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Asymmetric Disilylation of Spirocyclic Palladacyclopentanes via Tandem Heck/C–H Activation of Aryl Iodides

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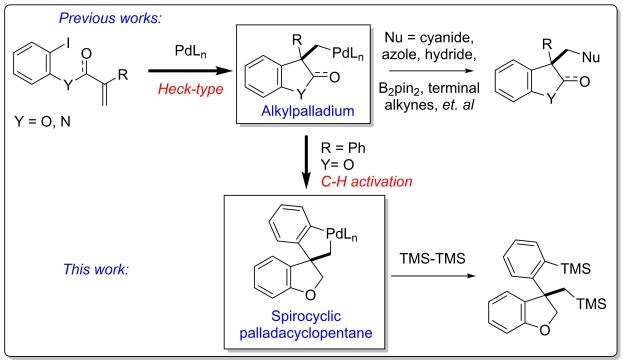
Abstract: The synthesis of chiral organosilicon compounds is highly appealing due to their wide and important applications in synthetic chemistry and medicinal science. However, catalytic asymmetric disilylation are surprisingly underrepresented because of the lack of enantioselective methods in the stereoselective control of silyl group transformations. Herein, an asymmetric palladium-catalyzed disilylation of ether-tethered aryl iodide contained a styrene moiety through Heck/C–H activation sequence was explored for the first time. Upon high-throughput screening of TADDOL-derived phosphoramidites, it was found that **L18** is a good match in combination with Pd(dtbpf)Cl_2 in the tandem Heck/C–H activation of aryl iodide with hexamethyldisilane to afford disilylated 2.3-dihydrobenzofunan derivatives in good yields with moderate enantioselectivity.

Organosilicon compounds are well applied in synthetic organic chemistry[1] materials,[2] pharmaceuticals,[3] agrochemicals,[4] and the new applications of organosilicon compounds continue to discover in each research area.[5] Transition metal-catalyzed C–H silylation is one of the most important synthetic method for the preparation of silyl-functionalized organic molecules,[6] In recent years, Zhang,[7] Liang,[8] Cheng,[9] and Lautens's[10] research groups have committed to developing an efficient disilylation reaction of hexamathylsilane with aryl halides in the presence of palladium catalyst to synthesis the corresponding disilylated products. In these strategies palladium-catalyzed tandem Heck/remote C–H activation of aryl halides bearing a styrene moiety via a linkage to generate a spirocyclic palladapentanecycle is a key intermediate to construct the disilylated products. Indeed, palladacycles generated through C–H activation of alkene-tethered aryl halides represents a type of attractive and utility intermediate for C–C and C-heteroatom bond formation.[11] Palladacycle intermediate holds great appeal, as this species is a key factor for subsequent C–H functionalization, which could not only react with hexamethyldisiliane,[12] but also trapped by carbenes,[13] alkynes,[14] arynes,[15] fullerene,[16] dibromomethane,[17] silacycles,[18] etc., lead to polysubstituted arenes and diverse heterocycles. Notably, recent effort has been focused on the development of new strategies for constructing complex cyclic molecules via palladium-catalyzed tandem reactions, however the scope of the chemistry of the palladacycles had not expanded to the enantioselective process. In contrast, considerable efforts have been devoted to the asymmetric transformation of its analogue, namely an α-alkylpalladium intermediate formed by asymmetric intramolecular Heck-type reaction, which could be trapped by various nucleophiles such as cyanide,[19] azole,[20] hydride,[21] B_2pin_2,[22] terminal alkynes,[23] and others (Scheme 1).

The development of a catalytic asymmetric disilylation of spirocyclic palladapentanecycles is highly desired due to the undiscovered status of the asymmetric transformation of spirocyclic palladapentanecycles intermediate, an essential intermediate for constructing a quaternary carbon chirality. On the basis of previous researches and our ongoing interest in the enantioselective transition metal-catalyzed reactions, we continue to explore the first example of asymmetric disilylation of spirocyclic palladacyclopentanes with hexamathylsilane to form disilylated cyclic products (Scheme 1).

At the outset of this project, alkene-tethered aryl iodide **1a** was used as a model substrate for optimizing reaction conditions (Scheme 2). In the presence of $Pd(OAc)_2$ with PPh_3, K_3PO_4 as the base, acetonitrile as the solvent, **1a** reacted with hexamethyldisilane **2a** smoothly to afford a racemic disilylated cyclic product **3a** in 95% isolated yield. Inspired by the result, a range of chiral ligands were tested in this process. Firstly, we summited Ar-BINMOL-Phos and Fei-Phos as the ligand, which originated in our group and were found useful multifunctional



Scheme 1. Palladium-catalyzed tandem reaction of aryl iodides.

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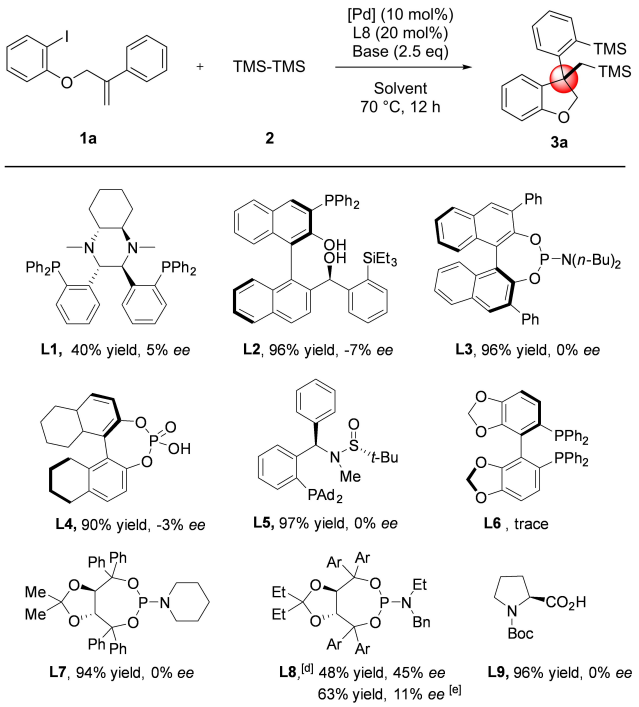
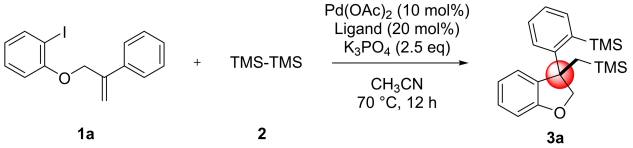


Scheme 2. The effect of chiral ligand. [a] Reaction conditions: **1 a** (0.2 mmol), **2 a** (1.6 mmol), $Pd(OAc)_2$ (10 mol%), Ligand (20 mol%), K_3PO_4 (2.5 eq.), solvent (2.0 mL), 70 °C, 12 h. [b] Determined by HPLC on a chiral stationary phase. [c] Isolated yield. [d] The Ar of L8 = 3,5-dimethylphenyl. [e] 2 equivalents of TMS-TMS were used.

Table 1. Optimization of reaction conditions.[a,b,c]



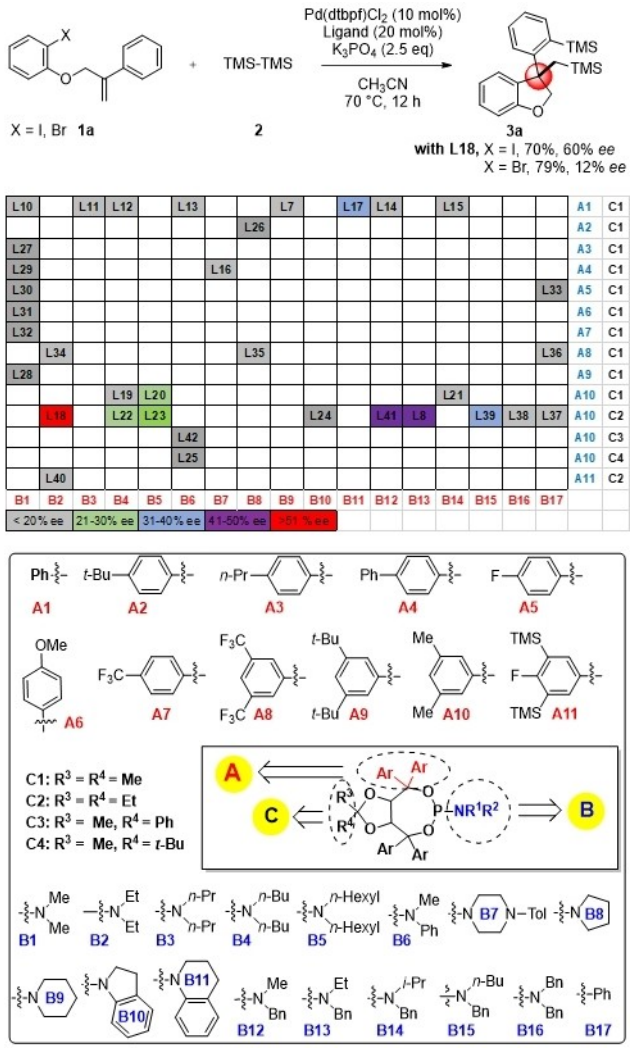
Entry	[Pd]	Base	Solvent	Yield [%]	*ee* [%]
1	$Pd(TFA)_2$	K_3PO_4	CH_3CN	97	0
2	$PdCl_2$	K_3PO_4	CH_3CN	91	0
3	$Pd(dtbpf)Cl_2$	K_3PO_4	CH_3CN	65	57
4	$Pd(dtbpf)Cl_2$	Na_2CO_3	CH_3CN	18	34
5	$Pd(dtbpf)Cl_2$	K_2CO_3	CH_3CN	25	25
6	$Pd(dtbpf)Cl_2$	Cs_2CO_3	CH_3CN	8	7
7	$Pd(dtbpf)Cl_2$	CsF	CH_3CN	29	25
8	$Pd(dtbpf)Cl_2$	TMG	CH_3CN	72	0
9	$Pd(dtbpf)Cl_2$	DBU	CH_3CN	62	0
10	$Pd(dtbpf)Cl_2$	DABCO	CH_3CN	26	0
11	$Pd(dtbpf)Cl_2$	K_3PO_4	DMF	99	3
12	$Pd(dtbpf)Cl_2$	K_3PO_4	DMA	99	4
13	$Pd(dtbpf)Cl_2$	K_3PO_4	THF	62	11
14	$Pd(dtbpf)Cl_2$	K_3PO_4	HMPA	38	16

[a] Reaction conditions: **1 a** (0.2 mmol), **2 a** (1.6 mmol), $Pd(OAc)_2$ (10 mol%), Ligand (20 mol%), K_3PO_4 (2.5 eq.), Solvent (2.0 mL), 70 °C, 12 h. [b] GC conversion and calibrated by GC yield. [c] Determined by HPLC on a chiral stationary phase.

chiral ligands in various catalytic asymmetric transformations.[24] Unexpectedly, Fei-Phos (**L1**) and Ar-BIMOL-Phos (**L2**) seemed to be unsuitable ligand in this transformation, as low enantioselective control was absorbed in both cases. BINOL-derived phosphonamidite (**L3**) and Octahydro BINOL-derived phosphate (**L4**) allowed the formation of disilylated 2.3-dihydrobenzofunan **3 a** in very good yield with poor enantioselectivity. Then, sulfinamide phosphine[25] and (*R*)-SEGPHOS[26] were the idea ligands that used for generating chiral α-alkylpalladium intermediates were tested, according to the result, we realized that **L5** result in a trace amount of **3 a** and no control of enantioselectivity on palladacycle intermediate in this process by using (*R*)-SEGPHOS **L6**. Next, TADDOL-derived phosphoramidite **L7** and *N*-Boc-*L*-Proline **L9** were used as the ligand lead to racemic product. Surprisingly, we observed promising enantioselectivity (45% *ee*) in the presence of **L8**, a modified structure of **L7**. Note that the conversion and enantioselectivity decreased when 2 equivalents of **2 a** were used in the process.

With these results in hand, further investigations were performed base on **L8** (Table 1). The replacement of the palladium acetate $Pd(OAc)_2$ by palladium(II) trifluoroacetate $Pd(TFA)_2$ and palladium chloride $PdCl_2$, lead to racemic disilylated product **3 a**, while 1,1′-bis (di-*t*-butylphosphino)ferrocene palladium dichloride ($Pd(dtbpf)Cl_2$) was submitted as the catalyst, **3 a** was obtained in moderate yield with 57% *ee* (entry 1–3). In addition, various bases were tested, such as, sodium carbonate (Na_2CO_3), potassium carbonate (K_2CO_3), cesium carbonate (Cs_2CO_3), cesium fluoride (CsF), tetramethylguanidine (TMG), 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and triethylenediamine (DABCO), it turned out all these bases did not provide any improvement in terms of enantioselectivity in this palladium-catalyzed tandem reaction process (entry 4–10). Finally, the solvent effect was studied. The reaction was carried out in *N*,*N*-dimethylformamide (DMF), *N*,*N*-dimethylacetamide (DMA), tetrahydrofuran (THF), and hexamethylphosphoramide (HMPA), respectively. CH_3CN exhibited an idea solvent among these solvents in terms of enantioselectivity. At this point, the model reaction of **1 a** and **2** under the combination of $Pd(dtbpf)Cl_2$, TADDOL-derived phosphoramidite **L8**, K_3PO_4 and acetonitrile allowed the formation of **3 a** in 65% yield with 57% *ee*.

Owing to structural modification and its flexibility of the chiral TADDOL-derived phosphoramidites, they have become one of the most popular and efficient ligands in various transition-metal-catalyzed asymmetric transformations.[27] We continued to investigate the palladium catalyzed disilylation of **1 a** via tandem Heck/C–H activation sequences with a varity of chiral TADDOL-derived phosphoramidites (**L10**–**L42**) bearing different substituents on ketal, aryl ring or amine of TADDOL-based backbone. As shown in Scheme 3, in general, the desired product was formed in varied yields (4–97% yields) and low to moderate enantioselectivities (0–60% *ee*), which revealed the importance of the combination of these substituents on chiral TADDOL-based phosphoramidites to the enantioselective construction of the disilylated product in this reaction. For example, the introduction of a bulky group (C3, C4) or less steric group (C1) on ketal part of the ligand, normally resulted in low enantioselectivity. On the other hand, the aryl ring requires an appropriate substituent to manage the aromatic interaction or steric repulsion for asymmetric tandem Heck/C–H activation of **1**. It was found that 3.5-dimethylphenyl group (A10) was an



Scheme 3. Screening of TADDOL-based phosphoramidites.

idea substituent, compared to 3.5-di-*tert*-butylphenyl (A8) and 3.5-di-trifluoromethylphenyl (A9). Likewise, amine (B1–B20) decorative TADDOL-derived phosphoramidites were investigated to give varied enantioselectivities. As a result, we identified **L18** (Ar = 3.5-dimethylphenyl, R^1=R^2=R^3=R^4=Et) was the best ligand in terms of enantioselectivity (60% *ee*) among these chiral TADDOL-derived phosphoramidites (see the SI for more details).

Although the optimized reaction conditions were not perfect in this reaction, so far the structural modification of TADDOL-derived phosphoramidites with high level of enantioselectivity for disilylation of spirocyclic palladacyclopentanes is not an easy task. We then used **L18** as the optimal ligand, and a range of ether-tethered aryl iodides were summited to the standard reaction conditions as shown in Scheme 4. *Para*-position of benzene ring on styrene side bearing a methyl group was first tested, the corresponding product **3b** was isolated in 70% yield with 42% *ee*. However, if the starting material was 1-bromo-2-((2-phenylallyl)oxy)benzene or 1-bromo-2-((2-(*p*-tolyl)allyl)oxy)benzene, the enantioselectivity was quite low (12% *ee* for **3a** or 9% *ee* for **3b** respectively), albeit the yield of the desired product was good (79% yield for **3a** and 49% yield for **3b** respectively). The replacement of methyl group by *t*-butyl group lead to higher isolated yield of **3c**, but lower enantioselectivity was observed. In contrast, *para*-methoxy substitute **3d** was isolated in moderate yield with 61% *ee*. Substrates bearing a halo atom were also tolerated, **3e**, **3f**, and **3g** were obtained in moderated yields (65–60%), while the enantioselectivity increased in the order of F < Cl < Br (36–76% *ee*). Next, substituent such as, methyl, halo, trifluoromethyl and *t*-butyl on the benzene ring of arylhalide were tested, In general, the reactions proceeded well and afforded the desired products in moderate to good yields (up to 98%), although varied enantioselectivities (up to 73 : 27 *er*) were obtained for most substrates.

According to previous studies on the general mechanism (scheme 5) the formation of spirocyclic palladacyclopentane intermediate[7] starts with oxidative addition of Pd(0) to C–X bond of aryl iodides, followed by a intramolecular carbopalladation to form alkylpalladium(II) intermediate **B**. Then a C–H activation step would give rise to spirocyclic palladacyclopentane intermediate **C** with the coordination of a suitable chiral ligand would allow to form a quaternary carbon chirality (**B** and **C**). However, the asymmertic transformation of spirocyclic palladacyclopentane intermediate **C** is more challenging compare to the alkylpalladium(II) intermediate **B**, cause the ligand should able to induce an optical alkylpalladium intermediate **B**, and remains high enantioselectivity in the follow C–H activation step to generate a chiral spirocyclic palladacyclopentane intermediate **C**. So far, TADDOL-derived phosphoramidite ligand **L18** was the best ligand to access chiral disilylated cyclic product although the results were not perfect.

In summary, it can be seen that the development of enantioselective disilylation of spirocyclic palladacyclopentanes is not an easy work at present, on the basis of high-throughput screening of TADDOL-derived phosphoramidites, we have tried explored for the first example of enantioselective palladium-catalyzed tandem reaction of ether-tethered aryl iodides with hexamethyldisilane. In general, ligand **L18** exhibited promising activity during the formation of the spirocyclic palladacyclopentane intermediates, leading to the corresponding disilylated products in moderate to good yield (up to 98%). Although the present palladium-catalyzed disilylation reaction of alkene-tethered aryl iodides **1** with hexamethyldisilane **2** resulted in only moderate enantioselectivities using TADDOL-derived phosphoramidite as the ligand, to our knowledge, these are the best results for an asymmetric disilylation of palladacyclopentanes via tandem Heck/C–H activation of aryl iodides in terms of enantioselectivity. The new chemistry in the asymmetric disilylation of palladacyclopentanes will possibly inspire researchers to explore more effective ligands in this field.

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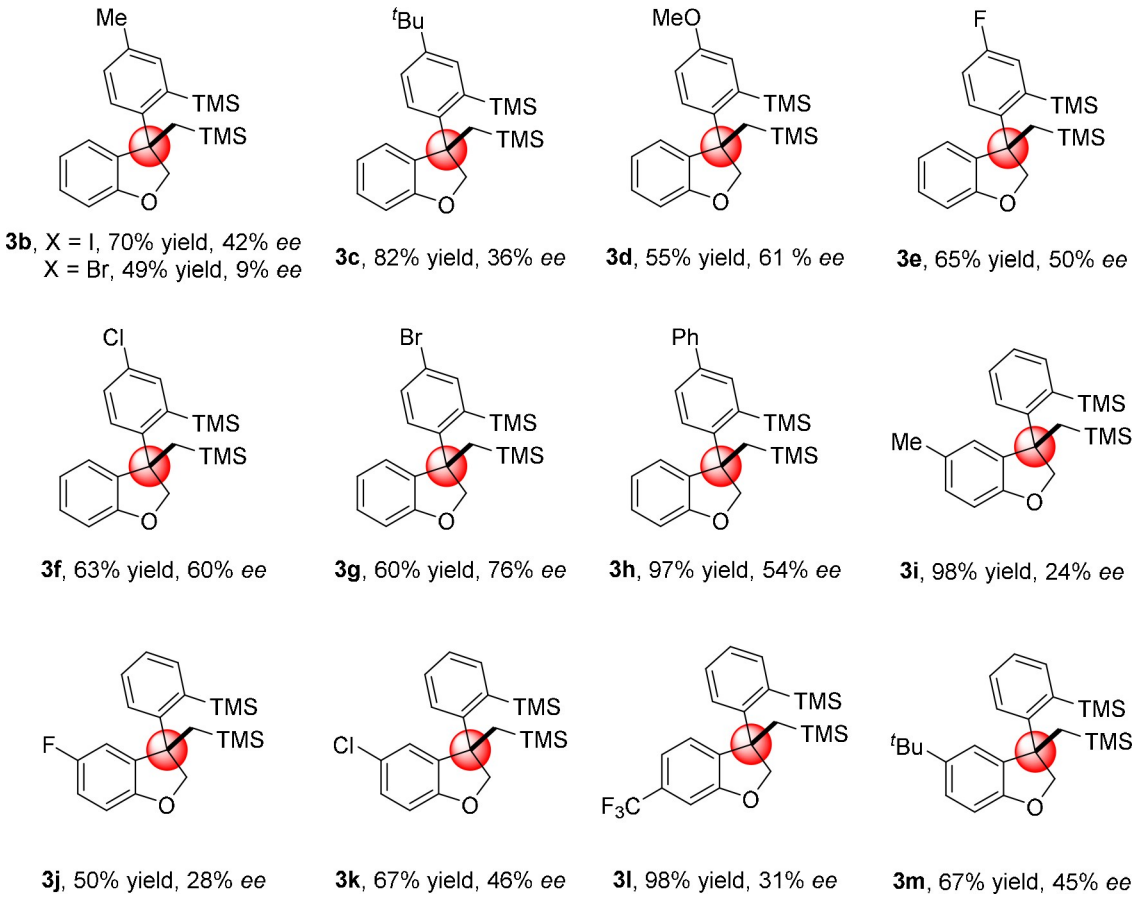
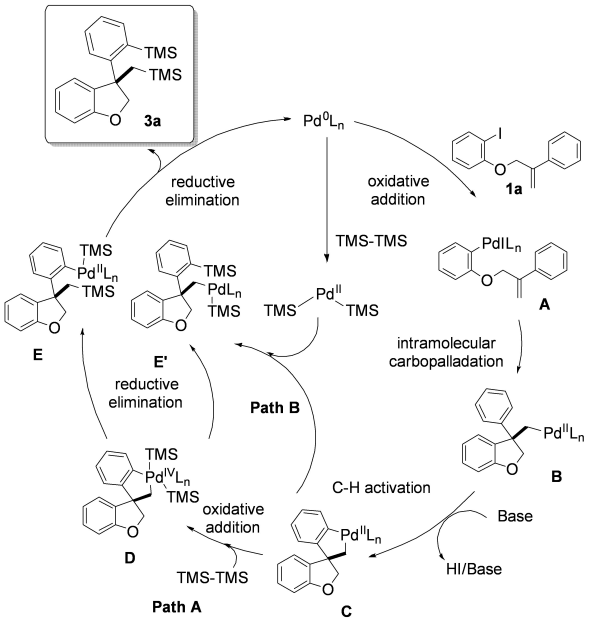


Scheme 4. Scope of Substrates. [a] Reaction conditions: **1 a** (0.2 mmol), **2 a** (1.6 mmol), Pd(dtbpf)Cl_2 (10 mol%), L18 (20 mol%), K_3PO_4 (2.5 eq.), CH_3CN (2.0 mL), 70 °C, 12 h. [b] Isolated yield. [c] Determined by HPLC on a chiral stationary phase.



Scheme 5. General mechanism for palladium-catalyzed tandem reaction of aryl iodides with hexamethyldisilane.

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Conflict of Interest

There are no conflicts to declare.

Keywords: Organosilicon · palladium · disilylation · spirocycle · chiral ligand

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