

Electronic Supplementary Information

Activation of Pd-precatalysts by organic compounds for vinyl-addition polymerization of norbornene derivatives

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Table of Contents

1. Materials	S2
2. Characterization of polymers	S2
3. General procedures for vinyl-addition polymerization	S3
4. Synthesis of (<i>p</i> -CF ₃ C ₆ H ₄)Pd(PPh ₃) ₂ I	S4
5. Table S1 Vinyl-addition polymerization of norbornene over Pd(dba) ₂ activated by various organic compounds	S5
6. Figure S1. ¹ H NMR spectrum of vinyl-addition polynorbornene	S6
7. Figure S2. The influence of monomer concentration on the polynorbornene yield	S7
8. Figure S3. ¹ H NMR spectrum of (<i>p</i> -CF ₃ C ₆ H ₄)Pd(PPh ₃) ₂ I	S8
9. Table S2 The influence of Pd(dba) ₂ /NO ₂ C ₆ H ₄ N ₂ ⁺ BF ₄ ⁻ molar ratio on the yield and the molecular weight of polynorbornene	S8
10. Table S3 The influence of solvent nature on the polynorbornene yield	S9
11. Table S4 The influence of temperature on the polynorbornene yield	S9
12. Crystallographic data	S9
13. References	S9

Materials

Commercial norbornene, 5-ethylidene-2-norbornene (ENB, mixture of *Z*- and *E*-isomers), 5-vinyl-2-norbornene (VNB, mixture of *endo*- and *exo*-isomers), 5-norbornene-2-methanol (mixture of *endo*- and *exo*-isomers), 5-norbornene-2-carboxylic acid (mixture of *endo*- and *exo*-isomers), phenyl bromide, phenyl iodide, *p*-NO₂C₆H₄Br, *p*-NO₂C₆H₄I, *p*-MeOC₆H₄I, *p*-CF₃C₆H₄I, C₆F₅Cl, C₆F₅Br, methyl iodide, methylene iodide, benzoyl chloride, 3,5-bis(trifluoromethyl)phenylbromide, *p*-tolylboronic acid pinacol ester, tricyclohexylphosphine (PCy₃), tri-*tert*-butylphosphine (P^tBu₃), Pd(dba)₂, Pd(OAc)₂, Pd(acac)₂, PdCl₂, NaBF₄ and solvents from Sigma-Aldrich were used in this study. PhN₂⁺BF₄⁻,¹ PhN₂⁺OTf,² *p*-CF₃C₆H₄N₂⁺BF₄⁻,¹ *p*-NC-C₆H₄N₂⁺BF₄⁻,¹ *p*-MeOC₆H₄N₂⁺BF₄⁻, *p*-NO₂C₆H₄N₂⁺BF₄⁻,¹ PhOTf,³ Pd₂(dba)₃·CHCl₃,⁴ Pd(PPh₃)₄,⁵ SIPrPdPCy₃⁶ were prepared according to published procedures. The monomers (5-*n*-hexyl-2-norbornene and 5-*n*-decyl-2-norbornene) were prepared as described in the literature.⁷

Chloroform was distilled over CaH₂ and it was kept in an inert atmosphere (dried argon) with CaH₂. 1,2-Dichloroethane was dried over P₂O₅ and distilled under argon. Toluene, ENB and VNB were distilled from sodium under argon before use. 5-Norbornene-2-methanol, 5-norbornene-2-carboxylic acid, Pd(dba)₂, Pd(OAc)₂, Pd(acac)₂, PdCl₂, NaBF₄, *p*-MeOC₆H₄I, *p*-CF₃C₆H₄I, *p*-MeOC₆H₄N₂⁺BF₄⁻, P^tBu₃, PCy₃ and *p*-tolylboronic acid pinacol ester were used without additional purification. Phenyl bromide, phenyl iodide, C₆F₅Cl, C₆F₅Br, methyl iodide, methylene iodide, benzoyl chloride, 3,5-bis(trifluoromethyl)phenylbromide were purified *via* distillation under vacuum. *p*-NO₂C₆H₄Br and *p*-NO₂C₆H₄I were recrystallized from hot methanol.

All manipulations with air- and moisture-sensitive compounds were carried out under dried and purified argon using standard Schlenk and vacuum-line techniques. The monomers were stored in an inert atmosphere.

Characterization of polymers

The NMR spectra were recorded on a Bruker Avance DRX 400 spectrometer at 400.1 MHz (¹H NMR) and 100.6 MHz (¹³C NMR) in CDCl₃ solution. Chemical shifts δ are reported in parts per million (ppm) relative to reference (residual CHCl₃ signal). ³¹P NMR spectra were obtained on a Bruker Avance DRX 400 (at 162 MHz) using H₃PO₄ (85% solution in water) sealed in a thin tube as an external reference.

Gel-permeation chromatography (GPC) analysis of the polymers was performed on a Waters system with a differential refractometer (Chromatopack Microgel-5; eluent, chloroform; flow rate, 1ml/min). The molecular weights and polydispersity were calculated by a standard procedure relative to monodispersed polystyrene standards.

General procedures for vinyl-addition polymerization

Addition polymerization of norbornene

$5.3 \cdot 10^{-3}$ M solution of catalyst was prepared by mixing Pd(dba)₂ (7.1 mg, $1.2 \cdot 10^{-2}$ mmol) and *p*-NO₂C₆H₄N₂⁺BF₄⁻ (8.6 mg, $3.6 \cdot 10^{-2}$ mmol) in 2.34 mL of chloroform in glass vial charged with magnetic stirrer an inert atmosphere. The mixture was allowed to stir for 5 min. 0.307 mL of 70.2 wt.% solution of norbornene in toluene (2.1 mmol) was mixed with 0.355 mL of chloroform in glass vial charged with magnetic stirrer. 0.4 mL of $5.3 \cdot 10^{-3}$ M solution of catalyst was added with stirring in air media. The reaction mixture was allowed to stir for 15 minutes at 25°C and was then precipitated into ethanol. The ethanol was removed, then the polymer was washed with 3×3 mL of ethanol and dried in vacuum. The polymer was reprecipitated twice from its chloroform solution into ethanol and dried in vacuum at 60 °C to a constant weight.

¹H NMR (CDCl₃, δ, ppm): 2.50-0.70 m (10H).

Vinyl-addition polymerization of 5-*n*-hexylnorbornene

$3.2 \cdot 10^{-2}$ M solution of Pd(dba)₂ (2.6 mg, $4 \cdot 10^{-3}$ mmol) and *p*-NO₂C₆H₄N₂⁺BF₄⁻ (3.2 mg, $1.2 \cdot 10^{-4}$ mmol) in 0.14 ml of chloroform was prepared in glass vial charged with magnetic stirrer an inert atmosphere and stirred for 5 min. 5-*n*-Hexylnorbornene (0.20 g, 1.1 mmol) was then added in air media and the reaction mixture was stirred at 25°C. After 30 minutes the reaction mixture was precipitated into ethanol. The ethanol was removed, then the polymer was washed with 3×3 mL of ethanol and dried in vacuum. The polymer was reprecipitated twice from its chloroform solution into ethanol and dried in vacuum at 60 °C to a constant weight.

¹H NMR (CDCl₃, δ, ppm): 2.70-0.40 m (22H).

Vinyl-addition poly(5-*n*-decyl-2-norbornene)

¹H NMR (C₆D₆, δ, ppm): 2.55-0.45 m (30H).

Vinyl-addition poly(5-ethylidene-2-norbornene)

¹H NMR (CDCl₃, δ, ppm): 6.00-4.9 m (1H), 2.80-0.69 m (12H).

Vinyl-addition poly(5-vinyl-2-norbornene)

¹H NMR (CDCl₃, δ, ppm): 6.18-4.7 m (olefinic protons), 2.60-0.75 m (carbocyclic protons).

Vinyl-addition polymerization of 5-norbornene-2-carboxylic acid

$2.8 \cdot 10^{-2}$ M solution of $\text{Pd}(\text{dba})_2$ (12 mg, 0.02 mmol) and $p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ (16 mg, 0.06 mmol) in 0.75 mL of chloroform was prepared in glass vial charged with magnetic stirrer an inert atmosphere and stirred for 5 min. 5-Norbornene-2-carboxylic acid (0.20 g, 1.4 mmol) was dissolved in 0.1 mL of chloroform in glass vial charged with magnetic stirrer in air media. 0.2 mL of $2.8 \cdot 10^{-2}$ M solution of catalyst was then added with stirring. After 24 hours reaction mixture was precipitated into hexane. The ethanol was removed, then the polymer was washed with 3×3 mL of hexane and dried in vacuum. The polymer was reprecipitated twice from its THF solution into hexane and dried in vacuum at 60°C to a constant weight. ^1H NMR spectrum of the polymer corresponded to the earlier published one.⁸

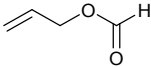
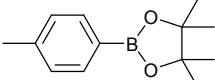
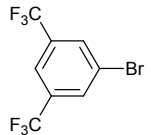
Synthesis of $(p\text{-CF}_3\text{C}_6\text{H}_4)\text{Pd}(\text{PPh}_3)_2\text{I}$

The reaction was carried out under argon atmosphere in a glove box. $\text{Pd}(\text{PPh}_3)_4$ (0.10 g, 0.08 mmol, 1 eq.) was stirred in 2 mL of dry THF in a 4 ml glass vial. After 5 minutes, $p\text{-CF}_3\text{C}_6\text{H}_4\text{I}$ (0.22 g, 0.8 mmol, 10 eq.) was added and the solution was stirred for 6 hours. The solvent was removed under reduced pressure. The residue was washed with 2×2 ml of dry diethyl ether and 2×2 ml of dry methanol to remove triphenylphosphine. After that, the product was dissolved in 0.3 ml of dry CH_2Cl_2 . The solution was layered with 3 ml of dry methanol and was kept overnight at -20°C . The desired complex crystallized as yellowish crystals and the solution was removed. Yield: 30 mg (45%).

^1H NMR (CDCl_3 , δ , ppm): 7.53-7.48 m (12 H), 7.34-7.22 m (18 H), 6.71 d (2H), 6.39 d (2H).

^{31}P NMR (CDCl_3 , δ , ppm): 23.59.

Table S1 Vinyl-addition polymerization of norbornene over Pd(dba)₂ activated by various organic compounds.^a

Cocatalyst	NB/Pd molar ratio	Pd/Cocatalyst molar ratio	Yield, %	M _w ×10 ⁻³	M _n ×10 ⁻³	M _w /M _n ^b
CH ₃ I	100/1	1/5	0	-	-	-
CH ₂ I ₂	100/1	1/5	0	-	-	-
	100/1	1/5	0	-	-	-
	100/1	1/5	0	-	-	-
C ₆ F ₅ Cl	100/1	1/5	0	-	-	-
PhC(O)Cl	100/1	1/5	11	-	-	-
PhBr	100/1	1/5	1	-	-	-
C ₆ F ₅ Br	100/1	1/5	5	-	-	-
C ₆ F ₅ Br/P ^t Bu ₃	100/1	1/3 ^c	20	5.1	2.3	2.2
<i>p</i> -NO ₂ C ₆ H ₄ Br	100/1	1/5	11	-	-	-
	100/1	1/50	4	-	-	-
	100/1	1/5	17	-	-	-
	100/1	1/5	36	8.8	4.9	1.8
PhI	250/1	1/5	12	7.0	3.5	2.0
	500/1	1/5	3	4.5	2.0	2.2
	100/1	1/3 ^d	4	-	-	-
<i>p</i> -MeOC ₆ H ₄ I	300/1	1/3 ^d	traces	-	-	-
	100/1	1/3 ^d	22	3.4	1.4	2.4
<i>p</i> -CF ₃ C ₆ H ₄ I	300/1	1/3 ^d	3	2.3	1.1	2.1
PhOTf	250/1	1/3 ^e	5	-	-	-
<i>p</i> -MeOC ₆ H ₄ N ₂ ⁺ BF ₄ ⁻	1000/1	f	0	-	-	-

^aThe polymerization conditions: 25°C, 24 h, solvent – toluene, [NB] – 6.4 M, in argon. ^bMolecular weights and PDI were determined by GPC according to polystyrene standards. ^cPd/P^tBu₃ molar ratio was 1/2. ^d[NB] – 3.5 M, the reaction time – 2 h. ^e[NB] – 2 M, the solvent – chloroform. ^f[NB] – 2.0 M, the reaction time – 2 h, the solvent – chloroform.

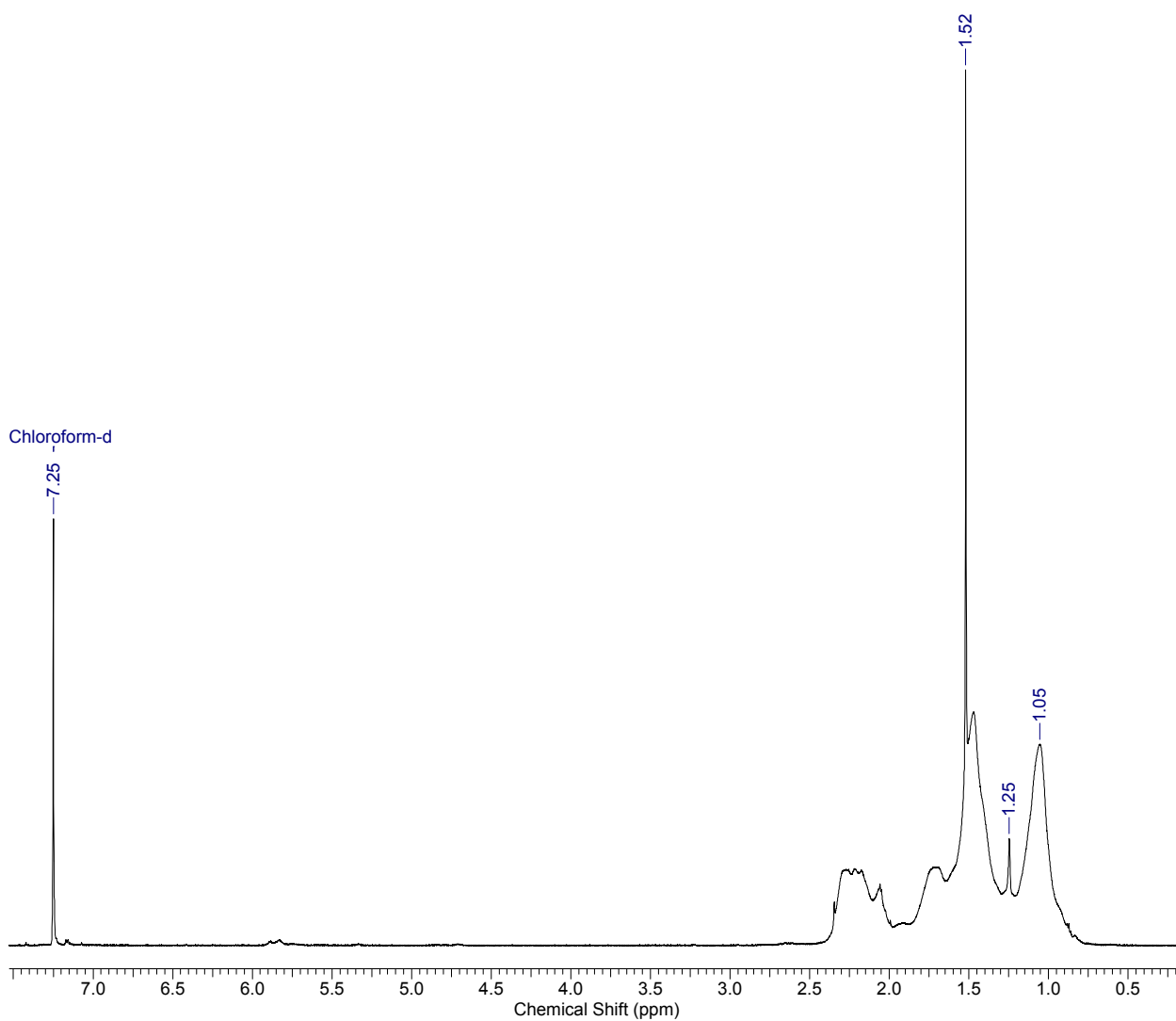


Figure S1. ^1H NMR spectrum of vinyl-addition polynorbornene prepared using $\text{Pd}(\text{dba})_2/p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ system (CDCl_3 , molar ratio norbornene/ $\text{Pd}/p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^- = 1000/1/3$, $[\text{NB}] = 2.0 \text{ M}$, reaction time – 25 minutes).

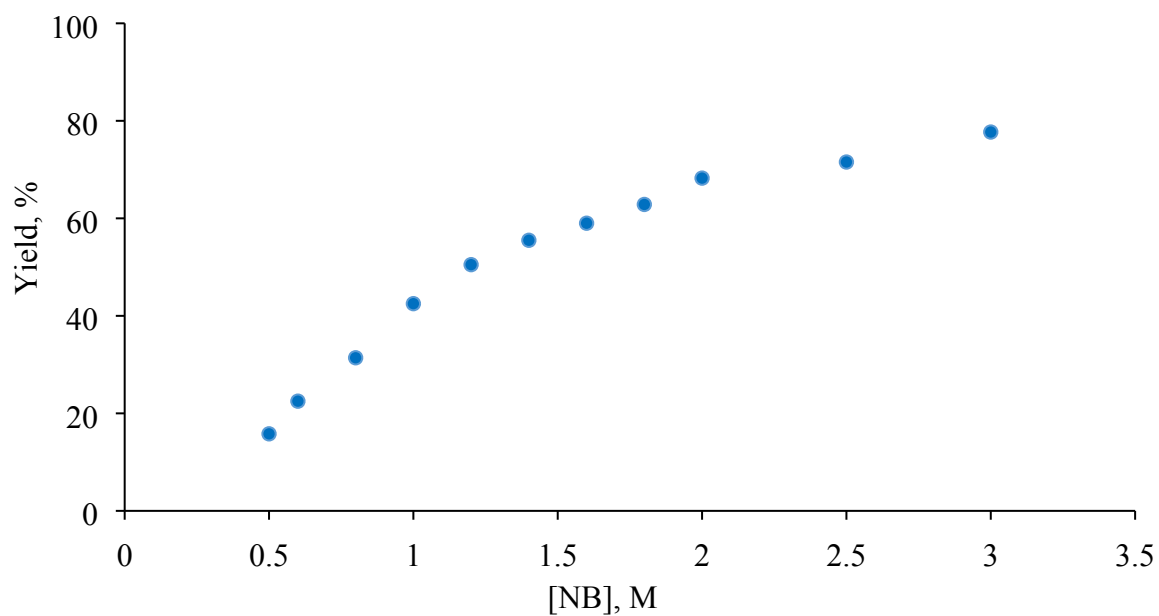


Figure S2. The influence of monomer concentration on the polynorbornene yield (catalyst – $\text{Pd}(\text{dba})_2/p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$; monomer/Pd molar ratio = 1000/1; molar ratio of $\text{Pd}(\text{dba})_2/p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^- = 1/3$; the solvent – chloroform; the reaction time – 15 min, the reaction temperature – 25°C, in air).

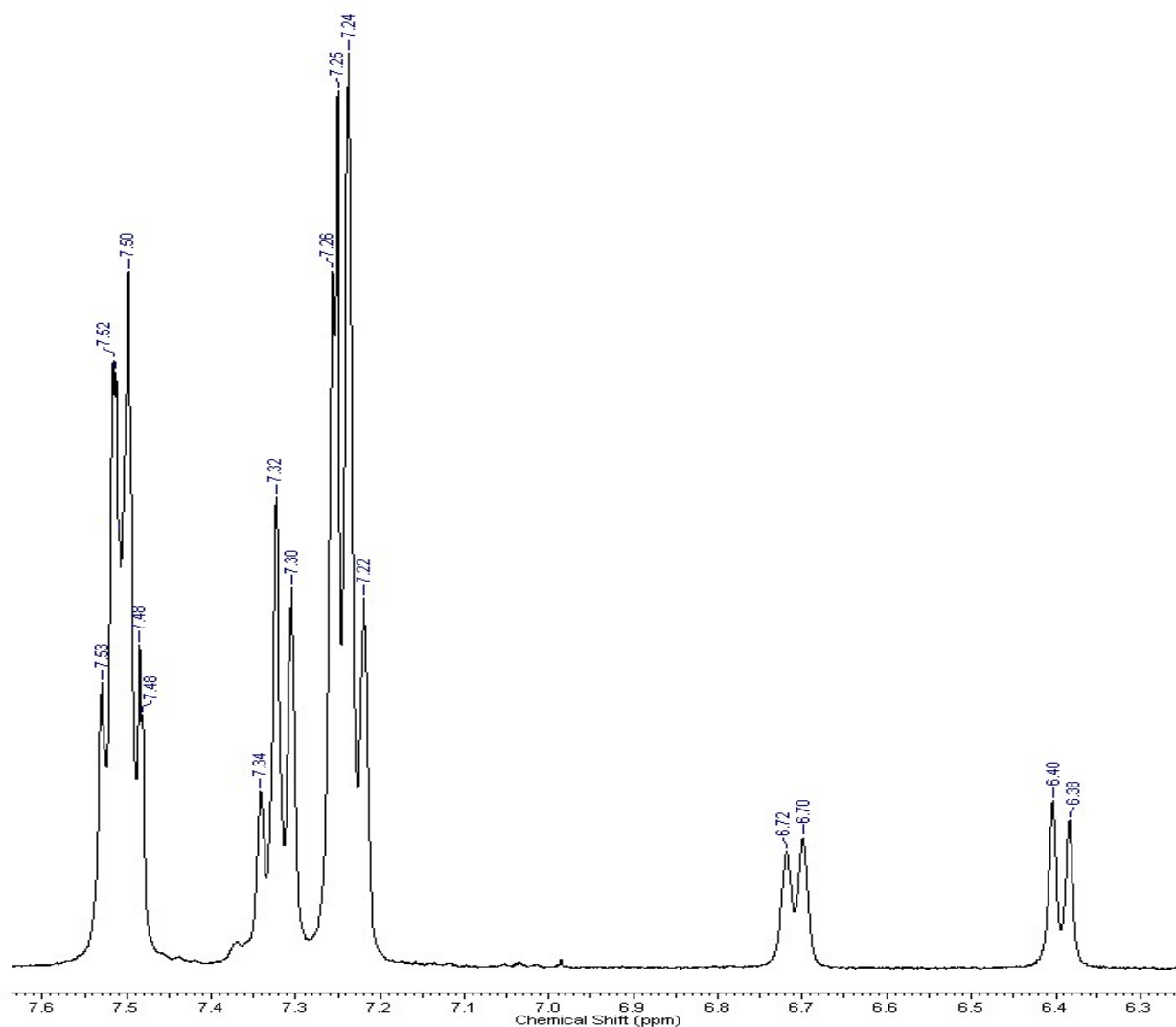


Figure S3. ^1H NMR spectrum of $(p\text{-CF}_3\text{C}_6\text{H}_4)\text{Pd}(\text{PPh}_3)_2\text{I}$ (CDCl_3).

Table S2 The influence of $\text{Pd}(\text{dba})_2/p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$ molar ratio on the yield and the molecular weight of polynorbornene (molar ratio of NB/Pd = 1000/1; $[\text{NB}] = 2 \text{ M}$; the solvent – chloroform, the reaction time – 25 min, the reaction temperature – 25°C , in air).

$\text{Pd}(\text{dba})_2/p\text{-NO}_2\text{C}_6\text{H}_4\text{N}_2^+\text{BF}_4^-$	Yield, %	$M_w \times 10^{-3}$	$M_n \times 10^{-3}$	M_w/M_n
1/1	86	58	42	1.4
1/3	87	59	43	1.4
1/3	65 ^a	44	26	1.7
1/3	60 ^b	55	31	1.8
1/5	90	47	32	1.5

^aThe reaction time was 15 min; the solvent was dry chloroform.

^bThe reaction time was 15 min; the solvent was reagent grade chloroform.

Table S3 The influence of solvent nature on the polynorbornene yield (catalyst - Pd(dba)₂/*p*-NO₂C₆H₄N₂⁺BF₄⁻; molar ratio of Pd(dba)₂/*p*-NO₂C₆H₄N₂⁺BF₄⁻ = 1/3; NB/Pd molar ratio = 2000/1; [NB] = 2 M; the solvent – chloroform, the reaction time – 2 h, in air).

Solvent	Yield, %	M _w × 10 ⁻³	M _n × 10 ⁻³	M _w /M _n
Toluene	2	3.7	1.9	2.0
1,2-Dichloroethane	9	23	18	1.3

Table S4 The influence of temperature on the polynorbornene yield (catalyst - Pd(dba)₂/*p*-NO₂C₆H₄N₂⁺BF₄⁻; molar ratio of Pd(dba)₂/*p*-NO₂C₆H₄N₂⁺BF₄⁻ = 1/3; NB/Pd molar ratio = 3000/1; [NB] = 2 M; the solvent – chloroform, the reaction time – 2 h, in air).

Reaction temperature, °C	Yield, %	M _w × 10 ⁻³	M _n × 10 ⁻³	M _w /M _n
25	44	62	48	1.3
45	7	41	5.7	7.2
60	3	33	6.6	5.0

Crystallographic data

Crystals of (*p*-CF₃C₆H₄)Pd(PPh₃)₂I (C₄₃H₃₄F₃IP₂Pd, M = 902.94) are monoclinic, space group C2/c, at 120 K: a = 25.1867(15), b = 13.4727(8), c = 11.4702(7) Å, β = 111.6700(10)°, V = 3617.1(4) Å³, Z = 4, d_{calc} = 1.658 g*cm⁻³, μ (MoKα) = 15.02 cm⁻¹, F(000) = 1792. Intensities of 23605 reflections were measured with a Bruker APEX2 DUO CCD diffractometer [μ (MoKα) = 0.71073 Å⁻¹, ω-scans, 2θ < 60°]; 5526 independent reflections [Rint 0.0772] were used in further refinement. Using Olex2,⁹ the structure was solved with the ShelXT¹⁰ structure solution program using Intrinsic Phasing and refined with the XL¹⁰ refinement package using Least-Squares minimization. Positions of hydrogen atoms were calculated and they were refined in the isotropic approximation within the riding model. The refinement converged to wR2 = 0.0862 and GOF = 1.006 for all the independent reflections (R1 = 0.0390 was calculated against F for 4028 observed reflections with I > 2σ (I)). CCDC 2068310 contains the supplementary crystallographic information for (*p*-CF₃C₆H₄)Pd(PPh₃)₂I.

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