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1-(α-Aminobenzyl)-2-naphthol as phosphine-free ligand for Pd-catalyzed Suzuki and one-pot Wittig-Suzuki reaction

A. R. Chaudhary and A. V. Bedekar*

Air stable and easily accessible, 1-(α-aminobenzyl)-2-naphthols are used as efficient phosphine-free ligands in palladium-catalyzed Suzuki reaction for a variety of substrates under conventional heating as well as ultrasonic conditions. Multi-brominated aromatic substrates were successfully converted to corresponding arylated moieties with good conversion and selectivity. A novel one-pot two-step cascade reaction strategy involving Wittig and Suzuki reactions is developed for efficient synthesis of 4-styryl biphenyls (C_6-C_2-C_6-C_6 unit). Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: 1-(α-aminobenzyl)-2-naphthols; phosphine-free Suzuki reaction; homogeneous palladium catalysis; one-pot Wittig–Suzuki reaction

Introduction

Palladium-catalyzed cross-coupling reactions,[1a,b] via Suzuki,[1c-j] Heck,[1k] Stille,[1l,m] Negishi[1n,1o] and Sonogashira[1p,q] protocols are powerful methods for C-C bond formation. The palladium-catalyzed Heck and Suzuki reactions have been used extensively for the synthesis of natural products, pharmaceutical intermediates, conducting polymers, pesticides and liquid crystals.[2–5] The significance of palladium catalysis and cross-coupling reactions has been acknowledged by the award of a Nobel Prize for Chemistry in 2010 to scientists who carried out pioneering work in this area.

The Suzuki reaction is proving to be an increasingly popular tool for the construction of unsymmetrical biaryls. It represents an attractive alternative to other methods using organometallic reagents as organoboranes are air and moisture stable and with relatively low toxicity.[1d,g,3a] These reactions, normally performed with 1–5 mol% of Pd catalyst along with equal or higher molar amounts of phosphine ligands, still suffer from two significant problems.[6a] Firstly, palladium is expensive and its contamination has to be particularly regulated in the case of consumption for biological systems. Secondly, many phosphine ligands are not readily available, and are not simple to work with owing to their poisonous character, air sensitivity and ease of degradation. However, most of these catalysts containing phosphines are generally sensitive to moisture and air, and require air-free conditions to minimize oxidation. Moreover, their large-scale application is limited in industry owing to their high cost and toxic nature[6b].

These reasons offer an option to develop Pd catalysts that can utilize inexpensive phosphine-free ligands. In this endeavor, a number of nitrogen donor ligands such as imine,[7a] oxime,[7b–d] diazabutadiene derivatives,[7e] bis(pyrimidine),[8] *N*-heterocyclic carbenes (NHC),[9] oxazolines,[10] amines,[11] Schiff bases,[12] pyridines,[13] hydrazones,[14] guanidines,[15] pyrazoles,[16] tetrazoles,[17] quinolines,[18] carbazones,[19] imidazoles,[20] thioureas,[21] and 1,3-dicarbonyl compounds[22] have been examined for palladium-catalyzed reactions.

Suzuki coupling for the production of biaryls has been applied under microwave[23] or ultrasonic irradiation.[24] Both conditions, in general, lead to reduction of reaction time and can offer some advantages.

Recently an application of 1-(α-aminobenzyl)-2-naphthols as air-stable phosphine-free ligands for the palladium-catalyzed Mizoroki–Heck coupling reaction has been reported.[25] The results obtained prompted us to extend our studies towards the palladium-catalyzed Suzuki coupling reactions. To the best of our knowledge, applications of 1-(α-aminobenzyl)-2-naphthols–Pd catalyst for Suzuki coupling reaction have not been developed.

Result and Discussion

A series of 1-(α-aminobenzyl)-2-naphthols **1** were prepared from 2-naphthols by aromatic Mannich reaction[25,26] and screened as a ligand for Suzuki reaction. The product **1** (Scheme 1), a derivative of Betti base,[27] and some analogous molecules have been investigated from different aspects of stereoselective transformations.[28]

The amino phenol of type **1** has a suitable arrangement of heteroatoms to form a six-membered stable chelate, a prerequisite for application as a ligand in metal-catalyzed reactions. Some examples of the applications of **1** as a ligand in catalytic reactions are available in the literature.[25,29–34] One of the basic types of reactivity in palladium-driven catalytic cycles is due to the ability of Pd(0) species to undergo oxidative addition to various C-X bonds. The ligand **1** stabilizes the Pd catalysts via formation of Pd(0) species and thus accelerates coupling in the reaction.

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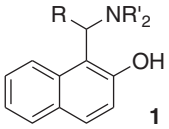
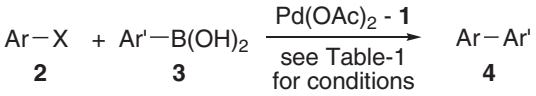


Scheme 1. General structure of the ligand for the present study



Scheme 2. Typical Suzuki–Miyaura reaction

A small group of these ligands **1a–d** were prepared with corresponding 2° amine, benzaldehyde and 2-naphthol for this study (Fig. 1).

The ligands were screened to determine standard reaction conditions for the Suzuki–Miyaura reaction with aryl halides and aryl boronic acids in the presence of a suitable base (Scheme 2). The results are presented in Table 1.

The results of the study of Suzuki–Miyaura coupling indicate very efficient conversion with aryl iodides and aryl bromides with a small quantity of tetra-*n*-butylammonium bromide (TBAB) when aqueous dioxane was used as solvent. Chlorobenzene was considerably less reactive after a long reaction time but iodobenzene gave biphenyls with good conversion amounts even with very low catalyst quantity. Variation of the amount of catalyst to as low as 0.01 mol% of Pd resulted in the formation of biphenyl in high yield and turnover number (TON).

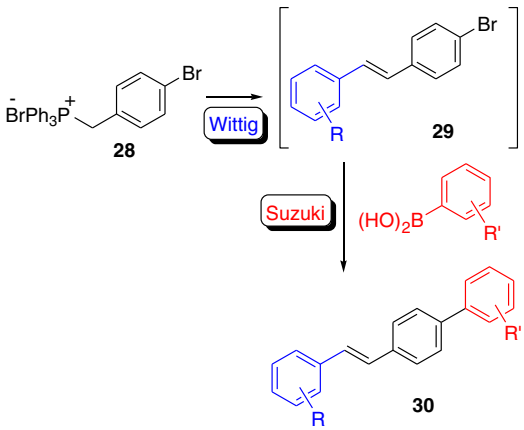
The efficacy of different ligands was ascertained by separate experiments (Table 1, entries 1, 2, 4 and 5). It was found that in the absence of any ligand, only $Pd(OAc)_2$ (Table 1, entry 3) could catalyze the Suzuki reaction, but the yield of biphenyl was low (20%). The reaction with ligand **1c** under controlled conditions increased the yield to 96% (Table 1, entry 4), clearly indicating the role of the ligand. Similarly, reaction carried out at room temperature (with neither heating nor sonication) gave the biphenyl in very poor yield (Table 1, entry 9), indicating the effect of ultrasonic irradiation.

The method of using readily accessible ligands was further extended for a number of examples (Table 2). A series of different biaryls **5–13** were prepared by using a ligand–Pd ratio (1/$Pd(OAc)_2$) of 0.12/0.10 mol%), while for dibromo, tribromo and tetrabromo substrates a higher ratio of phenylboronic acid and catalyst was needed. The method worked well for a series of compounds, establishing the generality of the present ligand system for the Suzuki–Miyaura coupling reaction.

The present reaction system was then investigated under ultrasonic/sonication conditions. The reaction was conducted in a normal cleaning immersion sonication bath and the reaction medium was agitated by a mechanical stirrer. Care was taken to maintain the bath temperature below 40°C by careful water circulation. A wide variety of substrates and boronic acids were used for Suzuki–Miyaura coupling under sonication and the results are summarized in Table 3.

The strategy for cascade reactions involved carrying out a sequence of transformations in which the product of the first step serves as the substrate for the second step. The process involved a number of steps until finally a stable product was formed. The cascade reaction reduces the consumption of reagents, number of purifications and shortens reaction time, contributing to better economy of the chemical process. Many combinations of different bond-making processes are combined for cascade reactions with reasonable success.[35] One-pot synthesis of stilbenes by dehydrohalogenation–Heck olefination and multi-component Wittig–Heck reaction was recently accomplished by the present authors.[10d] Cascade reactions involving Suzuki reaction as one of the steps have been reported in the literature, although almost all involve phosphine-based catalyst systems.[2e, 36–50] A few examples of double Suzuki reactions have been reported in which excellent control for two different reagents was achieved.[51] In this paper, the present authors report the initial efforts to apply this phosphine-free Pd catalyst system for a one-pot combination of Wittig and Suzuki–Miyaura coupling reactions. Very few references are reported in the literature describing an organophosphine-catalyzed one-pot Wittig–Suzuki reaction sequence with formylareneboronic acid[52] where the formyl group undergoes an olefination reaction. A case of one-pot Wittig–Suzuki reaction utilizing a phosphine-free catalyst system has not been reported.

The essential requirement of planning any one-pot multi-step reaction is the compatibility of the reagent system and reaction conditions. The stability of the phosphonium salt, while still reactive towards carbonyl groups, under a number of different reaction conditions offers the opportunity to combine the Wittig olefination reaction with another transformation in a one-pot procedure. Phosphonium salt **28** was prepared from 4-bromobenzyl bromide and triphenyl phosphine as the component which can undergo Suzuki coupling at its Ar-Br site. A separate aldehyde has been chosen to receive its carbanion/ylide for the olefination reaction. This approach is outlined in Scheme 3 considering the



Scheme 3. One-pot approach for synthesis of styryl biphenyls

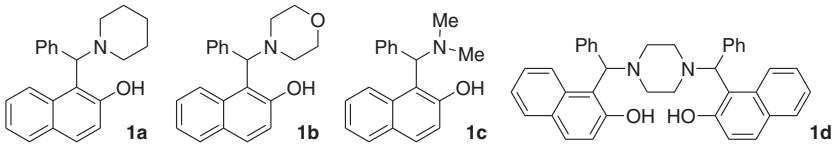


Figure 1. List of ligands for the present study

Table 1. Search for suitable conditions for Suzuki reaction with 1-(α-aminobenzyl)-2-naphthols **1** as ligand

Entry	PhX, X (mol eq.)	**1** ($Pd(OAc)_2$/ligand mol% ratio)	Temperature (°C) [Time (h)]	Yield (% of Ph–Ph) [TON]
1	**2c**, I	**1a**	95	92
	(1.0)	(0.1/0.12)	[4]	[920]
2	**2c**	**1b**	95	89
	(1.0)	(0.1/0.12)	[4]	[890]
3	**2c**	**1c**	95	20
	(1.0)	(0.1/0.00)	[4]	[200]
4	**2c**	**1c**	95	96
	(1.0)	(0.1/0.12)	[4]	[964]
5	**2c**	**1d**	95	85
	(1.0)	(0.1/0.12)	[4]	[854]
6	**2b**, Br	**1c**	95	82[a]
	(1.0)	(0.1/0.12)	[20]	[629]
7	**2a**, Cl	**1c**	95	26[a]
	(1.0)	(0.1/0.12)	[30]	[146]
8	**2c**	**1c**	95	93
	(1.0)	[0.01:0.012]	[24]	[9390]
9	**2c**	**1c**	r.t.	10
	(1.0)	(0.1/0.12)	[2]	[100]
10	**2c**	**1c**	Sonication	60
	(1.0)	(0.1/0.12)	Temp. ≤ 40 °C [2]	[603]
11	**2c**	**1c**	Sonication	70
	(1.0)	(0.5/0.60)	Temp. ≤ 40 °C [2]	[140]

All reactions in dioxane–water (1:1) with phenyl boronic acid (1.2 equiv.), K_2CO_3 (2.0 equiv.).
[a]With TBAB (20 mol%).

example of the *in situ* Wittig synthesis of stilbene and then the Suzuki reaction to form 4-styryl biphenyl. A similar class of molecules was synthesized by one-pot Heck–Suzuki sequence by Gruber *et al.*[36e]

In order to effectively carry out our practical one-pot strategy it was necessary to establish the efficacy of the solvent for both steps. It was also important to check whether the ratio of *Z* and *E* isomers was affected in the second step. To confirm this aspect an experiment was conducted in which the product 4-bromo stilbene **29** was separated and characterized. The ratio of *Z*:*E* isomer of **29** was established by ^{1}H-NMR analysis to be 48:52 and the isolated yield was 72%. The product **29** was then subjected to a separate step under Suzuki reaction conditions and the final product **30** was isolated in 67% yield, with a *Z*:*E* ratio of 50:50. Both steps were carried out in same solvent (anhydrous DMA) and the ratio of isomers was almost the same, indicating the compatibility of solvent and also establishing that negligible isomerization occurred in the second step of the one-pot sequence.

The overall reaction sequence involved three components or variables, although presently **28** has been used as the common element. By varying the other two components a series of styryl biphenyls were synthesized and the results are presented in Table 4.

The Wittig olefination reaction of aromatic aldehyde with phosphonium salt **28** took place even in the presence of a weak base like potassium carbonate (3 equiv.) in DMA under inert atmosphere at 130°C initially to form **29**, an intermediate 4-bromostilbene. Boronic acid (1.2 equiv.), potassium carbonate (2 equiv.), a catalytic quantity of $Pd(OAc)_2$–ligand **1c**, and TBAB as phase transfer catalyst were added after 6 h and the reaction mixture was continued to completion. In all cases, the *Z* isomer of stilbene derivatives **30** were obtained in excess in Wittig olefination.[53] The *Z*:*E* isomer ratios were close to ~55:45, except for product 4-nitrostyryl biphenyl **34**, where the nitro group controls the ratio in favor of the *E* isomer.

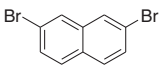
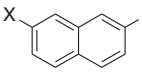
Experimental

Reagents were purchased from Sigma-Aldrich Chemicals Ltd, SD Fine, Qualigens Limited, etc. Thin-layer chromatography (TLC) was performed on Merck 60 F_{254} aluminium-coated plates. The spots were visualized under UV light or with iodine vapor. All the compounds were purified by column chromatography using silica gel (60–120 mesh). The ligands **1** were prepared by the general process[25] and characterized by usual spectral analysis before being used for the present work. All the products were characterized by ^{1}H-NMR IR, mass spectroscopy and by comparison of melting point with the reported values. ^{1}H-NMR spectra were recorded on a Bruker Avance 400 Spectrometer and were run in $CDCl_3$. Mass spectra were recorded on a Thermo Fisher DSQ II GCMS instrument. IR spectra were recorded on a PerkinElmer FTIR RXI spectrometer as KBr pallets. Melting points were recorded in Thiele's tube using paraffin oil and are uncorrected.

Typical Experimental Procedure for the Suzuki Reaction under Conventional Conditions (in Thermal Condition)

To an oven-dried two-necked round-bottom flask equipped with a stirrer bar was charged 4-iodoanisole (0.25 g, 1.07 mmol), potassium carbonate (0.295 g, 2.14 mmol), palladium acetate (0.24 mg,

Table 2. Application of 1-(α-aminobenzyl)-2-naphthols **1** as ligand for palladium-catalyzed Suzuki–Miyaura reaction with phenylboronic acid,*with *o*-tolylboronic acid.

Entry	ArX	$Pd(OAc)_2$–**1** [mol% ratio]	Temp. (°C) [Time (h)]	Ar–Ar′ [Yield (%)]
1	C_6H_5I	**1c** [0.1/0.12]	95 [4]	C_6H_5-C_6H_5 **4** [96]
2	4-$MeOC_6H_4I$	**1c** [0.1:0.12]	95 [4]	4-$MeOC_6H_4$–C_6H_5 **5** [98]
3	$AcHNC_6H_4I$	**1c** [0.1:0.12]	95 [8]	$AcHNC_6H_4$–C_6H_5 **6** [98][a]
4	4-$NO_2C_6H_4Br$	**1c** [0.1:0.12]	95 [15]	4-$NO_2C_6H_4$–C_6H_5 **7** [89]
5	3-$NO_2C_6H_4Br$	**1a** [0.1:0.12]	95 [15]	3-$NO_2C_6H_4$–C_6H_5 **8** [81]
6	4-$CH_3COC_6H_4Br$	**1a** [0.1:0.12]	95 [15]	4-$CH_3COC_6H_4$–C_6H_5 **9** [90]
7	1,2-$Br_2C_6H_4$	**1c** [0.1:0.12]	95 [15]	2-BrC_6H_4–C_6H_5 **10** [24] 1,2-$Ph_2C_6H_4$ **11** [68]
8		**1c** [0.1:0.12]	95 [15]	 **12**, X = Br [20] **13**, X = Ph [77]
9	2-MeC_6H_4I	**1c** [0.5:0.6]	95 [15]	2-MeC_6H_4–C_6H_5 **14** [94]
10	2-MeC_6H_4I	**1c** [0.5:0.6]	95 [15]	2-MeC_6H_4–2′-MeC_6H_4 **15** [96]*
11	1,2-$Br_2C_6H_4$	**1c** [2:2.2]	95 [24]	2-BrC_6H_4–Ar **16** [24][a,c*] 1,2-Ar_2–C_6H_4 **17** [74][a,c*] Ar = 2-MeC_6H_4
12	1,3,5-$Br_3C_6H_3$	**1c** [3:3.3]	95 [15]	1,3,5-$Ph_3C_6H_3$ **18** [89][a,c]
13	1,3,5-$Br_3C_6H_3$	**1c** [3:3.3]	95 [15]	1,3,5-$Ar_3C_6H_3$ **19** [86][a,c*] Ar = 2-MeC_6H_4
14	1,2,4,5-$Br_4C_6H_2$	**1c** [4:4.4]	95 [40]	1,2,4,5-$Ph_4C_6H_2$ **20** [90][a,a]

All reactions in dioxane-water (1:1) with K_2CO_3 (2.0 eq); [a]With TBAB (20% per halogen atom); [a]Dioxane-H_2O (2:1); [c]Dioxane-H_2O (3:1).

0.001 mmol) and **1c** (0.356 mg, 0.0013 mmol) in dioxane–water (1:1). To this reaction mixture phenylboronic acid (0.156 g, 1.28 mmol) was added. The reaction mixture was heated at 95 °C for 4 h. Following confirmation of consumption of the starting material by TLC, the reaction mixture was quenched with water and extracted with ethyl acetate (3 × 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel to afford 4-methoxybiphenyl **5** (0.194 g, 98%) (Table 2, entry 2).

General Procedure for the Suzuki Reaction under Sonochemical Conditions (in Ultrasonication)

To the mixture of iodobenzene (0.05 ml, 0.447 mmol), palladium acetate (0.5 mg, 0.002 mmol), **1c** (0.74 mg, 0.002 mmol), and potassium carbonate (0.185 mg, 1.34 mmol) in dioxane–water (1:1) was added 3-(hydroxymethyl)phenyl boronic acid (0.082 g, 0.536 mmol). The reaction mixture was then sonicated for the time mentioned in Table 3. The progress of the reaction was monitored by TLC. After completion of the reaction, the reaction mixture was quenched with water and extracted with ethyl acetate (3 × 25 ml). The combined organic phase was washed with water and dried over anhydrous sodium sulfate. Solvent was removed under vacuum and the crude product was purified by column chromatography on silica gel to afford 3-(hydroxymethyl)biphenyl **27** (0.078 g, 95%) (Table 3, entry 13).

Representative Procedure for the One-Pot Wittig–Suzuki Reaction

*4-(Chlorostyryl)biphenyl (**32**) (Table 4)*

In a dry N_2-flushed two-necked round-bottom flask a mixture of 4-chlorobenzaldehyde (0.2 g, 1.423 mmol), (4-bromobenzyl)triphenylphosphonium bromide **28** (0.729 g, 1.423 mmol) and dry potassium carbonate (0.59 g, 4.268 mmol) in dry *N*,*N*-dimethylacetamide (5 ml) was placed and kept under N_2 atmosphere. The reaction was heated to 130°C for 6 h and then phenylboronic acid (0.208 g, 1.707 mmol), potassium carbonate (0.393 g, 2.845 mmol), TBAB (0.092 g, 0.284 mmol), palladium acetate (3.19 mg,

Table 3. Application of **1c** as ligand for palladium-catalyzed Suzuki–Miyaura reaction under sonication

Entry	Ar-X	Ar-B(OH)$_2$ (mol. equiv.)	Pd(OAc)$_2$–**1c** [mol % ratio]	Temp. ≤ 40 °C [Time (h)]	Ar–Ph [Yield (%)]
1	4-$NO_2C_6H_4Br$	$C_6H_5B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[5]	4-$NO_2C_6H_4$–C_6H_5 **7** [89]
2	3-$NO_2C_6H_4Br$	$C_6H_5B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[5]	3-$NO_2C_6H_4$–C_6H_5 **8** [86]
3	4-$CH_3COC_6H_4Br$	$C_6H_5B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[4]	4-$CH_3COC_6H_4$–C_6H_5 **9** [84]
4	C_6H_5I	2-Me-$C_6H_4B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[5]	2-Me-C_6H_4–C_6H_5 **14** [66]
5	4-$NO_2C_6H_4Br$	2-Me-$C_6H_4B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[5]	4-$NO_2C_6H_4$–Ar **21** [90] Ar = 2-MeC_6H_4
6	4-$CH_3COC_6H_4Br$	2-Me-$C_6H_4B(OH)_2$ (1.2 eq.)	[0.5:0.6]	[5]	4-$CH_3COC_6H_4$–Ar **22** [94] Ar = 2-MeC_6H_4
7	4-$CHOC_6H_4Br$	$C_6H_5B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[7]	4-$CHOC_6H_4$–C_6H_5 **23** [89]
8	1,2-$Br_2C_6H_4$	$C_6H_5B(OH)_2$ (4.0 equiv.)	[1:1.2]	[5]	2-BrC_6H_4–C_6H_5 **10** [10][a] 1,2-$Ph_2C_6H_4$ **11** [87][a]
9	1,4-$Br_2C_6H_4$	$C_6H_5B(OH)_2$ (4.0 equiv.)	[1:1.2]	[5]	4-BrC_6H_4–C_6H_5 **24** [27][a] 1,4-$Ph_2C_6H_4$ **25** [52][a]
10	1,3,5-$Br_3C_6H_3$	$C_6H_5B(OH)_2$ (6.0 eqiov.)	[3:3.3]	[5]	1,3,5-$Ph_3C_6H_3$ **18** [91][a]
11	C_6H_5I	4-$CHOC_6H_4B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[4]	4-$CHOC_6H_4$–C_6H_5 **23** [57]
12	C_6H_5I	3-$HOC_6H_4B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[4]	3-HOC_6H_4–C_6H_5 **26** [92][b]
13	C_6H_5I	3-$HOCH_2C_6H_4B(OH)_2$ (1.2 equiv.)	[0.5:0.6]	[4]	3-$HOCH_2C_6H_4$–C_6H_5 **27** [95][b]

All reactions run in dioxane–water (1:1) with K_2CO_3 (2.0 equiv.).
[a]With TBAB (20% per halogen atom).
[b]With K_2CO_3 (3.0 equiv.).

0.014 mmol) and **1c** (4.71 mg, 0.017 mmol) were added and again heated to 130°C for 24 h. The reaction mixture was added to 20 ml of water and extracted with ethyl acetate (3 × 25 ml). The combined organic layer was washed with water (2 × 20 ml), dried with anhydrous sodium sulfate and concentrated under vacuum. The residue was purified by flash chromatography on silica gel to give the desired product 4-(chlorostyryl)biphenyl **32** (0.33 g, 80%) (Table 4, entry 2).

Analytical and spectral data for new compounds are reported in Table 4.

4-Styrylbiphenyl (**31**) (Table 4, entry 1). Yield 0.34 g (56%); *Z*:*E* = 55:45; m.p. 64–66 °C (*Z* isomer), 216–218°C (*E* isomer) (lit.[54,55] 209°C).

4-[2-(4-Chlorophenyl)vinyl]biphenyl (**32**) (Table 4, Entry 2). Yield: 0.33 g (80%); *Z*:*E* = 57:43; m.p. 100–102°C (*Z* isomer), 242–244°C (*E* isomer).[56]

2-Methyl-4′-styrylbiphenyl (**33**) (Table 4, entry 3). Yield 0.42 g (63%); *Z*:*E* = 59:41; m.p. 74–76 °C. IR (KBr): ν 3054, 3020, 2951, 2922, 1950, 1915, 1598, 1574, 1510, 1481, 1447, 1409, 1379, 1326, 1305, 966, 762, 729, 692 cm^{-1}. Anal. Calcd for $C_{21}H_{18}$: C, 93.29; H, 6.73. Found: C, 93.39; H, 6.79%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.35 (s, 3 H), 7.20 (s, 2 H), 7.28–7.32 (m, 5 H), 7.36–7.43 (m, 4 H), 7.57–7.62 (m, 4 H) (for *E* isomer). ^{13}C NMR ($CDCl_3$) δ 20.6, 20.63, 125.86, 125.92, 126.31, 126.6, 127.21, 127.3, 127.39, 127.71, 128.33, 128.4, 128.67, 128.74, 128.78, 128.94, 129.13, 129.65, 129.8, 130.01, 130.36, 130.45, 130.49, 135.36, 135.42, 135.7, 135.91, 137.42, 140.77, 141.35, 141.56, 141.6 (for mixture of *Z* and *E*). Mass (EI): 271.1 (21), 270.07 (100), 255.05 (12), 179 (12), 178 (14), 152.01 (3), 91 (3).

4-[2-(4-Nitrophenyl)vinyl]biphenyl (**34**) (Table 4, entry 4). Yield 0.307 g (77%); *Z*:*E* = 9 : 91; m.p. 212–214°C (lit.[57,58] 216–218°C).

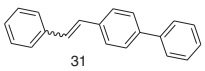
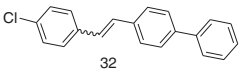
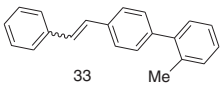
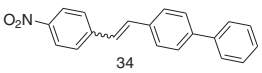
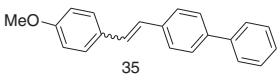
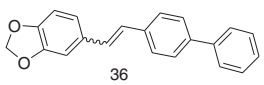
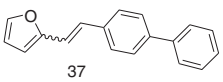
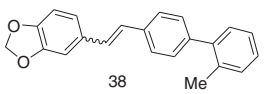
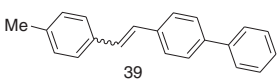
4-[2-(4-Methoxyphenyl)vinyl]biphenyl (**35**) (Table 4, entry 5). Yield for compound 35 is = 0.30 g (64%) ; *Z*:*E* = 55:45; m.p. 234–236 °C (lit.[59,60] 236–236.5°C).

5-(2-Biphenyl-4-ylvinyl)benzo[1, 3]dioxole (**36**) (Table 4, entry 6). Yield 0.29 g (73%); *Z*:*E* = 55:45; m.p. 176–178°C (lit.[60] 188–189°C).

2′-(2-Biphenyl-4-ylvinyl)furan (**37**) (Table 4, entry 7). Yield 0.28 g (55%); *Z*:*E* = 38:62 (tentatively established by ^{1}H-NMR compound was unstable); m.p. 134–136°C. IR (KBr): ν 3028, 2922, 1951, 1776, 1749, 1698, 1599, 1556, 1485, 1408, 1326, 1257, 963, 735, 693 cm^{-1}. Anal. Calcd for $C_{18}H_{14}O.1/4H_2O$: C, 86.2; H, 5.63. Found: C, 86.3; H, 4.95%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 6.36–6.54 (m, 2 H), 6.97 and 7.10 (two d, *J* = 16 Hz), 7.36–7.67 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 108.76, 111.74, 116.55, 126.63, 126.78, 126.93, 127.01, 127.36, 127.39, 128.85, 129.25, 136.09, 140.27, 140.66, 142.24, 153.31 (for mixture of *Z* and *E*). Mass (EI): 247.05 (19), 246.04 (100), 245.05 (16), 217.04 (30), 202.02 (22), 169.01 (4), 152.02 (3).

5-[2-(2′-Methylbiphenyl-4-yl)vinyl]benzo[1,3]dioxole (**38**) (Table 4, entry 8). Yield 0.28 g (67%); *Z*:*E* = 56:44; m.p. 94–96°C. IR (KBr): ν 3018, 2952, 1926, 1630, 1600, 1503, 1487, 1444, 1356, 1313,

Table 4. One-pot Wittig olefination–Suzuki coupling reaction variation of boronic acid and aldehyde components

No	Aldehyde (1.0 equiv.)	Boronic acid (1.2 equiv.)	Product	Yield[a] (%) (*Z*:*E* ratio)	m.p.[c] (°C) (lit. m.p.)[ref.]
1	C_6H_5CHO	$C_6H_5B(OH)_2$	 31	56 (55 : 45)	216–218 (209)[54]
2	4-ClC_6H_4CHO	$C_6H_5B(OH)_2$	 32	80 (57 : 43)	242–244 (NA)[56]
3	C_6H_5CHO	2-$MeC_6H_4B(OH)_2$	 33	63 (59 : 41)	74–76 (NA)
4	4-$NO_2C_6H_4CHO$	$C_6H_5B(OH)_2$	 34	77 (9 : 91)	212–314 (216–218)[57,58]
5	4-$MeOC_6H_4CHO$	$C_6H_5B(OH)_2$	 35	64 (55 : 45)	234–236 (236–236.5)[59]
6	Piperonal	$C_6H_5B(OH)_2$	 36	73 (55:45)	176–178 (188)[60]
7	Furfural	$C_6H_5B(OH)_2$	 37	55 (38:62)[b]	134–136 (NA)
8	Piperonal	2-$MeC_6H_4B(OH)_2$	 38	67 (56:44)	94–96 (NA)
9	4-MeC_6H_4CHO	$C_6H_5B(OH)_2$	 39	77 (55:45)	214–216 (219–220)[61]

All reactions run with aldehyde (1 equiv.), phosphonium salt **28** (1 equiv.), boronic acid (1.2 equiv.), K_2CO_3 (5.0 equiv.), TBAB (20%), $Pd(OAc)_2$ (1%), **1c** (1.2%) in DMA at 130 °C for 30 h.

[a]Isolated. *cis*:*trans* ratio determined by ^{1}H-NMR.

[b]Tentatively established by ^{1}H-NMR; compound was unstable.

[c]For *E* isomer.

1260, 1100, 1042, 968, 941, 851, 735, 612 cm^{-1}. Anal. Calcd For $C_{22}H_{18}O_2.1/4(H_2O)$: C, 82.86; H, 5.69. Found: C, 83.02; H, 5.3%. ^{1}H-NMR (400 MHz, $CDCl_3$) δ 2.32 and 2.33 (two s, 3 H, $-CH_3$ of *Z* and *E* isomers), 5.96 and 6.01 (two s, 2 H, $-CH_2-$ of *Z* and *E* isomer), 6.55 and 6.56 (two d, J = 12.4 Hz, 2 H), 6.69–6.85 (m, 1 H), 6.98–7.63 (m, 10 H). ^{13}C NMR ($CDCl_3$) δ 20.57, 29.75, 100.97, 101.18, 105.56, 108.26, 108.48, 108.95, 121.54, 122.97, 125.82, 125.86, 126.05,126.27, 126.67, 127.26, 127.31, 128.37, 128.58, 128.63, 128.99, 129.15, 129.59, 129.63, 129.76, 129.78, 129.89, 130.4, 130.43, 131.27, 131.94, 135.35, 135.39, 135.73, 135.95, 140.66, 141.04, 141.54, 141.57, 146.69, 147.36, 147.43, 148.2 (for mixture of *Z* and *E*). Mass (EI): 315.09 (24), 314.07 (100), 239.04 (15), 165.01 (12).

4-[2-(4-Methylphenyl)vinyl]biphenyl (**39**) (Table 4, entry 9). Yield 0.52 g (77%), *Z*:*E* = 55:45; m.p. of pure *E* isomer 214–216°C (lit.[61,62] 219 °C).

Conclusion

In this communication we have reported applications of 1-(α-aminobenzyl)-2-naphthols as air-stable phosphine-free

ligands for palladium-catalyzed Suzuki–Miyaura reaction and extended the study with development of a one-pot strategy for the combination of Wittig olefination and Suzuki–Miyaura coupling reaction to offer easy access to styryl biphenyls (C_6-C_2-C_6-C_6 unit). Such reactions carried out in one-pot or under cascade conditions reduce consumption of reagents such as solvent, save energy and offer many advantages which can make this a greener process.

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