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Catalytic asymmetric construction of 1,5-remote Si- and C-stereocenters *via* desymmetrizing ene reaction of bis(methallyl)silanes†

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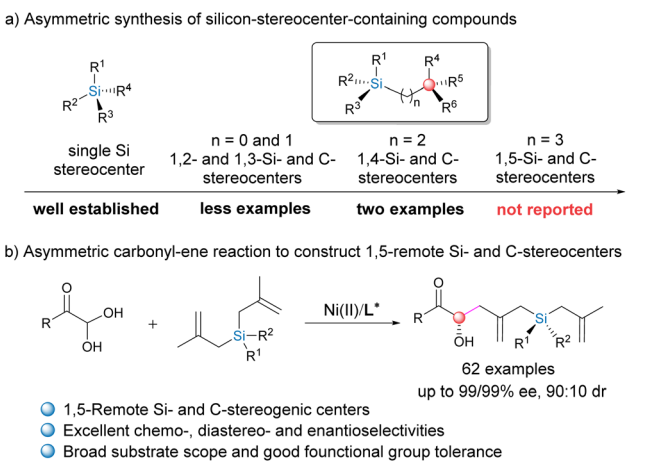
The catalytic enantioselective synthesis of chiral silanes has long been a challenging pursuit. Achieving simultaneous construction of remote Si- and C-stereogenic centers in an acyclic molecule *via* desymmetrization is particularly difficult. Herein, we realized an example of a chiral nickel(II) complex-catalyzed desymmetrizing carbonyl–ene reaction of bis(methallyl)silanes with α-keto aldehyde monohydrates, enabling the highly chemo-, diastereo- and enantioselective synthesis of chiral δ-hydroxy silanes featuring 1,5-remote Si- and C-stereocenters. This protocol demonstrated good functional group tolerance and a broad substrate scope. A bioactivity study revealed its potential applications in the synthesis of bioactive molecules.

Introduction

Enantiomerically enriched silicon-stereogenic silanes hold significant potential in the fields of functional materials,[1] medicinal chemistry[2] and organic synthesis.[3] As natural organosilicon compounds are nonexistent, accessing these compounds relies entirely on chemical synthesis. The desymmetrization of prochiral silanes represents the most prevalent and efficient approach.[4] Among these methods, the direct cleavage of Si–X (X = C, H, Cl) bonds or the conversion of functional groups bound to the silicon atom has been well established, yielding chiral silanes with a single silicon stereocenter (Scheme 1a).

In contrast, the construction of chiral molecules featuring both silicon- and carbon-stereogenic centers is more challenging due to the need for simultaneous control of diastereo- and enantioselectivity. To date, several intriguing studies have focused on the construction of 1,2-adjacent or 1,3-nonadjacent stereocenters. For examples, asymmetric protoboration[5] of divinyl-substituted silanes with B_2pin_2 was exploited to construct 1,2-Si- and C-stereocenters. Intramolecular asymmetric aryl-transfer[6] and the Heck reaction,[7] as well as intermolecular Peterson-olefination[8] of tetrasubstituted silanes, have generated 1,3-Si- and C-stereocenters. Hydrosilanes-participated catalytic asymmetric hydrosilation[9] with alkenes and Si–H insertion[10] with α-diazo acetates, have achieved chiral silanes containing 1,2-, 1,3-, or 1,2,3-Si- and C-stereocenters. For the construction of 1,4-remote Si- and C- stereocenters, only two examples have been reported: the homologation[11] of silacyclohexanones with CF_3CHN_2 and the benzoin reaction[12] of siladials, both leading to silicon-stereogenic silacycles. However, to our knowledge, protocols for synthesizing chiral silanes with 1,5-remote Si-and C-stereocenters remain unexplored.

Allyl silanes have traditionally served as allylation reagents in organic synthesis through the release of the silyl group. In recent years, bis(methallyl)silanes, a class of symmetrical



Scheme 1 Catalytic asymmetric synthesis of chiral silicon-stereogenic silanes.

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† Electronic supplementary information (ESI) available: ^1H, $^{13}C\{^1H\}$ and $^{19}F\{^1H\}$ NMR, HPLC and SFC spectra. CCDC 2393874 (**G**) and 2418295 (**L_4-RaCy$_2$**/Ni(NTf_2)$_2$). For ESI and crystallographic data in CIF or other electronic format see DOI: https://doi.org/10.1039/d5sc01054c

silanes, have been employed by the List group in carbon–carbon bond formation *via* silicon–hydrogen exchange[13] and cyclization.[14] These strategies have emerged as novel and efficient methods for constructing Si-stereogenic centers. Later, they also developed a dynamic kinetic asymmetric transformation of racemic allyl silanes.[15]

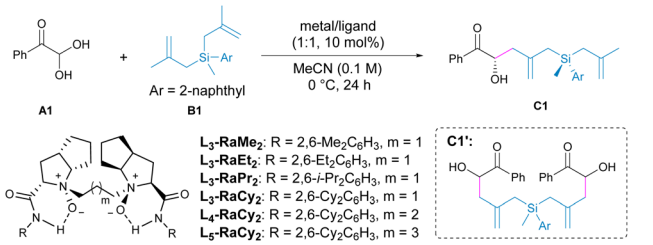
Results and discussion

Inspired by previous success in the carbonyl–ene reaction[16] utilizing chiral *N*,*N*′-dioxide-metal complexes,[17] and driven by our interest in organosilicon chemistry,[18] we envisioned that a desymmetrizing carbonyl–ene reaction with prochiral bis(methallyl)silanes could provide an entry to chiral silanes bearing 1,5-remote Si- and C-stereogenic centers. However, this approach faces important challenges, including: (i) Potential competitive reactions, such as allylation and the double carbonyl–ene reaction. (ii) Achieving diastereo- and enantioselective control of 1,5-remote stereogenic centers, especially in acyclic molecules with more flexible conformations. Herein, we describe a chiral *N*,*N*′-dioxide/Ni(II) complex-mediated asymmetric carbonyl–ene reaction of glyoxal monohydrates with bis(methallyl)silanes, delivering a wide range of chiral δ-hydroxy silanes with 1,5-remote Si- and C-stereocenters (Scheme 1b).

Initially, we chose phenylglyoxal monohydrate **A1** and bis(methallyl)silane **B1** as the model substrates to optimize the carbonyl–ene reaction conditions. With chiral *N*,*N*′-dioxide **L$_3$-RaCy$_2$** as the ligand and Ni(OTf)$_2$ as the metal precursor, the desired product **C1** was obtained in 54% yield with 89 : 11 dr and 99/99% ee (entry 1). Notably, the allylation product was not detected but the byproduct **C1′** which underwent a double carbonyl–ene reaction was isolated with 10% yield. The investigation of chiral ligands showed that efficient enantioselectivity could be achieved using different *N*,*N*′-dioxides, but the L-ramipril-derived ligand **L$_3$-RaCy$_2$** with larger steric hindrance at the 2,6-positions of the amide unit was superior to the ligands generated from other amino acid backbones in terms of diastereoselectivity (entries 2–4, see Table S3† for more details). The chain length linking the two amino amide units had a slight influence on this reaction, affording **C1** with 56% yield, 90 : 10 dr and 99/99% ee by employment of **L$_4$-RaCy$_2$** (entry 5). Switching the counterion of Ni^{2+} to NTf_2^- the yield of **C1** was improved to 67% (entry 7). Given the generation of byproduct **C1′**, the amount of **B1** was increased, leading to a higher yield (76%) of **C1** while maintaining stereoselectivity (entry 8). Upon extending the reaction time to 48 h, the yield of **C1** was further enhanced to 81% (entry 9). Screening of other parameters, including metal salt, solvent, temperature, additive and so on, did not yield a better result (see Tables S1–S8† for details). It is worth mentioning that kinetic resolution may be involved in the second carbonyl–ene reaction, which was verified by performing the control experiment that resulted in the formation of **C1′** and recovered **C1** with an increased dr value (see Fig. S1† for details).

With the optimized reaction conditions in hand (Table 1, entry 9), we proceeded to explore the substrate scope. As depicted in Scheme 2, regardless of the position or electronic

Table 1 Optimization of the reaction conditions[a]



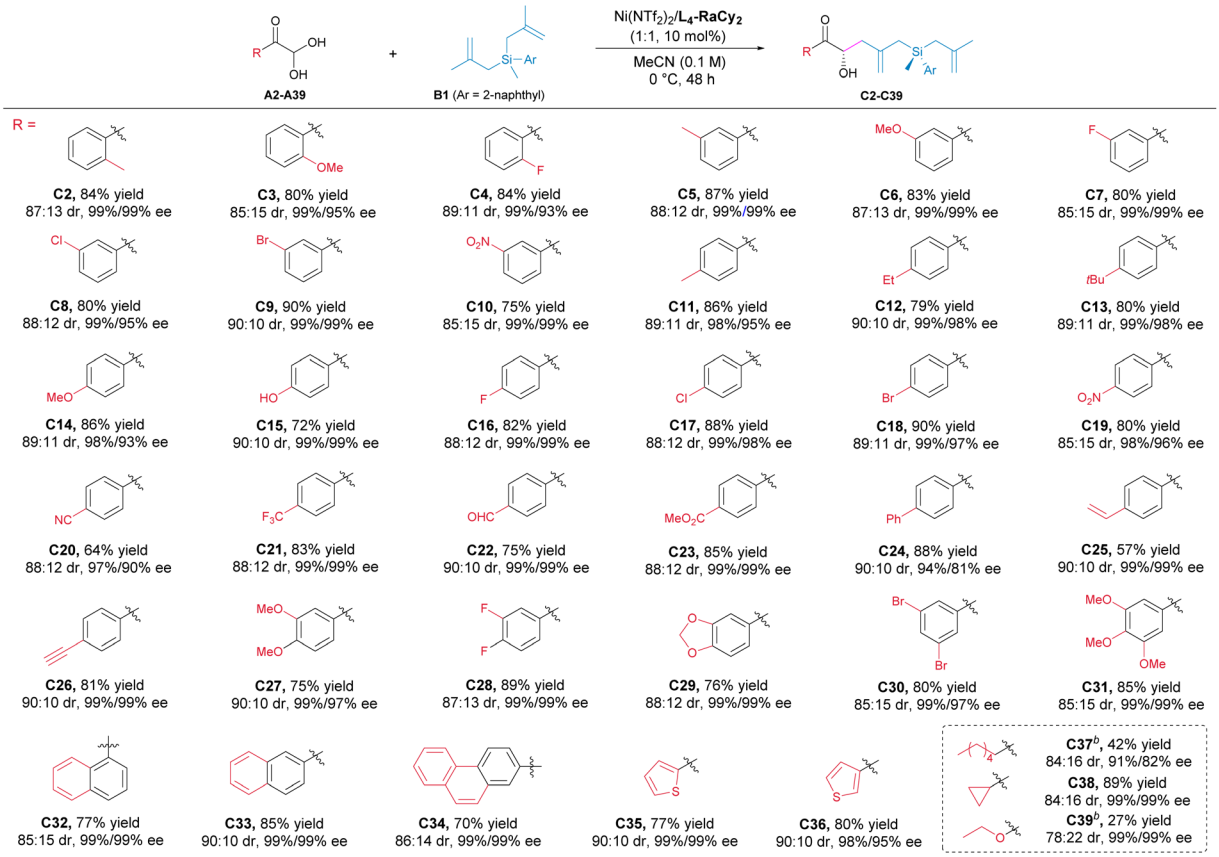
	Metal salt	Ligand	Yield[b]/%	ee[c]/%	dr[c]
1	Ni(OTf)$_2$	**L$_3$-RaCy$_2$**	54	99/99	89 : 11
2	Ni(OTf)$_2$	**L$_3$-RaPr$_2$**	43	97/89	82 : 18
3	Ni(OTf)$_2$	**L$_3$-RaEt$_2$**	46	99/99	75 : 25
4	Ni(OTf)$_2$	**L$_3$-RaMe$_2$**	33	95/92	62 : 38
5	Ni(OTf)$_2$	**L$_4$-RaCy$_2$**	56	99/99	90 : 10
6	Ni(OTf)$_2$	**L$_5$-RaCy$_2$**	47	99/99	90 : 10
7	Ni(NTf$_2$)$_2$	**L$_4$-RaCy$_2$**	67	99/99	90 : 10
8[d]	Ni(NTf$_2$)$_2$	**L$_4$-RaCy$_2$**	76	99/99	90 : 10
9[d,e]	Ni(NTf$_2$)$_2$	**L$_4$-RaCy$_2$**	81	99/99	90 : 10

[a] Unless otherwise noted, all reactions were carried out with **A1** (0.1 mmol), **B1** (0.1 mmol), and metal/ligand (1 : 1, 10 mol%) in MeCN (0.1 M) at 0 °C for 24 h. [b] Yield of the isolated product. [c] Determined by SFC analysis on a chiral stationary phase. [d] **B1** (0.2 mmol). [e] For 48 h.

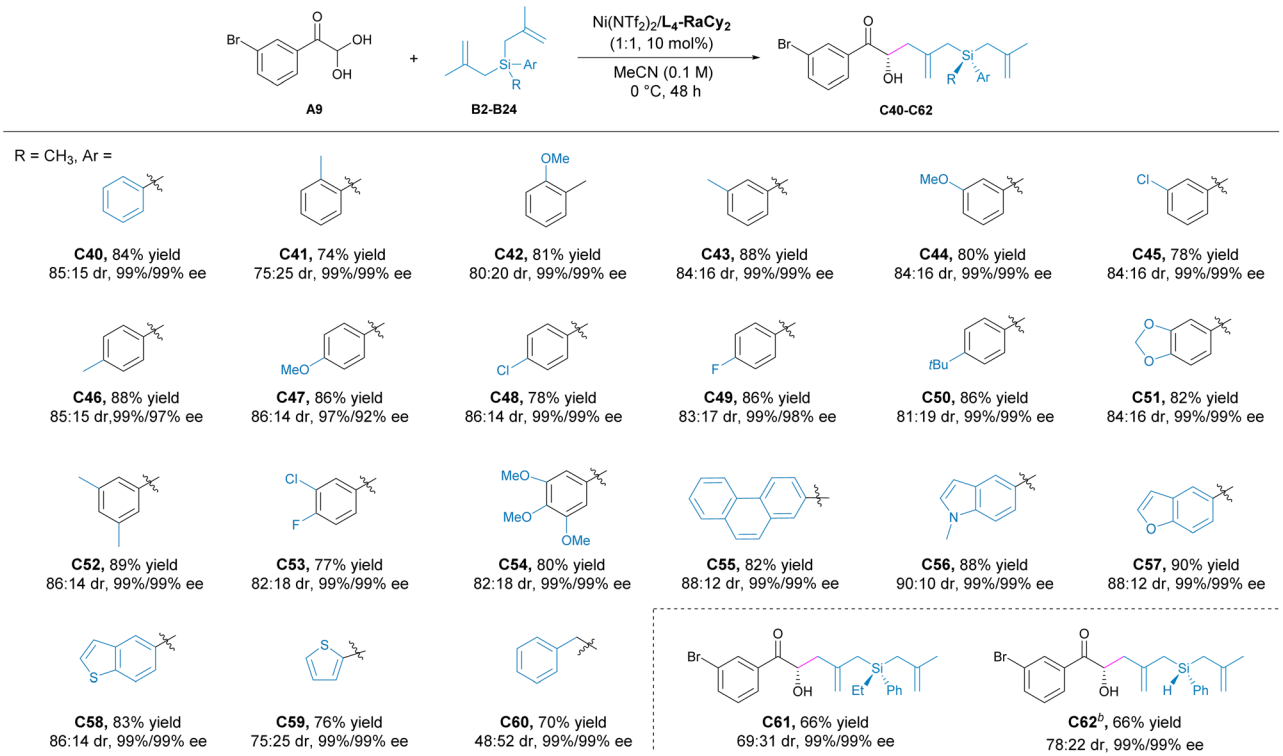
property of the substituents on the phenyl group, all the activated aryl aldehydes reacted with **B1** smoothly to deliver the corresponding products **C2–C26** with 57–90% yield, 85 : 15–90 : 10 dr, 90–99% ee, and exhibited excellent functional group tolerance, including hydroxyl, halogen, nitro, cyano, trifluoromethyl, formyl, ester group, carbonyl, phenyl, vinyl, and ethynyl. Di-, tri-substituted, condensed-ring and heteroaromatic substrates were also well tolerated (**C27–C36**). Furthermore, this catalytic system was also applicable to aliphatic glyoxal monohydrates. Linear alkyl substituted **A37** was converted into **C37** with decreased reactivity and stereoselectivity (42% yield, 84 : 16 dr, 91%/82% ee), but the cyclopropyl-derived one proved to be a suitable substrate (**C38**, 89% yield, 84 : 16 dr, 99%/99% ee). Additionally, the scope of this reaction was extended successfully to glyoxylate (**C39**).

Subsequently, we turned our attention to the scope of bis(methallyl)silanes (Scheme 3). A wide range of aryl methyl substituted bis(methallyl)silanes were successfully transformed into the desired products **C40–C59** in 74–90% yield with 92–99% ee and 75 : 25–90 : 10 dr. Wherein, the silanes (**B3–B4**) bearing a substituent at the *ortho*-position of phenyl exhibited lower diastereoselectivity. Benzyl methyl bis(methallyl)silane (**B22**) was also tested in this reaction, producing **C60** with high yield and enantioselectivity, but the diastereoselectivity was poor. A comparative analysis of the results between **C40** and **C61–C62** revealed that the alkyl substituent on silicon atom also influenced the diastereoselectivity significantly; decreased dr values were obtained with phenyl ethyl bis(methallyl)silane **B23** and monohydrosilane **B24** as substrates.

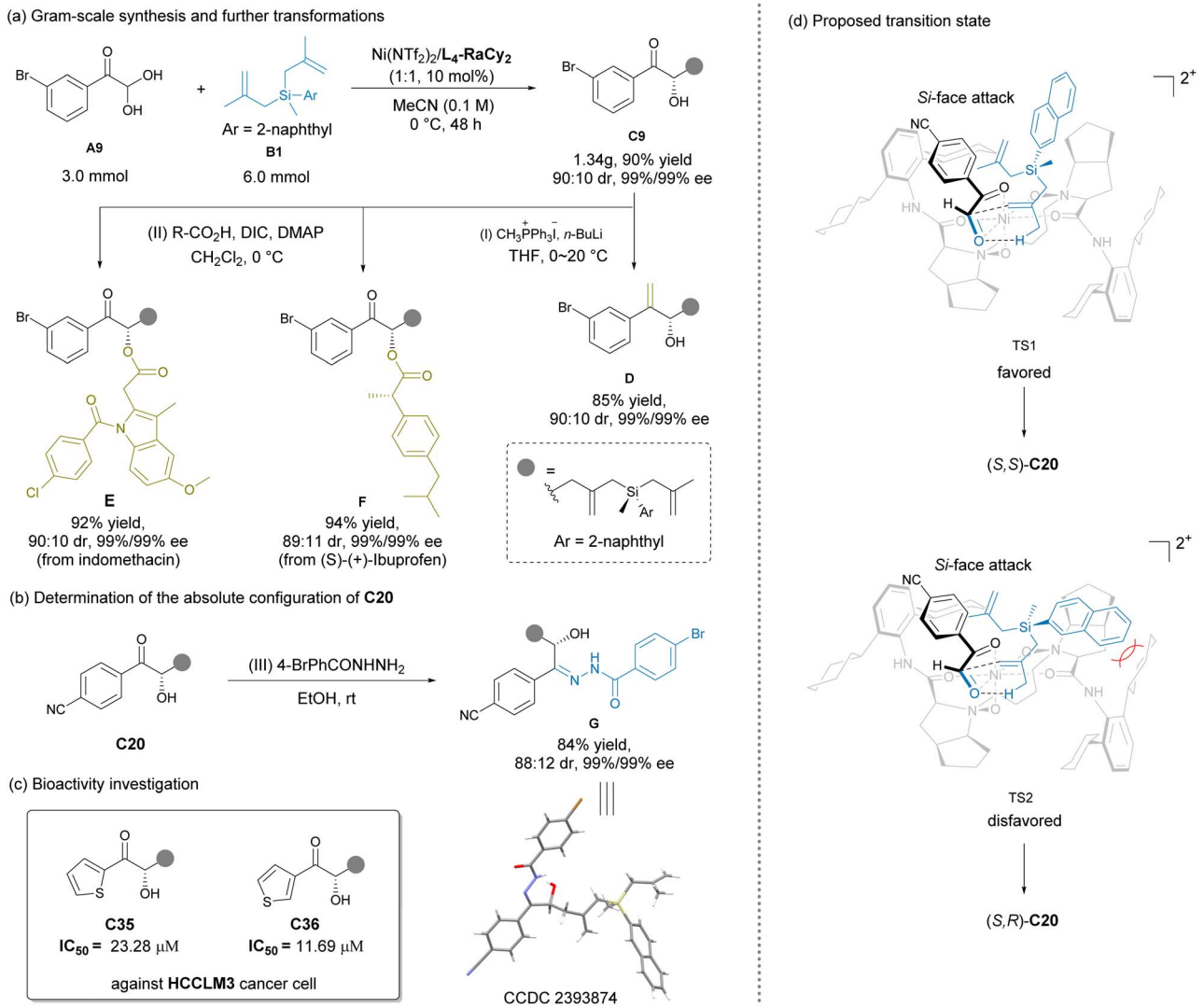
To evaluate the practicality of the catalytic system, a scale-up experiment was carried out between **A9** and **B1** under the



Scheme 2 Substrate scope of α-keto aldehyde monohydrates. [a] Unless otherwise noted, all reactions were carried out with **A** (0.1 mmol), **B1** (0.2 mmol), and $Ni(NTf_2)_2$/**L_4-RaCy$_2$** (1 : 1, 10 mol%) in MeCN (0.1 M) at 0 °C for 48 h under N_2. [b] For 72 h.



Scheme 3 Substrate scope of bis(methallyl)silanes. [a] Unless otherwise noted, all reactions were carried out with **A9** (0.1 mmol), **B** (0.2 mmol), and $Ni(NTf_2)_2$/**L_4-RaCy$_2$** (1 : 1, 10 mol%) in MeCN (0.1 M) at 0 °C for 48 h under N_2. [b] For 72 h.



Scheme 4 (a) Gram-scale synthesis and further transformations. (b) Determination of the absolute configuration of **C20**. (c) Bioactivity investigation. (d) Proposed transition state.

optimized reaction conditions, delivering the product **C9** in 90% yield with 90 : 10 dr and 99/99% ee (Scheme 4a). Further transformations of **C9** were also carried out. For instance, **C9** underwent a Wittig reaction to yield **D** while maintaining its stereoselectivity. It was also applied for the late-stage modification of drugs through the introduction of a Si-stereogenic center, as demonstrated by the synthesis of drug derivatives **E** and **F** *via* condensation reaction. Treatment of **C20** with 4-bromobenzohydrazide provided the corresponding hydrazone **G** in 84% yield with 99/99% ee, whose configuration was determined to be (*S*,*S*) by X-ray crystallographic analysis[19] (Scheme 4b). In light of the potential bioactivity of organosilicon compounds, their *in vitro* cytotoxicity against human hepatocellular carcinoma was investigated. The outcomes indicated that **C35** and **C36** had an inhibitory effect on the activity of HCCLM3 (Scheme 4c).

Based on the absolute configuration of product **C20** and the single-crystal structure of the **L$_4$-RaCy$_2$**/Ni(II) complex,[20] the possible working modes were proposed to understand the stereoselective control of this reaction. As shown in Scheme 4d, both the oxygen atoms of the amide and N-oxide units of the ligand coordinate with the central Ni(NTf$_2$)$_2$ to form the **L$_4$-RaCy$_2$**/Ni(II) complex in a tetradentate manner; this complex acts as a chiral Lewis acid to activate the glyoxal derivative **A20** *via* bidentate coordination with the dicarbonyl groups. Mechanistically, the carbonyl–ene reaction proceeds *via* a six-membered cyclic transition state. **B1** approaches from the *Si* face of **A20** because the *Re* face is blocked by the amide unit of the ligand (see the ESI† for details). Meanwhile, due to steric repulsion between the naphthyl of **B1** and the chiral ligand (Scheme 4d, bottom), the naphthyl group is directed toward the back side (Scheme 4d, top), producing (*S*,*S*)-**C20** as the major diastereoisomer.

Conclusions

In conclusion, an efficient catalytic asymmetric desymmetrization of bis(methallyl)silanes with α-keto aldehyde

monohydrates was accomplished by employing a chiral *N*,*N*′-dioxide/Ni(II) complex catalyst. This protocol provides facile access to acyclic chiral δ-hydroxy silanes bearing 1,5-remote Si- and C-stereocenters in excellent yields with good dr and ee values. The scale-up reaction and product transformations as well as good biological activity illustrate the potential practicality of this methodology. Further endeavor toward the enantioselective synthesis of chiral silanes is underway.

Data availability

Further details of the experimental procedure, ^{1}H, $^{13}C\{^{1}H\}$ and $^{19}F\{^{1}H\}$ NMR, HPLC spectra, SFC spectra, X-ray crystallographic data for **G** and the **L_4-RaCy$_2$**/Ni$(NTf_2)_2$ complex are available in the ESI.†

Author contributions

Q. H. C. performed experiments and prepared the manuscript and ESI.† Y. T. Y. participated in the synthesis of substrates. Y. W. M. repeated some experiments. M. H. J. and F. W. conducted bioactivity investigation. W. D. C. helped in modifying the paper and ESI.† W. D. C. and X. M. F. conceived and directed the project.

Conflicts of interest

There are no conflicts to declare.

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19 CCDC 2393874† for **G** contains the supplentary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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