



REGULAR ARTICLE

An unsymmetrical Schiff-base derived recyclable Pd-catalyst for Suzuki–Miyaura and Sonogashira reactions in aqueous media

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MS received 4 November 2020; revised 20 February 2021; accepted 23 March 2021

Abstract. A water-soluble palladium (II) complex containing an unsymmetrical Schiff-base ligand was synthesized and applied as catalyst Suzuki–Miyaura and Sonogashira cross-coupling reactions in aqueous media. Notably, moderate to excellent yields of biaryls were obtained in Suzuki reaction with usually less reactive aryl and heteroaryl chlorides under relatively mild condition. Moderate-to-high yields of aryl-alkynes were also obtained in Sonogashira reactions using aryl bromides. Apart from hydrophilic nature, the accomplishment of reactions in water, high recyclability, broad functional group tolerance, etc., are other advantages of the system.

Keywords. Water-soluble catalyst; Palladium; Unsymmetrical Schiff-base; Suzuki–Miyaura reaction; Sonogashira reaction.

1. Introduction

In the past decades, multidentate Schiff-base derived homogeneous palladium catalysts have gained enormous interests in carbon-carbon bond formation reactions such as Suzuki,^{1,2} Sonogashira,^{3,4} Heck,^{5–7} etc. Such ligands, by virtue of their low cost, easy synthetic accessibility and air and moisture sensitive properties, have the potentiality to act as a sustainable alternative to conventional phosphines in cross-coupling reactions.⁸ Moreover, like phosphines, the stereo-electronic properties in Schiff-bases can also be fine-tuned by properly selecting the condensing partners.⁹ Until now, most of Schiff-base related studies for cross-coupling reactions are confined with symmetric functionalization of diamines, where the ligands were synthesized *via* a double-condensation reaction between a symmetrical diamine with two equivalents of aldehydes, mostly salicylaldehyde.^{10,11} However, from a catalytic perspective, unsymmetrical Schiff-bases are more intriguing, and there are literature precedents available, at least in some cases with non-palladium systems,^{12,13} where unsymmetrical Schiff-bases exhibited superior activity and selectivity

compared to their symmetrical counterparts.¹⁴ Nevertheless, there also exist a few isolated cases of unsymmetrical Schiff-base ligands in Pd-catalyzed cross-coupling reactions; however, those systems are almost exclusively limited to application in non-aqueous media.^{15,16} Although, moderate to good yields of cross-coupling products were obtained with selected aryl bromides/iodides in Suzuki reaction, the system remained virtually ineffective with aryl chlorides as substrates. It needs to mention that despite significant advancements in Suzuki reaction, the activations of chloroarenes in an aqueous environment without using phosphines is still considered as one of the most difficult tasks.¹⁷

In one of our previous works, we developed a catalytic system comprised of unsymmetrical tetradentate N₂O₂-type Schiff-base ligands that showed the impressive result in activating aryl chlorides in the Suzuki reaction.¹⁸ However, the catalytic system was neither reusable nor applicable in an aqueous medium with aryl chlorides. It may be noted that from economical and environmental needs, it has become essential to develop new reusable catalytic systems for Suzuki reaction that works in a hydrophilic

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Electronic supplementary material: The online version contains supplementary material available at <https://doi.org/10.1007/s12039-021-01909-2>.

environment with chloroarenes.¹⁹ Literature precedents suggest that the aqueous-phase efficiency of a homogeneous Schiff-base system could be enhanced by introducing some ionic functionality, *viz.*, $-\text{COO}^-$, $-\text{SO}_3^-$ into the ligand moiety^{11,20,21} so that the complex becomes water-soluble. Moreover, such types of catalysts could be easily separated from the reaction system by a simple biphasic extraction strategy and hence enhance the prospect of recyclability.^{22,23}

Thus, in continuation with our works on Schiff-base system,^{18, 23–25} herein we present a recyclable water-soluble Pd-catalyst containing an unsymmetrical Schiff-base ligand for Suzuki–Miyaura reaction of chloroarenes in water. We have also expanded the scope of our catalytic system for Sonogashira reaction; another most widely studied Pd-catalyzed cross-coupling reaction.^{26–28}

2. Experimental

2.1 Synthesis of ligand and complex

The ligand, **L1** was prepared by reacting two equivalents of sodium salicylaldehyde-5-sulfonate with one equivalent of 2-aminobenzylamine in EtOH. Yield: 72%, Colour: Yellow, M.p. > 250 °C, ¹H NMR (500 MHz, D₂O): δ (ppm) = 8.73 (s, 1H, H), 8.47 (s, 1H, H), 8.03–7.92 (m, 8H, Ar–H), 6.94–6.88 (dd, 2H, H, H), 4.12 (s, 2H, CH₂), FTIR (KBr, cm⁻¹): 3501 ($\nu_{\text{O-H}}$), 1558 ($\nu_{\text{C=N}}$), 1427 ($\nu_{\text{C=C}}$), 1192, 1126 (ν_{SO_3}), UV–Vis (H₂O) λ (nm): 220, ¹³C NMR (400 MHz, D₂O): δ (ppm) = 161.93 (imine carbons), MS (ESI): m/z = 534 [M]⁺. The Pd complex, **C1** was prepared by adding a methanolic solution of Pd(OAc)₂ (1 mmol) to a methanolic solution of the ligand, **L1** (1 mmol). The resulting mixture was refluxed for 3 h and then the solvent was evaporated under reduced pressure, washed with methanol to obtain a pure crystalline solid. Yield: 78%, Colour: Yellowish brown, ¹H NMR (500 MHz, DMSO-d₆): δ (ppm) = 8.30 (s, 1H, H), 8.19 (s, 1H, H), 7.88–7.35 (m, 8H, Ar–H), 6.84–6.78 (dd, 2H, H, H), 4.84 (s, 2H, CH₂), FTIR (KBr, cm⁻¹): 3088 ($\nu_{\text{C-H}}$), 1524 ($\nu_{\text{C=N}}$), 1196, 1032 (ν_{SO_3}), 608 ($\nu_{\text{M-O}}$); 752 ($\nu_{\text{M-N}}$), ¹³C NMR (500 MHz, DMSO-d₆) δ (ppm) = 166.49 (imine carbons), MS (ESI): m/z = 641 [M + H]⁺.

2.2 General procedure of Suzuki–Miyaura reaction

A 50 mL round-bottomed reaction flask was charged with aryl chloride (0.5 mmol), arylboronic acid (0.65 mmol), base (1.3 mmol), required amount of **C1** and water (4 mL). The mixture was stirred in a

synthesizer at a particular temperature. The reaction was monitored with TLC and finally, yield of the product was determined by GC (Perkin Elmer, Clarus 480). The organic product was extracted with ethyl acetate (3 × 15 mL) and dried using Na₂SO₄. The solvent was evaporated under reduced pressure to obtain the crude organic product which was purified by column chromatography using hexanes/ethyl acetate (9:1) as eluent. The identities of the products were confirmed by ¹H NMR analysis.

2.3 General procedure of Sonogashira reaction

A 50 mL round-bottomed reaction flask was charged with aryl bromide (0.5 mmol), phenylacetylene (0.65 mmol), base (1.3 mmol), required amount of **C1** and water (4 mL). The rest of the monitoring and extraction procedures are the same as those used for Suzuki–Miyaura reaction. Finally, the identities of the desired products were confirmed by GC–MS analysis (Agilent 7820A GC, 5975 series mass detector).

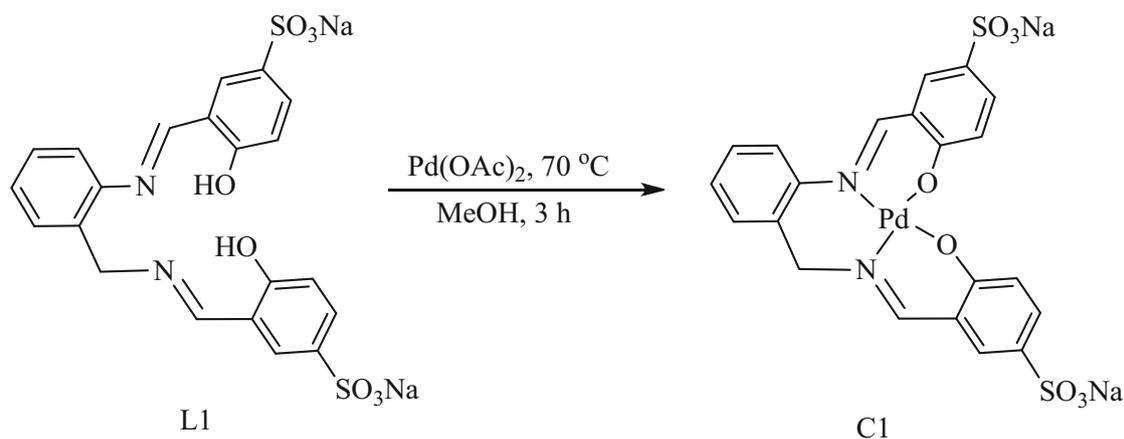
3. Results and Discussion

3.1 Catalyst preparation

The ligand, N, N'-bis(5-sulphosalicyliden)-2-aminobenzylamine, **L1** was prepared by reacting two equivalents of sodium salicylaldehyde-5-sulfonate with one equivalent of 2-aminobenzylamine in EtOH following a slightly modified reported protocol.²⁹ Then, its Pd-complex, **C1** was synthesized by reacting Pd(OAc)₂ and the **L1** in 1:1 molar ratio in MeOH under refluxing condition (Scheme 1). The ESI-mass spectrum of the complex showed a peak at m/z : 641 that corresponds to the [M + H]⁺ species. The FTIR spectrum of the complex showed a strong band at 1524 cm⁻¹ due to $\nu_{\text{C=N}}$ stretching, 34 cm⁻¹ lower compared to the free ligand. In the ¹H NMR spectrum of **C1**, the imine signals appeared at δ : 8.30 and 8.19 ppm which is significantly upfield compared to the free ligand consistent with coordination of the imine with Pd.²⁹ The ¹³C NMR spectrum of the complex also showed a characteristic downfield shift of the imine-carbons compared to the free ligand **L1**.

3.2 Application of the catalyst in Suzuki–Miyaura reaction

The catalytic activity of the complex **C1** was tested for Suzuki–Miyaura reactions of aryl chlorides with



Scheme 1. Synthesis of the water-soluble Pd (II) complex of unsymmetrical Schiff-base ligand.

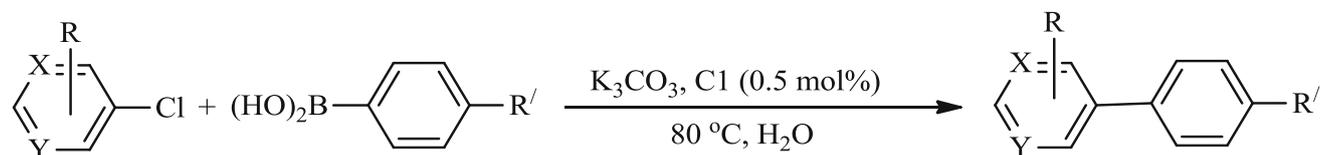
arylboronic acids. To evaluate the optimum condition in terms of base, solvent, temperature and catalyst quantity, 4-chloronitrobenzene and phenylboronic acid were chosen as model substrates. This initial optimization study revealed that 0.5 mol% of the catalyst at 80 °C in pure water was sufficient for the highest yield. Further, the efficiency of various organic and inorganic bases was also examined and it was observed that K_2CO_3 was the most suitable base (Table S1, Supplementary Information).

Thus, by using this optimum condition (H_2O , 80 °C, 0.5 mol% of C1 and K_2CO_3) we have expanded the scope of our catalyst for different substrates. In fact, our catalyst could effectively convert a range of aryl chlorides containing electron-withdrawing and electron-donating substituents. To cite examples, *para*-substituted aryl chlorides with activating $-NO_2$ group gave corresponding biphenyl with 97% yield while with deactivating $-OCH_3$ group, gave 83% yield (Table 1, entries 1, 2). Moderate to high yields of biaryls were also obtained with aryl chlorides containing electron-donating groups at relatively hindered *ortho* or *meta* positions, such as 2-chlorobenzaldehyde or 3-chloroanisole (Table 1, entries 5 and 14). However, with the presence of a deactivating $-CH_3$ group at *para* position, the yield increased to 84% (Table 1, entry 15). The catalyst was also found to be very efficient in coupling heteroaryl chlorides, which are generally considered very challenging. For instance, heteroaryl chlorides such as 3-chloropyridine, 5-chloropyrimidine and 2-chloro-3-methylthiophene underwent coupling with phenylboronic acid to give 89, 83 and 78% of products respectively (Table 1, entries 11-13). The catalyst was also found to be effective in activating aryl chlorides when neutral phenylboronic acid was replaced by phenylboronic

acid-containing electron-donating $-CH_3$ or electron-withdrawing $-Cl$ group (Table 1, entries 6-9). It is noteworthy to mention that the most striking feature of our catalytic system is the activation of chloroarenes exclusively in pure water without any additive or phase transfer agent. However, the addition of a phase transfer agent like cetyltrimethylammoniumbromide (CTAB) improved the yield marginally (Table 1, entry 2). Although the specific role of the ligand in our catalytic process could not be established, however, based on literature support on the mechanistic cycle of similar ligand promoted Pd (II)-catalyzed Suzuki reaction, it could be reasonable to assume that the Schiff-base ligand accelerates the oxidative addition pathway and thus increases the rate of the reaction.³⁰ Moreover, the ionic nature of the ligand in our catalyst facilitates easy cleavage of the $Ph-X$ bond in aqueous media, thereby activating substrates including comparatively challenging chloroarenes.³¹

3.3 Application of the catalyst in Sonogashira reaction

It may be noted that there exists at least one example where a water-soluble Pd-salen catalyst³² was used for aqueous-phase Sonogashira reaction, however, the system was effective only with aryl iodides. Therefore, we intended to expand the scope of our catalyst for aqueous-phase Sonogashira coupling of aryl bromides inspired by the excellent result in the aqueous Suzuki reaction. Initially, to evaluate the best conditions, the reaction between 4-bromoacetophenone and phenylacetylene in water was chosen as a model reaction. We were gratified to see that using neat water as solvent, 81% yield was formed at 100 °C and in presence

Table 1. Suzuki–Miyaura cross-coupling reaction of aryl/heteroaryl chlorides with arylboronic acids in water^a

Sl. No.	R	X	Y	R'	Time (h)	Yield (%) ^b
1	4-NO ₂	CH	CH	H	5	97
2	4-OCH ₃	CH	CH	H	8	83 (86) ^c
3	H	CH	CH	H	4	98
4	4-CHO	CH	CH	H	8	79
5	2-CHO	CH	CH	H	8	71
6	4-NO ₂	CH	CH	4-CH ₃	6	82
7	4-NO ₂	CH	CH	4-Cl	6	89
8	4-OCH ₃	CH	CH	4-CH ₃	8	77
9	4-OCH ₃	CH	CH	4-Cl	7	83
10	2, 5-di-OCH ₃	CH	C	H	8	66
11	H	N	CH	H	6	89
12	H	N	N	H	7	83
13 ^d	3-CH ₃	S	–	H	8	78
14	3-OCH ₃	CH	CH	H	8	80
15	4-CH ₃	CH	CH	H	8	84

^aReaction Conditions: boronic acid: 0.65 mmol, aryl halide: 0.5 mmol, K₂CO₃: 1.3 mmol, Catalyst (C1): 0.5 mol%. H₂O: 4 mL. ^bGC yield. ^cCTAB was used (0.5 mmol). ^daryl halide: 2-chloro-3-methylthiophene.

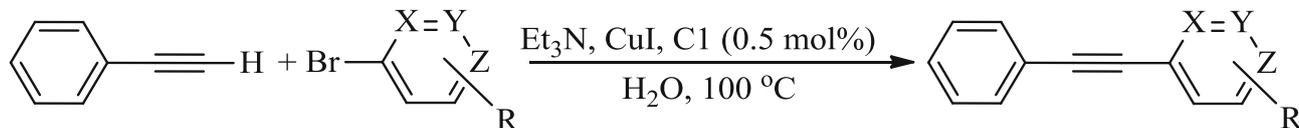
of 0.5 mol% of palladium loading. On increasing the temperature or catalyst quantity, yield of the desired product remained almost the same and on decreasing, the yield gradually decreased. Like the Suzuki reaction, in this case also, there was a slight improvement in the yield when CTAB was used as a phase transfer agent. Then, several organic and inorganic bases were screened and it was observed that maximum yield (81%) was observed using triethylamine. Thus, after screening various reaction variables, it was found that the best condition for the reaction was: H₂O, Et₃N, 100 °C, and 0.5 mol% of C1 (Table S2, Supplementary Information). Further, the compatibility of C1 was also tested under a copper-free condition which revealed that the coupling could not proceed significantly in absence of CuI providing only 30% of yield (Table S2, entry c8, Supplementary Information).

After finding the optimum condition, we then evaluated the scope of our catalytic system for different aryl bromides, containing electron-withdrawing and electron-donating substituents (Table 2). It was observed that aryl bromides with electron-withdrawing substituents like –COCH₃, –CHO, –NO₂ at *para* positions (Table 2, entries 1, 3, 5) gave the desired aryl-alkynes in excellent yields. On the other hand, aryl bromides containing electron-donating groups like

–CH₃, –OCH₃, –CH₂OH, etc. gave moderate-to-low yield. For instance, the yield of the reaction involving 4-CH₃ substituent was recorded 65% (Table 2, entry 6) which was significantly lower than bromoarenes with electron-withdrawing substituents (Table 2, entries 5, 8). Consequently, *para* and *meta*-nitro-bromobenzene reacted with phenylacetylene giving 98% and 82% yield of the desired product respectively (Table 2, entry 5, 8). Again, in presence of deactivating group like –CH₂OH at *ortho* position, the yield further decreased to 37% (Table 2, entry 10). The catalyst was also employed for activation of heteroaryl bromides *viz.*, 4, 2 and 3-bromopyridines which could easily couple with phenylacetylene with respective yields of 97, 82 and 87% (Table 2, entries 2, 4, 9).

3.4 Recycling of the catalyst

It may be noted that one of the major problems faced by conventional homogeneous catalysts is their difficulty in separation from the reaction mixture and their subsequent recycling. In that perspective, the water-soluble catalyst is often advantageous as it could be easily separated from the reaction mixture by simple biphasic extraction and hence increase the prospect of

Table 2. Sonogashira reaction of aryl/heteroaryl bromides with phenylacetylene in water.^a

Sl. No.	R	X	Y	Z	Time (h)	Yield (%) ^c
1	4-COCH ₃	CH	CH	C	7	81 (84) ^b
2	H	CH	CH	N	6	97
3	4-CHO	CH	CH	C	7	94
4	H	N	CH	CH	6	82
5	4-NO ₂	CH	CH	C	6	98
6	4-CH ₃	CH	CH	C	8	65
7	2,5-di-OCH ₃	C	CH	CH	9	47
8	3-NO ₂	CH	C	CH	7	82
9	H	CH	N	CH	6	87
10	2-CH ₂ OH	C	CH	CH	8	37

^aReaction Conditions: Phenylacetylene: 0.65 mmol, aryl bromide: 0.5 mmol, Et₃N: 1.3 mmol, CuI: 0.5 mol%, Catalyst (C1): 0.5 mol%. H₂O: 4 mL. ^bCTAB was used (0.5 mmol). ^cGC yield.

reusability. Thus, to check the reusability of our catalyst in the Suzuki reaction, we separated the catalyst after the initial reaction between 4-nitrochlorobenzene and phenylboronic acid by adding ethyl acetate. After the extraction, the organic layer contained the product while the aqueous layer contained the catalyst which was reused for subsequent runs by adding a fresh batch of reactants. By that way, the catalyst could be recycled at least for four cycles; however, a progressive decrease in activity was noticed from 97% in the first cycle to 83% in the fourth cycle which might be due to the handling loss of catalyst during recycling experiments. Like the Suzuki reaction, the catalyst was also recycled four times in the Sonogashira reaction and almost a similar trend in activity was observed (Figure 1).

4. Conclusions

In conclusion, a highly efficient and recyclable water-soluble Pd based catalyst, incorporating an unsymmetrical Schiff-base ligand was developed which could smoothly perform the Suzuki–Miyaura and the Sonogashira cross-coupling reactions in aqueous media under mild reaction conditions with a low loading of catalyst. Moreover, the catalyst could easily be recycled due to its water-soluble nature, although a progressive decrease in activity was observed in subsequent runs in both the coupling reactions.

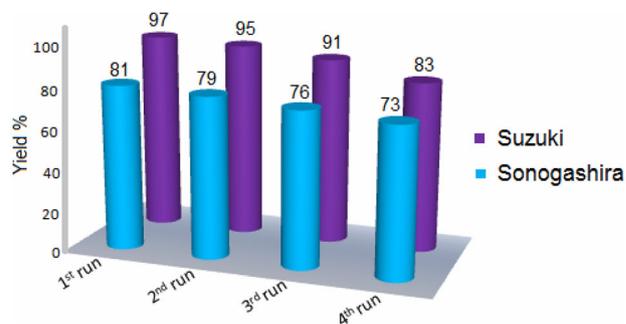


Figure 1. Recycling of the catalyst in Suzuki and Sonogashira reactions

Supplementary information (SI)

The SI includes NMR, ESI-MS and FTIR spectra of the ligand and the complex. Also, ¹H NMR of the Suzuki products and GCMS of the Sonogashira products along with optimization tables are available at www.ias.ac.in/chemsci.

Acknowledgement

DST, New Delhi is gratefully acknowledged for financial support (Grant nos. 2015/000021 and CRG/2018/001669) and UGC, New Delhi for SAP-DRS programme. The authors also acknowledge the NMR Research Centre, IISc, Bangalore and SAIF, Punjab University, Chandigarh for NMR and ESI-MS analyses respectively.

References

1. Das P and Linert W 2016 Schiff base-derived homogeneous and heterogeneous palladium catalysts for the Suzuki–Miyaura reaction *Coord. Chem. Rev.* **311** 1
2. Nagalakshmi V, Sathya M, Premkumar M, Kaleeswaran D, Venkatachalam G and Balasubramani K 2020 Palladium (II) complexes comprising naphthylamine and biphenylamine based Schiff-base ligands: Synthesis, structure and catalytic activity in Suzuki coupling reactions *J. Organomet. Chem.* **914** 121220
3. Kumar S 2019 Recent advances in the Schiff-bases and *N*-heterocyclic carbenes as ligands in the cross-coupling reactions: a comprehensive review *J. Heterocycl. Chem.* **56** 1168
4. Rao G K, Kumar A, Singh M P, Kumar A, Biradar A M and Singh A K 2014 Influence of pendent alkyl chains on Heck and Sonogashira C–C coupling catalyzed with palladium (II) complexes of selenated Schiff-bases having liquid crystalline properties *J. Organomet. Chem.* **753** 42
5. Andrade A P S, Arantes L M, Kadooca J Y, Carvalho R L, Fatima A and Sabino A A 2016 Palladium complexes with tetradentate Schiff-bases or their corresponding amines: synthesis and application in Heck reactions *ChemistrySelect* **1** 886
6. Chelmieniecka A S, Rzuchowska A, Szczupak A M, Schilf W and Rozwadowski Z 2020 New “one-pot” Pd (II) and Zn (II) complexes of Schiff-bases, derivatives of 1-amino-1-deoxy-d-sorbitol: Spectroscopic studies and biological and catalytic activities *Appl. Organomet. Chem.* **34** 5485
7. Keleş M, Keleş H and Emir D M 2015 Pd (II) complexes of Schiff-bases and their application as catalysts in Mizoroki–Heck and Suzuki–Miyaura cross-coupling reactions *Appl. Organomet. Chem.* **29** 543
8. Ansari R M and Bhat B R 2017 Schiff-base transition metal complexes for Suzuki–Miyaura cross-coupling reaction *J. Chem. Sci.* **129** 1483
9. Bhaskar R, Sharma A K, Yadav M K and Singh A K 2017 Sonogashira (Cu and amine free) and Suzuki coupling in air catalyzed via nanoparticles formed *in situ* from Pd (II) complexes of chalcogenated Schiff-bases of 1-naphthaldehyde and their reduced forms *Dalton Trans.* **46** 15235
10. Zhou J, Guo X, Tu C, Li X and Sun H 2009 Aqueous Suzuki coupling reaction catalyzed by water-soluble diiminesoluble diimine/Pd (II) systems *J. Organomet. Chem.* **694** 697
11. Liu Y, Gu N, Liu P, Ma X, Liu Y, Xie J and Dai B 2015 Water-soluble salen-Pd complex as an efficient catalyst for Suzuki–Miyaura reaction of sterically hindered substrates in pure water *Tetrahedron* **71** 7985
12. Renehan M F, Schanz H J, McGarrigle E M, Dalton C T, Daly A M and Gilheany D G 2005 Unsymmetrical chiral salen Schiff-base ligands: Synthesis and use in metal-based asymmetric epoxidation reactions *J. Mol. Catal. A: Chem.* **231** 205
13. Kim G J and Shin J H 1999 Application of new unsymmetrical chiral Mn (III), Co (II, III) and Ti (IV) salen complexes in enantioselective catalytic reactions *Catal. Lett.* **63** 83
14. Kleij A W 2009 Nonsymmetrical salen ligands and their complexes: synthesis and applications *Eur. J. Inorg. Chem.* **2009** 193
15. Sedighipoor M, Kianfar A H, Mohammadnezhad G, Görls H and Plass W 2018 Unsymmetrical palladium (II) N, N, O, O-Schiff-base complexes: Efficient catalysts for Suzuki coupling reactions *Inorg. Chim. Acta* **476** 20
16. Pratihari J L, Mandal P, Lai C K and Chattopadhyay S 2019 Tetradentate amido azo Schiff-base Cu (II), Ni (II) and Pd (II) complexes: Synthesis, characterization, spectral properties, and applications to catalysis in C–C coupling and oxidation reaction *Polyhedron* **161** 317
17. Lee J Y, Ghosh D, Lee J Y, Wu S S, Hu C H, Liu S D and Lee H M 2014 Zwitterionic palladium complexes: room-temperature Suzuki–Miyaura cross-coupling of sterically hindered substrates in an aqueous medium *Organometallics* **33** 6481
18. Puzari A, Shahnaz N and Das P 2018 Palladium complexes with two unsymmetrical Schiff-base ligands: Highly active catalyst for activation of chloroarenes in Suzuki–Miyaura reaction *J. Indian Chem. Soc.* **95** 837
19. Mak S Y, Kin Liew K H, Chua C C, Mohd, Yarmo M A, Yahaya B H, Samad W Z, Jamil M S M and Yusop R M 2019 Palladium nanoparticles supported on fluorine-doped tin oxide as an efficient heterogeneous catalyst for Suzuki coupling and 4-nitrophenol reduction *J. Chem. Sci.* **131** 111
20. Reimann M J, Salmon D R, Horton J T, Gier E C and Jefferies L R 2019 Water-soluble sulfonate Schiff-base ligands as fluorescent detectors for metal ions in drinking water and biological systems *ACS Omega* **4** 2874
21. Voronova K, Purgel M, Udvardy A, Benyei A C, Katho A and Joo F 2013 Hydrogenation and redox isomerization of allylic alcohols catalyzed by a new water-soluble Pd-tetrahydrosalen complex *Organometallics* **32** 4391
22. Nehra P, Khungar B, Pericherla K, Sivasubramanian S C and Kumar A 2014 Imidazolium ionic liquid-tagged palladium complex: an efficient catalyst for the Heck and Suzuki reactions in aqueous media *Green Chem.* **16** 4266
23. Shahnaz N, Puzari A, Paul B and Das P 2016 Activation of aryl chlorides in water for Suzuki coupling with a hydrophilic salen-Pd (II) catalyst *Catal. Commun.* **86** 55
24. Banik B, Tairai A, Shahnaz N and Das P 2012 Palladium (II) complex with a potential N₄-type Schiff-base ligand as highly efficient catalyst for Suzuki–Miyaura reactions in aqueous media *Tetrahedron Lett.* **53** 5627
25. Shahnaz N, Banik B and Das P 2013 A highly efficient Schiff-base derived palladium catalyst for the Suzuki–Miyaura reactions of aryl chlorides *Tetrahedron Lett.* **54** 2886
26. Chinchilla R and Nájera C 2011 Recent advances in Sonogashira reactions *Chem. Soc. Rev.* **40** 5084
27. Khairul W M, Wahab F F A, Soh S K C, Shamsuddin M and Daud A I 2020 Palladium (II)-pivaloyl thiourea complexes: Synthesis, characterisation and their catalytic activity in mild Sonogashira cross-coupling reaction *Chem. Phys. Lett.* **756** 137842
28. Anitha P, Manikandan R, Vijayan P, Prakash G, Viswanathamurthi P and Butcher R J 2015 Nickel (II)

- complexes containing ONS donor ligands: Synthesis, characterization, crystal structure and catalytic application towards C-C cross-coupling reactions *J. Chem. Sci.* **127** 597
29. Asadi M, Asadi Z, Zarei L, Sadi S B and Amirghofran Z 2014 Affinity to bovine serum albumin and anti-ancer activity of some new water-soluble metal Schiff-base complexes *Spectrochim. Acta A* **133** 697
30. Schmidt A F, Kurokhtina A A, Larina E V, Vidyaeva E V and Lagoda N A 2021 Nonclassical cooperative mechanism in Suzuki–Miyaura reaction-Is it possible? *Mol. Catal.* **499** 111321
31. Nehzat F and Grivani G 2020 Two efficient ligand-assisted systems of two different ionic Schiff-base ligands for palladium chloride catalyzed in Suzuki–Miyaura reaction *J. Chem. Sci.* **132** 33
32. Bakherad M, Keivanloo A, Bahramian B and Hashemi M 2009 Copper-free Sonogashira coupling reactions catalyzed by a water-soluble Pd-salen complex under aerobic conditions *Tetrahedron Lett.* **50** 1557