# PVC-Supported Palladium Nanoparticles: An Efficient Catalyst for Suzuki Cross-Coupling Reactions at Room Temperature

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**Abstract:** A simple and efficient protocol is described for a Suzuki reaction catalyzed by poly(vinyl chloride)-supported nanoparticles of metallic palladium at room temperature. Aryl iodides, bromides, and chlorides underwent smooth Suzuki reactions in aqueous ethanol, an environmentally friendly solvent, under ligand-free conditions to give good yields of the desired biaryl products. The heterogeneous catalyst could be used up to four times with no detectable metal leaching or loss of catalytic efficiency.

**Key words:** coupling reactions, supported catalysis, palladium, halides, biaryls, Suzuki reactions

Palladium-catalyzed cross-coupling reactions are indispensable tools for the construction of C–C bonds in syntheses of fine chemicals, pharmaceuticals, advanced functional materials, and natural products.[1] Among these reactions, the Suzuki–Miyaura cross-coupling reaction is widely used in the construction of biaryl and heterobiaryl compounds from aryl or hetaryl halides or triflates and arylboronic acids or their esters.[2] The Suzuki reaction has continued to garner attention because of the many applications that result from its tolerance toward a wide range of functional groups and because of the stability, low toxicity, and commercial availability of boronic acid and boronate ester reactants. The Suzuki reaction has been used on an industrial scale for the synthesis of the sartan family of hypertensive drugs and the fungicide boscalid.[3] Various modifications, such as new catalysts, new ligands, and even ligand-free conditions, have been developed during the past two decades to render the Suzuki reaction simple, mild, and efficient.[4]

The chemistry of metal nanoparticles has emerged as an interesting field with a wide range of applications in synthesis and in medicine.[5] The small size and high surface area of metal nanoparticles renders them useful in catalysis. Limitations on the use of palladium complexes, such as high costs, metal contamination, laborious reaction conditions, and problems with recycling of catalysts has led to the development of supported palladium nanoparticles as catalysts.[6] Various supports have been explored, including porous materials, ionic liquids, surfactants, dendrimers, functionalized polymers, biopolymers, various ligands, and silica (in supercritical carbon dioxide).[7] Immobilization of the metal on a matrix eliminates problems associated with agglomeration, metal contamination, and leaching of the metal, and it permits ready recycling of the catalyst.[8] Supported palladium nanoparticles are increasingly used in various reactions, such as hydrogenations, aerobic oxidations, and cross-coupling reactions.[9] Reetz and co-workers[10] reported the application of palladium nanoparticles in cross-coupling reactions. Das et al.[11] reported the use of palladium nanoparticles supported on borohydride-exchanged resin beads or microparticles for the synthesis of biaryl compounds through a ligand-free Suzuki reaction at 110 °C for six to twelve hours. Sayed and co-workers[12] used nanoparticles of poly(1-vinylpyrrolidone)-supported palladium in a ligand-free Suzuki reaction under reflux conditions for twelve hours. Pd(0)/polypyrrole nanoparticles have been used in a Suzuki reaction at a high temperature (100 °C) for six hours.[13] Palladium(0) nanoparticles supported on diphenylphosphinylated silica gel have also been used as a catalyst for the Suzuki reaction.[14] However, the high reaction temperatures, long reaction times, and limited substrate scope have limited the use of such reactions, and there is still considerable interest in developing readily prepared and versatile catalysts to permit efficient syntheses of biaryl and heterobiaryl compounds.

Poly(vinyl chloride) (PVC) is a widely used, commercially available, inexpensive polymer. Catalysts consisting of palladium(0) nanoparticles supported on 2-aminoethanol-modified PVC[15] or a PVC-derived Schiff base[16] have been used in Heck and Suzuki reactions. Our group has reported the preparation of palladium nanoparticles supported on unmodified PVC, and we have demonstrated their use in the reduction of a range of functional groups, as well as in the deprotection of some common protecting groups in peptide chemistry.[17] In continuation of our interest in metal nanoparticle-catalyzed reactions, we examined the use of unmodified PVC-supported palladium nanoparticles in ligand-free Suzuki cross-coupling reactions at room temperature.

The Pd(0)/PVC catalyst was freshly prepared in a single batch that was used in all the subsequent reactions. Inductively coupled plasma–optical emission spectroscopy (ICP–OES) analysis of the catalyst showed that its palladium content was 13% (for transmission electron micrographs and a histogram, see the Supporting Information). Initially, we examined the Suzuki reaction of 0.1 mmol of iodobenzene (**1a**) with 0.12 mmol of phenylboronic acid

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(**2a**) as model substrates in the presence of 0.815 mg of Pd(0)/PVC catalyst (0.106 mg of Pd) under air. In preliminary experiments, we tested sodium carbonate and cesium carbonate as bases, and we performed the reaction at room temperature in a 1:1 mixture of 1,2-dimethoxyethane and water as the solvent. Only traces of biphenyl (**3a**) were obtained in either case (Table 1, entries 1 and 2). Increasing the temperature to 85 °C led to slight increases in the yield of biphenyl (entries 3 and 4). Other common solvents, such as 1,4-dioxane, acetonitrile, or *N*,*N*-dimethylformamide, in 1:1 mixtures with water were also examined in the presence of sodium carbonate or cesium carbonate. Yields of the product in all the cases were unsatisfactory (<35%), even at high temperatures (entries 5–10). Finally, to our delight the use of a 1:1 mixture of ethanol and water as the solvent with sodium carbonate as the base resulted in efficient ligand-free synthesis of biphenyl (**3a**) from iodobenzene (**1a**) and phenylboronic acid (**2a**) at room temperature catalyzed by Pd(0)/PVC (Table 1, entry 12).

**Table 1** Screening of Solvents and Bases for the Suzuki–Miyaura Reaction of Iodobenzene with Phenylboronic Acid

| Entry | Solvent[a] | Base | Temp (°C) | Time (h) | Yield (%) of **3a** |
|---|---|---|---|---|---|
| 1 | DME–$H_2O$ | $Na_2CO_3$ | 25 | 10 | 10 |
| 2 | DME–$H_2O$ | $Cs_2CO_3$ | 25 | 10 | 8 |
| 3 | DME–$H_2O$ | $Na_2CO_3$ | 80 | 6 | 28 |
| 4 | DME–$H_2O$ | $Cs_2CO_3$ | 85 | 5 | 20 |
| 5 | 1,4-dioxane–$H_2O$ | $Na_2CO_3$ | 85 | 6 | 26 |
| 6 | 1,4-dioxane–$H_2O$ | $Cs_2CO_3$ | 85 | 5 | 18 |
| 7 | DMF–$H_2O$ | $Na_2CO_3$ | 87 | 7 | 32 |
| 8 | DMF–$H_2O$ | $Cs_2CO_3$ | 87 | 7 | 27 |
| 9 | MeCN–$H_2O$ | $Na_2CO_3$ | 74 | 6 | 23 |
| 10 | MeCN–$H_2O$ | $Cs_2CO_3$ | 74 | 6 | 16 |
| 11 | EtOH–$H_2O$ | $Cs_2CO_3$ | r.t. | 2 | 83 |
| 12 | EtOH–$H_2O$ | $Na_2CO_3$ | r.t. | 2 | 99 |

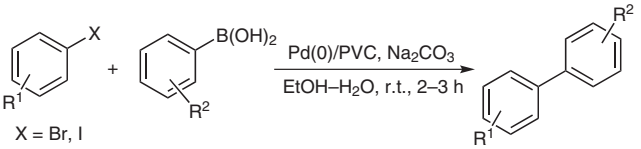
[a] 1:1 mixture.

Next, we examined the effect of the catalyst loading on the reaction of phenylboronic acid (**2a**) and iodobenzene (**1a**). A catalyst loading of 0.407 mg of Pd(0)/PVC in a 0.1-mmol-scale reaction resulted in a 95% yield of biphenyl (**3a**) in four hours, whereas the reaction was found to be complete in two hours with a 99% yield at a loading of 0.815 mg Pd(0)/PVC. Increasing the catalyst loading to 1.22 mg had no beneficial effect on the yield or rate of the reaction.

We therefore selected an optimal catalyst loading of 0.815 mg Pd(0)/PVC for the 0.1-mmol-scale Suzuki reactions of various aryl iodides or bromides **1** with various boronic acids **2**.

In a typical reaction, phenylboronic acid (**2a**; 0.12 mmol), sodium carbonate (0.2 mmol), and Pd(0)/PVC (0.106 mg of Pd) were added to a solution of iodobenzene (**1a**; 0.1 mmol) in 1:1 ethanol–water, and the mixture was stirred at room temperature for two hours while we monitored the course of the reaction by thin-layer chromatography. The pure product was isolated by simple workup without any column purification in this case. Under our optimized reaction conditions, the Suzuki reaction proceeded smoothly in two to three hours with various aryl halides **1** and arylboronic acids **2** bearing electron-rich or electron-deficient functional groups (Table 2). In most cases, the Suzuki product **3** was isolated after removal of the catalyst by filtration without the need for any column purification. The ortho-substituted reactant 1-iodo-2-methoxybenzene gave a slightly lower yield of the corresponding biphenyl **3c** (entry 3).

**Table 2** Synthesis of Biaryls **3** from Aryl Bromides or Iodides with Pd(0)/PVC Catalyst at Room Temperature




| Entry | Aryl halide | $R^2$ | Product | Yield (%) |
|---|---|---|---|---|
| 1 | PhI | H | **3a** | 99 |
| 2 | PhI | 4-$F_3C$ | **3b** | 97 |
| 3 | 2-$MeOC_6H_4I$ | H | **3c** | 93 |
| 4 | 4-$BnC_6H_4Br$ | H | **3d** | 97 |
| 5 | 4-$H_2NC_6H_4Br$ | H | **3e** | 96 |
| 6 | PhI | 4-pyridyl | **3f** | 98 |
| 7 | PhBr | 4-F | **3g** | 98 |
| 8 | PhBr | 4-Me | **3h** | 99 |
| 9 | 4-$MeOC_6H_4Br$ | 4-MeO | **3i** | 97 |
| 10 | 4-$O_2NC_6H_4Br$ | 4-F | **3j** | 98 |

We then turned our attention to the catalytic activity of Pd(0)/PVC for the reaction of aryl chlorides with arylboronic acids. Activation of aryl chlorides is much more sluggish than that of the analogous bromo or iodo compounds. For this reason, Suzuki reactions of aryl chlorides have been effected by using sterically demanding electron-rich ligands, which are often sensitive to air or moisture and which frequently require multistep syntheses.[18] The sensitivity and expense of these ligands led to investigate the use of ligand-free catalytic systems for the Suzuki cross-coupling reactions of aryl chlorides.[19] Diaconescu and co-workers[19d] reported the use of palladium(0) nanoparticles supported on polyaniline nanofibers



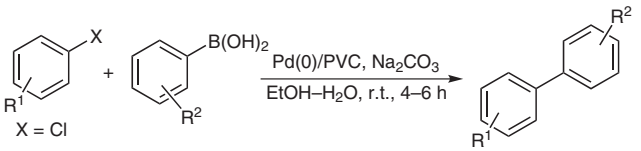
as active catalysts for the coupling of aryl chlorides in water at 80–100 °C for two to six hours. Liu and co-workers[19a] reported a ligand-free Suzuki reaction of aryl chlorides catalyzed by palladium nanoparticles generated in situ. Li and co-workers[20] reported a ligand-free Suzuki coupling reaction of aryl chlorides on the presence of magnetically separable iron(III) sulfate/silica-supported palladium(0) nanoparticles at 130 °C for 36 hours. Choudary et al.[21] reported the use of double-layer hydroxide-supported palladium nanoparticles for the Suzuki reaction of aryl chlorides at 100 °C for ten hours. The majority of these reported protocols therefore require harsh reaction conditions and long reaction times.

We examined the coupling of 4-chlorotoluene with phenylboronic acid under similar conditions to those that we employed for the coupling of iodides or bromides at room temperature. Interestingly, the reaction was found to be complete within 4.5 hours at room temperature, and the desired biaryl compound **3h** was obtained in excellent yield (97%). Furthermore, when we subjected a series of activated and nonactivated aryl chlorides to the Suzuki reaction, all the desired biaryl compounds were isolated in good yields within four to six hours (Table 3). In case of 2-chlorothiophene, a slight decrease in the yield was noticed (entry 3). Also, the reaction was slower with the nonactivated chlorides, although the desired biaryls were still obtained in good yields after six hours (entries 2, 6, and 8). Aryl chlorides with electron-withdrawing substituents showed higher reactivities and gave better yields when of the products (entries 4, 5, and 7) than did those with electron-donating substituents.

We tested the recyclability of the catalyst for the reaction between iodobenzene (**1a**) and phenylboronic acid (**2a**). When the reaction was complete, the catalyst was recovered by filtration, washed successively with water and ethanol, dried, and reused directly in the next cycle. The catalyst performed well when recycled up to three times, and the reaction was found to be complete within 2–2.3 hours with a consistent yield (Table 4). The palladium content of the recycled catalyst after the third round of recycling was found to be 12.7% by ICP–OES. This indicated negligible leaching of the active nanopalladium species during three recycling operations (0.3% in total). However, the efficiency of the nanocatalyst fell after a fourth round of recycling, and its palladium content (ICP-OES) fell markedly to 11.81%, indicating that considerable leaching of the catalytic species had occurred. These studies confirmed that Pd(0)/PVC nanoparticles can act as an efficient and recyclable catalyst system for the Suzuki reaction under mild conditions.

In conclusion, the Pd(0)/PVC catalyst was successfully used in ligand-free Suzuki cross-coupling reactions of aryl iodides, bromides, or chlorides at room temperature. The catalyst can be easily separated from the reaction mixture by simple filtration, and it can be reused up to three times without any significant loss of activity. Our present protocol offers several advantages over reported methods, including mild reaction conditions, a faster and cleaner reaction profile, and superior yields.

**Table 3** Suzuki Cross-Coupling Reaction of Aryl Chlorides with Arylboronic Acids at Room Temperature with Pd(0)/PVC Catalyst




| Entry | Aryl chloride | $R^2$ | Product | Yield% |
|---|---|---|---|---|
| 1 | 4-TolCl | H | **3h** | 97 |
| 2 | 2-$H_2NC_6H_4Cl$ | H | **3k** | 90 |
| 3 | 2-chlorothiophene | H | **3l** | 87 |
| 4 | 3-$MeO_2CC_6H_4Cl$ | H | **3m** | 94 |
| 5 | 4-$NCC_6H_4Cl$ | H | **3n** | 95 |
| 6 | 4-$H_2NC_6H_4Cl$ | 4-Me | **3o** | 91 |
| 7 | 4-$O_2NC_6H_4Cl$ | H | **3p** | 95 |
| 8 | 4-$HO_2CC_6H_4Cl$ | 4-OMe | **3q** | 89 |
| 9 | 3-$MeOC_6H_4Cl$ | 4-$NO_2$ | **3r** | 92 |
| 10 | 4-$HCOC_6H_4Cl$ | H | **3s** | 90 |
| 11 | 4-$MeCOC_6H_4Cl$ | H | **3t** | 91 |
| 12 | 3-$MeOC_6H_4Cl$ | H | **3u** | 94 |

**Table 4** Recycling of the Catalyst System

| Cycle | Time (h) | Yield (%) of **3a** |
|---|---|---|
| fresh | 2 | 99 |
| recycle 1 | 2 | 97 |
| recycle 2 | 2 | 98 |
| recycle 3 | 2.3 | 96 |
| recycle 4 | 3 | 90 |

PVC powder (low molecular weight: $M_w$ 48,000, K value 55–57; density: 1.4 g/mL at 25 °C) was purchased from Sigma-Aldrich and used directly. ICP–OES measurements were made on PerkinElmer Optima 5300 DV equipment. Melting points were recorded on a Thomas–Hoover capillary apparatus and are uncorrected. $^1H$ and $^{13}C$ NMR spectra were recorded with a Brucker FT NMR Avance-300 spectrometer at 300 and 75 MHz, respectively. Chemical shifts (δ) are reported relative to TMS as an internal standard. High-resolution mass spectra were recorded on a Micromass Q-TOF spectrometer operated in the ESI mode.

**Pd(0)/PVC Catalyst**

$PdCl_2$ (600 mg, 3.38 mmol) was added to a suspension of PVC powder (2.4 g) in EtOH (440 mL). The mixture was stirred for 2 h then

refluxed for 5 min while a soln of $NaBH_4$ (148 mg, 4 mmol) in EtOH (8 mL) was slowly added. The brownish mixture immediately became colorless, indicating reduction of the Pd(II) salt to Pd(0). The suspension was then allowed to cool before the black precipitate was collected by filtration. Excess $NaBH_4$ was quenched with $H_2O$ and the black powder of Pd(0)/PVC was washed successively with MeOH and $H_2O$ then dried under vacuum.

**Biaryls (3a–v); General Procedure**

Pd(0)/PVC (0.815 mg; 0.106 mg Pd) was added to a stirred soln of the appropriate aryl halide (0.1 mmol), arylboronic acid (0.12 mmol), and $Na_2CO_3$ (0.2 mmol) in 1:1 EtOH–$H_2O$ (4 mL), and the mixture was stirred at r.t. until the reaction was complete (TLC). The mixture was then filtered and the residue was washed with EtOH (3 mL). The solvent was evaporated under vacuum and the residue was extracted with EtOAc (2 ×5 mL). The separated organic layer was washed with brine (5 mL), dried ($Na_2SO_4$), and concentrated under vacuum. Where necessary, the product was purified by column chromatography (silica gel 100–200 mesh) using EtOAc–*n*-hexane (1–8% EtOAc) as eluent.

**Biphenyl (3a)**

White solid; yield: 15.4 mg (99%); mp 68–70 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.2–7.8 (m, 7 H), 8.21–8.37 (m, 3 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 127.90, 132.67, 133.43, 135.62.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{10}Na$: 177.0680; found: 177.0683.

**4-(Trifluoromethyl)biphenyl (3b)**

White solid; yield: 21.53 mg (97%); mp 69–72 °C

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.38 (t, *J* = 7.2 Hz, 1 H), 7.43 (t, *J* = 7 Hz, 2 H), 7.54 (d, *J* = 6.8 Hz, 2 H), 7.62 (s, 4 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 123.63, 124.82, 127.35, 127.46, 128.37, 129.12, 129.49, 136.13, 139.67.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{13}H_9F_3Na$: 245.0554; found: 245.0531.

**2-Methoxybiphenyl (3c)**

Colorless gummy liquid; yield: 17.12 mg (93%).

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.94–6.98 (m, 2 H), 7.25–7.30 (m, 3 H), 7.35–7.39 (m, 2 H), 7.48–7.51 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 55.45, 11.20, 120.75, 126.84, 127.91, 128.53, 129.42, 130.63, 130.76, 138.53, 156.41.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{13}H_{12}NaO$: 207.0786; found: 207.0782.

**4-(Benzyloxy)biphenyl (3d)**

Light-yellow solid; yield: 25.23 mg (97%); mp 298–300 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 5.18 (s, 2 H), 7.12–7.18 (m, 2 H), 7.30–7.70 (m, 12 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 71.3, 114.3, 127.1, 127.4, 126.9, 127.6, 128.2, 128.6, 128.7, 128.8, 136.1, 139.6, 159.2.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{19}H_{16}NaO$: 283.1099; found: 283.110.

**Biphenyl-4-amine (3e)**

Yellowish brown solid; yield: 16.23 mg (96%); mp 50–53 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 13.6–3.8 (br s, 2 H), 6.76–6.80 (m, 2 H), 7.20–7.35 (m, 1 H), 7.41–7.50 (m, 4 H), 7.56–7.60 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 115.33, 126.19, 126.33, 127.94, 128.59, 131.52, 141.10, 145.77.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{11}NNa$: 192.0789; found: 192.0786.

**4-Phenylpyridine (3f)**

White solid; yield: 15.19 mg (98%); mp 70–72 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.16 (m, 1 H), 7.26–7.30 (m, 2 H), 7.40–7.46 (m, 2 H), 7.49–7.56 (m, 2 H), 8.21 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 121.32, 126.84, 128.92, 129.16, 138.45, 147.17, 149.46.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{11}H_9NNa$: 178.0633; found: 178.0620.

**4-Fluorobiphenyl (3g)**

White solid; yield: 16.86 mg (98%); mp 77–80 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.10–7.18 (m, 2 H), 7.27–7.68 (m, 7 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 115.43, 115.72, 126.99, 127.23, 128.6, 128.71, 128.79, 137.31, 137.35, 137.95, 164.09.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_9FNa$: 195.0586; found: 195.0589.

**4-Methylbiphenyl (3h)**

White solid; yield: 16.64 mg (99%) from PhBr and 4-TolB$(OH)_2$, 16.30 mg (97%) from 4-TolCl and PhB$(OH)_2$; mp 44–46 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.39 (s, 3 H), 7.30 (d, *J* = 7.8 Hz, 2 H), 7.36–7.47 (m, 1 H), 7.57–7.60 (m, 2 H), 7.70 (d, *J* = 8.0 Hz, 2 H), 7.78–7.80 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 21.07, 126.91, 129.4 (4 C), 136.93, 138.14, 141.2.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{13}H_{12}Na$: 191.0837; found: 191.0842.

**4,4′-Dimethoxybiphenyl (3i)**

White solid; yield: 20.76 mg (97%); mp 178–181 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 6 H), 6.94 (d, *J* = 7.2 Hz, 4 H), 7.46 (d, *J* = 7.4 Hz, 4 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 55.32, 114.18, 127.72, 133.41, 158.62.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{14}H_{14}NaO_2$: 237.0891; found: 237.0897.

**4-Fluoro-4′-nitrobiphenyl (3j)**

White solid; yield: 21.27 mg (98%); mp 120–123 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.16–7.19 (m, 2 H), 7.60–7.63 (m, 2 H), 7.67 (d, *J* = 8.4 Hz, 2 H), 8.26 (d, *J* = 8.2 Hz, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 116.42, 121.26, 128.31, 129.14, 131.83, 141.92, 147.26, 161.38.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_8FNNaO_2$: 240.0437; found: 240.0441.

**Biphenyl-2-amine (3k)**

White solid; yield: 15.21 mg (90%); mp 48–50 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.68 (br s, 2 H), 6.70 (d, *J* = 8.2 Hz, 1 H), 6.78 (t, *J* = 7.2 Hz, 1 H), 7.08–7.13 (m, 2 H), 7.29 (m, 1 H), 7.37–7.42 (m, 4 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 115.2, 118.4, 127.3, 127.6, 128.2, 128.5, 129.1, 130.2, 139.4, 143.1.

HRMS: *m/z* $[M + Na]^+$ calcd for $C_{12}H_{11}NNa$: 192.0789; found: 192.0792.

**2-Phenylthiophene (3l)**

White solid; yield: 13.92 mg (87%); mp 33–35 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.05–7.12 (m, 1 H), 7.24–7.40 (m, 5 H), 7.62–7.71 (m, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 123.04, 124.76, 125.94, 127.42, 127.95, 128.84, 134.40, 144.42.



HRMS: *m/z* [M + Na]$^+$ calcd for $C_{10}H_8NaS$: 183.0244; found: 183.0251.

**Methyl Biphenyl-3-carboxylate (3m)**
White solid; yield: 19.93 mg (94%); mp 116–118 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 7.28–7.57 (m, 4 H), 7.60–7.62 (m, 3 H), 7.71–7.79 (m, 1 H), 8.01–8.13 (m, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 52.13, 127.08, 127.67, 128.19, 128.28, 128.81, 130.60, 131.46, 140.02, 141.38, 166.99.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{14}H_{12}NaO_2$: 235.0735; found: 235.0741.

**Biphenyl-4-carbonitrile (3n)**
White solid; yield: 17.01 mg (95%); mp 83–85 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.42 (t, *J* = 7.2 Hz, 1 H), 7.48 (t, *J* = 7.6 Hz, 2 H), 7.62 (d, *J* = 7.4 Hz, 2 H), 7.70–7.72 (m, 4 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 110.62, 118.65, 127.26, 127.43, 128.47, 129.04, 132.67, 139.21, 145.66.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{13}H_9NNa$: 202.0633; found: 202.0637.

**(4′-Methylbiphenyl-4-yl)amine (3o)**
Yellowish brown solid; yield: 16.66 mg (91%); mp 92–95 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.38 (s, 3 H), 3.67 (br s, 2 H), 6.72 (d, *J* = 8.4 Hz, 2 H), 7.16–7.20 (m, 2 H), 7.35–7.41 (m, 4 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 21.02, 115.44, 126.25, 127.53, 129.27, 131.64, 135.27, 138.42, 145.38.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{13}H_{13}NNa$: 206.0946; found: 206.0957.

**4-Nitrobiphenyl (3p)**
White solid; yield: 18.91 mg (95%); mp 110–112 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.40–7.51 (m, 3 H), 7.61 (d, *J* = 7 Hz, 2 H), 7.72 (d, *J* = 8.6 Hz, 2 H), 8.24 (d, *J* = 8.4 Hz, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 124.33, 127.24, 127.56, 128.62, 129.37, 138.45, 146.82, 147.23.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{12}H_9NNaO_2$: 222.0531; found: 222.0536.

**4′-Methoxybiphenyl-4-carboxylic Acid (3q)**
White solid; yield: 20.29 mg (89%); mp 263–265 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.82 (s, 3 H), 6.89 (d, *J* = 8.4 Hz, 2 H), 7.68 (d, *J* = 8.6 Hz, 2 H), 7.74 (d, *J* = 8.6 Hz, 2 H), 7.96 (d, *J* = 8.2 Hz, 2 H), 12.81 (s, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 55.32, 114.56, 126.31, 128.24, 128.63, 129.71, 131.45, 143.87, 159.30, 167.22.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{14}H_{12}O_3Na$: 251.0684; found: 251.0678.

**3-Methoxy-4′-nitrobiphenyl (3r)**
White solid; yield: 21.07 mg (92%); mp 84–86 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 6.86 (d, *J* = 8.2 Hz, 1 H), 7.10 (s, 1 H), 7.19 (d, *J* = 7.4 Hz, 1 H), 7.39 (t, *J* = 8.2 Hz, 1 H), 7.72 (d, *J* = 6.4 Hz, 2 H), 8.28 (d, *J* = 7 Hz, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 56.21, 111.34, 112.85, 119.60, 121.32, 128.48, 130.13, 137.16, 141.81, 147.47, 159.92.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{13}H_{11}NNaO_3$: 252.0637; found: 252.0637.

**Biphenyl-4-carbaldehyde (3s)**
White solid; yield: 16.38 mg (90%); mp 54–56 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 7.38 (t, *J* = 7.4 Hz, 1 H), 7.42 (t, *J* = 7.2 Hz, 2 H), 7.59 (d, *J* = 7 Hz, 2 H), 7.71 (d, *J* = 8.2 Hz, 2 H), 7.92 (d, *J* = 6.8 Hz, 2 H), 9.89 (s, 1 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 127.34, 127.66, 128.21, 128.84, 129.67, 135.48, 136.15, 141.63, 191.21.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{13}H_{10}NaO$: 205.0629; found: 205.0631.

**1-Biphenyl-4-ylethanone (3t)**
White solid; yield: 17.84 mg (91%); mp 119–122 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 2.68 (s, 3 H), 7.41–7.53 (m, 3 H), 7.62–7.71 (m, 4 H), 8.03–8.06 (d, *J* = 7 Hz, 2 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 26.72, 127.26, 127.35, 127.42, 128.64, 128.92, 135.86, 139.90, 145.73, 197.7.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{14}H_{12}NaO$: 219.0786; found: 219.0789.

**3-Methoxybiphenyl (3u)**
White solid; yield: 17.30 mg (94%); mp 87–90 °C.

$^1$H NMR (300 MHz, $CDCl_3$): δ = 3.86 (s, 3 H), 7.05–7.07 (m, 2 H), 7.25–7.60 (m, 7 H).

$^{13}$C NMR (75 MHz, $CDCl_3$): δ = 55.31, 114.18, 126.62, 126.70, 128.11, 128.68, 133.76, 140.80, 159.13.

HRMS: *m/z* [M + Na]$^+$ calcd for $C_{13}H_{12}NaO$: 207.0786; found: 207.0789.

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**Supporting Information** for this article is available online at http://www.thieme-connect.com/ejournals/toc/synthesis. Included are TEM and histogram data for PVC-Pd(0) and $^1$H and $^{13}$C NMR spectra and HRMS spectra for selected compounds.

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