

Cite this: *Chem. Sci.*, 2025, 16, 8454

All publication charges for this article have been paid for by the Royal Society of Chemistry

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

Qihui Cao,^a Yuntian Yang,^a Yiwen Mei,^a Minghui Ji,^b Fei Wang,^b Xiaoming Feng^{ID} ^{*a} and Weidi Cao^{ID} ^{*a}

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.

Received 10th February 2025
Accepted 27th March 2025

DOI: 10.1039/d5sc01054c

rsc.li/chemical-science

Introduction

Enantiomerically enriched silicon-stereogenic silanes hold significant potential in the fields of functional materials,¹ medicinal chemistry² 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 protoboration⁵ of divinyl-substituted silanes with B_2pin_2 was exploited to construct 1,2-Si- and C-stereocenters. Intramolecular asymmetric aryl-transfer⁶ and the Heck reaction,⁷ as well as intermolecular Peterson-olefination⁸ of tetrasubstituted silanes,

have generated 1,3-Si- and C-stereocenters. Hydrosilanes-participated catalytic asymmetric hydrosilation⁹ with alkenes and Si-H insertion¹⁰ 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 homologation¹¹ of silacyclohexanones with CF_3CHN_2 and the benzoin reaction¹² 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

a) Asymmetric synthesis of silicon-stereocenter-containing compounds



b) Asymmetric carbonyl-ene reaction to construct 1,5-remote Si- and C-stereocenters

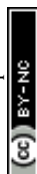


Scheme 1 Catalytic asymmetric synthesis of chiral silicon-stereogenic silanes.

^aKey Laboratory of Green Chemistry & Technology, Ministry of Education, College of Chemistry, Sichuan University, Chengdu, 610064, P. R. China. E-mail: xmfeng@scu.edu.cn; wdcao@scu.edu.cn

^bCenter for Natural Products Research, Chengdu Institute of Biology, Chinese Academy of Sciences, Chengdu, 610041, China

† Electronic supplementary information (ESI) available: ¹H, ¹³C{¹H} and ¹⁹F{¹H} NMR, HPLC and SFC spectra. CCDC 2393874 (G) and 2418295 (L4-RaCy₂/Ni(NTf₂)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 exchange¹³ 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 reaction¹⁶ 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 **L3-RaCy2** 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 **L3-RaCy2** 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 **L4-RaCy2** (entry 5). Switching the counterion of Ni²⁺ to NTF₂[−] 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	L3-RaCy2	54	99/99	89 : 11
2	Ni(OTf) ₂	L3-RaPr2	43	97/89	82 : 18
3	Ni(OTf) ₂	L3-RaEt2	46	99/99	75 : 25
4	Ni(OTf) ₂	L3-RaMe2	33	95/92	62 : 38
5	Ni(OTf) ₂	L4-RaCy2	56	99/99	90 : 10
6	Ni(OTf) ₂	L5-RaCy2	47	99/99	90 : 10
7	Ni(NTf ₂) ₂	L4-RaCy2	67	99/99	90 : 10
8 ^d	Ni(NTf ₂) ₂	L4-RaCy2	76	99/99	90 : 10
9 ^{d,e}	Ni(NTf ₂) ₂	L4-RaCy2	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 hetero-aromatic 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**).

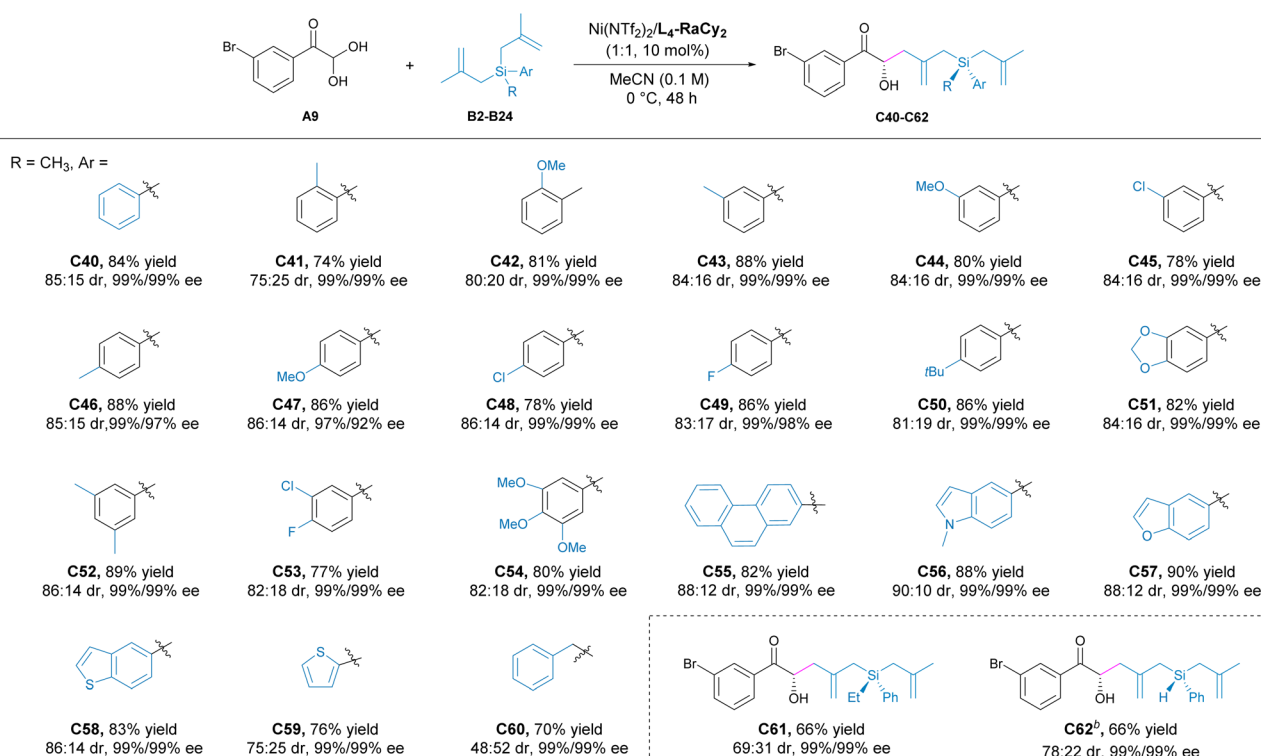
Subsequently, we turned our attention to the scope of bis(methallyl)silanes (Scheme 3). A wide range of aryl methyl substituted bis(methallyl)silanes were successfully transformed into the desired products **C40–C59** in 74–90% yield with 92–99% ee and 75 : 25–90 : 10 dr. Wherein, the silanes (**B3–B4**) 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





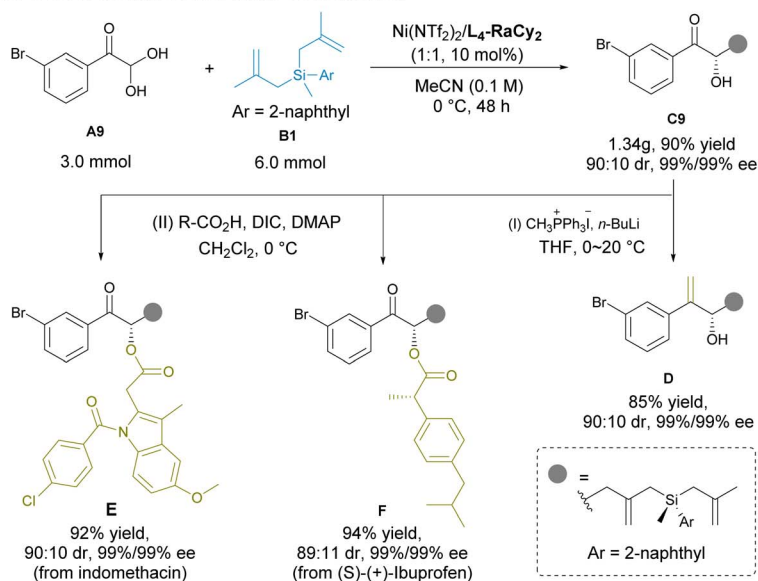
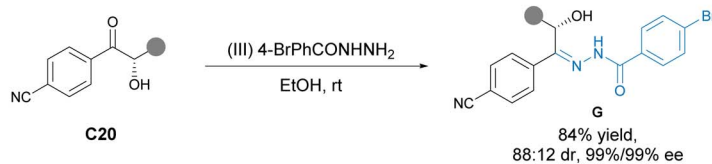
Scheme 2 Substrate scope of α -keto aldehyde monohydrates.^a Unless otherwise noted, all reactions were carried out with **A** (0.1 mmol), **B1** (0.2 mmol), and Ni(NTf₂)₂/L₄-RaCy₂ (1 : 1, 10 mol%) in MeCN (0.1 M) at 0 °C for 48 h under N₂. ^b For 72 h.



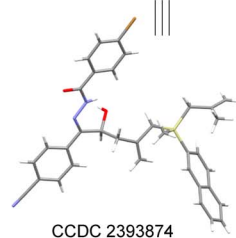
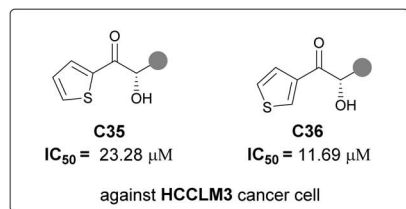
Scheme 3 Substrate scope of bis(methallyl)silanes.^a Unless otherwise noted, all reactions were carried out with **A9** (0.1 mmol), **B** (0.2 mmol), and Ni(NTf₂)₂/L₄-RaCy₂ (1 : 1, 10 mol%) in MeCN (0.1 M) at 0 °C for 48 h under N₂. ^b For 72 h.



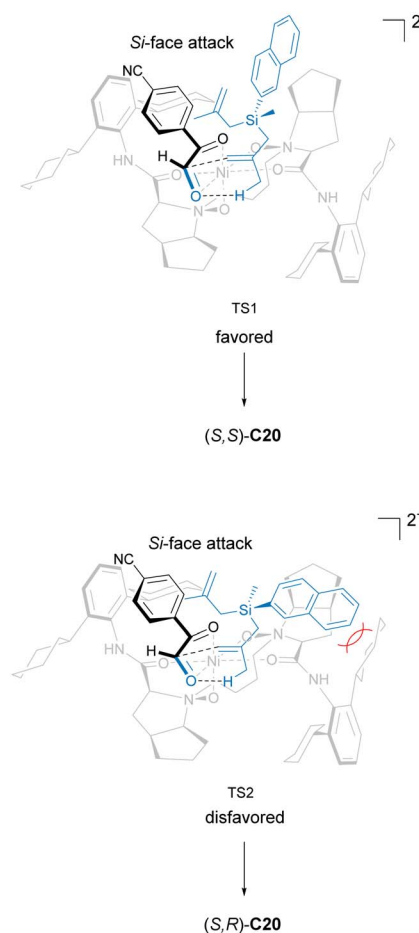
(a) Gram-scale synthesis and further transformations

(b) Determination of the absolute configuration of **C20**

(c) Bioactivity investigation



(d) Proposed transition state



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 analysis¹⁹ (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 **L4-RaCy2**/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(NTf₂)₂ to form the **L4-RaCy2**/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, ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{19}\text{F}\{^1\text{H}\}$ NMR, HPLC spectra, SFC spectra, X-ray crystallographic data for **G** and the $\text{L}_4\text{-RaCy}_2/\text{Ni}(\text{NTf}_2)_2$ 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.

Acknowledgements

We appreciate the National Key Research and Development Program of China (2022YFA1504301) and the National Natural Science Foundation of China (22471179 and 92256302) for financial support. We thank Dr Yuqiao Zhou (Sichuan University) for the X-ray single crystal diffraction analysis.

Notes and references

- (a) J. Chen and Y. Cao, *Macromol. Rapid Commun.*, 2007, **28**, 1714–1742; (b) Y. Kawakami, Y. Kakihana, O. Ooi, M. Oishi, K. Suzuki, S. Shinke and K. Uenish, *Polym. Int.*, 2009, **58**, 279–284; (c) T. Ikeno, T. Nagano and K. Hanaoka, *Chem.–Asian J.*, 2017, **12**, 1435–1446; (d) R. Shintani, N. Misawa, R. Takano and K. Nozaki, *Chem.–Eur. J.*, 2017, **23**, 2660–2665; (e) S. Koga, S. Ueki, M. Shimada, R. Ishii, Y. Kurihara, Y. Yamanoi, J. Yuasa, T. Kawai, T. Uchida, M. Iwamura, K. Nozaki and H. Nishihara, *J. Org. Chem.*, 2017, **82**, 6108–6117.
- (a) R. Tacke and U. Wannagat, *Syntheses and Properties of Bioactive Organo-Silicon Compounds*, Springer, Heidelberg, 1979; (b) R. Tacke, D. Reichel, M. Kropfgans, P. G. Jones, E. Mutschler, J. Gross, X. Hou, M. Waelbroeck and G. Lambrecht, *Organometallics*, 1995, **14**, 251–262; (c) M. Mutahi, T. Nittoli, L. Guo and S. M. Sieburth, *J. Am. Chem. Soc.*, 2002, **124**, 7363–7375; (d) A. K. Franz and S. O. Wilson, *J. Med. Chem.*, 2013, **56**, 388–405; (e) E. Remond, C. Martin, J. Martinez and F. Cavelier, *Chem. Rev.*, 2016, **116**, 11654–11684; (f) R. Ramesh and D. S. Reddy, *J. Med. Chem.*, 2018, **61**, 3779–3798.
- (a) C. E. Masse and J. S. Panek, *Chem. Rev.*, 1995, **95**, 1293–1316; (b) S. Rendler, G. Auer, M. Keller and M. Oestreicha, *Adv. Synth. Catal.*, 2006, **348**, 1171–1182; (c) L.-W. Xu, L. Li, G.-Q. Lai and J.-X. Jiang, *Chem. Soc. Rev.*, 2011, **40**, 1777–1790; (d) L. J. Li, Y. B. Zhang, L. Gao and Z. L. Song, *Tetrahedron Lett.*, 2015, **56**, 1466–1473; (e) J. O. Bauer and C. Strohmann, *Eur. J. Inorg. Chem.*, 2016, **18**, 2868–2881; (f) Y.-M. Cui, Y. Lin and L.-W. Xu, *Coord. Chem. Rev.*, 2017, **330**, 37–52; (g) R. Shintani, *Synlett*, 2018, **29**, 388–396; (h) M. Zhang, S. Gao, J. Tang, L. Chen, A. H. Liu, S. R. Sheng and A. Q. Zhang, *Chem. Commun.*, 2021, **57**, 8250–8263.
- (a) L.-W. Xu, *Angew. Chem., Int. Ed.*, 2012, **51**, 12932–12934; (b) R. Shintani, *Asian J. Org. Chem.*, 2015, **4**, 510–514; (c) L. Zheng, X.-X. Nie, Y. C. Wu and P. Wang, *Eur. J. Org. Chem.*, 2021, **44**, 6006–6014; (d) F. Ye, Z. Xu and L.-W. Xu, *Acc. Chem. Res.*, 2021, **54**, 452–470; (e) Y. C. Ge, X. F. Huang, J. Ke and C. He, *Chem Catal.*, 2022, **2**, 2898–2928; (f) Y. C. Wu, L. Zheng, Y. Wang and P. Wang, *Chem*, 2023, **10**, 3461–3514; (g) Y. Zeng and F. Ye, *Chin. J. Org. Chem.*, 2023, **43**, 3388–3413; (h) Y. C. Ge, J. Ke and C. He, *Acc. Chem. Res.*, 2025, **58**, 375–398.
- G. Zhang, Y. F. Li, Y. Wang, Q. Zhang, T. Xiong and Q. Zhang, *Angew. Chem., Int. Ed.*, 2020, **59**, 11927–11931.
- R. Kumar, Y. Hoshimoto, H. Yabuki, M. Ohashi and S. Ogoshi, *J. Am. Chem. Soc.*, 2015, **137**, 11838–11845.
- K.-L. Yin, S. Zhao, Y. Qin, S.-H. Chen, B. Li and D. B. Zhao, *ACS Catal.*, 2022, **12**, 13999–14005.
- W. G. Guo, Q. Li, Y. Liu and C. Li, *Sci. China: Chem.*, 2023, **66**, 2797–2802.
- (a) K. Tamao, K. Nakamura, H. Ishii, S. Yamaguchi and M. Shiro, *J. Am. Chem. Soc.*, 1996, **118**, 12469–12470; (b) Z.-Y. Zhao, Y.-X. Nie, R.-H. Tang, G.-W. Yin, J. Cao, Z. Xu, Y.-M. Cui, Z.-J. Zheng and L.-W. Xu, *ACS Catal.*, 2019, **9**, 9110–9116; (c) X. Chang, P.-L. Ma, H.-C. Chen, C.-Y. Li and P. Wang, *Angew. Chem., Int. Ed.*, 2020, **59**, 8937–8940; (d) Y.-H. Huang, Y. C. Wu, Z. L. Zhu, S. J. Zheng, Z. H. Ye, Q. Peng and P. Wang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202113052; (e) L. Wang, W. X. Lu, J. W. Zhang, Q. L. Chong and F. K. Meng, *Angew. Chem., Int. Ed.*, 2022, **61**, e202205624; (f) W. X. Lu, Y. M. Zhao and F. K. Meng, *J. Am. Chem. Soc.*, 2022, **144**, 5233–5240.
- (a) Y. Yasutomi, H. Suematsu and T. Katsuki, *J. Am. Chem. Soc.*, 2010, **132**, 4510–4511; (b) Y. Nakagawa, S. Chanthamath, I. Fujisawa, K. Shibatomi and S. Iwasa, *Chem. Commun.*, 2017, **53**, 3753–3756; (c) J. R. Jagannathan, J. C. Fettingner, J. T. Shaw and A. K. Franz, *J. Am. Chem. Soc.*, 2020, **142**, 11674–11679.
- S.-S. Li, S. Sun and J. B. Wang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202115098.
- H. Liu, P. Y. He, X. L. Liao, Y. P. Zhou, X. K. Chen, W. P. Ou, Z. H. Wu, C. Luo, L. M. Yang and J. F. Xu, *ACS Catal.*, 2022, **12**, 9864–9871.



- 13 H. Zhou, J. T. Han, N. Nöthling, M. M. Lindner, J. Jenniches, C. Kühn, N. Tsuji, L. Zhang and B. List, *J. Am. Chem. Soc.*, 2022, **144**, 10156–10161.
- 14 J. T. Han, N. Tsuji, H. Zhou, M. Leutzsch and B. List, *Nat. Commun.*, 2024, **15**, 5846.
- 15 H. Zhou, R. Properzi, M. Leutzsch, P. Belanzoni, G. Bistoni, N. Tsuji, J. T. Han, C. D. Zhu and B. List, *J. Am. Chem. Soc.*, 2023, **145**, 4994–5000.
- 16 (a) L. C. Dias, *Curr. Org. Chem.*, 2000, **4**, 305–342; (b) X. H. Liu, K. Zheng and X. M. Feng, *Synthesis*, 2014, **46**, 2241–2257; (c) M. Balha, C. Parida and S. C. Pan, *Asian J. Org. Chem.*, 2021, **10**, 2440–2453; (d) Y. Yang and C. R. Jones, *Synthesis*, 2022, **54**, 5042–5054; (e) K. Zheng, J. Shi, X. H. Liu and X. M. Feng, *J. Am. Chem. Soc.*, 2008, **130**, 15770–15771; (f) K. Zheng, X. H. Liu, J. N. Zhao, Y. Yang, L. L. Lin and X. M. Feng, *Chem. Commun.*, 2010, **46**, 3771–3773; (g) K. Zheng, Y. Yang, J. N. Zhao, C. K. Yin, L. L. Lin, X. H. Liu and X. M. Feng, *Chem.–Eur. J.*, 2010, **16**, 9969–9972; (h) K. Zheng, C. K. Yin, X. H. Liu, L. L. Lin and X. M. Feng, *Angew. Chem., Int. Ed.*, 2011, **50**, 2573–2577; (i) K. Zheng, X. H. Liu, S. Qin, M. S. Xie, L. L. Lin, C. W. Hu and X. M. Feng, *J. Am. Chem. Soc.*, 2012, **134**, 17564–17573; (j) W. W. Luo, J. N. Zhao, C. K. Yin, X. H. Liu, L. L. Lin and X. M. Feng, *Chem. Commun.*, 2014, **50**, 7524–7526; (k) W. W. Luo, J. N. Zhao, J. Ji, L. L. Lin, X. H. Liu, H. J. Mei and X. M. Feng, *Chem. Commun.*, 2015, **51**, 10042–10045; (l) H. Zhang, Q. Yao, W. D. Cao, S. L. Ge, J. X. Xu, X. H. Liu and X. M. Feng, *Chem. Commun.*, 2018, **54**, 12511–12514; (m) W. Liu, W. D. Cao, H. P. Hu, L. L. Lin and X. M. Feng, *Chem. Commun.*, 2018, **54**, 8901–8904; (n) W. Liu, P. F. Zhou, J. W. Lang, S. X. Dong, X. H. Liu and X. M. Feng, *Chem. Commun.*, 2019, **55**, 4479–4482; (o) L. Z. Hou, T. F. Kang, L. K. Yang, W. D. Cao and X. M. Feng, *Org. Lett.*, 2020, **22**, 1390–1395; (p) X. P. Sang, Y. H. Mo, S. Y. Li, X. H. Liu, W. D. Cao and X. M. Feng, *Chem. Sci.*, 2023, **14**, 8315–8320.
- 17 (a) X. H. Liu, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2011, **44**, 574–587; (b) X. H. Liu, H. F. Zheng, Y. Xia, L. L. Lin and X. M. Feng, *Acc. Chem. Res.*, 2017, **50**, 2621–2631; (c) M.-Y. Wang and W. Li, *Chin. J. Chem.*, 2021, **39**, 969–984; (d) S. X. Dong, X. H. Liu and X. M. Feng, *Acc. Chem. Res.*, 2022, **55**, 415–428; (e) D.-F. Chen and L.-Z. Gong, *Org. Chem. Front.*, 2023, **10**, 3676–3683; (f) S. X. Dong, W. D. Cao, M. P. Pu, X. H. Liu and X. M. Feng, *CCS Chem.*, 2023, **5**, 2717–2735; (g) Z. J. Xiao, M. P. Pu, Y. Z. Li, W. Yang, F. Wang, X. M. Feng and X. H. Liu, *Angew. Chem., Int. Ed.*, 2025, **64**, e202414712; (h) Q. F. Xu, L. C. Ning, W. T. Xu, L. L. Lin and X. M. Feng, *Org. Lett.*, 2024, **26**, 9665–9670; (i) L. K. Yang, S. Y. Li, L. C. Ning, H. S. Zhao, L. Zhou, W. D. Cao and X. M. Feng, *Nat. Commun.*, 2024, **15**, 10866.
- 18 (a) M. M. Guan, S. Y. Wang, Y. Luo, W. D. Cao, X. H. Liu and X. M. Feng, *Chem. Sci.*, 2021, **12**, 7498–7503; (b) L. Z. Hou, Y. Q. Zhou, H. Yu, T. Y. Zhan, W. D. Cao and X. M. Feng, *J. Am. Chem. Soc.*, 2022, **144**, 22140–22149; (c) L. L. Feng, X. F. Chen, N. Guo, Y. Q. Zhou, L. L. Lin, W. D. Cao and X. M. Feng, *Chem. Sci.*, 2023, **14**, 4516–4522; (d) N. Guo, Y. Luo, L. L. Feng, Z. L. Liu, W. D. Cao and X. M. Feng, *Asian J. Org. Chem.*, 2023, **12**, e202300164; (e) L. Z. Hou, W. D. Cao and X. M. Feng, *ChemCatChem*, 2024, **16**, e202400385.
- 19 CCDC 2393874† for **G** contains the supplementary 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.
- 20 CCDC 2418295† for the **L₄-RaCy₂/Ni(NTf₂)₂** complex contains the supplementary 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.

