Pd–Ni bimetallic nanoparticles supported on ZrO_2 as an efficient catalyst for Suzuki–Miyaura reactions

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Pd-Ni bimetallic nanoparticles (BMNPs) supported on ZrO_2 were prepared by an impregnation-reduction method. The BMNPs showed excellent catalytic performance in Suzuki carbon-carbon cross-coupling reactions and almost quantitative conversion of the substrates was obtained under mild conditions in the absence of ligand. The excellent catalytic performance of the bimetallic catalyst could be a result of the synergistic effect between the two metal components. The catalyst showed outstanding recyclability during the reaction process; no obvious decrease in catalytic performance was observed after five cycles.

Keywords: heterogeneous catalysis, alloys, nanochemistry, bimetallic nanoparticles, Suzuki-Miyaura coupling

The Suzuki carbon-carbon (C-C) cross-coupling reaction is among the most crucial catalytic conversions in organic chemistry; it is one of the vital players in diverse areas such as natural product synthesis, polymers and material science.¹⁻⁴ The Suzuki coupling reaction is predominantly catalysed by palladium catalysts.5-7 The search for such catalysts designed for Suzuki reactions is most challenging due to the high price and low abundance of Pd.^{8,9} In past decades, continuous efforts have been made on the development of novel catalysts with prominent catalytic activity and stability¹⁰⁻¹⁴ and these outstanding works laid a firm foundation for the development of novel catalysts with high activity. Although homogeneous palladium catalysts with various ligands are highly efficient in the Suzuki-Miyaura reactions,¹⁵⁻¹⁹ heterogeneous catalysts are preferable in industry due to their reusability and easy separation, which may lower the cost of industrial production.²⁰ Although many catalytic systems have been established, there is still a long way to go to achieve superior catalysts.^{21,22}

The active sites of heterogeneous catalysts are mainly distributed on the catalyst surface,²³ so nanoparticles have long been regarded as the bridge between homogeneous and heterogeneous catalysts due to their high surface area-to-volume ratio,²⁴ which could provide more contact opportunity between the reactant molecules and the active sites. The enhanced interaction could help to achieve a better reaction rate that is closer to its homogeneous counterpart.⁴ Bimetallic nanoparticles, composed of two different metal components, usually show a combination of the properties associated with monometallic counterparts and a significant enhancement due to synergistic effects.^{25–27} Several excellent reports have shown that bimetallic nanoparticles have great potential in catalyst development.^{13,28–32}

In this work, highly efficient Pd–Ni bimetallic nanoparticles were fabricated by the impregnation–reduction method. Our previous reports showed that Pd–Ni/ZrO₂ particles outperform the corresponding monometallic catalyst in the selective hydrogenolysis of lignin.³³ The same bimetallic catalyst showed extraordinary performance for Suzuki–Miyaura reactions. Control experiments showed that the catalytic activity of the Pd–Ni alloy catalyst was superior to the monometallic Pd catalyst and the main reason for the enhancement in catalytic performance could be ascribed to the improved electron flow on the catalyst surface on formation of a Pd–Ni alloy. The catalyst also showed outstanding recyclability during the reaction process; no obvious decrease

in catalytic performance was observed when the catalyst was reused four times and no activity discrepancy was observed when the reaction was conducted on a larger scale (5 mmol). Our work highlights the vital role of bimetallic nanoparticles (BMNPs) in catalyst development and we expect that more excellent catalysts based on bimetallic nanoparticles will be reported in the near future.

Results and discussion

$Characterisation\ of\ Pd-Ni\ bimetallic\ nanoparticles$

Nanocatalysts immobilised on ZrO_2 were prepared by an impregnation–reduction method using NaBH₄ as the reductant; composition of the bimetallic nanoparticles was controlled by adjusting the ratio of the metal precursors. The morphologies of ZrO_2 supported Pd–Ni alloy catalysts were well characterised in our previous work. The freshly prepared Pd–Ni alloy nanoparticles were well-proportioned and irregular spherical particles and the size of the BMNPs was mainly distributed between 6 and 8 nm. Area-selected scanning electronic microscope (SEM)–energy dispersive spectroscopy (EDS) mappings of the catalyst also verified the formation of a random homogeneous Pd–Ni alloy.³³

Suzuki–Miyaura reactions catalysed by bimetallic nanoparticles

At the outset of our study, p-tolylboronic acid and bromobenzene were chosen as the model substrates to evaluate the catalytic performance of the BMNPs (Table 1). Based on our previous experience on the catalytic performance of the Pd-Ni alloy catalyst, the Pd/Ni ratio was set as 1:4. Initially, 4 mol% catalyst was applied and the products were obtained in a 44% yield (Table 1, entry 1). The substrate was fully converted into products by increasing the catalyst amount to 8 mol% (Table 1, entry 2). Preliminary attempts to lower the reaction temperature showed that almost no reaction could proceed at a relatively low reaction temperature (40 °C) (Table 1, entry 3). Subsequently, we explored the effects of the base on the reaction and Na₂CO₃ was found to be the most suitable (Table 1, entries 4-6). Solvent effects on this reaction were also studied and similar reaction yields were obtained when using EtOH or H₂O as the solvent but a poor yield was obtained when CH₂CN was used (Table 1, entries 7–10).

Other alloy catalysts prepared by the same method were also tested in this reaction, but their catalytic performance was far inferior to the Pd–Ni alloy catalyst (Table 1, entries 11–13).

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Table 1 Evaluation of effect of the reaction parameters on the Suzuki-Miyaura reactions^a

	H_3C + $Cat., Solvent$ Base				
		1	2	3	
Entry	Ratio (2 /1)	Catalyst	Base	Solvent	Yield (%) ^e
1 ^b	1.5	Pd ₁ Ni ₄ /ZrO ₂	K ₂ CO ₃	Et0H:H ₂ 0	49
2	1.5	Pd ₁ Ni ₄ /ZrO ₂	K ₂ CO ₃	Et0H:H ₂ 0	97
3°	1.5	Pd ₁ Ni ₄ /ZrO ₂	K ₂ CO ₃	Et0H:H ₂ 0	3
4	1	Pd ₁ Ni ₄ /ZrO ₂	K ₂ CO ₃	Et0H:H ₂ 0	35
5	1	Pd ₁ Ni ₄ /ZrO ₂	Cs ₂ CO ₃	Et0H:H ₂ 0	17
6	1	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	Et0H:H ₂ 0	54
7	1.5	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	Et0H:H ₂ 0	97
8	1.5	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	CH ₃ CN	2
9	1.5	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	H ₂ 0	96
10	1.5	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	EtOH	99
11	1.5	Pd ₁ Cu₄/ZrO ₂	Na ₂ CO ₃	EtOH	39
12	1.5	Pd ₁ Fe ₄ /ZrO ₂	Na ₂ CO ₃	EtOH	51
13	1.5	Pd₁Zn₄/ZrO₂	Na ₂ CO ₃	EtOH	21
14 ^b	4	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	EtOH	99
15⁵	4	Pd/ZrO ₂	Na ₂ CO ₃	EtOH	82
16 ^{d,b}	4	Pd ₁ Ni ₄ /ZrO ₂	Na ₂ CO ₃	EtOH	67

^aReaction conditions: *p*-tolylboronic acid (0.15 mmol), catalyst (8 mol%, based on metal Pd), base (1 equiv.), solvent (2 mL) (for aqueous EtOH, EtOH:H₂O = 1:1), N₂ atmosphere, 80 °C, 4 h. ^bAmount of the catalyst was 4 mol%.

°Reaction temperature was 40 °C

^dReaction was carried out in air.

eYields were determined by gas chromatography.

Attempts to lower the catalyst loading were also made and a satisfactory yield was obtained while increasing the dosage of bromobenzene to 4 equiv. (Table 1, entry 14). Finally, several control experiments were also conducted. The monometallic catalyst showed relatively low catalytic performance compared with the alloy catalyst (Table 1, entry 14 versus entry 15), which highlights the importance of synergistic effects between two components for catalytic performance. When it comes to the catalytic performance enhancement, we think an electronic effect is the main cause. Due to the difference in electronegativity between Pd and Ni, electron transfer on the catalyst surface was accelerated because of the formation of an alloy, which further accelerated the reaction process.^{34,35} Moreover, it is worth noting that the reaction did not proceed smoothly under air (Table 1, entry 16), which may be due to the oxidation of nickel in the alloy catalyst.

With the optimised reaction conditions in hand, we explored the functional group tolerance of the established catalytic system. As shown in Table 2, a series of aryl boronic acids with different substituents could react with bromobenzene, furnishing the corresponding products (3a-n) in outstanding yields. No obvious reactivity difference was observed between aryl boronic acids with electron-withdrawing groups and electron-donating groups. However, when considering the reactivity of the substituted bromobenzenes, electronic effects play a vital role in the reaction (3o-v). For aryl bromides with electron-withdrawing groups, reduced yields of the products were observed, but the reactions proceeded smoothly when aryl bromides with electron-donating groups were used as the reactants. Finally, reusability of the Pd–Ni/ZrO₂ alloy catalyst was also investigated using *p*-tolylboronic acid and bromobenzene as the reactants (5 mmol scale) under the optimised conditions (Table 1, entry 14). After the reaction, the catalyst was easily separated from the mixture by simple filtration and directly reused in the next cycle after washing with water and ethanol. The alloy catalyst could be reused up to four times without significant loss in catalytic performance: the excellent stability of the catalyst could be ascribed to the formation of alloys and the mild reaction conditions. A transmission electron microscope (TEM) image of the Pd–Ni/ZrO₂ alloy catalyst after five cycles (Fig. 2) also clearly indicates that the nanoparticles still have a good dispersion on the matrix and no obvious agglomeration was observed.

CLI

Conclusions

In summary, a supported Pd–Ni alloy catalyst was fabricated by an impregnation–reduction method. The as-prepared alloy catalyst displayed outstanding catalytic activity for Suzuki– Miyaura reactions and we think the excellent performance could be ascribed to good dispersion of nanoparticles and improved electron flow on the catalyst surface. This catalytic system showed an excellent functional groups tolerance; a series of arylboronic acids and bromobenzene derivatives were transformed into corresponding products in an efficient way. Moreover, the catalyst could be reused for four cycles without significant loss in catalytic performance. Based on the excellent catalytic performance of the alloy nanoparticles, it is reasonable to propose that alloy nanoparticles could be an important platform for catalyst development.



Table 2 Pd-Ni alloy catalyst Suzuki-Miyaura reactions between substituted bromobenzenes and aryl boronic acidsª

^aReaction conditions: arylboronic acid (0.15 mmol), bromobenzene (4 equiv.), Na₂CO₃ (1 equiv.), Pd₁Ni₄/ZrO₂ (4 mol%), EtOH (2 mL). The mixture was stirred under an N₂ atmosphere at 80 °C for 4h.

*See SAFETY CAUTION in Experimental.

^bProduct yields were determined by gas chromatography and gas chromatography-mass spectrometry.



100nm

Fig. 1 Recycling of $\rm Pd-Ni/ZrO_{2}$ alloy catalyst in the Suzuki-Miyaura reactions.

Fig. 2 TEM image of Pd-Ni/ZrO, alloy catalyst after five cycles.

Experimental

All chemical reagents were obtained from commercial suppliers and used without further purification. Gas chromatography-mass spectrometry (GC-MS) was performed on an ISQ Trace 1300 instrument in the electron ionisation (EI) mode. Helium was used as carrier gas at a constant flow of 1 mL min⁻¹. The following temperature programme was used: 70 °C for 0 min, heating rate 16 °C min-1, 300°C for 5.625 min, injection temperature 250 °C, detection temperature 300 °C. Gas chromatography (GC) analyses were performed on an Agilent 7890A instrument (Column: Agilent 19091J-413: 30 m × 320 µm × 0.25 µm, carrier gas: H₂, FID detection. Nitrogen was used as carrier gas at a constant flow of 0.4 mL min-1. The following temperature programne was used: 75 °C for 0 min, heating rate 15 °C min-1, 175 °C for 5 min, heating rate 15 °C min-1, 300 °C for 5 min, injection temperature 250 °C, detection temperature 300 °C. TEM images were obtained using a Philips Tecnai 12 microscope operating at 120 kV. SEM images were obtained on a field-emission scanning electron microscope (HITACHI S-4800) and EDS was performed using an X-Max EDS system (Oxford Instruments). All compounds were known, the structures of the products were analysed by GC-MS and confirmed by comparing the GC traces with those of commercially available products. ¹H NMR spectra of the isolated products were recorded on an AVANCE III Bruker spectrometer operating at 500 MHz and chemical shifts were reported in ppm.

Catalyst preparation

The nanocatalyst immobilised on ZrO_2 was prepared by the impregnation–reduction method and the composition of the bimetallic nanoparticles was controlled by adjusting the ratio of the metal precursors. In a typical procedure, Pd₁Ni₄ BMNPs supported on ZrO_2 were prepared as follows: ZrO_2 (400 mg) was dispersed into an aqueous solution (50 mL) of metal precursors (10 mg PdCl₂ and 53.5 mg NiCl₂·6H₂O) under ultrasonic radiation. Lysine aqueous solution (200 mg dissolved in 2 mL water) was then added to the mixture with vigorous stirring for 30 min. Then, NaBH₄ aqueous solution (0.05 M, 22 mL) was added dropwise to this suspension. The colour of the mixture turned to black immediately, indicating the formation of metal particles. The mixture was further stirred for 30 min and then aged for 24 h. Finally, the solid was separated, washed (with water and ethanol) and dried at room temperature under reduced pressure.

Suzuki-Miyaura reactions; typical procedure

In a typical reaction procedure, bromobenzene (0.4 mmol), 4-methylbenzeneboronic acid (0.1 mmol), Pd_1Ni_4/ZrO_2 alloy catalyst and Na_2CO_3 (1 equiv.) were added into a reactor (10 mL) equipped with a magnetic stirrer and EtOH (2 mL) was added as the solvent. The reaction mixture was stirred at 80 °C under an N_2 atmosphere for 4 h. After reaction, the catalyst was separated by simple filtration and the solution was analysed by GC and GC–MS. For isolation of the products, the solvent was removed under reduced pressure. The residue was purified by flash chromatography on a silica column, using ethyl acetate and *n*-hexane as the eluent.

The NMR data for the products agreed with the literature.

4-Methylbiphenyl (**3a**): White solid; m.p. 46–48 °C (lit.⁶ 46–47 °C); yield 99%; MS (EI) *m/z*: 168 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.49 (dd, *J* = 8.3, 1.3 Hz, 2H), 7.43–7.38 (m, 2H), 7.34 (t, *J* = 7.8 Hz, 2H), 7.24 (td, *J* = 7.2, 1.3 Hz, 1H), 7.16 (d, *J* = 7.9 Hz, 2H), 2.31 (s, 3H). See literature⁶ NMR data.

Biphenyl (**3b**): White solid; m.p. 68–70 °C (lit.⁶ 69–70 °C); yield 100%; MS (EI) m/z: 154 [M⁺]; ¹ H NMR (500 MHz, CDCl₃): δ 7.25 (2H, t), 7.35 (4H, t), 7.51 (d, 4H). See literature⁶ NMR data.

4-Biphenylcarbonitrile (**3c**): White solid; m.p. 86–87 °C (lit.⁷ 85–87 °C); yield 100%; MS (EI) *m/z*: 179 [M⁺]; ¹ H NMR (500 MHz, CDCl₃): δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.58 (d, *J* = 8.4 Hz, 2H), 7.45 (d, *J* = 7.6 Hz, 2H), 7.35 (t, *J* = 7.05 Hz, 2H), 7.29 (t, *J* = 7.2 Hz, 1H). See literature⁷ NMR data.

CAUTION: The manufacture and use for all purposes of the compound 4-nitrobiphenyl (**3d**) is prohibited in the UK by the Control of Substances Hazardous to Health (COSHH) regulations. Compound **3d** is a potent human carcinogen and the *Journal of Chemical Research* strongly advises against its preparation.

4-*Nitrobiphenyl* (**3d**): Yellow solid; m.p. 111–115 °C (lit.⁶ 112–114 °C); yield 94%; MS (EI) *m/z*: 199 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.36–7.44 (m, 3H), 7.50–7.53 (m, 2H), 7.56–7.65 (m, 2H), 8.14–8.22 (m, 2H). See literature⁶ NMR data.

4-Biphenylcarbaldehyde (**3e**): White solid; m.p. 59–61 °C (lit.⁶ 59–60 °C); yield 99%; MS (EI) m/z: 182 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.31 (t, 1H), 7.38 (t, 2H), 7.53 (d, 2H), 7.65 (d, 2H), 7.85 (d, 2H), 9.95 (s, 1H). See literature⁶ NMR data.

4-*Fluorobiphenyl* (**3f**): Grey solid; m.p. 73–75 °C (lit.³⁶ 73–74 °C); yield 94%; MS (EI) *m/z*: 172 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.59–7.53 (m, 4H), 7.46 (dd, J = 7.5 Hz, 7.0 Hz, 2H), 7.35 (t, J = 7.5 Hz, 1H), 7.12 (dd, J = 8.0 Hz, 7.5 Hz, 2H). See literature³⁶ NMR data.

4-*Chlorobiphenyl* (**3g**): White solid; m.p. 77–80 °C (lit.⁶ 78–79 °C); yield 98%; MS (EI) *m/z*: 188 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.63–7.58 (m, 2H); 7.56 (d, J = 8.2 Hz, 2H), 7.52–7.39 (m, 5H). See literature⁶ NMR data.

4-tert-*Butylbiphenyl* (**3h**): White solid; m.p. 49–51 °C (lit.¹⁴ 49–50 °C); yield 95%; MS (EI) *m/z*: 210 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.71 (d, *J* = 7.8 Hz, 2H), 7.67 (d, *J* = 8.1 Hz, 2H), 7.58 (d, *J* = 8.3 Hz, 2H), 7.52 (t, *J* = 7.6 Hz, 3H), 7.43 (q, *J* = 7.4 Hz, 1H), 1.48 (m, 9H). See literature¹⁴ NMR data.

3-Methoxybiphenyl (**3i**): Colourless oil; Yield 99%; MS (EI) m/z: 184 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 3.58 (s, 3H), 6.64 (dd, J = 8.2, 2.4 Hz, 1H), 6.88–6.95 (m, 2H), 7.06–7.12 (m, 2H), 7.15 (t, J = 7.2 Hz, 2H), 7.33 (d, J = 7.2 Hz, 2H). See literature¹⁵ NMR data.

3-Methylbiphenyl (**3j**): Colourless oil; yield 96%; MS (EI) *m/z*: 168 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.44 (d, *J* = 7.6 Hz, 2H), 7.29 (d, *J* = 7.2 Hz, 2H), 7.25 (d, *J* = 8.8 Hz, 2H), 7.19 (t, *J* = 6.8 Hz, 2H), 7.02 (d, *J* = 7.2 Hz, 1H), 2.28 (s, 3H). See literature¹⁵ NMR data.

3,5-Difluorobiphenyl (**3k**): Colourless liquid; yield 99%; MS (EI) m/z: 190 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 6.68 (tt, 1H), 6.96 (dd, 2H), 7.29 (t, 1H), 7.36 (t, 2H), 7.46 (d, 2H). See literature⁶ NMR data.

3,4-Dimethylbiphenyl (**3**I): Colourless liquid; yield 94%; MS (EI) m/z: 182 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 2.27 (s, 3H), 2.30 (s, 3H), 7.03 (d, J = 7.6 Hz, 1H), 7.12 (d, J = 7.6 Hz, 1H), 7.19 (t, J = 7.6 Hz, 1H), 7.26 (d, J = 12.8 Hz, 2H), 7.41 (t, J = 6.4 Hz, 3H). See literature¹⁶ NMR data.

2-Phenylnaphthalene (**3m**): White solid; m.p. 97–99 °C (lit.⁶ 97–99 °C); yield 100%; MS (EI) m/z: 204 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.26–7.34 (m, 1H), 7.37–7.43 (m, 4H), 7.61–7.68 (m, 3H), 7.75–7.82 (m, 3H), 7.94 (s, 1H) See literature⁶ NMR data.

4-Phenoxybiphenyl (**3n**): Colourless oil; yield 89%; MS (EI) *m/z*: 246 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.67–7.57 (m, 4H), 7.48 (dd, *J* = 10.5, 4.7 Hz, 2H), 7.44–7.35 (m, 3H), 7.21–7.08 (m, 5H); ¹³C NMR (126 MHz, CDCl3): δ 156.2, 155.9, 139.6, 136.5, 135.3, 129.3, 128.9, 127.8, 127.5, 126.4, 126.1, 125.9, 122.4, 118.1, 118.0. See literature¹⁷ NMR data.

4-Biphenylol (**30**): White solid; m.p. 163–165 °C (lit.⁷ 163–164 °C); yield 99%; MS (EI) *m/z*: 170 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 1.01 (br, 1H), 7.05–7.21 (m, 5H), 7.28 (d, *J* = 7.2 Hz, 2H), 7.37 (d, *J* = 8.8 Hz, 2H). See literature⁷ NMR data.

4-Methoxybiphenyl (**3p**): White solid; m.p. 85-87 °C (lit.⁶ 86–87 °C); yield 99%; MS (EI) *m/z*: 184 [M⁺]; ¹H NMR (500 MHz, CDCl₃) δ 3.75 (s, 3H), 6.87 (d, 2H), 7.19 (t, 1H), 7.31 (t, 2H), 7.41 (m, 4H). See literature⁶ NMR data.

4-Biphenylsulfonamide (**3q**): White solid; m.p. 221–223 °C (lit.¹⁸ 221–222 °C); yield 95%; MS (EI) *m/z*: 217 [M⁺]; ¹H NMR (500MHz, DMSO– d_{o}): δ 6.62 (2H, s), 7.27 (3H, m), 7.59 (2H, d), 7.70 (2H, d), 7.84 (2H, d). See literature¹⁸ NMR data.

2-Methylbiphenyl (**3r**): Colourless oil; yield 92%; MS (EI) m/z: 168 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.28 (t, J = 8.0 Hz, 2H), 7.19 (m, 3H), 7.12 (m, 4H), 2.13 (s, 3H). See literature¹⁵ NMR data.

6-Methyl-2-biphenylcarboxylic acid (**3s**): Yellow solid; m.p. 157.0–158 °C (lit.³⁷ 157–158.1 °C); yield 99%; MS (EI) *m/z*: 212 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 7.78 (d, *J* = 7.8 Hz, 1H), 7.44 (d, *J* = 7.7 Hz, 1H), 7.38 (tt, *J* = 8.0, 1.9 Hz, 2H), 7.34 (dt, *J* = 7.3, 1.6 Hz, 1H), 7.32 (t, *J* = 7.7 Hz, 1H), 7.15 (dd, *J* = 8.1, 1.4 Hz, 2H), 2.09 (s, 3H). See literature³⁷ NMR data.

CAUTION: The manufacture and use for all purposes of the compound 4-aminobiphenyl (**3t**) is prohibited in the UK by the Control of Substances Hazardous to Health (COSHH) regulations. Compound **3t** is a potent human carcinogen and the Journal of Chemical Research strongly advises against its preparation.

4-Aminobiphenyl (**3t**): Colourless oil; yield 95%; MS (EI) *m/z*: 169 [M⁺]; ¹H NMR (500 MHz, CDCl₃): δ 3.53 (s, 2H), 6.58 (d, *J* = 8.4 Hz, 2H), 7.11 (d, *J* = 7.2 Hz, 1H), 7.27 (m, 4H), 7.39 (d, *J* = 7.2 Hz, 2H); ¹³C NMR (125 MHz, CDCl₃): δ 114.3, 125.2, 125.3, 126.9, 127.6, 130.5, 140.1, 144.8. See literature¹⁵ NMR data.

3-Biphenylmethanol (**3u**): White crystals; m.p. 51–53 °C (lit.¹⁹ 51.2–51.5 °C); yield 96%; MS (EI) m/z: 184 [M⁺]; ¹H NMR (400 MHz, CDCl₃): δ 7.68 (s, 1H), 7.49–7.41 (m, 2H), 7.32–7.28 (m, 3H), 7.28–7.14 (m, 3H), 4.38 (s, 2H, CH₂), 2.76 (s, 1H, OH). See literature¹⁹ NMR data.

4-Biphenylcarboxylic acid (**3v**): White solid; m.p. 224–228 °C (lit.⁶ 224–226 °C); yield 97%; MS (EI) m/z: 198 [M⁺]; ¹H NMR (500 MHz, DMSO- d_6): δ 12.82 (s, 1H), 7.88 (d, 2H), 7.65 (d, 2H), 7.59 (d, 2H), 7.36 (t, 2H), 7.29 (t, 1H). See literature⁶ NMR data.

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