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Reductive desymmetric silylation of biaryl bis(triflates) enabled by a chiral nickel/picolinamide complex

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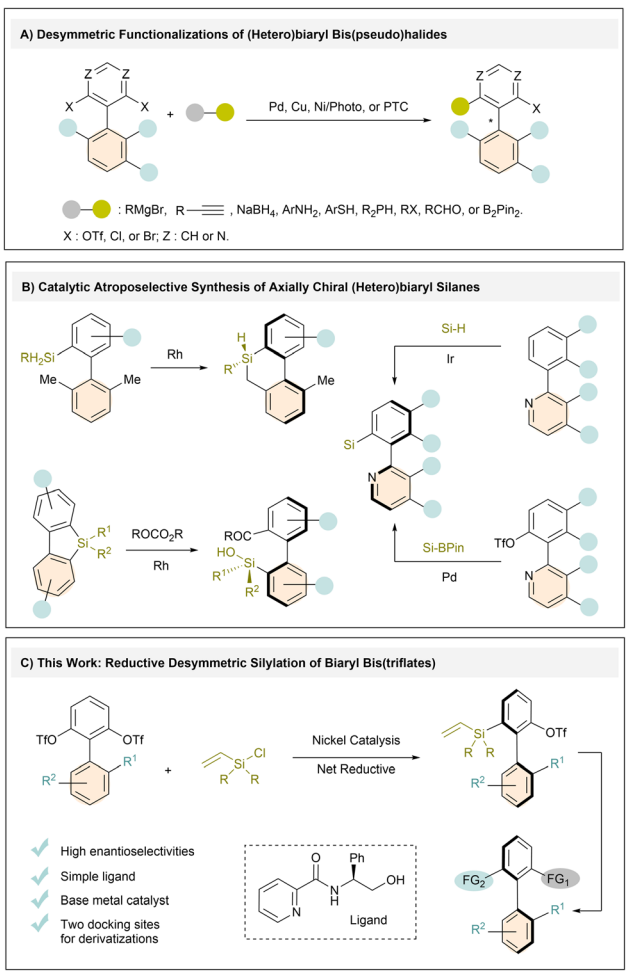
Given the importance of organosilicons and atropisomerism, there is a fundamental need to develop new methods to synthesize axially chiral biaryl silanes. By use of an easily accessible chiral picolinamide as a ligand and inexpensive nickel as a catalyst, we realize a desymmetric silylation of prochiral biaryl bis(triflates) with silyl chlorides under net reductive conditions. This cross-electrophile reaction offers a new approach to preparing highly enantioenriched C_1-symmetric axially chiral platform molecules, which incorporate both a silane and a triflate moiety as two distinct docking sites for various downstream derivatizations.

Introduction

Axially chiral biaryls are not only present as a core structure in numerous natural products[1] and pharmaceutically relevant molecules[2] but are also frequently used as privileged scaffolds for chiral ligands and organocatalysts in asymmetric catalysis.[3] To date, catalytic methods have emerged as a powerful tool to synthesize axially chiral biaryls based on different strategies, including aryl–aryl cross-coupling, *de novo* arene ring formation, (dynamic) kinetic resolution of racemic biaryls, and desymmetrization of prochiral biaryls.[4] In the desymmetrization variant, one of two distally positioned enantiotopic moieties is enantioselectively converted, and thus this unique reaction pattern circumvents direct construction of a sterically encumbered chiral axis while the unreacted functionality is available for further derivatizations.[5] In the 1990s, Hayashi realized the first examples of desymmetric functionalization of prochiral biaryl bis(triflates) *via* palladium-catalyzed Kumada[6] and Sonogashira coupling.[7] Recently, this reaction mode has been further extended by utilizing other coupling partners including borohydride,[8] aromatic amines,[9] thiols,[10] phosphines,[11] alkyl bromides,[12] aldehydes,[12] and B_2Pin_2 (ref. 13) (Scheme 1A). However, desymmetric silylation of biaryl bis(halides) or bis(sulfonates) *via* enantioselective C–Si bond formation remains elusive.

Organosilicons find broad applications in organic synthesis,[14] material science,[15] and medicinal chemistry.[16] Consequently, organic chemists have endeavoured to develop new and efficient approaches to preparing such compounds.[17] However, catalytic atroposelective synthesis of (hetero)biaryl silanes starting from achiral or racemic precursors is



Scheme 1 (A) Desymmetric functionalizations of (hetero)biaryl bis(pseudo)halides; (B) catalytic atroposelective synthesis of axially chiral (hetero)biaryl silanes; (C) reductive desymmetric silylation of biaryl bis(triflates).

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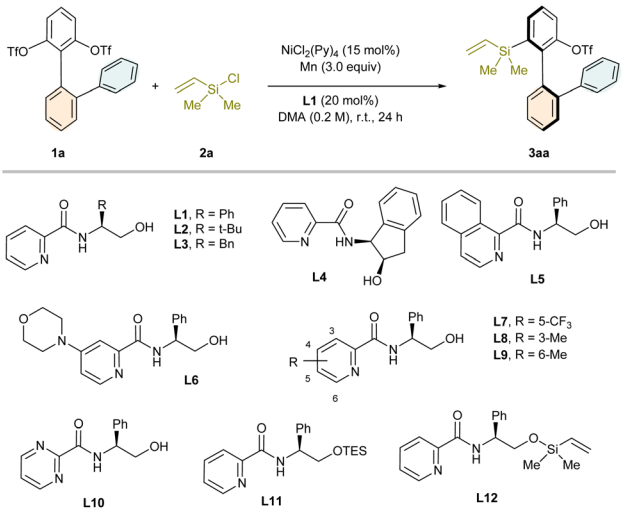
underdeveloped, and a handful of successful examples rely on either C–H silylation[18] or cross-coupling between silicon nucleophiles and carbon electrophiles[19] (Scheme 1B). On the other side, rapid progress has been witnessed in the transition metal-catalyzed cross-electrophile coupling (XEC) reactions between silyl halides and diverse carbon electrophiles, which provides new and efficient access to organosilanes.[20] Driven by these elegant results and our continued interest in the development of asymmetric XEC reactions for the synthesis of atropisomers,[21] we wondered whether reductive silylation of aryl (pseudo)halides with halo silanes could be applied as the enantiodetermining step of atroposelective desymmetrization. In this context, we realized a chiral nickel/picolinamide complex-catalyzed reductive desymmetric silylation of prochiral biaryl bis(triflates) with silyl chlorides towards the highly enantioselective synthesis of C_1-symmetric axially chiral biaryls, which contain both a nucleophilic silane and an electrophilic triflate moiety as two distinct docking sites to introduce new functionalities (Scheme 1C).

Results and discussion

For optimization of the reaction conditions, the biaryl bis(triflate) **1a** and chlorodimethyl(vinyl)silane (**2a**) were selected as the model substrates. While some privileged chiral ligands for asymmetric nickel catalysis, including BOX, BiOX, PyrOx, PyBOX, and PHOX, either could not promote the target reaction or only delivered a trace amount of the product as a racemic mixture, a ligand class of chiral picolinamides was surprisingly found to be effective for the intended desymmetric reductive silylation. To the best of our knowledge, enantioselective Ni-catalyzed cross-electrophile coupling reactions using chiral picolinamides as the ligands is unprecedented. Systematic screening of the reaction conditions revealed the optimized one as follows: $NiCl_2(Py)_4$ (15 mol%) as the precatalyst, the picolinamide **L1** derived from L-phenylglycinol (20 mol%) as the ligand, and Mn (3 equiv.) as the reducing agent in DMA (0.2 M) as the solvent at room temperature for 24 h. In this case, the desired product **3aa** was obtained in 80% yield and 91% ee (Table 1, entry 1). Notably, the formation of the bis(silylation) byproduct was not observed, revealing that this desymmetrization reaction is not followed by kinetic resolution. Next, we varied the reaction parameters from the optimized conditions to demonstrate their impact on the reaction outcome (Table 1, entries 2–17). Replacing Ph with *t*-Bu (**L2**) or Bn (**L3**) as the ligand arm resulted in decreased enantiocontrol (entries 2 and 3). The ligand **L4** bearing a chiral indane scaffold was also competent but provided lower enantioselectivity (entry 4). In the case of the chiral 1-isoquinolinecarboxamide **L5** as the ligand, both the reaction yield and the asymmetric induction were significantly reduced (entry 5). The introduction of an *N*-morpholinyl group to position 4 of the pyridine of the ligand did not improve the result (**L6**, entry 6), whereas the installation of CF_3 on position 5 attenuated both the selectivity and the efficiency to some degree (**L7**, entry 7). Notably, substitution on positions 3 and 6 deteriorated the ligand performance significantly (**L8** and **L9**, entries 8 and 9). Moreover, the reaction was almost shut down when using the ligand **L10** based on pyrimidine-2-carboxylic acid (entry 10). When the hydroxyl group of the ligand was protected by TES, both the yield and the enantiomeric excess of the product diminished dramatically (**L11**, entry 11). However, a nearly identical result was achieved in the case of the ligand **L12** with a pendant dimethylvinyl siloxy group, indicating that *in situ* silylation of the hydroxyl group of the ligand might occur (entry 12). When the nickel precatalysts lacking pyridine as a coligand were employed, the desired product was formed much less enantioselectively, suggesting that pyridine might remain coordinated to the catalyst species in the enantiodetermining step (entries 13 and 14). The use of

Table 1 Deviation from the optimized reaction conditions[a]



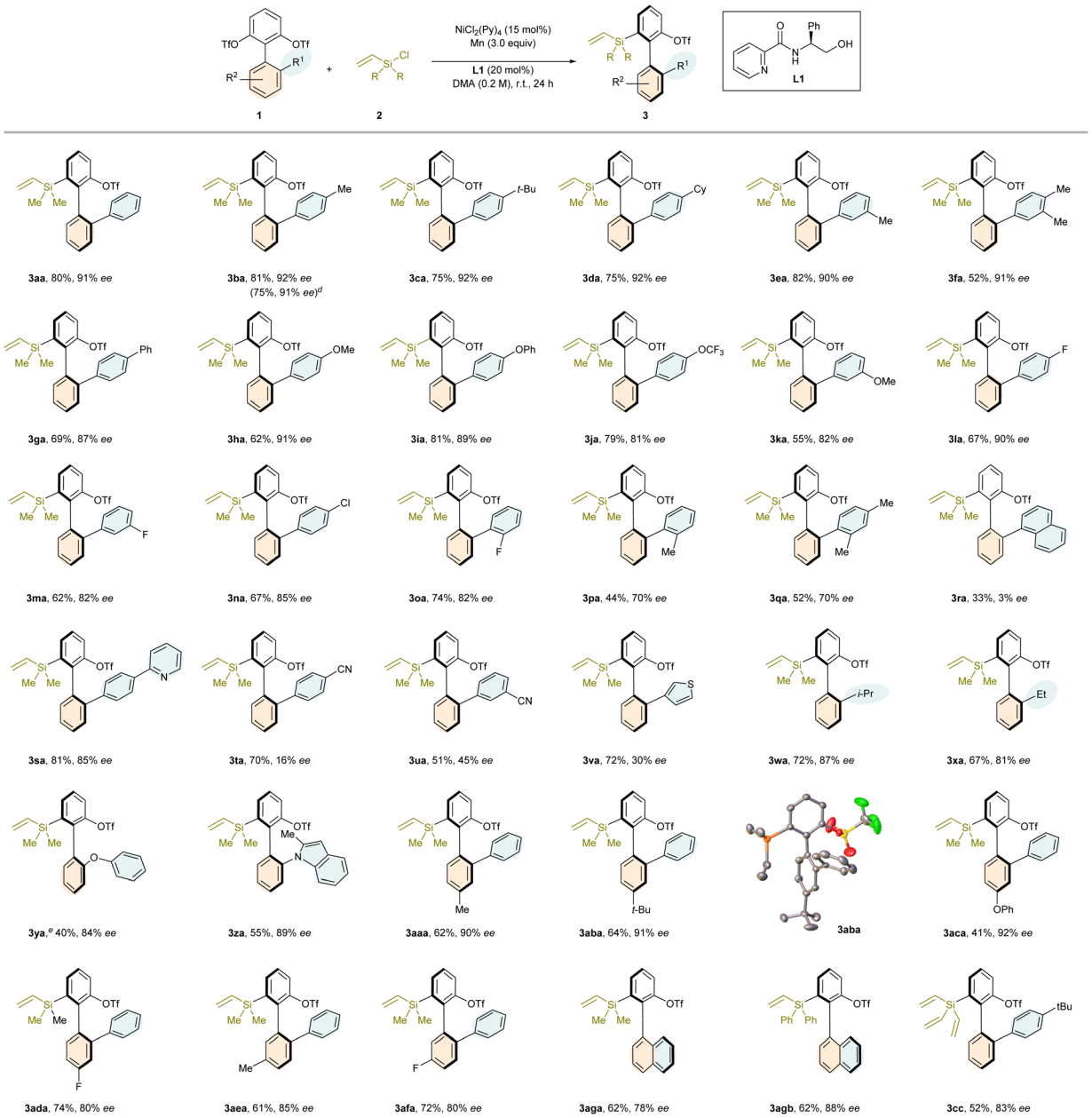
Entry	Deviation from the optimized conditions	Yield[b] (%)	ee[c] (%)
1	**None**	**80**	91
2	**L2** instead of **L1**	22	67
3	**L3** instead of **L1**	68	83
4	**L4** instead of **L1**	61	82
5	**L5** instead of **L1**	10	11
6	**L6** instead of **L1**	60	91
7	**L7** instead of **L1**	24	79
8	**L8** instead of **L1**	16	8
9	**L9** instead of **L1**	16	3
10	**L10** instead of **L1**	Trace	n.d.
11	**L11** instead of **L1**	19	21
12	**L12** instead of **L1**	78	91
13	$NiCl_2$ instead of $NiCl_2(Py)_4$	51	62
14	$Ni(COD)_2$ instead of $NiCl_2(Py)_4$	41	70
15[d]	$Ni(COD)_2$ instead of $NiCl_2(Py)_4$	63	72
16	DMF instead of DMA	53	84
17	NMP instead of DMA	61	83
18	Zn instead of Mn	Trace	n.d.

[a] Unless otherwise specified, the reactions were performed on a 0.2 mmol scale of the biaryl bis(triflate) **1a** using 3.0 equiv. of chlorodimethyl(vinyl)silane (**2a**), 15 mol% $NiCl_2(Py)_4$, 20 mol% ligand **L1**, and 3.0 equiv. of Mn in 1 mL DMA under N_2 atmosphere for 24 h at room temperature. [b] Yield of the isolated product. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The reaction was performed with 60 mol% pyridine as an additive.

60 mol% pyridine as an additive did not lead to significantly improved enantiocontrol (entry 15). The desired reaction proceeded in other polar aprotic solvents tested but afforded only inferior results (entries 16 and 17). Only a trace amount of compound **3aa** was generated when Zn was used as the reductant instead of Mn (entry 18).

With the optimized reaction conditions in hand, we commenced to evaluate the substrate scope of this nickel-catalyzed desymmetrization reaction (Table 2). First, we focused on investigating the generality of the biaryl bis(triflates) **1**. It turned out that suitable R^1 substituents of compounds **1** include phenyl bearing alkyl (**1b–1f**), phenyl (**1g**), OMe (**1h** and **1k**), OPh (**1i**), OCF_3 (**1j**), and halide (**1l–1n**) on *para* or/and *meta*-position, and the corresponding products **3ba–na** were obtained in 52–82% yields and 81–98% ee. The reaction also tolerated *o*-fluorine phenyl (**1o**), affording the product **3oa** in 74% yield and 82% ee. In contrast, bulkier methyl on the *ortho*-position of the phenyl substituent (**1j** and **1k**) had a significant

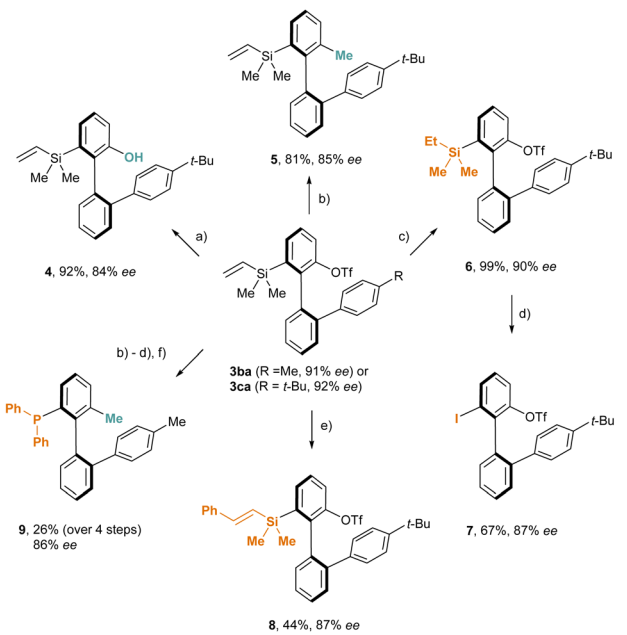
Table 2 Evaluation of the substrate scope[a,b,c,d,e]



[a] Unless otherwise specified, the reactions were performed on a 0.2 mmol scale of the biaryl bis(triflate) **1** using 3.0 equiv. of the silyl chlorides **2**, 15 mol% $NiCl_2(Py)_4$, 20 mol% ligand **L1**, and 3.0 equiv. of Mn in 1 mL DMA under N_2 atmosphere for 24 h at room temperature. [b] Yields of the isolated products. [c] Determined by HPLC analysis on a chiral stationary phase. [d] The reaction was performed on a 1 mmol scale of **1b**. [e] The reaction was performed using **L5** as the ligand instead of **L1**.

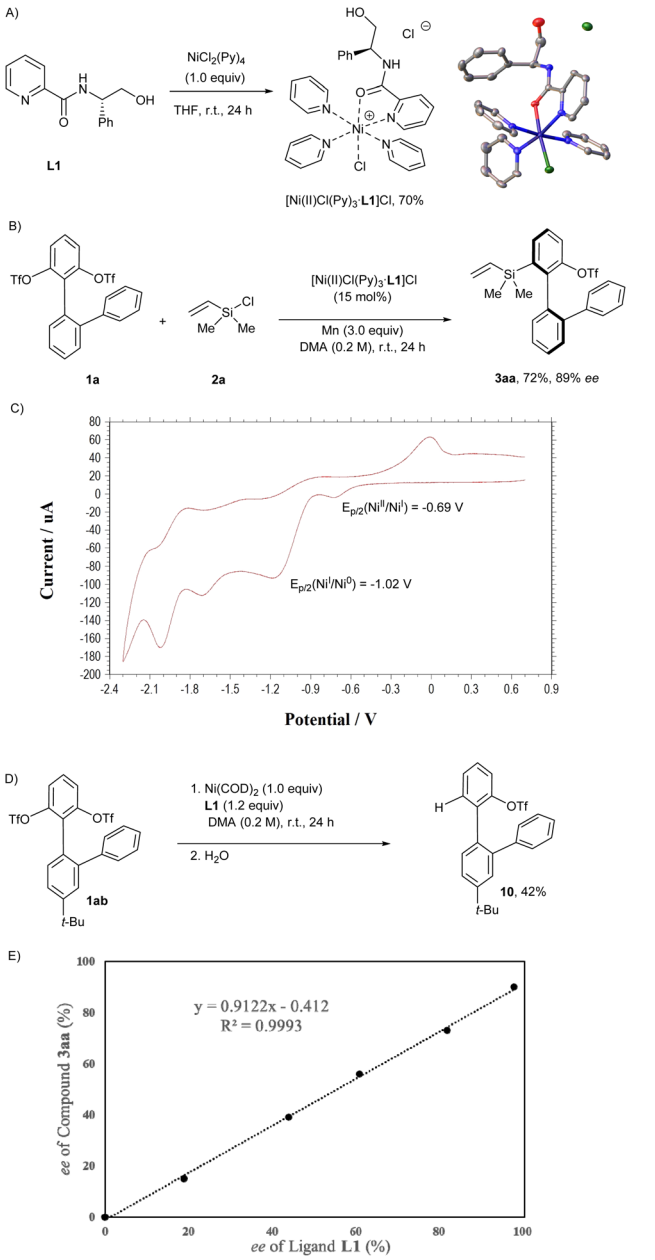
detrimental effect on the asymmetric induction of the studied reaction, yielding the products **3pa** and **3qa** in much lower enantiomeric excesses. The sterically more encumbering α-naphthyl (**1r**) led to the formation of a nearly racemic product **3ra**. Coordinative pyridine on the *para*-position of phenyl (**1s**) posed no problem, furnishing the product **3sa** in 81% yield and 85% ee. Strong electron-withdrawing cyano group (**1t** and **1u**) undermined the enantiocontrol of the studied reaction dramatically (**3ta** and **3ua**). Replacing phenyl by 3-thienyl as the R^1 substituent (**1v**) also resulted in a low enantiomeric excess (**3va**). In the case of isopropyl (**1w**) or ethyl (**1x**) as R^1, the desired reactions proceeded smoothly, providing the products **3wa** and **3xa** in 87% ee and 81% ee, respectively. Notably, phenoxy (**1y**) and *N*-indolyl (**1z**) were also found to be pertinent R^1 substituents, affording the products **3ya** and **3za** in 84% ee and 89% ee, respectively. Subsequently, permutation of the R^2 substituent was performed. It turned out that alkyl (**1aa**, **1ab**, and **1ae**), PhO (**1ac**), and F (**1ad** and **1af**) on either *para* or *meta* position were all compatible, delivering the corresponding products in **3aaa**–**3afa** 41–74% yields and 80–92% ee. Moreover, moderate results in terms of both yield and enantiomeric excess were obtained in the case of α-naphthyl (**3aga**). Next, we turned our attention to assessing the scope of silyl chlorides. Chlorodiphenyl(vinyl) silane (**2b**) and chlorotrivinylsilane (**2c**) were both suitable precursors, providing the products **3agb** and **3cc** in 88% ee and 83% ee, respectively. The vinyl substituent of silyl chlorides was confirmed to be vital for this transformation since its absence shut down this target desymmetrization. The coordination-assisted oxidative addition of vinyl substituted silyl chlorides to low-valent nickel is likely. However, it could also be attributed to higher ability of vinyl substituted silyl chlorides regarding oxidative addition to low-valent nickel. Moreover, the reaction for the synthesis of compound **3ba** on a 1 mmol scale afforded a similar result (75% yield, 91% ee). In addition, the absolute configuration of compound **3aba** was unambiguously determined to be *R* through X-ray crystallography (CCDC number: 2452324).

A variety of downstream derivatizations focusing on the transformations of the pendant triflate and/or silane moiety of the coupling products were carried out (Scheme 2). First, simple sodium hydroxide-mediated hydrolysis of the compound **3ca** provided a chiral phenol **4** in 92% yield and 84% ee. Furthermore, the nickel-catalyzed Kumada methylation of the aryl



a) Aq. NaOH (2 N), MeOH, 40 °C, 24 h; b) $NiCl_2$ dppp (5 mol%), MeMgBr (6 equiv), ether, 0 - 40 °C, 24 h; c) Pd/C, H_2, MeOH, r.t., 24 h; d) ICl (2 equiv), DCM, r.t., 24 h; e) Grubbs II (20 mol%), styrene (10 equiv), DCM, 40 °C, 24 h; f) PPh_2Cl (1.75 equiv), *n*-BuLi (1.5 equiv), THF, -78 °C - r.t., overnight.

Scheme 2 Derivatizations of the desymmetrization product.

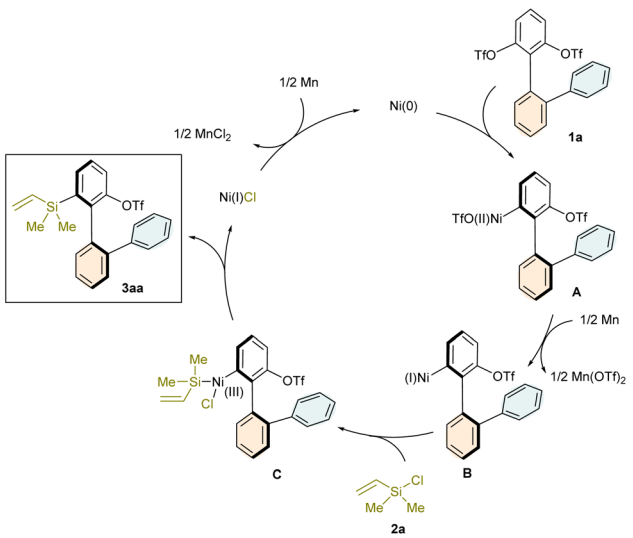


Scheme 3 (A) Preparation of [Ni(II)Cl(Py)$_3$·L1]Cl; (B) reaction using [Ni(II)Cl(Py)$_3$·L1]Cl as a catalyst; (C) cyclic voltammetry measurement; (D) stoichiometric reaction with $Ni(COD)_2$; (E) non-linear effect.

triflate **3ca** delivered a chiral silane **5** in 81% yield and 85% ee. Moreover, the vinyl group of **3ca** was successfully hydrogenated using Pd/C in 99% yield and 90% ee. Upon treatment with ICl, the resultant saturated silane **6** underwent iodination, affording a chiral aryl iodide 7 in 67% yield and 87% ee. Besides, the compound **3ca** was subjected to metathesis with styrene, furnishing a chiral silane **8** bearing an internal olefinic unit **8** in 44% yield and 86% ee. In addition, the sequential reactions consisting of Kumada methylation, hydrogenation, iodination, and *n*-BuLi-mediated phosphination with PPh_2Cl converted the compound **3ba** into a chiral phosphine **9** in 26% overall yield and 86% ee.

Next, a series of preliminary mechanistic studies were conducted, and the results were demonstrated in Scheme 3. First, it turned out that $NiCl_2(Py)_4$ could react with the picolinamide ligand **L1** to afford a cationic Ni(II) complex [Ni(II)Cl(Py)$_3$·**L1**]Cl, the structure of which was determined by X-ray crystallography (CCDC number: 2452325) (Scheme 3A). Furthermore, the direct use of [Ni(II)Cl(Py)$_3$·**L1**]Cl as the precatalyst for the desymmetrization of the biaryl bis(triflate) **1a** with chlorodimethyl(vinyl) silane (**2a**) provided a similar outcome to the one under the standard conditions (Scheme 3B). The cyclic voltammetry (CV) measurement of [Ni(II)Cl(Py)$_3$·**L1**]Cl gave irreversible reduction waves at −0.89 V and at −1.02 V (*vs.* Ag/AgCl in DMA), which could be assigned to the reduction of Ni(II) to Ni(I) and Ni(I) to Ni(0), respectively (Scheme 3C). According to the seminal work of Stahl *et al.*,[22] the thermodynamic potential of Mn^{2+}/Mn is $E^{O\prime} = -1.08$ V (*vs.* Ag/AgCl in DMA), suggesting that Mn is capable of reducing the Ni(II) precatalyst into a Ni(0) species *in situ*. Moreover, the stoichiometric reaction between the biaryl bis(triflate) **1ab** and $Ni(COD)_2$ in the presence of the ligand **L1** afforded the detriflated product **10** after quenching with water in 42% yield, indicating that the oxidative addition of biaryl bis(triflates) to Ni(0) is viable (Scheme 3D). The picolinamide ligand-enabled generation of Ni(0) *via* reduction might be the key for the success of this asymmetric silylation, since Mn is known to be unable to reduce Ni(II)PyrOx,[23] Ni(II)BiOX,[24] or Ni(II)BOX[25] into their corresponding Ni(0) species. In addition, the dependence of the enantiomeric excess of the product **3aa** on the enantiopurity of the ligand **L1** was investigated, and a linear relationship was obtained, revealing that no high-order catalytically active on-cycle species containing multiple units of the chiral entity is present in this nickel-catalyzed reaction (Scheme 3E).

Based on the preliminary mechanistic studies and the previous report,[20a] a plausible catalytic cycle exemplified by the precursors **1a** and **2a** was proposed in Scheme 4. Initially, Ni(0) is generated under reductive conditions and undergoes two-electron oxidative addition with the biaryl bis(triflate) **1a** in an enantioselective manner. The resultant axially chiral Ni(II) complex **A** is subsequently reduced by Mn into a Ni(I) species **B**, to which chlorodimethyl(vinyl)silane (**2a**) performs the second oxidative addition. Next, stereoretensive reductive elimination from the generated Ni(III) complex **C** provides the product **3aa** and Ni(I)Cl, and the latter is reduced by Mn to Ni(0) for the next catalytic cycle.



Scheme 4 Proposed catalytic cycle.

Conclusions

In conclusion, we have developed a reductive desymmetric silylation of prochiral biaryl bis(triflates) with silyl chlorides. This desymmetrization reaction is promoted by a simple chiral nickel/picolinamide complex, allowing for the synthesis of C_1-symmetric axially chiral biaryl silanes in a highly enantioselective fashion. The downstream derivatizations of the coupling products, focusing on the conversions of the pendant silane and triflate moieties, provide a variety of functionalized axially chiral biaryls. According to the preliminary mechanistic investigations, the picolinamide ligand enables the generation of a Ni(0) species *via* reduction, to which biaryl bis(triflates) perform enantiodiscriminating oxidative addition.

Author contributions

C. W. and Z. C. conceived and designed the experiments. Z. C. and J. Z. performed experiments and prepared the SI. C. W. directed the project and wrote the paper. All authors discussed the results and commented on the manuscript.

Conflicts of interest

There is no conflict to declare.

Data availability

CCDC 2452324 (**3aba**) and 2452325 ([Ni(II)Cl(Py)$_3$·**L1**]Cl) contain the supplementary crystallographic data for this paper.[26a,b]

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: experimental procedure, spectra data, NMR-data, and HPLC-data. See DOI: https://doi.org/10.1039/d5sc09250g.

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Notes and references

1 (*a*) M. H. McCormick, W. M. Stark, G. E. Pittenger, R. C. Pittenger and J. M. McGuire, *Antibiot. Annu.*, 1955, **3**, 606–611; (*b*) S. M. Kupchacn, R. W. Britton, M. F. Ziegler, C. J. Gilmore, R. J. Restivo and R. F. Bryan, *J. Am. Chem. Soc.*, 1973, **95**, 1335–1336; (*c*) Y. F. Hallock, K. P. Manfredi, J. W. Blunt, J. H. Cardellina II, M. Schaeffer, K.-P. Gulden, G. Bringmann, A. Y. Lee, J. Clardy, G. François and M. R. Boy, *J. Org. Chem.*, 1994, **59**, 6349–6355; (*d*) A. Zask, J. Murphy and G. A. Ellestad, *Chirality*, 2013, **25**, 265–274; (*e*) J. E. Smyth, N. M. Butler and P. A. Keller, *Nat. Prod. Rep.*, 2015, **32**, 1562–1583; (*f*) C. A. Bewley, G. A. Sulikowski, Z. J. Yang, G. Bifulco, H.-M. Cho and C. R. Fullenkamp, *Acc. Chem. Res.*, 2023, **56**, 414–424.

2 (*a*) S. R. LaPlante, L. D. Fader, K. R. Fandrick, D. R. Fandrick, O. Hucke, R. Kemper, S. P. F. Miller and P. J. Edwards, *J. Med. Chem.*, 2011, **54**, 7005–7022; (*b*) S. R. LaPlante, P. J. Edwards, L. D. Fader, A. Jakalian and O. Hucke, *ChemMedChem*, 2011, **6**, 505–513; (*c*) M. Basilaia, M. H. Chen, J. Secka and J. L. Gustafson, *Acc. Chem. Res.*, 2022, **55**, 2904–2919; (*d*) P. W. Glunz, *Bioorg. Med. Chem. Lett.*, 2018, **28**, 53–60; (*e*) S. Perreault, J. Chandrasekhar and L. Patel, *Acc. Chem. Res.*, 2022, **55**, 2581–2593; (*f*) Z. Wang, L. Meng, X. Liu, L. Zhang, Z. Yu and G. Wu, *Eur. J. Med. Chem.*, 2022, **243**, 114700.

3 (*a*) R. Noyori and H. Takaya, *Acc. Chem. Res.*, 1990, **23**, 345–350; (*b*) Y. Chen, S. Yekta and A. K. Yudin, *Chem. Rev.*, 2003, **103**, 3155–3212; (*c*) W. Tang and X. Zhang, *Chem. Rev.*, 2003, **103**, 3029–3070; (*d*) Y.-M. Li, F.-Y. Kwong, W.-Y. Yu and A. S. C. Chan, *Coord. Chem. Rev.*, 2007, **251**, 2119–2144; (*e*) T. Akiyama, *Chem. Rev.*, 2007, **107**, 5744–5758; (*f*) S. Shirakawa and K. Maruoka, *Angew. Chem., Int. Ed.*, 2013, **52**, 4312–4348; (*g*) D. Parmar, E. Sugiono, S. Raja and M. Rueping, *Chem. Rev.*, 2014, **114**, 9047–9153.

4 For reviews on atroposelective synthesis of atropisomers, see: (*a*) G. Bringmann and D. Menche, *Acc. Chem. Res.*, 2001, **34**, 615–624; (*b*) G. Bringmann, A. J. Price Mortimer, P. A. Keller, M. J. Gresser, J. Garner and M. Breuning, *Angew. Chem., Int. Ed.*, 2005, **44**, 5384–5427; (*c*) M. C. Kozlowski, B. J. Morgan and E. C. Linton, *Chem. Soc. Rev.*, 2009, **38**, 3193–3207; (*d*) G. Bringmann, T. Gulder, T. A. M. Gulder and M. Breuning, *Chem. Rev.*, 2011, **111**, 563–639; (*e*) P. G. Cozzi, E. Emer and A. Gualandi, *Angew. Chem., Int. Ed.*, 2011, **50**, 3847–3849; (*f*) G. Ma and M. P. Sibi, *Chem.–Eur. J.*, 2015, **21**, 11644–11657; (*g*) J. Wencel-Delord, A. Panossian, F. R. Leroux and F. Colobert, *Chem. Soc. Rev.*, 2015, **44**, 3418–3430; (*h*) Y.-N. Ma, S.-X. Li and S.-D. Yang, *Acc. Chem. Res.*, 2017, **50**, 1480–1492; (*i*) D. Bonne and J. Rodriguez, *Chem. Commun.*, 2017, **53**, 12385–12393; (*j*) Y.-B. Wang and B. Tan, *Acc. Chem. Res.*, 2018, **51**, 534–547; (*k*) A. Link and C. Sparr, *Chem. Soc. Rev.*, 2018, **47**, 3804–3815; (*l*) B. Zilate, A. Castrogiovanni and C. Sparr, *ACS Catal.*, 2018, **8**, 2981–2988; (*m*) A. J. Metrano and S. J. Miller, *Acc. Chem. Res.*, 2019, **52**, 199–215; (*n*) Y.-C. Zhang, F. Jiang and F. Shi, *Acc. Chem. Res.*, 2020, **53**, 425–446; (*o*) X. Bao, J. Rodriguez and D. Bonne, *Angew. Chem., Int. Ed.*, 2020, **59**, 12623–12634; (*p*) J. K. Cheng, S.-H. Xiang, S. Li, L. Ye and B. Tan, *Chem. Rev.*, 2021, **121**, 4805–4902; (*q*) T. A. Schmidt and C. Sparr, *Acc. Chem. Res.*, 2021, **54**, 2764–2774; (*r*) R. Song, Y. Xie, Z. Jin and Y. R. Chi, *Angew. Chem., Int. Ed.*, 2021, **60**, 26026–26037; (*s*) J. Wang, C. Zhao and J. Wang, *ACS Catal.*, 2021, **11**, 12520–12531; (*t*) C.-X. Liu, W.-W. Zhang, S.-Y. Yin, Q. Gu and S.-L. You, *J. Am. Chem. Soc.*, 2021, **143**, 14025–14040; (*u*) X. Zhang, K. Zhao and Z. Gu, *Acc. Chem. Res.*, 2022, **55**, 1620–1633; (*v*) X.-F. Bai, Y.-M. Cui, J. Cao and L.-W. Xu, *Acc. Chem. Res.*, 2022, **55**, 2545–2561; (*w*) W. Qin, Y. Liu and H. Yan, *Acc. Chem. Res.*, 2022, **55**, 2780–2795; (*x*) S. Choppin and J. Wencel-Delord, *Acc. Chem. Res.*, 2023, **56**, 189–202.

5 (*a*) J. Moon, S. Kim, S. Lee, H.-A. Cho, A. Kim, M. K. Ham, S. H. Kim, J. Jung and Y. Kwon, *ChemCatChem*, 2024, **16**, e202400690; (*b*) X.-P. Zeng, Z.-Y. Cao, Y.-H. Wang, F. Zhou and J. Zhou, *Chem. Rev.*, 2016, **116**, 7330–7396.

6 T. Hayashi, S. Niizuma, T. Kamikawa, N. Suzuki and Y. Uozumi, *J. Am. Chem. Soc.*, 1995, **117**, 9101–9102.

7 T. Kamikawa, Y. Uozumi and T. Hayashi, *Tetrahedron Lett.*, 1996, **37**, 3161–3164.

8 X. Li, G.-W. Wang, L.-X. Liu, C.-B. Yu and Y.-G. Zhou, *Angew. Chem., Int. Ed.*, 2023, **62**, e202301337.

9 X. Wang, W.-G. Liu, L.-T. Liu, X.-D. Yang, S. Niu, C.-H. Tung, L.-Z. Wu and H. Cong, *Org. Lett.*, 2021, **23**, 5485–5490.

10 R. J. Armstrong and M. D. Smith, *Angew. Chem., Int. Ed.*, 2014, **53**, 12822–12826.

11 R. Cui, Y. Zhang, Z. Huang, L. Yuwen, Y. Xu and Q.-W. Zhang, *Angew. Chem., Int. Ed.*, 2024, **63**, e202412064.

12 Y.-D. Zhu, Z.-Y. Dai, M. Jiang and P.-S. Wang, *ACS Catal.*, 2024, **14**, 13860–13866.

13 Y. Xiao, A. L. Bartelt, E. Irran and M. Oestreich, *Angew. Chem., Int. Ed.*, 2025, **64**, e202515234.

14 (*a*) Y. Nakao and T. Hiyama, *Chem. Soc. Rev.*, 2011, **40**, 4893–4901; (*b*) P. L. Fuchs, in *Handbook of Reagents for Organic Synthesis. Reagents for Silicon-Mediated Organic Synthesis*, Wiley, New York, 2011; (*c*) T. Komiyama, Y. Minami and T. Hiyama, *ACS Catal.*, 2017, **7**, 631–651.

15 (*a*) N. Auner and J. Weis, in *Organosilicon Chemistry V: From Molecules to Materials*, Wiley-VCH, Weinheim, 2003; (*b*) M. A. Brook, in *Silicon in Organic, Organometallic, and Polymer Chemistry*, Wiley, New York, 2000; (*c*) H. Wang, X. Zhang, Y. Li and L.-W. Xu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202210851.

16 (*a*) A. K. Franz and S. O. Wilson, *J. Med. Chem.*, 2013, **56**, 388–405; (*b*) R. Ramesh and D. S. Reddy, *J. Med. Chem.*, 2018, **61**, 3779–3798.

17 (*a*) M. Oestreich, E. Hartmann and M. Mewald, *Chem. Rev.*, 2013, **113**, 402–441; (*b*) G. K. Min, D. Hernández and T. Skrydstrup, *Acc. Chem. Res.*, 2013, **46**, 457–470; (*c*) Z. Xu, W.-S. Huang, J. Zhang and L.-W. Xu, *Synthesis*, 2015, **47**,

3645–3668; (*d*) Y. Nakajima and S. Shimada, *RSC Adv.*, 2015, **5**, 20603–20616; (*e*) L. Li, Y. Zhang, L. Gao and Z. Song, *Tetrahedron Lett.*, 2015, **56**, 1466–1473; (*f*) T. Hiyama, Y. Minami and A. Mori, in *Organosilicon Chemistry: Novel Approaches and Reactions*, ed. T. Hiyama and M. Oestreich, Wiley-VCH, Weinheim, 2019, pp. 271–332; (*g*) S. Bähr, W. Xue and M. Oestreich, *ACS Catal.*, 2019, **9**, 16–24; (*h*) X. Zhang, J. Fang, C. Cai and G. Lu, *Chin. Chem. Lett.*, 2021, **32**, 1280–1292; (*i*) J.-J. Feng, W. Mao, L. Zhang and M. Oestreich, *Chem. Soc. Rev.*, 2021, **50**, 2010–2073; (*j*) Y. Wu, L. Zheng, Y. Wang and P. Wang, *Chem*, 2023, **9**, 3461–3514; (*k*) M. Liu, L. Qi and D. Zhao, *Chin. J. Org. Chem.*, 2023, **43**, 3508–3525; (*l*) Y. Ge, J. Ke and C. He, *Acc. Chem. Res.*, 2025, **58**, 375–398.

18 (*a*) Y. Guo, M.-M. Liu, X. Zhu, L. Zhu and C. He, *Angew. Chem., Int. Ed.*, 2021, **60**, 13887–13891; (*b*) B. Yang, J. Gao, X. Tan, Y. Ge and C. He, *Angew. Chem., Int. Ed.*, 2023, **62**, e202307812.

19 (*a*) X. Bi, J. Feng, X. Xue and Z. Gu, *Org. Lett.*, 2021, **23**, 3201–3206; (*b*) Y. Xiao, A. L. Bartelt, E. Irran and M. Oestreich, *ACS Catal.*, 2025, **15**, 11307–11312.

20 (*a*) J. Duan, K. Wang, G.-L. Xu, S. Kang, L. Qi, X.-Y. Liu and X.-Z. Shu, *Angew. Chem., Int. Ed.*, 2020, **59**, 23083–23088; (*b*) L. Zhang and M. Oestreich, *Angew. Chem., Int. Ed.*, 2021, **60**, 18587–18590; (*c*) J. Duan, Y. Wang, L. Qi, P. Guo, X. Pang and X.-Z. Shu, *Org. Lett.*, 2021, **23**, 7855–7859; (*d*) Z.-Z. Zhao, X. Pang, X.-X. Wei, X.-Y. Liu and X.-Z. Shu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202200215; (*e*) C.-H. Xu, Z.-Q. Xiong, J.-H. Qin, X.-H. Xu and J.-H. Li, *Org. Lett.*, 2023, **25**, 7263–7267; (*f*) Q.-Q. Pan, L. Qi, X. Pang and X.-Z. Shu, *Angew. Chem., Int. Ed.*, 2023, **62**, e202215703; (*g*) C. Li, S. Yang and X. Zeng, *ACS Catal.*, 2023, **13**, 12062–12073; (*h*) X.-X. Wei, Z.-Z. Zhao, X. Pang and X.-Z. Shu, *Org. Lett.*, 2024, **26**, 6125–6129; (*i*) L.-Y. Yang, Y. Qin, Z. Zhao and D. Zhao, *Angew. Chem., Int. Ed.*, 2024, **63**, e202407773; (*j*) D. Xing, J. Liu, D. Cai, B. Huang, H. Jiang and L. Huang, *Nat. Commun.*, 2024, **15**, 4502; (*k*) T. Yin, S. Sui, S. Li, J. Chang and D. Bai, *Chem. Commun.*, 2024, **60**, 14204–14207; (*l*) L. Qiu, Y. Liu, H. Chen, L. Song and W. Xie, *Chem. Sci.*, 2025, **16**, 9454–9461.

21 (*a*) Z. Lin, W. Hu, L. Zhang and C. Wang, *ACS Catal.*, 2023, **13**, 6795–6803; (*b*) H. Dong and C. Wang, *J. Am. Chem. Soc.*, 2023, **145**, 26747–26755; (*c*) Y. Mao, W. Hu and C. Wang, *ACS Catal.*, 2024, **14**, 17039–17045; (*d*) X. Ding and C. Wang, *Org. Lett.*, 2025, **27**, 2897–2901.

22 Z.-M. Su, R. Deng and S. S. Stahl, *Nat. Chem.*, 2024, **16**, 2036–2043.

23 C. L. Wagner, G. Herrera, Q. Lin, C. T. Hu and T. Diao, *J. Am. Chem. Soc.*, 2021, **143**, 5295–5300.

24 L. Ju, Q. Lin, L. N. J. Bretto, C. L. Wagner, C. T. Hu, J. T. Miller and T. Diao, *J. Am. Chem. Soc.*, 2021, **143**, 14458–14463.

25 R. F. Turro, J. L. H. Wahlman, Z. J. Tong, X. Chen, M. Yang, E. P. Chen, X. Hong, R. G. Hadt, K. N. Houk, Y.-F. Yang and S. Reisman, *J. Am. Chem. Soc.*, 2023, **145**, 14705–14715.

26 (*a*) CCDC 2452324: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2n9v72; (*b*) CCDC 2452325: Experimental Crystal Structure Determination, 2026, DOI: 10.5517/ccdc.csd.cc2n9v83.