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Modified Amino Acid-Derived Phosphine-Imine Ligands for Palladium-Catalyzed Asymmetric Arylation of Cyclic *N*-Sulfonyl Imines

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Abstract: A series of chiral phosphine-imine ligands were synthesized starting with α-amino acids and examined for palladium-catalyzed asymmetric addition of arylboronic acids to cyclic *N*-sulfonyl imines. High catalytic activities (up to 99% yield) and high enantioselectivities (up to 98% ee) were achieved for cyclic *N*-sulfonyl aldimines and ketimines with five and six-membered ring structures.

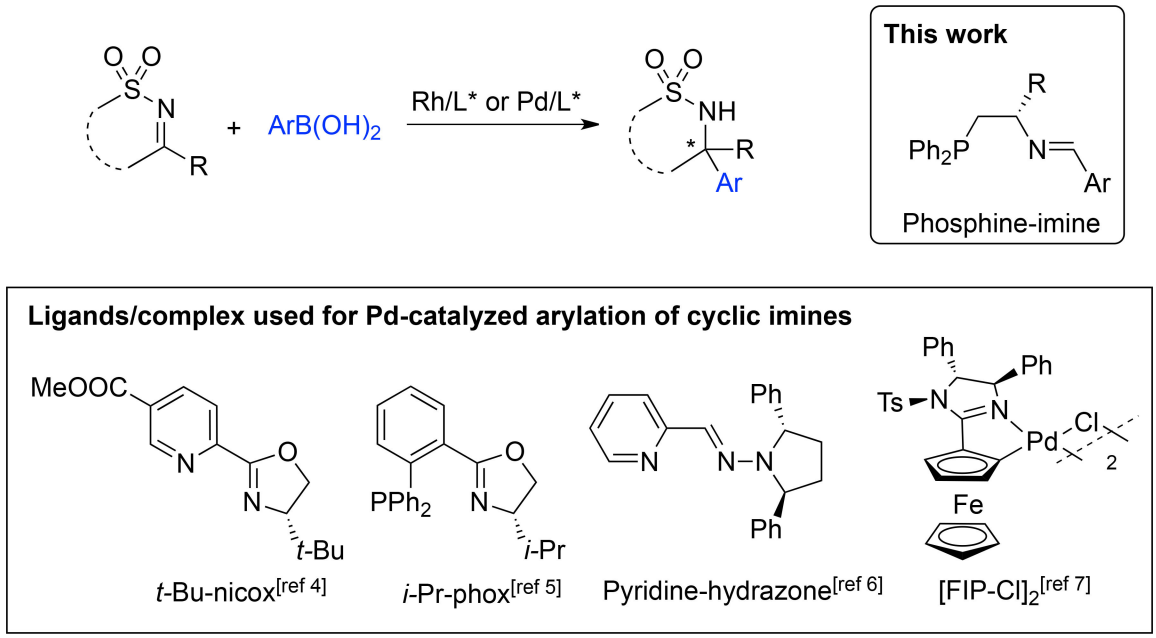
Keywords: asymmetric arylation; palladium; phosphine-imine; arylboronic acid; cyclic sulfonyl imine

Asymmetric arylation of imines catalyzed by chiral rhodium and palladium catalysts is one of the most efficient methods of producing chiral disubstituted and trisubstituted methylamines.[1,2] Recently, cyclic *N*-sulfonyl imines have attracted great attention in virtue of their general high reactivity and high enantioselectivity in the arylation reactions[3–7] (Scheme 1). Their cyclic structures make the enantioface differentiation of imines easier and simpler. The use of palladium catalysts for this asymmetric reaction was first reported by Zhang[4] where a chiral palladium complex generated from pyridinooxazoline and Pd $(OCOCF_3)_2$ catalyzed the asymmetric addition of arylboronic acids to cyclic *N*-sulfonyl ketimines. Subsequently, chiral palladium catalysts coordinated with a phosphinooxazoline,[5] a pyridinohydrazone,[6] and a ferrocene-derived palladacycle[7] were reported to be enantioselective catalysts for the asymmetric arylation of cyclic *N*-sulfonyl imines.

The design and synthesis of new chiral ligands is of essential importance for asymmetric metal catalysis. At the design, one of the factors to be considered is their tunability which makes the chiral ligands fit in with a given reaction with enantioselectivity as high as possible. On the other hand, α-amino acids are known to be most useful chiral pools because a series of them are available in enantiomerically pure forms and they are functionalized well with amino and carboxylic acid groups which are advantageous for their derivatization. The α-amino acids have been used for the synthesis of chiral ligands which coordinate to metals with nitrogen and phosphorus atoms.[8,9] The P,N ligands are an interesting class of ligands as they are easily tuned for their steric and electronic characters, as mentioned above.

In 1999, Morimoto reported a series of chiral phosphine-imine type P,N ligands, which are readily prepared from amino acids by way of β-aminoalkylphosphines, and their successful use for palladium-catalyzed asymmetric allylic alkylation reactions.[10] These phosphine-imine ligands[11] have a similar scaffold to phosphinooxazoline ligands.[12] The phosphinooxazoline ligands have demonstrated their high performance in a large scope of reactions.[5,8a,d] Here we report fine tuning of the phosphine-imine ligands for the asymmetric arylation of imines by modification of their imino moiety.

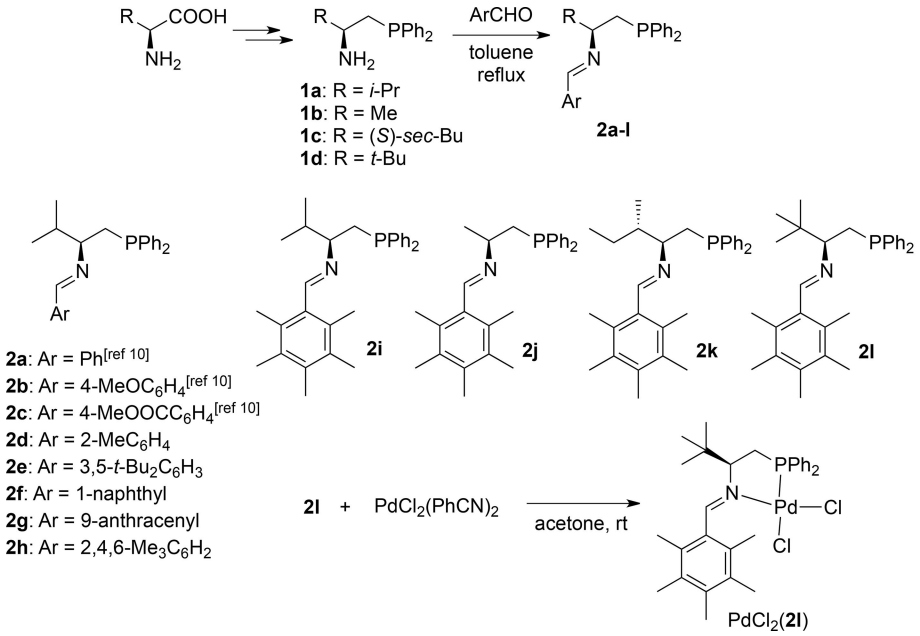
The chiral phosphine-imines **2** (Scheme 2), where R is *i*-Pr and Ar is Ph (**2a**), 4-$MeOC_6H_4$ (**2b**), and 4-$MeOOCC_6H_4$ (**2c**), have been reported by Morimo-



Scheme 1. Catalytic asymmetric arylation of cyclic *N*-sulfonyl imines.

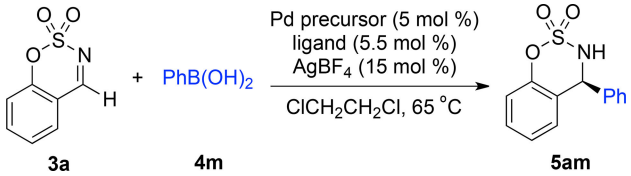
to[10] to be synthesized by condensation of β-aminoalkylphosphine **1a**[13] with the corresponding aldehydes in refluxing toluene. We have modified the phosphine-imines mainly by introducing bulkier aromatic groups on the imine moiety and changing alkyl groups on the stereogenic carbon center. A palladium complex $PdCl_2$(**2l**) was isolated by the reaction of phosphine-imine **2l** with $PdCl_2(PhCN)_2$ in acetone.

The phenylation of benzo[*e*][1,2,3]oxathiazine 2,2-dioxide **3a** with phenylboronic acid **4m** was examined in the presence of chiral phosphine-imine/palladium catalysts (Table 1). The cationic palladium complex generated in situ from ligand **2a** (5.5 mol%), $PdCl_2(PhCN)_2$ (5.0 mol%), and $AgBF_4$ (15 mol%) catalyzed the asymmetric phenylation in 1,2-dichloroethane at 65 °C to give the phenylation product **5am** with 77%



Scheme 2. Preparation of amino acid-derived phosphine-imine ligands.

Table 1. Optimization of reaction conditions.[a]



3a 4m 5am

Entry	Pd	Ligand	Time [h]	Yield **5am** [%][b]	ee **5am** [%][c]
1	$PdCl_2(PhCN)_2$	**2a**	12	91	77 (*S*)
2	$PdCl_2(MeCN)_2$	**2a**	12	38	77 (*S*)
3[d]	$PdCl_2(PhCN)_2$	**2a**	12	0	–
4[e]	$Pd(OCOCF_3)_2$	**2a**	12	trace	–
5	$PdCl_2(PhCN)_2$	**2b**	12	41	74 (*S*)
6	$PdCl_2(PhCN)_2$	**2c**	12	55	78 (*S*)
7	$PdCl_2(PhCN)_2$	**2d**	12	92	78 (*S*)
8	$PdCl_2(PhCN)_2$	**2e**	12	65	68 (*S*)
9	$PdCl_2(PhCN)_2$	**2f**	12	78	84 (*S*)
10	$PdCl_2(PhCN)_2$	**2g**	12	92	85 (*S*)
11	$PdCl_2(PhCN)_2$	**2h**	12	93	87 (*S*)
12	$PdCl_2(PhCN)_2$	**2i**	12	94	89 (*S*)
13	$PdCl_2(PhCN)_2$	**2j**	12	91	81 (*S*)
14	$PdCl_2(PhCN)_2$	**2k**	12	92	88 (*S*)
15	$PdCl_2(PhCN)_2$	**2l**	12	94	96 (*S*)
16	$PdCl_2(PhCN)_2$	**2l**	1	94	96 (*S*)
17[f]	$PdCl_2$(**2l**)	–	1	98	97 (*S*)
18[g]	$PdCl_2$(**2l**)	–	6	99	97 (*S*)

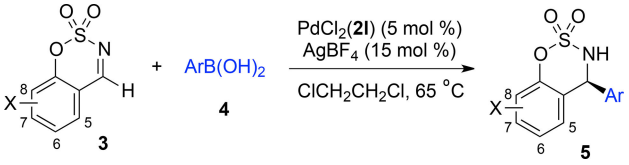
[a] *Reaction conditions*: **3a** (0.20 mmol), **4m** (0.40 mmol), Pd precursor (5 mol%), ligand (5.5 mol%), $AgBF_4$ (15 mol%) in $ClCH_2CH_2Cl$ (2.0 mL) at 65 °C.
[b] Isolated yield of **5am**.
[c] Determined by HPLC analysis with a chiral stationary phase. The absolute configuration of **5am** was determined by comparison of its optical rotation with the literature report.
[d] Reaction without $AgBF_4$.
[e] $Pd(OCOCF_3)_2$ instead of Pd precursor/$AgBF_4$.
[f] Isolated palladium complex $PdCl_2$(**2l**) was used in place of in situ generation from $PdCl_2(PhCN)_2$ and **2l** ligand.
[g] The reaction was performed with **3a** (458 mg, 2.50 mmol), **4m** (915 mg, 7.50 mmol), $PdCl_2$(**2l**) (1 mol%), $AgBF_4$ (3 mol%) in $ClCH_2CH_2Cl$ (25 mL).

ee in 91% yield (entry 1). The use of $PdCl_2(MeCN)_2$ as a catalyst precursor in place of $PdCl_2(PhCN)_2$ resulted in a lower yield of **5am** (entry 2). In the absence of $AgBF_4$, no phenylation was observed (entry 3), indicating that the generation of a cationic palladium species is essential for the high catalytic activity. The yield of **5am** is also very low with Pd $(OCOCF_3)_2$ as a palladium precursor (entry 4).

On modifying the aromatic group on imine moiety, it was found that the enantioselectivity was not strongly dependent on the electronic characters of the *para*-substituents (entries 5 and 6) or a bulky group at *meta*-positions (entry 8). Higher enantioselectivity was observed with conjugated aromatic rings, 1-naphthyl **2f** (84% ee) and 9-anthracenyl **2g** (85% ee), (entries 9 and 10) and with *ortho*-disubstituted phenyl groups, 2,4,6-trimethylphenyl **2h** (87% ee) and pentamethylphenyl **2i** (89% ee), (entries 11 and 12). With keeping the pentamethylphenyl group in the imine moiety, substituents at the stereogenic carbon center derived from α-amino acids were modified and compared for the enantioselectivity (entries 12–15). The highest enantioselectivity was obtained with *t*-Bu group **2l**, which gave a high yield (94%) of **5am** with 96% ee (entry 15). The reaction is so fast that the reaction time is shortened to 1 h without loss of yield of **5am** (entry 16). The use of isolated palladium complex $PdCl_2$(**2l**) showed a slightly better performance than the in situ generation from $PdCl_2(PhCN)_2$ and ligand **2l**. The product **5am** was obtained with 97% ee in 98% yield in the presence of 5 mol% of $PdCl_2$(**2l**) and 15 mol% of $AgBF_4$ (entry 17). We have also scaled up the experiment by using 1 mol% palladium catalyst, and the reaction proceeded well and the product **5am** was obtained in 99% yield and with 97% ee (entry 18).

Under the conditions shown in entry 17 in Table 1, the addition reactions of various arylboronic acids **4** to

Table 2. Scope of arylboronic acids and cyclic *N*-sulfonyl aldimines.[a]



Entry	X	Ar	Yield **5** [%][b]	ee **5** [%][c]
1	H (**3a**)	Ph (**4m**)	98	97 (*S*)
2	H (**3a**)	4-MeC_6H_4 (**4n**)	99	98 (*S*)
3	H (**3a**)	4-FC_6H_4 (**4o**)	98	98 (*S*)
4	H (**3a**)	4-ClC_6H_4 (**4p**)	99	98 (*S*)
5	H (**3a**)	4-BrC_6H_4 (**4q**)	99	98 (*S*)
6[d]	H (**3a**)	4-$CF_3C_6H_4$ (**4r**)	88	97 (*S*)
7	H (**3a**)	4-$MeOC_6H_4$ (**4s**)	99	80 (*S*)
8	H (**3a**)	3,4-$(OCH_2O)C_6H_3$ (**4t**)	97	92 (*S*)
9	H (**3a**)	3-ClC_6H_4 (**4u**)	99	98 (*S*)
10	H (**3a**)	3-MeC_6H_4 (**4v**)	99	97 (*S*)
11	H (**3a**)	2-MeC_6H_4 (**4w**)	99	39 (*S*)
12	H (**3a**)	1-naphthyl (**4x**)	85	12 (*S*)
13	H (**3a**)	2-naphthyl (**4y**)	99	98 (*S*)
14	6-Me (**3b**)	Ph (**4m**)	99	98 (*S*)
15	6-Cl (**3c**)	Ph (**4m**)	96	97 (*S*)
16	6-NO_2 (**3d**)	Ph (**4m**)	98	97 (*S*)
17	6-OMe (**3e**)	Ph (**4m**)	97	98 (*S*)
18	5,6-$(CH{=}CH)_2$ (**3f**)	Ph (**4m**)	99	97 (*S*)
19	7-Me (**3g**)	Ph (**4m**)	96	95 (*S*)
20	8-Me (**3h**)	Ph (**4m**)	99	98 (*S*)

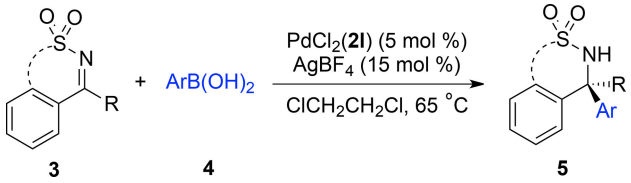
[a] *Reaction conditions*: **3** (0.20 mmol), **4** (0.40 mmol), $PdCl_2$(**2l**) (5 mol%), $AgBF_4$ (15 mol%) in $ClCH_2CH_2Cl$ (2.0 mL) at 65 °C for 1 h.
[b] Isolated yield of **5**.
[c] Determined by HPLC analysis with a chiral stationary phase. The absolute configuration of **5am** was determined by comparison of its optical rotation with the literature report, and the other compounds were estimated by stereochemical similarity to the reaction giving **5am**.
[d] Reaction time 3 h.

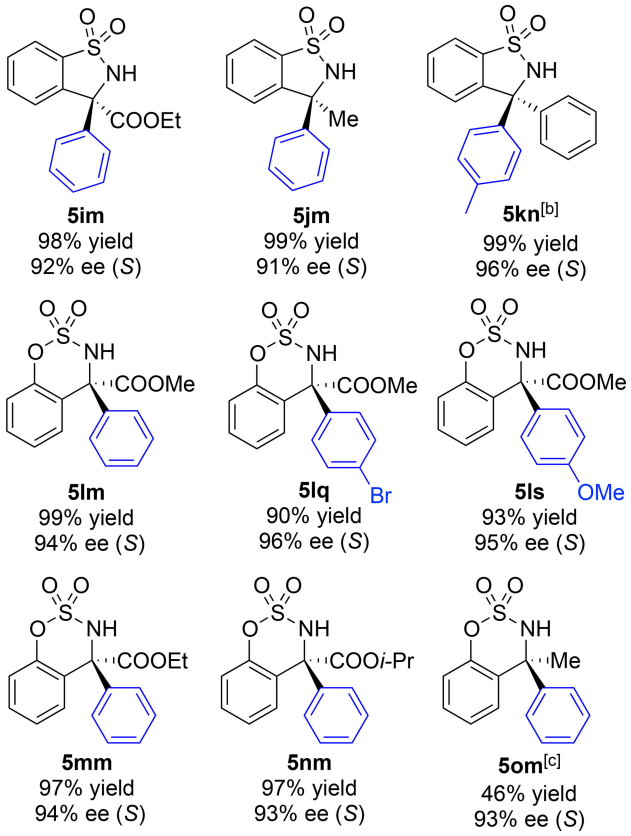
a range of cyclic *N*-sulfonyl aldimines **3** were investigated (Table 2). The enantioselectivity is generally high (97–98% ee) for the addition of phenylboronic acids substituted at 4 and 3 positions to aldimine **3a**, except for 4-$MeOC_6H_4$ (**4s**) (entry 7) and 3,4-$(OCH_2O)C_6H_3$ (**4t**) (entry 8). Unfortunately, the enantioselectivity was low for *ortho*-substituted arylboronic acids, 2-MeC_6H_4 (**4w**) (entry 11) and 1-naphthyl (**4x**) (entry 12), while the yields are kept high. In addition, the aryl moieties of the aldimines (**3b**–**3h**) could also be varied by installing substituents with different electronic nature and substitution patterns, and the arylation reactions proceeded extremely well and afforded the desired addition products in very high yields and excellent ee values (entries 14–20).

The present catalyst system $PdCl_2$(**2l**)/$AgBF_4$ for asymmetric arylation was successfully applied to the more challenging substrates, namely cyclic *N*-sulfonyl ketimines (Table 3). High yields and high ee values were achieved in the addition to five-membered ring ketimines bearing ester (**3i**), methyl (**3j**), and phenyl (**3k**) groups on the imine carbon. The six-membered ketimine esters (**3l**–**3n**) also gave high yields and ee values with various boronic acids. The SO_2 group in the arylation products could be readily removed without affecting stereochemical integrity of the products, with a concurrent reduction of the ester group.[4b] However, methyl-substituted the six-membered ring ketimine (**3o**) remains as a less reactive substrate for this reaction.

The X-ray crystal structure of $PdCl_2$(**2l**)[14] (Figure 1) provides us with significant information on the structure of the chiral palladium catalyst. The phosphine–imine ligand **2l** coordinates to Pd with both diphenylphosphino group and imine nitrogen to form five-membered chelate ring. The *t*-Bu group adopts pseudo axial position in the five-membered ring chelate, which forces the pentamethylphenyl group on the imine to direct towards the substrate coordination site where the enantioface-selective arylpalladation takes place as one of the key steps in the catalytic cycle.[15] The absolute configurations (*S*)

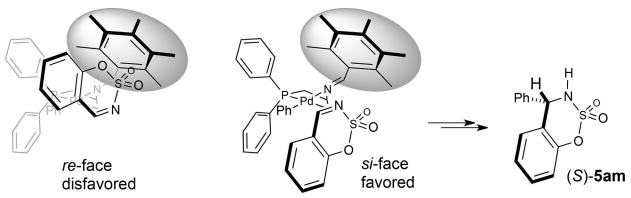
Table 3. Scope of cyclic *N*-sulfonyl ketimines.[a]





[a] *Reaction conditions*: **3** (0.20 mmol), **4** (0.40 mmol), $PdCl_2$(**2l**) (5 mol%), $AgBF_4$ (15 mol%) in $ClCH_2CH_2Cl$ (2.0 mL) at 65 °C for 1 h. The yields are isolated yields, and ee values were determined by HPLC analysis with chiral stationary phase. The absolute configurations of **5jm**, **5kn**, **5lm**, **5mm**, and **5om** were determined by comparison of their optical rotations with literature reports, and the other compounds were estimated by similarity of the stereochemical pathway.
[b] Boronic acid **4n** (1.00 mmol) was used.
[c] **4m** (1.00 mmol), $PdCl_2$(**2l**) (10 mol%), and $AgBF_4$ (25 mol%) for 12 h.

of the products are rationalized by the stereochemical model shown in Scheme 3. Thus, for example, imine **3a** approaches a phenyl-palladium intermediate with its *si*-face to prevent the coordination from steric



Scheme 3. Stereochemical pathway giving (*S*)-**5am**.

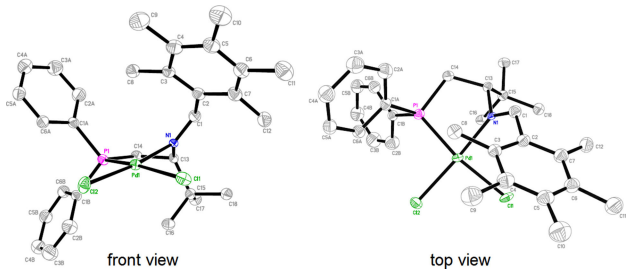


Figure 1. X-ray structure of $PdCl_2$(**2l**).

repulsions between the sulfonyl group of the imine and pentamethylphenyl ring on the ligand. The

phenylpalladation of **3a** on its *si*-face will lead to the product **5am** with *S* configuration. The coordination with *re*-face would suffer from a serious steric repulsion caused by the pentamethylphenyl ring and the sulfonyl group.

In summary, a series of amino acid-derived phosphine-imine ligands were designed and synthesized for palladium-catalyzed arylation of cyclic *N*-sulfonyl imines. The easily prepared phosphine-imine ligands demonstrated high catalytic activities and useful level of enantioselectivities.

Experimental Section

Synthesis of Amino Acid-Derived Phosphine-Imine Ligands 2a–2l and $PdCl_2$(2l) Complex

A modified procedure based on Morimoto's report[10b] for synthesis of phosphine-imine ligands: A 25 mL flask was charged with β-aminoalkylphosphine (0.30 mmol) and aldehyde (0.36 mmol) in toluene (15.0 mL). The mixture was heated at reflux for 4 h under argon with Dean-Stark trap. The solvent was removed under vacuum. The crude mixture was subjected to a short silica gel column with hexane/ethyl acetate (25:1) to give crude product (the column was pretreated with 5% Et_3N in hexane, and then flushed with hexane). The crude product was heated to 200 °C under vacuum to remove excess aldehyde, and gave pure product.

A 25 mL round bottle flask was charged with $PdCl_2(PhCN)_2$ (1.00 mmol, 383.6 mg) in acetone (5.0 mL) under argon. Phosphine-imine ligand **2l** (1.00 mmol, 443.6 mg) in acetone (10.0 mL) was added slowly over 5 min at room temperature. The mixture was stirred at room temperature for 2 h, in the meantime yellow precipitates were formed. The mixture was concentrated to 5 mL, and filtrated. The residue was washed with hexane (10 mL ×3), and dried under vacuum to give pure product $PdCl_2$(**2l**) (528.0 mg, 85% yield) as yellow solid.

General Procedure for Asymmetric Palladium-Catalyzed Arylation Reactions

$PdCl_2$(**2l**) (6.2 mg, 0.01 mmol), *N*-sulfonyl imine (0.20 mmol), and boronic acid (0.40 mmol) were placed in a Schlenk tube. To the tube, 1,2-dichloroethane (1.0 mL) was added, and then $AgBF_4$ (5.8 mg, 0.03 mmol) in 1,2-dichloroethane (1.0 mL) was added. The mixture was stirred at 65 °C for 1 h, and it was directly subjected to flash chromatography on silica gel using hexane/ethyl acetate as an eluent to give pure product.

Acknowledgements

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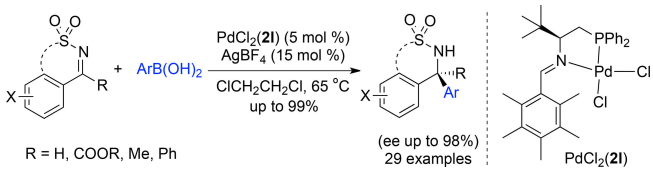
Modified Amino Acid-Derived Phosphine-Imine Ligands for Palladium-Catalyzed Asymmetric Arylation of Cyclic *N*-Sulfonyl Imines



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