t-Bu₃P-Coordinated 2-Phenylaniline-Based Palladacycle Complex as a Precatalyst for the Suzuki Cross-coupling Polymerization of Aryl Dibromides with Aryldiboronic Acids

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Supporting Information

General: ^{1}H, ^{31}P, ^{13}C NMR spectra were recorded on Varian 600 MHz NMR spectrometer. Chemical shifts were determined relative to internal $(CH_3)_4Si$ (TMS). All yields reported refer to isolated yields unless otherwise indicated. *M*n and *M*w/*M*n (PDI) value of polymers were measured with gel permeation chromatography (Waters alliance GPC 2000) using THF as eluent (1 mL/min) at 40 ^{o}C, which were calibrated with polystyrene standards. Melting points were measured on a Fisher-Johns Melting Point Apparatus and uncorrected.

1,4-Dibromo-2,5-bis(hexyloxy)benzene, 2,5-bis(hexyloxy)-1,4-phenylenediboronic acid were prepared according to the reported procedure.[1] 7-Dibromo-9,9-dioctyl-9*H*-fluorene, 2,7-dibromo-9,9-dihexyl-9*H*-fluorene, 9,9-dioctyl-2,7-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene and 9,9-dihexyl-2,7-bis(4,4',5,5'-tetramethyl-1,3,2-dioxaborolan-2-yl)-9H-fluorene are prepared in a way similar to the literature.[2] Ferrocenylmethyl alcohol was also prepared according to reported literature.[3] Complexes **1b** and **1d** were prepared by following reported method.[4] The purity of these monomers was estimated to be greater than 98% as determined by ^{1}H NMR or GC-MS. The product purity was estimated to be greater than 95% as determined by ^{1}H NMR. THF was freshly distilled from sodium/benzophenone. Unless otherwise mentioned, other solvents and reagents were purchased from commercial sources and used as received.
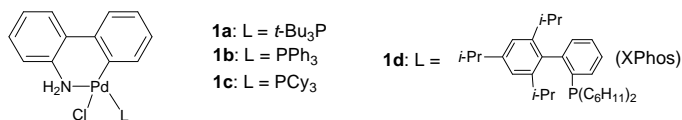

General Procedure for the Synthesis of precatalyst 1a and 1c: In a glovebox, a mixture of Pd(OAc)₂ (336 mg, 1.5 mmol) and 2-aminobiphenyl (264 mg, 1.5 mmol) in anhydrous toluene (10 mL) was heated at 60 ^{o}C under N₂ atmosphere for 30 min. After the reaction was cooled to room temperature, the toluene was removed. The remaining solid was washed with anhydrous toluene (2 x 2 mL) and then suspended in anhydrous acetone (10 mL). Lithium chloride (191 mg, 4.5 mmol) was added to the suspension and the mixture was stirred at room temperature under N₂ atmosphere for

1 h. t-Bu$_3$P or PCy$_3$ (1.4 mmol) was then added to the solution. The mixture was stirred at room temperature for 2.5 h. Removal of about 90% of the solvent under vacuum afforded yellow slurry, which was treated with methyl t-butyl ether (5 mL) and pentane (10 mL). The mixture was then placed in refrigerator for 1 h. Then, the mixture was filtered, washed with water and pentane and dried under vacuum to afford complex **1a** or **1c**.
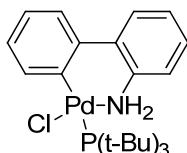

1a: Yield: 58% Yellow solid. Mp: 164.0-164.4 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.47 (dd, J = 3.6 Hz, J = 7.2 Hz, 1 H), 7.42 (d, J = 7.8 Hz, 1 H), 7.14 ~ 7.20 (m, 4 H), 7.02 (t, J = 7.2 Hz, 1 H), 6.96 (t, J = 7.2 Hz, 1 H), 5.08 (s, 1 H), 4.41 (s, 1 H), 1.31 (d, J = 12.6 Hz, 27 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 146.4, 140.1, 139.0, 138.2, 138.2, 136.1, 128.1, 126.7, 126.4, 125.0, 124.7, 119.0, 39.9, 32.6 ppm. ^{31}P NMR (121 MHz, CDCl$_3$): δ 77.79ppm. HRMS (ESI) Calcd for: C$_{24}$H$_{37}$NPPd ([M+H-HCl]$^+$) 476.1698. Found: 476.1703.
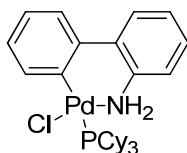

1c:[5] Yield: 63% Gray solid. Mp: 228.9-229.3 °C. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.41 (d, J = 6.6 Hz, 1 H), 7.31 (dd, J = 1.8 Hz, J = 7.2 Hz, 1 H), 7.16 ~ 7.23 (m, 4 H), 7.07 (t, J = 7.2 Hz, 1 H), 7.03 (t, J = 7.2 Hz, 1 H), 4.70 (br, 1 H), 4.61 (br, 1 H), 2.08 (q, J = 12.0 Hz, 3 H), 1.93 (d, J = 11.4 Hz, 3 H), 1.72 (s, 3 H), 1.54 ~ 1.62 (m, 9 H), 1.35 ~ 1.48 (m, 6 H), 1.11 ~ 1.19 (m, 6 H), 0.88 ~ 0.90 (m, 3 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 153.2, 140.3, 140.1, 137.5, 135.5, 127.9, 127.4, 127.2, 125.4, 125.0, 124.9, 119.9, 33.7 (d, J = 19 Hz), 30.0, 29.2, 27.6 (d, J = 9.2 Hz), 27.4 (d, J = 8.7 Hz), 26.3 ppm. ^{31}P NMR (121 MHz, CDCl$_3$): δ 42.08 ppm. HRMS (ESI) Calcd for: C$_{30}$H$_{43}$NPPd ([M+H-HCl]$^+$) 554.2168. Found: 554.2174.

General Procedure for the Suzuki cross-coupling polymerization: Under N$_2$ atmosphere, to a solution of dibromide monomer (0.101 mmol) and diboronic acid monomer (0.1 mmol) in dry THF (0.5 mL), precatalyst **1a** (0.002 mmol, 2 mmol%) was added. K$_3$PO$_4$ solution (2 M, 0.2 mL) was then added to the mixture. After stirring at 60 °C for 1 h, the mixture was poured into HCl solution (5 M, 10 mL) with stirring. The product was extracted with CH$_2$Cl$_2$ (3 x 15 mL), the combined organic layer was washed with brine and dried over Na$_2$SO$_4$. After removal of solvents under vacuum, the residue was dissolved in a small amount of THF and added slowly to methanol with stirring. The precipitation formed was collected by filtration, washed with methanol. The dissolution-precipitation process was repeated two more times to
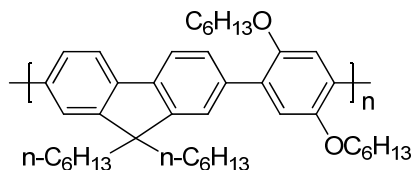
afford the final product, which was dried under vacuum for 4 h.
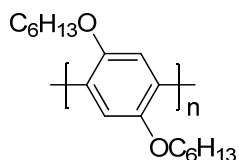
Yellow solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.09 (s, 2 H), 3.92 (s, 4 H), 1.67 ~ 1.68 (m, 4 H), 1.27 ~ 1.36 (m, 12 H), 0.87 (t, J = 6.0 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.0, 127.5, 117.2, 69.5, 31.6, 29.5, 25.7, 22.6, 14.0 ppm. GPC profile: Mn = 19 800 (PDI = 2.25).
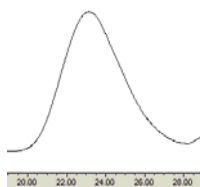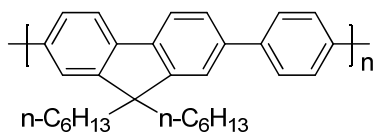

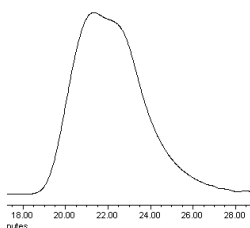The polymerization was repeated and the polymer was obtained with a Mn = 19 500 (PDI = 2.35).

Yellow solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.71 ~ 7.81 (m, 4 H), 7.58 ~ 7.63 (m, 2 H), 7.14 (s, 2 H), 3.99 (t, J = 6.0 Hz, 4 H), 2.04 (br, 4 H), 1.75 (t, J = 6.6 Hz, 4 H), 1.30 ~ 1.41 (m, 16 H), 1.05 ~ 1.21 (m, 12 H), 0.88 (t, J = 6.6 Hz, 6 H), 0.82 (t, J = 6.6 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 150.5, 150.4, 139.8, 137.0, 131.2, 127.9, 124.4, 121.5, 119.1, 116.7, 69.8, 55.0, 40.6, 31.6, 31.5, 29.9, 29.4, 25.7, 22.7, 22.6, 14.0, 14.0 ppm. GPC profile: Mn = 11 500 (PDI = 2.38).
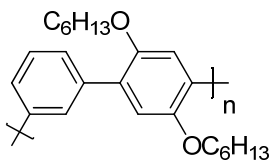
22.00   24.00   26.00   28.00
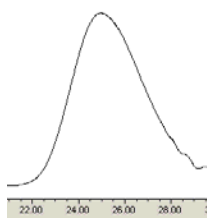
The polymerization was repeated and the polymer was obtained with a Mn = 10 800 (PDI = 2.17).

n-C$_6$H$_{13}$ n-C$_6$H$_{13}$

Brown solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.80 ~ 7.84 (m, 6 H), 7.66 ~ 7.69 (m, 4 H), 2.10 (br, 4 H), 1.10 ~ 1.16 (m, 12 H), 0.76 ~ 0.80 (m, 10 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.8, 140.7, 140.0, 139.5, 127.6, 126.2, 121.4, 119.9, 55.2, 40.6, 31.4, 29.6, 23.8, 22.5, 14.0 ppm. GPC profile: Mn = 42 000 (PDI = 2.85).


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The polymerization was repeated and the polymer was obtained with a Mn = 44 000 (PDI = 2.23).

C$_6$H$_{13}$O

OC$_6$H$_{13}$

Brown solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.85 (s, 1 H), 7.64 (d, J = 5.4 Hz, 2 H), 7.47 (t, , J = 4.8 Hz, 2 H), 7.10 (s, 2 H), 3.96 (t, J = 6.0 Hz, 4 H), 1.72 (s, 4 H), 1.24 ~ 1.37 (m, 16 H), 0.84 (s, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$, ppm): δ 150.3, 138.1, 130.8, 130.3, 128.3, 127.3, 116.4, 116.2, 69.6, 31.5, 29.4, 25.8, 22.5, 22.5, 14.0, 14.0, 14.0 ppm. GPC profile: Mn = 9 400 (PDI = 1.86).
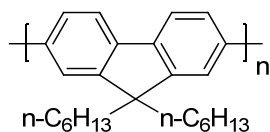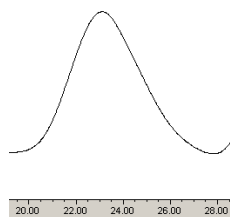
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The polymerization was repeated and the polymer was obtained with a Mn = 8 100 (PDI = 2.10).
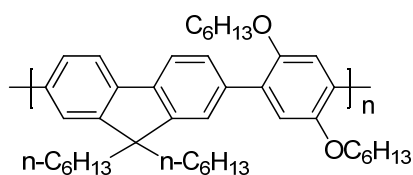
Brown solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.71 ~ 7.81 (m, 4 H), 7.58 ~ 7.63 (m, 2 H), 7.14 (s, 2 H), 3.99 (t, J = 6.0 Hz, 4 H), 2.04 (br, 4 H), 1.75 (t, J = 6.6 Hz, 4 H), 1.30 ~ 1.41 (m, 16 H), 1.05 ~ 1.21 (m, 12 H), 0.88 (t, J = 6.6 Hz, 6 H), 0.82 (t, J = 6.6 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.5, 150.4, 139.8, 137.0, 131.2, 127.9, 124.4, 121.5, 119.1, 116.7, 69.8, 55.0, 40.6, 31.6, 31.5, 29.9, 29.4, 25.7, 22.7, 22.6, 14.0, 14.0 ppm. GPC profile: Mn 20 900 (PDI = 2.52).

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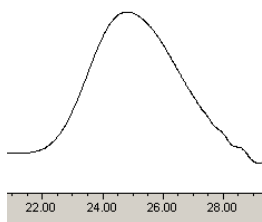
The polymerization was repeated and the polymer was obtained with a Mn = 20 500 (PDI = 2.26).

Brown solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.84 (d, J = 7.8 Hz, 2 H), 7.67 ~ 7.70 (m,

4 H), 2.12 (br, 4 H), 1.13 ~ 1.17 (m, 16 H), 0.79 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.8, 140.5, 140.0, 126.1, 121.0, 119.9, 55.4, 40.2, 31.4, 29.6, 22.5, 14.0 ppm. GPC profile: Mn 19 300 (PDI = 2.83).
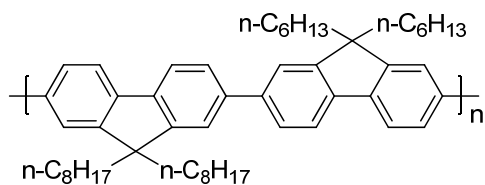

The polymerization was repeated and the polymer was obtained with a Mn = 18 900 (PDI = 3.04).
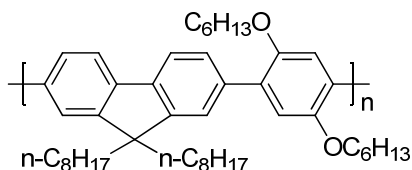

Brown solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.72 ~ 7.80 (m, 4 H), 7.58 (d, J = 6.0 Hz, 2 H), 7.13 (s, 2 H), 3.98 (t, J = 6.0 Hz, 4 H), 2.04 (br, 4 H), 1.74 (t, J = 7.2 Hz, 4 H), 1.30 ~ 1.41 (m, 16 H), 1.08 ~ 1.16 (m, 20 H), 0.88 (t, J = 7.2 Hz, 6 H), 0.78 (t, J = 7.2 Hz, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.5, 150.4, 139.8, 137.0, 131.2, 127.9, 124.4, 119.1, 116.8, 69.8, 55.0, 40.5, 31.8, 31.5, 30.3, 29.4, 29.4, 29.4, 29.1, 29.1, 25.8, 24.1, 22.6, 22.6, 14.0, 14.0 ppm. GPC profile: Mn 19 800 (PDI = 2.67).
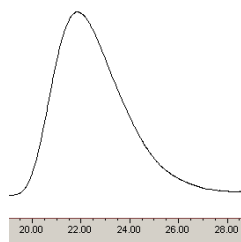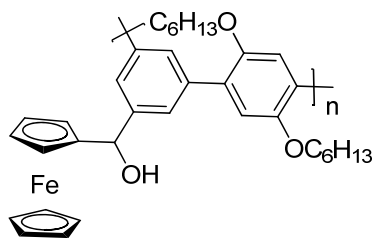

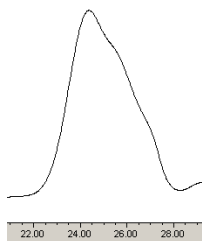The polymerization was repeated and the polymer was obtained with a Mn = 18 900 (PDI = 2.11).

Yellow solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.84 (d, J = 7.2 Hz, 4 H), 7.67 ~ 7.70 (m, 8 H), 2.12 (br, 4 H), 1.14 ~ 1.22 (m, 36 H), 0.78 ~ 0.84 (m, 20 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 152.5, 151.7, 140.5, 139.9, 139.0, 130.1, 126.1, 121.4, 121.1, 119.9, 55.3, 40.3, 40.1, 31.7, 31.4, 30.0, 29.8, 29.6, 29.2, 23.9, 23.8, 23.9, 22.6, 22.5, 14.0, 14.0 ppm. GPC profile: Mn 45 300 (PDI = 2.10).
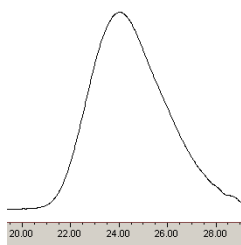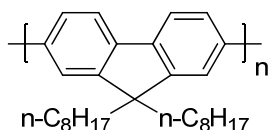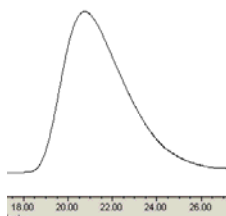

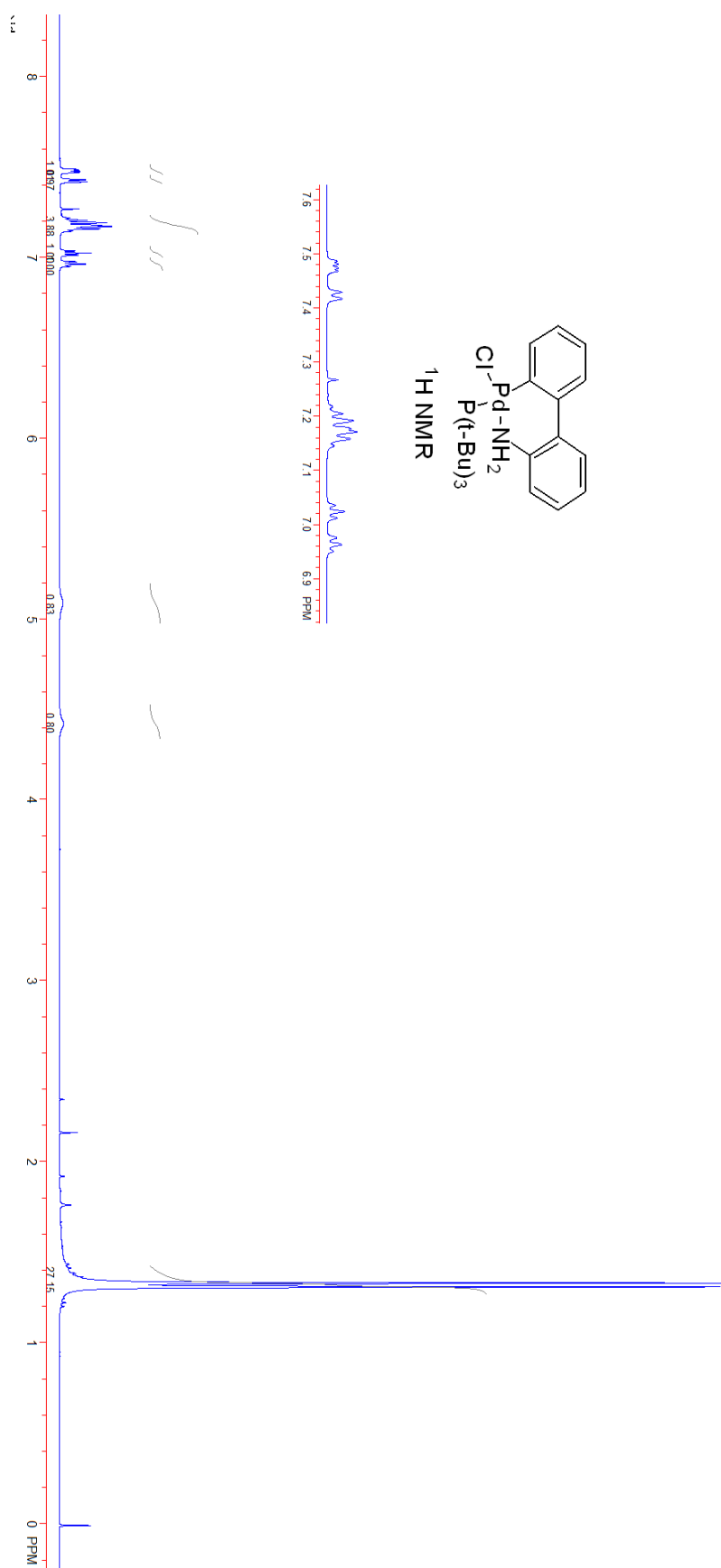
The polymerization was repeated and the polymer was obtained with a Mn = 40 700 (PDI = 2.30).

Red solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.65 ~ 7.69 (m, 3 H), 7.04 (s, 2 H), 5.57 (s, 1 H), 4.17 ~ 4.34 (m, 9 H), 3.90 (t, J = 6.0 Hz, 4 H), 2.45 (s, 1 H), 1.66 ~ 1.69 (m, 4 H), 1.22 ~ 1.33 (m, 16 H), 0.83 (s, 6 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 150.3, 142.3, 138.0, 130.7, 126.3, 116.3, 94.2, 72.4, 69.6, 68.4, 68.07, 68.0, 67.5, 66.1, 31.5, 29.4, 25.8, 22.6, 14.0 ppm. GPC profile: Mn = 7 900 (PDI = 1.69).
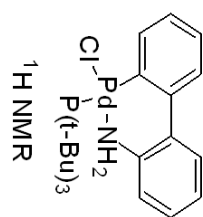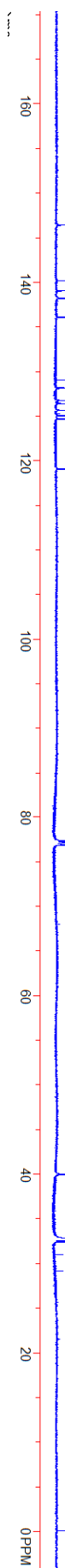
22.00 24.00 26.00 28.00

The polymerization was repeated and the polymer was obtained with a Mn = 8 400 (PDI = 1.70).

n-C$_8$H$_{17}$ n-C$_8$H$_{17}$

Yellow solid. ^{1}H NMR (600 MHz, CDCl$_3$): δ 7.84 (d, J = 7.2 Hz, 2 H), 7.67 ~ 7.70 (m, 4 H), 2.12 (br, 4 H), 1.14 ~ 1.24 (m, 24 H), 0.79 ~ 0.84 (m, 10 H) ppm. ^{13}C NMR (125 MHz, CDCl$_3$): δ 151.8, 140.4, 140.0, 126.1, 121.4, 119.9, 55.3, 40.3, 31.7, 30.0, 29.2, 24.8, 23.8, 22.6, 14.0 ppm. GPC profile: Mn = 77 600 (PDI = 2.45).
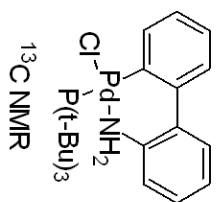

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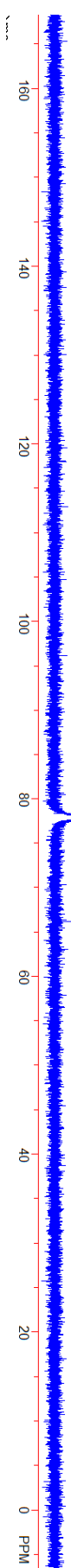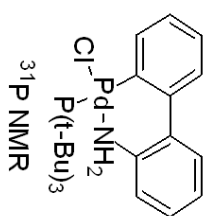The polymerization was repeated and the polymer was obtained with a Mn = 88 300 (PDI = 2.26).

References:

1. Maruyama, S.; Kawanishi, Y., *J. Mater. Chem.* **2002,** *12*, 2245-2249.
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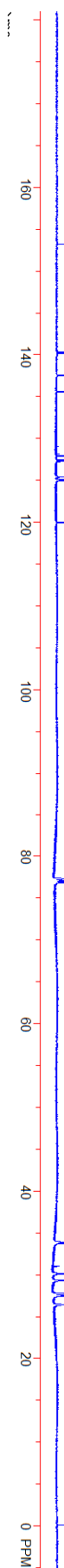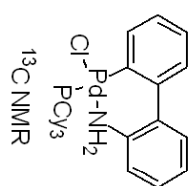6. Albert, J.; Granell, J.; Zafrilla, J.; Font-Bardia, M.; Solans, X., *J. Organomet.*
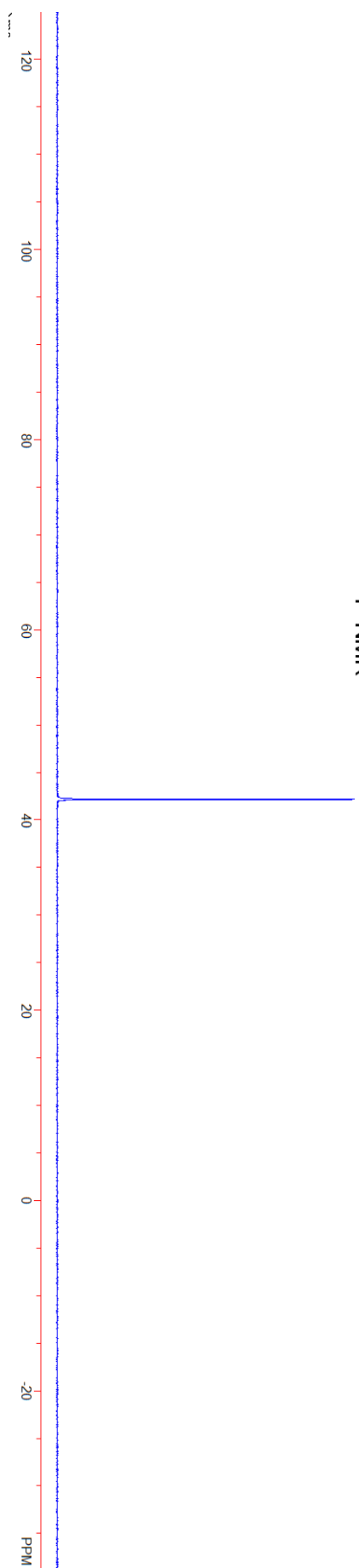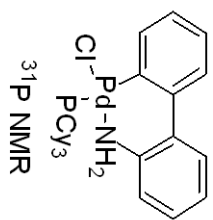
Chem. **2005,** *690*, 422-429.

^{1}H NMR

¹³C NMR

31P NMR

^{1}H NMR

^{13}C NMR

31P NMR

¹H NMR

C₆H₁₃O / OC₆H₁₃

^{13}C NMR

^{1}H NMR

^{13}C NMR

^{1}H NMR

n-C$_6$H$_{13}$ n-C$_6$H$_{13}$

^{13}C NMR

^{1}H NMR

^{13}C NMR

^{1}H NMR

n–C$_6$H$_{13}$ n–C$_6$H$_{13}$

^{13}C NMR

1H NMR

C_6H_{13}O

n-C_8H_{17} n-C_8H_{17}

OC_6H_{13}

C_6H_{13}

8   7   6   5   4   3   2   1   0 PPM

3.46 1.66 1.82 4.00 3.25 3.93 14.21 20.75 6.65.41

^{13}C NMR

^{1}H NMR

^{13}C NMR

^{1}H NMR

^{13}C NMR

^{1}H NMR

^{13}C NMR