Nickel/Brønsted Acid-Catalyzed Chemo- and Enantioselective Intermolecular Hydroamination of Conjugated Dienes

HIGHLIGHTS

- Dual catalysis
- High chemo- and enantioselectivity
- Broad amine scope
- Wide functional group tolerance

> 50 examples
up to 99% yield, > 99% ee

91% yield, > 99% ee
83% yield, 98% ee
94% yield, 99% ee
59% yield, 90% ee
95% yield, > 99% ee
40% yield, > 99% ee
Nickel/Brønsted Acid-Catalyzed Chemo- and Enantioselective Intermolecular Hydroamination of Conjugated Dienes

Jiao Long,1 Peng Wang,1 Wang Wang,1 Yuqiang Li,1 and Guoyin Yin1,2,*

SUMMARY
A novel nickel/Brønsted acid-catalyzed asymmetric hydroamination of acyclic 1,3-dienes has been established. A wide array of primary and secondary amines can be transformed into allylic amines with high yields and high enantioselectivities under very mild conditions. Moreover, our method is compatible with various functional groups and heterocycles, allowing for late-stage functionalization of biologically active complex molecules. Remarkably, this protocol exhibits good chemoselectivity with respect to amines bearing two different nucleophilic sites. Mechanistic studies reveal that the enantioselective carbon-nitrogen bond-forming step is reversible.

INTRODUCTION
Chiral amines represent a privileged pharmacophore and are present in a myriad of natural products and drugs (Figure 1A) (Francotte and Lindner, 2006; Lough and Wainer, 2002; Nugent, 2010). Therefore, organic chemists have made considerable efforts toward their synthesis during the last decade (Groghan, 2018; Li and Zhang, 2014; Nugent and El-Shazly, 2010; Patil et al., 2018; Robak et al., 2010). Among them, asymmetric hydroamination of unsaturated C-C bonds serves as an efficient and powerful tool in organic synthesis, particularly hydroamination using free amines (Aillaud et al., 2007; Clement and Jerome, 2017; Dondoni, 2015; Hannedouche and Schulz, 2013, 2018; Hii, 2006; Huang et al., 2015; Huo et al., 2019; Jerome, 2018; Müller et al., 2008; Patel et al., 2017; Pirnot et al., 2016; Reznichenko and Hultzsch, 2016; Zi, 2009, 2011). In this context, transition-metal-catalyzed intermolecular asymmetric hydroamination of allenes (Berthold and Breit, 2018, 2019; Cooke et al., 2012; Dion and Beauachemin, 2011; Lin et al., 2019; Parveen et al., 2017; Xu et al., 2016), alkynes (Athira et al., 2018; Liu et al., 2011; Lutete et al., 2004; Patil et al., 2006; Xu et al., 2019), and conjugated dienes (Adamson et al., 2017; Dion and Beauachemin, 2011; Lin et al., 2019; Lober et al., 2001; Park and Malcolmson, 2018; Xiong et al., 2018; Yang and Dong, 2017; Zhou and Hartwig, 2008) has been extensively studied (Figure 1B). Nevertheless, the use of noble transition metals such as rhodium and palladium are often mandatory (Adamson et al., 2017; Aillaud et al., 2007; Athira et al., 2018; Berthold and Breit, 2018; Clement and Jerome, 2017; Cooke et al., 2012; Dion and Beauachemin, 2011; Dondoni, 2015; Hannedouche and Schulz, 2013, 2018; Hii, 2006; Huang et al., 2015; Huo et al., 2019; Jerome, 2018; Lin et al., 2019; Liu et al., 2011; Lober et al., 2001; Lutete et al., 2004; Müller et al., 2008; Park and Malcolmson, 2018; Parveen et al., 2017; Patel et al., 2017; Patil et al., 2006; Pirnot et al., 2016; Reznichenko and Hultzsch, 2016; Xiong et al., 2018; Xu et al., 2016, 2019; Yang and Dong, 2017; Zhou and Hartwig, 2008, 2009, 2011); in addition, these methods suffer from limited amine scope (Adamson et al., 2017; Dion and Beauachemin, 2011; Lin et al., 2019; Lober et al., 2001; Park and Malcolmson, 2018; Xiong et al., 2018; Yang and Dong, 2017; Zhou and Hartwig, 2008), as well as excessive quantities of the unsaturated substrate are always required to achieve a high level of efficiency (Adamson et al., 2017; Dion and Beauachemin, 2011; Lin et al., 2019; Lober et al., 2001; Park and Malcolmson, 2018; Yang and Dong, 2017; Zhou and Hartwig, 2008).

In recent years, research toward nickel-catalyzed oxidative addition with X-H (X = C, O, ...) bonds has become a hot theme owing to earth-abundance of nickel and its great potential in oxidative addition (Ananikov, 2015; Tasker et al., 2014; Wang, 2016; Figure 1C). Significant progress has been made in the asymmetric hydrofunctionalization of alkenes through nickel-catalyzed reactions (Bezenine-Lafollee et al., 2017; Cai et al., 2019; Chen and Lu, 2018; Cheng et al., 2018, 2019; Diesel et al., 2018, 2019; Donets and Cramer, 2013; Li et al., 2018, 2019a; Lv et al., 2018; Richmond and Moran, 2018; Woźniak and Cramer, 2018).
Chiral centers are generally induced via a carbon-carbon bond-forming process, involving the direct oxidative addition of C-H bonds (Cai et al., 2019; Cheng et al., 2018, 2019, Diesel et al., 2018, 2019; Donets and Cramer, 2013; Li et al., 2019a; Lv et al., 2018; Wozniak and Cramer, 2019; Zhang et al., 2019) or an external stoichiometric reductant, such as alcohol (Chen et al., 2019) or hydrosiloxane (Ahlin and Cramer, 2016). However, nickel-catalyzed asymmetric hydrofunctionalization of unsaturated compounds involving a carbon-heteroatom bond formation has not been studied much (Tran et al., 2019). As an extension of our studies with nickel-catalyzed carbon-carbon bond formations (Li et al., 2019b; Wang et al., 2019), we turned our attention to carbon-heteroatom bonds. Inspired by the recent reports on metal/Brønsted acid dual catalysis (Adamson et al., 2017; Dion and Beauchemin, 2011; Han et al., 2018; Kathe and Fleischer, 2019; Lin et al., 2019; Liu and Feng, 2018; Löber et al., 2001; Park and Malcolmson, 2018; Yang and Dong, 2017; Zhou and Hartwig, 2008), we have developed a novel, room temperature nickel/Brønsted acid-catalyzed asymmetric hydroamination using conjugated dienes as a limiting reagent (Figure 1D). This protocol can transform a wide array of primary and secondary amines into allylic amines in high yields with excellent enantioselectivities. Significantly, good regio-, chemo-, and enantioselectivity have been achieved using amines bearing potentially competitive nucleophilic sites. It is noteworthy that the nickel-catalyzed racemic hydroamination of cyclic dienes has only been reported by the Hartwig group before, wherein they also demonstrated the challenge for the development of an enantioselective variant (Pawlas et al., 2002).

Figure 1. Reaction Design
(A) Representative drugs containing chiral amines.
(B) Toward chiral allylic amines by asymmetric intermolecular hydroamination.
(C) Ni-catalyzed asymmetric hydrofunctionalization.
(D) Nickel/Brønsted acid-catalyzed chemo- and enantioselective intermolecular hydroamination of conjugated dienes.
RESULTS

Optimization Reaction Conditions

We initiated this study by choosing phenyl-1,3-diene (1a) and morpholine (2a) as model substrates. Ligand evaluations were conducted using Ni(COD)2 as the precatalyst and TsOH·H2O as a cocatalyst. As shown in Figure 2, a series of bisphosphine ligands were examined; the 1,2-hydroamination product 3a (Wang et al., 2014) was obtained in a moderate yield with a low enantiomeric excess (ee) when chiral BINAP (L1) or SEGPHOS (L2) was used, which demonstrated the feasibility of this hydroamination reaction. Unfortunately, (S)-SKP (L3), (R)-SDP (L4), and (R)-DIOP (L5) as ligand were not effective for this transformation, although (S,S)-BDPP (L6), a flexible bisphosphine ligand, yielded 3a in an excellent yield, but with low enantioselectivity (23% ee). However, both high yields and enantioselectivities were achieved by (R,C,S)-DuanPhos (L7). To our delight, excellent ee (95% ee) was obtained when (S,S)-Me-DuPhos (L8), as a more rigid ligand, was used. In addition, the Brønsted acid cocatalyst can also affect the efficiency and enantioselectivity of this hydroamination reaction. Further studies demonstrated that the desired product can also be obtained in high yields without a decrease in enantioselectivity when switching the acid cocatalyst to phenylphosphonic acid (A3) or phthalic acid (A4). To easily weighout, we selected A4 as cocatalyst. Moreover, control experiments indicated that both nickel catalysts and the Brønsted acids were crucial to the success of this reaction. Notably, no other regioisomers were detected in these reactions.

Substrate Scope Study

With the optimal conditions in hand, we shifted our attention to investigate the generality of this Ni-catalyzed asymmetric hydroamination reaction. Utilizing 1a, we examined the scope of the amines. As illustrated in Figure 3, a series of primary amines bearing various functional groups produced the
Figure 3. Scope of Primary and Secondary Amines
Reactions were conducted at 0.2 mmol scale, see Supplemental Information for reaction condition details. *Reactions were conducted at 5 mmol scale. \[a\] 12 h; \[b\] 36 h; \[c\] 48 h. See also Scheme S3.
corresponding hydroamination products
3b-3l with good to excellent yields with excellent enantioselectivities. Notably, (R)-(+)-1-Phenylethylamine, a chiral amine, also gave the hydroamination product in a moderate yield with an excellent diastereomeric ratio (dr > 20:1, 3m). In addition to the aliphatic amines, primary arylamines were also suitable for the reaction to generate the chiral amine products with excellent enantioselectivities, albeit in lower yields under the current reaction conditions. It is noteworthy that the aryl bromide is compatible with this nickel-catalyzed reaction (3p). To assess the practicality of this
asymmetric hydroamination reaction, a gram-scale experiment was conducted. When the reaction of 1a with 2g was performed on a 5 mmol scale, it still was able to furnish 3g without loss of reaction efficiency and optical enantioselectivities, even in the presence of 1 mol % catalysts.

Next, the scope of secondary amines was tested. Various secondary cyclic amines afforded the chiral allylic amines in both remarkable yields and enantioselectivities (3a-3v). Moreover, acyclic secondary amines were also able to produce the desired hydroamination products with excellent enantioselectivities under the same reaction conditions (3w-3aa). Interestingly, although catalytic amount of Brønsted acid was used as a cocatalyst, amines containing other nitrogen atoms did not affect this asymmetric transformation (3j and 3v). Additionally, a series of functional groups, including ethers (3i and 3a), esters (3l), thioethers (3q), terminal alkenes (3h and 3w), and heterocycles such as furan (3f) and pyrimidines (3v), all were well tolerated in this reaction.

Subsequently, the scope of 1,3-dienes was studied. A set of aryl-substituted linear 1,3-butadienes were examined with both primary and secondary amines under the optimal conditions. As shown in Figure 4, both electron-rich and deficient substituents did not affect the efficiency or enantioselectivity. Alkyl-substituted butadienes were also capable of producing the Markovnikov hydroamination products (3ai, 3aj, 3ar, 3as, and 3at) in excellent yields with an excellent ee value. Notably, no other regioisomers were detected in these reactions. Furthermore, the hydroamination product (3au) could also be synthesized from 1,3-cyclohexadiene, albeit in low yields and enantioselectivity under the current conditions.

As we have highlighted earlier, both primary and secondary alkyl and aryl amines can produce satisfactory results in this nickel/Brønsted acid-catalyzed reaction. We were curious about the chemoselectivity when using one substrate containing two different nucleophilic sites. Guided by this idea, a set of more complex amines were examined under the optimal conditions and the results have been displayed in Figure 5. With aminoethanol, only the 1,2-hydroamination product (3av) was isolated with an excellent yield and ee value. Notably, the less sterically encumbered primary amine was found to be more reactive than the secondary amine when N-benzylethylediamine was used (3aw). Interestingly, the acidic phenol did not affect the amination (3ax), and the hydroamination reaction of the aryl amine (3ay) was not affected by the presence of an alcohol. Moreover, a single isomer with both excellent ee and yield could be obtained from tryptamine (3az). Finally, high chemoselectivity was shown at the alphatic amine part when 4-aminobenzylamine was used (3ba). Collectively, these results suggest that this nickel-catalyzed reaction exhibits...
good chemoselectivity toward hydroamination and also demonstrates the potential of this method in the late-stage diversification of biomolecules.

**DISCUSSION**

**Mechanism Study**

To get more details of this transformation, a preliminary mechanistic investigation was conducted. In Hartwig’s reaction, a reversible carbon-nitrogen bond formation was observed. To determine if this phenomenon also exists in our reaction, amine exchange experiments were performed first. When the enantioenriched 3t and stoichiometric morpholine were subjected to the optimal conditions, both 3t and 3a were detected (Scheme 1-1). A similar phenomenon was also observed in the reaction of 3t with a primary amine (Scheme 1-2). This reversible effect was also found when a primary amine-based product was used (Schemes 1-3 and 1-4). These findings strongly suggested that a reversibility of carbon-nitrogen bond formation was involved in this reaction. These results are in consistence with Hartwig’s results (Pawlas et al., 2002) but inconsistent with the results of Mazet’s conditions (Tran et al., 2019).

Furthermore, a decrease in enantioselectivity over time has been observed in the palladium-catalyzed hydroamination reactions (Lober et al., 2001; Pawlas et al., 2002). To determine if this phenomenon also exists in our reaction, time course experiments were conducted for both primary and secondary amines (Figure 6). To our surprise, significant racemization was observed for the reaction with a secondary amine.
Figure 6. Reaction Profiles
(A) Time course experiments of secondary amine.
(B) Time course experiments of primary amine.
Data are represented as mean value of three times; see also Scheme S6 and Figure S246.

(Figure 6A), whereas there was nearly no alteration of enantioselectivity in a reaction with a primary amine (Figure 6B). Moreover, similar results were also obtained switching A4 to A3.

Finally, based on precedent studies (Adamson et al., 2017; Dion and Beauchemin, 2011; Lin et al., 2019; Löber et al., 2001; Park and Malcolmson, 2018; Xiong et al., 2018; Yang and Dong, 2017; Zhou and Hartwig, 2008) and the above-mentioned findings (see Supplemental Information for more results), a mechanistic profile is proposed for this transformation. As illustrated in Scheme 2, the reaction is initiated by a Ni(0) species (I), which undergoes oxidative addition to form a Ni(II)-H species (II). Subsequently, a 1,3-diene migratory insertion leads to the formation of a π-allylNi(II) intermediate (III). The hydroamination product 3 is ultimately generated from the π-allylNi(II) complex by an amine nucleophilic attack (McDonald et al., 2011), accompanied by releasing of a Ni(0) species and regeneration of the acid cocatalyst.

Conclusion
In summary, we have developed a novel nickel and Brønsted acid-cocatalyzed asymmetric hydroamination reaction. The choice of chiral bisphosphine ligand and the use of a suitable Brønsted acid in catalytic amount are crucial to the success of this transformation. This protocol allows access to a series of
enantiopure secondary and tertiary allylic amines from linear conjugated dienes and free amines. This method provides high enantioselectivity and a broad substrate scope for the synthesis of various chiral amines. Importantly, a set of complex amines have been accomplished with excellent chemo- and enantioselectivity in this system. The good functional group tolerance and the scalability demonstrates the potential of this method in the synthesis of enantiopure amines. Mechanistic studies indicate that the C-N bond formation is a reversible step. Moreover, racemization over time exists in the reaction with secondary amines but not for primary amines. We believe this chemistry will greatly benefit medicinal chemistry and further reaction development.

Limitations of the Study
The disubstituted diene was not suitable in this methodology.

METHODS
All methods can be found in the accompanying Transparent Methods supplemental file.

DATA AND CODE AVAILABILITY
All data and methods can be found in the Supplemental Information.

SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.11.008.

ACKNOWLEDGMENTS
We thank Profs. Xumu Zhang, Hui Lv, and Xiuqin Dong at Wuhan University for lending laboratory space and sharing the basic instruments. We are grateful for the financial support from National Natural Science Foundation of China (21702151, 21871211) and the Fundamental Research Funds for Central Universities (2042019k0208).

AUTHOR CONTRIBUTIONS
G.Y. conceived the project and designed the experiments. J.L. discovered the reported process and designed and carried out almost all the experiments. P.W. participated in synthesizing partial substrates. W.W. helped in executing isotopic labeling studies, and Y.L. helped in analyzing the data. G.Y. wrote the manuscript. J.L. wrote Supplemental Information. All the authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS
The authors declare no competing interests.

Received: September 10, 2019
Revised: November 2, 2019
Accepted: November 5, 2019
Published: December 20, 2019

REFERENCES
Adamson, N.J., Hull, E., and Malcolmson, S.J. (2017). Enantioselective intermolecular addition of aliphatic amines to acyclic dienes with a Pd–PHOX catalyst. J. Am. Chem. Soc. 139, 7180–7183.

Ahlin, J.S.E., and Cramer, N. (2016). Chiral N-heterocyclic carbene ligand enabled nickel(0)-catalyzed enantioselective three-component couplings as direct access to silylated indanols. Org. Lett. 18, 3242–3245.

Aillaud, I., Collin, J., Hannedouche, J., and Schulz, E. (2007). Asymmetric hydroamination of non-activated carbon-carbon multiple bonds. Dalton Trans. 5105–5118.

Ananikov, V.P. (2015). Nickel: the “spirited horse” of transition metal catalysis. ACS Catal. 5, 1964–1971.

Athira, C., Changotra, A., and Sunoj, R.B. (2018). Rhodium catalyzed asymmetric hydroamination of internal alkynes with indoline: mechanism, origin of enantioselectivity, and role of additives. J. Org. Chem. 83, 2627–2639.

Berthold, D., and Breit, B. (2018). Chemo-, regio-, and enantioselective rhodium-catalyzed allylation of triazoles with internal alkynes and terminal allenes. Org. Lett. 20, 598–601.

Berthold, D., Geissler, A.G.A., Giofre, S., and Breit, B. (2019). Rhodium-catalyzed asymmetric intramolecular hydroamination of allenes. Angew. Chem. Int. Ed. 58, 9994–9997.

Bezzenine-Lafollee, S., Gil, R., Prim, D., and Hannedouche, J. (2017). First-Row late transition metals for catalytic alkyne hydrofunctionalisation: recent advances in C-N, C-O and C-P bond formation. Molecules 22, 1901–1930.
Cai, Y., Ye, X., Liu, S., and Shi, S.-L. (2019). Nickel/NHC-Catalyzed asymmetric C-H alkylation of fluoroarenes with alkenes: synthesis of enantioenriched fluorotrotonals. Angew. Chem. Int. Ed. https://doi.org/10.1002/anie.201907367.

Chen, J., and Lu, Z. (2018). Asymmetric hydrofunctionalization of minimally functionalized alkenes via earth abundant transition metal catalysis. Org. Chem. Front. 5, 260–272.

Chen, Y.-G., Shuai, B., Xu, X.-T., Li, Y.-Q., Yang, Q.-L., Qiu, H., Zhang, K., Fang, P., and Mei, T.-S. (2019). Nickel-catalyzed enantioselective hydroarylation and hydrogenalkylation of styrenes. J. Am. Chem. Soc. 141, 3395–3399.

Cheng, L., Li, M.-M., Xiao, L.-J., Xie, J.-H., and Zhou, Q.-L. (2018). Nickel(0)-Catalyzed hydroalkylation of 1,3-dienes with simple functionalized alkenes via earth abundant transition metals. Organometallics 37, 4313–4326.

Hii, K.K. (2006). Development of palladium catalysts for asymmetric hydroamination reactions. Pure Appl. Chem. 78, 341–349.

Huang, L., Arndt, M., Gooßen, K., Heydt, G., and Gooßen, L.J. (2015). Late transition metal-catalyzed hydroamination and hydroamidation. Chem. Rev. 115, 2996–2977.

Huo, J., He, G., Chen, W., Hu, X., Deng, Q., and Gooßen, L.J. (2019). A minireview of hydroamination catalysis: alkenes and alkylene substrate selective, metal complex design. BMC Chem. 13, 89–101.

Jerome, H. (2018). Mechanistic insights into first-row late transition metal-catalysed (formal) hydroamination of unactivated alkenes. Chimia 72, 635–641.

Kathe, P., and Fleischer, I. (2019). Cooperative use of brønsted acids and metal catalysts in tandem isomerization reactions of olefins. ChemCatChem 11, 3343–3354.

Li, R., Ju, C.-W., and Zhao, D. (2019a). Rhodium(III) vs. Cobalt(III): a mechanistically distinct three-component C-H bond addition cascade using a Cp(RHII) catalyst. Chem. Commun. (Camb.) 55, 695–699.

Li, L., Li, M.-L., Zhang, Q., Zhu, S.-F., and Zhou, Q.-L. (2018). Highly enantioselective nickel catalyzed intramolecular hydroalkenylation of N- and O-tethered 1,6-diienes to form six-membered heterocycles. J. Am. Chem. Soc. 140, 7458–7461.

Li, Y., Fang, H., Wu, D., Li, Z., Wang, W., Wei, H., Fu, Y., and Yin, G. (2019b). Nickel-catalyzed 1,1-alkylboration of electronically unbiased terminal alkenes. Angew. Chem. Int. Ed. 58, 8872–8876.

Li, W., and Zhang, X. (2014). Stereoselective Formation of Amines (springer verlag).

Lin, J.-S., Li, T.-T., Jiao, G.-Y., Guo, Q.-S., Cheng, J.-T., Lv, L., and Liu, X.-Y. (2019). Chiral branched acid catalyzed dynamic kinetic asymmetric hydroamination of racemic alkenes and asymmetric hydroamination of dienes. Angew. Chem. Int. Ed. 58, 7092–7096.

Liu, W., Chen, C., and Zhang, Q. (2011). Highly stereoselective synthesis of tetrasubstituted alkenes via hydroalkenylation of alkynes and C=H acetoxylation. Org. Biomol. Chem. 9, 6484–6486.

Liu, X., and Feng, X. (2018). Dual nickel and bransted acid catalysis for hydroalkenylation. Angew. Chem. Int. Ed. 57, 16604–16605.

Löber, O., Kawatsura, M., and Hartwig, J.F. (2001). Palladium-catalyzed hydroamination of 1,3-dienes: a colorimetric assay and enantioselective additions. J. Am. Chem. Soc. 123, 4366–4367.

Lough, W.J., and Wainer, I.W. (2002). Chirality in Natural and Applied Science (Oxford University Press).

Lutete, L.M., Kadota, I., and Yamamoto, Y. (2004). Palladium-catalyzed intramolecular asymmetric hydroamination of alkynes. J. Am. Chem. Soc. 126, 1622–1623.

Lv, H., Xiao, L.-J., Zhao, D., and Zhou, Q.-L. (2018). Nickel(0)-Catalyzed linear-selective hydroarylation of unactivated alkenes and styrenes with aryl boronic acids. Chem. Sci. 9, 6689–6693.

McDonald, R.I., Liu, G., and Stahl, S.S. (2011). Palladium(0)-Catalyzed alkenyl functionalization via nucleopalladation: stereocchemical pathways and enantioselective catalytic applications. Chem. Rev. 111, 2981–3019.

Müller, T.E., Hultsch, K.C., Yus, M., Foubelo, F., and Tada, M. (2008). Hydroamination: direct addition of amines to alkenes and alkynes. Chem. Rev. 108, 3795–3892.

Nugent, T.C. (2010). Chiral Amine Synthesis: Methods, Developments and Applications (Wiley-VCH Verlag GmbH).

Nugent, T.C., and El-Shazly, M. (2010). Chiral amine synthesis - recent developments and trends for enamide reduction, reductive amination, and imine reduction. Adv. Synth. Catal. 352, 753–819.

Park, S., and Malcolmson, S.J. (2018). Development and mechanistic investigations of enantioselective Pd-catalyzed intramolecular hydroaminations of internal dienes. ACS Catal. 8, 8468–8476.

Parveen, S., Li, C., Hassan, A., and Breit, B. (2017). Chemo-, regio-, and enantioselective rhodium-catalyzed allylation of pyridazinones with terminal alkenes. Org. Lett. 19, 2326–2329.

Patel, M., Saunthwal, R.K., and Verma, A.K. (2017). Base-mediated hydroamination of alkenes. Acc. Chem. Res. 50, 240–254.

Patil, M.D., Grogan, G., Bommarius, A., and Yun, H. (2018). Oxidoreductase-catalyzed synthesis of chiral amines. ACS Catal. 8, 10985–11015.

Patil, N.T., Lutete, L.M., Wu, H., Phadai, N.K., Gridnev, I.D., and Yamamoto, Y. (2006). Palladium-catalyzed intramolecular asymmetric hydroamination, hydroalkoxylation, and hydrocarbonation of alkenes. J. Org. Chem. 71, 4270–4279.

Pawlas, J., Nakao, Y., Kawatsura, M., and Hartwig, J.F. (2002). A general nickel-catalyzed hydroamination of 1,3-diienes by alkylamines: catalyst selection, scope, and mechanism. J. Am. Chem. Soc. 124, 3669–3679.

Pirnot, M.T., Wang, Y.M., and Buchwald, S.L. (2016). Copper hydride catalyzed hydroamination of alkynes and alkenes. Angew. Chem. Int. Ed. 55, 48–57.

Reznichenko, A.L., and Hultsch, K.C. (2016). Hydroamination of alkenes. Organic Reactions 88, 1–554.

Richmond, E., and Morán, J. (2018). Recent advances in nickel catalysis enabled by

378 iScience 22, 369–379, December 20, 2019
During we are preparing this manuscript, a Ni-catalyzed enantioselective hydroamination of branched 1,3-dienes has been reported: Tran, G., Shao, W., and Mazet, C. (2019). Ni-catalyzed enantioselective intermolecular hydroamination of branched 1,3-dienes using primary aliphatic amines J. Am. Chem. Soc. https://doi.org/10.1021/jacs.9b07253.

The absolute configuration of compound 3a was assigned by comparison of the optical rotation with that reported in the literature: Wang, T.-T., Wang, F.-X., Yang, F.-L., and Tian, S.-K. (2014). Palladium-catalyzed aerobic oxidative coupling of enantioenriched primary allylic amines with sulfonyl hydrazides leading to optically active allylic sulfones Chem. Commun. (Camb.) 50, 3802–3805.

Xiong, Y., Sun, Y., and Zhang, G. (2018). Recent advances on catalytic asymmetric difunctionalization of 1,3-dienes. Tetrahedron Lett. 59, 347–355.

Xu, C., Feng, Y., Li, F., Han, J., He, Y.-M., and Fan, Q.-H. (2019). A synthetic route to chiral benzo-fused N-heterocycles via sequential intramolecular hydroamination and asymmetric hydrogenation of anilino-alkynes. Organometallics. https://doi.org/10.1021/acs.organomet.9b00183.

Wang, Z. (2016). Nickel-based catalysts. RSC Green Chemistry Series 38, 407–468.

Wu, Z., and Cramer, N. (2019). Enantioselective C-H bond functionalizations by 3d transition-metal catalysts. Trends Chem. 1, 471–484.

Xiao, L.-J., Ye, M.-C., and Zhou, Q.-L. (2018). Nickel-catalyzed highly atom-economical C–C coupling reactions with π components. Synlett 30, 361–369.

Zi, G. (2009). Asymmetric hydroamination/cyclization catalyzed by organolanthane complexes with chiral biaryl-based ligands. Dalton Trans. 42, 9101–9109.

Yang, X.-H., and Dong, V.M. (2017). Rhodium-catalyzed hydrofunctionalization: enantioselective coupling of indolines and 1,3-dienes. J. Am. Chem. Soc. 139, 1774–1777.

Zhang, W.-B., Yang, X.-T., Ma, J.-B., Su, Z.-M., and Shi, S.-L. (2019). Regio- and enantioselective C–H cyclization of pyridines with alkenes enabled by a nickel/N-heterocyclic carbene catalysis. J. Am. Chem. Soc. 141, 5628–5634.

Zhou, J., and Hartwig, J.F. (2008). Intermolecular, catalytic asymmetric hydroamination of bicyclic alkenes and dienes in high yield and enantioselectivity. J. Am. Chem. Soc. 130, 12220–12221.
Supplemental Information

Nickel/Brønsted Acid-Catalyzed
Chemo- and Enantioselective Intermolecular
Hydroamination of Conjugated Dienes

Jiao Long, Peng Wang, Wang Wang, Yuqiang Li, and Guoyin Yin
Supplemental figures for $^1$H, $^{13}$C and $^{19}$F-NMR spectra of substrate 1a-1j.

Figure S1. $^1$H NMR spectra of substrate 1a, related to Figure 2.

Figure S2. $^{13}$C NMR spectra of substrate 1a, related to Figure 2.
Figure S3. $^1$H NMR spectra of substrate 1b, related to Figure 4.

Figure S4. $^{13}$C NMR spectra of substrate 1b, related to Figure 4.
**Figure S5.** $^1$H NMR spectra of substrate 1c, related to Figure 4.

**Figure S6.** $^{13}$C NMR spectra of substrate 1c, related to Figure 4.
Figure S7. $^1$H NMR spectra of substrate 1d, related to Figure 4.

Figure S8. $^{13}$C NMR spectra of substrate 1d, related to Figure 4.
Figure S9. $^1$H NMR spectra of substrate 1e, related to Figure 4.

Figure S10. $^{13}$C NMR spectra of substrate 1e, related to Figure 4.
Figure S11. $^{19}$F NMR spectra of substrate 1e, related to Figure 4.

Figure S12. $^1$H NMR spectra of substrate 1f, related to Figure 4.
**Figure S13.** $^{13}$C NMR spectra of substrate 1f, related to Figure 4.

**Figure S14.** $^{19}$F NMR spectra of substrate 1f, related to Figure 4.
Figure S15. $^1$H NMR spectra of substrate 1g, related to Figure 4.

Figure S16. $^{13}$C NMR spectra of substrate 1g, related to Figure 4.
Figure S17. $^1$H NMR spectra of substrate $1h$, related to Figure 4.

Figure S18. $^{13}$C NMR spectra of substrate $1h$, related to Figure 4.
Figure S19. $^1$H NMR spectra of substrate 1i, related to Figure 4.

Figure S20. $^{13}$C NMR spectra of substrate 1i, related to Figure 4.
**Figure S21.** $^1$H NMR spectra of substrate 1j, related to Figure 4.

**Figure S22.** $^{13}$C NMR spectra of substrate 1j, related to Figure 4.
Supplemental figures for $^1$H, $^{13}$C and $^{19}$F-NMR spectra of products 3a-3bd.

Figure S23. $^1$H NMR spectra of 3a, related to Figure 3.

Figure S24. $^{13}$C NMR spectra of 3a, related to Figure 3.
Figure S25. $^1$H NMR spectra of 3b, related to Figure 3.

Figure S26. $^{13}$C NMR spectra of 3b, related to Figure 3.
Figure S27. $^1$H NMR spectra of 3c, related to Figure 3.

Figure S28. $^{13}$C NMR spectra of 3c, related to Figure 3.
Figure S29. $^1$H NMR spectra of 3d, related to Figure 3.

Figure S30. $^{13}$C NMR spectra of 3d, related to Figure 3.
Figure S31. $^1$H NMR spectra of 3e, related to Figure 3.

Figure S32. $^{13}$C NMR spectra of 3e, related to Figure 3.
Figure S33. $^1$H NMR spectra of 3f, related to Figure 3.

Figure S34. $^{13}$C NMR spectra of 3f, related to Figure 3.
Figure S35. $^1$H NMR spectra of $3g$, related to Figure 3.

Figure S36. $^{13}$C NMR spectra of $3g$, related to Figure 3.
Figure S37. $^1$H NMR spectra of $3h$, related to Figure 3.

Figure S38. $^{13}$C NMR spectra of $3h$, related to Figure 3.
Figure S39. $^1$H NMR spectra of 3i, related to Figure 3.

Figure S40. $^{13}$C NMR spectra of 3i, related to Figure 3.
Figure S41. $^1$H NMR spectra of 3j, related to Figure 3.

Figure S42. $^{13}$C NMR spectra of 3j, related to Figure 3.
Figure S43. $^1$H NMR spectra of 3k, related to Figure 3.

Figure S44. $^{13}$C NMR spectra of 3k, related to Figure 3.
Figure S45. $^1$H NMR spectra of 3I, related to Figure 3.

Figure S46. $^{13}$C NMR spectra of 3I, related to Figure 3.
Figure S47. $^1$H NMR spectra of 3m, related to Figure 3.

Figure S48. $^{13}$C NMR spectra of 3m, related to Figure 3.
Figure S49. $^1$H NMR spectra of 3n, related to Figure 3.

Figure S50. $^{13}$C NMR spectra of 3n, related to Figure 3.
Figure S51. $^1$H NMR spectra of 3o, related to Figure 3.

Figure S52. $^{13}$C NMR spectra of 3o, related to Figure 3.
Figure S53. $^1$H NMR spectra of 3p, related to Figure 3.

Figure S54. $^{13}$C NMR spectra of 3p, related to Figure 3.
Figure S55. $^1$H NMR spectra of 3q, related to Figure 3.

Figure S56. $^{13}$C NMR spectra of 3q, related to Figure 3.
Figure S57. $^1$H NMR spectra of 3r, related to Figure 3.

Figure S58. $^{13}$C NMR spectra of 3r, related to Figure 3.
Figure S59. $^1$H NMR spectra of $3s$, related to Figure 3.

Figure S60. $^{13}$C NMR spectra of $3s$, related to Figure 3.
Figure S61. $^1$H NMR spectra of $3t$, related to Figure 3.

Figure S62. $^{13}$C NMR spectra of $3t$, related to Figure 3.
Figure S63. $^1$H NMR spectra of 3u, related to Figure 3.

Figure S64. $^{13}$C NMR spectra of 3u, related to Figure 3.
Figure S65. $^1$H NMR spectra of 3v, related to Figure 3.

Figure S66. $^{13}$C NMR spectra of 3v, related to Figure 3.
Figure S67. $^1$H NMR spectra of 3w, related to Figure 3.

Figure S68. $^{13}$C NMR spectra of 3w, related to Figure 3.
Figure S69. $^1$H NMR spectra of 3x, related to Figure 3.

Figure S70. $^{13}$C NMR spectra of 3x, related to Figure 3.
Figure S71. $^1$H NMR spectra of 3y, related to Figure 3.

Figure S72. $^{13}$C NMR spectra of 3y, related to Figure 3.
Figure S73. $^1$H NMR spectra of 3z, related to Figure 3.

Figure S74. $^{13}$C NMR spectra of 3z, related to Figure 3.
Figure S75. $^1$H NMR spectra of 3aa, related to Figure 3.

Figure S76. $^1$H NMR spectra of 3aa, related to Figure 3.
Figure S77. $^1$H NMR spectra of 3ab, related to Figure 4.

Figure S78. $^{13}$C NMR spectra of 3ab, related to Figure 4.
Figure S79. $^1$H NMR spectra of 3ac, related to Figure 4.

Figure S80. $^{13}$C NMR spectra of 3ac, related to Figure 4.
Figure S81. $^1$H NMR spectra of 3ad, related to Figure 4.

Figure S82. $^{13}$C NMR spectra of 3ad, related to Figure 4.
Figure S83. $^1$H NMR spectra of 3ae, related to Figure 4.

Figure S84. $^{13}$C NMR spectra of 3ae, related to Figure 4.
Figure S85. $^{19}$F NMR spectra of 3ae, related to Figure 4.

Figure S86. $^1$H NMR spectra of 3af, related to Figure 4.
Figure S87. $^{13}$C NMR spectra of 3af, related to Figure 4.

Figure S88. $^{19}$F NMR spectra of 3af, related to Figure 4.
Figure S89. $^1$H NMR spectra of 3ag, related to Figure 4.

Figure S90. $^{13}$C NMR spectra of 3ag, related to Figure 4.
Figure S91. $^1$H NMR spectra of 3ah, related to Figure 4.

Figure S92. $^{13}$C NMR spectra of 3ah, related to Figure 4.
Figure S93. $^1$H NMR spectra of 3ai, related to Figure 4.

Figure S94. $^{13}$C NMR spectra of 3ai, related to Figure 4.
Figure S95. $^1$H NMR spectra of 3aj, related to Figure 4.

Figure S96. $^{13}$C NMR spectra of 3aj, related to Figure 4.
Figure S97. $^1$H NMR spectra of 3ak, related to Figure 4.

Figure S98. $^{13}$C NMR spectra of 3ak, related to Figure 4.
**Figure S99.** $^1$H NMR spectra of 3al, related to Figure 4.

**Figure S100.** $^{13}$C NMR spectra of 3al, related to Figure 4.
Figure S101. $^1$H NMR spectra of 3am, related to Figure 4.

Figure S102. $^{13}$C NMR spectra of 3am, related to Figure 4.
Figure S103. $^1$H NMR spectra of 3an, related to Figure 4.

Figure S104. $^{13}$C NMR spectra of 3an, related to Figure 4.
Figure S105. $^{19}\text{F}$ NMR spectra of 3an, related to Figure 4.

Figure S106. $^1\text{H}$ NMR spectra of 3ao, related to Figure 4.
Figure S107. $^{13}$C NMR spectra of 3ao, related to Figure 4.

Figure S108. $^{19}$F NMR spectra of 3ao, related to Figure 4.
Figure S109. $^1$H NMR spectra of 3ap, related to Figure 4.

Figure S110. $^{13}$C NMR spectra of 3ap, related to Figure 4.
Figure S111. $^1$H NMR spectra of 3aq, related to Figure 4.

Figure S112. $^{13}$C NMR spectra of 3aq, related to Figure 4.
Figure S113. $^1$H NMR spectra of 3ar, related to Figure 4.

Figure S114. $^{13}$C NMR spectra of 3ar, related to Figure 4.
Figure S115. $^1$H NMR spectra of 3as, related to Figure 4.

Figure S116. $^{13}$C NMR spectra of 3as, related to Figure 4.
Figure S117. $^1$H NMR spectra of 3at, related to Figure 4.

Figure S118. $^{13}$C NMR spectra of 3at, related to Figure 4.
Figure S119. $^1$H NMR spectra of 3au, related to Figure 4.

Figure S120. $^{13}$C NMR spectra of 3au, related to Figure 4.
Figure S121. $^1$H NMR spectra of 3av, related to Figure 5.

Figure S122. $^{13}$C NMR spectra of 3av, related to Figure 5.
Figure S123. $^1$H NMR spectra of 3aw, related to Figure 5.

Figure S124. $^{13}$C NMR spectra of 3aw, related to Figure 5.
Figure S125. $^1$H NMR spectra of 3ax, related to Figure 5.

Figure S126. $^{13}$C NMR spectra of 3ax, related to Figure 5.
Figure S127. $^1$H NMR spectra of 3ay, related to Figure 5.

Figure S128. $^{13}$C NMR spectra of 3ay, related to Figure 5.
Figure S129. $^1$H NMR spectra of 3az, related to Figure 5.

Figure S130. $^{13}$C NMR spectra of 3az, related to Figure 5.
Figure S131. $^1$H NMR spectra of 3ba, related to Figure 5.

Figure S132. $^{13}$C NMR spectra of 3ba, related to Figure 5.
Figure S133. $^1$H NMR spectra of 3ba.

Figure S134. $^{13}$C NMR spectra of 3ba.
Figure S135. $^1$H NMR spectra of 3bc.

Figure S136. $^{13}$C NMR spectra of 3bc.
Figure S137. $^1$H NMR spectra of 3bd.

Figure S138. $^{13}$C NMR spectra of 3bd.
Supplemental figures for $^1$H and $^2$H-NMR spectra of deuterium labeling studies

**Figure S139.** $^1$H NMR spectra of $d$-3t, related to Scheme S7.

**Figure S140.** $^2$H NMR spectra of $d$-3t, related to Scheme S7.
**Supplemental Figures for HPLC spectra**

Data File: D:\DATA\GUAN YUQING\LJ-0306\LJ-0306 2019-03-06 14-33-09\002-0301.D
Sample Name: 1d-100-7-RAC

---

**Figure S141.** HPLC spectra of *rac-3a*, related to Figure 3.

| Peak RetTime | Width | Area | Height | Area |
|--------------|-------|------|--------|------|
| 11.192 min  | 0.302 s | 1.02861e4 | 486.24136 | 50.3351 |
| 14.395 min  | 0.3613 | 1.01890e4 | 488.17218 | 49.7649 |

**Area Percent Report**

---

**Sorted By:** Signal

Signal 1: DAB1 B, Sig=254,4 Ref=off

| # | Width | Area | Height | Area |
|---|-------|------|--------|------|
| 1 | 0.302 s | 1.02861e4 | 486.24136 | 50.3351 |
| 2 | 0.3613 | 1.01890e4 | 488.17218 | 49.7649 |

**Totals:** 2.04759e4 894.41354
Figure S142. HPLC spectra of 3a, related to Figure 3.
Figure S143. HPLC spectra of rac-3b, related to Figure 3.
Figure S144. HPLC spectra of 3b, related to Figure 3.
Figure S145. HPLC spectra of rac-3c, related to Figure 3.
Figure S146. HPLC spectra of 3c, related to Figure 3.
Figure S147. HPLC spectra of rac-3d, related to Figure 3.
Figure S148. HPLC spectra of 3d, related to Figure 3.
Figure S149. HPLC spectra of rac-3e, related to Figure 3.
Figure S150. HPLC spectra of 3e, related to Figure 3.
Figure S151. HPLC spectra of rac-3f, related to Figure 3.
Figure S152. HPLC spectra of 3f, related to Figure 3.
Figure S153. HPLC spectra of rac-3g, related to Figure 3.
Figure S154. HPLC spectra of 3g, related to Figure 3.
Figure S155. HPLC spectra of rac-3h, related to Figure 3.
Figure S156. HPLC spectra of 3h, related to Figure 3.
Figure S157. HPLC spectra of rac-3i, related to Figure 3.
Figure S158. HPLC spectra of 3i, related to Figure 3.
Figure S159. HPLC spectra of rac-Bz-3j, related to Figure 3.
Figure S160. HPLC spectra of Bz-3j, related to Figure 3.
Figure S161. HPLC spectra of rac-3k, related to Figure 3.
**Figure S162.** HPLC spectra of 3k, related to Figure 3.
Figure S163. HPLC spectra of rac-3I, related to Figure 3.
Figure S164. HPLC spectra of 3l, related to Figure 3.
Figure S165. HPLC spectra of rac-3n, related to Figure 3.
Figure S166. HPLC spectra of 3n, related to Figure 3.
**Figure S167.** HPLC spectra of rac-3o, related to Figure 3.
Figure S168. HPLC spectra of 3o, related to Figure 3.
Figure S169. HPLC spectra of rac-3p, related to Figure 3.
Figure S170. HPLC spectra of 3p, related to Figure 3.
Figure S171. HPLC spectra of rac-3q, related to Figure 3.
Figure S172. HPLC spectra of 3q, related to Figure 3.
Figure S173. HPLC spectra of rac-3r, related to Figure 3.
Figure S174. HPLC spectra of 3r, related to Figure 3.
Figure S175. HPLC spectra of rac-3s, related to Figure 3.
Figure S176. HPLC spectra of 3s, related to Figure 3.
**Figure S177.** HPLC spectra of rac-3t, related to Figure 3.
Figure S178. HPLC spectra of 3t, related to Figure 3.
Figure S179. HPLC spectra of rac-3u, related to Figure 3.
Figure S180. HPLC spectra of *rac-3u*, related to Figure 3.
Figure S181. HPLC spectra of rac-3v, related to Figure 3.
Figure S182. HPLC spectra of 3v, related to Figure 3.
Figure S183. HPLC spectra of rac-3w, related to Figure 3.
Figure S184. HPLC spectra of 3w, related to Figure 3.
Figure S185. HPLC spectra of rac-3x, related to Figure 3.
Figure S186. HPLC spectra of 3x, related to Figure 3.
Figure S187. HPLC spectra of rac-3y, related to Figure 3.
Figure S188. HPLC spectra of 3y, related to Figure 3.
Figure S189. HPLC spectra of rac-3z, related to Figure 3.
Figure S190. HPLC spectra of 3z, related to Figure 3.
Figure S191. HPLC spectra of rac-3aa, related to Figure 3.
Figure S192. HPLC spectra of 3aa, related to Figure 3.
Figure S193. HPLC spectra of rac-3ab, related to Figure 4.
Figure S194. HPLC spectra of 3ab, related to Figure 4.
Figure S195. HPLC spectra of rac-3ac, related to Figure 4.
Figure S196. HPLC spectra of 3ac, related to Figure 4.
Figure S197. HPLC spectra of rac-3ad, related to Figure 4.
Figure S198. HPLC spectra of 3ad, related to Figure 4.
Figure S199. HPLC spectra of rac-3ae, related to Figure 4.
Figure S200. HPLC spectra of 3ae, related to Figure 4.
Figure S201. HPLC spectra of rac-3af, related to Figure 4.
Figure S202. HPLC spectra of 3af, related to Figure 4.
Figure S203. HPLC spectra of rac-3ag, related to Figure 4.
Figure S204. HPLC spectra of 3ag, related to Figure 4.
Figure S205. HPLC spectra of rac-3ah, related to Figure 4.
Figure S206. HPLC spectra of 3ah, related to Figure 4.
Figure S207. HPLC spectra of rac-3ai, related to Figure 4.
Figure S208. HPLC spectra of 3ai, related to Figure 4.
Figure S209. HPLC spectra of rac-3aj, related to Figure 4.
Figure S210. HPLC spectra of 3aj, related to Figure 4.
Figure S211. HPLC spectra of rac-3ak, related to Figure 4.
**Figure S212.** HPLC spectra of 3ak, related to Figure 4.
Figure S213. HPLC spectra of rac-3al, related to Figure 4.
Figure S214. HPLC spectra of 3al, related to Figure 4.
Figure S215. HPLC spectra of rac-3am, related to Figure 4.
Figure S216. HPLC spectra of 3am, related to Figure 4.
Figure S217. HPLC spectra of rac-3an, related to Figure 4.
Figure S218. HPLC spectra of 3an, related to Figure 4.
Figure S219. HPLC spectra of rac-3ao, related to Figure 4.
Figure S220. HPLC spectra of 3ao, related to Figure 4.
Figure S221. HPLC spectra of rac-3ap, related to Figure 4.
Figure S222. HPLC spectra of 3ap, related to Figure 4.
Figure S223. HPLC spectra of rac-3aq, related to Figure 4.
Figure S224. HPLC spectra of 3aq, related to Figure 4.
Figure S225. HPLC spectra of *rac-3ar*, related to Figure 4.
Figure S226. HPLC spectra of 3ar, related to Figure 4.
Figure S227. HPLC spectra of rac-3as, related to Figure 4.
Figure S228. HPLC spectra of 3as, related to Figure 4.
Figure S229. HPLC spectra of rac-3at, related to Figure 4.
Figure S230. HPLC spectra of 3at, related to Figure 4.
**Figure S231.** HPLC spectra of *rac-3au*, related to Figure 4.
Figure S232. HPLC spectra of 3au, related to Figure 4.
Figure S233. HPLC spectra of rac-Bz-3av, related to Figure 5.
Figure S234. HPLC spectra of Bz-3av, related to Figure 5.
Figure S235. HPLC spectra of rac-Bz-3aw, related to Figure 5.
Figure S236. HPLC spectra of Bz-3aw, related to Figure 5.
Figure S237. HPLC spectra of rac-3ax, related to Figure 5.
Figure S238. HPLC spectra of 3ax, related to Figure 5.
Figure S239. HPLC spectra of rac-3ay, related to Figure 5.
Figure S240. HPLC spectra of 3ay, related to Figure 5.
Figure S241. HPLC spectra of rac-3az, related to Figure 5.
Figure S242. HPLC spectra of 3az, related to Figure 5.
Figure S243. HPLC spectra of \textit{rac-3ba}, related to Figure 5.
Figure S244. HPLC spectra of 3ba, related to Figure 5.
Transparent Methods

General Information

Unless otherwise noted, all reagents and solvents were purchased from commercial suppliers (Energy Chemical, Adamas-beta®, J&K and so on) and used without further purification. All reactions were performed under a dry argon atmosphere fitted on a glass tube or vial unless otherwise specified. All new compounds were characterized by \(^1\)H NMR, \(^{13}\)C NMR, \(^{19}\)F NMR and HRMS. The known compounds were characterized by \(^1\)H NMR, \(^{13}\)C NMR, \(^1\)H, \(^{13}\)C and \(^{19}\)F NMR data were recorded with Bruker 400 MHz with TMS as the internal standard. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd = doublet of doublet, dt = doublet of triplet, m = multiplet, br = broad), coupling constants and integration. All chemical shifts (δ) were reported in ppm and coupling constants (J) in Hz. All chemical shifts were reported relative to TMS (0.00 ppm) for \(^1\)H NMR, CDCl\(_3\) (77.00 ppm) for \(^{13}\)C NMR, respectively. High resolution mass spectra (HRMS) were measured with a Waters Micromass GCT instrument. GC-MS spectra were recorded on a Varian GC-MS 3900 - 2100 T. GC analysis was performed on an Agilent 7890B gas chromatograph with an FID detector using a J & W DB-1 column (10 m, 0.1 mm I.D.). Optical rotation was determined using a Perkin Elmer 343 polarimeter. HPLC analysis was conducted on an Agilent 1260 Series instrument. Column Chromatography was performed with silica gel Merck 60 (300-400 mesh). Purification of the product amine were performed on deactivated silica gel. The deactivated silica gel was prepared by washing the silica gel with petroleum ether/triethylamine (20:1 v/v) prior to purification.

General Procedures for the Synthesis of Conjugated Dienes

Dienes 1a-1i were prepared from commercially available cinnamic acids or cinnamaldehydes, the following scheme shows general procedures (Preuss et al, 2013; Sardini & Brown, 2017):

Scheme S1 (related to Figure 4):

Step A: A mixture of aldehyde (125 mmol, 1.0 equiv) and malonic acid (28.7 g, 275 mmol, 2.2 equiv) was suspended in 65 mL pyridine. Piperidine (2.0 mL) was added and the mixture was
heated to 100 °C until no more gas formation was observed through a gas-washing bottle. The reaction mixture was then poured into ice-cold aqueous HCl solution (2 M, 500 mL) under continuous stirring. The pH-value was checked and adjusted with additional aqueous HCl solution to be strong acidic. The resulting suspension was filtered and the solid cinnamic acid was washed with aqueous HCl (2 M) until no basic reaction of the filtrate was observed. The cinnamic acid was obtained as a white solid which was dried under reduced pressure.

**Step B:** The cinnamic acid (50 mmol, 1.0 equiv) was suspended in 100 mL MeOH (2 mL per mmol acid) and SOCl₂ (5.4 mL, 75 mmol, 1.5 equiv) was added. The reaction mixture was heated to 65 °C for 2 h. Subsequently, the MeOH was removed under reduced pressure and the resulting solid was dissolved in dry n-hexane under an atmosphere of N₂. The solution was cooled to -50 °C and a solution of DIBAL-H in n-hexane (1 M, 100 mL, 100 mmol, 2.0 equiv) was added slowly. After complete addition, the reaction mixture was stirred for 2.5 h at -50 °C. Then 10 mL MeOH and 50 mL aqueous NaHCO₃ solution were added slowly and the mixture was allowed to reach room temperature. The resulting slurry was carefully acidified with aqueous HCl (1 M) until all solid was dissolved. The layers were separated and the aqueous layer was extracted with n-hexane (3×100 mL). The combined organic layers were dried with Na₂SO₄ and the solvents were removed under reduced pressure.

**Step C:** The resulting crude allylic alcohol was dissolved in 400 mL n-hexane. Then manganese dioxide (65.2 g, 750 mmol, 20.0 equiv) was added and the reaction mixture was stirred under an atmosphere of N₂. The progress of the reaction was monitored by thin layer chromatography and after complete conversion, the reaction mixture was filtered through silica gel. The solid residue was washed with EtOAc and the solvent was removed under reduced pressure. Finally, the crude product was purified by flash column chromatography to give the corresponding cinnamaldehyde.

**Step D:** To a flame-dried round bottom flask was added phosphonium (1.25 equiv) and KOt-Bu (1.3 equiv). The flask was evacuated and backfilled with N₂ three times. THF (0.25 M) was then added via syringe. The solution was allowed to stir at ambient temperature for 30 min before adding aldehyde (1.0 equiv) dropwise over 10 minutes. The reaction was then allowed to stir at room temperature for 12 h. The reaction was then quenched with 100 mL saturated NH₄Cl solution, and the aqueous layer was extracted with diethyl ether (3×100 mL). The combined organic extracts were washed with brine (1×100 mL), dried over Na₂SO₄, and gravity filtered. The solvent was removed under reduced pressure, and the crude product was purified via silica gel column chromatography to give the desired diene.

**(E)-buta-1,3-dien-1-ylbenzene (1a) (Preuß et al, 2013):** colorless liquid, 88% yield, step D. ¹H NMR (400 MHz, CDCl₃) δ 7.42-7.39 (m, 2H), 7.34-7.29 (m, 2H), 7.25-7.20 (m, 1H), 6.82-6.75 (m, 1H), 6.58-6.46 (m, 2H), 5.36-5.31 (m, 1H), 5.19-5.16
(E)-1-(buta-1,3-dien-1-yl)-2-methoxybenzene (1b) (Davenport & Fernandez, 2018): colorless liquid, 80% yield, step D. ¹H NMR (400 MHz, CDCl₃) δ 7.47 (dd, J = 7.7, 1.7 Hz, 1H), 7.24-7.19 (m, 1H), 6.94-6.77 (m, 4H), 6.54 (dt, J = 16.9, 10.1 Hz, 1H), 5.33-5.28 (m, 1H), 5.15-5.12 (m, 1H), 3.85 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 156.7, 137.9, 130.2, 128.6, 127.6, 126.4, 120.6, 117.0, 110.8, 55.4 ppm.

(E)-1-(buta-1,3-dien-1-yl)-3-methoxybenzene (1c) (Preuß et al, 2013): colorless solid, 41% yield, steps A-D. ¹H NMR (400 MHz, CDCl₃) δ 7.25-7.21 (m, 1H), 7.01-6.99 (m, 1H), 6.94 (dd, J = 2.6, 1.6 Hz, 1H), 6.81-6.74 (m, 2H), 6.56-6.45 (m, 2H), 5.36-5.31 (m, 1H), 5.19-5.16 (m, 1H), 3.82 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 159.8, 138.6, 137.1, 132.7, 129.9, 129.5, 119.2, 117.8, 113.4, 111.6, 55.19 ppm.

(E)-1-(buta-1,3-dien-1-yl)-4-methoxybenzene (1d) (Preuß et al, 2013): colorless solid, 85% yield, step D. ¹H NMR (400 MHz, CDCl₃) δ 7.36-7.34 (m, 2H), 6.88-6.84 (m, 2H), 6.70-6.64 (m, 1H), 6.53-6.44 (m, 2H), 5.28 (d, J = 16.0 Hz, 1H), 5.11 (d, J = 8.5 Hz, 1H), 3.81 (s, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 159.2, 137.3, 132.4, 129.9, 127.6, 116.5, 114.0, 55.3 ppm.

(E)-1-(buta-1,3-dien-1-yl)-4-fluorobenzene (1e) (Hu et al, 2018): colorless liquid, 90% yield, step D. ¹H NMR (400 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.03-6.97 (m, 2H), 6.73-6.66 (m, 1H), 6.53-6.43 (m, 2H), 5.32 (d, J = 15.6 Hz, 1H), 5.17 (d, J = 9.2 Hz, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 162.3 (d, J = 247.2 Hz), 136.9, 133.2 (d, J = 3.4 Hz), 131.5, 129.3 (d, J = 2.4 Hz), 127.9 (d, J = 8.0 Hz), 117.7, 115.5 (d, J = 21.7 Hz) ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -114.18 ppm.

(E)-1-(buta-1,3-dien-1-yl)-4-(trifluoromethyl)benzene (1f) (Adamson & Malcolmson, 2017): colorless liquid, 28% overall yield, steps B-D. ¹H NMR (400 MHz, CDCl₃) δ 7.57-7.55 (m, 2H), 7.49-7.47 (m, 2H), 6.85 (dd, J = 15.7, 10.5 Hz, 1H), 6.59-6.47 (m, 2H), 5.43-5.38 (m, 1H), 5.28-5.25 (m, 1H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 140.5 (q, J = 1.4 Hz), 136.6, 131.9, 131.2, 129.2 (q, J = 32.4 Hz), 126.5, 125.5 (q, J = 3.9 Hz), 124.2 (q, J = 271.5 Hz), 119.4 ppm; ¹⁹F NMR (376 MHz, CDCl₃) δ -62.40 ppm.
(E)-4-(buta-1,3-dien-1-yl)-N,N-dimethylaniline (1g) (Davenport & Fernandez, 2018): yellow solid, 37% yield, step D. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.31-7.29 (m, 2H), 6.69-6.67 (m, 2H), 6.63 (dd, $J$ = 15.7, 10.4 Hz, 1H), 6.53-6.44 (m, 2H), 5.25-5.20 (m, 1H), 5.04 (d, $J$ = 9.8 Hz, 1H), 2.96 (s, 6H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.0, 137.8, 133.1, 127.5, 125.6, 115.0, 112.4, 40.5 ppm. 

(E)-2-(buta-1,3-dien-1-yl)furan (1h) (Preuß et al, 2013): slight yellow liquid, 75% yield, step D. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (d, $J$ = 1.9 Hz, 1H), 6.73-6.67 (m, 1H), 6.48-6.41 (m, 1H), 6.39-6.34 (m, 2H), 6.27 (d, $J$ = 3.2 Hz, 1H), 5.35-5.30 (m, 1H), 5.17-5.14 (m, 1H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 152.9, 142.2, 136.7, 128.2, 120.4, 117.8, 111.6, 108.5 ppm.

(E)-buta-1,3-dien-1-ylcyclohexane (1i) (Preuß et al, 2013): colorless liquid, 32% overall yield, steps A-D. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.35-6.25 (m, 1H), 6.05-5.98 (m, 1H), 5.66 (dd, $J$ = 15.3, 6.9 Hz, 1H), 5.12-5.07 (m, 1H), 4.97-4.94 (m, 1H), 2.04-1.95 (m, 1H), 1.75-1.70 (m, 4H), 1.67-1.62 (m, 1H), 1.33-1.03 (m, 5H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.3, 137.6, 128.3, 114.7, 40.6, 32.7, 26.1, 26.0 ppm.

Scheme S2 (related to Figure 4):

Synthesis of (E)-hexa-3,5-dien-1-yllbenzene (1j) (Adamson & Malcolmson, 2017): To a solution of diethyl allylphosphonate (4.28 g, 24 mmol, 1.2 equiv) in anhydrous THF (45 mL) was added dropwise n-BuLi (2.5 M in hexanes, 9.6 mL, 24 mmol, 1.2 equiv) at -78 °C. After stirring for 45 min, a solution of phenylpropyl aldehyde (2.6 mL, 20 mmol, 1.0 equiv) in DMPU (2.4 mL, 20 mmol, 1.0 equiv) was added dropwise via cannula. The resulting solution was stirred for 2 h at -78 °C, and then allowed to warm to room temperature. Stirring was continued overnight at room temperature before quenching with saturated aqueous NH$_4$Cl solution. The mixture was extracted with diethyl ether (3×45 mL). The combined organic phases were washed with brine (100 mL), dried (Na$_2$SO$_4$) and concentrated to afford the crude product. Purification by flash chromatography (PE as eluent) gave the desired diene 1j (1.23 g, 39% yield) as a colorless oil. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.30-7.26 (m, 2H), 7.20-7.17 (m, 3H), 6.35-6.26 (m, 1H), 6.12-6.05 (m, 1H), 5.78-5.71 (m, 1H), 5.12-5.07 (m, 1H), 4.99-4.96 (m, 1H), 2.73-2.69 (m, 2H), 2.44-2.38 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 141.7, 137.1, 134.2, 131.4, 128.4, 128.3, 125.8, 115.2, 35.6, 34.4 ppm.

Reaction Optimization
A reaction vial was charged with Ni(COD)$_2$ (2.8 mg, 0.01 mmol, 0.05 equiv vs amine), ligand (0.01 mmol, 0.05 equiv vs amine), morpholine (17 μL, 0.2 mmol, 1.0 equiv), 1-phenylbutadiene (40 μL, 0.3 mmol, 1.5 equiv), and 1.0 mL of solvent (toluene, THF, MTBE, EA, n-hexane, i-PrOH, CH$_3$CN or PhCN) in an argon-filled glovebox, then acid (0.00-0.20 equiv vs amine) was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

**Table S1.** Solvent screening for the Ni-catalyzed asymmetric hydroamination of 1a, related to Figure 2.\[a\]

| Entry | Solvent | Yield [%]\[b\] | ee [%]\[c\] |
|-------|---------|----------------|-------------|
| 1     | i-PrOH  | trace          | ND\[d\]     |
| 2     | PhMe    | 90             | 23          |
| 3     | THF     | 42             | 9           |
| 4     | MTBE    | trace          | ND          |
| 5     | EtOAc   | trace          | ND          |
| 6     | CH$_3$CN| trace          | ND          |
| 7     | PhCN    | 53             | 14          |
| 8     | n-hexane| NP\[e\]        | ND          |

\[a\] Unless otherwise noted, all reactions were carried out with 0.10 mmol amine, 0.15 mmol diene, 5.0 mol % Ni(COD)$_2$, 5.0 mol % (S,S)-BDPP, 5.0 mol % TsOH·H$_2$O in 1 mL solvent at 25 °C for 24 h. \[b\] Yield was determined by gas chromatogram analysis, using naphthalene as the internal standard. \[c\] Determined by HPLC analysis using a chiral stationary phase. \[d\] Not determined. \[e\] No product.

**Table S2.** Ligand screening for Ni-catalyzed asymmetric hydroamination of 1a, related to Figure 2.\[a\]

| Entry | Ligand | Yield [%]\[b\] | ee [%]\[c\] |
|-------|--------|----------------|-------------|
| 1     | L1     | 65             | 30          |
| 2     | L2     | 42             | 21          |
[a] Unless otherwise noted, all reactions were carried out with 0.10 mmol amine, 0.15 mmol diene, 5.0 mol % Ni(COD)$_2$, 5.0 mol % ligand, 5.0 mol % TsOH·H$_2$O in 1 mL toluene at 25 °C for 24 h. [b] Yield was determined by gas chromatogram analysis, using naphthalene as the internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Not determined. [e] The catalyst was stirred at room temperature one hour in advance. [f] Isolated yield.

Table S3. Acid additives screening for Ni-catalyzed asymmetric hydroamination of 1a, related to Figure 2. 

| Entry | Acid | Yield[%][b] | ee[%][c] |
|-------|------|-------------|----------|
| 1     | A1   | 86          | 86       |
| 2     | A2   | 86          | 98       |
| 3     | A3   | 98          | 98       |
| 4     | A4   | 94[d]       | 96       |
Unless otherwise noted, all reactions were carried out with 0.20 mmol diene, 0.40 mmol amine, 5.0 mol % Ni(COD)$_2$/((S,S)-Me-DuPhos, 5.0 mol % acid in 1 mL toluene at 25 °C for 24 h; The catalyst was stirred at room temperature one hour in advance. [b] Yield was determined by gas chromatogram analysis, using naphthalene as the internal standard. [c] Determined by HPLC analysis using a chiral stationary phase. [d] Isolated yield. [e] With 0.30 mmol amine.

General Procedure for Ni-catalyzed Asymmetric Hydroamination of Conjugated Dienes
Scheme S3 (related to Figure 3, Figure 4 and Figure 5):

A stock solution was made by mixing Ni(COD)$_2$ with L8 in a 1:1 molar ratio in toluene (0.01 M) at room temperature for 1 h in a argon-filled glovebox. An aliquot of the catalyst solution (1.0 mL, 0.01 mmol) was transferred by syringe into the vials charged with different 1,3-diienes (0.2 mmol for each) and amines (0.3 mmol for each), and then 0.01 mmol A4 was added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 12-48 h. The product was purified by column chromatography on deactivated silica gel using PE/EtOAc. The ee values of all compounds were determined by HPLC on a chiral stationary phase.

(S,E)-4-(4-phenylbut-3-en-2-yl)morpholine (3a): with A3, 12 h, obtained pale yellow oil 43.4 mg; Isolated yield: 99%; 98% ee; $[\alpha]_D^{25} = -72.0$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm, $t_R$ = 11.4 min (minor), 14.4 min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.17 (dd, $J = 15.9$, 8.2 Hz, 1H), 3.73 (t, $J = 4.7$ Hz, 4H), 3.05-2.99 (m, 1H), 2.61-2.52 (m, 4H), 1.26 (d, $J = 6.6$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 136.8, 132.0, 131.2, 128.6, 127.5, 126.2, 67.2, 63.1, 50.8, 17.8 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{14}$H$_{19}$NNaO = 240.1359, found: 240.1359.

(S,E)-N-butyl-4-phenylbut-3-en-2-amine (3b): with A4, 24 h, obtained colorless oil 37.7 mg; Isolated yield: 93%; > 99% ee; $[\alpha]_D^{25} = -60.3$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm, $t_R$ = 9.2 min (major), 9.7 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.19 (m, 1H), 6.46 (d, $J = 15.9$ Hz, 1H), 6.08 (dd, $J = 15.9$, 8.0 Hz, 1H), 3.39-3.32 (m, 1H), 2.67-2.53 (m, 2H), 1.52-1.43 (m, 2H), 1.38-1.29 (m, 2H), 1.25 (d, $J = 6.5$ Hz, 3H), 0.91 (t, $J = 7.3$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 137.1, 134.4, 129.7, 128.5, 127.2, 126.2, 56.4, 47.3, 32.4, 22.0, 20.5, 14.0 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{14}$H$_{21}$NNaO = 226.1566, found: 226.1565.
(S,E)-N-phenethyl-4-phenylbut-3-en-2-amine (3c): with A4, 24 h, obtained pale yellow oil 50.3 mg; Isolated yield: 99%; 92% ee; [α]_D^25 = -76.8 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm, \( t_{20} = 13.9 \text{ min (major), } 15.0 \text{ min (minor); } ^1\text{H NMR} \) (400 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.32-7.26 (m, 4H), 7.23-7.18 (m, 4H), 6.44 (d, J = 15.9 Hz, 1H), 6.05 (dd, J = 15.9, 8.0 Hz, 1H), 3.41-3.34 (m, 1H), 2.96-2.79 (m, 4H), 1.23 (d, J = 6.5 Hz, 3H) ppm; \(^{13}\text{C NMR} \) (100 MHz, CDCl₃) δ 139.9, 136.9, 133.9, 129.9, 128.7, 128.5, 128.4, 127.3, 126.2, 126.1, 56.2, 48.8, 36.4, 21.9 ppm; HRMS (ESI) calculated [M+Na]^+ for C₁₆H₁₃NNa = 274.1566, found: 274.1563.

(S,E)-N-(4-phenylbut-3-en-2-yl)cyclopropanamine (3d): with A4, 24 h, obtained colorless oil 22.9 mg; Isolated yield: 61%; > 99% ee; [α]_D^25 = -91.8 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, \( t_{20} = 10.5 \text{ min (major), } 10.9 \text{ min (minor); } ^1\text{H NMR} \) (400 MHz, CDCl₃) δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.49 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9, 7.9 Hz, 1H), 3.52-3.45 (m, J = 6.7 Hz, 1H), 2.18-2.13 (m, 1H), 2.02 (br, s, 1H), 1.25 (d, J = 6.5 Hz, 3H), 0.47-0.33 (m, 4H) ppm; \(^{13}\text{C NMR} \) (100 MHz, CDCl₃) δ 137.2, 134.4, 129.4, 128.5, 127.2, 126.2, 56.5, 28.6, 21.8, 6.6, 6.4 ppm; HRMS (ESI) calculated [M+Na]^+ for C₁₆H₁₃NNa = 210.1253, found: 210.1254.

(S,E)-N-(4-phenylbut-3-en-2-yl)cyclohexanamine (3e): with A4, 24 h, obtained pale yellow oil 34.9 mg; Isolated yield: 76%; 92% ee; [α]_D^25 = -66.1 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, \( t_{20} = 11.0 \text{ min (major), } 12.1 \text{ min (minor); } ^1\text{H NMR} \) (400 MHz, CDCl₃) δ 7.49-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9, 8.1 Hz, 1H), 3.59-3.52 (m, 1H), 2.55-2.48 (m, 1H), 2.01-1.97 (m, 1H), 1.84-1.58 (m, 3H), 1.69 (br, s, 1H), 1.26-0.98 (m, 9H) ppm; \(^{13}\text{C NMR} \) (100 MHz, CDCl₃) δ 137.1, 134.8, 129.3, 128.5, 127.2, 126.2, 53.5, 52.5, 34.4, 33.2, 26.1, 25.3, 25.0, 22.5 ppm. HRMS (ESI) calculated [M+Na]^+ for C₁₈H₂₁NNa = 252.1723, found: 252.1722.

(S,E)-N-(furan-2-ylmethyl)-4-phenylbut-3-en-2-amine (3f): with A4, 24 h, obtained pale yellow oil 45.5 mg; Isolated yield: 99%; 99% ee; [α]_D^25 = -49.2 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, \( t_{20} = 17.0 \text{ min (minor), } 20.0 \text{ min (major); } ^1\text{H NMR} \) (400 MHz, CDCl₃) δ 7.40-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 1H), 6.49 (d, J = 15.9 Hz, 1H), 6.31 (dd, J = 3.1, 1.9 Hz, 1H), 6.16 (dd, J = 3.1, 0.5 Hz, 1H), 6.07 (dd, J = 15.9, 8.1 Hz, 1H), 3.83 (d, J = 14.4 Hz, 1H), 3.73 (d, J = 14.4 Hz, 1H), 3.42-3.35 (m, 1H),
1.26 (d, J = 6.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 153.9, 141.8, 137.0, 133.7, 130.5, 128.5, 127.4, 126.3, 110.1, 106.8, 55.3, 43.8, 22.0 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{15}$H$_{18}$NO = 228.1383, found: 228.1380.

(S,E)-N-(2-(cyclohex-1-en-1-yl)ethyl)-4-phenylbut-3-en-2-amine (3g): with A$_4$, 24 h, obtained pale yellow oil 50.9 mg; Isolated yield: 99%; 96% ee; $[^\alpha]_D^{25}$ = -66.1 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 11.0 min (minor), 11.6 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9, 8.0 Hz, 1H), 5.48-5.45 (m, 1H), 3.38-3.31 (m, 1H), 2.74-2.59 (m, 2H), 2.14 (t, $J$ = 6.9 Hz, 2H), 2.01-1.97 (m, 2H), 1.92-1.88 (m, 2H), 1.64-1.51 (m, 4H), 1.46 (br, s, 1H), 1.24 (d, $J$ = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.1, 135.4, 134.4, 129.7, 128.5, 127.2, 126.2, 122.8, 56.2, 45.2, 38.4, 28.1, 25.2, 22.9, 22.4, 22.1 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{15}$H$_{18}$N = 256.2060, found: 256.2057.

(S,E)-N-allyl-4-phenylbut-3-en-2-amine (3h): with A$_4$, 24 h, obtained pale yellow oil 29.1 mg; Isolated yield: 78%; > 99% ee; $[^\alpha]_D^{25}$ = -60.4 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 11.9 min (major), 12.7 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d, J = 15.9 Hz, 1H), 6.06 (dd, J = 15.9, 8.1 Hz, 1H), 5.97-5.87 (m, 1H), 5.20-5.15 (m, 1H), 5.12-5.08 (m, 1H), 3.44-3.36 (m, 1H), 3.34-3.28 (m, 1H), 3.24-3.18 (m, 1H), 1.86 (br, s, 1H), 1.26 (d, J = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.0, 136.8, 133.9, 130.1, 128.5, 127.3, 126.2, 115.9, 55.6, 50.0, 22.0 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{20}$H$_{26}$NNa = 210.1253, found: 210.1258.

(2S,E)-4-phenyl-N-((tetrahydrofuran-2-yl)methyl)but-3-en-2-amine (3i): with A$_4$, 24 h, obtained pale yellow oil 46.4 mg; Isolated yield: 99%; 99% ee; dr = 1:1; $[^\alpha]_D^{25}$ = -53.1 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm, t$_{R1}$ = 15.3 min (major), 16.9 min (minor), t$_{R2}$ = 19.8 min (minor), 21.2 min (major); 3i: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.50 (d, J = 5.7 Hz, 1H), 6.08 (dd, J = 8.1, 3.2 Hz, 1H), 4.08-3.98 (m, 1H), 3.88-3.82 (m, 1H), 3.78-3.72 (m, 1H), 3.45-3.38 (m, 1H), 2.77 (dd, J = 11.9, 3.4 Hz, 1H), 2.68 (d, J = 1.9 Hz, 1H), 2.02-1.84 (m, 3H), 1.58-1.46 (m, 1H), 1.29 (d, J = 3.3 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.9, 133.7, 130.4, 128.5, 127.3, 126.3, 78.5, 67.9, 56.8, 52.3, 29.4, 25.7, 21.9 ppm; 3i$: $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.46 (d, J = 5.7 Hz, 1H), 6.12 (dd, J = 8.1, 3.2 Hz, 1H), 4.08-3.98 (m, 1H), 3.88-3.82 (m, 1H), 3.78-3.72 (m, 1H), 3.45-3.38 (m, 1H),
2.70 (s, 1H), 2.58 (dd, $J = 11.9, 8.5$ Hz, 1H), 2.02-1.84 (m, 3H), 1.58-1.46 (m, 1H), 1.27 (d, $J = 3.3$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 136.9, 133.7, 130.2, 128.5, 127.3, 126.3, 77.9, 67.9, 56.2, 51.7, 29.3, 25.7, 21.8 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{15}$H$_{22}$NO = 232.1696, found: 232.1693.

(S,E)-$N^1$,N$^1$-dimethyl-N$^2$-(4-phenylbut-3-en-2-yl)ethane-1,2-diamine (3j): with A4, 24 h, obtained pale yellow oil 42.0 mg; Isolated yield: 96%; 97% ee; [α]$_D^{25}$ = -71.1 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by (converting it to compound Bz-3j) HPLC on Chiralpak AS-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm, $t_R$ = 43.1 min (major), 50.8 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.47 (d, $J = 15.9$ Hz, 1H), 6.08 (dd, $J = 15.9, 8.0$ Hz, 1H), 3.39-3.32 (m, 1H), 2.78-2.62 (m, 2H), 2.46-2.43 (m, 3H), 2.22 (s, 6H), ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.0, 134.0, 130.0, 128.5, 127.3, 126.2, 59.0, 56.5, 45.4, 44.7, 22.0 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{14}$H$_{23}$N$_2$ = 219.1856, found: 219.1856.

(S,E)-$N$-benzyl-4-phenylbut-3-en-2-amine (3k): with A4, 24 h, obtained pale yellow oil 43.3 mg; Isolated yield: 91%; 95% ee; [α]$_D^{25}$ = -99.5 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, $t_R$ = 11.3 min (major), 12.2 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.40-7.38 (m, 2H), 7.33-7.30 (m, 6H), 7.27-7.20 (m, 2H), 6.48 (d, $J = 15.9$ Hz, 1H), 6.11 (dd, $J = 15.9, 8.0$ Hz, 1H), 3.85 (d, $J = 13.1$ Hz, 1H), 3.73 (d, $J = 13.1$ Hz, 1H), 3.44-3.37 (m, 1H), ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.5, 137.1, 134.0, 130.0, 128.5, 127.3, 126.2, 59.0, 56.5, 45.4, 44.7, 22.0 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{17}$H$_{19}$NNa = 260.1410, found: 260.1405.

methyl (S,E)-(4-phenylbut-3-en-2-yl)glycinate (3l): with A3, 48 h, obtained pale yellow oil 35.1 mg; Isolated yield: 80%; > 99% ee; [α]$_D^{25}$ = -154.7 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, $t_R$ = 27.2 min (major), 28.4 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.35 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.45 (d, $J = 15.8$ Hz, 1H), 6.01 (dd, $J = 15.8, 8.2$ Hz, 1H), 3.69 (s, 3H), 3.42 (d, $J = 3.1$ Hz, 2H), 3.39-3.32 (m, 1H), 2.17 (br, s, 1H), 1.27 (d, $J = 6.5$ Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.2, 136.8, 133.2, 130.7, 128.5, 127.5, 126.3, 55.5, 51.5, 22.1 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{13}$H$_{18}$NO$_2$ = 220.1332, found: 220.1331.
(S,E)-4-phenyl-N-((R)-1-phenylethyl)but-3-en-2-amine (3m): with A4, 48 h, obtained pale yellow oil 28.2 mg; isolated yield: 56%; > 20:1 dr; [α]D25 = -55.3 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.34-7.27 (m, 8H), 7.25-7.19 (m, 2H), 6.42 (d, J = 15.9 Hz, 1H), 6.07 (dd, J = 15.9, 7.7 Hz, 1H), 3.95-3.90 (m, 1H), 3.38-3.31 (m, 1H), 1.76 (br, s, 1H), 1.37 (d, J = 6.6 Hz, 3H), 1.22 (d, J = 6.4 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 145.8, 137.1, 134.6, 129.2, 128.5, 127.2, 126.8, 126.5, 126.2, 54.8, 53.0, 23.7, 21.2 ppm; HRMS (ESI) calculated [M+Na]+ for C18H17NNa = 274.1566, found: 274.1566.

(S,E)-N-(4-phenylbut-3-en-2-yl)aniline (3n): with A3, 24 h, obtained colorless oil 34.7 mg; isolated yield: 78%; 86% ee; [α]D25 = -80.6 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, tR = 11.6 min (major), 13.4 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.36-7.34 (m, 2H), 7.30-7.27 (m, 2H), 7.22-7.13 (m, 3H), 6.70-6.63 (m, 3H), 6.57 (d, J = 16.0 Hz, 1H), 6.21 (dd, J = 16.0, 5.8 Hz, 1H), 4.17-4.11 (m, 1H), 1.40 (d, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 147.4, 136.9, 133.2, 129.2, 129.1, 128.5, 127.3, 126.3, 117.3, 113.4, 50.8, 22.1 ppm; HRMS (ESI) calculated [M+Na]+ for C18H17NNa = 246.1253, found: 246.1253.

(S,E)-4-methyl-N-(4-phenylbut-3-en-2-yl)aniline (3o): with A4, 48 h, obtained reddish orange oil 10.8 mg (or with A3, 36 h, obtained reddish orange oil 43.9 mg); isolated yield: 23% (or 93%); 93% (or 73%) ee; [α]D25 = -99.5 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tR = 14.6 min (major), 16.5 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.36-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.22-7.18 (m, 1H), 6.97 (d, J = 8.2 Hz, 2H), 6.59-6.55 (m, 3H), 6.21 (dd, J = 16.0, 5.9 Hz, 1H), 4.14-4.08 (m, 1H), 2.22 (s, 3H), 1.39 (d, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 145.1, 137.1, 133.4, 129.6, 129.1, 128.5, 127.3, 126.5, 126.3, 113.6, 51.1, 22.1, 20.4 ppm; HRMS (ESI) calculated [M+Na]+ for C19H18NNa = 260.1410, found: 260.1405.

(S,E)-4-bromo-N-(4-phenylbut-3-en-2-yl)aniline (3p): with A3, 36 h, obtained reddish orange oil 29.2 mg; isolated yield: 48%; 92% ee; [α]D25 = -111.6 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, tR = 13.5 min (minor), 17.2 min (major); 1H NMR (400 MHz, CDCl3) δ 7.35-7.32 (m, 2H), 7.31-7.27 (m, 2H), 7.24-7.19 (m, 3H), 6.56-6.49 (m, 3H), 6.16 (dd, J = 16.0, 5.8 Hz, 1H), 4.12-4.05 (m, 1H), 3.75 (br, s, 1H), 1.40 (d, J = 6.7 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 146.3, 136.7, 132.5, 131.8, 129.5, 128.5,
127.5, 126.3, 114.9, 108.8, 50.9, 22.0 ppm; **HRMS (ESI)** calculated [M+H]^+ for C_{10}H_{17}BrN = 302.0539, found: 302.0524.

(S,E)-4-(4-phenylbut-3-en-2-yl)thiomorpholine (3q): with A4, 24 h, obtained colorless oil 42.9 mg; Isolated yield: 92%; 96% ee; [α]_D^{25} = -59.0 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm, t_R = 8.7 min (minor), 9.7 min (major); ^1H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (m, 2H), 7.33-7.30 (m, 2H), 7.25-7.21 (m, 1H), 6.44 (d, J = 16.0 Hz, 1H), 6.21 (dd, J = 16.0, 7.2 Hz, 1H), 3.27-3.20 (m, 1H), 2.90-2.80 (m, 4H), 2.69 (t, J = 5.0 Hz, 4H), 1.25 (d, J = 6.7 Hz, 3H) ppm; ^13C NMR (100 MHz, CDCl₃) δ 136.9, 131.7, 130.9, 128.5, 127.4, 126.2, 62.7, 51.6, 28.3, 16.3 ppm; **HRMS (ESI)** calculated [M+Na]^+ for C_{14}H_{19}NNaS = 256.1130, found: 256.1130.

(S,E)-1-(4-phenylbut-3-en-2-yl)piperidine (3r): with A4, 24 h, obtained pale yellow oil 40.8 mg; Isolated yield: 95%; 95% ee; [α]_D^{25} = -55.7 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, t_R = 8.6 min (minor), 9.8 min (major); ^1H NMR (400 MHz, CDCl₃) δ 7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.24-7.19 (m, 1H), 6.43 (d, J = 16.0 Hz, 1H), 6.24 (dd, J = 15.9, 8.0 Hz, 1H), 3.11-3.05 (m, 1H), 2.52-2.50 (m, 4H), 1.63-1.57 (m, 4H), 1.46-1.42 (m, 2H), 1.26 (d, J = 6.6 Hz, 3H) ppm; ^13C NMR (100 MHz, CDCl₃) δ 137.2, 132.7, 130.5, 128.5, 127.2, 126.2, 63.0, 51.0, 26.2, 24.6, 17.7 ppm; **HRMS (ESI)** calculated [M+Na]^+ for C_{15}H_{21}NNa = 238.1566, found: 238.1568.

(S,E)-1-(4-phenylbut-3-en-2-yl)pyrrolidine (3s): with A4, 24 h, obtained pale yellow oil 36.7 mg; Isolated yield: 91%; 97% ee; [α]_D^{25} = -92.4 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, t_R = 7.6 min (minor), 8.1 min (major); ^1H NMR (400 MHz, CDCl₃) δ 7.38-7.36 (m, 2H), 7.32-7.28 (m, 2H), 7.23-7.19 (m, 1H), 6.47 (d, J = 15.9 Hz, 1H), 6.24 (dd, J = 15.8, 8.6 Hz, 1H), 2.95-2.88 (m, 1H), 2.61-2.55 (m, 4H), 1.81-1.78 (m, 4H), 1.30 (d, J = 6.5 Hz, 3H) ppm; ^13C NMR (100 MHz, CDCl₃) δ 137.1, 133.9, 129.6, 128.5, 127.2, 126.2, 63.1, 52.2, 23.3, 21.0 ppm; **HRMS (ESI)** calculated [M+Na]^+ for C_{15}H_{19}NNa = 224.1410, found: 224.1410.

(S,E)-1-(4-phenylbut-3-en-2-yl)indoline (3t): with A3, 24 h, obtained pale yellow oil 43.6 mg; Isolated yield: 87%; 97% ee; [α]_D^{25} = -109.4 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min; UV detection at 254 nm, t_R = 13.8 min (major), 14.6 min (minor); ^1H NMR (400 MHz, CDCl₃) δ 7.37-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 7.07-7.02 (m, 2H), 6.64-6.60 (m, 1H),
(S,E)-2-(4-phenylbut-3-en-2-yl)-1,2,3,4-tetrahydroisoquinoline (3u): with A4, 24 h, obtained pale yellow oil 52.6 mg; Isolated yield: 99%; > 99% ee; [α]D^{25} = -51.5 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tₘₐᵣᵳ = 11.0 min (minor), 14.5 min (major); ¹H NMR (400 MHz, CDCl₃) δ 7.41-7.39 (m, 2H), 7.34-7.30 (m, 2H), 7.24-7.22 (m, 1H), 7.12-7.07 (m, 3H), 7.03-7.01 (m, 1H), 6.53 (d, J = 16.0 Hz, 1H), 6.30 (dd, J = 16.0, 7.9 Hz, 1H), 3.83-3.74 (m, 2H), 3.34-3.27 (m, 1H), 2.97-2.90 (m, 3H), 2.84-2.73 (m, 1H), 1.37 (d, J = 6.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 137.0, 134.9, 134.4, 132.3, 130.9, 128.6, 128.5, 127.4, 126.8, 126.3, 126.0, 125.5, 61.9, 53.0, 47.3, 29.4, 17.9 ppm; HRMS (ESI) calculated [M+Na]^+ for C₁₉H₁₉NNa = 272.1410, found: 272.1412.

(S,E)-2-(4-phenylbut-3-en-2-yl)piperazin-1-yl)pyrimidine (3v): with A4, 48 h, obtained pale yellow oil 58.9 mg; Isolated yield: 99%; 95% ee; [α]D^{25} = -68.1 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tₘₐᵳ = 12.7 min (major), 15.2 min (minor); ¹H NMR (400 MHz, CDCl₃) δ 8.29 (d, J = 4.7 Hz, 2H), 7.39-7.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.49-6.45 (m, 2H), 6.22 (dd, J = 15.9, 8.0 Hz, 1H), 3.84 (t, J = 5.2 Hz, 4H), 3.16-3.09 (m, 1H), 2.68-2.58 (m, 4H), 1.30 (d, J = 6.6 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 161.6, 157.7, 136.9, 132.1, 131.1, 128.6, 127.4, 126.3, 109.7, 62.6, 49.9, 43.9, 17.8 ppm; HRMS (ESI) calculated [M+Na]^+ for C₁₉H₁₂NNa = 317.1737, found: 317.1730.

(S,E)-N-allyl-N-methyl-4-phenylbut-3-en-2-amine (3w): with A4, 24 h, obtained pale yellow oil 33.2 mg; Isolated yield: 82%; 99% ee; [α]D^{25} = -49.2 (c = 1.0, CHCl₃); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, tₘₐᵳ = 8.0 min (minor), 9.3 min (major); ¹H NMR (400 MHz, CDCl₃) δ 7.39-7.36 (m, 2H), 7.33-7.28 (m, 2H), 7.24-7.20 (m, 1H), 6.45 (d, J = 16.0 Hz, 1H), 6.22 (dd, J = 16.0, 7.6 Hz, 1H), 5.93-5.83 (m, 1H), 5.20-5.11 (m, 2H), 3.34-3.27 (m, 1H), 3.19-3.13 (m, 1H), 3.09-3.03 (m, 1H), 2.25 (s, 3H), 1.25 (d, J = 6.7 Hz, 3H) ppm; ¹³C NMR (100 MHz, CDCl₃) δ 137.2, 136.3, 131.9, 130.8, 128.5, 127.3, 126.3, 117.3, 60.4, 57.4, 37.7, 17.2 ppm; HRMS (ESI) calculated [M+Na]^+ for C₁₄H₁₉NNa = 224.1410, found: 224.1412.
(S,E)-N-benzyl-N-methyl-4-phenylbut-3-en-2-amine (3x): with A3, 24 h, obtained pale yellow oil 44.2 mg; Isolated yield: 88%; 98% ee; [α]D 25 = -91.9 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, tR = 5.0 min (minor), 6.0 min (major); 1H NMR (400 MHz, CDCl3) δ 7.41-7.39 (m, 2H), 7.36-7.30 (m, 6H), 7.26-7.21 (m, 2H), 6.47 (d, J = 16.1 Hz, 1H), 6.31 (dd, J = 16.0, 7.3 Hz, 1H), 3.65 (d, J = 13.2 Hz, 1H), 3.51 (d, J = 13.2 Hz, 1H), 3.39-3.32 (m, 1H), 2.22 (s, 3H), 1.30 (d, J = 6.7 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 139.8, 137.2, 132.0, 130.8, 128.9, 128.5, 128.2, 127.3, 126.8, 126.2, 60.4, 58.2, 37.9, 16.9 ppm; HRMS (ESI) calculated [M+Na]+ for C21H23NNa = 274.1566, found: 274.1563.

(S,E)-N,N-dibenzyl-4-phenylbut-3-en-2-amine (3y): with A3, 24 h, obtained pale yellow oil 34.6 mg; Isolated yield: 53%; 96% ee; [α]D 25 = -193.7 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 90:10, flow rate = 1.0 mL/min, UV detection at 254 nm, tR = 7.6 min (major), 10.5 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.42-7.38 (m, 6H), 7.34-7.29 (m, 6H), 7.24-7.20 (m, 3H), 6.43 (d, J = 16.2 Hz, 1H), 6.32 (dd, J = 16.1, 6.6 Hz, 1H), 3.71 (d, J = 13.9 Hz, 2H), 3.59 (d, J = 13.9 Hz, 2H), 3.51-3.44 (m, 1H), 1.29 (d, J = 6.8 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 140.6, 137.3, 131.6, 130.9, 128.52, 128.50, 128.2, 127.2, 126.7, 126.2, 54.8, 53.7, 15.8 ppm; HRMS (ESI) calculated [M+Na]+ for C24H25NNa = 350.1873, found: 350.1873.

(S,E)-N,N-diethyl-4-phenylbut-3-en-2-amine (3z): with A3, 36 h, obtained pale yellow oil 11.0 mg; Isolated yield: 27%; 96% ee; [α]D 25 = -26.8 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tR = 7.7 min (minor), 8.0 min (major); 1H NMR (400 MHz, CDCl3) δ 7.39-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.44 (d, J = 16.0 Hz, 1H), 6.24 (dd, J = 16.0, 7.5 Hz, 1H), 3.50-3.43 (m, 1H), 2.69-2.53 (m, 4H), 1.24 (d, J = 6.6 Hz, 3H), 1.06 (t, J = 7.2 Hz, 6H) ppm; 13C NMR (100 MHz, CDCl3) δ 137.2, 133.0, 130.0, 128.5, 127.2, 126.2, 57.5, 43.4, 17.4, 12.8 ppm; HRMS (ESI) calculated [M+Na]+ for C24H25NNa = 226.1566, found: 226.1568.

(S,E)-N-methyl-N-(4-phenylbut-3-en-2-yl)aniline (3aa): with A3, 36 h, obtained pale yellow oil 10.4 mg; Isolated yield: 22%; 90% ee; [α]D 25 = -169.9 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, tR = 11.7 min (major), 15.0 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.38-7.35 (m, 2H), 7.32-7.20 (m, 5H), 6.86-6.83 (m, 2H), 6.75-6.71 (m, 1H), 6.48 (dd, J = 16.2, 1.9 Hz, 1H), 6.30 (dd, J = 16.2, 4.4 Hz, 1H), 4.69-4.62 (m, 1H), 2.79 (s, 3H), 1.37 (d, J = 6.8 Hz, 3H) ppm;
\(^{13}\text{C} \text{NMR} \quad (100 \text{ MHz, CDCl}_3) \ \delta 150.0, 137.1, 131.3, 130.0, 129.2, 128.6, 127.4, 126.3, 116.8, 113.4, 54.9, 31.7, 16.2 \text{ ppm}; \text{HRMS (ESI)} \text{ calculated } [\text{M+Na}^+] \text{ for } C_{17}H_{19}NNa = 260.1410, \text{ found: 260.1411.}

\((S,E)-N-(\text{furan-2-ylmethyl})-4-(2\text{-methoxyphenyl})\text{-but-3-en-2-amine (3ab)}: \text{ with A4, 24 h, obtained pale yellow oil 51.5 mg; Isolated yield: 99%; > 99% ee; } [\alpha]_D^{25} = -114.1 \ (c = 1.0, \text{CHCl}_3); \text{ The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, } t_R = 27.5 \text{ min (major), 32.5 min (minor); } \ ^1\text{H NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta 7.46 \ (dd, \ J = 7.6, 1.8 \text{ Hz, 1H}), 7.36 \ (d, \ J = 1.9, 0.9 \text{ Hz, 1H}), 7.23-7.19 \ (m, 1H), 6.94-6.90 \ (m, 1H), 6.87 \ (dd, \ J = 8.2, 1.1 \text{ Hz, 1H}), 6.81 \ (d, \ J = 16.0 \text{ Hz, 1H}), 6.31 \ (dd, \ J = 3.2, 1.8 \text{ Hz, 1H}), 6.17 \ (dd, \ J = 3.2, 0.8 \text{ Hz, 1H}), 6.07 \ (dd, \ J = 16.0, 8.2 \text{ Hz, 1H}), 3.85 \ (s, 3H), 3.83 \ (d, \ J = 14.7 \text{ Hz, 1H}), 3.74 \ (d, \ J = 14.4 \text{ Hz, 1H}), 3.43-3.36 \ (m, 1H), 1.26 \ (d, \ J = 6.4 \text{ Hz, 3H}) \text{ ppm; HRMS (ESI) calculated } [\text{M+H}^+] \text{ for } C_{16}H_{20}NO_2 = 258.1484, \text{ found: 258.1484.}

\((S,E)-N-(\text{furan-2-ylmethyl})-4-(3\text{-methoxyphenyl})\text{-but-3-en-2-amine (3ac)}: \text{ with A4, 24 h, obtained pale yellow oil 51.0 mg; Isolated yield: 99%; > 99% ee; } [\alpha]_D^{25} = -104.0 \ (c = 1.0, \text{CHCl}_3); \text{ The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, } t_R = 28.0 \text{ min (major), 29.9 min (minor); } \ ^1\text{H NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta 7.36 \ (dd, \ J = 1.9, 0.9 \text{ Hz, 1H}), 7.23 \ (t, \ J = 7.9 \text{ Hz, 1H}), 6.99-6.96 \ (m, 1H), 6.93-6.92 \ (m, 1H), 6.79 \ (dd, \ J = 8.2, 2.6, 0.9 \text{ Hz, 1H}), 6.46 \ (d, \ J = 15.9 \text{ Hz, 1H}), 6.31 \ (dd, \ J = 3.1, 1.9 \text{ Hz, 1H}), 6.16 \ (dd, \ J = 3.2, 0.8 \text{ Hz, 1H}), 6.07 \ (dd, \ J = 15.9, 8.1 \text{ Hz, 1H}), 3.83 \ (d, \ J = 14.4 \text{ Hz, 1H}), 3.82 \ (s, 3H), 3.74 \ (d, \ J = 14.4 \text{ Hz, 1H}), 3.42-3.35 \ (m, 1H), 1.88 \ (br, s, 1H), 1.26 \ (d, \ J = 6.4 \text{ Hz, 3H}) \text{ ppm; HRMS (ESI) calculated } [\text{M+H}^+] \text{ for } C_{16}H_{20}NO_2 = 258.1489, \text{ found: 258.1481.}

\((S,E)-N-(\text{furan-2-ylmethyl})-4-(4\text{-methoxyphenyl})\text{-but-3-en-2-amine (3ad)}: \text{ with A4, 24 h, obtained pale yellow oil 51.5 mg; Isolated yield: 99%; > 99% ee; } [\alpha]_D^{25} = -159.0 \ (c = 1.0, \text{CHCl}_3); \text{ The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, } t_R = 33.8 \text{ min (major), 35.4 min (minor); } \ ^1\text{H NMR} \quad (400 \text{ MHz, CDCl}_3) \ \delta 7.36 \ (dd, \ J = 2.0, 0.8 \text{ Hz, 1H}), 7.34-7.30 \ (m, 2H), 6.88-6.84 \ (m, 2H), 6.43 \ (d, \ J = 15.9 \text{ Hz, 1H}), 6.31 \ (dd, \ J = 3.2, 1.8 \text{ Hz, 1H}), 6.16 \ (dd, \ J = 3.1, 0.8 \text{ Hz, 1H}, 6.07 \ (dd, \ J = 15.9, 8.1 \text{ Hz, 1H}) \text{ ppm; HRMS (ESI) calculated } [\text{M+H}^+] \text{ for } C_{16}H_{20}NO_2 = 258.1489, \text{ found: 258.1481.}
1H, 5.93 (dd, J = 15.8, 8.2 Hz, 1H), 3.83 (d, J = 13.2 Hz, 1H), 3.81 (s, 3H), 3.73 (d, J = 14.4 Hz, 1H), 3.39-3.33 (m, 1H), 1.86 (br, s, 1H), 1.25 (d, J = 6.4 Hz, 3H) ppm; \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 159.0, 153.9, 141.8, 131.4, 130.0, 129.7, 127.4, 113.9, 110.1, 106.8, 55.3, 55.2, 54.8 ppm; \(\text{HRMS (ESI)}\) calculated [M+Na]\(^+\) for C\(_{16}\)H\(_{18}\)N\(_2\)NaO\(_2\) = 280.1308, found: 280.1310.

(S,E)-4-(4-fluorophenyl)-N-(furan-2-ylmethyl)but-3-en-2-amine (3ae): with A4, 24 h, obtained pale yellow oil 49.1 mg; Isolated yield: 99%; > 99% ee; \([\alpha]_D^{25}\) = -137.4 (c = 1.0, CHCl\(_3\)); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, \(t_R = 25.0\) min (major), 27.4 min (minor); \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.37-7.32 (m, 3H), 7.03-6.97 (m, 2H), 6.45 (d, J = 15.8 Hz, 1H), 6.31 (dd, J = 3.1, 1.9 Hz, 1H), 6.16 (dd, J = 3.2, 0.8 Hz, 1H), 5.99 (dd, J = 15.8, 8.1 Hz, 1H), 3.82 (d, J = 14.4 Hz, 1H), 3.73 (d, J = 14.4 Hz, 1H), 3.41-3.34 (m, 1H), 1.83 (br, s, 1H), 1.25 (d, J = 6.4 Hz, 3H) ppm; \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 162.1 (d, J = 246.5 Hz), 153.8, 141.8, 133.4 (d, J = 2.2 Hz), 133.1 (d, J = 3.2 Hz), 129.3, 127.7 (d, J = 7.9 Hz), 115.4 (d, J = 21.4 Hz), 110.1, 106.8, 55.2, 43.8, 22.0 ppm; \(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)) \(\delta\) -114.82 ppm; \(\text{HRMS (ESI)}\) calculated [M+Na]\(^+\) for C\(_{16}\)H\(_{16}\)F\(_3\)NO = 268.1108, found: 268.1103.

(S,E)-N-(furan-2-ylmethyl)-4-(4-(trifluoromethyl)phenyl)but-3-en-2-amine (3af): with A4, 24 h, obtained pale yellow oil 59.2 mg; Isolated yield: 99%; 96% ee; \([\alpha]_D^{25}\) = -99.8 (c = 1.0, CHCl\(_3\)); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, \(t_R = 11.5\) min (major), 13.0 min (minor); \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.56 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.2 Hz, 2H), 7.37 (dd, J = 1.9, 0.8 Hz, 1H), 6.52 (d, J = 15.9 Hz, 1H), 6.31 (dd, J = 3.2, 1.8 Hz, 1H), 6.21-6.15 (m, 2H), 3.82 (d, J = 14.5 Hz, 1H), 3.74 (d, J = 14.5 Hz, 1H), 3.45-3.38 (m, 1H), 1.82 (br, s, 1H), 1.27 (d, J = 6.5 Hz, 3H) ppm; \(^{13}\text{C NMR}\) (100 MHz, CDCl\(_3\)) \(\delta\) 153.7, 141.8, 140.5 (q, J = 1.6 Hz), 136.5, 129.11 (q, J = 32.2 Hz), 129.09, 126.4, 125.5 (q, J = 3.9 Hz), 124.2 (q, J = 270.5 Hz), 110.1, 106.9, 55.1, 43.8, 21.8 ppm; \(^{19}\text{F NMR}\) (376 MHz, CDCl\(_3\)) \(\delta\) -62.36 ppm; \(\text{HRMS (ESI)}\) calculated [M+H]\(^+\) for C\(_{16}\)H\(_{17}\)F\(_3\)NO = 296.1257, found: 296.1250.

(S,E)-4-(3-(furan-2-ylmethyl)amino)but-1-en-1-yl)-N,N-dimethylaniline (3ag): with A4, 24 h, obtained pale yellow oil 49.8 mg; Isolated yield: 99%; > 99% ee; \([\alpha]_D^{25}\) = -167.1 (c = 1.0, CHCl\(_3\)); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.6 mL/min, UV detection at 254 nm, \(t_R = 29.8\) min (minor), 32.1 min (major); \(^1\text{H NMR}\) (400 MHz, CDCl\(_3\)) \(\delta\) 7.36 (dd, J = 1.9, 0.8 Hz, 1H), 7.29-7.27 (m, 2H), 6.70-
6.67 (m, 2H), 6.39 (d, J = 15.8 Hz, 1H), 6.31 (dd, J = 3.2, 1.9 Hz, 1H), 6.16 (dd, J = 3.1, 0.8 Hz, 1H), 5.85 (dd, J = 15.8, 8.2 Hz, 1H), 3.83 (d, J = 14.4 Hz, 1H), 3.73 (d, J = 14.4 Hz, 1H), 3.38-3.31 (m, 1H), 2.95 (s, 6H); 2.24 (br, s, 1H); 1.25 (d, J = 6.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 153.9, 150.0, 141.7, 130.6, 129.1, 127.2, 125.4, 112.5, 110.0, 106.8, 55.5, 43.6, 40.6, 22.1 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{11}$H$_{23}$N$_2$O = 271.1805, found: 271.1805.

(S,E)-4-(furan-2-yl)-N-(furan-2-ylmethyl)but-3-en-2-amine (3ah): with A4, 36 h, obtained pale yellow oil 37.0 mg; Isolated yield: 85%; [a]$_D^{25} = -124.5$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, $t_R$ = 19.1 min (major), 24.9 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (dd, J = 1.9, 0.9 Hz, 1H), 7.34 (d, J = 1.8 Hz, 1H), 6.36 (dd, J = 3.3, 1.8 Hz, 1H), 6.34-6.30 (m, 2H), 6.21 (d, J = 3.2 Hz, 1H), 6.16 (dd, J = 3.2, 0.8 Hz, 1H), 6.02 (dd, J = 15.8, 8.0 Hz, 1H), 3.82 (d, J = 14.5 Hz, 1H), 3.72 (d, J = 14.4 Hz, 1H), 3.37-3.30 (m, 1H), 1.24 (d, J = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.5, 152.6, 141.8, 141.7, 132.5, 118.9, 111.2, 110.1, 107.2, 106.8, 54.9, 43.8, 22.0 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{13}$H$_{16}$NO = 218.1176, found: 218.1177.

(S,E)-4-cyclohexyl-N-(furan-2-ylmethyl)but-3-en-2-amine (3ai): with A4, 24 h, obtained pale yellow oil 45.4 mg; Isolated yield: 97%; [a]$_D^{25} = -51.0$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm, $t_R$ = 8.7 min (major), 9.4 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (dd, J = 1.9, 0.9 Hz, 1H), 6.30 (dd, J = 3.2, 1.8 Hz, 1H), 6.13 (dd, J = 3.1, 0.9 Hz, 1H), 5.48 (dd, J = 15.4, 6.6 Hz, 1H), 5.24-5.18 (m, 1H), 3.77 (d, J = 14.5 Hz, 1H), 3.67 (d, J = 14.4 Hz, 1H), 3.16-3.09 (m, 1H), 1.99-1.90 (m, 1H), 1.74-1.69 (m, 4H), 1.67-1.64 (m, 1H), 1.29-1.16 (m, 3H), 1.14 (d, J = 6.4 Hz, 3H), 1.11-1.02 (m, 2H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 154.2, 141.6, 137.9, 130.9, 110.0, 106.6, 55.1, 43.6, 40.4, 33.1, 33.0, 26.2, 26.0, 22.1 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{15}$H$_{20}$NO = 234.1852, found: 234.1853.

(S,E)-N-(furan-2-ylmethyl)-6-phenylhex-3-en-2-amine (3aj): with A4, 24 h, obtained pale yellow oil 51.0 mg; Isolated yield: 99%; [a]$_D^{25} = -41.1$ (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm, $t_R$ = 17.6 min (minor), 18.7 min (major); $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (dd, J = 1.9, 0.9 Hz, 1H), 7.29-7.25 (m, 2H), 7.19-7.15 (m, 3H), 6.29 (dd, J = 3.1, 1.9 Hz, 1H), 6.10 (dd, J = 3.2, 0.7 Hz, 1H), 5.55 (dt, J = 15.2, 6.6 Hz, 1H), 5.27 (ddt, J = 15.4, 8.1, 1.4 Hz, 1H), 3.69 (d, J = 14.4 Hz, 1H), 3.60 (d, J = 14.4 Hz, 1H), 3.17-3.10 (m, 1H), 2.76-2.65 (m, 2H), 2.39-2.33 (m, 2H), 1.12
(d, J = 6.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 154.2, 141.8, 141.6, 134.6, 130.7, 128.5, 128.3, 125.8, 110.0, 106.6, 54.9, 43.6, 35.8, 34.0, 22.0 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{17}$H$_{22}$NO = 256.1696, found: 256.1691.

(S,E)-4-(4-(2-methoxyphenyl)but-3-en-2-yl)morpholine (3ak): with A4, 24 h, obtained pale yellow oil 49.5 mg; Isolated yield: 99%; > 99% ee; [α]$_D^{25}$ = -61.6 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 22.1 min (minor), 24.2 min (major);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.44 (dd, J = 7.6, 1.7 Hz, 1H), 7.23 - 7.19 (m, 1H), 6.93 - 6.89 (m, 1H), 6.86 (dd, J = 8.2, 1.2 Hz, 1H), 6.17 (dd, J = 16.0, 8.3 Hz, 1H), 3.84 (s, 3H), 3.73 (t, J = 4.7 Hz, 4H), 3.06 - 2.99 (m, 1H), 2.62 - 2.52 (m, 4H), 1.26 (d, J = 6.6 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 156.5, 132.5, 128.5, 126.6, 125.9, 125.8, 120.6, 110.9, 67.2, 63.6, 55.4, 50.8, 17.9 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{15}$H$_{22}$NO$_2$ = 248.1645, found: 248.1641.

(S,E)-4-(4-(3-methoxyphenyl)but-3-en-2-yl)morpholine (3al): with A4, 24 h, obtained pale yellow oil 49.5 mg; Isolated yield: 99%; 98% ee; [α]$_D^{25}$ = -58.7 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 21.2 min (major), 24.6 min (minor);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.23 (t, J = 7.9 Hz, 1H), 6.96 (d, J = 7.7 Hz, 1H), 6.92 - 6.91 (m, 1H), 6.79 (dd, J = 8.2, 2.4 Hz, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.17 (dd, J = 15.9, 8.3 Hz, 1H), 3.81 (s, 3H), 3.73 (t, J = 4.7 Hz, 4H), 3.06 - 2.99 (m, 1H), 2.61 - 2.52 (m, 4H), 1.26 (d, J = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.8, 138.3, 132.3, 131.1, 129.5, 118.9, 113.2, 111.4, 67.1, 63.0, 55.1, 50.7, 17.6 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{15}$H$_{22}$NO$_2$ = 248.1645, found: 248.1637.

(S,E)-4-(4-(4-methoxyphenyl)but-3-en-2-yl)morpholine (3am): with A4, 24 h, obtained pale yellow oil 49.3 mg; Isolated yield: 99%; > 99% ee; [α]$_D^{25}$ = -80.8 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 1.0 mL/min, UV detection at 254 nm, t$_R$ = 20.6 min (minor), 29.0 min (major);

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31 (d, J = 8.7 Hz, 2H), 6.85 (d, J = 8.7 Hz, 2H), 6.41 (d, J = 15.9 Hz, 1H), 6.02 (dd, J = 15.9, 8.3 Hz, 1H), 3.81 (s, 3H), 3.74 (t, J = 4.7 Hz, 4H), 3.03 - 2.96 (m, 1H), 2.61 - 2.53 (m, 4H), 1.26 (d, J = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.1, 130.8, 129.6, 129.5, 127.4, 113.9, 67.10, 63.2, 55.3, 50.7, 17.8 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{15}$H$_{21}$NNaO$_2$ = 270.1465, found: 270.1464.
(S,E)-4-(4-(4-fluorophenyl)but-3-en-2-yl)morpholine (3an): with A4, 24 h, obtained pale yellow oil 47.2 mg; Isolated yield: 99%; > 99% ee; [α]D25 = -70.3 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tr = 16.0 min (minor), 17.5 min (major); 1H NMR (400 MHz, CDCl3) δ 7.36-7.31 (m, 2H), 7.03-6.97 (m, 2H), 6.43 (d, J = 15.9 Hz, 1H), 6.08 (dd, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 162.2 (d, J = 246.6 Hz), 133.0 (d, J = 3.3 Hz), 131.8 (d, J = 2.1 Hz), 130.0, 127.7 (d, J = 7.9 Hz), 115.4 (d, J = 21.6 Hz), 67.2, 63.0, 50.7, 17.7 ppm; 19F NMR (376 MHz, CDCl3) δ -114.64 ppm; HRMS (ESI) calculated [M+H]+ for C14H19FNO = 236.1445, found: 236.1442.

(S,E)-4-(4-(4-(trifluoromethyl)phenyl)but-3-en-2-yl)morpholine (3ao): with A4, 24 h, obtained pale yellow oil 57.1 mg; Isolated yield: 99%; 93% ee; [α]D25 = -48.3 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, tr = 15.0 min (major), 17.8 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.56 (d, J = 8.2 Hz, 2H), 7.46 (d, J = 8.4 Hz, 2H), 6.50 (d, J = 16.0 Hz, 1H), 6.28 (dd, J = 16.0, 8.0 Hz, 1H), 3.75-3.72 (m, 4H), 3.10-3.02 (m, 1H), 2.58-2.55 (m, 4H), 1.27 (d, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 162.2 (d, J = 246.6 Hz), 133.0, 129.9, 129.2 (q, J = 32.4 Hz), 126.4, 125.5 (q, J = 3.8 Hz), 124.1 (q, J = 270.9 Hz), 67.1, 62.9, 50.7, 17.5 ppm; 19F NMR (376 MHz, CDCl3) δ -62.38 ppm; HRMS (ESI) calculated [M+H]+ for C15H19F3NO = 286.1413, found: 286.1412.

(S,E)-N,N-dimethyl-4-(3-morpholinobut-1-en-1-yl)aniline (3ap): with A4, 24 h, obtained pale yellow oil 38.8 mg; Isolated yield: 74%; > 99% ee; [α]D25 = -98.5 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, tr = 19.5 min (major), 21.3 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.28-7.25 (m, 2H), 6.69-6.67 (m, 2H), 6.37 (d, J = 15.8 Hz, 1H), 5.94 (dd, J = 15.9, 8.3 Hz, 1H), 3.73 (t, J = 4.7 Hz, 4H), 3.00-2.97 (m, 1H), 2.95 (s, 6H), 2.61-2.52 (m, 4H), 1.25 (d, J = 6.5 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 150.0, 131.2, 127.5, 127.1, 125.4, 112.5, 67.2, 63.4, 50.8, 40.6, 18.0 ppm; HRMS (ESI) calculated [M+H]+ for C16H25N2O = 261.1961, found: 261.1960.
(S,E)-4-(4-(furan-2-yl)but-3-en-2-yl)morpholine (3a): with A4, 36 h, obtained pale yellow oil 41.4 mg; Isolated yield: 99%; 96% ee; [α]D25 = -73.8 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tR = 16.6 min (minor), 18.7 min (major); 1H NMR (400 MHz, CDCl3) δ 7.33 (d, J = 1.8 Hz, 1H), 6.36 (dd, J = 3.3, 1.8 Hz, 1H), 6.31-6.27 (m, 1H), 6.20 (d, J = 3.3 Hz, 1H), 6.11 (dd, J = 15.9, 8.1 Hz, 1H), 3.72 (t, J = 4.7 Hz, 4H), 3.04-2.97 (m, 1H), 2.60-2.50 (m, 4H), 1.23 (d, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 152.5, 141.7, 130.7, 119.7, 111.2, 107.3, 67.2, 62.7, 50.5, 17.5 ppm; HRMS (ESI) calculated [M+H]+ for C12H18NO2 = 208.1332, found: 208.1333.

(S,E)-2-(4-(4-cyclohexylbut-3-en-2-yl)piperazin-1-yl)pyrimidine (3ar): with A4, 24 h, obtained colourless oil 34.7 mg; Isolated yield: 58%; 96% ee; [α]D25 = -17.7 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OJ-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tR = 8.8 min (minor), 9.5 min (major); 1H NMR (400 MHz, CDCl3) δ 8.29 (d, J = 4.7 Hz, 2H), 6.46 (t, J = 4.7 Hz, 2H), 6.50 (t, J = 15.6, 6.4 Hz, 1H), 5.37-5.31 (m, 1H), 3.83-3.81 (m, 4H), 2.93-2.86 (m, 1H), 2.62-2.49 (m, 4H), 1.99-1.90 (m, 1H), 1.72-1.69 (m, 4H), 1.66-1.62 (m, 1H), 1.28-1.22 (m, 3H), 1.18 (d, J = 6.6 Hz, 3H), 1.14-1.02 (m, 2H) ppm; 13C NMR (100 MHz, CDCl3) δ 161.6, 157.7, 138.5, 128.7, 109.6, 62.5, 49.6, 43.8, 40.4, 33.04, 32.97, 26.1, 26.0, 18.1 ppm; HRMS (ESI) calculated [M+H]+ for C18H29N4 = 301.2387, found: 301.2380.

(S,E)-2-(4-(6-phenylhex-3-en-2-yl)piperazin-1-yl)pyrimidine (3as): with A4, 24 h, obtained colorless oil 63.5 mg; Isolated yield: 98%; > 99% ee; [α]D25 = -14.2 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 254 nm, tR = 19.2 min (major), 21.7 min (minor); 1H NMR (400 MHz, CDCl3) δ 8.30 (d, J = 4.7 Hz, 2H), 7.28-7.24 (m, 2H), 7.17-7.13 (m, 3H), 6.46 (t, J = 4.7 Hz, 1H), 5.52 (dt, J = 15.3, 6.5 Hz, 1H), 5.37 (ddt, J = 15.4, 8.0, 1.2 Hz, 1H), 3.78 (t, J = 5.2 Hz, 4H), 2.91-2.84 (m, 1H), 2.76-2.64 (m, 2H), 2.51-2.41 (m, 4H), 2.39-2.33 (m, 2H), 1.14 (d, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 161.6, 157.7, 131.2, 128.5, 128.2, 125.8, 109.6, 62.3, 49.6, 43.8, 35.6, 34.0, 17.9 ppm; HRMS (ESI) calculated [M+H]+ for C20H27N4 = 323.2280, found: 323.2224.
(S,E)-4-(6-phenylhex-3-en-2-yl)morpholine (3at): with A4, 24 h, obtained colorless oil 43.1 mg; Isolated yield: 88%; > 99% ee; [α]_D = -21.8 (c = 1.0, CHCl_3); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 95:5, flow rate = 0.5 mL/min, UV detection at 220 nm, t_R = 13.1 min (minor), 14.4 min (major); ^1H NMR (400 MHz, CDCl_3) δ 7.28-7.24 (m, 2H), 7.18-7.15 (m, 3H), 5.52 (dd, J = 15.2, 6.6 Hz, 1H), 5.32 (ddt, J = 15.3, 8.1, 1.4 Hz, 1H), 3.66 (t, J = 5.2 Hz, 4H), 2.79-2.64 (m, 3H), 2.40-2.33 (m, 6H), 1.10 (d, J = 6.5 Hz, 3H) ppm; ^13C NMR (100 MHz, CDCl_3) δ 141.7, 132.8, 131.3, 128.5, 128.3, 125.8, 7.35 (dd, J = 15.9, 8.1 Hz, 1H), 3.76 (m, 2H), 3.23 (m, 2H), 2.33 (m, 6H), 2.13 (m, 6H), 1.71 (m, 1H), 1.60 (d, J = 6.5 Hz, 3H) ppm; HRMS (ESI) calculated [M+H]^+ for C_{18}H_{24}NO = 246.1852, found: 246.1847.

(S)-N-(furan-2-ylmethyl)cyclohex-2-en-1-amine (3au): with A4, 24 h, obtained pale yellow oil 17.4 mg; Isolated yield: 28%; 22% ee; [α]_D = -13.5 (c = 1.0, CHCl_3); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 220 nm, t_R = 13.1 min (minor), 21.9 min (major); ^1H NMR (400 MHz, CDCl_3) δ 7.35 (dd, J = 1.9, 0.9 Hz, 1H), 6.31 (dd, J = 3.1, 1.9 Hz, 1H), 6.18 (dd, J = 3.1, 0.8 Hz, 1H), 5.80-5.75 (m, 1H), 5.70-5.66 (m, 1H), 3.89-3.80 (m, 2H), 3.23-3.17 (m, 1H), 2.02-1.96 (m, 2H), 1.90-1.85 (m, 1H), 1.78-1.71 (m, 1H), 1.60-1.41 (m, 2H) ppm; ^13C NMR (100 MHz, CDCl_3) δ 154.0, 141.7, 129.4, 129.2, 110.1, 106.7, 52.0, 43.4, 29.2, 25.2, 20.1 ppm; HRMS (ESI) calculated [M+H]^+ for C_{11}H_{10}NO = 178.1226, found: 178.1221.

(S,E)-2-((4-phenylbut-3-en-2-yl)amino)ethan-1-ol (3av): with A4, 24 h, obtained pale yellow oil 34.8 mg; Isolated yield: 91%; > 99% ee; [α]_D = -54.8 (c = 1.0, CHCl_3); The enantiomeric excess was determined by (converting it to compound Bz-3av) HPLC on Chiralpak AS-H column, hexane: isopropanol = 85:15; flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 20.0 min (major), 24.7 min (minor); ^1H NMR (400 MHz, CDCl_3) δ 7.39-7.37 (m, 2H), 7.32-7.29 (m, 2H), 7.25-7.21 (m, 1H), 6.50 (d, J = 15.9 Hz, 1H), 6.12 (dd, J = 15.9, 8.1 Hz, 1H), 3.76-3.67 (m, 2H), 3.53-3.41 (m, 1H), 3.41 (br, s, 1H), 3.32 (br, s, 1H), 2.93-2.79 (m, 2H), 1.35 (d, J = 6.5 Hz, 3H) ppm; ^13C NMR (100 MHz, CDCl_3) δ 136.4, 131.6, 131.5, 128.5, 128.3, 126.4, 60.3, 56.3, 48.5, 21.2 ppm; HRMS (ESI) calculated [M+H]^+ for C_{12}H_{18}NO = 192.1383, found: 192.1381.

(S,E)-N1-benzyl-N1-(4-phenylbut-3-en-2-yl)ethane-1,2-diamine (3aw): with A4, 24 h, obtained pale yellow oil 46.5 mg; Isolated yield: 83%; 98% ee; [α]_D = -56.6 (c = 1.0, CHCl_3); The enantiomeric excess was determined by (converting it to compound Bz-3aw) HPLC on Chiralpak AD-H column, hexane: isopropanol = 85:15, flow rate = 1.0 mL/min, UV detection at 254 nm, t_R = 24.4 min (minor), 27.6 min (major); ^1H NMR (400 MHz, CDCl_3) δ 7.41-7.37 (m, 2H), 7.32-7.28 (m, 6H), 7.25-7.19 (m, 2H), 6.44 (d, J = 15.9 Hz, 1H), 5.66 (m, 1H), 3.89 (m, 2H), 3.23 (m, 2H), 2.33 (m, 6H), 2.13 (m, 6H), 1.71 (m, 1H), 1.60 (d, J = 6.5 Hz, 3H) ppm; HRMS (ESI) calculated [M+H]^+ for C_{18}H_{24}NO = 285.1842, found: 285.1841.
6.05 (dd, J = 15.9, 7.9 Hz, 1H), 3.79 (s, 2H), 3.35-3.28 (m, 1H), 2.81-2.65 (m, 4H), 1.25 (br, s, 2H), 1.25 (d, J = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 140.3, 137.0, 134.2, 129.9, 128.5, 128.4, 128.1, 127.3, 126.9, 126.3, 56.3, 53.8, 48.8, 46.9, 22.0 ppm; HRMS (ESI) calculated [M+H]$^+$ for C$_{19}$H$_{25}$N$_2$ = 281.2012, found: 282.2011.

(S,E)-2-(((4-phenylbut-3-en-2-yl)amino)methyl)phenol (3ax): with A4, 24 h, obtained pale yellow oil 47.6 mg; Isolated yield: 94%; 97% ee; [α]$_D^{25}$ = -110.6 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 31.9 min (major), 37.2 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.38-7.30 (m, 4H), 7.26-7.22 (m, 1H), 7.18-7.14 (m, 1H), 6.96-6.94 (m, 1H), 6.84 (dd, J = 8.1, 1.2 Hz, 1H), 6.78-6.74 (m, 1H), 6.46 (d, J = 15.9 Hz, 1H), 6.03 (dd, J = 15.9, 8.2 Hz, 1H), 4.07 (d, J = 14.0 Hz, 1H), 3.91 (d, J = 13.9 Hz, 1H), 3.45-3.38 (m, 1H), 1.32 (d, J = 6.5 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.2, 136.5, 131.7, 131.5, 128.6, 128.3, 127.7, 126.3, 122.7, 119.1, 116.4, 55.1, 50.0, 21.7 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{17}$H$_{19}$NO = 276.1359, found: 276.1361.

(S,E)-2-(((4-phenylbut-3-en-2-yl)amino)phenyl)ethanol (3ay): with A3, 24 h, obtained white solid 31.4 mg; Isolated yield: 59%; 91% ee; [α]$_D^{25}$ = -114.1 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak OD-H column, hexane: isopropanol = 80:20, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 24.7 min (major), 28.9 min (minor); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.37-7.34 (m, 2H), 7.31-7.27 (m, 2H), 7.23-7.19 (m, 1H), 7.03-7.00 (m, 2H), 6.63-6.60 (m, 2H), 6.57-6.54 (m, 1H), 6.20 (dd, J = 15.9, 1.3 Hz, 1H), 4.15-4.08 (m, 1H), 3.78 (t, J = 6.5 Hz, 2H), 2.74 (t, J = 6.5 Hz, 2H), 1.40 (d, J = 6.6 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 146.0, 136.9, 133.2, 129.8, 129.2, 128.5, 127.3, 126.7, 126.3, 113.6, 63.9, 51.0, 38.2, 22.1 ppm; HRMS (ESI) calculated [M+Na]$^+$ for C$_{18}$H$_{21}$NNaO = 290.1532, found: 290.1531.

(S,E)-N-(2-((1H-indol-3-yl)ethyl)-4-phenylbut-3-en-2-amine (3az): with A4, 24 h, obtained pale yellow oil 58.2 mg; Isolated yield: 99%; > 99% ee; [α]$_D^{25}$ = -76.2 (c = 1.0, CHCl$_3$); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 99:1, flow rate = 0.5 mL/min, UV detection at 254 nm, t$_R$ = 69.3 min (minor), 75.3 min (major); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (s, 1H), 7.62 (d, J = 7.9 Hz, 1H), 7.37-7.27 (m, 5H), 7.23-7.17 (m, 2H), 7.10 (t, J = 7.5 Hz, 1H), 7.04 (d, J = 2.3 Hz, 1H), 6.42 (d, J = 15.9 Hz, 1H), 6.06 (dd, J = 15.9, 8.0 Hz, 1H), 3.41-3.34 (m, 1H), 3.04-2.92 (m, 4H), 1.97 (br, s, 1H), 1.22 (d, J = 6.4 Hz, 3H) ppm; $^{13}$C NMR (100 MHz, CDCl$_3$) δ 137.0, 136.4, 134.1, 129.9, 128.5, 127.4, 127.3, 126.2, 122.02, 121.98, 119.2, 118.9, 113.8, 111.1,
(S,E)-4-(((4-phenylbut-3-en-2-yl)amino)methyl)aniline (3ba): with A3, 24 h, obtained pale yellow oil 20.4 mg; Isolated yield: 40%; > 99% ee; [α]D25 = -148.5 (c = 1.0, CHCl3); The enantiomeric excess was determined by HPLC on Chiralpak AS-H column, hexane: isopropanol = 90:10, flow rate = 0.5 mL/min, UV detection at 254 nm, tR = 25.8 min (major), 28.8 min (minor); 1H NMR (400 MHz, CDCl3) δ 7.40-7.37 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 7.12-7.09 (m, 2H), 6.67-6.63 (m, 2H), 6.47 (d, J = 15.9 Hz, 1H), 6.11 (dd, J = 15.9, 8.0 Hz, 1H), 3.73 (d, J = 12.8 Hz, 1H), 3.61 (d, J = 12.9 Hz, 1H), 3.43-3.36 (m, 1H), 1.25 (d, J = 6.5 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 145.2, 137.1, 134.2, 130.4, 130.1, 129.3, 128.5, 127.3, 126.2, 115.1, 55.3, 51.0, 22.0 ppm; HRMS (ESI) calculated [M+H]+ for C20H22N2Na = 313.1675, found: 313.1675.

(S,E)-4-((4-cyclohexylbut-3-en-2-yl)morpholine (3bb): with A4, 24 h, obtained pale yellow oil 29.8 mg; Isolated yield: 67%; The enantiomeric excess couldn’t be determined; [α]D25 = -25.2 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 5.47 (dd, J = 15.5, 6.5 Hz, 1H), 5.32-5.26 (m, 1H), 3.71 (t, J = 4.7 Hz, 4H), 2.81-2.74 (m, 1H), 2.55-2.42 (m, 4H), 1.97-1.89 (m, 1H), 1.74-1.67 (m, 4H), 1.67-1.62 (m, 1H), 1.32-1.16 (m, 3H), 1.14 (d, J = 6.5 Hz, 3H), 1.12-1.01 (m, 2H) ppm; 13C NMR (100 MHz, CDCl3) δ 138.6, 128.9, 67.2, 62.9, 50.5, 40.4, 33.1, 33.0, 26.2, 26.0, 18.0 ppm; HRMS (ESI) calculated [M+H]+ for C14H26NO = 224.2011, found: 224.2011.

(S,E)-1-((4-phenylbut-3-en-2-yl)piperidine-4-carboxamide (3bc): white solid 44.9 mg; Isolated yield: 87%; The enantiomeric excess couldn’t be determined; [α]D25 = -35.4 (c = 1.0, CHCl3); 1H NMR (400 MHz, CDCl3) δ 7.38-3.36 (m, 2H), 7.33-7.29 (m, 2H), 7.24-7.20 (m, 1H), 6.44 (d, J = 15.9 Hz, 1H), 6.20 (dd, J = 15.9, 7.9 Hz, 1H), 5.52 (br, s, 2H), 3.16-3.07 (m, 2H), 3.05-3.00 (m, 1H), 2.18-2.09 (m, 3H), 1.94-1.87 (m, 2H), 1.80-1.67 (m, 2H), 1.25 (d, J = 6.6 Hz, 3H) ppm; 13C NMR (100 MHz, CDCl3) δ 177.7, 137.0, 132.2, 130.7, 128.5, 127.3, 126.2, 62.4, 49.7, 49.5, 43.0, 29.2, 29.1, 17.6 ppm; HRMS (ESI) calculated [M+H]+ for C16H23N2O = 218.1176, found: 218.1177.
(S,E)-8-chloro-11-(1-(4-phenylbut-3-en-2-yl)piperidin-4-ylidene)-6,11-dihydro-5H-benzo[5,6]cyclohepta[1,2-b]pyridine (3bd): with A4, 48 h, obtained reddish orange oil 88.1 mg; Isolated yield: 99%; The enantiomeric excess couldn’t be determined; \([\alpha]_D^{25} = -64.3 \; (c = 1.0, \text{CHCl}_3); 3ay: \text{^1H NMR} \; (400 \text{ MHz, CDCl}_3) \delta 8.40-8.38 (m, 1H), 7.42 (dd, \; J = 7.7, 1.7 \text{ Hz, 1H}), 7.37-7.28 (m, 4H), 7.24-7.20 (m, 1H), 7.14-7.11 (m, 3H), 7.09-7.06 (m, 1H), 6.42 (d, \; J = 15.9 \text{ Hz, 1H}), 6.25-6.19 (m, 1H), 3.44-3.32 (m, 2H), 3.20-3.11 (m, 1H), 2.93-2.74 (m, 4H), 2.56-2.32 (m, 6H), 1.26 (d, \; J = 6.6 \text{ Hz, 3H}) ppm; \text{^13C NMR} \; (100 \text{ MHz, CDCl}_3) \delta 157.62, 146.57, 139.46, 139.09, 137.72, 137.20, 136.93, 133.40, 132.38, 132.08, 130.90, 130.82, 128.93, 128.51, 127.34, 126.24, 125.94, 122.04, 62.38, 51.63, 51.42, 31.83, 31.40, 31.08, 30.87, 17.83 ppm; \text{HRMS (ESI)} \; \text{calculated} \; [\text{M+Na}]^+ \; \text{for C}_{29}\text{H}_{29}\text{ClN}_2\text{Na} = 463.1911, \text{found: 463.1907.}

Non-reactive and inefficient substrates

we also have prepared two disubstituted dienes 1k and 1l, and examined them in the hydroamination reaction. It was found that substrate 1k could participate in the reaction to afford the corresponding product 3be in 22% yield and 68% ee. However, substrate 1l failed to provide the desired product (3bf and 3bg) under standard reaction condition.

![Figure S245](image.png)

Figure S245. Non-reactive and inefficient dienes, related to Figure 4.

Scalability of Asymmetric Hydroamination

Scheme S4 (related to Figure 3):
To a 20 mL vial was added the catalyst precursor Ni(COD)$_2$ (13.8 mg, 0.05 mmol), L8 (15.3 mg, 0.05 mmol) and toluene (5 mL) in an argon-filled glovebox. The mixture was stirred for 1 h at room temperature to give a clear orange solution. Then 1-phenylbutadiene (651.0 mg, 5.0 mmol, 1.0 equiv), amine (939.1 mg, 7.5 mmol, 1.5 equiv), A4 (41.5 mg, 0.25 mmol) and another 5 mL toluene was added in the catalyst solution. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 96 h. The product was purified by column chromatography on deactivated silica gel with PE/EtOAc=1:1 to yield 1.23 g of 3g (96% yield, 96% ee), the enantiomeric excess was determined by HPLC on Chiralpak AD-H column.

Transamination Experiments

Scheme S5 (related to Scheme 1):

Transamination Experiments

Scheme S5 (related to Scheme 1):
A stock solution was made by mixing Ni(COD)$_2$ with L8 in a 1:1 molar ratio in toluene (0.01 M) at room temperature for 1 h in an argon-filled glovebox. An aliquot of the catalyst solution (0.5 mL, 0.005 mmol) was transferred by syringe into the vials charged with 3t or 3k (0.1 mmol, 1.0 equiv), amines (2a or 2f, 0.1 mmol, 1.0 equiv) and naphthalene (3.2 mg, 0.025 mmol, 0.25 equiv), then 0.005 mmol A4 and another 0.5 mL toluene were added. The reaction vessel was sealed using a PTFE septum and removed from the glovebox, and the mixture was stirred at 25 °C for 24 h. Yields were determined by gas chromatogram analysis, using naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.

**Reaction Profiles**

**Scheme S6 (related to Figure 6):**

A stock solution was made by mixing Ni(COD)$_2$ with L8 in a 1:1 molar ratio in toluene (0.01 M) at room temperature for 1 h in an argon-filled glovebox. An aliquot of the catalyst solution (1.0 mL, 0.01 mmol) was transferred by syringe into the vials charged with 1a (0.4 mmol), amines (0.6 mmol for each) and naphthalene (12.8 mg, 0.1 mmol, 0.25 equiv), then A3 (3.2 mg, 0.02 mmol) or A4 (3.3 mg, 0.02 mmol) and another 1.0 mL toluene were added. The reaction vessel was sealed using a PTFE septum and stirred at 25 °C in the glovebox. The reaction progress was monitored by GC with naphthalene as the internal standard. The ee values were determined by HPLC on a chiral stationary phase.
| Time [h] | Yield [%] | ee [%] | Yield [%][b] | ee [%][b] | Yield [%][c] | ee [%][c] | Yield [%][d] | ee [%][d] |
|---------|-----------|--------|-------------|-----------|-------------|-----------|-------------|----------|
| 6 h     | 84        | 98     | 86          | 97        | 12          | 98        | 91          | 98       |
| 12 h    | 99        | 94     | 99          | 96        | 19          | 98        | 95          | 98       |
| 24 h    | 99        | 91     | 99          | 92        | 38          | 97        | 98          | 98       |
| 36 h    | 99        | 88     | 99          | 90        | 39          | 97        | 98          | 98       |
| 48 h    | 99        | 99     | 99          | 92        | 38          | 97        | 98          | 98       |

Reaction conditions: [a] 0.40 mmol 1a, 0.60 mmol 2a, 5.0 mol % Ni(COD)/L8, 5.0 mol % A3, 1 mL toluene, 25 °C, 48 h. [b] A4 instead of A3. [c] 2f instead of 2a. [d] 2f instead of 2a, A4 instead of A3.

Figure S246. Time Course of Scheme S6.

Deuterium Labeling Experiments

Scheme S7:

\[
\begin{align*}
\text{Ph} &= \text{C} = \text{C} \\
1a &+ d\text{-}2t \quad \text{65\% D} \\
\text{Ni(COD)}_2/L8 \quad (5 \text{ mol \%}) \\
&\quad \text{A3} \quad (5 \text{ mol \%}) \\
toluene, 25 ^\circ C, 24 h \\
\text{Ph} &\quad \text{Me} \\
d\text{-}3t &\quad 0.82 \text{ D} \\
91\% \text{ yield}
\end{align*}
\]

Reaction was carried as described in General Procedure for Ni-catalyzed Asymmetric Hydroamination of Conjugated Dienes. d-indoline was prepared by a known previously established method (Yi & Lee, 2009). The d-3t was determined by \(^1\)H NMR and \(^2\)H NMR analysis.

Amines Benzoylation for ee Determination (Wang et al, 2014)

Scheme S8 (related to Figure 3 and Figure 5):
To a solution of chiral amine 3 (0.20 mmol, 1.0 equiv) and triethylamine (42 μL, 0.30 mmol, 1.5 equiv) in DCM (0.8 mL) at 0 °C was added dropwise a solution of benzoyl chloride (28 μL, 0.24 mmol, 1.2 equiv) in DCM (0.2 mL). The mixture was warmed to room temperature and stirred overnight. The mixture was quenched with water (1.0 mL) and extracted with DCM (5.0 mL), and the aqueous layer was extracted with DCM (3.0 mL). The organic layers were combined, dried over sodium sulfate, and concentrated. The residue was purified by silica gel chromatography, eluting with ethyl acetate/petroleum ether, to give amide Bz-3.

Supplemental References

Adamson, N. J., Hull, E., and Malcolmson, S. J. (2017). Enantioselective Intermolecular Addition of Aliphatic Amines to Acyclic Dienes with a Pd–PHOX Catalyst. J. Am. Chem. Soc. 139, 7180−7183.

Davenport, E., and Fernandez, E. (2018). Transition-Metal-Free Synthesis of Vicinal Triborated Compounds and Selective Functionalisation of the Internal C–B Bond. Chem. Commun. 54, 10104-10107.

Hu, M.-Y., He, Q., Fan, S.-J., Wang, Z.-C., Liu, L.-Y., Mu, Y.-J., Peng, Q., and Zhu, S.-F. (2018). Ligands with 1,10-Phenanthroline Scaffold for Highly Regioselective Iron-Catalyzed Alkene Hydrosilylation. Nat. Commun. 9, 1-11.

Preuβ, T., Saak, W., and Doye, S. (2013). Titanium-Catalyzed Intermolecular Hydroaminoalkylation of Conjugated Dienes. Chem. Eur. J. 19, 3833-3837.

Sardini, S. R., and Brown, M. K. (2017). Catalyst Controlled Regiodivergent Arylboration of Dienes. J. Am. Chem. Soc. 139, 9823-9826.

Wang, Y., Li, M., Ma, X., Liu, C., Gu, Y., and Tian, S.-K. (2014). Deammoniative Condensation of Primary Allylic Amines with Nonallylic Amines. Chin. J. Chem. 32, 741-751.

Yi, C. S., and Lee, D. W. (2009). Efficient Dehydrogenation of Amines and Carbonyl Compounds Catalyzed by a Tetranuclear Ruthenium-μ-oxo-μ-hydroxo-hydride Complex. Organometallics 28, 947-949.