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Palladium-Catalyzed Asymmetric Synthesis of Silicon-Stereogenic Dibenzosiloles via Enantioselective C−H Bond Functionalization

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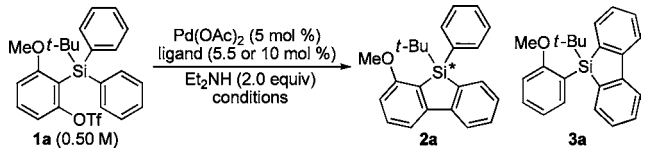
Supporting Information

ABSTRACT: A Pd-catalyzed asymmetric synthesis of Si-stereogenic dibenzosiloles is developed through enantioselective C−H bond functionalization of prochiral 2-(arylsilyl)aryl triflates. High chemo- and enantioselectivities are achieved by employing a Josiphos-type ligand under mild conditions.

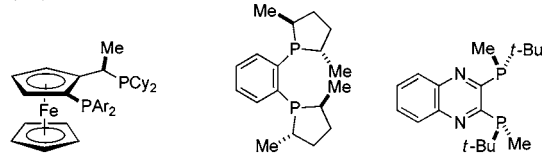
Dibenzosiloles constitute a class of compounds that can be applied to various useful materials[1] such as light-emitting diodes,[2] thin-film transistors,[3] solar cells,[4] and detectors for explosives,[5] due to their unique optoelectronic properties based on the π-conjugation system. Considering this wide utility of the dibenzosilole structural motif in materials science, the preparation of enantioenriched chiral dibenzosiloles would be of high significance in view of their potential future applications. Unfortunately, however, no synthetic methods are available to date for enantioenriched dibenzosiloles as far as we are aware. In this context, we envisioned that the preparation of Si-stereogenic dibenzosiloles would be highly attractive because the requisite biaryl moiety of the dibenzosilole can be flexibly tuned without the necessity of introducing extra C stereocenters, but available methods for the construction of Si stereocenters, particularly in a catalytic asymmetric manner, are very limited compared to those for the construction of C stereocenters.[6,7] Here we describe a new way of synthesizing such Si-stereogenic dibenzosiloles with high enantioselectivity through Pd-catalyzed enantioselective C−H bond functionalization of 2-(arylsilyl)aryl triflates.[8,9]

Our investigation was initiated by employing prochiral aryl triflate **1a** having a (*tert*-butyl)diphenylsilyl group as a model substrate for the Pd-catalyzed intramolecular C−H bond arylation reaction, a non-asymmetric variant of which was recently reported by Shimizu et al.[10] Under their reported conditions that were highly effective for yielding various achiral dibenzosiloles (PCy_3 as the ligand in DMA at 100 °C), an almost 1:1 mixture of desired product **2a** and its isomeric achiral dibenzosilole **3a** was obtained in 81% combined yield (Table 1, entry 1). In contrast, the formation of undesired **3a** was significantly suppressed by using (R,S_p)-**L1** (Josiphos),[11] an electron-rich bisphosphine ligand, and product **2a** was obtained in 57% yield with 82% ee at 60 °C (entry 2). Higher yield and ee were achieved by conducting the reaction in toluene instead of DMA, giving **2a** in 84% yield with 87% ee (entry 3). The change of diphenylphosphino group of ligand (R,S_p)-**L1** to bis(3,5-dimethyl-4-methoxyphenyl)phosphino group ((R,S_p)-**L2**)[11c] led to further improvement of both yield and enantioselectivity (95% yield, 94% ee; entry 4). In comparison, other chiral electron-rich bisphosphine ligands such as (S,S)-**L3** (Me-DuPhos)[12] and (R,R)-**L4** (QuinoxP*)[13] also gave **2a** selectively over **3a**, but the yields and ee values were significantly lower than those with Josiphos-type ligands (entries 5 and 6).[14]

Table 1. Pd-Catalyzed Synthesis of Dibenzosiloles from 1a: Optimization



entry	ligand (mol%)	conditions	yield of **2a** (%)[a]	yield of **3a** (%)[a]	ee of **2a** (%)[b]
1	PCy_3 (10)	DMA, 100 °C, 24 h	44	37	—
2	(R,S_p)-**L1** (5.5)	DMA, 60 °C, 48 h	57	4	82 (*S*)
3	(R,S_p)-**L1** (5.5)	toluene, 60 °C, 48 h	84	4	87 (*S*)
4	(R,S_p)-**L2** (5.5)	toluene, 60 °C, 48 h	95	3	94 (*S*)
5	(S,S)-**L3** (5.5)	toluene, 60 °C, 48 h	19	<1	19 (*R*)
6	(R,R)-**L4** (5.5)	toluene, 60 °C, 48 h	25	3	54 (*R*)



(R,S_p)-**L1**: Ar = Ph (Josiphos)
(R,S_p)-**L2**: Ar = 3,5-Me_2-4-$MeOC_6H_2$
(S,S)-**L3** (Me-Duphos)
(R,R)-**L4** (QuinoxP*)

[a]Determined by ^{1}H NMR against an internal standard ($MeNO_2$). [b]Determined by chiral HPLC on a Chiralcel OD-H column with hexane/2-propanol = 90/10.

Under the optimized conditions described in Table 1, entry 4, 4-substituted 5-(*tert*-butyl)-5-phenyl-5*H*-dibenzosiloles **2a**−**2c** were effectively prepared with high enantioselectivity (91−98% ee; Table 2, entries 1−3). Dibenzosiloles **2d**−**2f** having substituents at the 2- or 3-position were also synthesized in high yield, albeit with somewhat reduced ee values (75−80% ee; entries 4−6). In addition, dibenzosiloles **2g** and **2h** derived from 2-naphthyl and 5-indolyl triflates, respectively, were

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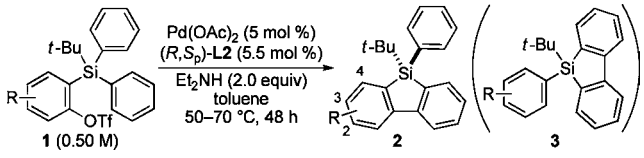
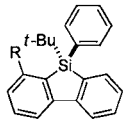
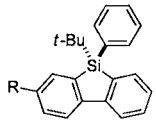
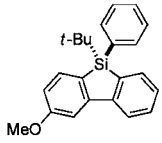
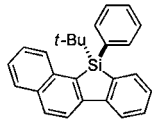
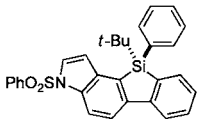
Table 2. Pd-Catalyzed Asymmetric Synthesis of Si-Stereogenic Dibenzosiloles 2: Scope 1



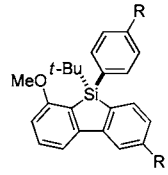
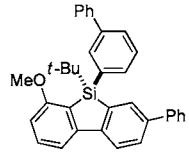
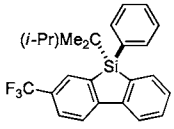
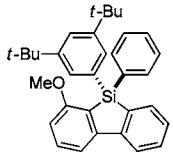
entry	structure of **2** (R)		temp (°C)	yield (%)[a]	**2**/**3**[b]	ee of **2** (%)[c]
1		**2a** (OMe)	60	92[d]	97/3	94
2		**2b** (Me)	50	70	97/3	91
3[e,f]		**2c** (CH=CMe$_2$)	60	64	>99/1	98
4		**2d** (CF_3)	50	99	>99/1	80
5[e]		**2e** (Me)	50	72	>99/1	80
6		**2f**	60	94	>99/1	75
7		**2g**	50	84	98/2	94
8		**2h**	70	95	97/3	96

[a]Combined isolated yield of **2** and **3** unless otherwise noted. [b]Determined by ^{1}H NMR. [c]Determined by chiral HPLC with hexane/2-propanol. [d]Isolated yield of **2a**. [e]Conducted in the presence of 10 mol% of Pd(OAc)$_2$ and 10.5 mol% of ligand. [f](R,S_p)-**L1** was used as the ligand.

obtained with high enantioselectivity (94–96% ee; entries 7 and 8). The absolute configuration of product **2g** in entry 7 was determined to be (*S*) by X-ray crystallographic analysis with Cu Kα radiation.[15]

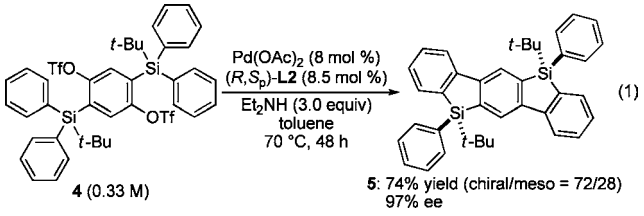
In addition to aryl triflates having a (*tert*-butyl)diphenylsilyl group at the 2-position as described in Table 2, several other 2-silylated aryl triflates can also be employed for the present catalysis. For example, substrates **1**, having two of the same substituted phenyl groups on the Si atom, were converted to the corresponding dibenzosiloles **2** with good to excellent ee (81–97% ee; Table 3, entries 1–4). It is worth noting that **1l**, having a (*tert*-butyl)di(3-phenylphenyl)silyl group, selectively undergoes C–H bond functionalization at the less hindered site, giving **2l** with extended π-conjugation of the *p*-terphenyl moiety (entry 4).[16] Other dibenzosiloles such as **2m** and **2n**, having bulky 1,1,2-trimethylpropyl and 3,5-di-*tert*-butylphenyl groups, respectively, were also synthesized with relatively high enantioselectivity (79–89% ee; entries 5 and 6).[17] The result in entry 6 represents an interesting example that effectively differentiates the two phenyl groups on the Si atom in the presence of another substituted phenyl group. Furthermore, the reaction of aryl ditriflates **4** gives doubly cyclized product **5** in 74% combined yield of chiral and meso isomers (ratio = 72/28) with 97% ee for the chiral isomer through the two-fold enantioselective C–H bond functionalization (eq 1).[18] The

Table 3. Pd-Catalyzed Asymmetric Synthesis of Si-Stereogenic Dibenzosiloles 2: Scope 2[a]

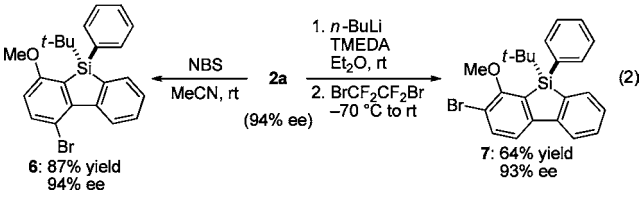
entry	structure of **2** (R)		temp (°C)	yield (%)[b]	**2**/**3**[c]	ee of **2** (%)[d]
1		**2i** (Me)	70	84[e]	94/6	81
2		**2j** (Ph)	60	97	99/1	97
3		**2k** (2-Np)	60	94	98/2	95
4[f]		**2l**	60	93	99/1	96
5[f]		**2m**	50	93	>99/1	79
6		**2n**	60	94	96/4	89

[a]The reaction conditions are the same as those in Table 2 unless otherwise noted. [b]Combined isolated yield of **2** and **3**. [c]Determined by ^{1}H NMR. [d]Determined by chiral HPLC with hexane/2-propanol. [e]Contaminated with small impurity (<5%). [f]Conducted in the presence of 10 mol% of Pd(OAc)$_2$ and 10.5 mol% of ligand.

absolute configuration of chiral **5** was determined to be (*S*,*S*) by X-ray crystallographic analysis.[15]



We have also begun to explore derivatizations of enantioenriched dibenzosiloles **2** obtained in these reactions. In our preliminary experiments, bromination of **2a** (94% ee) with NBS in MeCN proceeds regioselectively at the 1-position to give **6** in 87% yield with 94% ee (eq 2, left).[19] On the other



hand, lithiation of **2a** with *n*-BuLi/TMEDA, followed by bromination, results in the formation of 3-bromo compound **7** in 64% yield (eq 2, right). These bromination products could be of further use with rich chemistry of aryl halides (cross-coupling, homocoupling, metal–halogen exchange, etc.).

To gain some mechanistic insight into the present catalysis, we conducted several competition experiments. Electron-deficient aryl triflate **1d**, having a trifluoromethyl group at the

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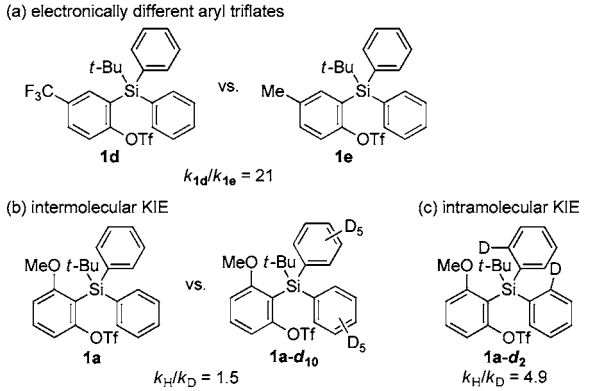
4-position, reacted 21 times faster than structurally similar but more electron-rich 4-methyl substrate **1e** (Scheme 1a). In

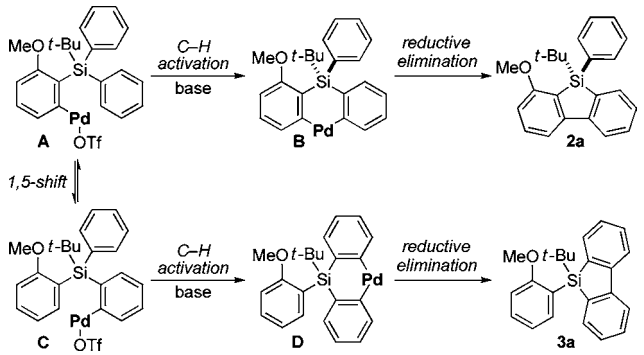
Scheme 1. Reactivity Difference between 1d and 1e and Observed Inter- and Intramolecular Kinetic Isotope Effects



addition, an intermolecular competition reaction between 2-(*tert*-butyl)diphenylsilyl aryl triflate **1a** and 2-(*tert*-butyl)di(pentadeuteriophenyl)silyl aryl triflate **1a-d_{10}** showed k_H/k_D = 1.5 (Scheme 1b). On the other hand, k_H/k_D = 4.9 was observed for an intramolecular competition reaction of 2-(*tert*-butyl)di(2-deuteriophenyl)silyl aryl triflate **1a-d_2** (Scheme 1c).

A proposed reaction pathway for the present reaction of **1a** is illustrated in Scheme 2. Thus, oxidative addition of the C−O

Scheme 2. Proposed Reaction Pathways to Dibenzosilole 2a and Its Isomer 3a



bond of aryl triflate **1a** to Pd(0) gives arylpalladium triflate **A**. A base-assisted intramolecular C−H bond activation then gives diarylpalladium species **B**,[20] reductive elimination of which leads to the formation of chiral dibenzosilole **2a** along with regeneration of Pd(0). Formation of undesired achiral isomer **3a** could be explained by 1,5-Pd migration[21,22] from **A** to arylpalladium triflate **C**, which then undergoes C−H bond activation toward diarylpalladium **D** followed by reductive elimination. On the basis of the competition experiment in Scheme 1a (k_{1d}/k_{1e} = 21) and the result of intermolecular KIE in Scheme 1b (k_H/k_D = 1.5), oxidative addition of aryl triflate to Pd(0) (formation of **A**) is most likely the turnover-limiting step of the catalytic cycle, and the subsequent C−H bond activation (**A**→**B**) occurs faster.[20i,j] The intramolecular KIE in Scheme 1c (k_H/k_D = 4.9), which is consistent with the one for related intramolecular arylation reactions of aryl bromides,[20c] may indicate that this C−H bond activation step proceeds through a transition state (Figure 1a) with intermolecular assistance of the

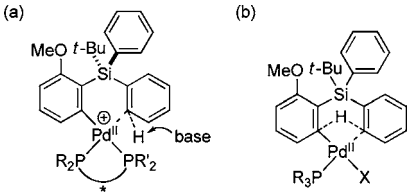


Figure 1. Possible transition states for (a) **A**→**B** and (b) **A**→**C**.

base, as proposed by Maseras and Echavarren.[20c] On the other hand, based on the report by Dedieu and Suffert for the reaction involving a 1,5-Pd migration,[21] the undesired step from **A** to **C** could proceed through a four-centered H atom transfer of a Pd(II)L_1 species (Figure 1b),[23,24] and this pathway seems effectively suppressed by using bisphosphine ligands such as **L1**−**L4** in the present catalysis (Table 1).

In summary, we have developed a Pd-catalyzed asymmetric synthesis of Si-stereogenic dibenzosiloles through enantioselective C−H bond functionalization of prochiral 2-(arylsilyl)aryl triflates. High chemo- and enantioselectivities have been achieved by employing Josiphos-type ligand (R,S_p)-**L2** under mild conditions. This method also represents the first example of catalytic asymmetric construction of Si stereocenters by enantioselective C−H bond activation. Future studies will explore further expansion of the reaction scope, and we hope this methodology will open the door for various applications using enantioenriched chiral dibenzosiloles.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Experimental procedures and compound characterization data. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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