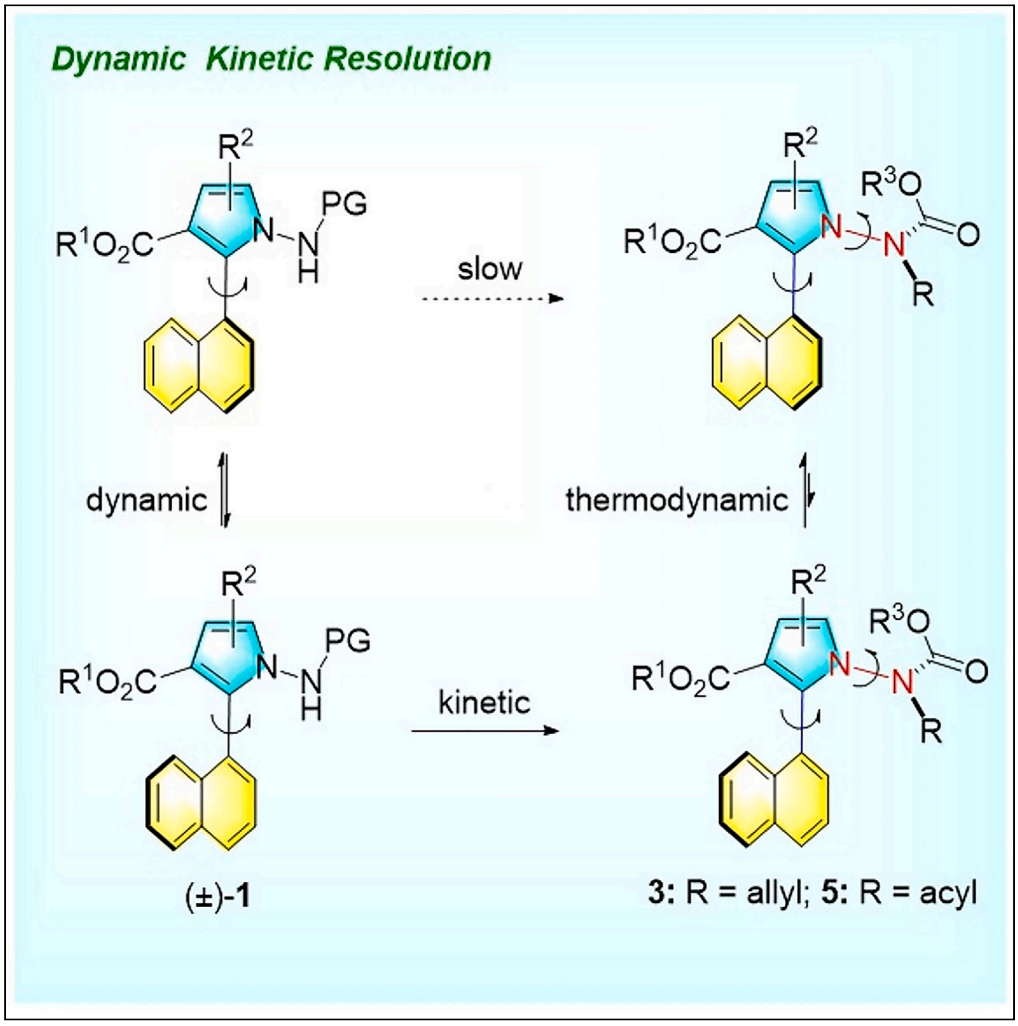
iScience

CellPress
OPEN ACCESS

Article

Catalytic atroposelective synthesis of heterobiaryls with vicinal C–C and N–N diaxes via dynamic kinetic resolution



Tian-Jiao Han, Chun-Yan Guan, Na Li, ..., Xiao Xiao, Min-Can Wang, Guang-Jian Mei

wangmincan@zzu.edu.cn (M.-C.W.)
meigj@zzu.edu.cn (G.-J.M.)

Highlights

Heterobiaryls with vicinal C–C and N–N diaxes

Dynamic kinetic resolution

Wide range of substrates, good yields and excellent enantioselectivities

Han et al., iScience 26, 107978
October 20, 2023
https://doi.org/10.1016/j.isci.2023.107978

iScience

CellPress
OPEN ACCESS

Article

Catalytic atroposelective synthesis of heterobiaryls with vicinal C–C and N–N diaxes via dynamic kinetic resolution

Tian-Jiao Han,[1,4] Chun-Yan Guan,[1,4] Na Li,[2] Rui Dong,[1] Li-Ping Xu,[2] Xiao Xiao,[3] Min-Can Wang,[1,*] and Guang-Jian Mei[1,5,*]

SUMMARY

Reported herein is a highly efficient dynamic kinetic resolution protocol for the atroposelective synthesis of heterobiaryls with vicinal C–C and N–N diaxes. Atropisomers bearing vicinal diaxes mainly exist in *o*-triaryls, while that of biaryls is highly challenging in terms of the concerted rotation and deplanarization effects. The combination of C–C biaryl with N–N nonbiaryl delivers a novel class of vicinal-diaxis heterobiaryls. For their atroposelective synthesis, the dynamic kinetic resolution enabled by either quinine-catalyzed allylation or isothiourea-catalyzed acylation has been developed, allowing the preparation of a wide range of vicinal-axis heterobiaryls in good yields with excellent enantioselectivities. Atropisomerization experiments revealed that the C–C bond rotation led to diastereomers, and the N–N bond rotation offered enantiomers. Besides, this protocol could be extended to kinetic resolution by employing substrates with a more hindered axis.

INTRODUCTION

Atropisomeric biaryls arising from axially restricted aryl–aryl bond rotation are known for their wide prevalence in natural products, organocatalysts, chiral ligands, pharmaceuticals, and functional materials.[1–5] The past decades have witnessed significant progress in the preparation of atropisomeric biaryls with a single stereogenic axis.[6–11] Atropisomers bearing vicinal diaxes are particularly intriguing for materials sciences, as they mainly exist in *o*-triaryls (Figure 1A).[12] Nevertheless, the concerted rotation of 1,2-diaxes poses a daunting challenge to enantiocontrol.[13] To date, only a few successful catalytic asymmetric methods have been reported to access *o*-triaryls, which include the *de novo* construction of (hetero)arenes,[14–20] the central-to-axial chirality conversion,[21] and the atroposelective C–H activation.[22–24] Although one can certainly design an *o*-triaryl atropisomer by merging two readily available biaryls, it is hard to imagine an atropisomeric biaryl with vicinal diaxes. To make that possible, the key is to find a suitable nonbiaryl system that can be merged. However, under equal conditions, the lower rotation barrier induced by the deplanarization renders a less stable conformer of nonbiaryls.[25–30] This is the case in the pioneering contributions of the groups of Hsung building chiral *ortho*-disubstituted *N,O*-biaryls by combining the C–C and C–N axial chirality.[31] Later, the preparation of 1,2-diaxially chiral biaryl benzamides had been achieved by Tanaka.[32] More recently, the He group accomplished the synthesis of diaxially chiral *B,N*-heterobiaryls bearing vicinal C–B and C–N axes via a stepwise asymmetric allylic substitution-isomerization strategy.[33] Although these creative studies showcased the concept of biaryl atropisomers with vicinal diaxes, the catalytic atroposelective synthesis is still in its infancy and developing new structural types is highly desirable yet challenging.

The N–N bond is ubiquitous in natural products and bioactive compounds,[33–35] while its atropisomerism has been largely overlooked. Although the first consideration of N–N atropisomers can be traced back to 1931,[36] catalytic asymmetric synthesis has not been reported until recently.[37,38] With the appropriate bulkiness and electronic properties, N–N heterobiaryls can be atropisomeric in analogy to C–C biaryls (Figure 1B). In this context, enantioselective synthetic approaches to access structurally diverse indole-pyrrole, indole-carbazole, bispyrrole, and bisindole atropisomers with an N–N axis has been reported by Liu, Shi and others.[39–49] More importantly, nitrogen atom can assume a stable planar geometry beyond the aromatic ring since the unpaired electrons could conjugate with a carbonyl group. As a result, N–N axial chirality can be found in nonbiaryl systems. The seminal work came from the Lu group, in which they accomplished the asymmetric synthesis of N–N atropisomeric 1-aminopyrroles and 3-aminoquinazolinones.[50–52] Furthermore, Bencivenni et al. described the catalytic stereoselective synthesis of hydrazides containing a rotationally stable N–N axis by a sequential catalysis protocol.[53] Inspired by these impressive

[1]College of Chemistry, Pingyuan Laboratory, Zhengzhou University, Zhengzhou 450001, China
[2]School of Chemistry and Chemical Engineering, Shandong University of Technology, Zibo 255000, Shandong, China
[3]Collaborative Innovation Center of Yangtze River Delta Region Green Pharmaceuticals, Zhejiang University of Technology, Hangzhou 310014, People's Republic China
[4]These authors contribute equally
[5]Lead contact
*Correspondence: wangmincan@zzu.edu.cn (M.-C.W.), meigj@zzu.edu.cn (G.-J.M.)
https://doi.org/10.1016/j.isci.2023.107978

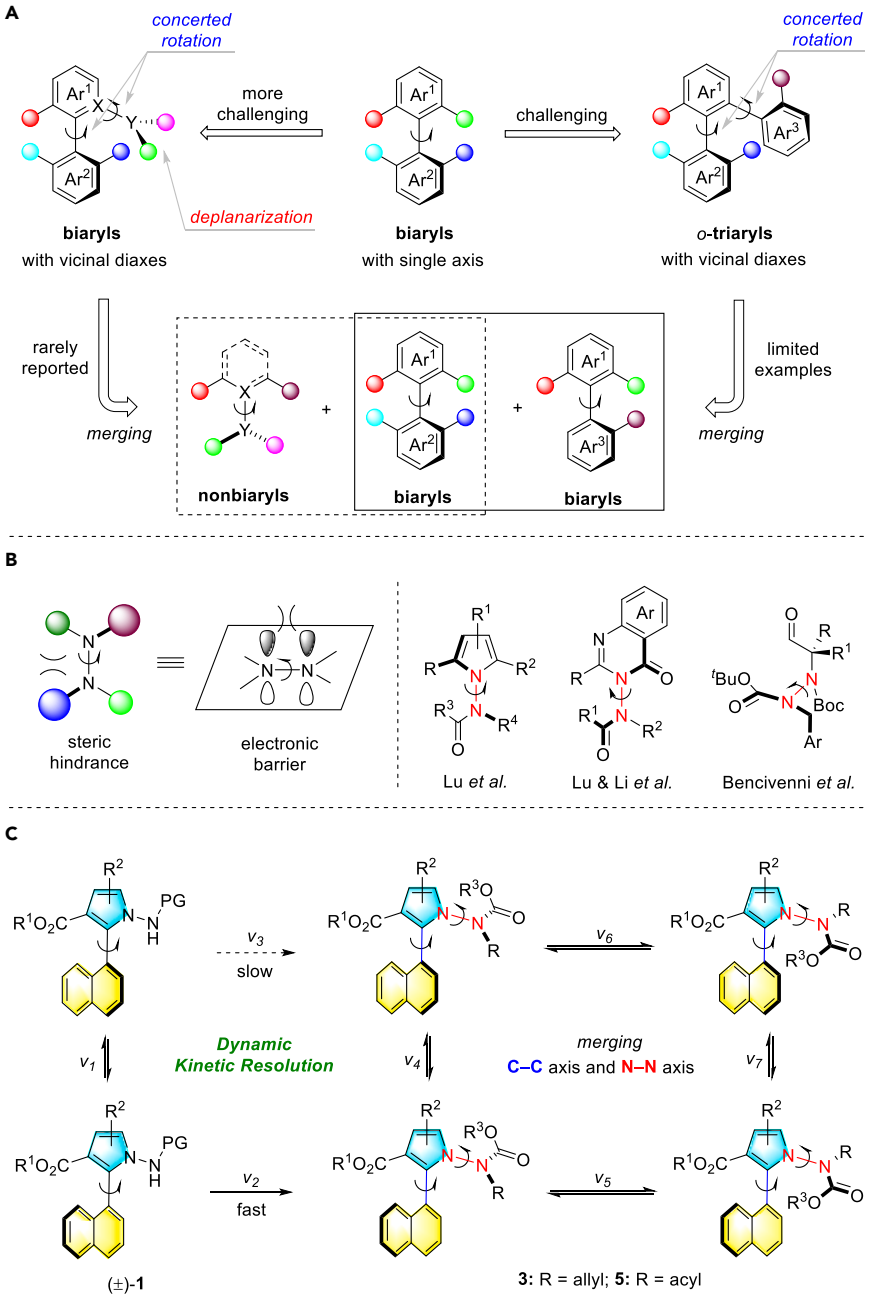
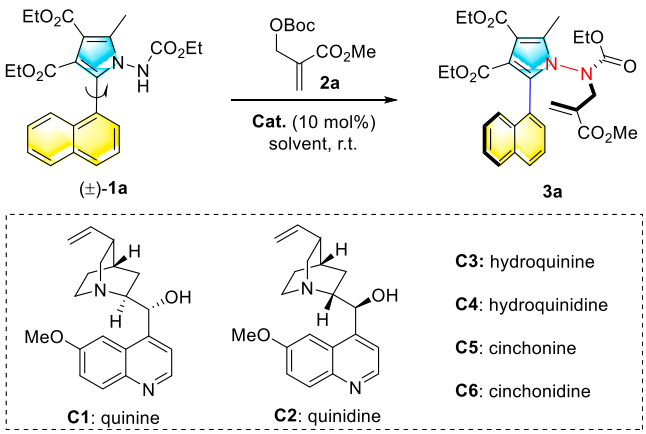


Figure 1. Enantioselective synthesis of atropisomers with vicinal diaxes

(A–C) (A) Vicinal-diaxis systems; (B) N-N Axial chirality in nonbiaryls; (C) This work.

achievements, we envision that a biaryl atropisomer bearing vicinal C−C and N−N diaxes is feasible and with a suitable synthetic strategy its asymmetric synthesis can be achieved.

Dynamic kinetic resolution (DKR) represents a particularly appealing strategy for the synthesis of atropisomers from preformed racemic biaryls.[7,54] The dynamics of atropisomers well conform to the requirement of DKR for the racemization of starting materials during reaction process. Consequently, DKR has been exploited with success in preparing various biaryls with a single stereogenic axis.[55–64] However, when it comes to multi-axis systems, especially the vicinal-axis system, the stereocontrol is problematic. To our knowledge, the Miller group has successfully achieved the DKR of configurationally labile axes for atropisomerically enriched two-axis systems.[13,65,66] DKR of racemic biaryls with a configurationally stable axis remains challenging and elusive. Our group has a continuous interest in developing effective methods to access structurally important axially chiral compounds.[28,52,67] Along this line, we envision that the enantioselective synthesis of vicinal-axis



Scheme 1. Reaction optimization

atropisomers could be enabled by DKR (Figure 1C). However, an effective DKR should fit the following criterions: (1) the catalyst must precisely discriminate the two enantiomers of starting material (v_2>v_3); (2) the enantioselective transformation must be slower than the racemization of the starting materials but faster than the racemization of the products (v_1>v_2>v_4/v_6 *or* v_5/v_7).

To address these issues, herein, we report in detail the catalytic atroposelective synthesis of heterobiaryls with vicinal C−C and N−N diaxes via DKR (Figure 1C). Notably, this DKR reaction can be enabled by either quinine-catalyzed allylation or isothiourea-catalyzed acylation, allowing the formation of vicinal-axis biaryls 3 and 5 in good yields and with excellent enantioselectivities. Not only are the products a new addition to atropisomeric biaryls with vicinal diaxes, but the protocol enriches the DKR strategy in atroposelective synthesis.

RESULTS

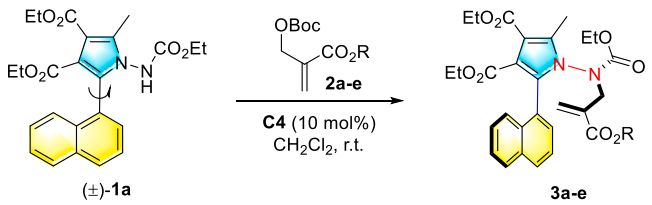
The rational design of starting materials is crucial for an effective DKR. In our recent work on atroposelective synthesis of axially chiral C2-arylpyrrole-derived amino alcohols,[67] we found that heterobiaryl **1a** possesses an atropoisomeric C–C bond which can rotate dynamically at room temperature (see the supplemental information for HPLC analysis on a chiral stationary phase). Considering that the *N*-functionalization could introduce sufficient rotation constraint for C–C and N–N bonds, **1a** was chosen as our model substrate for our development of DKR. Asymmetric allylation of **1a** with the Morita–Baylis–Hillman (MBH) adduct **2a** in the presence of various quinolines was examined (Scheme 1) and the results are summarized in Table 1. To our delight, the DKR of **1a** occurred under the catalysis of **C1** in CH_2Cl_2 at room temperature, delivering the desired vicinal-axis product **3a** as diastereoisomers in a moderate yield (entry 1). The screening of catalysts indicated that **C4** was the best choice in terms of yield and stereoselectivity (entry 4). The solvent effect was then examined. Although toluene could increase the *ee* value, the yield decreased significantly (entry 7). Acetonitrile and tetrahydrofuran failed to afford enhancements (entries 8 & 9). At −20°C, the product **3a** was obtained in a good enantioselectivity, however, the yield and the diastereoselectivity declined (entry 10).

Further improvements were achieved by utilizing various MBH carbonates with different ester moieties (Scheme 2). The results implied that the steric effect had some influence on the enantio-control (Table 2). Changing the small methyl group (**2a**) to the sterically bulky groups such

Table 1. Reaction optimization

Entry	Cat.	Solvent	Yield (%)	dr	*ee* (%)
1	C1	CH_2Cl_2	53	1.7:1	85/84
2	C2	CH_2Cl_2	32	2.5:1	86/83
3	C3	CH_2Cl_2	96	2.6:1	74/74
4	C4	CH_2Cl_2	94	3.2:1	86/80
5	C5	CH_2Cl_2	33	2.8:1	78/75
6	C6	CH_2Cl_2	67	2.7:1	75/75
7	C4	toluene	10	1.3:1	90/86
8	C4	CH_3CN	84	2.4:1	72/66
9	C4	THF	77	2.4:1	69/66
10[a]	C4	CH_2Cl_2	50	1.6:1	90/89

Reaction conditions: **1a** (0.1 mmol), **2a** (0.15 mmol), and **Cat.** (10 mol %) in the solvent specified (1 mL) at RT for 12 h; Yields refer to isolated yields; The ee values were determined by HPLC analysis on a chiral stationary phase; The dr ratios were determined by ^{1}H NMR.
[a]Performed at −20°C.



Scheme 2. Further optimization by screening MBH carbonates

as ethyl (**2b**), benzyl (**2c**), and *n*-butyl (**2d**) resulted in enhanced enantioselectivities (entries 2–4). Notably, with the employment of *t*-butyl MBH carbonate (**2e**), the allylation product **3e** was obtained in 96% yield with 2.8:1 dr and 95%/93% *ee* (entry 5).

With the best conditions established, the generality of the substrate was studied. As shown in Figure 2, this *N*-alkylation enabled DKR protocol was applicable to a broad range of racemic heterobiaryls **1**. Firstly, the *N*-protecting group ($-CO_2R^4$) could be varied, giving the consistently good yields and excellent enantioselectivities (**3f**–**i**). Among them, the bulky fluorenylmethyl ester group led to a higher diastereoselectivity (**3h**). The tolerance of the ester group far from the central axis ($-CO_2R^2$) was also investigated, while almost no influence on the reaction was observed (**3j**–**m**). The ester group $-CO_2R^1$ was supposed to have an impact on the C–C bond rotation. However, the small methyl group (**3n**) and sterically bulky propyl groups (**3o** and **3p**) gave the similar good results. Different R^3 group (**3q**–**t**) at the pyrrole ring were also well tolerated. In addition to the excellent yields and *ee* values, *n*-propyl (**3r**) and benzyl (**3t**) afforded the increased diastereoselectivities. Next, a variety of heterobiaryls **1** bearing different substituents at the naphthyl ring were employed. From the excellent yields and *ee* values of the products **3u**–**3b′**, it seems that both the electronic nature and the patterns of the substituents have little effect on the reaction efficiency and stereoselectivity. Remarkably, substrates with 5,7-dimethyl naphthyl group (**3c′**) or anthranyl group (**3d′**) were also compatible with this reaction.

Encouraged by the success of *N*-allylation, we preliminarily attempted other asymmetric *N*-functionalization reactions for this DKR protocol (see the supplemental information for details). We were pleased to discover that the DKR of heterobiaryls **1** could also be achieved by the isothiourea-catalyzed acylation. As shown in Figure 3, under the catalysis of chiral isothiourea **C7** in CH_2Cl_2 at room temperature, racemic **1e** reacted with cinnamic anhydride **4a** in a DKR manner, delivering the corresponding vicinal-diaxis product **5a** in moderate enantioselectivity. The subsequent reaction optimization revealed that the chiral isothiourea **C9** was the best catalyst, affording the correspond product in 95% yield with 1.3:1 dr and 90%/90% *ee* values. With the best conditions in hand, the substrate scope of this catalytic asymmetric acylation had been investigated (Figure 4). Remarkably, in all the substrates tested, the asymmetric DKR reaction took place smoothly, affording the corresponding vicinal-diaxis heterobiaryls **5a**–**5l** in good yields with excellent enantioselectivities.

Furthermore, the atropisomerization of **3b′** was conducted to investigate the configurational stability, which showed that the C–C and N–N axes are of different rotational barriers (Figure 5A). Rotation over the lower-barrier axis determines the dr value and that of the higher-barrier axis determines the *ee* value. The two diastereomers (*R,S*)-**3b′** and (*S,S*)-**3b′** are separable, and their interconversion over the C–C bond could be readily observed at the ambient temperature. Given the difference of the two diastereomers in structural stability, their energy barriers for interconversion should be slightly different. This analysis is consistent with experiments that complete erosion of dr values of the major isomer (*R,S*)-**3b′** to equilibrium, requiring 24.0 kcal/mol, while that of the minor isomer (*S,S*)-**3b′** only needs 23.5 kcal/mol. On the other hand, the racemization over the both axes occurs at about 130°C. The rotation barrier is determined to be 31.8 kcal/mol, which is similar to that 31.2 kcal/mol of compound **6** with a single N–N axis (Figure 5B). Thus, the rotation over the N–N axis dominates the atropisomerization of **3b′**. In addition, the rotational barrier on the C-C bond of substrate **1f** was calculated to be 22.9 kcal/mol, so, there was a slight increase in the energy of the C-C bond after reaction. Substrate **7** with a Bn-protected naphthol motif caused a higher rotation barrier (32.8 kcal/mol). The rotational energy barrier of **7** was so high that it does not racemate at room temperature and results in a kinetic resolution. To verify this hypothesis, hereobiaryl **7** was employed (Figure 5C). Under similar conditions, the catalytic asymmetric allylation occurred smoothly in a kinetic resolution manner. The corresponding vicinal-diaxis compound **8** was obtained in 46% yield with 7.7:1 dr and 92%/94% *ee* values, and the compound **7** was recovered in 43% yield and with 90% *ee*. In terms of the high *s*-factor (*s* = 95) achieved, this kinetic resolution is synthetically useful and will be fully investigated in the future. Finally, kinetic experiments were performed to shed light on the mechanism. As shown

Table 2. Further optimization by screening MBH carbonates

Entry	R/2	3	Yield (%)	dr	*ee* (%)
1	Me (**2a**)	**3a**	94	3.2:1	86/80
2	Et (**2b**)	**3b**	95	3.2:1	93/91
3	Bn (**2c**)	**3c**	93	3:1	93/91
4	^{n}Bu (**2d**)	**3d**	94	2.8:1	94/92
5	^{t}Bu (**2e**)	**3e**	96	2.8:1	95/93

Reaction conditions: **1a** (0.1 mmol), **2** (0.15 mmol), and **C4** (10 mol %) in CH_2Cl_2 (1 mL) at RT for 12 h; Yields refer to isolated yields; The *ee* values were determined by HPLC analysis on a chiral stationary phase; The dr ratios were determined by ^{1}H NMR.

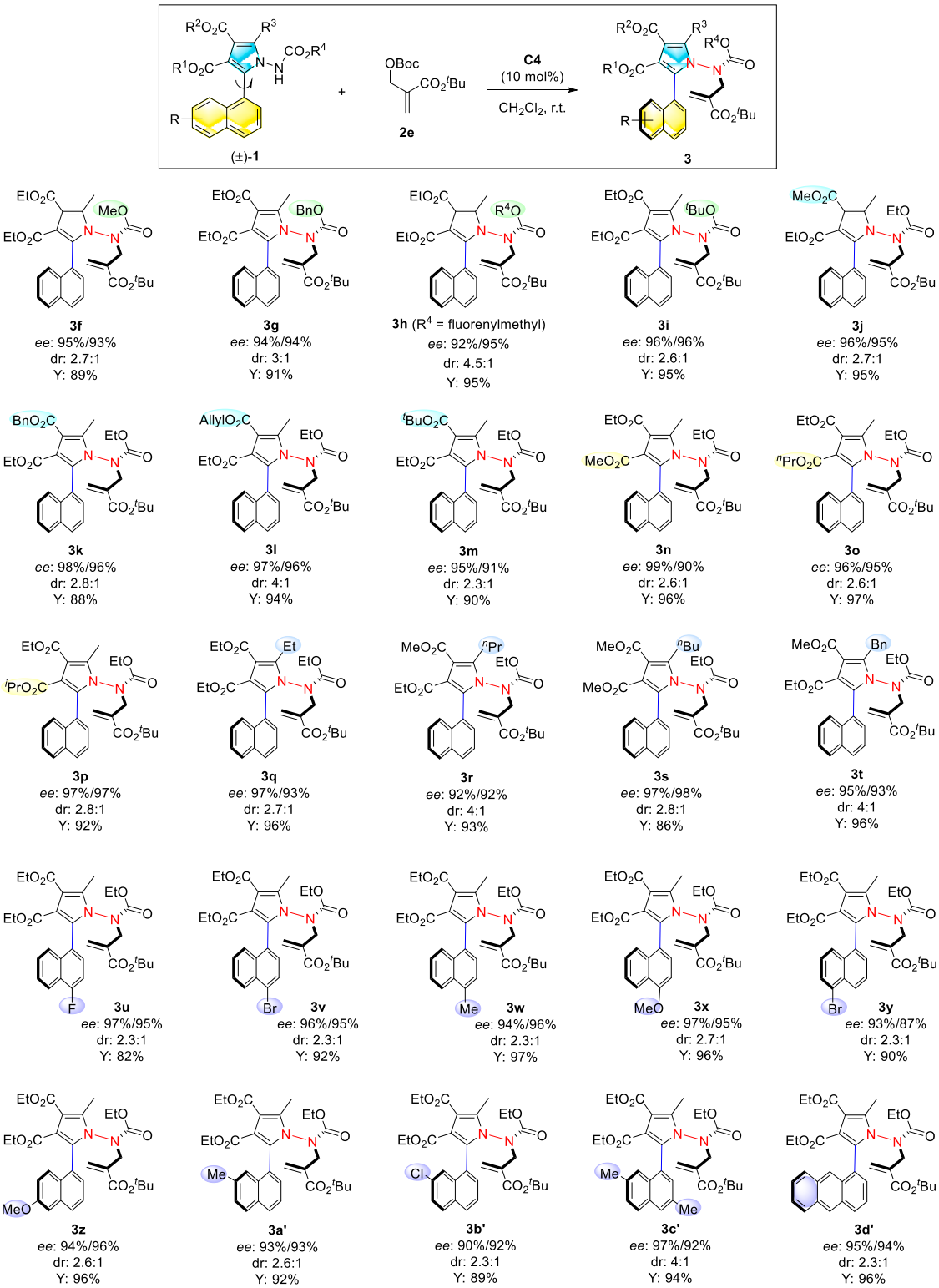


Figure 2. Substrate scope for allylation

Reaction conditions: **1a** (0.1 mmol), **2e** (0.15 mmol), and **C4** (10 mol %) in CH_2Cl_2 (1 mL) at RT for 12 h; Yields refer to isolated yields; The *ee* values were determined by HPLC analysis on a chiral stationary phase; The dr ratios were determined by ^1H NMR.

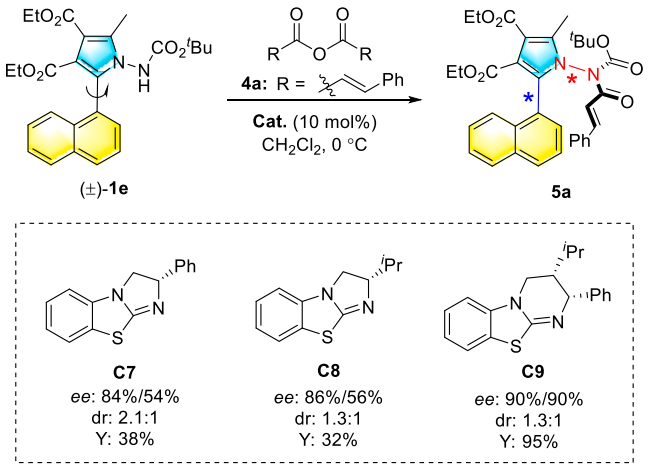


Figure 3. DKR via acylation

Reaction conditions: **1e** (0.1 mmol), **4a** (0.15 mmol), and the **Cat.** (0.01 mmol) in CH_2Cl_2 (1 mL) at 0°C for 12 h. Isolated yields. The dr and *ee* values were determined by HPLC analysis on a chiral stationary phase.

in Figure 5D, the dr value of the product underwent a reversal over time, and the *ee* value of the substrate **1b′** always remained at a low level. At the beginning, the dr and ee values of the product were very high, indicating that the enantioselectivity was set under kinetic control. However, the dr value decreased over reaction time, and even reversed finally (from 1:10 to 1.9:1). So, the final dr was set under thermodynamic control.

DISCUSSION

In conclusion, we have established a highly efficient DKR protocol for the atroposelective synthesis of heterobiaryls with vicinal C−C and N−N diaxes. Atropisomers bearing vicinal diaxes mainly exist in *o*-triaryls, vicinal-diaxis biaryls has traditionally been regarded as challenging structural motifs. By using this protocol, a wide range of vicinal-axis heterobiaryls were readily prepared in good yields with excellent enantioselectivities under mild conditions. Notably, this dynamic kinetic resolution reaction can be enabled by either quinine-catalyzed allylation or isothiourea-catalyzed acylation. Atropisomerization experiments revealed that the C−C bond rotation led to diastereomers, while that of N−N bond of enantiomers. Besides, this protocol could be extended to kinetic resolution by employing substrates with a more hindered axis. Further investigation along this line is ongoing, and will be reported in due course.

Limitations of the study

The diastereoselectivities are relatively low, which can be attributed to the low rotational barrier at the C-C stereogenic axis in the products. The limited configurational stability at the C-C axes may hinder the practical application of the obtained products.

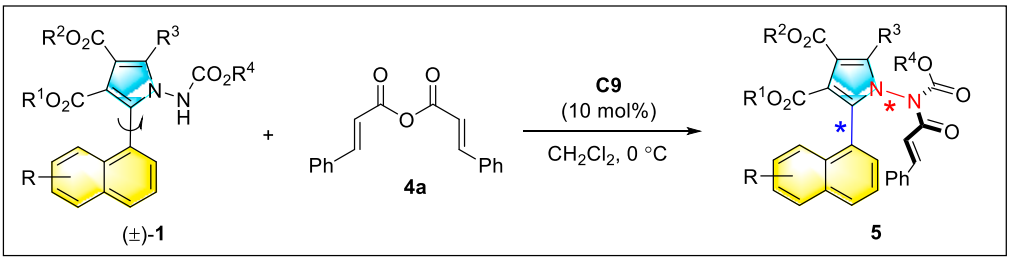
STAR★METHODS

Detailed methods are provided in the online version of this paper and include the following:

- KEY RESOURCES TABLE
- RESOURCE AVAILABILITY
  - Lead contact
  - Materials availability
  - Data and code availability
- METHODS DETAILS
  - General procedures for asymmetric allylation
  - (*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3e
  - General procedures for asymmetric acylation
  - General procedure for asymmetric synthesis of compound 6
  - General procedure for kinetic resolution of 7

SUPPLEMENTAL INFORMATION

Supplemental information can be found online at https://doi.org/10.1016/j.isci.2023.107978.



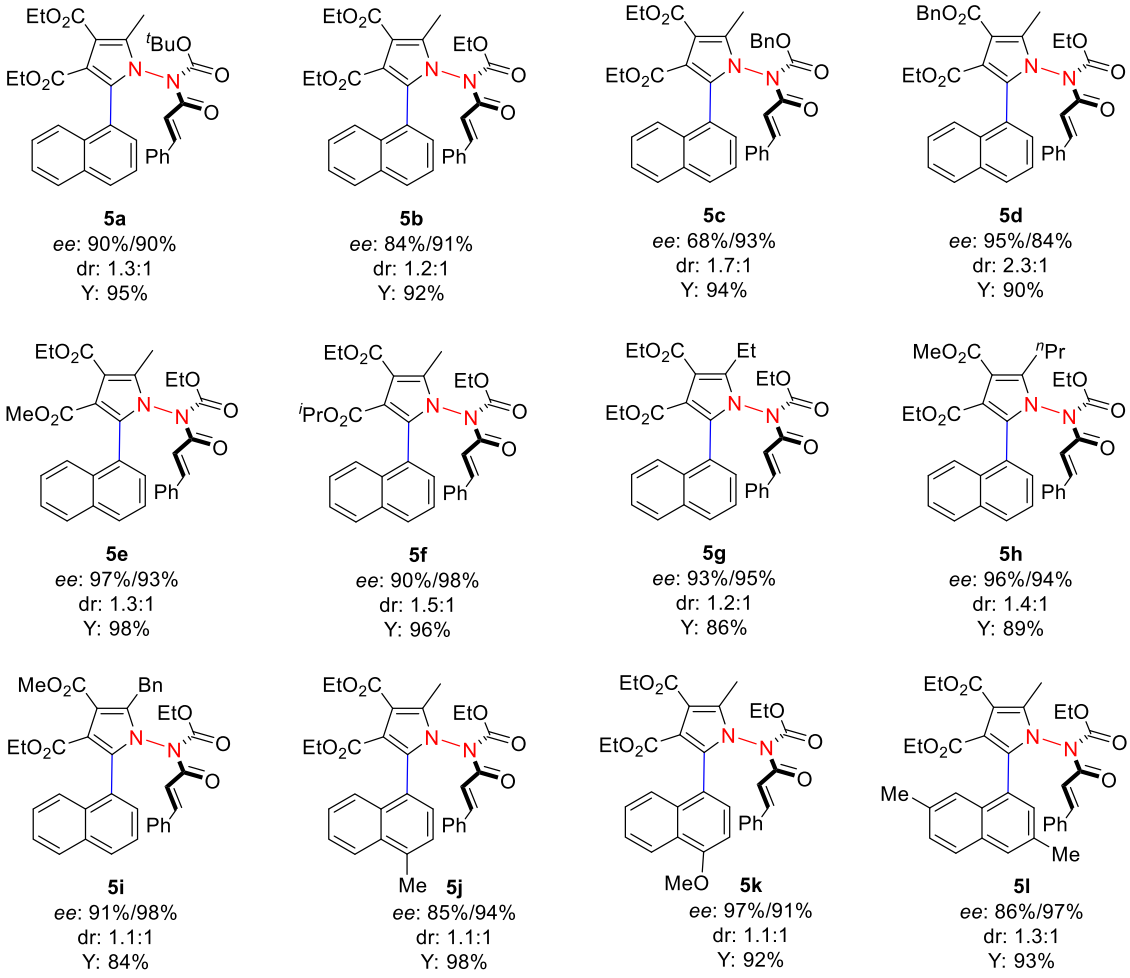


Figure 4. Substrate scope for acylation

Reaction conditions: **1** (0.1 mmol), **4a** (0.15 mmol), and the **C9** (0.01 mmol) in CH_2Cl_2 (1 mL) at 0°C for 12 h. Isolated yields. The dr and *ee* values were determined by HPLC analysis on a chiral stationary phase.

ACKNOWLEDGMENTS

Financial supports from National Natural Science Foundation of China (22371265 to G.-J. Mei, 22208302 to X. Xiao), Natural Science Foundation of Henan Province (222300420084 to G.-J. Mei), and Application Research Plan of Key Scientific Research Projects in Colleges and Universities of Henan Province (22A150056 to G.-J. Mei) are gratefully acknowledged.

AUTHOR CONTRIBUTIONS

T-J.H. and C-Y.G. performed and analyzed the experiments. R.D., X.X., and M-C.W. participated in the early development of the project. N.L. and L-P.X. performed the calculations. G-J.M. conceived and designed the project. G-J.M. overall supervised the project. All authors prepared this manuscript.

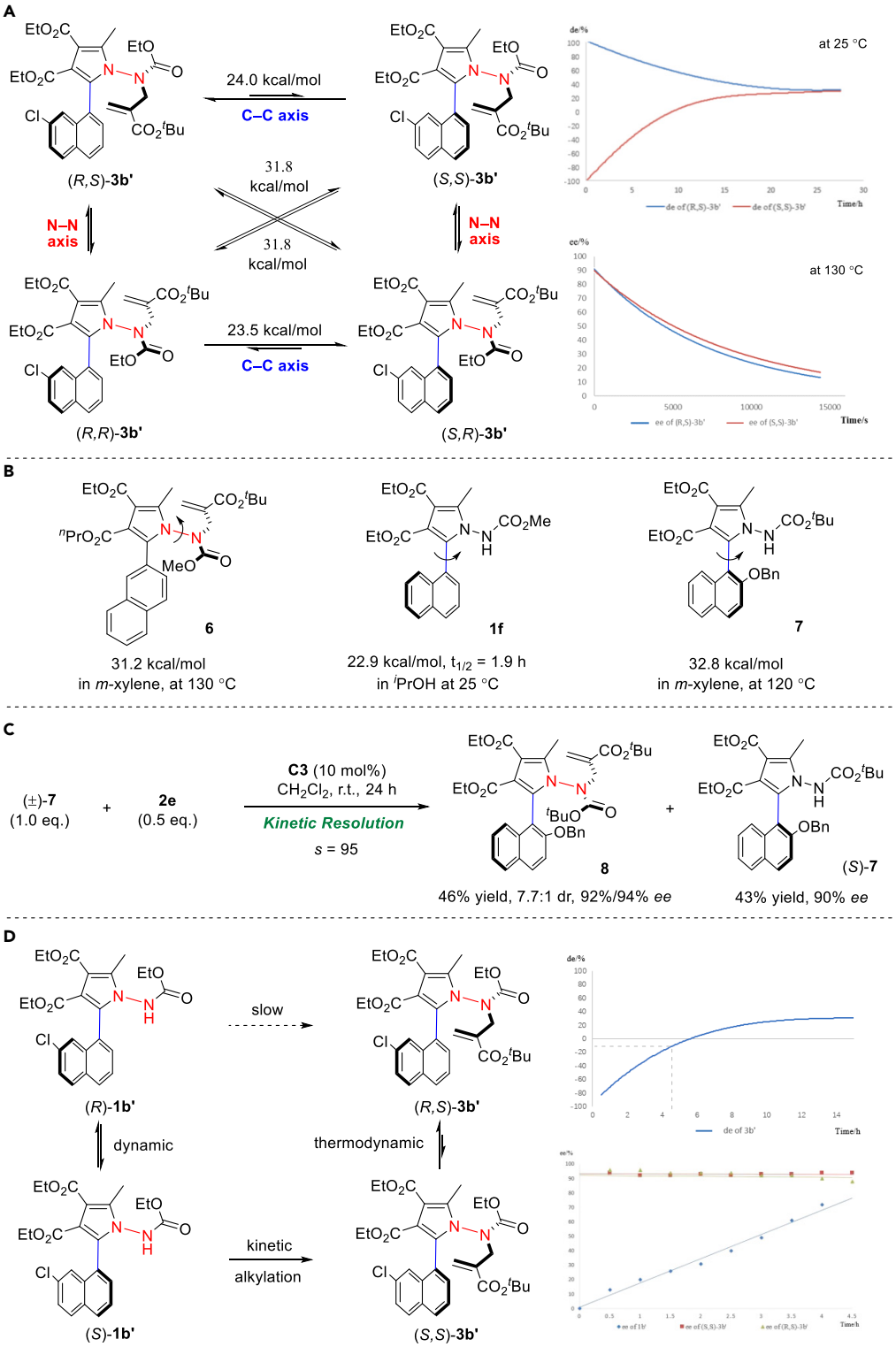


Figure 5. Atropisomerization and kinetic resolution

(A–D) (A) Racemization experiments; (B) Rotational energy barriers; (C) Kinetic resolution; (D) Mechanism considerations. After 4.5 h, **1b'** was fully consumed, the de value was determined by HPLC.

DECLARATION OF INTERESTS

The authors declare no competing interests.

Received: July 5, 2023
Revised: September 7, 2023
Accepted: September 15, 2023
Published: September 20, 2023

REFERENCES

1. Laplante, S.R., D Fader, L., Fandrick, K.R., Fandrick, D.R., Hucke, O., Kemper, R., Miller, S.P.F., Edwards, P.J., and Edwards, P.J. (2011). Assessing atropisomer axial chirality in drug discovery and development. J. Med. Chem. *54*, 7005–7022. https://doi.org/10.1021/jm200584g.
2. Cozzi, P.G., Emer, E., and Gualandi, A. (2011). Atroposelective organocatalysis. Angew. Chem. Int. Ed. *50*, 3847–3849. https://doi.org/10.1002/anie.201008031.
3. Bringmann, G., Gulder, T., Gulder, T.A.M., and Breuning, M. (2011). Atroposelective Total Synthesis of Axially Chiral Biaryl Natural Products. Chem. Rev. *111*, 563–639. https://doi.org/10.1021/cr100155e.
4. Kozlowski, M.C., Morgan, B.J., and Linton, E.C. (2009). Total synthesis of chiral biaryl natural products by asymmetric biaryl coupling. Chem. Soc. Rev. *38*, 3193–3207. https://doi.org/10.1039/B821092F.
5. Bringmann, G., and Menche, D. (2001). Stereoselective Total Synthesis of Axially Chiral Natural Products via Biaryl Lactones. Acc. Chem. Res. *34*, 615–624. https://doi.org/10.1021/ar000106z.
6. Cheng, J.K., Xiang, S.H., Li, S., Ye, L., and Tan, B. (2021). Recent Advances in Catalytic Asymmetric Construction of Atropisomers. Chem. Rev. *121*, 4805–4902. https://doi.org/10.1021/acs.chemrev.0c01306.
7. Carmona, J.A., Rodríguez-Franco, C., Fernández, R., Hornillos, V., and Lassaletta, J.M. (2021). Atroposelective transformation of axially chiral (hetero)biaryls. From desymmetrization to modern resolution strategies. Chem. Soc. Rev. *50*, 2968–2983. https://doi.org/10.1039/D0CS00870B.
8. Li, T.Z., Liu, S.J., Tan, W., and Shi, F. (2020). Catalytic Asymmetric Construction of Axially Chiral Indole-Based Frameworks: An Emerging Area. Chem. Eur J. *26*, 15779–15792. https://doi.org/10.1002/chem.202001397.
9. Zhang, S., Liao, G., and Shi, B. (2019). Enantioselective Synthesis of Atropisomers Featuring Pentatomic Heteroaromatics. Chin. J. Org. Chem. *39*, 1522–1528. https://doi.org/10.6023/cjoc201904030.
10. Liao, G., Zhou, T., Yao, Q.J., and Shi, B.F. (2019). Recent advances in the synthesis of axially chiral biaryls via transition metal-catalysed asymmetric C-H functionalization. Chem. Commun. *55*, 8514–8523. https://doi.org/10.1039/c9cc03967h.
11. Bringmann, G., Price Mortimer, A.J., Keller, P.A., Gresser, M.J., Garner, J., and Breuning, M. (2005). Atroposelective synthesis of axially chiral biaryl compounds. Angew. Chem. Int. Ed. *44*, 5384–5427. https://doi.org/10.1002/anie.200462661.
12. Bao, X., Rodriguez, J., and Bonne, D. (2020). Enantioselective Synthesis of Atropisomers with Multiple Stereogenic Axes. Angew. Chem. Int. Ed. *59*, 12623–12634. https://doi.org/10.1002/anie.202002518.
13. Barrett, K.T., Metrano, A.J., Rablen, P.R., and Miller, S.J. (2014). Spontaneous transfer of chirality in an atropisomerically enriched two-axis system. Nature *509*, 71–75. https://doi.org/10.1038/nature13189.
14. Zhang, S.-C., Liu, S., Wang, X., Wang, S.-J., Yang, H., Li, L., Yang, B., Wong, M.W., Zhao, Y., and Lu, S. (2023). Enantioselective Access to Triaryl-2-pyrones with Monoaxial or Contiguous C–C Diaxes via Oxidative NHC Catalysis. ACS Catal. *13*, 2565–2575. https://doi.org/10.1021/acscatal.2c05570.
15. Zhang, S., Wang, X., Han, L.L., Li, J., Liang, Z., Wei, D., and Du, D. (2022). Atroposelective Synthesis of Triaryl alpha-Pyranones with 1,2-Diaxes by N-Heterocyclic Carbene Organocatalysis. Angew. Chem. Int. Ed. *61*, e202212005. https://doi.org/10.1002/anie.202212005.
16. Xu, D., Huang, S., Hu, F., Peng, L., Jia, S., Mao, H., Gong, X., Li, F., Qin, W., and Yan, H. (2022). Diversity-Oriented Enantioselective Construction of Atropisomeric Heterobiaryls and N-Aryl Indoles via Vinylidene Ortho-Quinone Methides. CCS Chem. *4*, 2686–2697. https://doi.org/10.31635/ccschem.021.202101154.
17. Moser, D., and Sparr, C. (2022). Synthesis of Atropisomeric Two-Axis Systems by the Catalyst-Controlled syn- and anti-Selective Arene-Forming Aldol Condensation. Angew. Chem. Int. Ed. *61*, e202202548. https://doi.org/10.1002/anie.202202548.
18. Lotter, D., Castrogiovanni, A., Neuburger, M., and Sparr, C. (2018). Catalyst-Controlled Stereodivergent Synthesis of Atropisomeric Multiaxis Systems. ACS Cent. Sci. *4*, 656–660. https://doi.org/10.1021/acscentsci.8b00204.
19. Lotter, D., Neuburger, M., Rickhaus, M., Häussinger, D., and Sparr, C. (2016). Stereoselective Arene-Forming Aldol Condensation: Synthesis of Configurationally Stable Oligo-1,2-naphthylenes. Angew. Chem. Int. Ed. *55*, 2920–2923. https://doi.org/10.1002/anie.201510259.
20. Shibata, T., Tsuchikama, K., and Otsuka, M. (2006). Enantioselective intramolecular [2+2+2] cycloaddition of triynes for the synthesis of atropisomeric chiral ortho-diarylbenzene derivatives. Tetrahedron: Asymmetry *17*, 614–619. https://doi.org/10.1016/j.tetasy.2005.12.033.
21. Wei, L., Shen, C., Hu, Y.Z., Tao, H.Y., and Wang, C.J. (2019). Enantioselective synthesis of multi-nitrogen-containing heterocycles using azoalkenes as key intermediates. Chem. Commun. *55*, 6672–6684. https://doi.org/10.1039/c9cc02371b.
22. Wang, B.-J., Xu, G.-X., Huang, Z.-W., Wu, X., Hong, X., Yao, Q.-J., and Shi, B.-F. (2022). Single-Step Synthesis of Atropisomers with Vicinal C−C and C−N Diaxes by Cobalt-Catalyzed Atroposelective C−H Annulation. Angew. Chem. Int. Ed. *61*, e202208912. https://doi.org/10.1002/anie.202208912.
23. Gao, Q., Wu, C., Deng, S., Li, L., Liu, Z.S., Hua, Y., Ye, J., Liu, C., Cheng, H.G., Cong, H., et al. (2021). Catalytic Synthesis of Atropisomeric o-Terphenyls with 1,2-Diaxes via Axial-to-Axial Diastereoinduction. J. Am. Chem. Soc. *143*, 7253–7260. https://doi.org/10.1021/jacs.1c02405.
24. Dherbassy, Q., Djukic, J.P., Wencel-Delord, J., and Colobert, F. (2018). Two Stereoinduction Events in One C-H Activation Step: A Route towards Terphenyl Ligands with Two Atropisomeric Axes. Angew. Chem. Int. Ed. *57*, 4668–4672. https://doi.org/10.1002/anie.201801130.
25. Wu, Y.-J., Liao, G., and Shi, B.-F. (2022). Stereoselective construction of atropisomers featuring a C–N chiral axis. Green Synth. Catal. *3*, 117–136. https://doi.org/10.1016/j.gresc.2021.12.005.
26. Wu, S., Xiang, S.-H., Cheng, J.K., and Tan, B. (2022). Axially chiral alkenes: Atroposelective synthesis and applications. Tetrahedron Chem *1*, 100009. https://doi.org/10.1016/j.tchem.2022.100009.
27. Rodríguez-Salamanca, P., Fernández, R., Hornillos, V., and Lassaletta, J.M. (2022). Asymmetric Synthesis of Axially Chiral C-N Atropisomers. Chem. Eur J. *28*, e202104442. https://doi.org/10.1002/chem.202104442.
28. Mei, G.-J., Koay, W.L., Guan, C.-Y., and Lu, Y. (2022). Atropisomers beyond the C–C axial chirality: Advances in catalytic asymmetric synthesis. Chem *8*, 1855–1893. https://doi.org/10.1016/j.chempr.2022.04.011.
29. Kitagawa, O. (2021). Chiral Pd-Catalyzed Enantioselective Syntheses of Various N-C Axially Chiral Compounds and Their Synthetic Applications. Acc. Chem. Res. *54*, 719–730. https://doi.org/10.1021/acs.accounts.0c00767.
30. Kumarasamy, E., Raghunathan, R., Sibi, M.P., and Sivaguru, J. (2015). Nonbiaryl and Heterobiaryl Atropisomers: Molecular Templates with Promise for Atropselective Chemical Transformations. Chem. Rev. *115*, 11239–11300. https://doi.org/10.1021/acs.chemrev.5b00136.
31. Oppenheimer, J., Hsung, R.P., Figueroa, R., and Johnson, W.L. (2007). Stereochemical Control of Both C−C and C−N Axial Chirality in the Synthesis of Chiral N. Org. Lett. *9*, 3969–3972. https://doi.org/10.1021/ol701692m.
32. Suda, T., Noguchi, K., Hirano, M., and Tanaka, K. (2008). Highly enantioselective synthesis of n,n-dialkylbenzamides with aryl-carbonyl axial chirality by rhodium-catalyzed [2+2+2] cycloaddition. Chem. Eur J. *14*, 6593–6596. https://doi.org/10.1002/chem.200800953.
33. Zhang, X.L., Gu, J., Cui, W.H., Ye, Z., Yi, W., Zhang, Q., and He, Y. (2022). Stepwise Asymmetric Allylic Substitution-Isomerization Enabled Mimetic Synthesis of Axially Chiral

B,N-Heterocycles. Angew. Chem. Int. Ed. *61*, e202210456. https://doi.org/10.1002/anie.202210456.

34. Blair, L.M., and Sperry, J. (2013). Natural products containing a nitrogen-nitrogen bond. J. Nat. Prod. *76*, 794–812. https://doi.org/10.1021/np400124n.
35. Reddy, P.S., and Bhavani, A.K.D. (2015). In Advances in Heterocyclic Chemistry, *114*, E.F.V. Scriven and C.A. Ramsden, eds. (Academic Press), pp. 271–391.
36. Chang, C., and Adams, R. (1931). STEREOCHEMISTRY OF N,N′-DIPYRRYLS. RESOLUTION OF N,N′,2,5,2′,5′-TETRAMETHYL-3,3′-DICARBOXYDIPYRRYL. XVI. J. Am. Chem. Soc. *53*, 2353–2357. https://doi.org/10.1021/ja01357a049.
37. Song, T., Li, R., Huang, L., Jia, S., and Mei, G. (2023). Catalytic Asymmetric Synthesis of N-N Atropisomers. Chin. J. Org. Chem. *43*, 1977–1990. https://doi.org/10.6023/cjoc202212003.
38. Centonze, G., Portolani, C., Righi, P., and Bencivenni, G. (2023). Enantioselective Strategies for The Synthesis of N-N Atropisomers. Angew. Chem. Int. Ed. *62*, e202303966. https://doi.org/10.1002/anie.202209895.
39. Yin, S.Y., Zhou, Q., Liu, C.X., Gu, Q., and You, S.L. (2023). Enantioselective Synthesis of N-N Biaryl Atropisomers through Iridium(I)-Catalyzed C-H Alkylation with Acrylates. Angew. Chem. Int. Ed. *62*, e202305067. https://doi.org/10.1002/anie.202305067.
40. Yao, W., Lu, C.J., Zhan, L.W., Wu, Y., Feng, J., and Liu, R.R. (2023). Enantioselective Synthesis of N-N Atropisomers by Palladium-Catalyzed C-H Functionalization of Pyrroles. Angew. Chem. Int. Ed. *62*, e202218871. https://doi.org/10.1002/anie.202218871.
41. Wang, L.Y., Miao, J., Zhao, Y., and Yang, B.M. (2023). Chiral Acid-Catalyzed Atroposelective Indolization Enables Access to 1,1′-Indole-Pyrroles and Bisindoles Bearing a Chiral N-N Axis. Org. Lett. *25*, 1553–1557. https://doi.org/10.1021/acs.orglett.3c00237.
42. Sparr, C., and Hutskalova, V. (2023). Control over Stereogenic N–N Axes by Pd-Catalyzed 5-endo-Hydroaminocyclizations. Synthesis *55*, 1770–1782. https://doi.org/10.1055/a-1993-6899.
43. Chen, Z.H., Li, T.Z., Wang, N.Y., Ma, X.F., Ni, S.F., Zhang, Y.C., and Shi, F. (2023). Organocatalytic Enantioselective Synthesis of Axially Chiral N,N′-Bisindoles. Angew. Chem. Int. Ed. *62*, e202300419. https://doi.org/10.1002/anie.202300419.
44. Zhang, P., Xu, Q., Wang, X.M., Feng, J., Lu, C.J., Li, Y., and Liu, R.R. (2022). Enantioselective Synthesis of N-N Bisindole Atropisomers. Angew. Chem. Int. Ed. *61*, e202212101. https://doi.org/10.1002/anie.202212101.
45. Xu, Q., Zhang, H., Ge, F.B., Wang, X.M., Zhang, P., Lu, C.J., and Liu, R.R. (2022). Cu(I)-Catalyzed Asymmetric Arylation of Pyrroles with Diaryliodonium Salts toward the Synthesis of N-N Atropisomers. Org. Lett. *24*, 3138–3143. https://doi.org/10.1021/acs.orglett.2c00812.
46. Pu, L.Y., Zhang, Y.J., Liu, W., and Teng, F. (2022). Chiral phosphoric acid-catalyzed dual-ring formation for enantioselective construction of N-N axially chiral 3,3′-bisquinazolinones. Chem. Commun. *58*, 13131–13134. https://doi.org/10.1039/d2cc05172a.
47. Gao, Y., Wang, L.Y., Zhang, T., Yang, B.M., and Zhao, Y. (2022). Atroposelective Synthesis of 1,1′-Bipyrroles Bearing a Chiral N-N Axis: Chiral Phosphoric Acid Catalysis with Lewis Acid Induced Enantiodivergence. Angew. Chem. Int. Ed. *61*, e202200371. https://doi.org/10.1002/anie.202200371.
48. Chen, K.W., Chen, Z.H., Yang, S., Wu, S.F., Zhang, Y.C., and Shi, F. (2022). Organocatalytic Atroposelective Synthesis of N-N Axially Chiral Indoles and Pyrroles by De Novo Ring Formation. Angew. Chem. Int. Ed. *61*, e202116829. https://doi.org/10.1002/anie.202116829.
49. Wang, X.M., Zhang, P., Xu, Q., Guo, C.Q., Zhang, D.B., Lu, C.J., and Liu, R.R. (2021). Enantioselective Synthesis of Nitrogen-Nitrogen Biaryl Atropisomers via Copper-Catalyzed Friedel-Crafts Alkylation Reaction. J. Am. Chem. Soc. *143*, 15005–15010. https://doi.org/10.1021/jacs.1c07741.
50. Pan, M., Shao, Y.B., Zhao, Q., and Li, X. (2022). Asymmetric Synthesis of N-N Axially Chiral Compounds by Phase-Transfer-Catalyzed Alkylations. Org. Lett. *24*, 374–378. https://doi.org/10.1021/acs.orglett.1c04028.
51. Lin, W., Zhao, Q., Li, Y., Pan, M., Yang, C., Yang, G.H., and Li, X. (2021). Asymmetric synthesis of N-N axially chiral compounds via organocatalytic atroposelective N-acylation. Chem. Sci. *13*, 141–148. https://doi.org/10.1039/d1sc05360d.
52. Mei, G.-J., Wong, J.J., Zheng, W., Nangia, A.A., Houk, K.N., and Lu, Y. (2021). Rational design and atroposelective synthesis of N–N axially chiral compounds. Chem *7*, 2743–2757. https://doi.org/10.1016/j.chempr.2021.07.013.
53. Portolani, C., Centonze, G., Luciani, S., Pellegrini, A., Righi, P., Mazzanti, A., Ciogli, A., Sorato, A., and Bencivenni, G. (2022). Synthesis of Atropisomeric Hydrazides by One-Pot Sequential Enantio- and Diastereoselective Catalysis. Angew. Chem. Int. Ed. *61*, e202209895. https://doi.org/10.1002/anie.202209895.
54. Ma, G., and Sibi, M.P. (2015). Catalytic Kinetic Resolution of Biaryl Compounds. Chem. Eur J. *21*, 11644–11657. https://doi.org/10.1002/chem.201500869.
55. Dai, L., Liu, Y., Xu, Q., Wang, M., Zhu, Q., Yu, P., Zhong, G., and Zeng, X. (2023). A Dynamic Kinetic Resolution Approach to Axially Chiral Diaryl Ethers by Catalytic Atroposelective Transfer Hydrogenation. Angew. Chem. Int. Ed. *62*, e202216534. https://doi.org/10.1002/anie.202216534.
56. Carmona, J.A., Rodríguez-Franco, C., López-Serrano, J., Ros, A., Iglesias-Sigüenza, J., Fernández, R., Lassaletta, J.M., and Hornillos, V. (2021). Atroposelective Transfer Hydrogenation of Biaryl Aminals via Dynamic Kinetic Resolution. Synthesis of Axially Chiral Diamines. ACS Catal. *11*, 4117–4124. https://doi.org/10.1021/acscatal.1c00571.
57. Zhao, K., Duan, L., Xu, S., Jiang, J., Fu, Y., and Gu, Z. (2018). Enhanced Reactivity by Torsional Strain of Cyclic Diaryliodonium in Cu-Catalyzed Enantioselective Ring-Opening Reaction. Chem *4*, 599–612. https://doi.org/10.1016/j.chempr.2018.01.017.
58. Zhang, J., and Wang, J. (2018). Atropoenantioselective Redox-Neutral Amination of Biaryl Compounds through Borrowing Hydrogen and Dynamic Kinetic Resolution. Angew. Chem. Int. Ed. *57*, 465–469. https://doi.org/10.1002/anie.201711126.
59. Hornillos, V., Carmona, J.A., Ros, A., Iglesias-Sigüenza, J., López-Serrano, J., Fernández, R., and Lassaletta, J.M. (2018). Dynamic Kinetic Resolution of Heterobiaryl Ketones by Zinc-Catalyzed Asymmetric Hydrosilylation. Angew. Chem. Int. Ed. *57*, 3777–3781. https://doi.org/10.1002/anie.201713200.
60. Carmona, J.A., Hornillos, V., Ramírez-López, P., Ros, A., Iglesias-Sigüenza, J., Gómez-Bengoa, E., Fernández, R., and Lassaletta, J.M. (2018). Dynamic Kinetic Asymmetric Heck Reaction for the Simultaneous Generation of Central and Axial Chirality. J. Am. Chem. Soc. *140*, 11067–11075. https://doi.org/10.1021/jacs.8b05819.
61. Staniland, S., Adams, R.W., McDouall, J.J.W., Maffucci, I., Contini, A., Grainger, D.M., Turner, N.J., and Clayden, J. (2016). Biocatalytic Dynamic Kinetic Resolution for the Synthesis of Atropisomeric Biaryl N-Oxide Lewis Base Catalysts. Angew. Chem. Int. Ed. *55*, 10755–10759. https://doi.org/10.1002/anie.201605486.
62. Hazra, C.K., Dherbassy, Q., Wencel-Delord, J., and Colobert, F. (2014). Synthesis of axially chiral biaryls through sulfoxide-directed asymmetric mild C-H activation and dynamic kinetic resolution. Angew. Chem. Int. Ed. *53*, 13871–13875. https://doi.org/10.1002/anie.201407865.
63. Bhat, V., Wang, S., Stoltz, B.M., and Virgil, S.C. (2013). Asymmetric Synthesis of QUINAP via Dynamic Kinetic Resolution. J. Am. Chem. Soc. *135*, 16829–16832. https://doi.org/10.1021/ja409383f.
64. Gustafson, J.L., Lim, D., and Miller, S.J. (2010). Dynamic Kinetic Resolution of Biaryl Atropisomers via Peptide-Catalyzed Asymmetric Bromination. Science *328*, 1251–1255. https://doi.org/10.1126/science.1188403.
65. Beleh, O.M., Miller, E., Toste, F.D., and Miller, S.J. (2020). Catalytic Dynamic Kinetic Resolutions in Tandem to Construct Two-Axis Terphenyl Atropisomers. J. Am. Chem. Soc. *142*, 16461–16470. https://doi.org/10.1021/jacs.0c08057.
66. Fugard, A.J., Lahdenperä, A.S.K., Tan, J.S.J., Mekareeya, A., Paton, R.S., and Smith, M.D. (2019). Hydrogen-Bond-Enabled Dynamic Kinetic Resolution of Axially Chiral Amides Mediated by a Chiral Counterion. Angew. Chem. Int. Ed. *58*, 2795–2798. https://doi.org/10.1002/anie.201814362.
67. Han, T.J., Zhang, Z.X., Wang, M.C., Xu, L.P., and Mei, G.J. (2022). The Rational Design and Atroposelective Synthesis of Axially Chiral C2-Arylpyrrole-Derived Amino Alcohols. Angew. Chem. Int. Ed. *61*, e202207517. https://doi.org/10.1002/anie.202207517.

STAR★METHODS

KEY RESOURCES TABLE

REAGENT or RESOURCE	SOURCE	IDENTIFIER
Chemicals, peptides, and recombinant proteins		
1′-Acetonaphthone	Bidepharm	CAS: 941-98-0
Diethyl carbonate	Energy Chemical	CAS: 105-58-8
Ethyl acetoacetate	Bidepharm	CAS: 141-97-9
Ethyl carbazate	Bidepharm	CAS: 4114-31-2
N-Chlorosuccinimide	Bidepharm	CAS: 128-09-6
4-Methylbenzenesulfonic acid hydrate	Bidepharm	CAS: 6192-52-5
NaH	Damas-beta	CAS: 7646-69-7
tert-Butyl acrylate	Bidepharm	CAS: 1663-39-4
1,4-Diazabicyclo[2.2.2]octane	Bidepharm	CAS: 280-57-9
Polyformaldenyde	Bidepharm	CAS: 9002-81-7
tert-Butyloxycarbonyl anhydride	Bidepharm	CAS: 24424-99-5
Cinnamic acid	Bidepharm	CAS: 140-10-3
1-(2-Hydroxynaphthalen-1-yl)ethanone	Bidepharm	CAS: 574-19-6
Benzyl bromide	Bidepharm	CAS: 100-39-0
Cinchonidine	Bidepharm	CAS: 485-71-2
Hydroquinidine	Bidepharm	CAS: 1435-55-8
Hydroquinine	Bidepharm	CAS: 522-66-7
Quinine	Bidepharm	CAS: 130-95-0
Quinidine	Bidepharm	CAS: 56-54-2
Cinchonine	Bidepharm	CAS: 118-10-5
(*S*)-2-Phenyl-2,3-dihydrobenzo[*d*]imidazo [2,1-*b*]thiazole	Bidepharm	CAS: 950194-37-3
(*S*)-2-Isopropyl-2,3-dihydrobenzo[*d*]imidazo [2,1-*b*]thiazole	Bidepharm	CAS: 1214921-55-7
(2*R*,3*S*)-3-Isopropyl-2-phenyl-3,4-dihydro-2*H*-pyrimido[2,1-*b*][1,3]benzothiazole	Bidepharm	CAS: 1699751-03-5
(*S*)-2-(*tert*-Butyl)-2,3-dihydrobenzo[*d*]imidazo [2,1-*b*]thiazole	Bidepharm	CAS: 1213233-51-2
Deposited data		
CIF of **6**	CCDC	CCDC 2265925
Software and algorithms		
ChemDraw Ultra 12.0	PerkinElmer	https://www.perkinelmer.com/category/chemdraw
Other		
X-ray diffraction	Bruker	https://bruker.com
AVIII 400 MHz	Bruker	https://bruker.com

RESOURCE AVAILABILITY

Lead contact

Further information and requests for resources should be directed to and will be fulfilled by the lead contact, Guang-Jian Mei (meigj@zzu.edu.cn).

Materials availability

All other data supporting the findings of this study are available within the article and the supplemental information or from the lead contact upon reasonable request.

Data and code availability

- All data reported in this paper will be shared by the lead contact upon request. The crystallographic, catalysts and catalysis are provided in supplemental information as referenced in the main text. All original crystal structures have been deposited at CCDC and are publicly available as of the date of publication. CCDC numbers are listed in the key resources table.
- This paper does not report original code.
- Any additional information required to reanalyze the data reported in this paper is available from the lead contact upon request.

METHODS DETAILS

General procedures for asymmetric allylation

Racemic axial chiral compound **1** (0.10 mmol), MBH carbonic ester **2e** (0.15 mmol) were dissolved in CH_2Cl_2 (1 mL), and **C4** (10 mol %) were added. The reaction mixture was stirred for 12 h at room temperature. The solvent was removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1–2:1) to afford the product **3**.

(R,S)-Diethyl 1-((ethoxycarbonyl)(2-(methoxycarbonyl)allyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3a

A colorless oil; 50.4 mg; isolated yield = 94%; dr = 3.2:1. $[\alpha]^{31.0}_D$ = +7.00 (*c* 0.20, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 14.65 min (major), t_2 = 40.56 min (minor), *ee* = 86%; minor product: t_1 = 18.11 min (major), t_2 = 34.12 min (minor), *ee* = 80%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.59 (m, 3H), 7.60–7.30 (m, 4H), 6.27–5.62 (m, 1H), 5.36–5.16 (m, 1H), 4.46–4.22 (m, 4H), 4.22–3.67 (m, 4H), 3.66–3.49 (m, 3H), 2.30–2.20 (m, 3H), 1.42–1.20 (m, 6H), 0.74–0.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 164.5, 164.3, 154.8, 136.4, 133.8, 133.5, 133.3, 132.9, 131.9, 130.9, 130.2, 129.7, 128.4, 128.3, 127.0, 126.7, 126.1, 126.1, 125.4, 125.0, 115.7, 110.7, 63.4, 60.4, 60.2, 52.0, 51.0, 14.7, 14.3, 13.3, 10.5. HRMS (ESI) m/z calcd for $C_{29}H_{32}N_2O_8Na^+$ $[M + Na]^+$ = 559.2051, found = 559.2053.

(R,S)-Diethyl 1-((ethoxycarbonyl)(2-(ethoxycarbonyl)allyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3b

A colorless oil; 52.3 mg; isolated yield = 95%; dr = 3.2:1. $[\alpha]^{31.4}_D$ = −19.33 (*c* 0.30, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 13.07 min (major), t_2 = 33.40 min (minor), *ee* = 93%; minor product: t_1 = 15.20 min (major), t_2 = 25.06 min (minor), *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.62 (m, 3H), 7.61–7.32 (m, 4H), 6.20–5.72 (m, 1H), 5.39–5.17 (m, 1H), 4.43–4.23 (m, 4H), 4.20–3.96 (m, 3H), 3.96–3.40 (m, 3H), 2.31–2.20 (m, 3H), 1.42–1.08 (m, 9H), 0.78–0.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.5, 164.3, 154.8, 136.5, 134.1, 133.7, 133.5, 132.9, 131.9, 130.7, 130.6, 130.2, 129.7, 128.4, 128.3, 127.0, 126.7, 126.2, 126.1, 125.4, 125.1, 115.7, 110.6, 63.3, 61.0, 60.4, 60.2, 51.0, 14.7, 14.3, 14.0, 13.3, 10.6. HRMS (ESI) m/z calcd for $C_{30}H_{34}N_2O_8Na^+$ $[M + Na]^+$ = 573.2207, found = 573.2210.

(R,S)-Diethyl 1-((2-((benzyloxy)carbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3c

A colorless oil; 56.9 mg; isolated yield = 93%; dr = 3.0:1. $[\alpha]^{31.5}_D$ = −59.20 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.28 min (major), t_2 = 27.54 min (minor), *ee* = 93%; minor product: t_1 = 13.07 min (major), t_2 = 20.61 min (minor), *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90–7.82 (m, 2H), 7.74–7.56 (m, 1H), 7.56–7.25 (m, 9H), 6.23–5.98 (m, 1H), 5.43–4.85 (m, 3H), 4.48–4.21 (m, 4H), 4.17–3.33 (m, 4H), 2.36–2.07 (m, 3H), 1.43–1.05 (m, 6H), 0.78–0.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.5, 164.3, 154.8, 136.5, 135.4, 133.5, 133.4, 132.9, 131.9, 131.3, 130.2, 129.7, 128.6, 128.6, 128.4, 128.3, 127.0, 126.7, 126.1, 126.1, 125.4, 125.0, 124.7, 115.7, 110.7, 66.8, 63.4, 60.4, 60.2, 51.0, 14.7, 14.3, 13.3, 10.5. HRMS (ESI) m/z calcd for $C_{35}H_{36}N_2O_8Na^+$ $[M + Na]^+$ = 635.2364, found = 635.2369.

(R,S)-Diethyl 1-((2-(butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3d

A colorless oil; 54.3 mg; isolated yield = 94%; dr = 2.8:1. $[\alpha]^{25}_D$ = −41.75 (*c* 0.40, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.60 min (major), t_2 = 27.15 min (minor), *ee* = 94%; minor product: t_1 = 12.93 min (major), t_2 = 19.85 min (minor), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.62 (m, 3H), 7.59–7.32 (m, 4H), 6.25–5.68 (m, 1H), 5.37–5.15 (m, 1H), 4.45–4.25 (m, 4H), 4.19–3.36 (m, 6H), 2.31–2.20 (m, 3H), 1.65–1.44 (m, 2H), 1.40–1.15 (m, 8H), 0.95–0.90 (m, 3H), 0.78–0.48 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.5, 164.3, 154.8, 136.6, 134.1, 133.6, 133.5, 132.9, 131.8, 130.7, 130.2, 129.7, 128.4, 128.3, 127.0, 126.7, 126.2, 125.4, 125.1, 115.7, 110.6, 64.9, 63.3, 60.4, 60.2, 51.0, 30.4, 19.1, 14.7, 14.3, 13.7, 13.3, 10.6. HRMS (ESI) m/z calcd for $C_{32}H_{38}N_2O_8Na^+$ $[M + Na]^+$ = 601.2520, found = 601.2522.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3e

A colorless oil; 55.5 mg; isolated yield = 96%; dr = 2.8:1. $[\alpha]^{31.1}_D$ = −49.71 (*c* 0.35, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 21.74 min (major), t_2 = 32.15 min (minor), *ee* = 95%; minor product: t_1 = 16.05 min (major),

t_2 = 17.42 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.61 (m, 3H), 7.59–7.32 (m, 4H), 6.27–5.61 (m, 1H), 5.42–5.09 (m, 1H), 4.54–4.26 (m, 4H), 4.18–3.08 (m, 4H), 2.44–2.14 (m, 3H), 1.47–1.39 (m, 9H), 1.38–1.20 (m, 6H), 0.85–0.44 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.5, 164.3, 154.7, 137.0, 135.5, 134.9, 133.5, 132.9, 131.7, 130.2, 130.1, 129.8, 128.4, 128.3, 127.1, 126.7, 126.2, 125.4, 125.1, 115.7, 110.4, 81.4, 63.3, 60.4, 60.2, 50.9, 27.9, 14.8, 14.3, 13.3, 10.7. HRMS (ESI) m/z calcd for $C_{32}H_{38}N_2O_8Na^+$ $[M + Na]^+$ = 601.2520, found = 601.2530.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(methoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3f

A colorless oil; 50.1 mg; isolated yield = 89%; dr = 2.7:1. $[\alpha]^{31.4}_D$ = −42.67 (*c* 0.45, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 21.74 min (major), t_2 = 32.15 min (minor), *ee* = 95%; minor product: t_1 = 16.05 min (major), t_2 = 17.42 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.59 (m, 3H), 7.58–7.28 (m, 4H), 6.18–5.92 (m, 1H), 5.46–5.10 (m, 1H), 4.59–4.18 (m, 3H), 4.11–3.11 (m, 6H), 2.36–2.16 (m, 3H), 1.48–1.38 (m, 9H), 1.37–1.33 (m, 3H), 0.74–0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.5, 164.3, 155.3, 136.9, 134.9, 133.5, 133.4, 132.9, 131.6, 130.3, 130.1, 129.8, 128.4, 128.2, 127.0, 126.7, 126.2, 126.0, 125.4, 125.2, 124.6, 115.8, 110.5, 81.5, 60.4, 60.2, 54.1, 51.0, 27.9, 14.3, 13.3, 10.7. HRMS (ESI) m/z calcd for $C_{31}H_{36}N_2O_8Na^+$ $[M + Na]^+$ = 587.2364, found = 587.2369.

(*R,S*)-Diethyl 1-(((benzyloxy)carbonyl)(2-(tert-butoxycarbonyl)allyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3g

A colorless oil; 55.5 mg; isolated yield = 91%; dr = 3.0:1. $[\alpha]^{31.6}_D$ = −38.25 (*c* 0.40 CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 12.87 min (major), t_2 = 16.93 min (minor), *ee* = 94%; minor product: t_1 = 9.29 min (major), t_2 = 10.97 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.56 (m, 3H), 7.52–6.85 (m, 9H), 6.15–5.89 (m, 1H), 5.49–4.64 (m, 3H), 4.53–3.04 (m, 6H), 2.32–2.23 (m, 3H), 1.55–1.29 (m, 12H), 0.72–0.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.4, 164.2, 154.6, 136.9, 135.3, 134.9, 133.4, 132.8, 131.9, 130.2, 130.0, 129.6, 129.1, 128.8, 128.7, 128.9, 128.6, 128.5, 128.5, 128.4, 128.0, 126.8, 126.6, 126.1, 125.4, 125.1, 124.6, 115.7, 110.6, 81.4, 68.7, 60.4, 60.1, 51.0, 27.8, 14.3, 13.3, 10.7. HRMS (ESI) m/z calcd for $C_{37}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 633.2677, found = 633.2672.

(*R,S*)-Diethyl 1-((((9H-fluoren-9-yl)methoxy)carbonyl)(2-(tert-butoxycarbonyl)allyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3h

A colorless oil; 69.2 mg; isolated yield = 95%; dr = 4.5:1. $[\alpha]^{31.8}_D$ = +30.71 (*c* 0.28, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 23.83 min (major), t_2 = 31.33 min (minor), *ee* = 92%; minor product: t_1 = 18.75 min (major), t_2 = 22.28 min (minor), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.62 (m, 5H), 7.58–7.26 (m, 9H), 7.22–6.55 (m, 1H), 6.20–5.73 (m, 1H), 5.53–4.84 (m, 1H), 4.78–4.06 (m, 6H), 3.97–3.01 (m, 3H), 2.33–1.91 (m, 3H), 1.50–1.29 (m, 12H), 0.77–0.54 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.2, 164.2, 154.4, 143.2, 143.0, 141.6, 141.4, 136.8, 134.7, 133.3, 132.8, 131.3, 130.2, 129.5, 128.5, 128.4, 128.1, 127.9, 127.2, 127.1, 126.8, 126.6, 126.0, 125.2, 125.2, 124.5, 124.2, 120.5, 120.3, 115.8, 110.2, 81.4, 68.8, 60.2, 60.0, 50.6, 46.7, 27.9, 14.4, 13.4, 10.3. HRMS (ESI) m/z calcd for $C_{44}H_{44}N_2O_8Na^+$ $[M + Na]^+$ = 751.2990, found = 751.2982.

(*R,S*)-Diethyl 1-((*tert*-butoxycarbonyl)(2-(tert-butoxycarbonyl)allyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3i

A colorless oil; 57.6 mg; isolated yield = 95%; dr = 2.6:1. $[\alpha]^{31.6}_D$ = −16.18 (*c* 0.34, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 20.67 min (major), t_2 = 22.65 min (minor), *ee* = 96%; minor product: t_1 = 12.94 min (major), t_2 = 13.56 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.66 (m, 3H), 7.61–7.34 (m, 4H), 6.27–5.72 (m, 1H), 5.42–4.94 (m, 1H), 4.48–3.10 (m, 6H), 2.32 (s, 3H), 1.55–1.43 (m, 9H), 1.42–1.29 (m, 12H), 0.67–0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 164.3, 153.3, 137.2, 136.8, 135.5, 135.1, 133.5, 133.4, 133.0, 132.0, 129.8, 129.7, 129.6, 128.9, 128.5, 128.4, 127.4, 126.6, 126.1, 126.0, 125.5, 125.0, 124.9, 115.4, 110.2, 82.8, 81.3, 60.3, 60.1, 50.3, 28.2, 27.9, 14.3, 13.3, 10.7. HRMS (ESI) m/z calcd for $C_{34}H_{42}N_2O_8Na^+$ $[M + Na]^+$ = 629.2833, found = 629.2837.

(*R,S*)-3-ethyl 4-methyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-5-methyl-2-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3j

A colorless oil; 53.6 mg; isolated yield = 95%; dr = 2.7:1. $[\alpha]^{30.8}_D$ = −32.00 (*c* 0.50 CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 15.13 min (major), t_2 = 26.82 min (minor), *ee* = 96%; minor product: t_1 = 11.29 min (major), t_2 = 13.48 min (minor), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.60 (m, 3H), 7.57–7.32 (m, 4H), 6.16–5.90 (m, 1H), 5.43–5.09 (m, 1H), 4.60–4.00 (m, 3H), 4.00–3.11 (m, 6H), 2.38–2.20 (m, 3H), 1.45–1.41 (m, 9H), 1.35–1.19 (m, 3H), 0.72–0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.5, 164.2, 154.7, 137.1, 135.5, 134.9, 133.5, 132.9, 132.0, 130.2, 130.1, 129.8, 128.5, 128.3, 127.1, 126.7, 126.2, 125.4, 125.1, 115.5, 110.2, 81.4, 63.3, 60.2, 51.5, 50.8, 27.9, 14.7, 13.3, 10.7. HRMS (ESI) m/z calcd for $C_{31}H_{36}N_2O_8Na^+$ $[M + Na]^+$ = 587.2364, found = 587.2363.

(*R,S*)-3-benzyl 4-ethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3k

A colorless oil; 56.3 mg; isolated yield = 88%; dr = 2.8:1. $[\alpha]^{31.9}_D$ = +17.00 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 10.21 min (major), t_2 = 34.60 min (minor), *ee* = 98%; minor product: t_1 = 8.99 min (major), t_2 = 14.28 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98–7.61 (m, 3H), 7.59–7.27 (m, 9H), 6.15–5.90 (m, 1H), 5.47–5.05 (m, 3H), 4.50–3.13

(m, 6H), 2.32–2.31 (m, 3H), 1.44–1.37 (m, 9H), 1.35–1.18 (m, 3H), 0.63–0.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.4, 164.3, 154.7, 137.5, 136.2, 135.5, 134.9, 133.5, 132.8, 131.6, 130.2, 130.2, 129.8, 128.4, 128.4, 128.0, 126.9, 126.7, 126.2, 125.4, 125.1, 116.0, 110.0, 81.4, 66.4, 63.3, 60.2, 50.9, 27.9, 14.8, 13.2, 10.8. HRMS (ESI) m/z calcd for $C_{37}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 663.2677, found = 663.2672.

(*R,S*)-3-allyl 4-ethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3l

A colorless oil; 55.5 mg; isolated yield = 94%; dr = 4.0:1. $[\alpha]^{30.8}_D$ = +25.88 (*c* 0.34 CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 23.83 min (major), t_2 = 34.54 min (minor), *ee* = 97%; minor product: t_1 = 16.41 min (major), t_2 = 17.77 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.61 (m, 3H), 7.59–7.30 (m, 4H), 6.23–5.73 (m, 2H), 5.53–4.98 (m, 3H), 4.79–4.78 (m, 2H), 4.48–3.16 (m, 6H), 2.33–2.32 (m, 3H), 1.45–1.41 (m, 9H), 1.36–1.19 (m, 3H), 0.73–0.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.3, 164.2, 154.7, 137.3, 135.5, 134.9, 133.5, 132.9, 132.5, 131.8, 130.2, 130.1, 129.8, 128.5, 128.3, 127.0, 126.7, 126.2, 125.4, 125.1, 118.0, 115.8, 110.0, 81.4, 65.2, 63.3, 60.3, 50.8, 27.9, 14.8, 13.3, 10.8. HRMS (ESI) m/z calcd for $C_{33}H_{38}N_2O_8Na^+$ $[M + Na]^+$ = 613.2520, found = 613.2522.

(*R,S*)-3-(*tert*-butyl) 4-ethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3m

A colorless oil; 54.5 mg; isolated yield = 90%; dr = 2.3:1. $[\alpha]^{31.6}_D$ = −46.67 (*c* 0.48 CH_2Cl_2; HPLC (IE column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.77 min (major), t_2 = 28.54 min (minor), *ee* = 95%; minor product: t_1 = 10.11 min (major), t_2 = 10.86 min (minor), *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.62 (m, 3H), 7.62–7.30 (m, 4H), 6.16–5.89 (m, 1H), 5.41–5.08 (m, 1H), 4.46–3.83 (m, 4H), 3.81–3.25 (m, 2H), 2.31–2.30 (m, 3H), 1.60–1.54 (m, 9H), 1.45–1.41 (m, 9H), 1.37–1.19 (m, 3H), 0.72–0.47 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.5, 163.7, 154.8, 136.5, 135.6, 134.9, 133.5, 133.4, 132.9, 131.2, 130.1, 129.9, 129.6, 128.4, 128.3, 127.2, 126.6, 126.1, 126.0, 125.9, 125.5, 125.1, 124.6, 116.0, 111.7, 81.4, 80.7, 63.2, 60.1, 50.9, 28.2, 27.9, 14.8, 13.3, 10.6. HRMS (ESI) m/z calcd for $C_{34}H_{42}N_2O_8Na^+$ $[M + Na]^+$ = 629.2833, found = 629.2835.

(*R,S*)-3-ethyl 4-methyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3n

A colorless oil; 54.1 mg; isolated yield = 96%; dr = 2.6:1. $[\alpha]^{31.7}_D$ = −33.78 (*c* 0.45, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 15.78 min (major), t_2 = 28.43 min (minor), *ee* = 99%; minor product: t_1 = 11.03 min (major), t_2 = 18.67 min (minor), *ee* = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.61 (m, 3H), 7.59–7.32 (m, 4H), 6.14–5.89 (m, 1H), 5.40–5.06 (m, 1H), 4.47–4.24 (m, 4H), 4.23–3.18 (m, 5H), 2.33–2.31 (m, 3H), 1.44–1.41 (m, 9H), 1.38–1.19 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.5, 164.4, 154.7, 137.1, 135.5, 134.9, 133.5, 133.5, 132.7, 131.6, 130.1, 129.9, 128.5, 128.4, 126.7, 126.2, 125.2, 125.1, 115.5, 110.2, 81.4, 63.3, 63.0, 60.3, 51.6, 27.9, 14.7, 14.3, 10.7. HRMS (ESI) m/z calcd for $C_{31}H_{36}N_2O_8Na^+$ $[M + Na]^+$ = 587.2364, found = 587.2368.

(*R,S*)-3-ethyl 4-propyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3o

A colorless oil; 57.2 mg; isolated yield = 97%; dr = 2.6:1. $[\alpha]^{31.7}_D$ = −38.37 (*c* 0.43, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 13.06 min (major), t_2 = 18.69 min (minor), *ee* = 95%; minor product: t_1 = 10.11 min (major), t_2 = 10.74 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.63 (m, 3H), 7.58–7.33 (m, 4H), 6.24–5.84 (m, 1H), 5.42–5.07 (m, 1H), 4.46–4.25 (m, 4H), 4.24–3.20 (m, 4H), 2.32–2.31 (m, 3H), 1.45–1.41 (m, 9H), 1.37–1.32 (m, 5H), 1.23–1.19 (m, 3H), 0.45–0.32 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 164.4, 154.7, 136.8, 135.6, 134.9, 133.5, 132.9, 131.6, 130.1, 130.0, 129.8, 128.4, 128.3, 127.1, 126.7, 126.2, 125.4, 125.1, 115.7, 110.6, 81.4, 66.0, 63.2, 60.4, 50.9, 27.9, 21.3, 14.8, 14.3, 10.7, 10.0. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 615.2677, found = 615.2684.

(*R,S*)-3-ethyl 4-isopropyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3p

A colorless oil; 54.5 mg; isolated yield = 92%; dr = 2.8:1. $[\alpha]^{31.6}_D$ = −35.31 (*c* 0.32, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 14.22 min (major), t_2 = 20.54 min (minor), *ee* = 97%; minor product: t_1 = 11.03 min (major), t_2 = 18.67 min (minor), *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.62 (m, 3H), 7.60–7.31 (m, 4H), 6.17–5.91 (m, 1H), 5.43–5.10 (m, 1H), 4.77–4.64 (m, 1H), 4.53–3.21 (m, 6H), 2.32–2.31 (m, 3H), 1.45–1.41 (m, 9H), 1.39–1.17 (m, 6H), 0.81–0.36 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 163.7, 154.7, 136.9, 135.6, 135.0, 133.5, 133.0, 131.6, 130.1, 129.9, 129.6, 128.8, 128.3, 127.3, 126.1, 125.6, 125.0, 116.1, 110.4, 81.4, 67.5, 63.2, 60.4, 50.9, 27.9, 21.3, 20.7, 14.8, 14.2, 10.7. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 615.2677, found = 615.2676.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-ethyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3q

A colorless oil; 56.8 mg; isolated yield = 96%; dr = 2.7:1. $[\alpha]^{31.2}_D$ = −17.81 (*c* 0.32, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.14 min (major), t_2 = 14.10 min (minor), *ee* = 97%; minor product: t_1 = 9.09 min (major), t_2 = 9.54 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.64 (m, 3H), 7.63–7.30 (m, 4H), 6.13–5.84 (m, 1H), 5.33–5.00 (m, 1H), 4.55–4.26 (m, 4H), 4.22–3.26 (m, 4H), 2.93–2.45 (m, 2H), 1.49–1.38 (m, 9H), 1.39–1.14 (m, 9H), 0.69–0.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.4,

164.3, 155.1, 142.0, 134.9, 133.5, 133.1, 132.6, 131.5, 130.1, 129.8, 129.5, 129.2, 128.4, 128.4, 127.2, 126.7, 126.2, 125.8, 125.4, 125.0, 116.0, 110.2, 81.3, 63.3, 60.4, 60.2, 51.4, 27.9, 18.3, 14.6, 14.2, 13.4, 13.3. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 615.2677, found = 615.2680.

(*R,S*)-3-ethyl 4-methyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-(naphthalen-1-yl)-5-propyl-1*H*-pyrrole-3,4-dicarboxylate: 3r

A colorless oil; 55.1 mg; isolated yield = 93%; dr = 4:1. $[\alpha]^{31.1}{}_D$ = −49.00 (*c* 0.30, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 21.99 min (major), t_2 = 41.20 min (minor), *ee* = 92%; minor product: t_1 = 19.64 min (minor), t_2 = 24.37 min (major), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.92–7.83 (m, 2H), 7.75–7.66 (m, 1H), 7.65–7.33 (m, 4H), 6.26–5.72 (m, 1H), 5.28–4.97 (m, 1H), 4.59–4.08 (m, 3H), 3.96–3.75 (m, 5H), 3.72–3.33 (m, 1H), 2.92–2.30 (m, 2H), 1.66–1.59 (m, 2H), 1.47–1.40 (m, 9H), 1.37–1.12 (m, 3H), 0.99–0.95 (m, 3H), 0.67–0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.4, 164.3, 155.1, 140.7, 134.8, 133.4, 133.1, 132.0, 130.0, 129.8, 129.1, 128.9, 128.4, 128.3, 127.2, 126.8, 126.2, 125.3, 125.0, 115.6, 110.4, 81.3, 63.3, 60.2, 51.6, 27.9, 26.9, 22.4, 14.6, 14.4, 13.3. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 615.2677, found = 615.2685.

(*R,S*)-4-ethyl 3-methyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-butyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3s

A colorless oil; 52.1 mg; isolated yield = 86%; dr = 2.8:1. $[\alpha]^{31.7}{}_D$ = −27.33 (*c* 0.30, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 20.38 min (major), t_2 = 35.83 min (minor), *ee* = 97%; minor product: t_1 = 17.76 min (minor), t_2 = 22.78 min (major), *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99–7.64 (m, 3H), 7.60–7.31 (m, 4H), 6.12–5.80 (m, 1H), 5.28–4.94 (m, 1H), 4.50–3.96 (m, 3H), 3.93–3.74 (m, 5H), 3.67–3.33 (m, 1H), 3.03–2.34 (m, 2H), 1.67–1.53 (m, 2H), 1.49–1.33 (m, 12H), 1.17–0.81 (m, 5H), 0.67–0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.4, 164.3, 155.1, 140.9, 135.4, 134.8, 133.4, 133.2, 133.0, 132.0, 130.1, 129.8, 129.0, 128.4, 128.4, 127.2, 126.7, 126.1, 125.3, 125.0, 115.7, 110.3, 81.3, 63.3, 60.2, 51.7, 51.5, 31.1, 27.9, 24.8, 22.9, 14.6, 13.8, 13.3. HRMS (ESI) m/z calcd for $C_{34}H_{42}N_2O_8Na^+$ $[M + Na]^+$ = 629.2833, found = 629.2841.

(*R,S*)-4-ethyl 3-methyl 2-benzyl-1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3t

A colorless oil; 61.4 mg; isolated yield = 96%; dr = 4:1. $[\alpha]^{31.6}{}_D$ = −24.32 (*c* 0.37, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.22 min (major), t_2 = 17.52 min (minor), *ee* = 95%; minor product: t_1 = 10.38 min (major), t_2 = 12.28 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.62 (m, 3H), 7.59–7.32 (m, 4H), 7.31–7.13 (m, 5H), 6.15–5.56 (m, 1H), 5.36–4.58 (m, 1H), 4.47–4.11 (m, 2H), 4.06–3.65 (m, 7H), 3.57–3.23 (m, 2H), 1.48–1.31 (m, 9H), 1.05–0.77 (m, 3H), 0.68–0.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 164.5, 163.9, 154.7, 137.7, 137.4, 135.4, 134.8, 133.4, 133.2, 130.1, 129.9, 129.5, 128.4, 128.4, 128.3, 127.1, 126.8, 126.4, 126.2, 125.3, 124.9, 115.3, 112.1, 81.4, 63.0, 60.2, 51.7, 51.4, 30.6, 27.9, 14.2, 13.3. HRMS (ESI) m/z calcd for $C_{37}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 663.2677, found = 663.2675.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-(4-fluoronaphthalen-1-yl)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3u

A colorless oil; 48.9 mg; isolated yield = 82%; dr = 2.3:1. $[\alpha]^{31.2}{}_D$ = −32.67 (*c* 0.30, CH_2Cl_2); HPLC (IE column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.51 min (major), t_2 = 19.94 min (minor), *ee* = 97%; minor product: t_1 = 9.02 min (major), t_2 = 9.95 min (minor), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16–8.11 (m, 1H), 7.88–7.61 (m, 1H), 7.60–7.28 (m, 3H), 7.19–7.14 (m, 1H), 6.18–5.89 (m, 1H), 5.45–5.08 (m, 1H), 4.43–4.22 (m, 4H), 4.00–3.31 (m, 4H), 2.31 (s, 3H), 1.45–1.41 (m, 9H), 1.38–1.23 (m, 6H), 0.79–0.65 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.4, 164.4, 164.3, 160.7, 158.2 (*J* = 250 Hz), 154.7, 136.9, 135.6, 135.0, 134.5, 134.4, 131.0, 129.9, 128.5, 128.4, 127.6, 126.6, 125.6, 125.5, 123.1, 121.0, 120.9, 120.7 (*J* = 25 Hz), 115.9, 110.6, 109.1, 108.9, 81.5, 63.3, 60.4, 60.3, 51.0, 27.9, 14.8, 14.3, 13.4, 10.7. ^{19}F NMR (376 MHz, $CDCl_3$) δ −119.93, −119.97, −120.39. HRMS (ESI) m/z calcd for $C_{32}H_{37}N_2O_8FNa^+$ $[M + Na]^+$ = 619.2426, found = 619.2430.

(*R,S*)-Diethyl 2-(4-bromonaphthalen-1-yl)-1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3v

A colorless oil; 60.4 mg; isolated yield = 92%; dr = 2.3:1. $[\alpha]^{31.7}{}_D$ = −9.72 (*c* 0.36, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 10.90 min (major), t_2 = 28.45 min (minor), *ee* = 96%; minor product: t_1 = 11.79 min (major), t_2 = 17.65 min (minor), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.31–8.26 (m, 1H), 7.84–7.80 (m, 2H), 7.70–7.15 (m, 3H), 6.61–5.89 (m, 1H), 5.44–5.09 (m, 1H), 4.48–4.25 (m, 4H), 4.20–3.15 (m, 4H), 2.31 (s, 3H), 1.45–1.41 (m, 9H), 1.37–1.29 (m, 6H), 0.86–0.53 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.3, 164.1, 154.6, 137.0, 135.6, 135.0, 134.0, 132.0, 130.8, 130.3, 130.1, 129.3, 128.9, 128.5, 127.7, 127.5, 127.2, 126.1, 124.9, 115.9, 110.7, 81.5, 63.4, 60.3, 60.3, 51.0, 27.9, 14.8, 14.3, 13.4, 10.7. HRMS (ESI) m/z calcd for $C_{32}H_{37}N_2O_8BrNa^+$ $[M + Na]^+$ = 679.1625, found = 679.1628.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(4-methylnaphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3w

A colorless oil; 57.4 mg; isolated yield = 97%; dr = 2.3:1. $[\alpha]^{31.3}{}_D$ = −39.50 (*c* 0.40, CH_2Cl_2); HPLC (ID column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 15.40 min (major), t_2 = 26.04 min (minor), *ee* = 94%; minor product: t_1 = 12.25 min (major),

t_2 = 31.14 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.98 (m, 1H), 7.86–7.59 (m, 1H), 7.57–7.21 (m, 4H), 6.16–5.92 (m, 1H), 5.44–5.12 (m, 1H), 4.57–4.22 (m, 4H), 4.20–3.05 (m, 4H), 2.73 (s, 3H), 2.46–2.16 (m, 3H), 1.45–1.42 (m, 9H), 1.38–1.19 (m, 6H), 0.79–0.62 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 164.5, 154.7, 136.9, 136.3, 135.6, 135.0, 132.8, 132.7, 132.0, 130.3, 129.8, 128.1, 126.2, 126.0, 126.0, 125.5, 125.2, 124.6, 124.2, 115.7, 110.2, 81.4, 63.2, 60.3, 60.2, 50.8, 27.9, 19.7, 14.8, 14.3, 13.4, 10.7. dr = 2.3:1. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 615.2677, found = 615.2677.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-(4-methoxynaphthalen-1-yl)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3x

A colorless oil; 58.4 mg; isolated yield = 96%; dr = 2.7:1. $[\alpha]^{31.6}_D$ = −22.08 (*c* 0.48, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 12.16 min (major), t_2 = 24.36 min (minor), *ee* = 97%; minor product: t_1 = 15.18 min (major), t_2 = 17.40 min (minor), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.39–8.06 (m, 1H), 7.83–7.56 (m, 1H), 7.51–7.19 (m, 3H), 6.83–6.81 (m, 1H), 6.18–5.93 (m, 1H), 5.47–5.14 (m, 1H), 4.55–4.23 (m, 4H), 4.04 (s, 3H), 3.98–3.04 (m, 4H), 2.31–2.30 (m, 3H), 1.45–1.42 (m, 9H), 1.37–1.29 (m, 6H), 0.88–0.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 164.5, 156.4, 154.8, 136.8, 135.6, 135.0, 133.8, 132.7, 131.8, 130.5, 130.4, 128.8, 127.1, 126.3, 125.8, 125.5, 125.4, 125.3, 125.2, 122.4, 122.0, 118.8, 115.8, 110.1, 103.2, 81.4, 63.2, 60.3, 60.2, 55.6, 50.8, 27.9, 14.8, 14.3, 13.5, 10.7. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_9Na^+$ $[M + Na]^+$ = 631.2626, found = 631.2629.

(*R,S*)-Diethyl 2-(5-bromonaphthalen-1-yl)-1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3y

A colorless oil; 59.0 mg; isolated yield = 90%; dr = 2.3:1. $[\alpha]^{31.3}_D$ = −21.88 (*c* 0.48, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 30.69 min (major), t_2 = 76.70 min (minor), *ee* = 93%; minor product: t_1 = 28.75 min (major), t_2 = 76.70 min (minor), *ee* = 87%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.37–8.35 (m, 1H), 7.85–7.39 (m, 4H), 7.34–7.16 (m, 1H), 6.30–5.72 (m, 1H), 5.44–5.05 (m, 1H), 4.53–4.23 (m, 4H), 4.20–3.09 (m, 4H), 2.31 (s, 3H), 1.45–1.41 (m, 9H), 1.37–1.26 (m, 6H), 0.78–0.65 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 164.3, 164.2, 154.6, 136.9, 135.0, 134.2, 132.0, 131.2, 131.1, 130.4, 129.9, 129.3, 129.0, 127.7, 126.5, 125.6, 123.3, 115.8, 110.6, 81.5, 63.4, 60.4, 60.3, 51.0, 27.9, 14.8, 14.3, 13.4, 10.7. HRMS (ESI) m/z calcd for $C_{32}H_{37}N_2O_8BrNa^+$ $[M + Na]^+$ = 679.1625, found = 679.1622.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-(6-methoxynaphthalen-1-yl)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3z

A colorless oil; 58.4 mg; isolated yield = 96%; dr = 2.6:1. $[\alpha]^{31.4}_D$ = −7.81 (*c* 0.32, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 23.66 min (major), t_2 = 57.86 min (minor), *ee* = 94%; minor product: t_1 = 20.25 min (major), t_2 = 30.16 min (minor), *ee* = 96%; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.81–7.79 (m, 1H), 7.73–7.49 (m, 1H), 7.45–7.19 (m, 2H), 7.16–7.00 (m, 2H) 6.16–5.90 (m, 1H), 5.42–5.07 (m, 1H), 4.51–4.22 (m, 4H), 4.18–3.16 (m, 7H), 2.40–2.12 (m, 3H), 1.45–1.41 (m, 9H), 1.37–1.28 (m, 6H), 0.77–0.66 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.5, 164.5, 164.4, 157.7, 154.8, 136.9, 135.5, 134.9, 134.8, 131.8, 130.1, 128.6, 128.3, 127.8, 127.0, 126.9, 126.0, 125.8, 125.3, 119.5, 118.8, 115.6, 110.3, 106.1, 81.4, 63.2, 60.4, 60.2, 55.3, 50.9, 27.9, 14.8, 14.3, 13.4, 10.7. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_9Na^+$ $[M + Na]^+$ = 631.2626, found = 631.2635.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-methyl-5-(7-methylnaphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 3a′

A colorless oil; 54.5 mg; isolated yield = 92%; dr = 2.6:1. $[\alpha]^{31.3}_D$ = +63.75 (*c* 0.40, CH_2Cl_2); HPLC (IF column, *i*-propanol/*n*-hexane = 10/90, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 34.27 min (minor), t_2 = 49.31 min (major), *ee* = 93%; minor product: t_1 = 24.28 min (major), t_2 = 43.71 min (minor), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.54 (m, 4H), 7.46–7.32 (m, 2H), 6.07–6.06 (m, 1H), 5.36–5.27 (m, 1H), 4.59–4.24 (m, 5H), 4.16–4.06 (m, 2H), 3.69–3.35 (m, 1H), 2.53–2.52 (m, 3H), 2.32–2.30 (m, 3H), 1.40 (s, 9H), 1.39–1.29 (m, 6H), 1.17–0.98 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.5, 164.3, 154.9, 137.2, 136.9, 136.8, 136.3, 135.0, 133.4, 132.7, 131.3, 131.2, 129.2, 129.1, 128.8, 128.1, 127.6, 126.8, 126.7, 125.6, 114.9, 110.0, 81.5, 63.3, 60.8, 60.2, 50.3, 27.8, 21.8, 14.9, 14.3, 14.0, 10.7. HRMS (ESI) m/z calcd for $C_{33}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 615.2677, found = 615.2672.

(*R,S*)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-(7-chloronaphthalen-1-yl)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3b′

A colorless oil; 54.5 mg; isolated yield = 89%; dr = 2.3:1. $[\alpha]^{31.0}_D$ = −57.71 (*c* 0.35, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 10.80 min (major), t_2 = 25.94 min (minor), *ee* = 90%; minor product: t_1 = 8.47 min (major), t_2 = 14.80 min (minor), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.90–7.88 (m, 1H), 7.85–7.62 (m, 2H), 7.63–7.34 (m, 3H), 6.19–5.93 (m, 1H), 5.42–5.09 (m, 1H), 4.48–4.26 (m, 4H), 4.22–3.11 (m, 4H), 2.33–2.31 (m, 3H), 1.45–1.42 (m, 9H), 1.40–1.24 (m, 6H), 0.79–0.74 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 164.4, 164.4, 154.7, 137.1, 135.5, 134.9, 133.6, 132.9, 132.3, 131.7, 131.3, 130.8, 130.4, 130.2, 130.1, 129.9, 129.8, 129.6, 129.5, 127.3, 127.2, 126.6, 125.4, 125.0, 124.4, 116.0, 110.5, 81.6, 63.3, 60.4, 60.3, 51.0, 27.9, 14.8, 14.3, 13.4, 10.7. HRMS (ESI) m/z calcd for $C_{32}H_{37}N_2O_8ClNa^+$ $[M + Na]^+$ = 635.2131, found = 635.2129.

(R,S)-Diethyl 1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-2-(3,7-dimethylnaphthalen-1-yl)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3c′

A colorless oil; 57.0 mg; isolated yield = 94%; dr = 4.0:1. $[\alpha]^{31.0}_{D}$ = −72.25 (*c* 0.40, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.99 min (major), t_2 = 27.75 min (minor), *ee* = 97%; minor product: t_1 = 10.85 min (major), t_2 = 16.64 min (minor), *ee* = 92%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.62 (m, 2H), 7.48 (s, 1H), 7.36–7.12 (m, 2H), 6.23–5.82 (m, 1H), 5.29–5.14 (m, 1H), 4.55–4.26 (m, 4H), 4.25–3.09 (m, 4H), 2.47–2.46 (m, 3H), 2.42–2.40 (m, 3H), 2.35–2.27 (m, 3H), 1.48–1.39 (m, 9H), 1.38–1.29 (m, 6H), 0.81–0.60 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.60, 164.5, 154.8, 137.3, 137.1, 135.5, 135.3, 135.1, 133.6, 133.6, 132.5, 132.1, 132.0, 131.8, 131.2, 130.9, 130.6, 130.3, 130.2, 129.7, 128.7, 128.6, 128.4, 127.7, 127.6, 127.3, 126.0, 124.0, 115.7, 110.1, 81.4, 63.2, 60.3, 60.2, 50.8, 27.9, 21.8, 21.5, 14.9, 14.3, 13.4, 10.7. HRMS (ESI) m/z calcd for $C_{34}H_{42}N_2O_8Na^+$ $[M + Na]^+$ = 629.2833, found = 629.2834.

(R,S)-Diethyl 2-(anthracen-1-yl)-1-((2-(*tert*-butoxycarbonyl)allyl)(ethoxycarbonyl)amino)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 3d′

A colorless oil; 60.3 mg; isolated yield = 96%; dr = 2.3:1. $[\alpha]^{31.3}_{D}$ = −86.22 (*c* 0.45, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 11.65 min (major), t_2 = 30.67 min (minor), *ee* = 95%; minor product: t_1 = 10.29 min (major), t_2 = 15.51 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.58–8.16 (m, 2H), 8.16–7.80 (m, 3H), 7.65–7.34 (m, 4H), 6.16–5.85 (m, 1H), 5.41–5.07 (m, 1H), 4.50–4.24 (m, 4H), 4.24–3.09 (m, 4H), 2.37–2.36 (m, 3H), 1.46–1.44 (m, 3H), 1.42–1.11 (m, 12H), 0.79–0.42 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.6, 164.5, 164.4, 154.8, 137.1, 135.0, 132.0, 131.7, 131.5, 130.9, 130.1, 130.0, 128.4, 128.2, 128.0, 127.2, 127.0, 125.9, 125.9, 125.7, 124.5, 124.1, 116.0, 110.4, 81.4, 63.3, 60.4, 60.2, 50.9, 27.8, 14.8, 14.3, 13.4, 10.8. HRMS (ESI) m/z calcd for $C_{36}H_{40}N_2O_8Na^+$ $[M + Na]^+$ = 651.2677, found = 651.2684.

General procedures for asymmetric acylation

Racemic axial chiral compound **1** (0.10 mmol), cinnamic anhydride **4a** (0.15 mmol) were dissolved in CH_2Cl_2 (1 mL), and **C9** (10 mol %) was added. The reaction mixture was stirred for 12 h at 0°C. The solvent was removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1–2:1) to afford the product 5.

(S)-Diethyl 1-(N-(*tert*-butoxycarbonyl)cinnamamido)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5a

A colorless oil; 56.6 mg; isolated yield = 95%; dr = 1.3:1. $[\alpha]^{20.0}_{D}$ = −80.01 (*c* 0.55, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 31.00 min (minor), t_2 = 36.52 min (major), *ee* = 90%; minor product: t_1 = 10.87 min (major), t_2 = 22.25 min (minor), *ee* = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–6.43 (m, 14H), 4.31–3.96 (m, 2H), 3.65–3.56 (m, 2H), 2.17–2.16 (m, 3H), 1.30 (s, 3H), 1.14 (t, *J* = 7.1 Hz, 3H), 0.96 (s, 6H), 0.42–0.33 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 164.6, 164.6, 164.3, 150.0, 147.0, 136.1, 134.3, 133.3, 133.1, 132.9, 130.9, 129.6, 128.9, 128.8, 128.7, 128.6, 128.3, 128.0, 126.7, 126.5, 126.1, 125.9, 125.0, 117.9, 115.5, 111.1, 86.0, 60.4, 60.1, 27.4, 14.3, 13.3, 10.3. HRMS (ESI) m/z calcd for $C_{35}H_{37}N_2O_7^+$ $[M + H]^+$ = 597.2595, found = 597.2587.

(S)-Diethyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5b

A colorless oil; 52.3 mg; isolated yield = 92%; dr = 2.3:1. $[\alpha]^{20.0}_{D}$ = −51.20 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 25.735 min (minor), t_2 = 28.659 min (major), *ee* = 84%; minor product: t_1 = 12.086 min (major), t_2 = 17.613 min (minor), *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.97–7.49 (m, 5H), 7.48–6.78 (m, 9H), 4.56–3.56 (m, 6H), 2.38–2.21 (m, 3H), 1.39–1.35 (m, 4H), 1.04–1.00 (m, 2H), 0.66–0.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.6, 164.3, 164.2, 151.7, 147.6, 136.0, 134.2, 133.4, 133.1, 132.9, 131.0, 129.7, 129.0, 128.6, 128.4, 128.1, 126.5, 126.1, 126.0, 125.0, 117.2, 115.7, 111.2, 64.5, 60.4, 60.1, 14.3, 13.7, 13.3, 10.3. HRMS (ESI) m/z calcd for $C_{33}H_{33}N_2O_7^+$ $[M + H]^+$ = 569.2282, found = 569.2277.

(S)-Diethyl 1-(N-((benzyloxy)carbonyl)cinnamamido)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5c

A colorless oil; 59.2 mg; isolated yield = 94%; dr = 1.7:1. $[\alpha]^{20.0}_{D}$ = −73.10 (*c* 0.55, CH_2Cl_2); HPLC (ID column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 15.874 min (minor), t_2 = 25.353 min (major), *ee* = 68%; minor product: t_1 = 19.745 min (minor), t_2 = 69.702 min (major), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07–7.51 (m, 4H), 7.50–6.71 (m, 15H), 5.36–4.61 (m, 2H), 4.50–4.20 (m, 2H), 4.08–3.59 (m, 2H), 2.30–2.28 (m, 3H), 1.39–1.35 (m, 3H), 0.63–0.57 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 164.5, 164.2, 164.1, 151.6, 147.8, 136.0, 134.1, 133.9, 133.6, 133.4, 132.9, 131.1, 129.8, 129.1, 128.9, 128.9, 128.8, 128.6, 128.5, 128.0, 127.7, 126.5, 126.3, 126.1, 126.0, 124.9, 117.1, 115.7, 111.5, 69.5, 60.4, 60.1, 14.3, 13.3, 10.3. HRMS (ESI) m/z calcd for $C_{38}H_{35}N_2O_7^+$ $[M + H]^+$ = 631.2439, found = 631.2440.

(S)-3-Benzyl 4-ethyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5d

A colorless oil; 56.7 mg; isolated yield = 90%; dr = 2.3:1. $[\alpha]^{20.0}_{D}$ = −54.00 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 26.903 min (minor), t_2 = 37.429 min (major), *ee* = 95%; minor product: t_1 = 13.964 min (major), t_2 = 19.710 min (minor), *ee* = 84%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–6.85 (m, 19H), 5.35 (s, 2H), 4.55–3.56 (m, 4H), 2.38–2.37 (m, 3H), 1.37–0.99 (m, 3H), 0.57–0.59 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.3, 164.3, 164.2, 151.7, 147.7, 136.5, 136.3, 134.2, 133.4, 133.1, 132.9, 131.1, 129.8, 129.0, 128.6, 128.5, 128.4, 128.0, 127.7, 126.5, 126.4, 126.1, 126.0, 125.0, 117.2, 115.9, 110.7, 66.4, 64.5, 60.1, 13.7, 13.3, 10.4. HRMS (ESI) m/z calcd for $C_{38}H_{35}N_2O_7^+$ $[M + H]^+$ = 631.2439, found = 631.2426.

(*S*)-3-Ethyl 4-methyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5e

A colorless oil; 54.3 mg; isolated yield = 98%; dr = 1.3:1. $[\alpha]^{20.0}_{D}$ = −85.61 (*c* 0.50, CH_2Cl_2); HPLC (IF column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 18.255 min (minor), t_2 = 33.880 min (major), *ee* = 97%; minor product: t_1 = 12.078 min (minor), t_2 = 13.395 min (major), *ee* = 93%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.49 (m, 5H), 7.49–6.80 (m, 9H), 4.57–3.61 (m, 4H), 3.44–3.41 (m, 3H), 2.39–2.38 (m, 3H), 1.39–1.34 (m, 4H), 1.04–1.00 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.2, 165.0, 164.5, 164.3, 151.6, 147.7, 136.2, 134.2, 133.4, 133.0, 132.7, 131.0, 129.9, 129.0, 128.8, 128.6, 128.4, 128.2, 127.8, 126.4, 126.2, 126.0, 125.9, 125.0, 117.2, 115.4, 111.1, 64.5, 60.4, 51.5, 14.3, 13.7, 10.3. HRMS (ESI) m/z calcd for $C_{32}H_{31}N_2O_7^+$ $[M + H]^+$ = 555.2126, found = 555.2119.

(*S*)-3-Ethyl 4-isopropyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-methyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5f

A colorless oil; 56.0 mg; isolated yield = 96%; dr = 1.5:1. $[\alpha]^{20.0}_{D}$ = −109.63 (*c* 0.53, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 10.810 min (major), t_2 = 14.810 min (minor), *ee* = 90%; minor product: t_1 = 16.521 min (major), t_2 = 27.272 min (minor), *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.49 (m, 5H), 7.48–6.86 (m, 9H), 4.85–4.54 (m, 1H), 4.50–3.67 (m, 4H), 2.38–2.37 (m, 3H), 1.39–1.36 (m, 4H), 1.05–1.01 (m, 2H), 0.73–0.65 (m, 3H), 0.59–0.45 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.6, 164.3, 163.6, 151.7, 147.6, 135.9, 134.2, 133.3, 133.2, 133.0, 133.0, 131.0, 129.6, 128.9, 128.6, 128.4, 128.0, 126.7, 126.7, 126.3, 125.9, 124.9, 117.2, 116.1, 111.2, 67.3, 64.5, 60.4, 21.3, 20.7, 14.3, 13.7, 10.2. HRMS (ESI) m/z calcd for $C_{34}H_{35}N_2O_7^+$ $[M + H]^+$ = 583.2439, found = 583.2439.

(*S*)-Diethyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-ethyl-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5g

A colorless oil; 50.1 mg; isolated yield = 86%; dr = 1.2:1. $[\alpha]^{20.0}_{D}$ = −79.32 (*c* 0.50, CH_2Cl_2); HPLC (IF column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 9.443 min (minor), t_2 = 11.384 min (major), *ee* = 93%; minor product: t_1 = 12.997 min (minor), t_2 = 24.180 min (major), *ee* = 95%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.50 (m, 5H), 7.47–6.83 (m, 9H), 4.53–3.53 (m, 6H), 2.97–2.53 (m, 2H), 1.39–1.35 (m, 4H), 1.24–0.94 (m, 5H), 0.65–0.56 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.4, 164.3, 164.3, 151.9, 147.6, 141.1, 134.2, 133.4, 132.9, 132.9, 131.0, 129.7, 129.0, 128.8, 128.6, 128.4, 128.1, 127.6, 126.7, 126.5, 126.2, 125.9, 125.0, 117.3, 115.9, 110.9, 64.4, 60.4, 60.1, 18.4, 14.3, 13.6, 13.4, 13.3. HRMS (ESI) m/z calcd for $C_{34}H_{35}N_2O_7^+$ $[M + H]^+$ = 583.2439, found = 583.2429.

(*S*)-3-Ethyl 4-methyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-(naphthalen-1-yl)-5-propyl-1*H*-pyrrole-3,4-dicarboxylate: 5h

A colorless oil; 51.8 mg; isolated yield = 89%; dr = 1.4:1. $[\alpha]^{20.0}_{D}$ = −63.52 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 15.843 min (major), t_2 = 20.782 min (minor), *ee* = 96%; minor product: t_1 = 10.11 min (major), t_2 = 10.74 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05–7.50 (m, 5H), 7.49–6.85 (m, 9H), 4.43–3.53 (m, 7H), 2.97–2.45 (m, 2H), 1.72–1.32 (m, 3H), 1.00–0.96 (m, 5H), 0.63–0.55 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.0, 164.3, 164.2, 151.8, 147.7, 139.8, 134.2, 133.4, 132.9, 131.0, 129.8, 129.0, 128.6, 128.4, 128.1, 126.6, 126.5, 126.2, 125.9, 125.0, 117.2, 115.6, 111.2, 64.4, 60.1, 51.6, 26.8, 22.2, 14.2, 13.6, 13.3. HRMS (ESI) m/z calcd for $C_{34}H_{35}N_2O_7^+$ $[M + H]^+$ = 583.2439, found = 583.2429.

(*S*)-4-Ethyl 3-methyl 2-benzyl-1-(N-(ethoxycarbonyl)cinnamamido)-5-(naphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5i

A colorless oil; 52.9 mg; isolated yield = 84%; dr = 1.1:1. $[\alpha]^{20.0}_{D}$ = −79.10 (*c* 0.55, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 9.738 min (major), t_2 = 14.429 min (minor), *ee* = 91%; minor product: t_1 = 22.438 min (major), t_2 = 28.628 min (minor), *ee* = 98%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.49 (m, 5H), 7.49–6.70 (m, 14H), 4.66–4.52 (m, 1H), 3.91 (s, 3H), 3.90–2.99 (m, 5H), 1.12–1.08 (m, 1H), 0.71–0.41 (m, 5H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.1, 164.3, 164.0, 151.3, 147.7, 137.4, 136.9, 134.3, 134.1, 133.3, 132.7, 131.0, 129.7, 129.0, 128.7, 128.5, 128.1, 126.6, 126.4, 126.2, 126.0, 125.9, 117.3, 115.5, 112.2, 64.2, 60.2, 51.8, 31.0, 13.2, 13.1. HRMS (ESI) m/z calcd for $C_{38}H_{35}N_2O_7^+$ $[M + H]^+$ = 631.2439, found = 631.2433.

(*S*)-Diethyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-methyl-5-(4-methylnaphthalen-1-yl)-1*H*-pyrrole-3,4-dicarboxylate: 5j

A colorless oil; 57.0 mg; isolated yield = 98%; dr = 1.1:1. $[\alpha]^{20.0}_{D}$ = −111.01 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 13.074 min (major), t_2 = 26.493 min (minor), *ee* = 85%; minor product: t_1 = 21.433 min (minor), t_2 = 40.600 min (major), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.49 (m, 4H), 7.49–6.85 (m, 9H), 4.60–3.66 (m, 6H), 2.66 (s, 3H), 2.38–2.37 (m, 3H), 1.39–1.35 (m, 4H), 1.05–1.01 (m, 2H), 0.71–0.63 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 165.1, 164.3, 164.0, 151.3, 147.7, 137.4, 136.9, 134.3, 134.1, 133.3, 132.7, 131.0, 129.7, 129.0, 128.7, 128.5, 128.1, 126.6, 126.4, 126.2, 126.0, 125.9, 124.9, 117.3, 115.5, 112.2, 64.2, 60.2, 51.8, 31.0, 13.9, 13.3, 13.2, 13.1. HRMS (ESI) m/z calcd for $C_{34}H_{35}N_2O_7^+$ $[M + H]^+$ = 583.2439, found = 583.2441.

(*S*)-Diethyl 1-(N-(ethoxycarbonyl)cinnamamido)-2-(4-methoxynaphthalen-1-yl)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 5k

A colorless oil; 55.0 mg; isolated yield = 92%; dr = 1.1:1. $[\alpha]^{20.0}_{D}$ = −83.81 (*c* 0.50, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 19.525 min (minor), t_2 = 40.537 min (major), *ee* = 97%; minor product: t_1 = 12.895 min (major), t_2 = 24.465 min (minor), *ee* = 91%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.32–7.96 (m, 1H), 7.85–7.43 (m, 3H), 7.40–6.99 (m, 8H), 6.92–6.55 (m, 1H), 4.38–3.56 (m, 9H), 2.30–2.29 (m, 3H), 1.31–1.27 (m, 4H), 0.97–0.93 (m, 2H), 0.63–0.58 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.3, 164.6, 164.4, 164.3, 156.4, 151.8, 147.5, 135.8, 134.2, 133.8, 133.3, 131.0, 129.3, 129.0, 128.6, 128.4, 126.7, 126.4, 125.9, 125.4, 125.2, 122.0, 118.3, 117.3, 115.8, 111.0, 103.0, 64.4, 60.4, 60.1, 55.5, 14.3, 13.7, 13.5, 10.3. HRMS (ESI) m/z calcd for $C_{34}H_{35}N_2O_8^+$ $[M + H]^+$ = 599.2388, found = 599.2388.

(S)-Diethyl 2-(3,7-dimethylnaphthalen-1-yl)-1-(N-(ethoxycarbonyl)cinnamamido)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 5l

A colorless oil; 55.4 mg; isolated yield = 93%; dr = 1.3:1. $[\alpha]^{20.0}_{D}$ = −95.41 (*c* 0.50, CH_2Cl_2); HPLC (IF column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 6.500 min (major), t_2 = 7.417 min (minor), *ee* = 86%; minor product: t_1 = 9.564 min (minor), t_2 = 26.629 min (minor), *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96–7.49 (m, 4H), 7.49–6.74 (m, 8H), 4.61–3.57 (m, 6H), 2.45–2.39 (m, 6H), 2.31–2.30 (m, 3H), 1.39–1.32 (m, 4H), 1.00–0.97 (m, 2H), 0.71–0.65 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 164.7, 164.5, 164.3, 151.7, 147.4, 136.1, 134.6, 134.2, 133.4, 133.3, 132.0, 131.2, 131.0, 130.9, 129.0, 128.9, 128.6, 128.4, 128.2, 125.6, 125.1, 124.6, 117.4, 115.6, 111.1, 64.3, 60.4, 60.1, 21.8, 21.4, 14.3, 13.6, 13.4, 10.3. HRMS (ESI) m/z calcd for $C_{35}H_{37}N_2O_7^+$ $[M + H]^+$ = 597.2595, found = 597.2603.

General procedure for asymmetric synthesis of compound 6

Compound **1e′** (0.10 mmol), MBH carbonic ester **2e** (0.15 mmol) were dissolved in DCM (1 mL), and **C3** (10 mol %) were added. The reaction mixture was stirred for 6 h at room temperature. The solvent was removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1–2:1) to afford the product **6**. A colorless solid; 52.0 mg; isolated yield = 90%; m.p. 72.2°C–72.8°C; $[\alpha]^{20}_{D}$ = +51.34 (c 0.025, THF); HPLC (IC column, *i*-propanol/*n*-hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 9.22 min (minor), t_2 = 11.05 min (major), *ee* = 97%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91–7.77 (m, 4H), 7.56–7.48 (m, 2H), 7.46–7.33 (m, 1H), 6.13–6.01 (m, 1H), 5.43–5.23 (m, 1H), 4.55–4.37 (m, 1H), 4.34–4.22 (m, 2H), 4.11–3.94 (m, 2H), 3.93–3.84 (m, 3H), 3.63–3.41 (m, 1H), 2.37–2.24 (m, 3H), 1.55–1.43 (m, 2H), 1.39 (s, 9H), 1.36–1.28 (m, 3H), 0.70–0.51 (m, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.4, 164.4, 164.2, 155.9, 155.4, 137.1, 136.7, 135.0, 134.7, 133.2, 133.0, 132.5, 131.4, 129.5, 128.7, 128.6, 128.5, 128.3, 128.3, 128.1, 127.8, 127.2, 127.1, 126.9, 126.8, 126.6, 126.6, 126.5, 125.7, 115.2, 110.2, 81.6, 68.2, 66.5, 66.4, 62.9, 60.3, 60.2, 54.3, 54.1, 51.2, 50.5, 27.8, 21.8, 21.4, 20.9, 19.2, 18.9, 14.3, 14.0, 13.5, 10.7, 10.2, 9.9; HRMS (ESI) m/z calcd for $C_{32}H_{38}N_2O_8Na^+$ $[M+Na]^+$ = 601.2520, found = 601.2525.

General procedure for kinetic resolution of 7

Racemic axial chiral compound **7** (0.2 mmol), MBH carbonic ester **2e** (0.1 mmol) were dissolved in DCM (10 mL), and **C3** (10 mol %) was added. The reaction mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and the crude product was separated by flash column chromatography on silica gel (petroleum ether/ethyl acetate = 4:1) to afford the product 8 and recover compound **7**.

(S)-Diethyl 2-(2-(benzyloxy)naphthalen-1-yl)-1-((*tert*-butoxycarbonyl)amino)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 7

A colorless oil; 49.2 mg; isolated yield = 43%; $[\alpha]^{32.6}_{D}$ = +187.36 (*c* 0.30, CH_2Cl_2); HPLC (IC column, *i*-propanol/hexane = 30/70, flow rate 1.0 mL/min, λ = 254 nm), product: t_1 = 8.06 min (minor), t_2 = 14.24 min (major), *ee* = 90%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (d, *J* = 9.0 Hz, 1H), 7.74 (s, 2H), 7.40–7.28 (m, 6H), 7.23–7.17 (m, 2H), 7.00–6.89 (m, 1H), 5.21–5.08 (m, 2H), 4.45–4.15 (m, 2H), 3.99–3.55 (m, 2H), 2.45 (s, 3H), 1.37 (t, *J* = 7.1 Hz, 3H), 0.91 (s, 9H), 0.57 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.8, 164.4, 154.1, 153.9, 137.2, 136.5, 134.1, 131.2, 129.6, 128.7, 128.2, 127.4, 126.8, 124.5, 116.2, 115.1, 110.5, 82.0, 72.9, 60.2, 59.9, 27.3, 14.3, 13.3, 10.5; HRMS (ESI) m/z calcd for $C_{33}H_{37}N_2O_7^+$ $[M + H]^+$ = 573.2595, found = 573.2590.

(R,R)-Diethyl 2-(2-(benzyloxy)naphthalen-1-yl)-1-((*tert*-butoxycarbonyl)(2-(*tert*-butoxycarbonyl)allyl)amino)-5-methyl-1*H*-pyrrole-3,4-dicarboxylate: 8

A colorless oil; 65.5 mg; isolated yield = 46%; dr = 7.7:1. $[\alpha]^{20.0}_{D}$ = −98.00 (*c* 0.30, CH_2Cl_2); HPLC (IC column, *i*-propanol/*n*-hexane = 20/80, flow rate 1.0 mL/min, λ = 254 nm), major product: t_1 = 6.26 min (minor), t_2 = 6.98 min (major), *ee* = 92%; minor product: t_1 = 5.74 min (major), t_2 = 7.84 min (minor), *ee* = 94%; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–7.47 (m, 3H), 7.43–7.14 (m, 8H), 5.77–5.67 (m, 1H), 5.24–5.04 (m, 2H), 4.92–4.70 (m, 1H), 4.47–3.73 (m, 6H), 2.37–2.34 (m, 3H), 1.47–1.43 (m, 9H), 1.41–1.35 (m, 3H), 1.33–1.09 (m, 9H), 0.78–0.49 (m, 3H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 164.8, 164.4, 155.6, 153.0, 136.9, 136.8, 134.9, 131.4, 130.0, 128.9, 128.5, 127.9, 127.6, 127.1, 126.6, 126.3, 124.0, 115.4, 114.7, 113.9, 110.5, 82.8, 81.1, 71.2, 60.2, 59.8, 50.8, 14.3, 13.4, 10.9. HRMS (ESI) m/z calcd for $C_{41}H_{49}N_2O_9^+$ $[M + H]^+$ = 713.3433, found = 713.3442.