Supporting Information

One-by-One Hydrogenation, Cross-Coupling Reaction, and Knoevenagel Condensations Catalyzed by PdCl₂ and Downstream Palladium Residue

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1. General remarks

AP-grade methyl acrylate, butyl acrylate, methyl methacrylate, ethyl acrylate, 2,2,2-trifluorethyl methacrylate, acrylic acid 2-hydroxyethyl ester, 2-hydroxyethyl methacrylate, 2-hydroxypropyl methylacrylate, allyl methylacrylate, Co(OAc)$_2$, TsOH, and chlorofrom were used as received. The molecular weight of PMHS was about 8684 g/mol. $^1$H NMR spectra were recorded on a Bruker AM-400 instrument in CDCl$_3$ without TMS. Attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy was performed on VERTEX70 IR (Bruker). The data were collected over 32 scans with a resolution of 4 cm$^{-1}$ at room temperature. The glass transition temperature ($T_g$) of the polymers were determined by differential scanning calorimetry (DSC) using Q100 (TA) at a heating rate of 10°C min$^{-1}$ under nitrogen atmosphere. Data were collected from the second scan curves. Thermogravimetric analysis (TGA) was performed on a TG209C instrument (Netzsch) under nitrogen atmosphere in a temperature range of 50-700°C at a heating rate of 10°C min$^{-1}$. The morphology of the polymer fracture surface was characterized by scanning electron micrograph (SEM, Hitachi S3000N). The samples were frozen in liquid nitrogen and snapped immediately. Transmission electron microscopy (TEM) was carried out with the phosphotungstic acid staining method on a Hitachi H-7650 transmission electron microscope.

2. Synthesis of PMHS/PA semi-IPN material

In a typical reaction, a PMHS/PEA semi-IPN was prepared as follows: ethyl acrylate (1.07 g), PMHS (2.01 g), TsOH (0.0184 g) and Co(OAc)$_2$ (0.026 g) were mixed in a reactor and stirred for 24 h at 70 °C. The resulting mixture was washed with the distilled water and dried for 24 h at 60 °C under vacuum. The PMHS-based semi-interpenetrating networks (PMHSIPN) is a novel organosilicon material and the research work about the synthesis of PMHSIPN will be reported elsewhere in the future.
3. A typical procedure for the reduction of ketones and benzylic alcohols to corresponding alkanes

Under nitrogen atmosphere, aromatic ketones (1mmol) was added to a dry tube containing PdCl₂ (5mol% or 10mol%), SPINs of PMHS/PEA (0.2mL: 5eq, calculated on the Si-H hydrogen content) and methanol 2 mL. the mixture was stirring at 40 °C for 24 hours. After the completion of the reaction, the product was dissolve in n-hexane, the reaction course was monitored by GC-MS or TLC. The combined organic layers were dried (Na₂SO₄), concentrated in vacuo, and purified by column chromatography on silica gel to gain the pure product.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple:

After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol and hexane.

All the products are known compounds and confirmed by GC-MS, NMR, and IR.[1]

4. General Procedure of the palladium-catalyzed Suzuki reaction with aryl bromides and arylboronic acids

A mixture of aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), recovery palladium catalyst residue (A) of the C-O Hydrogenolysis reaction (0.1544g, PdCl₂: 5mol%), K₂CO₃ (1 mmol) was stirred in ethanol (2 mL) at room temperature in air for the indicated time (18h). The reaction course was monitored by GC-MS or TLC. After the completion of the reaction, the mixture was quenched by brine, and extracted with n-hexane (4×10 mL). The combined organic phase was dried by anhydrous MgSO₄, concentrated under vacuum. The product was purified by column chromatography on silica gel.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple:
After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol, water, and hexane.

All the products are known compounds and confirmed by GC-MS, NMR, and IR. For example:

**6a**

![Image of compound 6a]

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.60$ (d, J = 1.6 Hz, 1H) ; 7.57 (d, J = 2.0 Hz, 2H) ; 7.55 (t, J = 3.2 Hz, 1H) ; 7.44 (m, 2H) ; 7.33 (t, J = 7.2 Hz, 1H) ; 7.01 (d, J = 8.8 Hz, 2H) , 3.87 (s, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 159.21, 140.88, 132.28, 128.76, 128.19, 126.78, 115.78, 114.27, 55.38.

**6b**

![Image of compound 6b]

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.51$ (m, 4H) ; 7.39 (d, J = 9.2 Hz, 1H) ; 6.98 (d, J = 8.8 Hz, 2H) ; 6.80 (d, J = 9.2 Hz, 1H) ; 3.86 (s, 3H) ; 1.38 (s, 9H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 158.97, 149.63, 137.96, 133.66, 132.26, 128.02, 126.39, 125.68, 115.76, 114.18, 55.35, 34.51, 31.98, 29.75, 22.74, 14.16.

**6c**

![Image of compound 6c]

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 8.03$ (d, J = 8.4 Hz, 2H) ; 7.69 (d, J = 8.4 Hz, 2H) ; 7.59 (d, J = 8.4 Hz, 2H) ; 7.51 (d, J = 8.4 Hz, 2H) ; 2.64 (s, 3H) ; 1.38 (s, 9H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 197.76, 151.48, 145.65, 136.94, 135.66, 128.93, 127.08, 126.95, 125.96, 34.67, 31.35, 26.66.

**6d**

![Image of compound 6d]
$^1$H-NMR (400 MHz, CDCl$_3$) : δ = 7.71 (d, J = 8.0 Hz, 2H) ; 7.66 (t, J = 6.8 Hz, 2H) ; 7.59 (d, J = 8.0 Hz, 2H); 7.54 (t, J = 7.6 Hz, 2H); 7.43 (t, J = 7.6 Hz, 1H); 1.49 (d, J = 1.6 Hz, 9H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 150.34, 141.10, 138.45, 128.81, 127.14, 127.09, 126.91, 125.82, 125.75, 34.64, 31.52.

6e

$^1$H-NMR (400 MHz, CDCl$_3$) : δ = 7.96 (m, 2H); 7.91 (d, J = 8.0 Hz, 1H) ; 7.62 (m, 6H), 7.48 (d, J = 6.8 Hz, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz): 140.85, 140.35, 130.15, 128.33, 127.70, 127.30, 127.0, 126.10, 125.83, 125.45.

6f

$^1$H-NMR (400 MHz, CDCl$_3$) : δ = 8.04 (d, J = 8.4 Hz, 2H); 7.69 (d, J = 8.4 Hz, 2H); 7.63 (d, J = 7.2 Hz, 2H); 7.48 (t, J = 7.6 Hz, 2H); 7.41 (t, J = 6.8 Hz, 1H); 2.64 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 197.74, 145.79, 139.89, 135.90, 128.99, 128.95, 128.27, 127.29, 127.24, 26.68.

6g

$^1$H-NMR (400 MHz, CDCl$_3$) : δ = 7.70 (m, 4H) ; 7.54 (m, 4H) ; 1.38 (s, 9H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 151.99, 145.52, 136.23, 132.58, 127.57, 126.92, 126.13, 119.06, 110.61, 34.72, 31.32.

6h
$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.81$ (d, J = 8.0 Hz, 1H) ; 7.63 (m, 5H) ; 7.47 (m, 2H); 3.17 (m, 2H); 2.69 (m, 2H); $^1$C-NMR (CDCl$_3$, 100 MHz) : 206.63, 155.88, 147.71, 140.23, 128.98, 128.35, 127.50, 126.79, 125.17, 124.09, 36.56, 25.91.

6i

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.81$ (d, J = 8.0 Hz, 1H) ; 7.67 (s, 1H) ; 7.59 (t, J = 8.4 Hz, 3H); 7.50 (d, J = 8.0 Hz, 2H) ; 3.19 (t, J = 6.4 Hz, 2H) ; 2.73 (q, J = 6.0 Hz, 2H); 1.37 (s, 9H); $^1$C-NMR (CDCl$_3$, 100 MHz) : 206.65, 155.89, 151.61, 147.58, 137.26, 135.79, 127.16, 126.62, 125.96, 124.89, 124.07, 36.56, 34.69, 31.34, 25.92.

6j

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.76$ (d, J = 8.0 Hz, 1H) ; 7.70 (s, 1H) ; 7.63 (d, J = 8.0 Hz, 1H) ; 7.45 (dd, J = 2.4 Hz, 1H) ; 7.39 (dd, J = 4.0 Hz, 1H) ; 7.13 (m, 1H) ; 3.17 (t, J = 6.8 Hz, 2H) ; 2.73 (m, 2H) ; $^1$C-NMR (CDCl$_3$, 100 MHz) : 206.18, 156.07, 143.16, 140.38, 135.98, 128.45, 126.71, 125.22, 124.95, 124.32, 123.33, 36.49, 25.83.

6k

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.39$ (m, 4H) ; 6.80 (m, 4H) ; 3.80 (s, 6H) ; $^1$C-NMR (CDCl$_3$, 100 MHz) : 158.71, 132.26, 115.74, 112.83, 55.46.

6l
1H-NMR (400 MHz, CDCl3) : δ = 7.98 (d, J = 8.4 Hz, 2H) ; 7.71 (dd, J = 5.2 Hz, 2H) ; 7.45 (dd, J = 2.8 Hz, 1H) ; 7.38 (dd, J = 4.0 Hz, 1H); 7.13 (q, J = 4.0 Hz, 1H) ; 2.62 (s, 3H); 13C-NMR (CDCl3, 100 MHz) : 197.36, 142.96, 138.80, 135.76, 131.92, 129.87, 129.15, 128.40, 126.50, 125.69, 124.64, 26.63.

5. General Procedure of the Palladium-catalyzed Sonogashira reaction of aryl iodide with aryl alkyne

A mixture of aryl iodide (0.5 mmol), aryl alkyne (0.55 mmol), recovery palladium catalyst residue (B catalyst) of the C-O Hydrogenolysis reaction (0.1544g, PdCl2: 5 mol%), K2CO3 (1 mmol), PhCl (10mol%) was stirred in ethanol (2 mL) at room temperature in air for the indicated time (18h). And the reaction course was monitored by GC-MS or TLC. After the completion of the reaction, the mixture was quenched by brine, extracted with n-hexane (4×10 mL). The combined organic phase was dried by anhydrous MgSO4, concentrated under vacuum. The product was purified by column chromatography on silica gel.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple:

After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol, water, and hexane.

All the products 9 are known compounds and confirmed by GC-MS, NMR, and IR. For example:

9a

\[ \text{Cl} \quad \text{CH} \quad \text{Cl} \]

1H-NMR (400 MHz, CDCl3) : δ = 7.46 (d, J = 8.4 Hz, 4H) ; 7.23 (d, J = 8.4 Hz, 4H).

9b
$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.43$ (t, $J = 8.4$ Hz, 4H) ; 7.31 (d, $J = 8.4$ Hz, 2H) ; 7.16(d, $J = 7.6$ Hz, 2H) ; 2.37 (s, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 134.54, 132.82, 131.74, 130.74, 129.18, 128.89, 128.78, 128.55, 128.40, 127.71, 121.45, 89.20, 29.75.

9c

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.44$ (q, $J = 8.4$ Hz, 4H) ; 7.31 (d, $J = 7.6$ Hz, 2H) ; 6.88 (d, $J = 8.4$ Hz, 2H) ; 3.83 (s, 2H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 159.81, 133.89, 133.10, 132.67, 128.67, 122.16, 115.04, 114.08, 90.40, 87.03, 55.34.

9d

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.52$ (q, $J = 3.6$ Hz, 2H) ; 7.45 (d, $J = 8.4$ Hz, 2H) ; 7.33 (q, $J = 4.0$Hz, 4H) ; 7.30 (s 1H).

9e

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.44$ (q, $J = 8.4$ Hz, 4H) ; 7.31 (d, $J = 7.6$ Hz, 2H) ; 6.878 (d, $J = 8.4$ Hz, 2H) ; 3.83 (s, 2H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 159.81, 133.89, 133.10, 132.67, 128.67, 122.16, 115.04, 114.08, 90.40, 87.03, 55.34.

9f

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta = 7.49$ (q, $J = 8.0$ Hz, 4H) ; 7.32 (d, $J = 7.2$ Hz, 2H) ; 6.874 (d, $J = 8.8$ Hz, 2H) ; 3.82 (s, 3H) ; 1.26 (s, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) :
159.64, 133.07, 131.48, 128.34, 123.62, 115.41, 114.03, 89.40, 88.10, 77.06, 70.75, 55.34.

9g

\[
\text{MeO} - \text{C} = \text{C} - \text{C} = \text{C} - \text{Me} \text{MeO}
\]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) : \(\delta = 7.45 \text{ (d, } J = 9.2 \text{ Hz, } 4\text{H)} \); \(6.87 \text{ (d, } J = 8.4 \text{ Hz, } 4\text{H)} \); 3.82 (s, 6H); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) : 159.42, 132.91, 115.75, 114.0, 88.0, 55.31, 29.77.

9h

\[
\text{MeO} - \text{C} = \text{C} - \text{C} = \text{C}
\]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) : \(\delta = 7.51 \text{ (dd, } J = 8.0 \text{ Hz, } 2\text{H)} \); \(7.47 \text{ (d, } J = 8.8 \text{ Hz, } 2\text{H)} \); \(7.32 \text{ (m, } 3\text{H)} \); \(6.87 \text{ (d, } J = 8.8 \text{ Hz, } 2\text{H)} \); 3.820 (s, 3H); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) : 159.65, 133.70, 131.49, 128.76, 128.21, 127.98, 127.76, 127.44, 114.04, 55.34.

9i

\[
\text{F} - \text{C} = \text{C} - \text{Cl}
\]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) : \(\delta = 7.53 \text{ (s, } 2\text{H)} \); \(7.48 \text{ (d, } J = 6.0 \text{ Hz, } 2\text{H)} \); \(7.36 \text{ (d, } J = 6.0 \text{ Hz, } 2\text{H)} \); \(7.09 \text{ (t, } J = 8.4 \text{ Hz, } 2\text{H)} \); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) : 134.37, 133.57, 133.48, 132.78, 128.76, 121.62, 115.86, 115.64.

9j

\[
\text{F} - \text{C} = \text{C} - \text{Me}
\]

\(^1\)H-NMR (400 MHz, CDCl\(_3\)) : \(\delta = 7.49 \text{ (m, } 2\text{H)} \); \(7.41 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H)} \); \(7.15 \text{ (d, } J = 8.0 \text{ Hz, } 2\text{H)} \); \(7.027 \text{ (d, } J = 8.4 \text{ Hz, } 2\text{H)} \); 2.36 (s, 2H); \(^{13}\)C-NMR (CDCl\(_3\), 100 MHz) : 138.51, 133.46, 133.38, 131.47, 129.17, 120.02, 115.73, 115.51, 21.55.

9k
1H-NMR (400 MHz, CDCl₃) : δ = 7.47 (m, 4H) ; 7.02 (t, J = 8.4 Hz, 2H) ; 6.87 (d, J = 7.2 Hz, 2H) ; 3.81 (s, 3H) ; 13C-NMR (CDCl₃, 100 MHz) : 159.70, 133.35, 133.27, 133.04, 115.72, 115.50, 114.06, 55.32.

91

1H-NMR (400 MHz, CDCl₃) : δ = 7.52 (q, J = 3.6 Hz, 2H) ; 7.45 (d, J = 8.4 Hz, 2H) ; 7.33 (q, J=4.0Hz, 4H) ; 7.30 (s 1H).

6. General Procedure of the Knoevenagel condensation reaction of aldehyde with Ethyl cyanoacetate

A mixture of aldehyde (0.5 mmol), ethyl cyanoacetate (0.55 mmol), recovery palladium catalyst residue (C catalyst) of the Suzuki or Sonogashira cross-coupling reaction was stirred in ethanol (2 mL) at room temperature in air for the indicated time (18h). The reaction course was monitored by GC-MS or TLC. The combined organic layers were dried (Na₂SO₄), concentrated in vacuo, and purified by column chromatography on silica gel to gain the pure product.

The preparation of Pd@silicone-based SIPN catalysts after every reaction is simple: After the certain reaction was completed, the palladium catalyst embedded in the silicone-based SIPN was filtered through a Büchner funnel and the cake washed with methanol, water, and hexane.

All the products 11 are known compounds and confirmed by GC-MS, NMR, and IR. For example:

11a
$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.25$ (s, 1H); 7.99 (d, J = 7.6 Hz, 2H); 7.53 (m, 3H); 4.39 (q, J = 7.6 Hz, 2H); 1.40 (t, J = 7.2 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 162.50, 155.06, 133.32, 131.50, 131.09, 129.30, 115.50, 103.06, 62.76, 29.72, 14.19.

11b

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.21$ (s, 1H); 7.90 (d, J = 8.0 Hz, 2H); 7.30 (d, J = 7.6 Hz, 2H); 4.37 (q, J = 7.2 Hz, 3H); 2.43 (s 3H); 1.39 (t, J = 7.2 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 162.79, 154.99, 144.65, 131.27, 130.05, 128.92, 115.78, 101.66, 62.61, 21.88, 14.20.

11c

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.76$ (s, 1H); 8.29 (d, J = 8.0 Hz, 1H); 7.52 (t, J = 8.0 Hz, 1H); 7.06 (t, J = 7.6 Hz, 1H); 6.96 (d, J = 7.6 Hz, 1H); 4.38 (q J = 7.6 Hz, 2H); 3.91 (s 3H); 1.40 (t, J = 6.8 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 159.23, 149.79, 135.02, 129.34, 120.96, 120.70, 115.94, 111.19, 102.34, 62.52, 55.79, 14.22.

11d

$^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 8.16$ (s, 1H); 7.99 (d, J = 7.2 Hz, 2H); 6.98 (d, J = 8.8 Hz, 2H); 4.36 (q, J = 7.2 Hz, 2H); 3.88 (s 3H); 1.38 (t, J = 7.2 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 163.80, 163.12, 154.37, 133.64, 124.41, 116.21, 114.79, 99.44, 62.43, 55.63, 14.22.

11e
$^{1}$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 8.14 (s, 1H); 7.29 (s 2H); 4.38 (q, $J =$ 7.2 Hz, 2H); 3.95 (s, 3H); 3.95 (s 6H); 1.40 (t, $J =$ 6.8 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 162.75, 154.81, 153.31, 126.58, 115.98, 108.67, 101.35, 62.65, 61.12, 56.341, 14.21.

$^{11f}$

![Structure 11f](image)

$^{1}$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 8.20 (s, 1H); 7.94 (d, $J =$ 8.4 Hz, 2H); 7.48 (d, $J =$ 8.4 Hz, 2H); 7.39 (q, $J =$ 7.2 Hz, 2H); 1.40 (t, $J =$ 7.2 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 162.24, 153.41, 139.60, 132.23, 129.89, 129.69, 115.29, 103.504, 62.90, 14.18.

$^{11g}$

![Structure 11g](image)

$^{1}$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 8.62 (s, 1H); 7.99 (s, 1H); 7.14 (s, 1H); 4.40 (q, $J =$ 7.2 Hz, 2H); 3.95 (s, 6H); 1.41 (t, $J =$ 7.2 Hz, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 162.50, 153.41, 153.08, 148.55, 132.41, 120.79, 115.88, 115.83, 102.33, 62.73, 56.49, 56.35, 14.22.

$^{11h}$

![Structure 11h](image)

$^{1}$H-NMR (400 MHz, CDCl$_3$): $\delta =$ 8.18 (s, 1H); 7.49 (d, $J =$ 8.8 Hz, 1H); 6.95 (d, $J =$ 8.8 Hz, 1H); 6.85 (s, 1H); 3.94 (s 3H); 3.91 (m 2H); 1.27 (s, 3H); $^{13}$C-NMR (CDCl$_3$, 100 MHz): 165.98, 165.18, 157.60, 149.02, 130.73, 113.72, 100.38, 61.75, 56.04, 29.73, 14.31.

$^{11i}$

![Structure 11i](image)
$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta$ = 8.29 (s, 1H) ; 7.43 (s, 1H) ; 7.41 (s, 1H) ; 7.35 (t, $J$ = 6.8 Hz, 1H) ; 4.435 (q, $J$ = 7.2 Hz, 2H) ; 1.43 (t, $J$ = 7.2 Hz, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 160.65, 151.17, 134.11, 131.70, 130.33, 128.55, 113.98, 113.35, 63.22, 14.11.

11j

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta$ = 8.61 (s, 1H) ; 8.21 (d, $J$ = 8.4 Hz, 1H) ; 7.54 (d, $J$ = 6.4 Hz, 1H) ; 7.40 (dd, $J$ = 6.4 Hz, 1H) ; 4.41 (q, $J$ = 7.2 Hz, 2H) ; 1.41 (q, $J$ = 7.2 Hz, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 161.62, 149.70, 139.41, 137.25, 130.53, 130.35, 128.37, 128.02, 114.68, 106.68, 106.45, 63.11, 14.16.

11k

$^1$H-NMR (400 MHz, CDCl$_3$) : $\delta$ = 8.22 (s, 1H) ; 8.05 (d, $J$ = 8.8 Hz, 2H) ; 7.04 (d, $J$ = 8.8 Hz, 2H) ; 4.33 (q, $J$ = 7.2 Hz, 2H) ; 1.344 (t, $J$ = 7.2 Hz, 3H) ; $^{13}$C-NMR (CDCl$_3$, 100 MHz) : 205.33, 162.69, 162.46, 154.16, 149.99, 123.59, 116.00, 98.55, 61.89, 13.59.

Selected Recent References, and references cited therein:


Figure S1. The picture of PdCl₂-catalyzed deoxygenated reduction of aromatic ketone and the desired supported palladium residue formed at the end of the deoxygenated reduction: (a) 1 min; (b) after 1 h; (c) at the last.
Table S1. Recovered palladium (A) catalyzed Suzuki reaction:

Optimization of reaction conditions

![Chemical structure of reaction](image)

<table>
<thead>
<tr>
<th>Entry (^{(a)})</th>
<th>Cat</th>
<th>Solvent</th>
<th>Base</th>
<th>Time / h</th>
<th>Yield(%)-6a (^{(b)})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Pd-A</td>
<td>EtOH</td>
<td>K₂CO₃</td>
<td>18</td>
<td>81</td>
</tr>
<tr>
<td>2</td>
<td>Pd-A</td>
<td>MeOH</td>
<td>K₃PO₄</td>
<td>18</td>
<td>18</td>
</tr>
<tr>
<td>3</td>
<td>Pd-A</td>
<td>DMF-H₂O/(V:9:1)</td>
<td>K₃PO₄</td>
<td>18</td>
<td>33</td>
</tr>
<tr>
<td>4</td>
<td>Pd-A</td>
<td>DMF</td>
<td>CS₂CO₃</td>
<td>18</td>
<td>trace</td>
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<tr>
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<td>MeOH</td>
<td>KOH</td>
<td>18</td>
<td>10</td>
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<tr>
<td>6</td>
<td>Pd-A</td>
<td>H₂O</td>
<td>Na₂CO₃</td>
<td>18</td>
<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Pd-A</td>
<td>H₂O</td>
<td>CS₂CO₃</td>
<td>18</td>
<td>trace</td>
</tr>
</tbody>
</table>

\(^{(a)}\) Reaction conditions: aryl bromide (0.5 mmol), arylboronic acid (0.75 mmol), the Recovered palladium catalyst residue (A) (0.1544g, PdCl₂:5mol%), K₂CO₃ (1 mmol) was stirred in ethanol (2 mL) at room temperature in air. 
\(^{(b)}\) Isolated yields.
Table S2. Recovered palladium (B) catalyzed Sonogashira reaction:

Optimization of reaction conditions

\[
\begin{array}{cccccc}
\text{Entry} & \text{SM1} & \text{Solvent} & \text{Base} & \text{Additive (10mol%)} & \text{Yield(%)—9} \\
1 & 4-Iodoanisole & H_2O & K_2CO_3 & \text{None} & \text{trace} \\
2 & 4-Iodoanisole & EtOH & K_2CO_3 & \text{None} & \text{trace} \\
3 & 1-Chloro-4-iodobenzene & EtOH & K_2CO_3 & \text{None} & 92 \\
4 & 1-Chloro-4-iodobenzene & EtOH & K_2CO_3 & \text{None} & 77^{[b]} \\
5 & 1-Chloro-4-iodobenzene & EtOH & K_2CO_3 & \text{None} & 49^{[c]} \\
6 & 1-Fluoro-4-iodobenzene & EtOH & K_2CO_3 & \text{None} & \text{trace} \\
7 & Iodobenzene & EtOH & K_2CO_3 & \text{None} & \text{trace} \\
8 & 1-Fluoro-4-iodobenzene & EtOH & K_2CO_3 & PhCl & 87 \\
9 & 4-Iodoanisole & EtOH & K_2CO_3 & PhCl & 92 \\
10 & Iodobenzene & EtOH & K_2CO_3 & PhCl & 88 \\
11 & 1-iodo-4-methylbenzene & EtOH & K_2CO_3 & \text{None} & \text{trace} \\
\end{array}
\]

[a] Isolated yield. [b] The recovered Pd (B) catalyst was recycled for reusing in the second cycle. [c] The recovered Pd (B) catalyst was recycled for reusing in the third cycle.
**Figure S2.** Catalyst recycling in the recovered palladium (B)-catalyzed Knoevenagel condensation
**Figure 3 of Text.** TEM images (larger size) of the recovered palladium catalyst embedded in the silicone-based SIPN (B catalyst) at the end of the deoxygenated reduction
Figure S6. The SEM picture and EDS spectra of palladium/silicone-based PN material

(a) Before reduction (the mixture of PdCl$_2$ + PA semi-IPN material): The palladium catalyst embedded in the silicone-based SIPN (A catalyst)
(b) After deoxygenated reduction of aromatic ketones or benzylic alcohols: The palladium catalyst embedded in the silicone-based SIPN (B catalyst)
(c) After Suzuki cross-coupling reaction: The palladium catalyst embedded in the silicone-based SIPN (C catalyst)
Figure S7. TEM images of the recovered palladium catalyst embedded in the silicone-based SIPN (C catalyst) at the end of the cross-coupling reactions
7. The characterization of PMHS/PA-semi-IPN material

\[ \left[ \begin{array}{c} \text{Si} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \\ \text{H} \end{array} \right] \times n + \] 

3 eq. (refer to Si-H, MW = 8700) 

\[ \text{OCH}_2\text{CH}_3 \] 

1 eq. 

\[ \text{H}_3\text{CH}_2\text{CO} \] 

94% conversion 

Co(OAc)\(_2\) (1 mol%) 

TsOH (1 mol%) 

PA polysiloxane 

no Co(OAc)\(_2\): no conversion 

no TsOH: no conversion
SEM images of the fracture surface of PMHS/PEA SIPN a) ×100 times, b) ×200 times
TEM images of PMHS/PEA SIPN

$1H$ NMR spectra of the PHMS/PEA SIPN
8. The Raman spectra of the palladium@silicone-based SIPNs: The Raman spectrum of the residue of palladium@silicone-based SIPN after the Knoevenagel condensation (down) was similarly to that of palladium catalyst B (up), which revealed there are no obvious changes for the structure of silicone-based SIPNs during these reactions in this work.
**IR spectra of Palladium@silicon-based SIPN material**

Pd@silicone-based SIPN before reduction: the solid sample was obtained from mixture of PdCl₂ and silicone-based SPIN in MeOH

Pd@silicone-based SIPN after reduction or before cross-coupling reaction

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Pd@silicone-based SIPN after cross-coupling reaction
9. $^{1}H$-NMR and $^{13}C$-NMR spectra