0%), 2,3-dibromo-1,4-naphthoquinone (Br₂-nq, Tokyo Chemical Industry, > 95.0%), *N,N,N',N'*-tetramethylethylenediamine (tmeda, Tokyo Chemical Industry, > 98.0%), *N,N,N',N'*-tetraethylethylenediamine (teeda, Tokyo Chemical Industry, > 98.0%), *N,N,N',N'*-tetramethyl-1,3-propanediamine (tmpda, Tokyo Chemical Industry, > 98.0%), sodium tetrphenylborate (NaBPh₄, Tokyo Chemical Industry, > 99.5%), hydrochloric acid (Nacalai Tesque, 35-37%), Na₂SO₄ (Nacalai Tesque, > 98.5%), and CaH₂ (Nacalai Tesque, > 90.0%) were used as received.

Synthesis of monomers. Ethyl diazoacetate (EDA)¹ was prepared according to the literature, and dried over CaH₂ and stored as a dichloromethane solution. The concentration of EDA was determined with trichloroethylene (Katayama Chemical) as an internal standard by using ¹H NMR spectroscopy. Benzyl diazoacetate (BDA), cyclohexyl diazoacetate (*c*-HDA), and 1-naphthylmethyl diazoacetate (NpCH₂DA) were synthesized according to the general procedure reported by Fukuyama and co-workers.² The characterization data for BDA,² *c*-HDA,³ and NpCH₂DA⁴ were reported in the literature. **Caution!** Extra care must be taken for syntheses and handling of the diazocarbonyl compounds because of their potential explosiveness.

Synthesis of Pd complexes. Pd₂(dba)₃·CHCl₃ (dba = *trans,trans*-dibenzylideneacetone),⁵ **1** [Pd(nq)₂ (nq = 1,4-naphthoquinone)],⁶ and **2** [(cod)PdCl(Cl-naphthoquinonyl) (cod = 1,5-cyclooctadiene)]⁶ were prepared according to the literature. Pd complexes **3–11** were synthesized in a similar procedure as for the preparation of **2**. The detail synthetic procedures and the characterization data for **3–11** were described as below.

Synthesis of 3. Under a nitrogen atmosphere, Pd₂(dba)₃·CHCl₃ (0.15 g, 0.15 mmol), dichlone (0.26 g, 1.2 mmol), and triphenylphosphine (0.15 g, 0.58 mmol) were dissolved in acetone (5 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (3 mL) was added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding yellow crystals (30 mg, 12%). ¹H NMR (500 MHz, CDCl₃, δ): 7.80–7.76 (m, 12H, P[C₆H₅]₃), 7.63–7.61 (m, 1H), 7.45–7.40 (m, 2H), 7.37–7.33 (m, 1H), 7.26–7.22 (m, 18H, P[C₆H₅]₃). ³¹P NMR (202 MHz, CDCl₃, δ): 22.8. Anal. Calcd for C₄₆H₃₄Cl₂O₂P₂Pd: C, 64.38; H, 4.00; N, 0.00. Found: C, 63.99; H, 4.77; N, 0.14.

Synthesis of 4. Under a nitrogen atmosphere, Pd₂(dba)₃·CHCl₃ (60 mg, 0.058 mmol), Cl₂-qu(anth)⁷ (0.16 g, 0.46 mmol), and triphenylphosphine (61 mg, 0.23 mmol) were dissolved in THF (5 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (4 mL) was added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding yellow crystals (33 mg, 29%). ¹H NMR (500 MHz, CDCl₃, δ): 7.77–7.62 (m), 7.43–7.41 (m), 7.30–7.25 (m), 7.11 (m), 5.30 (s, 1H), 5.28 (s, 1H). ¹³C NMR (126 MHz, CDCl₃, δ): 186.7, 184.2, 174.2, 147.3, 134.9 (t, *J* = 6.6 Hz), 132.4, 131.8, 131.1, 130.6 (t, *J* = 24 Hz),

130.5, 128.3 (t, $J = 5.7$ Hz), 126.0, 125.8. One of quaternary carbon signals was likely to be overlapping with others. ^{31}P NMR (202 MHz, CDCl_3 , δ): 22.8. Anal. Calcd for $\text{C}_{36}\text{H}_{40}\text{Cl}_2\text{O}_2\text{P}_2\text{Pd}$: C, 68.32; H, 4.10; N, 0.00. Found: C, 68.72; H, 4.26; N, 0.17.

Synthesis of 5. Under a nitrogen atmosphere, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (60 mg, 0.058 mmol), dichlone (0.21 g, 0.93 mmol), and dppf (64 mg, 0.12 mmol) were dissolved in acetone (3 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (1 mL) was added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding yellow crystals (15 mg, 15%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.12 (br, 5H), 7.79–7.78 (m, 2H), 7.51–7.45 (m, 12H), 7.01 (br, 5H), 4.95 (br, 2H), 4.58 (m, 2H), 4.16 (s, 2H), 3.37 (s, 2H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 31.0 (d), 13.7 (d). Anal. Calcd for $\text{C}_{44}\text{H}_{32}\text{Cl}_2\text{FeO}_2\text{P}_2\text{Pd} \cdot \text{CHCl}_3$: C, 53.66; H, 3.30; N, 0.00. Found: C, 54.16; H, 3.61; N, 0.00.

Synthesis of 6. Under a nitrogen atmosphere, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (60 mg, 0.058 mmol), dichlone (0.11 g, 0.46 mmol), and xantphos (84 mg, 0.15 mmol) were dissolved in THF (3 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (4 mL) was added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding yellow crystals (15 mg, 15%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.22–8.19 (m, 4H), 7.80 (d, $J = 8$ Hz, 1H), 7.66 (d, $J = 8$ Hz, 2H), 7.48–7.36 (m, 7H), 7.24–7.21 (m, 2H), 7.17–7.14 (m, 3H), 6.93–6.90 (m, 4H), 6.82 (d, $J = 8$ Hz, 1H), 6.77–6.74 (m, 4H), 6.71–6.68 (m, 2H), 1.93 (s, 3H), 1.75 (s, 3H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 6.3. Anal. Calcd for $\text{C}_{49}\text{H}_{36}\text{Cl}_2\text{N}_2\text{O}_4\text{Pd} \cdot \text{C}_4\text{H}_8\text{O}$: C, 64.68; H, 4.51; N, 0.00. Found: C, 64.25; H, 4.56; N, 0.00.

Synthesis of 7. Under a nitrogen atmosphere, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (60 mg, 0.058 mmol), Cl_2 -qu(anth) (0.16 g, 0.46 mmol), and xantphos (84 mg, 0.15 mmol) were dissolved in THF (5 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (4 mL) was added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding red crystals (86 mg, 71%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.08–8.05 (m, 4H), 7.66–7.64 (m, 2H), 7.42–7.40 (m, 2H), 7.36–7.33 (m, 4H), 7.28–7.27 (m, 2H), 7.18–7.13 (m, 4H), 7.05–7.03 (m, 2H), 7.00–6.98 (m, 4H), 6.81–6.77 (m, 4H), 6.45–6.42 (m, 4H), 6.40–6.36 (m, 2H), 5.34 (s, 1H), 4.69 (s, 1H), 1.93 (s, 3H), 1.73 (s, 3H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 6.3. Anal. Calcd for $\text{C}_{59}\text{H}_{42}\text{Cl}_2\text{O}_3\text{P}_2\text{Pd} \cdot 2(\text{C}_4\text{H}_8\text{O})$: C, 68.06; H, 4.94; N, 0.00. Found: C, 67.99; H, 4.90; N, 0.00.

Synthesis of 8. Under a nitrogen atmosphere, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (60 mg, 0.058 mmol), dichlone (0.11 g, 0.46 mmol), and tmeda (0.069 mL, 0.46 mmol) were dissolved in acetone (3 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (5 mL) and *n*-hexane (1 mL) were added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding red crystals (12 mg, 24%). ^1H NMR (500 MHz, CDCl_3 , δ): 8.07–8.05 (m, 2H, Ar-*H*), 7.48–7.46 (m, 2H, Ar-*H*), 2.60 (s, 6H, CH_3), 2.53–2.48 (m, 2H, CH_2), 2.43–2.38 (m, 2H, CH_2), 2.34 (s, 6H, CH_3). ^{13}C NMR (126 MHz, CDCl_3 , δ): 171.1, 135.1, 131.6, 125.5, 78.3, 59.6, 49.4, 48.8. Anal. Calcd for $\text{C}_{16}\text{H}_{20}\text{Cl}_2\text{N}_2\text{O}_2\text{Pd}$: C, 42.74; H, 4.48; N, 6.23. Found: C, 42.64; H, 4.50; N, 6.21.

Synthesis of 9. Under a nitrogen atmosphere, $\text{Pd}_2(\text{dba})_3 \cdot \text{CHCl}_3$ (60 mg, 0.058 mmol), dichlone (0.11 g, 0.46 mmol), and teeda (0.099 mL, 0.46 mmol) were dissolved in THF (3 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (3 mL) was added to the solution and the mixture was

left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding red crystals (26 mg, 44%). ¹H NMR (500 MHz, CDCl₃, δ): 8.07–8.05 (m, 2H, Ar-*H*), 7.48–7.47 (m, 2H, Ar-*H*), 2.82 (q, *J* = 7 Hz, 4H, NCH₂CH₃), 2.68–2.61 (m, 2H, NCH₂CH₂N), 2.60–2.53 (m, 4H, NCH₂CH₃), 2.52–2.46 (m, 2H, NCH₂CH₂N), 1.33 (t, *J* = 7 Hz, 4H, NCH₂CH₃), 0.89 (t, *J* = 7 Hz, 4H, NCH₂CH₃). ¹³C NMR (126 MHz, CDCl₃, δ): 173.5, 134.9, 131.7, 126.0, 77.3, 52.1, 51.6, 51.1, 11.9, 11.2. Anal. Calcd for C₂₀H₂₈Cl₂N₂O₂Pd·0.25(C₄H₈O): C, 48.15; H, 5.77; N, 5.35. Found: C, 48.12; H, 5.75; N, 5.30.

Synthesis of 10. Under a nitrogen atmosphere, Pd₂(dba)₃·CHCl₃ (60 mg, 0.058 mmol), dichlone (53 mg, 0.26 mmol), and tmpda (0.077 mL, 0.46 mmol) were dissolved in THF (3 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (2 mL) and *n*-hexane (2 mL) were added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding red crystals (18 mg, 34%). ¹H NMR (500 MHz, CDCl₃, δ): 8.09–8.07 (m, 2H, Ar-*H*), 7.51–7.49 (m, 2H, Ar-*H*), 2.68–2.63 (m, 2H, NCH₂CH₂CH₂N), 2.56 (s, 6H, CH₃), 2.34–2.29 (m, 2H, NCH₂CH₃CH₂N), 2.21 (s, 6H, CH₃), 1.71–1.63 (m, 2H, NCH₂CH₂CH₂N), 1.53–1.47 (m, 2H, NCH₂CH₂CH₂N). ¹³C NMR (126 MHz, CDCl₃, δ): 172.4, 135.1, 131.8, 125.6, 77.3, 63.3, 51.9, 48.4, 22.9. Anal. Calcd for C₁₇H₂₂Cl₂N₂O₂Pd: C, 44.03; H, 4.78; N, 6.04. Found: C, 44.06; H, 4.85; N, 5.89.

Synthesis of 11. Under a nitrogen atmosphere, Pd₂(dba)₃·CHCl₃ (60 mg, 0.058 mmol), 2,3-dibromo-1,4-naphthoquinone (73 mg, 0.23 mmol), and tmpda (0.077 mL, 0.46 mmol) were dissolved in THF (3 mL). The resulting mixture was stirred at room temperature for 60 min. After filtration, diethyl ether (2 mL) and *n*-hexane (2 mL) were added to the solution and the mixture was left to stand at 4 °C for overnight. The precipitated crystals were collected by vacuum filtration and washed by rinsing with a small amount of ice-cold diethyl ether, yielding red crystals (33 mg, 51%). ¹H NMR (500 MHz, CDCl₃, δ): 8.10–8.06 (m, 2H, Ar-*H*), 7.51–7.48 (m, 2H, Ar-*H*), 2.66–2.60 (m, 2H, NCH₂CH₂CH₂N), 2.58 (s, 6H, CH₃), 2.35–2.31 (m, 2H, NCH₂CH₃CH₂N), 2.22 (s, 6H, CH₃), 1.67–1.62 (m, 2H, NCH₂CH₂CH₂N), 1.56–1.51 (m, 2H, NCH₂CH₂CH₂N). ¹³C NMR (126 MHz, CDCl₃, δ): 173.7, 135.0, 131.9, 126.1, 69.8, 63.4, 52.0, 48.9, 22.9. Anal. Calcd for C₁₇H₂₂Br₂N₂O₂Pd: C, 36.95; H, 4.01; N, 5.07. Found: C, 36.92; H, 4.04; N, 4.91.

Polymerization procedure. As a representative example, the procedure for the polymerization of EDA with **10**/NaBPh₄ (run 10 in Table 2) is described as follows. In a Schlenk tube filled with nitrogen, **10** (4.64 mg, 1.0×10⁻² mmol) was dissolved in THF (3.0 mL). NaBPh₄ (3.76 mg, 1.1×10⁻² mmol) was added to the Schlenk tube cooled at -78 °C. After stirring for 10 min at the temperature, a dichloromethane solution of EDA (1.44 M, 0.69 mL) was added to the Schlenk tube. The reaction mixture was stirred at -78 °C for 10 min and then warmed to 50 °C. After the polymerization period (13 h), volatiles were removed with a vacuum pump. HCl/methanol (1 M, 10 mL), hydrochloric acid (1 M, 10 mL), and chloroform (20 mL) were added to the residue, and the resulting mixture was extracted with chloroform. The organic layer was washed with brine and water, dried over Na₂SO₄, and concentrated under reduced pressure. Purification with preparative recycling SEC gave a polymer (41 mg, 48% yield).

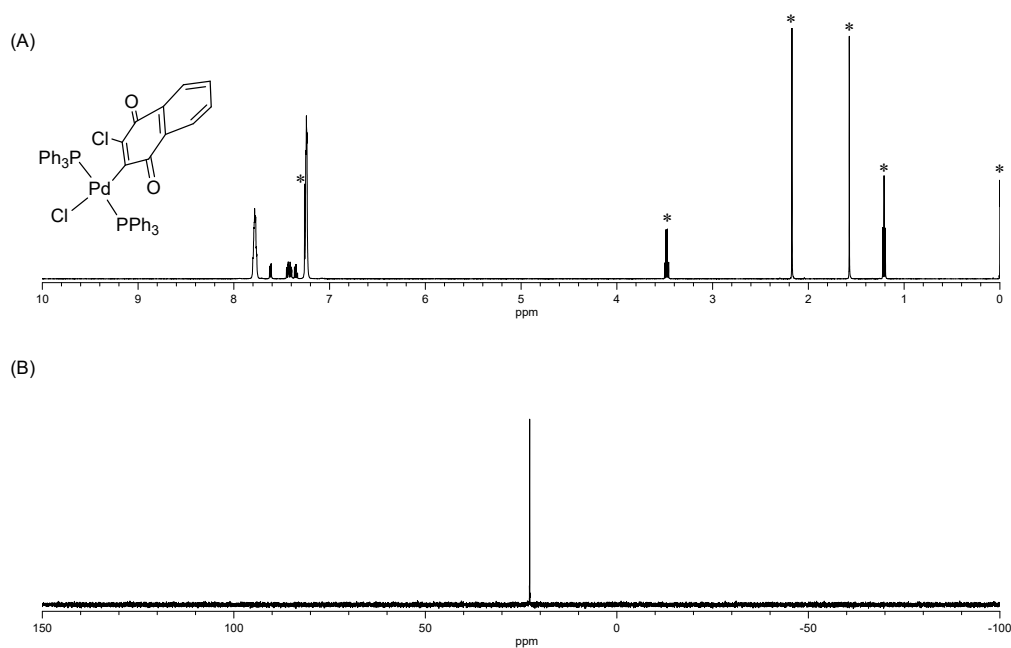
Measurements. The polymers' molar mass distributions were measured via SEC in THF (flow rate = 1.0 mL/min) at 40 °C on polystyrene gel columns [Styragel HR4 and Styragel HR2 (Waters, molar-mass exclusion limit = 600 kDa and 20 kDa for polystyrene, respectively)] connected to a pump (JASCO, PU-4180), a column oven (JASCO, CO-2065 Plus), an ultraviolet detector (JASCO, UV-4075), and a refractive index detector (JASCO, RI-

2031 Plus). The number-average molar mass (M_n) and dispersity [D ; weight-average molar mass/number-average molar mass (M_w/M_n)] were calculated from the chromatographs on the basis of six poly(methyl methacrylate) (PMMA) standards (Shodex M-75; $M_p = 2400\text{--}212000$, $D < 1.1$) and dibutyl sebacate (molar mass = 314.5). The absolute molecular weight of the polymers was determined by SEC coupled with multiangle light scattering (SEC-MALS) on a Dawn HELEOS II 8+ (Wyatt Technology; $\lambda = 661.5$ nm). The refractive index increment (dn/dc) values were measured assuming 100% mass recovery. Purification by preparative recycling SEC was performed on a JAI LC-918R equipped with a combination of JAIGEL-3H and JAIGEL-2H (Japan Analytical Industry, molar mass exclusion limit = 70 kDa and 5 kDa for polystyrene, respectively; column size = 600 mm \times 20 mm i.d.) using chloroform as eluent at a flow rate of 3.8 mL/min at room temperature. Matrix-assisted laser desorption/ionization time-of-flight mass (MALDI-TOF-MS) spectrometry data were recorded on a JMS-S3000 (JEOL, spiral mode) using super-DHB (Merck, a mixture of 2,5-dihydroxybenzoic acid and 2-hydroxy-5-methoxybenzoic acid) as a matrix and sodium trifluoroacetate as an ion source. The calibration was carried out using poly(ethylene glycol) ($M_n = 2700\text{--}3500$). ^1H (500 MHz), ^{13}C (126 MHz), and ^{31}P (202 MHz) NMR spectra were recorded on a Bruker Avance III HD 500 spectrometer in CDCl_3 at room temperature or at 50 $^\circ\text{C}$. Elemental analyses were performed on a YANAKO CHN Corder MT-5. X-ray diffraction analyses were performed with a Rigaku VariMax with RAPID diffractometer using multilayer mirror monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073$ \AA) at 100 K. The glass transition temperature (T_g) of polymers was determined by differential scanning calorimetry (DSC; Seiko Instruments Inc., EXSTAR DSC6000) in the range from -100 $^\circ\text{C}$ to 100 $^\circ\text{C}$ for product polymers. The heating and cooling rates were 10 $^\circ\text{C}/\text{min}$. The T_g of the polymers was defined as the temperature of the midpoint of a heat capacity change on the second heating scan. Thermogravimetric analysis (TGA) was performed with Exstar TG/DTA6200 (Seiko Instruments). The experiments were carried out with about 10 mg of a sample under a nitrogen atmosphere (25 mL/min) at a heating rate of 10 $^\circ\text{C}/\text{min}$.

Supplementary Tables and Figures

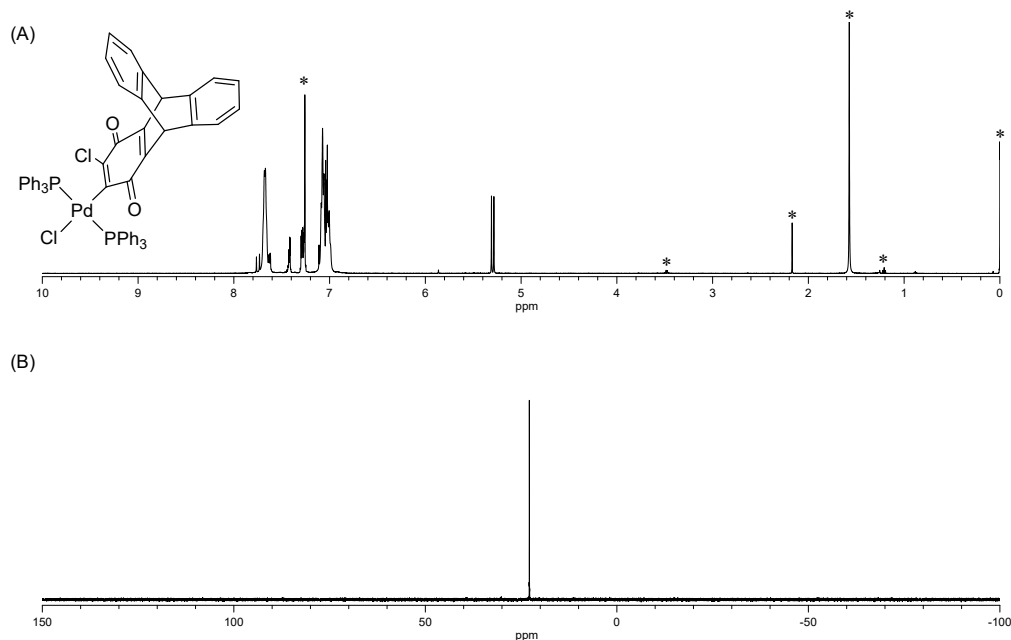
Table S1. X-ray crystallographic data of **3**, **5**, **6**, **7**, **8**, **10**, and **11**

	3	5	6	7	8	10	11
CCDC No.	2191524	2191472	2191475	2207432	2191409	2191416	2191419
Formula	C ₄₆ H ₃₄ Cl ₂ O ₂ P ₂ Pd, 1.45(C ₃ H ₆ O)	C ₄₄ H ₃₂ Cl ₂ FeO ₂ P ₂ Pd , CHCl ₃	C ₄₉ H ₃₆ Cl ₂ O ₃ P ₂ Pd, 2(C ₄ H ₈ O)	C ₅₉ H ₄₂ Cl ₂ O ₃ P ₂ Pd, 0.5(C ₄ H ₁₀ O), 0.5(C ₄ H ₈ O)	C ₁₆ H ₂₀ Cl ₂ N ₂ O ₂ Pd	C ₁₇ H ₂₂ Cl ₂ N ₂ O ₂ Pd	C ₁₇ H ₂₂ Br ₂ N ₂ O ₂ Pd
Formula weight	942.00	1007.15	1056.22	1111.28	449.64	463.67	552.57
Radiation	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α	Mo K α
Temperature [K]	100	100	100	100	100	100	100
Crystal system	monoclinic	orthorhombic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	<i>P</i> 2 ₁ / <i>n</i>	<i>Pna</i> 2 ₁	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>	<i>C</i> 2/ <i>c</i>	<i>C</i> 2/ <i>m</i>
<i>a</i> [Å]	12.4623(3)	32.1117(4)	12.6300	20.2129(9)	8.5369(2)	16.7813(9)	12.3508(5)
<i>b</i> [Å]	10.8537(3)	12.4315(2)	13.0697(5)	13.6540(4)	12.0251(2)	8.4205(3)	14.1078(5)
<i>c</i> [Å]	32.8318(8)	10.0614(1)	16.0599(6)	20.7338(8)	17.0606(4)	26.3272(13)	10.6617(5)
α [deg]	90	90	67.524(4)	90	90	90	90
β [deg]	93.985(2)	90	81.219(4)	116.670(5)	96.799(2)	103.427(5)	101.286(4)
γ [deg]	90	90	78.077(4)	90	90	90	90
<i>V</i> [Å ³]	4430.2(2)	4016.48(9)	2388.82(18)	5113.4(4)	1739.07(6)	3618.5(3)	1821.80(13)
<i>Z</i>	4	4	2	4	4	8	4
ρ [g/cm ⁻³]	1.412	1.666	1.468	1.444	1.717	1.702	2.015
μ [mm ⁻¹]	0.655	1.261	0.618	0.581	1.384	1.333	5.417
<i>F</i> (000)	1929.0	2040.0	1088.0	2284.0	904.0	1872.0	1080.0
<i>R</i> ¹	0.0574	0.0276	0.0443	0.0504	0.0376	0.0453	0.0379
w <i>R</i> ²	0.1417	0.0558	0.0996	0.1187	0.0913	0.0990	0.0942
GOF	1.029	1.066	1.048	1.050	1.057	1.047	1.028



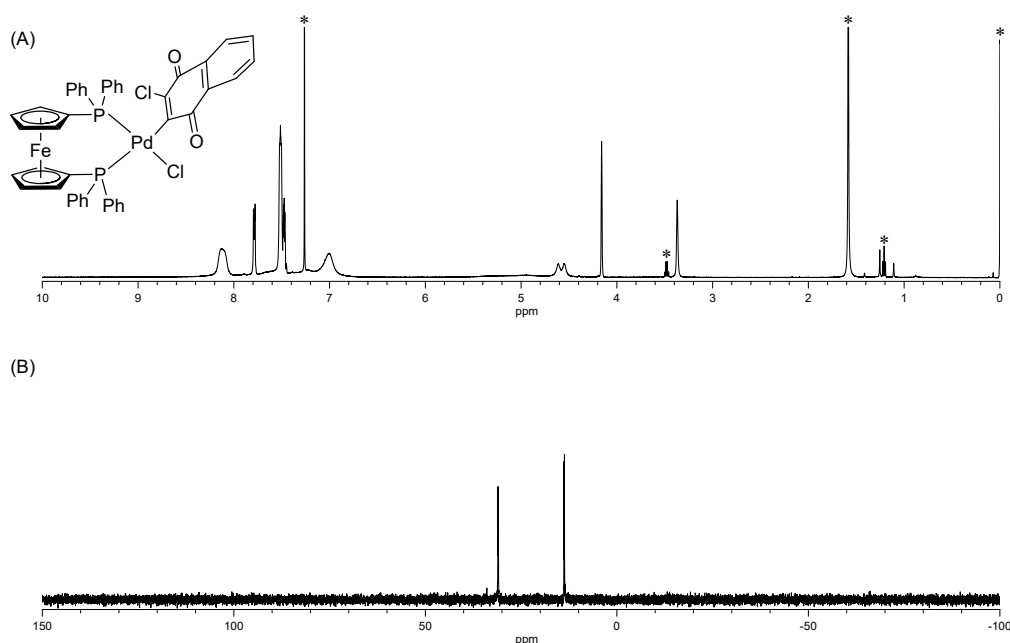
^1H NMR (500 MHz, CDCl_3 , δ): 7.80–7.76 (m, 12H, $\text{P}[\text{C}_6\text{H}_5]_3$), 7.63–7.61 (m, 1H), 7.45–7.40 (m, 2H), 7.37–7.33 (m, 1H), 7.26–7.22 (m, 18H, $\text{P}[\text{C}_6\text{H}_5]_3$). ^{31}P NMR (202 MHz, CDCl_3 , δ): 22.8.

Figure S1. (A) ^1H and (B) ^{31}P NMR spectra of **3** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



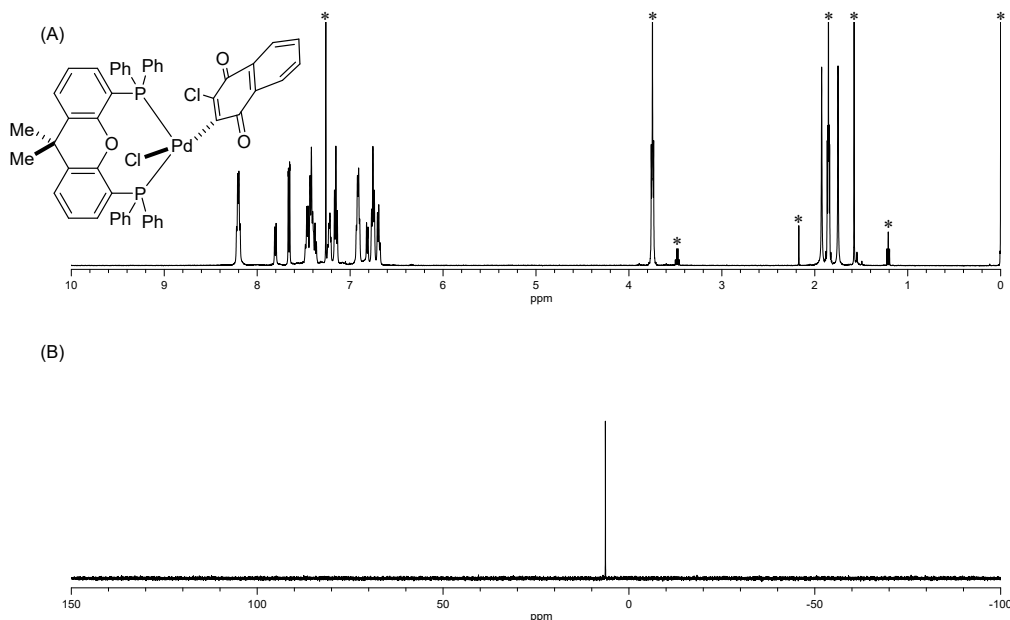
^1H NMR (500 MHz, CDCl_3 , δ): 7.77–7.62 (m), 7.43–7.41 (m), 7.30–7.25 (m), 7.11 (m), 5.30 (s, 1H), 5.28 (s, 1H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 22.8.

Figure S2. (A) ^1H and (B) ^{31}P NMR spectra of **4** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



^1H NMR (500 MHz, CDCl_3 , δ): 8.12 (br, 5H), 7.79–7.78 (m, 2H), 7.51–7.45 (m, 12H), 7.01 (br, 5H), 4.95 (br, 2H), 4.58 (m, 2H), 4.16 (s, 2H), 3.37 (s, 2H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 31.0 (d), 13.7 (d).

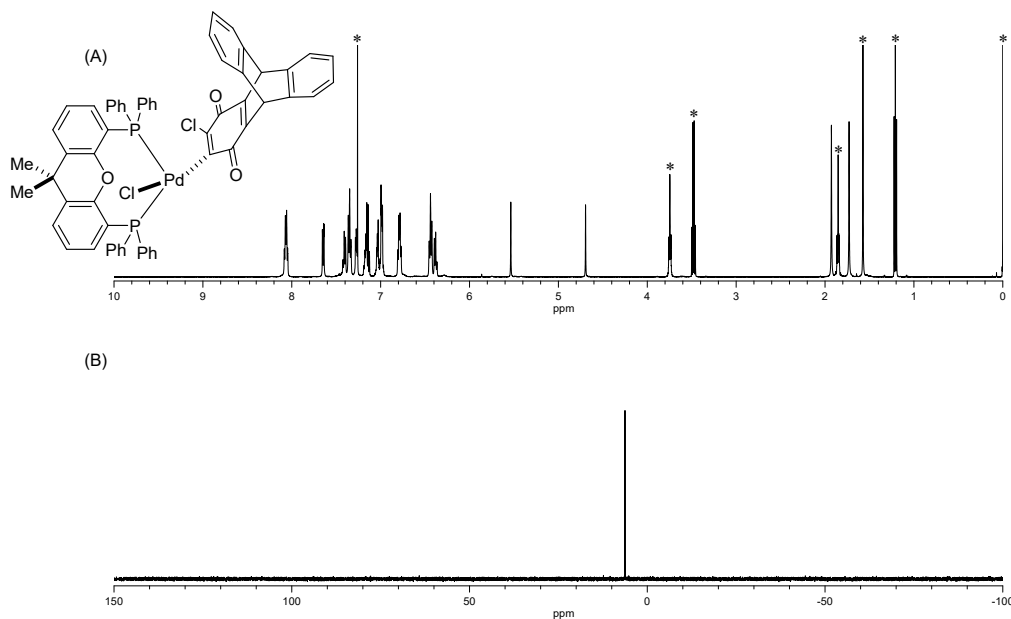
Figure S3. (A) ^1H and (B) ^{31}P NMR spectra of **5** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



^1H NMR (500 MHz, CDCl_3 , δ): 8.22–8.19 (m, 4H), 7.80 (d, $J = 8$ Hz, 1H), 7.66 (d, $J = 8$ Hz, 2H), 7.48–7.36 (m, 7H), 7.24–7.21 (m, 2H), 7.17–7.14 (m, 3H), 6.93–6.90 (m, 4H), 6.82 (d, $J = 8$ Hz, 1H), 6.77–6.74 (m, 4H), 6.71–6.68 (m, 2H), 1.93 (s, 3H), 1.75 (s, 3H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 6.3.

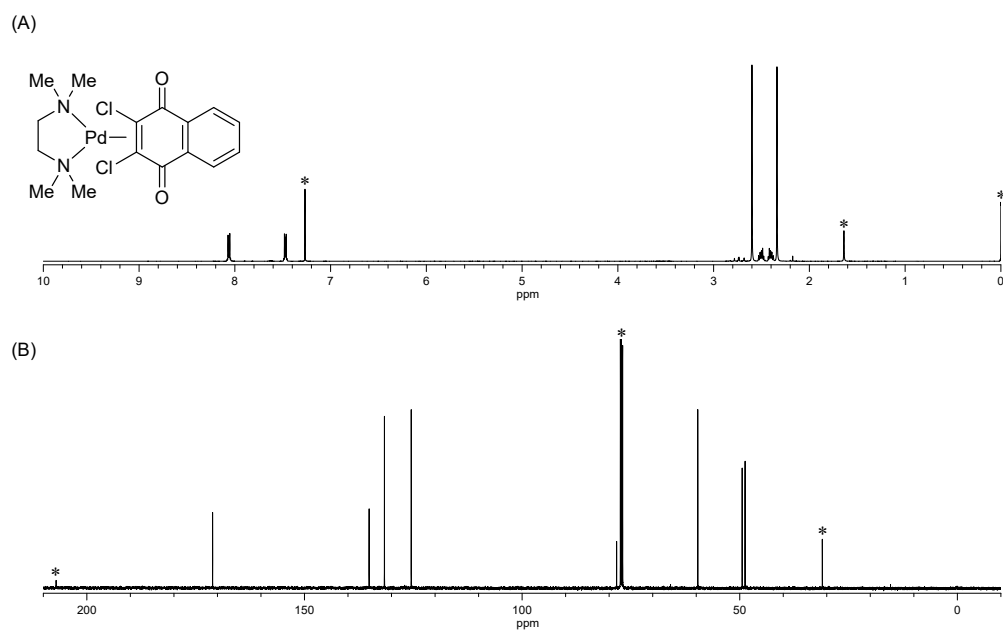
Figure S4. (A) ^1H and (B) ^{31}P NMR spectra of **6** recorded in CDCl_3 at room temperature (*solvent,

tetramethylsilane, or water).



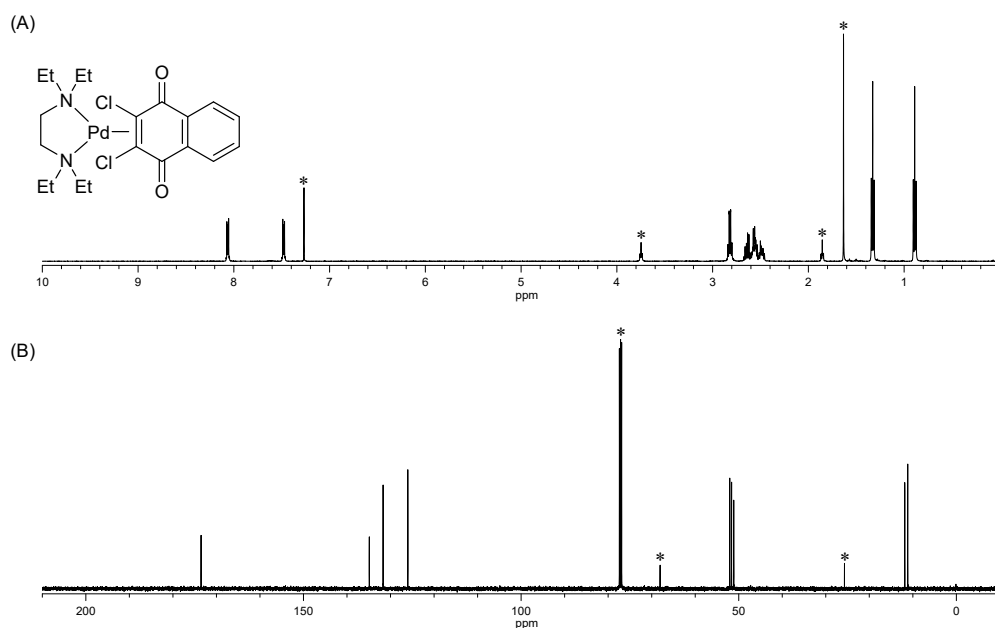
^1H NMR (500 MHz, CDCl_3 , δ): 8.08–8.05 (m, 4H), 7.66–7.64 (m, 2H), 7.42–7.40 (m, 2H), 7.36–7.33 (m, 4H), 7.28–7.27 (m, 2H), 7.18–7.13 (m, 4H), 7.05–7.03 (m, 2H), 7.00–6.98 (m, 4H), 6.81–6.77 (m, 4H), 6.45–6.42 (m, 4H), 6.40–6.36 (m, 2H), 5.34 (s, 1H), 4.69 (s, 1H), 1.93 (s, 3H), 1.73 (s, 3H). ^{31}P NMR (202 MHz, CDCl_3 , δ): 6.3.

Figure S5. (A) ^1H and (B) ^{31}P NMR spectra of **7** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



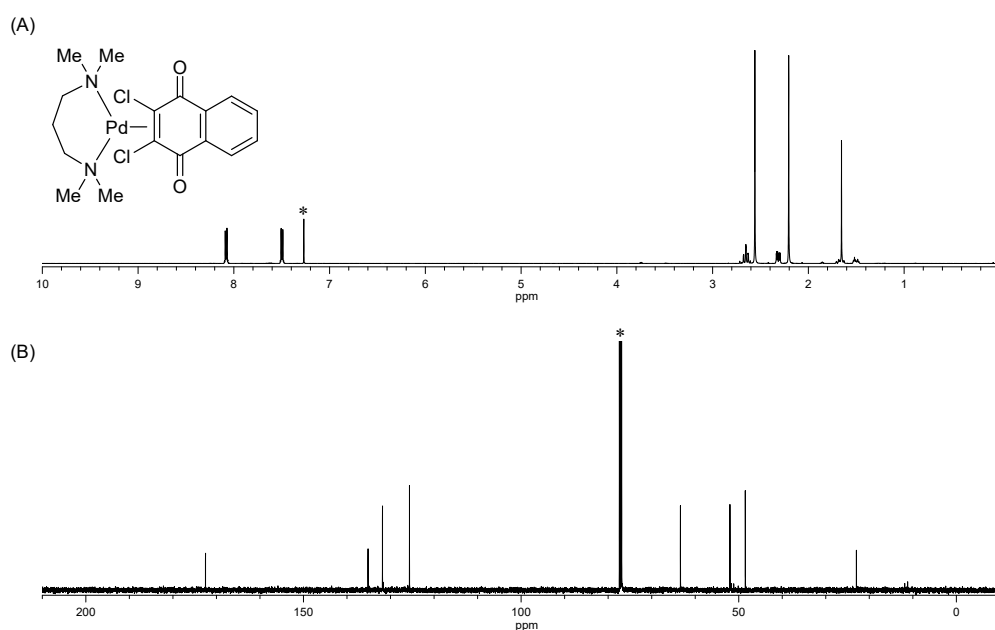
^1H NMR (500 MHz, CDCl_3 , δ): 8.07–8.05 (m, 2H, Ar-*H*), 7.48–7.46 (m, 2H, Ar-*H*), 2.60 (s, 6H, CH_3), 2.53–2.48 (m, 2H, CH_2), 2.43–2.38 (m, 2H, CH_2), 2.34 (s, 6H, CH_3). ^{13}C NMR (126 MHz, CDCl_3 , δ): 171.1, 135.1, 131.6, 125.5, 78.3, 59.6, 49.4, 48.8.

Figure S6. (A) ^1H and (B) ^{13}C NMR spectra of **8** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



^1H NMR (500 MHz, CDCl_3 , δ): 8.07–8.05 (m, 2H, Ar-*H*), 7.48–7.47 (m, 2H, Ar-*H*), 2.82 (q, $J = 7$ Hz, 4H, NCH_2CH_3), 2.68–2.61 (m, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 2.60–2.53 (m, 4H, NCH_2CH_3), 2.52–2.46 (m, 2H, $\text{NCH}_2\text{CH}_2\text{N}$), 1.33 (t, $J = 7$ Hz, 4H, NCH_2CH_3), 0.89 (t, $J = 7$ Hz, 4H, NCH_2CH_3). ^{13}C NMR (126 MHz, CDCl_3 , δ): 173.5, 134.9, 131.7, 126.0, 77.3, 52.1, 51.6, 51.1, 11.9, 11.2.

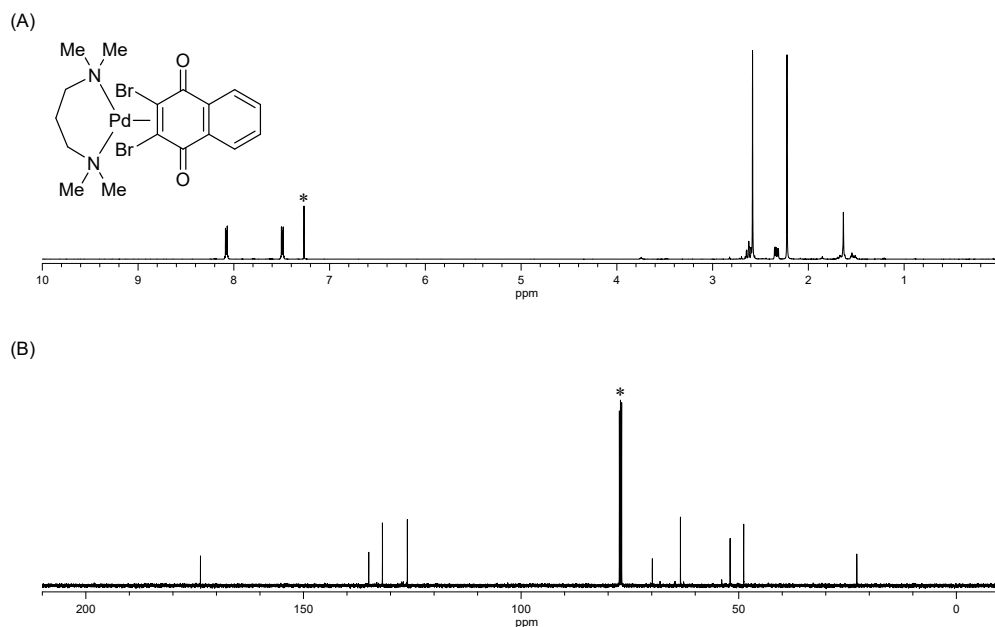
Figure S7. (A) ^1H and (B) ^{13}C NMR spectra of **9** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



^1H NMR (500 MHz, CDCl_3 , δ): 8.09–8.07 (m, 2H, Ar-*H*), 7.51–7.49 (m, 2H, Ar-*H*), 2.68–2.63 (m, 2H,

$\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.56 (s, 6H, CH_3), 2.34–2.29 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.21 (s, 6H, CH_3), 1.71–1.63 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.53–1.47 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$). ^{13}C NMR (126 MHz, CDCl_3 , δ): 172.4, 135.1, 131.8, 125.6, 77.3, 63.3, 51.9, 48.4, 22.9.

Figure S8. (A) ^1H and (B) ^{13}C NMR spectra of **10** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).



^1H NMR (500 MHz, CDCl_3 , δ): 8.10–8.06 (m, 2H, Ar-H), 7.51–7.48 (m, 2H, Ar-H), 2.66–2.60 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.58 (s, 6H, CH_3), 2.35–2.31 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 2.22 (s, 6H, CH_3), 1.67–1.62 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$), 1.56–1.51 (m, 2H, $\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}$). ^{13}C NMR (126 MHz, CDCl_3 , δ): 173.7, 135.0, 131.9, 126.1, 69.8, 63.4, 52.0, 48.9, 22.9.

Figure S9. (A) ^1H and (B) ^{13}C NMR spectra of **11** recorded in CDCl_3 at room temperature (*solvent, tetramethylsilane, or water).

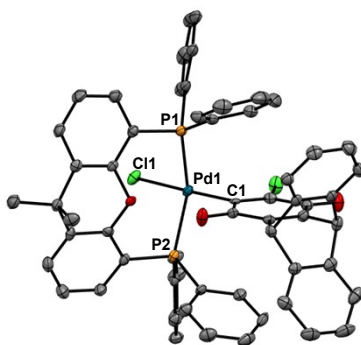


Figure S10. X-ray structure of **7** with 50% thermal ellipsoids. Hydrogen atoms and solvents are omitted for clarity. Selected bond lengths (\AA) and angles (deg): Pd1–P1 = 2.2933(9), Pd1–P2 = 2.2931(9), Pd1–C1 = 1.991(4), Pd1–C11 = 2.003(4), P1–Pd1–P2 = 152.54(4), C1–Pd1–C11 = 176.1(1), P1–Pd1–C11 = 90.7(1).

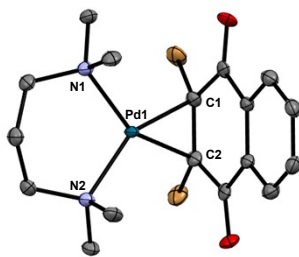


Figure S11. X-ray structure of **11** with 50% thermal ellipsoids. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): Pd1–N1 = 2.176, Pd1–N2 = 2.176, Pd1–C1 = 2.077, Pd1–C2 = 2.077, N1–Pd1–N2 = 95.0.

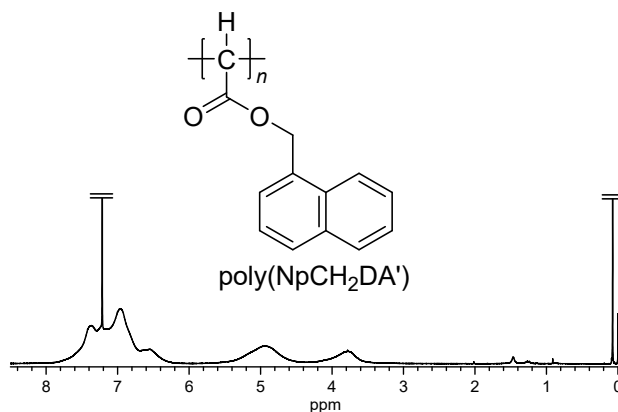


Figure S12. ^1H NMR spectrum of poly(NpCH₂DA) obtained by **8**/NaBPh₄ (run 5 in Table 3) recorded in CDCl₃ at 50 °C.

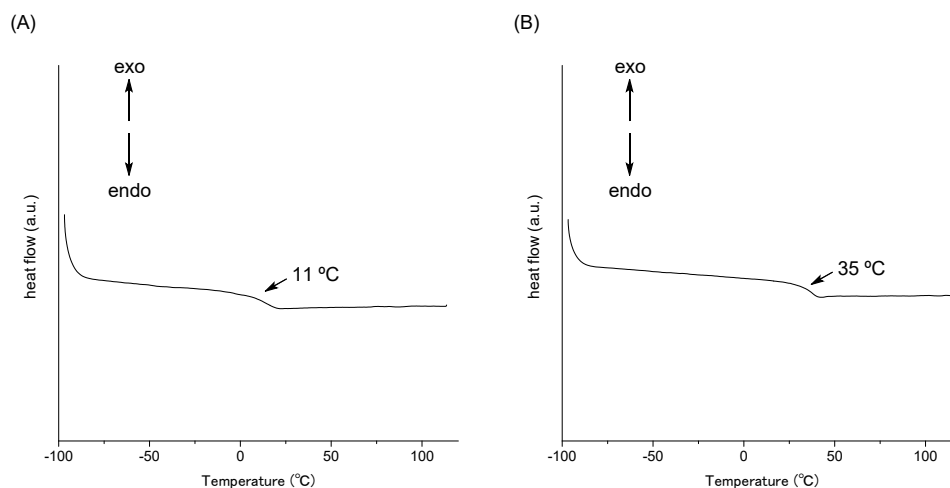


Figure S13. DSC curves of (A) polyEDA' ($M_n = 28100$, $M_w/M_n = 2.13$) and (B) polyBDA' ($M_n = 15100$, $M_w/M_n = 2.45$).

Note: DSC measurements were carried out for the obtained moderately syndiotactic polymers (**Figure S13**). Glass transition temperature (T_g) of polyEDA' obtained with the **10**/NaBPh₄ system was observed at 11 °C. The value is lower than that of a highly syndiotactic polymer obtained with a Rh(diene) initiator [22 °C ($M_w = 150$ kDa, $M_w/M_n = 3.6$)]⁸ but higher than that of an atactic polymer obtained with the (NHC)Pd/NaBPh₄ system [6 °C ($M_n = 19300$,

$M_w/M_n = 1.37$)]⁹. The same trend was observed for BDA polymers; the T_g of a moderately syndiotactic polyBDA' obtained with the **10**/NaBPh₄ system was observed at 35 °C, which is in between 14 °C for an atactic polyBDA' obtained with (NHC)Pd/NaBPh₄ system ($M_n = 22900$, $M_w/M_n = 1.60$)⁹ and 52 °C for a highly syndiotactic polyBDA' obtained with a Rh(diene) initiator ($M_w = 370$ kDa, $M_w/M_n = 2.4$).⁸ These comparisons of T_g s clearly show an effect of tacticity on the thermal behavior.

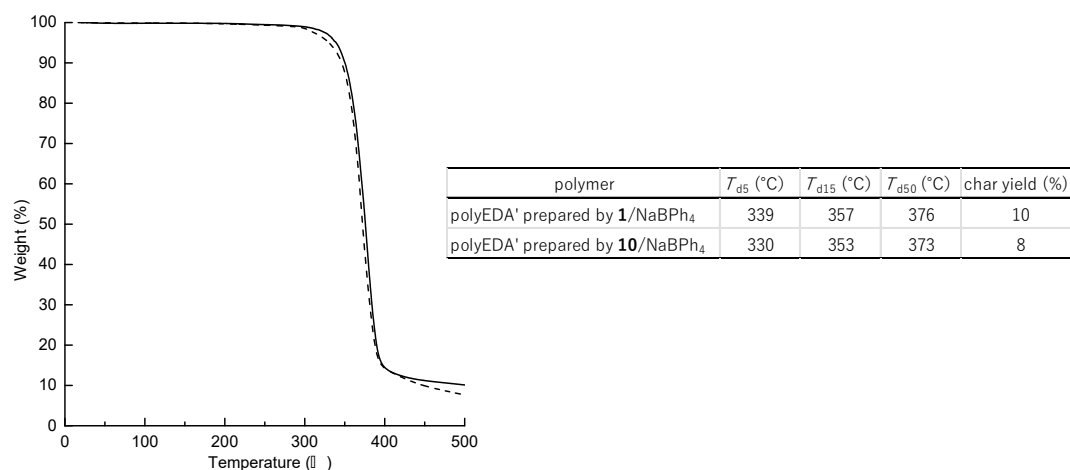


Figure S14. TGA curves of polyEDA's prepared by **1**/NaBPh₄ (solid line; $M_n = 17200$, $M_w/M_n = 1.27$) and **10**/NaBPh₄ (dashed line; $M_n = 28100$, $M_w/M_n = 2.13$).

Note: As shown in Figure S14, there was no significant difference in thermogravimetric behavior between an atactic polyEDA' prepared by **1**/NaBPh₄ and a moderately syndiotactic polyEDA' prepared by **10**/NaBPh₄. Temperatures of 15 and 50% mass loss (T_{d15} and T_{d50} , respectively) and the amounts of residue at 500 °C (char yield) for the polyEDA's were very similar as those for polymers with the same repeating unit prepared by radical polymerization of ethyl fumarate ($T_{d15} = 355\text{--}362$ °C, $T_{d50} = 385$ °C, char yield = 7.0–7.5%).¹⁰

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