

# Synthesis of biphenyl-based arsine ligands by microwave-assisted Suzuki-Miyaura coupling and their applications

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## INTRODUCTION

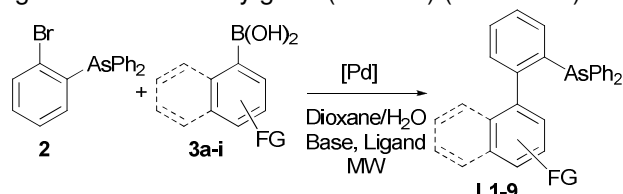
Over the past few years, there has been a growing interest in the synthesis and application of biphenyl-based monophosphine ligands.<sup>1</sup> Although tertiary phosphines constitute the group of ligands most widely used in metal-catalyzed reactions, arsines have been shown to be excellent ligands and there are several examples where arsine complexes give more active or selective catalysts than phosphines.

We have developed a versatile methodology that allow for C-As bond formation through a Pd-catalyzed arsination with stannane *n*-Bu<sub>3</sub>SnAsPh<sub>2</sub>.<sup>2</sup> By this methodology we carried out the synthesis of a novel biphenylarsine ligand biphenyl-2-ylidiphenylarsine, and also the preliminary investigation of its performance as a ligand.<sup>2a</sup>

Herein, we report the synthesis of a family of biarylarsine ligands (Figure 1) by an approach, including first the Pd-catalyzed arsination, and then the microwave-assisted Suzuki-Miyaura coupling as the key synthetic tool for biaryl construction. Additionally, the activity of new biarylarsine ligands in Pd-catalyzed reactions is also reported.

## RESULTS AND DISCUSSION

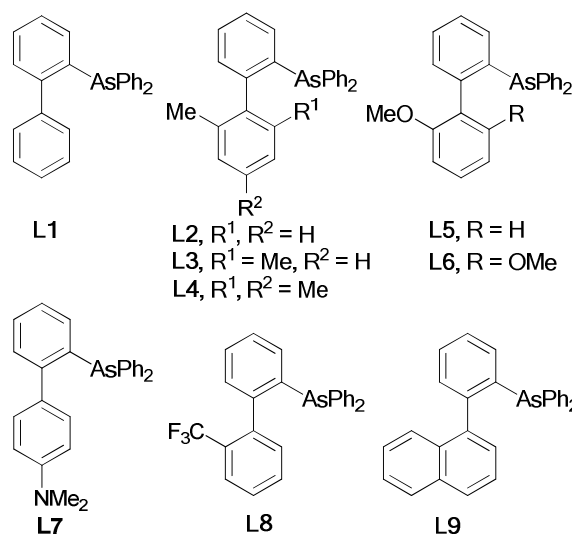
By the Pd-catalyzed arsination with *n*-Bu<sub>3</sub>SnAsPh<sub>2</sub> (**1**), the (2-bromophenyl)diphenylarsine (**2**, 83%) was obtained.<sup>2a</sup> The Suzuki-Miyaura coupling reaction between bromoarsine **2** and aryl boronic acids bearing different substituents provided biarylarsine ligands **L1-L9** in very good (66-99%) (Scheme 1).



FG = H (**3a**); 2-Me (**3b**); 2,6-diMe (**3c**); 2,4,6-triMe (**3d**); 2-OMe (**3e**); 2,6-diOMe (**3f**); 4-NMe<sub>2</sub> (**3g**); 2-CF<sub>3</sub> (**3h**); Naph (**3i**)

**Scheme1.** Insert the figure caption her

The coupling reaction conditions were thoroughly optimized, and we explored different methods and system for MW irradiation.



**Figure1.** Insert the figure caption her

Despite of the considerably bulky -AsPh<sub>2</sub> moiety in **2** and boronic acids with two groups in the *ortho* positions, the reaction was successfully carried out. The efficiency of catalysts derived from the new biarylarsine ligands was evaluated in Pd-catalyzed Stille and Heck. The Pd/**L4** and **L6** based catalysts demonstrated significant activity for both coupling reactions with 4-bromoanisole.

## CONCLUSION

We have synthesized a new family of biarylarsine ligands with different steric and electronic properties, varying the substituents in the biaryl backbone. Our newly prepared biphenylarsine ligands show promised activity for Pd-catalyzed reactions.

## ACKNOWLEDGEMENTS

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## REFERENCES

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