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Nickel(0)-Catalyzed Enantio- and Diastereoselective Synthesis of Benzoxasiloles: Ligand-Controlled Switching from Inter- to Intramolecular Aryl-Transfer Process

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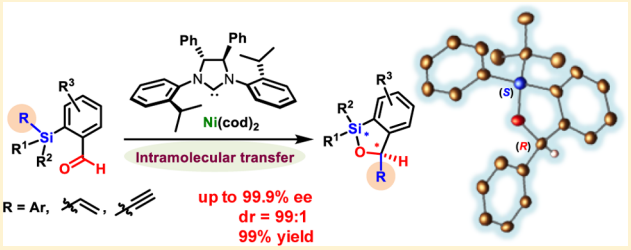
Supporting Information

ABSTRACT: A highly enantioselective synthesis of 3-aryl-, vinyl-, and alkynyl-2,1-benzoxasiloles (up to 99.9% ee and 99% yield) was achieved via the sequential activation of an aldehyde and a silane by nickel(0). This strategy was applied to a simultaneous generation of carbon- and silicon-stereogenic centers with excellent selectivity (dr = 99:1) via diastereotopic aryl transfer. Initial mechanistic studies revealed the complete switching of an aryl-transfer process from an intermolecular (racemic synthesis in the presence of IPr) to an intramolecular (enantioselective synthesis using chiral NHC, **L5**) fashion. A plausible rationale for the switching of the aryl-transfer process is given by a preliminary DFT calculation, which suggests that the coordination of **1** to the nickel(0)/**L5** fragment in an η^2-arene:η^2-aldehyde fashion would be a key to the intramolecular process, while the formation of the corresponding intermediate is not possible in the presence of IPr. Owing to the chemically labile nature of its C−Si and O−Si bonds, enantioenriched benzoxasiloles are utilized for the synthesis of chiral building blocks and antihistaminic and anticholinergic drug molecules such as (*R*)-orphenadrine and (*S*)-neobenodine with no erosion of the enantiomeric excess.



INTRODUCTION

The transition-metal-catalyzed enantioselective addition of organometallic reagents to prochiral carbonyl groups is a venerable area of fundamental research in organic chemistry.[1] Indeed, various combinations of organometallic reagents and transition metals have been developed to achieve corresponding chiral products with high enantioselectivities. These methods primarily follow the η^1 coordination of a carbonyl group to a metal, particularly Lewis acidic metals in their higher oxidation states. In contrast, examples of catalytic enantioselective reactions via the η^2 coordination of aldehydes toward low-valent transition metals are limited,[2−4] despite many contributions from the field of coordination chemistry.[5] In addition to its fundamental importance, the existing methodology of an enantioselective addition to an aldehyde would be conceptually more appealing if the resultant chiral product could serve as a versatile precursor for further transformations to useful products. Benzoxasilole has privileged structural features that make it useful for further transformations due to chemically labile C−Si and O−Si bonds. Several synthetic methods and applications of benzoxasiloles have been reported,[6] while their asymmetric version remains underdeveloped.[7] Furthermore, such an asymmetric strategy would allow the creation of a silicon stereogenic center. Very recently, Ryberg and Hartwig et al. reported the first asymmetric synthesis of 3-aryl-2,1-benzoxasiloles employing the Ir-catalyzed hydrosilylation of symmetrical diarylketone followed by Rh-catalyzed intramolecular enantioselective silylation of an arene C−H bond through the desymmetrization of diarylmethanol silyl ether.[7] However, this strategy has not been utilized to generate a silicon stereogenic center.

We recently reported the racemic synthesis of 3-aryl-, vinyl-, and alkynyl-2,1-benzoxasiloles proceeded via an activation of organosilanes with (η^2-aldehyde)Ni(IPr) complex, where IPr is 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene.[8] Initial mechanistic studies of this reaction revealed the involvement of an intermolecular aryl-transfer from the silicon center to a formyl carbon (Scheme 1). While the mild reaction conditions suggest the development of a rational asymmetric version, the mechanistic outcome offered further challenges to achieve high enantioselectivity. Herein, we report the nickel(0)-catalyzed enantio- and diastereoselective synthesis of benzoxasiloles with the simultaneous generation of carbon- and silicon-stereogenic centers by changing the ligand from IPr to a chiral NHC **L5** with a complete switching of the aryl-transfer

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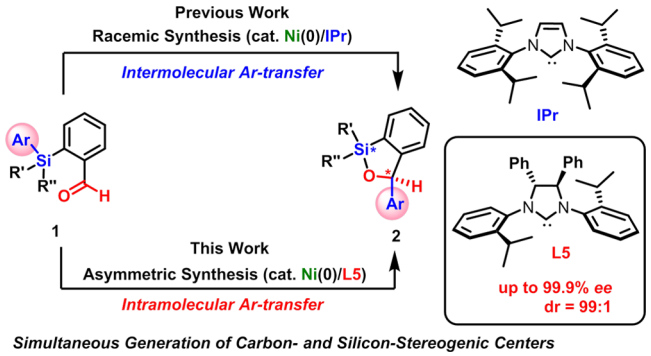
Scheme 1. Enantio- and Diastereoselective Synthesis of Benzoxasiloles via Ligand-Controlled Switching of Aryl-Transfer Process

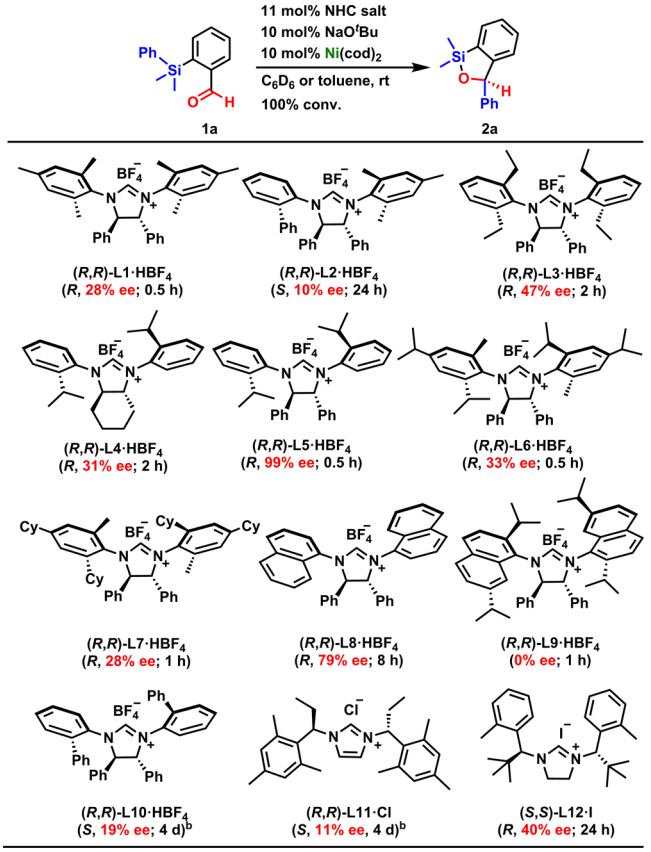


process from intermolecular to intramolecular (Scheme 1). The results of a preliminary density functional theory (DFT) calculation are also presented to rationalize the observed change in mechanism.

RESULTS AND DISCUSSION

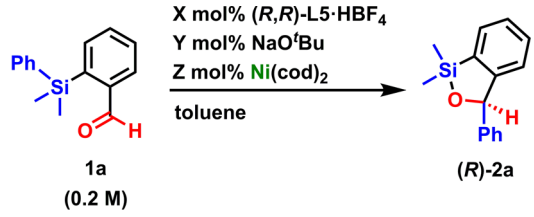
Our study began with an evaluation of potential chiral ligands. A set of chiral phosphines[9] and N-heterocyclic carbenes (NHCs) **L1**−**L12** (10 mol %; generated *in situ* by treating corresponding imidazolinium salt with NaO^{t}Bu) was surveyed using *o*-dimethylphenylsilylbenzaldehyde (**1a**) as a model substrate (Scheme 2). Most of the NHCs (**L1**−**L9**) yielded almost quantitative formation of benzoxasilole **2a**, which proved the robustness of this strategy. However, the enantioselectivity and reaction times varied with the structure of ligands (Scheme 2). For example, reactions were completed within 2 h in the presence of NHCs (**L1**−**L9** except **L8** and C_1-symmetric NHC **L2**) with a range of enantioselectivities. Excellent results in both the yield and enantioselectivity (99% ee) were observed with **L5**. This NHC was pioneered by Grubbs et al. and employed for the Ru-catalyzed enantioselective ring-closing metathesis reactions.[10] *N*-(1-Naphthyl)-substituted NHC **L8** gave **2a** with good enantioselectivity (79% ee), while *N*-(2,7-diisopropylnaphthyl)-substituted NHC **L9**[11] resulted in racemic-**2a**, and the reactions were completed in 8 and 1 h, respectively. Following 4 days at 60 °C, the reactions of **1a** with *N*-(2-biphenyl)-substituted NHC **L10** and *N*-(1-mesitylpropyl) NHC **L11** resulted in 50 and 10% conversion, respectively. The enantioselectivities (19 and 11% ee, respectively) were evaluated at these conversions. Kündig's NHC **L12**[12] delivered **2a** with moderate enantioselectivity (40% ee). It is noteworthy that benzoxasilole **2a** was sensitive to silica column chromatography[13] and HPLC. Hence, the enantiomeric composition of **2a** was evaluated after converting it into **3a** by Tamao−Fleming oxidation[6o] (*vide infra*, Figure 2). The feasibility of the reaction was also examined with other nickel source Ni(acac)$_2$ as well as in the absence of Ni(cod)$_2$ (Table 1, entries 2 and 3, respectively). However, no reaction was observed in either case. These results suggest that reactions are neither catalyzed by NHCs nor do they appear to be promoted by Lewis acidic Ni(II) species. The efficiency of the catalyst using Ni(cod)$_2$ was further examined by the lower catalyst loading of 2 mol %, which delivered **2a** with no erosion of the enantiomeric excess (entry 4; 99% yield and ee). The reaction produced high enantioselectivity even when 1 mol % of the catalyst was used (entry 5; 97% ee), but a longer reaction time was required (>2 days, entry 5). (*S*,*S*)-**L5** was equally effective to give (*S*)-**2a** (99% yield and ee, entry 6).

Scheme 2. Survey of Chiral NHC Ligands[a]



[a]Reaction was examined at 0.2 mmol scale. Enantioselectivity was determined by HPLC/SFC equipped with a chiral stationary phase. [b]Reaction was monitored at 60 °C, and ee was measured from aliquot collected at 50 and 10% conversion in case of **L10** and **L11**, respectively.

Table 1. Further Optimization with L5·HBF$_4$



entry	X	Y	Z	temp (°C)	time (h)	yield (%)[a]	ee (%)[b]
1	11.0	10.0	10.0	rt	0.5	100	>99
2[c]	11.0	10.0	10.0	rt	24.0	0	–
3	11.0	10.0	–	80	48.0	0	–
4	2.2	2.0	2.0	rt	1.0	99	99
5	1.1	1.0	1.0	rt	48.0	95	97
6[d]	2.2	2.0	2.0	rt	1.0	99[e]	99

[a]Yields were determined by GC using *n*-pentadecane as an internal standard. [b]Enantioselectivity was determined by SFC equipped with a chiral stationary phase. [c]Ni(acac)$_2$ was used as a Ni(II) source. [d](*S*,*S*)-**L5**·HBF$_4$ was employed. [e](*S*)-**2a** was obtained as a major product.

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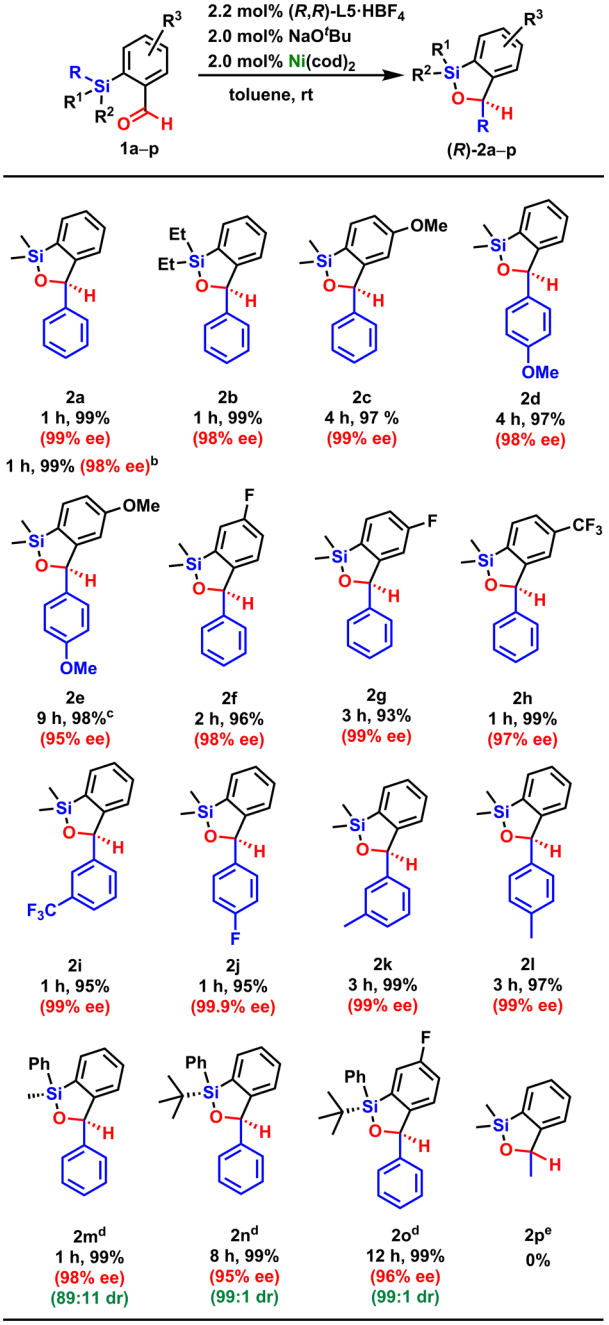
The generality of the present catalytic enantioselective process was evaluated for the synthesis of various chiral benzoxasiloles using 2 mol % of the catalyst with (*R*,*R*)-**L5** (Table 2). Enantioselectivities were determined either for the corresponding oxidation or for the desilylation products (**3** or **4**, respectively, *vide infra*, Figure 2). In the case of **2h**, enantiomeric composition was examined after both trans-formations (**3h** and **4h**) resulted in the same enantioselectivity.[9] The substituents on the silicon affected neither the yields nor the enantioselectivities of the products (**2a** and **2b**). When either, or both, of the aryl groups were substituted with electron-donating groups (**1c**–**e**), the reaction was relatively slow by comparison with the use of electron-withdrawing groups (**1f**–**j**). A fluorine atom at the para-position, with respect to either a formyl (**1f**) or a dimethylphenylsilyl group (**1g**), resulted in almost the same results. The reactions of **1h** and **1i**, which are equipped with an electron-withdrawing CF_3 group at the meta-position of either of the aryl groups, were completed in a relatively shorter time (1 h) with high enantioselectivity. The reactions of **1**, with either a *meta*- or a *para*-tolyl group on the silicon, were completed in 3 h with excellent yields and enantioselectivity (**2k** and **2l**). The absolute configuration of **2h** was determined to be (*R*) by X-ray crystallography (Figure 1a), and other compounds were assigned either by analogy to **2h** or by the elution order of enantiomers reported in the literature. To demonstrate the practical nature of the present catalytic process, a gram-scale reaction of **1a** (5.0 mmol, 1.22 g) was conducted under identical conditions and gave **2a** in 99% yield and 98% ee (Table 2).

Table 2. Catalytic Enantio- and Diastereoselective Synthesis of 3-Arylbenzoxasiloles[a]



[a]Reaction was examined at 0.2 to 2.0 mmol scale (0.2 M). Isolated yields are given. Enantioselectivity was determined by HPLC/SFC equipped with a chiral stationary phase. [b]Reaction was examined at 5.0 mmol scale. [c]**L5**·HBF_4/NaO^tBu/$Ni(cod)_2$ (4.4/4.0/4.0 mol %) was used. [d]**L5**·HBF_4/NaO^tBu/$Ni(cod)_2$ (2.2/2.2/2.0 mol %) was used.[16] [e]**L5**·HBF_4/NaO^tBu/$Ni(cod)_2$ (11/10/10 mol %) was employed and heated at 80 °C for 24 h.

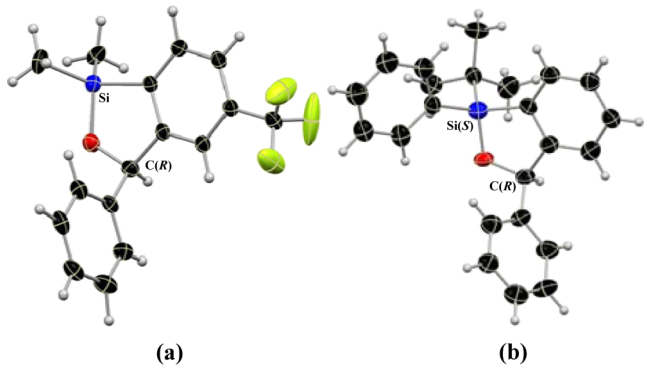


Figure 1. ORTEP representation with thermal ellipsoid at 50% probability level (a) (*R*)-**2h** (Flack parameter = 0.02(3)) and (b) (C(*R*),Si(*S*))-**2n** (Flack parameter = −0.03(2)).

As the chirality of carbon is a key element for natural products, the central chirality of silicon is an attractive and potentially useful attribute for unnatural chiral molecules due to the unique chemical and physical properties of silicon.[14] Therefore, much recent attention has been paid to the asymmetric construction of silicon stereogenic centers,[15] and catalytic asymmetric desymmetrization is one of the most promising approaches among them.[15a,b] In order to demonstrate our asymmetric approach to the diastereoselective activation of silicon, which in turn leads to the generation of a silicon stereogenic center, a prochiral silane (having two phenyl groups) was introduced. Diphenylmethylsilane derivative **1m** gave **2m** with a moderate degree of diastereoselectivity (dr = 89:11) and high enantioselectivity (98% ee). The diastereoselectivity was improved to almost one diastereomer by the introduction of a *tert*-butyldiphenylsilyl group (**2n** and **2o**; dr = 99:1) with negligible erosion of the enantioselectivity (95 and 96% ee, respectively). A single diastereomer of **2n** was isolated by recrystallization (hexane at −20 °C), and the absolute configurations of both the carbon and the silicon centers were unambiguously determined by X-ray crystallography to be C(*R*) and Si(*S*) (Figure 1b). The overall catalytic

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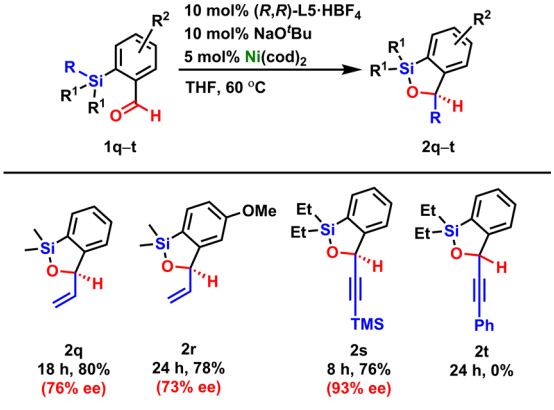
process is comprised of the first example of a synchronized generation of enantioenriched carbon and silicon stereogenic centers at the 1, 3 positions.[15d]

In order to check the feasibility of an alkyl group transfer from silicon to carbonyl carbon to get **2p**, *o*-trimethylsilylbenzaldehyde **1p** was treated with 10 mol % of catalyst. No reaction took place even at elevated temperatures (80 °C, Table 2), but a dimeric ester was formed as a single product via a nickel-catalyzed Tishchenko reaction under Ni(0)/IPr catalytic conditions.[8,4d]

We have also examined the enantioselective migration of vinyl and alkynyl groups to form corresponding 3-substituted benzoxasiloles (Table 3). We previously reported that the 1:2

Table 3. Catalytic Enantioselective Synthesis of 3-Vinyl- and Alkynylbenzoxasiloles[a]



[a]Isolated yields are given. Enantioselectivity was determined by SFC equipped with a chiral stationary phase.

mixture of $Ni(cod)_2$ and IPr in THF was effective for the catalytic transformation of substrates with vinyl- and alkynylsilyl groups.[8] Thus, we conducted the reaction of **1q** and **1r** with 5 mol % of $Ni(cod)_2$ and 10 mol % of **L5**·HBF_4 and NaO^{t}Bu each in THF at 60 °C, which gave **2q** (80% yield, 76% ee) and **2r** (78% yield, 73% ee), respectively. The enantioselective synthesis of 3-vinyl-2,1-benzoxasiloles required a much longer time than that of the corresponding racemic reaction.[8] The reaction of **1q** with a 1:1:1 mixture of **L5**·HBF_4, NaO^{t}Bu, and $Ni(cod)_2$ (10 mol % each) failed to give the required product. 3-Alkynyl-2,1-benzoxasilole (**2s**) was synthesized from diethyl(trimethylsilylethynyl)silyl benzaldehyde **1s** in a 76% yield with a high degree of enantioselectivity (93% ee), whereas phenylethynyl variant **1t** resulted in no reaction. The enantiomeric compositions of **2q–s** were determined for the corresponding oxidation products (allylic and propargylic alcohols;[8] Figure 2).

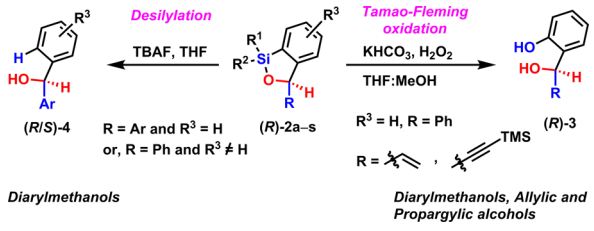
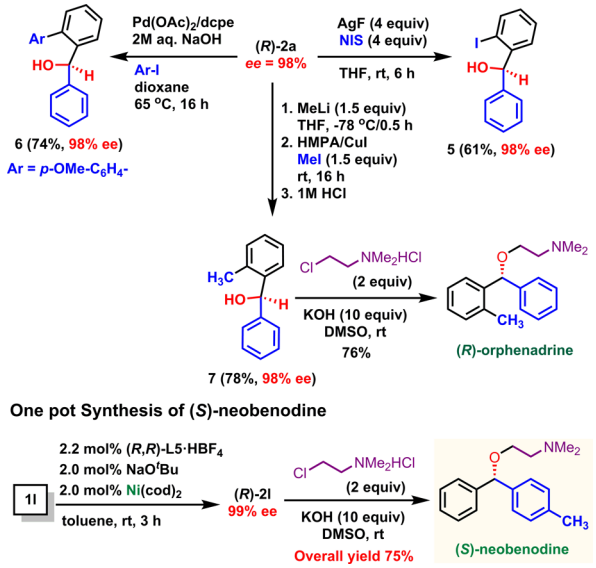


Figure 2. Synthetic transformations of benzoxasiloles for the determination of enantioselectivity.

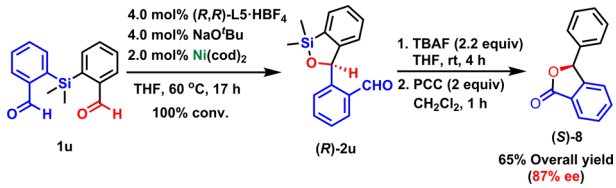
The synthetic utility of enantioenriched benzoxasiloles **2** was demonstrated by exploiting the chemically labile O–Si and C–Si bonds (Schemes 3 and 4). Benzoxasilole (*R*)-**2a** was

Scheme 3. Synthetic Utilities to Enantioenriched Diarylmethanol and Antihistaminic Drug Molecules[a]



[a]Isolated yields are given. Enantioselectivity was determined by SFC equipped with a chiral stationary phase.

Scheme 4. Synthetic Utility to Enantioselective Synthesis of 3-Phenylphthalide[a]



[a]Isolated yields are given. Enantioselectivity was determined by SFC equipped with a chiral stationary phase.

converted into 2-iododiarylmethanol (**5**) in a 61% yield in the presence of AgF, which served as a chiral building block for various coupling reactions and an asymmetric synthesis of alkylidene phthalans[17] that are known for fungal metabolites. The aryl and alkyl groups were introduced using Hiyama coupling reaction[6o] and anion relay chemistry[6p] to afford **6** and **7** in 74 and 78% yields, respectively. The enantioselectivity remained consistent following all transformations (Scheme 3). After establishment of an efficient method for the synthesis of enantioenriched diarylmethanols, which are important pharmacophores and found frequently in many biologically active molecules,[18] we further explored the synthesis of enantiomerically pure antihistaminic and anticholinergic drug molecules such as (*R*)-orphenadrine and (*S*)-neobenodine.[19] (*R*)-Orphenadrine was synthesized in one step from **7**, whereas (*S*)-neobenodine was achieved in a 75% overall yield via a one-pot procedure that started from **1l**. The synthesis of (*R*)-orphenadrine, however, can be achieved directly from an *o*-tolylsilyl varient of **1**, herein, we demonstrated the synthetic utility of both C–Si and O–Si bonds of benzoxasilole **1a**.

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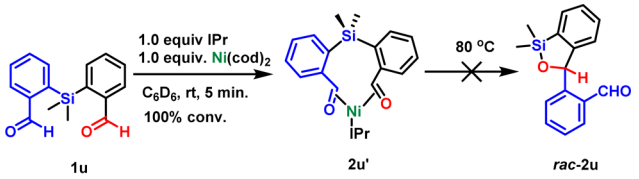
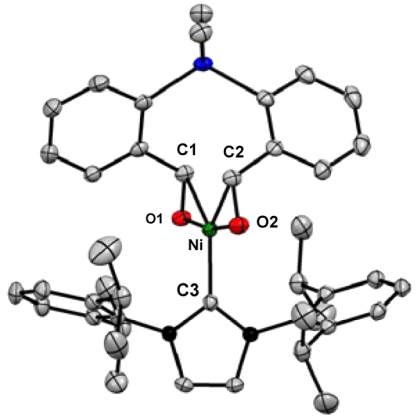
Another demonstration of the synthetic utility of enantioenriched benzoxasilole as a useful product was accomplished when designed benzoxasilole **2u** was converted into 3-phenylphthalides (*S*)-**8** via a desilylation−oxidation reaction sequence with an overall isolated yield of 65% (Scheme 4). In medicinal chemistry, 3-substituted phthalides are valuable pharmacological compounds.[20]Benzoxasilole **2u** was efficiently synthesized by modifying the reaction conditions that were employed for **1q−t** using 2 mol % of Ni(cod)$_2$ and 4 mol % of **L5**·HBF$_4$ and NaO^{t}Bu each. The formation of benzoxasilole **2u** was completely hampered when using a 1:1 mixture of Ni(cod)$_2$ and IPr due to the formation of an unreactive (η^2:η^2-dialdehyde)Ni complex (Scheme 5). That result was

Scheme 5. Isolation and Reaction of (η^2:η^2-dialdehyde)Ni-complex (2u′)[a]



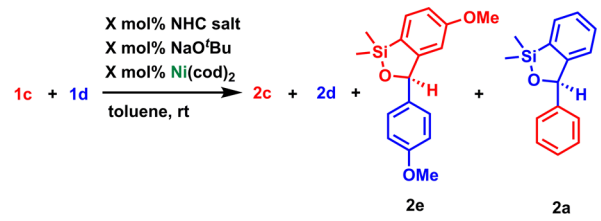


[a]ORTEP representation of **2u′** with thermal ellipsoid at 50% probability level. H atoms are omitted for clarity. Selected bond lengths (Å): O1−C1 1.303(3), O2−C2 1.309(3), O1−Ni 1.8922(15), C1−Ni 1.9653(19), O2−Ni 1.8923(15), C2−Ni 1.9749(19), C3−Ni 1.9255(18).

confirmed by the stoichiometric reaction of **1u** with an equimolar mixture of Ni(cod)$_2$ and IPr, which gave **2u′** as the sole product. The molecular structure of **2u′** was confirmed by NMR and X-ray analyses, which clearly shows the simultaneous η^2 coordination of two formyl groups to the nickel center. This is a rare example of direct isolation and confirmation of the use of a transition metal with bis-η^2-aldehyde ligands.[5k]

In the case of a Ni(0)/IPr catalyst system (racemic synthesis of benzoxasiloles), an intermolecular aryl-transfer mechanism was proposed based on the results of a crossover experiment.[8] Since excellent enantioselectivities were observed in the present optimized Ni(0)/**L5** catalytic system, we re-examined the crossover experiment in order to confirm whether the reaction proceeds via an inter- or an intramolecular aryl-transfer process. When the crossover experiment was conducted with **1c** and **1d** in the presence of 4 mol % of a chiral catalyst, the formation of crossover products was not observed, which indicated a complete switching of the aryl-migration process from intermolecular (Ni/IPr)[8] to intramolecular (Ni/**L5**) fashion (Table 4, entries 1 and 2). To exclude the influence of a base

Table 4. Crossover Experiments with 1c and 1d[a]



entry	NHC salt	mol (X, %)	yield (2c, %)	yield (2d, %)	yield (2e, %)	yield (2a, %)
1	(*R*,*R*)-L5·HBF$_4$	4	80	80	0	0
2[b]	IPr	2	52	60	42	46
3	IPr·HCl	2	15	50	25	27
4[b]	IPr/NaBF$_4$	5	27	54	30	32
5	SIPr·HBF$_4$	4	64	56	38	44

Crossover Products

[a]Reaction was monitored by GC analysis, and yields were determined with *n*-pentadecane as an internal standard. [b]IPr was used without NaO^{t}Bu.

(used for *in situ* generation of NHC **L5**) in this switching, a crossover experiment was conducted under similar conditions using IPr·HCl/NaO^{t}Bu. Crossover products were obtained in almost equal yields as produced in the case of the Ni(0)/IPr system (entry 3), which showed that NaO^{t}Bu was not responsible for the switching of an aryl-transfer process. The effect of NaBF$_4$ (generated from **L5**·HBF$_4$ and NaO^{t}Bu) was also ruled out after examining the reaction using NaBF$_4$ (5 mol %) as an additive to 5 mol % Ni/IPr experimental conditions (entry 4). A crossover experiment was also conducted with SIPr (having backbone of sp^3-carbons like **L5**) generated *in situ* from SIPr·HBF$_4$ and NaO^{t}Bu (entry 5), however crossover products were obtained. This experiment also supported the above result (entry 4) with *in situ* generation of NaBF$_4$. These sets of experiments clearly demonstrate that switching is absolutely controlled by ligands. In order to establish that the present enantioselective pathway is completely intramolecular, we sought to measure the enantioselectivities of crossover products. However, the corresponding desilylation products (**4c** and **4d**) could not be isolated in pure form to evaluate their enantiopurities due to their almost same polarity toward column chromatography. Therefore, another set of crossover experiments was carried out with **1c** and **1k** in the presence of 4 mol % of chiral catalyst (Table 5). As expected, no crossover products were obtained, whereas 37 and 39% of crossover products (**2v** and **2a**, respectively) were formed under similar reaction conditions using IPr·HCl. The enantioselectivities were measured for the corresponding benzoxasiloles **2c** (99% ee) and **2k** (99% ee) after the crossover experiment, which were compatible with the results obtained in each of the experiments (Table 5, entry 2; cf. Table 2). These results revealed the involvement of a complete intramolecular aryl-transfer process in the present catalytic asymmetric reaction.

Comparing the diastereoselectivities observed during the enantioselective and racemic versions of the reaction provides further support for a change in reaction mechanism. A higher degree of diastereoselectivities were observed for **2m−o**, the

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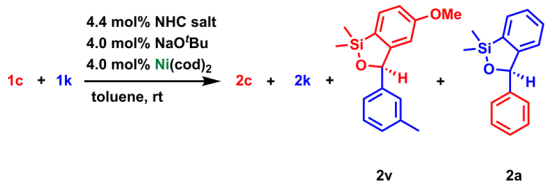
Table 5. Crossover Experiments with 1c and 1k[a]



NHC salt	yield (2c, %)	yield (2k, %)	yield (2v, %)	yield (2a, %)
IPr·HCl	53	61	37	39
(*R*,*R*)-L5·HBF$_4$	91 (99% ee)[b]	99 (99% ee)[b]	0	0
			Crossover Products	

[a]Reaction was monitored by GC analysis, and yields were determined with *n*-pentadecane as an internal standard. [b]Enantioselectivity was determined by SFC equipped with a chiral stationary phase.

present Ni(0)/**L5** enantioselective catalytic system compared with the racemic Ni(0)/IPr catalytic system (Figure 3).

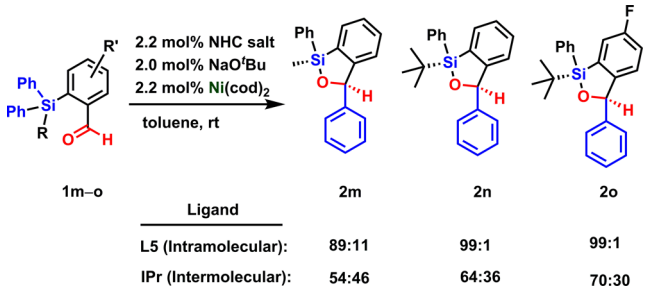
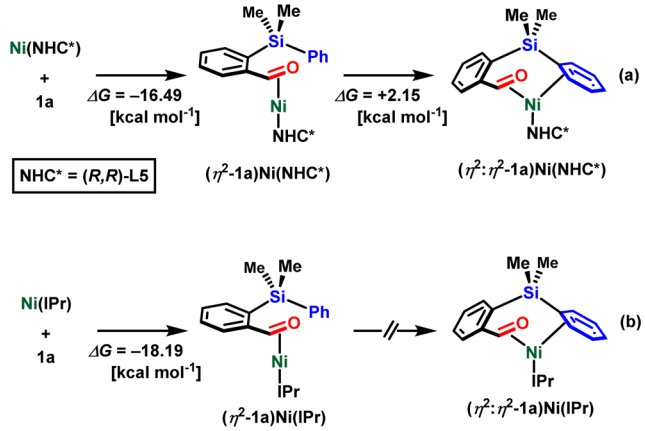


Figure 3. Comparison of diastereoselectivity (**L5** vs **IPr**).

We previously proposed the involvement of an η^2-aldehyde nickel intermediate, which was directly observed by NMR analyses at −50 °C. This η^2-aldehyde nickel complex was converted into a benzoxasilole quantitatively by warming to room temperature.[8] Similarly, the coordination of aldehyde **1** to a Ni(0)/**L5** moiety gives rise to the formation of an enantioenriched η^2-aldehyde nickel intermediate (η^2-**1**)Ni(**L5**) which undergoes intramolecular aryl-transfer from the silicon to the formyl carbon to yield benzoxasilole **2** in excellent enantio- and diastereoselectivity. A plausible rationale for the change in reaction mechanism using IPr and the chiral NHC (*R*,*R*)-**L5**, respectively, is in the difference for Ni(NHC) complexes to access coordination of substrate **1** through two η^2 interactions involving the formyl and phenyl moieties, respectively (Scheme 6).[21] A preliminary DFT calculation employing **1a** as a model substrate indicated that the chiral ligand **L5** enabled the coordination of substrate to the Ni(0)/**L5** fragment in an η^2:η^2-manner, yielding (η^2:η^2-**1a**)Ni((*R*,*R*)-**L5**) (Scheme 6a). Such intriguing behavior of formation of η^2:η^2 intermediate in the case of **L5** would facilitate an intramolecular aryl-transfer from the silicon to the formyl group giving (*R*)-**2a**. On the other hand, an energy minima was not found for similar η^2:η^2-intermediate when IPr was used. It might be due to the steric hindrance exerted by its two isopropyl groups attached to each of the N-aryl rings at the 2,6 positions (Scheme 6b). As a result, in the transformation reaction from **1a** to **2a**, the use of IPr as a ligand might be forced to undergo intermolecular aryl transfer. Further theoretical studies on the full intramolecular reaction mechanism are ongoing by our group.

Scheme 6. Plausible Rationale for Switching of Aryl-Transfer Process



CONCLUSION

In summary, the nickel(0)-catalyzed enantioselective syntheses of 3-aryl-, vinyl-, and alkynyl-2,1-benzoxasiloles were achieved. The silicon stereogenic center was generated sequentially with excellent selectivity through the desymmetrization of prochiral silane. Enantioenriched benzoxasiloles were successfully utilized for the synthesis of diarylmethanols including antihistaminic types of drug molecules such as (*R*)-orphenadrine and (*S*)-neobenodine. Crossover experiments clearly demonstrate a complete switching of the aryl-transfer process from an inter- to an intramolecular fashion by changing the ligand from IPr to **L5**, which could also account for the excellent enantio- and diasteoselectivity. This ligand-controlled switching mechanism was rationalized by the coordination of **1** to the Ni(0)/**L5** fragment in an η^2-arene:η^2-aldehyde fashion, as found by DFT calculation. As far as we could ascertain, this is the first example of ligand-controlled switching from an inter- to an intramolecular aryl-transfer process, and the asymmetric desymmetrization of silane with a (η^2-aldehyde)Ni complex could represent a novel tool for the generation of an enantioenriched silicon-stereogenic center. Detailed studies on the reaction mechanism and the utilization of silicon stereogenic centers are ongoing in our laboratory.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.5b07827.

(TXT)
Experimental and computational details and spectral data (PDF)

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Notes

The authors declare no competing financial interest.

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