Enantioselective [4+2] Annulation to the Concise Synthesis of Chiral Dihydrocarbazoles

HIGHLIGHTS

- Good yields with high enantioselectivity
- Concise synthesis of chiral analgesic agent
- Mild conditions
- Broad substrate scope

Wang et al., iScience 23, 100840 February 21, 2020 © 2020 The Author(s).
https://doi.org/10.1016/j.isci.2020.100840
Enantioselective [4+2] Annulation to the Concise Synthesis of Chiral Dihydrocarbazoles

Haiyang Wang, Qingdong Hu, Mingxu Wang, and Chang Guo

SUMMARY
A highly efficient phosphine-catalyzed enantioselective [4 + 2] annulation of allenoates with 3-nitroindoles or 3-nitrobenzothiophenes has been developed. The protocol represents a unique dearomatization-aromatization process to access functionalized dihydrocarbazoles or dihydrodibenzothiophenes with high optical purity (up to 97% ee) under mild reaction conditions. The synthetic utility of the highly enantioselective [4 + 2] annulation enables a concise synthesis of analgesic agent.

INTRODUCTION
Fused polycyclic indoles are common structural motifs found in a vast array of natural and biologically active molecules (Saxton, 1996; Knölker and Reddy, 2002; Schmidt et al., 2012; Tan and Cheng, 2019), such as kopsihaiinanine A, isoeelliptitoxin, and analgesic agents (Scheme 1A) (Madalengoitia and Macdonald, 1993; Carmosin et al., 2000; Chen et al., 2011). In this regard, the development of efficient methods for enantioselective construction of hydrocarbazole skeleton is still highly demanded (Sings et al., 2001; Lu et al., 2012; Zhou et al., 2015; Gu et al., 2016). The group of Jørgensen disclosed a novel [4 + 2] annulation by trienamine catalysis, thus obtaining dihydrocarbazoles in good yields and enantioselectivities (Li et al., 2016). In this context, we hypothesized that the development of new methods through the enantioselective phosphine-catalyzed [4 + 2] dearomatization would provide practical and efficient approach to this class of enantoenriched heterocycles (Scheme 1B).

Phosphine catalysis has been recognized as a reliable tool for the development of unique transformations of allenoates, allowing for the discovery of novel asymmetric synthetic methodology (Lu et al., 2001; Methot and Roush, 2004; Ye et al., 2008; Cowen and Miller, 2009; Wei and Shi, 2010, 2017; Fan and Kwon, 2013; Wang et al., 2014; 2016; López and Mascareñas, 2014; Xie and Huang, 2015; Li and Zhang, 2016a; Li and Lu, 2017; Ni et al., 2018; Guo et al., 2018). Considerable research efforts have been devoted to the development of new methods for the phosphine-catalyzed enantioselective reactions. The use of phosphine catalysts has introduced a set of elementary steps that operate via discrete reactive species, allowing access to natural products and pharmaceuticals (Tran and Kwon, 2005; Andrews and Kwon, 2012; Han et al., 2012; Wang and Knoche, 2003; Cai et al., 2016). One particularly versatile and reactive species is the phosphine-mediated 1,4-dipole generated upon addition of the phosphine catalyst to an allenoate substrate, thus providing a concise approach for accessing enantioselective annulations. Specially, Kwon group reported the result of their pioneering studies toward the development of a novel [4 + 2] annulation reaction of allenoates and N-tosylimines in the presence of phosphine catalyst (Zhu et al., 2003). Later, Fu group reported the phosphine-catalyzed highly enantioselective [4 + 2] annulation of N-tosylimines with allenoates (Wurz and Fu, 2005). Although great achievements have been made, concise syntheses of useful heterocycles involving phosphine-catalyzed [4 + 2] annulations in asymmetric versions were still rare (Tran and Kwon, 2007; Wang and Ye, 2010; Tran et al., 2011; Xiao et al., 2011; Baskar et al., 2011; Yu and Ma, 2012; Zhong et al., 2012; Takiyama et al., 2014; Yu et al., 2014; Liu et al., 2016; Wang and Guo, 2019). Moreover, the development of an enantioselective phosphine-catalyzed [4 + 2] dearomatization reaction would provide an attractive and complementary approach for construction of privileged motifs, which will be of great value for the synthesis of bioactive molecules (Scheme 1C).

Enantioselective dearomatization reactions of heteroaromatic compounds are very powerful transformations because they provide direct access to a wide variety of chiral heterocycles (You, 2016; Roche and Porco, 2011; Zhuo et al., 2012; Zhuo et al., 2014; Zheng and You, 2016; Sun et al., 2016; Wu et al., 2016). In recent years, 3-nitroindole was demonstrated to be a good substrate for various dearomatization
processes, and a number of enantioselective approaches have been reported (Awata and Arai, 2014; Zhao et al., 2015a, 2015b, 2018, 2019; Gerten and Stanley, 2016; Tröst et al., 2014; Cheng et al., 2018; Zhang et al., 2018; Sun et al., 2018; Yue et al., 2017; Yang et al., 2019). Importantly, Lu group (Li et al., 2019) and Zhang group (Wang et al., 2019b) independently reported the efficient phosphine-catalyzed enantioselective [3 + 2] annulation of 3-nitroindoles with allenoates to afford cyclopentaindoline products in high yields and excellent enantioselectivities. We envisaged that heteroaromatic systems bearing an electron-withdrawing group could react with phosphine-mediated zwitterionic intermediate in a process involving the [4 + 2] reaction to achieve the chiral dihydrocarbazole scaffold (Scheme 1C). With this objective in mind, a readily available 3-nitroindole derivative was selected as a model substrate to investigate the optimum reaction condition for the enantioselective [4 + 2] dearomatization reaction using a phosphine catalyst.

RESULTS AND DISCUSSION

Based on our previous work on phosphine chemistry (Wang and Guo, 2019a), we initiated the study by investigating the reaction between 1a and 2a in the presence of the phosphine 4a (Table 1, entry 1). Initially, diverse chiral phosphine catalysts were examined (entries 1–5). However, the catalyst 4a to 4c did not work for this reaction (entries 1–3). To our great delight, the desired dihydrocarbazole 3a could be obtained when the chiral phosphine 4d was employed (entry 4). After surveying an array of additives, we determined that silica gel can promote elimination of HNO2 for the aromatization process to afford the corresponding adduct in 92% yield with 94% ee (entry 4) (So and Mattson, 2012; Long et al., 2016). Other additives, such as Sc(OTf)3, Et3N, and SnCl2 led to byproducts (for further details, see Table S1 in the Supplemental Information). Furthermore, the ee values of the 3a decreased to 80% with low yield in the presence of 4e as catalyst (entry 5). Varying the solvents led to no improvement in the reaction, and toluene was proven to be the best choice (entries 4 vs 6–8). Further optimization studies revealed that the protection group of the 3-nitroindole was also sensitive to the reaction, and the variation of the N-substituent of the 3-nitroindole 1a' or 1a'' generated no product at all (entries 9 and 10) (Rivinoja et al., 2017; Suo et al., 2018).
With the optimal reaction conditions in hand, we set out to explore the substrate scope of the procedure. As shown in Scheme 2, various electron-withdrawing or donating groups on the indole ring were well tolerated and resulted in excellent levels of enantioselectivities ranging from 86% to 97% ee (3a–3j). The extension of the protocol to the 3-nitroindole with a variety of substitution patterns at the 5-position was successful to afford corresponding adducts with excellent enantioselectivities (3b–3f). To our delight, substrates bearing substituents on different positions of the indole ring also facilitate the annulation with high yields and ee values (3b, 3g, and 3j). The absolute configuration of the enantiopure 3i, recrystallized from ethyl acetate and petroleum ether, was assigned by single-crystal X-ray diffraction analysis.

The generality of the reaction with respect to the scope of the allenoates 2 was also investigated using 3-nitroindole 1a as the reaction partner under the optimized conditions. A diverse array of allenoates (2) with a variety of functional groups (methyl, fluoro, chloro, bromo, ester, trifluoromethyl, and cyano) performed well in this annulation reaction, and the corresponding products were isolated in good yields with high ee values (3k–3q). Remarkably, this method was compatible with alkyl allenoate, affording the desired products in good yields with good enantioselectivity (3v–3x). Additionally, all reactions with different esters attached to the allenoates proceeded smoothly, giving the corresponding products in good yields and excellent ee (3y and 3z). To test the synthetic utility of the current annulation, we performed the reaction on a 1 mmol scale with the formation of 3z in 56% yield and 92% ee.

Table 1. Optimization of Reaction Conditions

| Entry | 1     | 4     | Solvent | Yield (%)a | ee (%)b |
|-------|-------|-------|---------|------------|---------|
| 1     | 1a    | 4a    | Toluene | nr         | –       |
| 2     | 1a    | 4b    | Toluene | nr         | –       |
| 3     | 1a    | 4c    | Toluene | nr         | –       |
| 4     | 1a    | 4d    | Toluene | 92         | 94      |
| 5     | 1a    | 4e    | Toluene | 26         | 80      |
| 6     | 1a    | 4d    | CH2Cl2  | 23         | 73      |
| 7     | 1a    | 4d    | THF     | 73         | 84      |
| 8     | 1a    | 4d    | Dioxane | 57         | 90      |
| 9     | 1a’   | 4d    | Toluene | nr         | –       |
| 10    | 1a”   | 4d    | Toluene | nr         | –       |

Unless indicated otherwise, the reactions were conducted with 1 (0.1 mmol), 2a (0.15 mmol), and 4 (0.01 mmol) in toluene (1.0 mL) at room temperature for 18 h. Then silica gel (200 mg) was added to the reaction mixture to complete elimination of HNO₂. nr = no reaction.

aYield of isolated product.
bDetermined by HPLC analysis.
The scope of 3-nitroindoles 1:

3a, 92%, 94% ee
3b, 84%, 92% ee
3c, 52%, 91% ee
3d, 76%, 92% ee
3e, 61%, 97% ee
3f, 50%, 92% ee
3g, 86%, 95% ee
3h, 51%, 86% ee
3i, 61%, 91% ee
3j, 55%, 90% ee

The scope of alkenoates 2:

3k, 77%, 94% ee
3l, 92%, 94% ee
3m, 91%, 94% ee
3n, 70%, 93% ee
3o, 80%, 94% ee
3p, 88%, 94% ee
3q, 87%, 94% ee
3r, 58%, 92% ee
3s, 52%, 92% ee
3t, 62%, 94% ee
3u, 88%, 93% ee
3v, 65%, 92% ee
3w, 75%, 90% ee
3x, 70%, 81% ee
3y, 69%, 93% ee
3z, 76%, 92% ee
Encouraged by the excellent results with various 3-nitroindoles, we then investigated the [4 + 2] annulation reaction with a range of 3-nitrobenzothiophenes (5). Remarkably, process where the 3-nitrobenzothiophene as a reactive partner for asymmetric annulation has been much less studied (Tran and Kwon, 2007; Wang and Ye, 2010; Tran et al., 2011; Xiao et al., 2011; Baskar et al., 2011; Yu and Ma, 2012; Zhong et al., 2012; Takizawa et al., 2014; Yu et al., 2014; Liu et al., 2016; Wang and Guo, 2019a; Cheng et al., 2000; Cheng et al., 2017; Suo et al., 2018; Yue et al., 2018; Chen et al., 2019). Using phosphine 4d in toluene at 0°C, we were able to access dihydrodibenzothiophene products 6 (Scheme 3). Under the optimized reaction condition (for further details, see Table S2 in the Supplemental Information), a broad range of allenotes 2 and 3-nitrobenzothiophenes 5 were investigated. Allenotes with different substituents on the aromatic ring underwent this catalytic transformation smoothly in good yields with excellent ee (6a and 6b). Furthermore, various substitutions of 3-nitrobenzothiophenes 5 at the aromatic ring had little impact on the reactions (6c–6h, 91%–97% ee).

To highlight the synthetic potential of the present method, the dihydrocabazole 3v, which was obtained from the enantioselective [4 + 2] annulation, can be easily converted into analgesic agent 9 (Scheme 4). In 2000, Carmosin and co-workers obtained the racemic analgesic agent 9 via the Diels-Alder reaction,
and the optical product was obtained by using preparative chromatography (Carmosin et al., 2000). Taking advantage of our current phosphine-catalyzed enantioselective [4 + 2] reaction, we can easily obtain the analgesic agent \( \text{9} \) with excellent enantioselectivity. Hydrogenation of \( \text{3v} \) in the presence of a catalytic amount of Pd/C, followed by amidation with MeNH₂ gave rise to the desired amide \( \text{7} \) in 84% yield over two steps. The configuration of compound \( \text{7} \) was assigned by X-ray analysis. The subsequent chlorination of alcohol, deprotection of the N-Boc group and cyclization furnished \( \text{8} \) in good yield. Finally, the amide \( \text{8} \) was reduced to generate the corresponding analgesic agent \( \text{9} \) in 78% yield and 92% ee.

The proposed catalytic cycle for the enantioselective [4 + 2] annulation is illustrated in Figure 1. The addition of phosphine catalyst \( \text{4d} \) to the allenoate \( \text{2} \) gives the intermediate \( \text{A} \), which could react with the 3-nitroindole \( \text{1} \) or 3-nitrobenzothiophenes \( \text{5} \) to form the intermediate \( \text{B} \). Following migration and intramolecular conjugate addition give rise to the intermediate \( \text{D} \) and regenerate the phosphine \( \text{4d} \). This species \( \text{D} \) then undergoes elimination of HNO₂ through the aromatization process to furnish the final dihydrocarbazole \( \text{3} \) or dihydrodibenzothiophene \( \text{6} \).

In summary, we have developed simple and efficient synthetic routes to highly enriched hydrocarbozoles through chiral phosphine-catalyzed [4 + 2] annulation utilizing 3-nitroindole and allenoates as starting materials. This phosphine-catalyzed enantioselective [4 + 2] annulation procedure involving tandem dearomatization and aromatization steps proceeds under mild conditions. This reaction displays a broad substrate scope with respect to the substituents. Additionally, the obtained dihydrocarbozole could be efficient transformed to an analgesic agent containing polycyclic indole frameworks.

Limitations of the Study
The synthesis of the products needs two steps in one pot. No product was formed with the initial addition of silica gel.

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

DATA AND CODE AVAILABILITY
Crystallographic data for the structures reported in this article have been deposited at the Cambridge Crystallographic Data Center (CCDC) under accession numbers CCDC 1938371 (3i) and CCDC 1955757 (7). Copies of the data can be obtained free of charge from www.ccdc.cam.ac.uk/structures/.
SUPPLEMENTAL INFORMATION
Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2020.100840.

ACKNOWLEDGMENTS
The authors acknowledge financial support from the National Natural Science Foundation of China (grant no. 21702198), the Anhui Provincial Natural Science Foundation (grant no. 1808085MB30), "1000-Youth Talents Plan,"* and the Fundamental Research Funds for the Central Universities (WK2340000090).

AUTHOR CONTRIBUTIONS
H.W. carried out the experimental and data analysis work. Q.H. and M.W. prepared some starting materials. C.G. designed the reaction and directed the project. The paper was written by C.G. with assistance of H.W., Q.H., and M.W.

DECLARATION OF INTERESTS
The authors declare no conflict of interest.

Received: November 14, 2019
Revised: December 31, 2019
Accepted: January 9, 2020
Published: February 21, 2020

REFERENCES
Andrews, I.P., and Kwon, O. (2012). Enantioselective total synthesis of (+)-ibophyllidine via an asymmetric phosphine-catalyzed [3 + 2] annulation. Chem. Sci. 3, 2510–2514.

Awata, A., and Arai, T. (2014). Pyridine/Copper catalyst: asymmetric exo’-selective [3+2] cycloaddition using imino ester and electrophilic indole. Angew. Chem. Int. Ed. 53, 10462–10465.

Baskar, B., Dakas, P.-Y., and Kumar, K. (2011). Natural product biosynthesis inspired concise and stereoselective synthesis of benzopyrones and related scaffolds. Org. Lett. 13, 1988–1991.

Cai, L., Zhang, K., and Kwon, O. (2016). Catalytic asymmetric total synthesis of (-)-actinophyllic acid. J. Am. Chem. Soc. 138, 3298–3301.

Carmosin, R.J., Carson, J.R., and Pitis, P.M. (2000). Octahydropyrrolo-(3,4-C)-carbazoles useful as analgesic agents. US Patent No. 6063803.
Chen, J., Chen, J.-J., Yao, X., and Gao, X. (2011). Kopsiahaneamines A and B, two unusual alkaloids from kopsiaahaneanism. Org. Biomol. Chem. 9, 5334–5336.

Chen, X.-M., Lei, C.-W., Yue, D.-F., Zhao, J.-Q., Wang, Z.-H., Zhang, X.-M., Xu, X.-Y., and Yuan, W.-C. (2019). Organocatalytic asymmetric dearomatization of 3-nitroindoles and 3-nitrobenzothiophenes via thiol-triggered diastereo- and enantioselective double michael addition reaction. Org. Lett. 21, 5452–5456.

Cheng, Q., Zhang, F., Cai, Y., Guo, Y.-L., and You, S.-L. (2018). Stereodivergent synthesis of tetrahydrofuroindoles through Pd-catalyzed diastereo- and enantioselective double Michael addition reaction. Tetrahedron Lett. 59, 2134–2138.

Cheng, Q., Zhang, H.-J., Yue, W.-J., and You, S.-L. (2020). Organo- and propargylsulfonamides and allylic acetates: synthesis of pyrroloindolines by Pd-catalyzed tertiary amine-catalyzed formal [4+2] cycloadditions of allenes, alkynes, and MBHADs. Chem. Commun. (Camb.) 46, 5198–5201.

Cowen, B.J., and Miller, S.J. (2009). Enantioselective de arylation. In: C. Wipf and J.A. Porco (Eds.), Concise construction of diverse heterocyclic compounds: the chemistry of the monoterpenoid indole alkaloids. Wiley: Hoboken, NJ, pp. 235–250.

Cowen, B.J., and Miller, S.J. (2009). Enantioselective de arylation. In: C. Wipf and J.A. Porco (Eds.), Concise construction of diverse heterocyclic compounds: the chemistry of the monoterpenoid indole alkaloids. Wiley: Hoboken, NJ, pp. 235–250.

Cowan, B., and Miller, S.J. (2009). Enantioselective de arylation. In: C. Wipf and J.A. Porco (Eds.), Concise construction of diverse heterocyclic compounds: the chemistry of the monoterpenoid indole alkaloids. Wiley: Hoboken, NJ, pp. 235–250.

Cowan, B., and Miller, S.J. (2009). Enantioselective de arylation. In: C. Wipf and J.A. Porco (Eds.), Concise construction of diverse heterocyclic compounds: the chemistry of the monoterpenoid indole alkaloids. Wiley: Hoboken, NJ, pp. 235–250.
Wang, T., Han, X., Zhong, F., Yao, W., and Lu, Y. (2016). Multifunctional chiral phosphate organocatalysts in catalytic asymmetric Morita–Baylis–Hillman and related reactions. Acc. Chem. Res. 49, 1369–1378.

Wang, Z., Xu, X., and Kwon, O. (2014). Phosphine catalysis of alkenes with electrophiles. Chem. Soc. Rev. 43, 2927–2940.

Wei, Y., and Shi, M. (2010). Multifunctional chiral phosphate organocatalysts in catalytic asymmetric Morita–Baylis–Hillman and related reactions. Acc. Chem. Res. 43, 1005–1018.

Wei, Y., and Shi, M. (2017). Lu’s 3 + 2 cycloaddition of allenes with electrophiles: discovery, development and synthetic application. Org. Chem. Front. 4, 1876–1890.

Wu, W.-T., Zhang, L., and You, S.-L. (2016). Catalytic asymmetric dearomatization (CADA) reactions of phenol and aniline derivatives. Chem. Soc. Rev. 45, 1570–1580.

Wurz, R.P., and Fu, G.C. (2005). Catalytic asymmetric synthesis of piperidine derivatives through the [4 + 2] annulation of imines with allenes. J. Am. Chem. Soc. 127, 12234–12235.

Xiao, H., Chai, Z., Wang, H.-F., Wang, X.-W., Cao, D.-D., Liu, W., Lu, Y.-P., Yang, Y.-Q., and Zhao, G. (2011). Bifunctional N-acyl-aminophosphine-D. D., Liu, W., Lu, Y.-P., Yang, Y.-Q., and Zhao, G. (2011). Bifunctional N-acyl-aminophosphine-catalyzed asymmetric [4+2] cycloadditions of allenoates and imines with aldehydes: synthesis of sulfamate-fused tetrahydropyridines. Tetrahedron 70, 340–348.

Yu, S., and Ma, S. (2012). Allenes in catalytic asymmetric synthesis and natural product synthesis. Angew. Chem. Int. Ed. 51, 3074–3112.

Yue, D.-F., Zhao, J.-Q., Chen, X.-Z., Zhou, Y., Zhang, X.-M., Xu, X.-Y., and Yuan, W.-C. (2017). Multiple hydrogen-bonding bifunctional thiourea-catalyzed asymmetric dearomative (4 + 2) annulation of 3-nitroindoles: highly enantioselective access to hydrocarbazole skeletons. Org. Lett. 19, 4508–4511.

Zhao, J.-Q., Wu, Z.-J., Zhou, X.-J., Zhou, Y., Xu, X.-Y., Zhang, X.-M., and Yuan, W.-C. (2019). Phosphine-catalyzed dearomative (3 + 2) annulation of 2-nitrobenzofurans with 3-isothiocyanato oxindoles. Org. Lett. 20, 909–912.

Zhao, J.-Q., Yang, L., You, Y., Wang, Z.-H., Xie, K.-X., Zhang, X.-M., Xu, X.-Y., and Yuan, W.-C. (2019). Phosphine-catalyzed dearomative (3 + 2) annulation of 2-nitrobenzofurans and nitrobenzothiophenes with allenoates. Org. Biomol. Chem. 17, 5294–5304.

Yu, H., Zhang, L., Li, Z., Liu, H., Wang, B., Xiao, Y., and Guo, H. (2014). Phosphine-catalyzed [4+2] cycloaddition of sulfamate-derived cyclic imines with allenoates: synthesis of sulfamate-fused tetrahydropyridines. Tetrahedron 70, 340–348.

Zhong, F., Han, X., Wang, Y., and Lu, Y. (2012). Highly enantioselective [4 + 2] annulations catalyzed by amino acid-based phosphines: synthesis of functionalized cyclohexenes and 3-spirocyclohexene-2-oxindoles. Chem. Sci. 3, 1231–1234.

Zhou, L., Xu, B., and Zhang, J. (2015). Metal-Free dehydrogenative Diels–Alder reactions of 2-methyl-3-alkylindoles with dienophiles: rapid access to tetrahydrocarbazoles, carbazoles, and heteroaromatics. Angew. Chem. Int. Ed. 54, 9092–9096.

Zhao, J.-Q., Wu, Z.-J., Zhou, M.-Q., Xu, X.-Y., Zhang, X.-M., and Yuan, W.-C. (2015a). Zn-catalyzed diastereo- and enantioselective cascade reaction of 3-isothiocyanato oxindoles and 3-nitroindoles: stereocontrolled syntheses of polycyclic spirooxindoles. Org. Lett. 17, 5020–5023.

Zhu, X.-F., Lan, J., and Kwon, O. (2003). An expedient phosphine-catalyzed [4 + 2] annulation: synthesis of highly functionalized tetrahydropyridines. J. Am. Chem. Soc. 125, 4716–4717.

Zhao, C.-X., Zhang, W., and You, S.-L. (2012). Catalytic asymmetric dearomatization reactions. Angew. Chem. Int. Ed. 51, 12662–12666.

Zhuo, C.-X., Zheng, C., and You, S.-L. (2014). Transition-metal-catalyzed asymmetric allylic dearomatization reactions. Acc. Chem. Res. 47, 2558–2573.

Ye, L.-W., Zhou, J., and Tang, Y. (2008). Phosphine-triggered synthesis of functionalized cyclic compounds. Chem. Soc. Rev. 37, 1140–1152.

You, S.-L. (2016). Asymmetric Dearomatization Reactions [WileyVCH].
Supplemental Information

Enantioselective [4+2] Annulation
to the Concise Synthesis
of Chiral Dihydrocarbazoles

Haiyang Wang, Qingdong Hu, Mingxu Wang, and Chang Guo
Supplemental Figures for NMR spectrums:

**Figure S1.** $^1$H NMR spectrum of 3a, related to Scheme 2.

**Figure S2.** $^{13}$C NMR spectrum of 3a, related to Scheme 2.
Figure S3. $^1$H NMR spectrum of 3b, related to Scheme 2.

Figure S4. $^{13}$C NMR spectrum of 3b, related to Scheme 2.
Figure S5. $^1$H NMR spectrum of 3c, related to Scheme 2.

Figure S6. $^{13}$C NMR spectrum of 3c, related to Scheme 2.
Figure S7. $^{19}$F NMR spectrum of 3c, related to Scheme 2.
Figure S8. $^1$H NMR spectrum of 3d, related to Scheme 2.

Figure S9. $^{13}$C NMR spectrum of 3d, related to Scheme 2.
Figure S10. $^1$H NMR spectrum of 3e, related to Scheme 2.

Figure S11. $^{13}$C NMR spectrum of 3e, related to Scheme 2.
Figure S12. $^1$H NMR spectrum of 3f, related to Scheme 2.

Figure S13. $^{13}$C NMR spectrum of 3f, related to Scheme 2.
Figure S14. $^1$H NMR spectrum of 3g, related to Scheme 2.

Figure S15. $^{13}$C NMR spectrum of 3g, related to Scheme 2.
Figure S16. $^1$H NMR spectrum of 3h, related to Scheme 2.

Figure S17. $^{13}$C NMR spectrum of 3h, related to Scheme 2.
Figure S18. $^1$H NMR spectrum of 3i, related to Scheme 2.

Figure S19. $^{13}$C NMR spectrum of 3i, related to Scheme 2.
Figure S20. $^1$H NMR spectrum of 3j, related to Scheme 2.

Figure S21. $^{13}$C NMR spectrum of 3j, related to Scheme 2.
Figure S22. $^1$H NMR spectrum of 3k, related to Scheme 2.

Figure S23. $^{13}$C NMR spectrum of 3k, related to Scheme 2.
Figure S24. $^1$H NMR spectrum of 3l, related to Scheme 2.

Figure S25. $^{13}$C NMR spectrum of 3l, related to Scheme 2.
Figure S26. $^{19}\text{F}$ NMR spectrum of 3I, related to Scheme 2.
Figure S27. $^1$H NMR spectrum of 3m, related to Scheme 2.

Figure S28. $^{13}$C NMR spectrum of 3m, related to Scheme 2.
Figure S29. $^1$H NMR spectrum of 3n, related to Scheme 2.

Figure S30. $^{13}$C NMR spectrum of 3n, related to Scheme 2.
Figure S31. $^1$H NMR spectrum of 3o, related to Scheme 2.

Figure S32. $^{13}$C NMR spectrum of 3o, related to Scheme 2.
Figure S33. $^{19}$F NMR spectrum of 3o, related to Scheme 2.
Figure S34. $^1$H NMR spectrum of 3p, related to Scheme 2.

Figure S35. $^{13}$C NMR spectrum of 3p, related to Scheme 2.
Figure S36. $^1$H NMR spectrum of 3q, related to Scheme 2.

Figure S37. $^{13}$C NMR spectrum of 3q, related to Scheme 2.
Figure S38. $^1$H NMR spectrum of 3r, related to Scheme 2.

Figure S39. $^{13}$C NMR spectrum of 3r, related to Scheme 2.
Figure S40. $^1$H NMR spectrum of 3s, related to Scheme 2.

Figure S41. $^{13}$C NMR spectrum of 3s, related to Scheme 2.
Figure S42. $^1$H NMR spectrum of 3t, related to Scheme 2.

Figure S43. $^{13}$C NMR spectrum of 3t, related to Scheme 2.
Figure S44. $^1$H NMR spectrum of 3u, related to Scheme 2.

Figure S45. $^{13}$C NMR spectrum of 3u, related to Scheme 2.
Figure S46. $^1$H NMR spectrum of 3v, related to Scheme 2.

Figure S47. $^{13}$C NMR spectrum of 3v, related to Scheme 2.
Figure S48. $^1$H NMR spectrum of 3w, related to Scheme 2.

Figure S49. $^{13}$C NMR spectrum of 3w, related to Scheme 2.
Figure S50. $^1$H NMR spectrum of 3x, related to Scheme 2.

Figure S51. $^{13}$C NMR spectrum of 3x, related to Scheme 2.
Figure S52. $^1$H NMR spectrum of 3y, related to Scheme 2.

Figure S53. $^{13}$C NMR spectrum of 3y, related to Scheme 2.
Figure S54. $^1$H NMR spectrum of 3z, related to Scheme 2.

Figure S55. $^{13}$C NMR spectrum of 3z, related to Scheme 2.
Figure S56. $^1$H NMR spectrum of 6a, related to Scheme 3.

Figure S57. $^{13}$C NMR spectrum of 6a, related to Scheme 3.
Figure S58. $^1$H NMR spectrum of $6b$, related to Scheme 3.

Figure S59. $^{13}$C NMR spectrum of $6b$, related to Scheme 3.
Figure S60. $^1$H NMR spectrum of 6c, related to Scheme 3.

Figure S61. $^{13}$C NMR spectrum of 6c, related to Scheme 3.
Figure S62. $^1$H NMR spectrum of 6d, related to Scheme 3.

Figure S63. $^{13}$C NMR spectrum of 6d, related to Scheme 3.
Figure S64. $^1$H NMR spectrum of 6e, related to Scheme 3.

Figure S65. $^{13}$C NMR spectrum of 6e, related to Scheme 3.
Figure S66. $^1$H NMR spectrum of 6f, related to Scheme 3.

Figure S67. $^{13}$C NMR spectrum of 6f, related to Scheme 3.
Figure S68. $^1$H NMR spectrum of 6g, related to Scheme 3.

Figure S69. $^{13}$C NMR spectrum of 6g, related to Scheme 3.
Figure S70. $^{19}$F NMR spectrum of 6g, related to Scheme 3.
**Figure S71.** $^1$H NMR spectrum of 6h, related to Scheme 3.

**Figure S72.** $^{13}$C NMR spectrum of 6h, related to Scheme 3.
Figure S73. $^1$H NMR spectrum of 7, related to Scheme 4.

Figure S74. $^{13}$C NMR spectrum of 7, related to Scheme 4.
Figure S75. $^1$H NMR spectrum of 8, related to Scheme 4.

Figure S76. $^{13}$C NMR spectrum of 8, related to Scheme 4.
Figure S77. $^1$H NMR spectrum of 9, related to Scheme 4.

Figure S78. $^{13}$C NMR spectrum of 9, related to Scheme 4.
Figure S79. $^1$H NMR spectrum of 10, related to Table 1.

Figure S80. $^{13}$C NMR spectrum of 10, related to Table 1.
Supplemental Figures for HPLC spectra

Figure S81. HPLC spectra of rac-3a, related to Scheme 2.

Figure S82. HPLC spectra of 3a, related to Scheme 2.
Figure S83. HPLC spectra of rac-3b, related to Scheme 2.

Figure S84. HPLC spectra of 3b, related to Scheme 2.
Figure S85. HPLC spectra of rac-3c, related to Scheme 2.

Figure S86. HPLC spectra of 3c, related to Scheme 2.
Figure S87. HPLC spectra of rac-3d, related to Scheme 2.

**SAMPLE INFORMATION**

| Sample Name       | why-g05-100.1-IA-1.5%       | Acquired By: | System          |
|-------------------|----------------------------|--------------|-----------------|
| Sample Type       | Unknown                    | Sample Set Name |                |
| Vial              | 29                         | Acq. Method Set | 15%             |
| Injection #       | 1                          | Processing Method | 5.100 1        |
| Injection Volume  | 10.00 ul                   | Channel Name   | 2998 Ch1 254nm@1.2nm |
| Run Time          | 100.0 Minutes              | Proc. Chnl. Descr.: | 2998 Ch1 254nm@1.2nm |
| Date Acquired     | 5/6/2019 8:44:04 PM CST    |              |                 |
| Date Processed    | 7/19/2019 4:29:17 PM CST    |              |                 |

| RT    | Area     | % Area | Height |
|-------|----------|--------|--------|
| 1     | 6.968    | 1977187| 50.74  | 119534 |
| 2     | 9.439    | 1919556| 49.26  | 102818 |

Figure S88. HPLC spectra of 3d, related to Scheme 2.

**SAMPLE INFORMATION**

| Sample Name       | why-g05-100.2-IA-1.5%       | Acquired By: | System          |
|-------------------|----------------------------|--------------|-----------------|
| Sample Type       | Unknown                    | Sample Set Name |                |
| Vial              | 9                          | Acq. Method Set | 15%             |
| Injection #       | 1                          | Processing Method | 5.100 2        |
| Injection Volume  | 10.00 ul                   | Channel Name   | 2998 Ch1 254nm@1.2nm |
| Run Time          | 100.0 Minutes              | Proc. Chnl. Descr.: | 2998 Ch1 254nm@1.2nm |
| Date Acquired     | 5/6/2019 8:58:25 PM CST    |              |                 |
| Date Processed    | 7/19/2019 4:29:46 PM CST    |              |                 |

| RT    | Area     | % Area | Height |
|-------|----------|--------|--------|
| 1     | 6.997    | 297406 | 3.95   | 12618  |
| 2     | 9.436    | 5042981| 96.05  | 278668 |
Figure S89. HPLC spectra of rac-3e, related to Scheme 2.

Figure S90. HPLC spectra of 3e, related to Scheme 2.
Figure S91. HPLC spectra of rac-3f, related to Scheme 2.

Figure S92. HPLC spectra of 3f, related to Scheme 2.
Figure S93. HPLC spectra of rac-3g, related to Scheme 2.

Figure S94. HPLC spectra of 3g, related to Scheme 2.
Figure S95. HPLC spectra of rac-3h, related to Scheme 2.

Figure S96. HPLC spectra of 3h, related to Scheme 2.
Figure S97. HPLC spectra of rac-3i, related to Scheme 2.

Figure S98. HPLC spectra of 3i, related to Scheme 2.
Figure S99. HPLC spectra of rac-3j, related to Scheme 2.

Figure S100. HPLC spectra of 3j, related to Scheme 2.
Figure S101. HPLC spectra of rac-3k, related to Scheme 2.

Figure S102. HPLC spectra of 3k, related to Scheme 2.
**Figure S103.** HPLC spectra of rac-3l, related to Scheme 2.

![HPLC spectra of rac-3l](image)

| RT  | Area  | % Area  | Height |
|-----|-------|---------|--------|
| 6.195 | 1193006 | 50.69  | 121836 |
| 8.193 | 1180651 | 49.31  | 99218  |

**Figure S104.** HPLC spectra of 3l, related to Scheme 2.

![HPLC spectra of 3l](image)

| RT  | Area  | % Area  | Height |
|-----|-------|---------|--------|
| 5.579 | 847402  | 2.94   | 83595  |
| 7.380 | 27946081 | 97.06  | 2114242 |
Figure S105. HPLC spectra of rac-3m, related to Scheme 2.

Figure S106. HPLC spectra of 3m, related to Scheme 2.
Figure S107. HPLC spectra of rac-3n, related to Scheme 2.

![HPLC spectra of rac-3n](image)

| RT  | Area  | % Area | Height |
|-----|-------|--------|--------|
| 1   | 6.428 | 2345053| 49.77  | 232209 |
| 2   | 7.903 | 2367186| 50.23  | 202032 |

Figure S108. HPLC spectra of 3n, related to Scheme 2.

![HPLC spectra of 3n](image)

| RT  | Area  | % Area | Height |
|-----|-------|--------|--------|
| 1   | 5.733 | 112010 | 3.49   | 9656   |
| 2   | 7.021 | 3096909| 96.51  | 251145 |
**Figure S109.** HPLC spectra of rac-3o, related to Scheme 2.

| RT  | Area  | % Area | Height |
|-----|-------|--------|--------|
| 1   | 5.670 | 5001622| 50.69  |
| 2   | 6.865 | 4864935| 49.31  |

**Figure S110.** HPLC spectra of 3o, related to Scheme 2.

| RT  | Area  | % Area | Height |
|-----|-------|--------|--------|
| 1   | 5.666 | 262467 | 25190  |
| 2   | 6.856 | 7924190| 96.79  | 724173 |
Figure S111. HPLC spectra of rac-3p, related to Scheme 2.

Figure S112. HPLC spectra of 3p, related to Scheme 2.
Figure S113. HPLC spectra of rac-3q, related to Scheme 2.

Figure S114. HPLC spectra of 3q, related to Scheme 2.
Figure S115. HPLC spectra of rac-3r, related to Scheme 2.

Figure S116. HPLC spectra of 3r, related to Scheme 2.
Figure S117. HPLC spectra of rac-3{s}, related to Scheme 2.

![HPLC spectra of rac-3{s}](image)

| RT  | Area | % Area | Height |
|-----|------|--------|--------|
| 1   | 5.235| 4473670| 449631 |
| 2   | 7.823| 4461737| 409.93 | 342190 |

Figure S118. HPLC spectra of 3{s}, related to Scheme 2.

![HPLC spectra of 3{s}](image)

| RT  | Area  | % Area | Height |
|-----|-------|--------|--------|
| 1   | 5.392 | 322979 | 3.95   | 28962  |
| 2   | 7.824 | 7850224| 96.05  | 631496 |
Figure S119. HPLC spectra of rac-3t, related to Scheme 2.

Figure S120. HPLC spectra of 3t, related to Scheme 2.
Figure S121. HPLC spectra of rac-3u, related to Scheme 2.

Figure S122. HPLC spectra of 3u, related to Scheme 2.
Figure S123. HPLC spectra of rac-3v, related to Scheme 2.

![HPLC spectrum of rac-3v](image1)

| RT   | Area  | % Area | Height |
|------|-------|--------|--------|
| 1    | 8.131 | 1819009| 50.38  | 119730 |
| 2    | 9.905 | 1791927| 49.62  | 82895  |

Figure S124. HPLC spectra of 3v, related to Scheme 2.

![HPLC spectrum of 3v](image2)

| RT   | Area  | % Area | Height |
|------|-------|--------|--------|
| 1    | 8.146 | 10277030| 95.77  | 76342  |
| 2    | 9.940 | 453768 | 4.23   | 27838  |
Figure S125. HPLC spectra of rac-3w, related to Scheme 2.

Figure S126. HPLC spectra of 3w, related to Scheme 2.
Figure S127. HPLC spectra of rac-3x, related to Scheme 2.

Figure S128. HPLC spectra of 3x, related to Scheme 2.
Figure S129. HPLC spectra of rac-3y, related to Scheme 2.

Figure S130. HPLC spectra of 3y, related to Scheme 2.

Figure S131. HPLC spectra of rac-3z, related to Scheme 2.
Figure S132. HPLC spectra of 3z, related to Scheme 2.
**Figure S133.** HPLC spectra of rac-6a, related to Scheme 3.

**Figure S134.** HPLC spectra of 6a, related to Scheme 3.
Figure S135. HPLC spectra of rac-6b, related to Scheme 3.

| RT  | Area | % Area | Height |
|-----|------|--------|--------|
| 1   | 15.244 | 4234718 | 50.06 | 213977 |
| 2   | 18.515 | 4220834 | 49.92 | 181236 |

Figure S136. HPLC spectra of 6b, related to Scheme 3.

| RT  | Area | % Area | Height |
|-----|------|--------|--------|
| 1   | 15.315 | 467017  | 4.94  | 236896 |
| 2   | 18.930 | 8989230 | 95.06 | 376102 |
Figure S137. HPLC spectra of rac-6c, related to Scheme 3.

![HPLC spectrum of rac-6c](image1)

| RT  | Area   | % Area | Height |
|-----|--------|--------|--------|
| 1   | 19.108 | 49.92  | 112252 |
| 2   | 21.720 | 50.08  | 100552 |

Figure S138. HPLC spectra of 6c, related to Scheme 3.

![HPLC spectrum of 6c](image2)

| RT  | Area   | % Area | Height |
|-----|--------|--------|--------|
| 1   | 18.977 | 4.61   | 21417  |
| 2   | 21.557 | 95.39  | 391481 |
Figure S139. HPLC spectra of rac-6d, related to Scheme 3.

| Sample Name: | why-g05-189-1-IA-10% | Sample Type: | Unknown |
| Sample Set Name: | Acquired By: | System |
| Vial: | 4 | Acq. Method Set: | 10% |
| Injection #: | 1 | Processing Method: | 5198.1 |
| Injection Volume: | 10.00 ul | Channel Name: | 2998 Ch1 254nm@1.2nm |
| Run Time: | 100.0 Minutes | Proc. Chnl. Descr.: | 2998 Ch1 254nm@1.2nm |

Date Acquired: 7/2/2019 7:50:10 PM CST
Date Processed: 8/3/2019 3:31:12 PM CST

Figure S140. HPLC spectra of 6d, related to Scheme 3.

| Sample Name: | why-g05-189-2-IA-10% | Sample Type: | Unknown |
| Sample Set Name: | Acquired By: | System |
| Vial: | 2 | Acq. Method Set: | 10% |
| Injection #: | 1 | Processing Method: | 5198.2 |
| Injection Volume: | 10.00 ul | Channel Name: | 2998 Ch1 254nm@1.2nm |
| Run Time: | 100.0 Minutes | Proc. Chnl. Descr.: | 2998 Ch1 254nm@1.2nm |

Date Acquired: 7/2/2019 2:03:03 PM CST
Date Processed: 8/3/2019 3:31:41 PM CST

| RT | Area | % Area | Height |
|----|------|--------|--------|
| 1  | 16.442 | 3299513 | 49.87 | 159858 |
| 2  | 20.400 | 3307902 | 58.13 | 131836 |

| RT | Area | % Area | Height |
|----|------|--------|--------|
| 1  | 16.117 | 385610  | 4.75  | 19275  |
| 2  | 19.619 | 7731158 | 95.25 | 303811 |
Figure S141. HPLC spectra of rac-6e, related to Scheme 3.

Figure S142. HPLC spectra of 6e, related to Scheme 3.
Figure S143. HPLC spectra of rac-6f, related to Scheme 3.

Figure S144. HPLC spectra of 6f, related to Scheme 3.
Figure S145. HPLC spectra of rac-6g, related to Scheme 3.

Figure S146. HPLC spectra of 6g, related to Scheme 3.
Figure S147. HPLC spectra of rac-6h, related to Scheme 3.

Table: Sample Information

| Sample Name       | why-g05-197-1-A-10% |
|-------------------|---------------------|
| Sample Type       | Unknown             |
| Vial              | 73                  |
| Injection #:      | 2                   |
| Injection Volume: | 10.00 µl            |
| Run Time:         | 100.0 Minutes       |
| Date Acquired:    | 7/29/2019 7:29:54 PM CST |
| Date Processed:   | 8/3/2019 3:36:10 PM CST |
| Acquired By:      | System              |
| Sample Set Name   |                     |
| Acq. Method Set:  | 10%                 |
| Processing Method | 5 197.1             |
| Channel Name:     | 2998 Ch1 254 nm@1.2 nm |
| Proc. Chnl. Descr.:| 2998 Ch1 254 nm@1.2 nm |

![HPLC Spectra of rac-6h](image)

RT | Area  | % Area | Height
---|-------|--------|-------
1  | 7.311 | 2912330| 49.94 | 314167 |
2  | 8.324 | 2919807| 50.06 | 281933 |

Figure S148. HPLC spectra of 6h, related to Scheme 3.

Table: Sample Information

| Sample Name       | why-g05-194-1-A-10% |
|-------------------|---------------------|
| Sample Type       | Unknown             |
| Vial              | 97                  |
| Injection #:      | 1                   |
| Injection Volume: | 10.00 µl            |
| Run Time:         | 100.0 Minutes       |
| Date Acquired:    | 7/28/2019 7:42:43 PM CST |
| Date Processed:   | 8/3/2019 3:37:24 PM CST |
| Acquired By:      | System              |
| Sample Set Name   |                     |
| Acq. Method Set:  | 10%                 |
| Processing Method | 5 194.1             |
| Channel Name:     | 2998 Ch1 254 nm@1.2 nm |
| Proc. Chnl. Descr.:| 2998 Ch1 254 nm@1.2 nm |

![HPLC Spectra of 6h](image)

RT | Area  | % Area | Height
---|-------|--------|-------
1  | 7.333 | 176263 | 1.42  | 19997 |
2  | 8.357 | 12249669| 98.58 | 1208965 |

![HPLC Spectra of 6h](image)
Figure S149. HPLC spectra of rac-7, related to Scheme 4.

Figure S150. HPLC spectra of 7, related to Scheme 4.
**Figure S151.** HPLC spectra of rac-8, related to **Scheme 4**.

| RT   | Area  | % Area | Height |
|------|-------|--------|--------|
| 1    | 7.279 | 50.95  | 73830  |
| 2    | 8.662 | 49.05  | 81938  |

**Figure S152.** HPLC spectra of 8, related to **Scheme 4**.

| RT   | Area  | % Area | Height |
|------|-------|--------|--------|
| 1    | 7.481 | 4.23   | 30981  |
| 2    | 8.714 | 95.77  | 667895 |
Figure S153. HPLC spectra of rac-9, related to Scheme 4.

**Figure S154. HPLC spectra of 9, related to Scheme 4.**
Figure S155. HPLC spectra of rac-10, related to Table 1.

Figure S156. HPLC spectra of 10, related to Table 1.
Supplemental figures and tables for X-Ray structures

Figure S157. X-Ray crystal data of 3i, related to Scheme 2.

| Chemical formula | C_{26}H_{26}BrNO_{4} |
|------------------|----------------------|
| Formula weight   | 496.39               |
| Space group      | P1                   |
| Z                | 4                    |
| \( \alpha \), Å  | 9.1215(5)            |
| \( \beta \), Å   | 13.5175(7)           |
| \( \gamma \), Å  | 19.4869(10)          |
| \( \alpha \), °   | 99.498(3)            |
| \( \beta \), °   | 93.402(3)            |
| \( \gamma \), °  | 96.017(3)            |
| \( V \), Å³      | 2349.5(2)            |
| \( \rho \), g/cm³ | 1.403                |
Figure S15. X-Ray crystal data of 7, related to Scheme 4.

|                          |                  |                  |
|--------------------------|------------------|------------------|
| Chemical formula         | C$_{20}$H$_{26}$N$_2$O$_4$ |                  |
| Formula weight           | 358.43           |                  |
| Space group              | P2$_1$2$_1$2$_1$  |                  |
| Z                        | 4                |                  |
| $\alpha$, $\AA$          | 7.87500(10)      |                  |
| $b$, $\AA$               | 10.1406(2)       |                  |
| $c$, $\AA$               | 23.0161(4)       |                  |
| $\alpha$, $^\circ$       | 90               |                  |
| $\beta$, $^\circ$        | 90               |                  |
| $\gamma$, $^\circ$       | 90               |                  |
| $V$, $\AA^3$             | 1838.00(5)       |                  |
| $\rho, g/cm^3$           | 1.295            |                  |
Transparent Methods

General Information

Unless otherwise noted, all reagents were purchased from commercial suppliers and used without further purification. NMR spectra were recorded on a Brucker-400 MHz spectrometer. Chemical shifts (δ) are given in ppm relative to TMS. The residual solvent signals were used as references and the chemical shifts converted to the TMS scale (CHCl₃: δ 7.26 for proton and δ 77.16 for carbon; DMSO: δ 2.49 for proton and δ 39.51 for carbon; Acetone: δ 2.05 for proton and δ 206.68 for carbon). Multiplicities were given as: s (singlet); d (doublet); t (triplet); q (quartet); dd (doublet of doublets); dt (doublet of triplets); m (multiplets); brs (broad signal). Coupling constants are reported as a J value in Hz. High resolution mass spectral analysis (HRMS) was performed on Waters XEVO G2 Q-TOF. The measurement of enantiomeric excesses was performed on Waters-Alliance (2998. Photodiode Array Detector, UV detection monitored at 254 nm). Chiralpak IA, AD-H and AS-H columns were purchased from Daicel Chemical Industries, LTD. The absolute configuration of 3i and 7 were assigned by the X-ray analysis. Optical rotations were determined at 589 nm (sodium D line) by using a Perkin-Elmer-343 polarimeter.

Preparation of Substrates

Preparation of 3-Nitroindoles 1 and 3-Nitrobenzothiophenes 5

The 3-nitroindoles 1 (You et al, 2018), 3-nitrobenzothiophenes 5 (You et al, 2017) and Allenoates 2 (Kwon et al, 2007) were synthesized according to the literature.

Optimize reaction conditions

Table S1: Additives effect the reaction of 3-nitroindoles 1a and allenoates 2a, related to Table 1[a].

| Entry | Additive | T (°C) | t (h) | 10 [%] | ee [%] | 3a [%] | ee [%] | 11 [%] |
|-------|----------|--------|-------|--------|--------|--------|--------|--------|
| 1     | -        | rt     | -     | 74     | 94     | 21     | 94     | -      |
| 2     | Silica gel (200 mg) | rt | 3 | 8 | 94 | 92 | 94 | - |
| 3     | Sc(OTf)₃ (20 mol%) | 50 | 6 | - | - | 10 | 90 | 59 |
| 4     | SnCl₂ (20 mol%) | 50 | 6 | 24 | 94 | 44 | 94 |
| 5     | PhCOOH (20 mol%) | 50 | 3 | 67 | 94 | 15 | 94 |
| 6     | Et₃N (1.0 eqive) | 50 | 3 | 66 | 94 | 16 | 94 |
| 7     | DABCO (1.0 eqive) | 50 | 3 | 52 | 94 | 14 | 94 |

[a] Reactions were conducted with 1a (0.1 mmol), 2a (0.15 mmol) and catalyst 4d (0.01 mmol) in toluene (1.0 mL) at room temperature. [b] Yield of the isolated product after purification by chromatography on silica gel. [c] Enantiomeric excess determined by HPLC.

Table S2: Optimization of the reaction of 3-nitrobenzothiophenes 5a and allenoate 2h, related to Scheme 3[a].
General procedure
All the racemic products were obtained by use of Cy3P as catalyst.

Scheme S1. General procedure for phosphine-catalyzed enantioselective [4+2] annulation reaction of 3-nitroindoles 1 and allenates 2, related to Scheme 2.

A dried tube with a magnetic stir bar was charged with 3-nitroindole derivative 1 (0.10 mmol), allenate derivative 2 (0.15 mmol, 1.5 equiv.), catalyst 4d (10 mol%), followed by the addition of toluene (1.0 mL), and the reaction mixture was stirred at room temperature. When the reaction was finished (determined by TLC). The mixture were added silica gel and toluene (1.0 mL) continued stir at room temperature when the aromatization process was finished (determined by TLC). Then solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the products 3.

Scheme S2. General procedure for phosphine-catalyzed enantioselective [4+2]
annulation reaction of 3-nitrobenzothiophene 5 and allenoate 2, related to Scheme 3.

A dried tube with a magnetic stir bar was charged with 3-nitrobenzothiophenes derivative 5 (0.10 mmol), allenoate derivative 2 (0.15 mmol, 1.5 equiv.), catalyst 4d (10 mol%), followed by the addition of toluene (1.0 mL), and the reaction mixture was stirred at 0 °C. When the reaction was finished (determined by TLC). The mixture were added silica gel and toluene (1.0 mL) continued stir at room temperature when the aromatization process was finished (determined by TLC). Then solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the products 6.

Scheme S3. 1-mol scale reaction, related to Scheme 2.

A dried tube with a magnetic stir bar was charged with 3-nitroindole derivative 1a (1.0 mmol), allenoate derivative 2o (1.5 mmol, 1.5 equiv.), catalyst 4d (10 mol%), followed by the addition of toluene (10.0 mL), and the reaction mixture was stirred at room temperature. When the reaction was finished (determined by TLC). The mixture were added silica gel (2.0 g) and toluene (10.0 mL) continued stir at room temperature when the aromatization was finished (determined by TLC). Then solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the products 3x (251.4 mg, 56%, 92% ee).

Scheme S3. Synthesis procedure of derivatization reaction, related to Scheme 4.

A dried tube with a magnetic stir bar was charged with 3-nitroindole derivative 1a (1.00 mmol), allenoate derivative 2m (1.50 mmol, 1.5 equiv.), catalyst 4d (10 mol%), followed by the addition
of toluene (10.0 mL), and the reaction mixture was stirred at room temperature. When the reaction was finished (determined by TLC). The mixture were added silica gel (2.0 g) and toluene (10.0 mL) continued stir at room temperature when the aromatization process was finished (determined by TLC). Then solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the products 3v (261.6 mg, 57%, 92% ee).

A suspension of 3v (261.6 mg, 0.57 mmol) and 10% palladium on carbon (130.0 mg) in MeOH (10.0 mL) was maintained under an atmosphere of hydrogen gas for 8 h at rt. The insoluble solids were removed by filtration and the filtrate was concentrated. The residue was dissolved in MeNH₂ (30 wt. % in absolute EtOH 4.0 mL), and the resulting mixture was stirred 1 h. Then solvent was evaporated and the residue was purified by column chromatography on silica gel using hexane/ethyl acetate as the eluent to afford the product 7 (179.2 mg, 84%, 92% ee).

To a solution of 7 (28.8 mg, 0.12 mmol) in anhydrous THF (5 mL) was added LiAlH₄ (45.6 mg, 1.2 mmol) at 0 °C. The suspension was allowed to warm to room temperature and continues to stir at 40 °C for 36 h. After that, saturated aqueous Na₂SO₄ (4 mL) was added. The solid formed was filtered and washed with DCM. The organic layers were combined and dried with MgSO₄. The solvent was removed and the residue was purified by column chromatography (DCM/MeOH/Et₃N = 100/5/1) to give 8 (21.2 mg, 78%, 92% ee).

Characterization of products

9-(Tert-butyl) 3-ethyl (S)-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3a)

Step 1: 18 h; Step 2: 3 h (Silica gel 200 mg); Total yield: 38.4 mg (92%); ¹H NMR (400 MHz, CDCl₃) δ 8.07 (d, J = 8.3 Hz, 1H), 7.35 – 7.30 (m, 2H), 7.24 – 7.15 (m, 5H), 7.13 – 7.03 (m, 2H), 5.18 (t, J = 5.9 Hz, 1H), 4.18 – 4.00 (m, 4H), 1.70 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 166.41, 150.73, 143.15, 136.25, 134.87, 132.60, 130.82, 128.95, 128.27, 128.24, 126.62, 123.91, 122.73, 118.90, 118.13, 115.51, 84.03, 60.69, 40.49, 28.57, 28.43, 14.21. ESI-MS: calculated [C₂₆H₂₇NO₄ + Na⁺]: 440.1832, found: 440.1833. [d]D₀ = 26.8 (c = 0.96, CH₂Cl₂). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 5.72 min, t₂(major) =7.46 min.
late (3b)

Step 1: 20 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 36.3 mg (84%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.93 (d, \(J = 8.4\) Hz, 1H), 7.36 – 7.30 (m, 2H), 7.24 – 7.17 (m, 3H), 7.14 – 7.08 (m, 1H), 7.05 – 6.97 (m, 2H), 5.16 (t, \(J = 5.8\) Hz, 1H), 4.18 – 4.00 (m, 4H), 2.31 (s, 3H), 1.69 (s, 9H), 1.22 (t, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.46, 150.78, 143.24, 134.93, 134.45, 132.72, 132.15, 130.89, 128.95, 128.42, 128.28, 126.59, 125.25, 118.86, 117.93, 115.17, 83.85, 60.70, 40.45, 28.62, 28.47, 21.46, 14.23. ESI-MS: calculated [C\textsubscript{27}H\textsubscript{29}NO\textsubscript{4} + Na\textsuperscript{+}]: 454.1989, found: 454.1989. \([\alpha]\)\textsubscript{D}\textsuperscript{20} = 4.8 (c = 0.98, CH\textsubscript{2}Cl\textsubscript{2}). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH = 97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), \(t_1\) (minor) = 5.12 min, \(t_2\) (major) = 10.56 min.

9-(Tert-butyl) 3-ethyl (S)-6-fluoro-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3c)

Step 1: 24 h; Step 2: 4 h (Silica gel 400 mg); Total yield: 22.8 mg (52%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.05 – 7.97 (m, 1H), 7.34 – 7.26 (m, 2H), 7.25 – 7.18 (m, 3H), 7.17 – 7.10 (m, 1H), 6.93 – 6.83 (m, 2H), 5.12 (t, \(J = 5.9\) Hz, 1H), 4.18 – 3.99 (m, 4H), 1.70 (s, 9H), 1.21 (t, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.31, 159.13 (\(J = 239.3\) Hz), 150.46, 142.75, 134.62, 132.61, 132.51, 129.27, 129.18, 128.89, 128.43, 126.84, 117.93 (d, \(J = 3.8\) Hz), 116.48 (d, \(J = 8.9\) Hz), 111.46 (d, \(J = 24.8\) Hz), 104.62 (d, \(J = 23.9\) Hz), 84.37, 60.78, 40.46, 28.63, 28.44, 14.22. \textsuperscript{19}F NMR (377 MHz, CDCl\textsubscript{3}) \(\delta\) -120.41. ESI-MS: calculated [C\textsubscript{26}H\textsubscript{27}FNO\textsubscript{4} + H\textsuperscript{+}]: 436.1919, found: 436.1924. \([\alpha]\)\textsubscript{D}\textsuperscript{20} = 21.3 (c = 1.07, CH\textsubscript{2}Cl\textsubscript{2}). The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (CHIRALPAK IA, hexane/i-PrOH = 98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), \(t_1\) (minor) = 7.04 min, \(t_2\) (major) = 9.21 min.

9-(Tert-butyl) 3-ethyl (S)-6-chloro-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3d)

Step 1: 24 h; Step 2: 12 h (Silica gel 400 mg); Total yield: 34.4 mg (76%); \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 7.99 (d, \(J = 8.8\) Hz, 1H), 7.34 – 7.27 (m, 2H), 7.26 – 7.17 (m, 4H), 7.17 – 7.10 (m, 2H), 5.13 (t, \(J = 5.8\) Hz, 1H), 4.18 – 3.99 (m, 4H), 1.70 (s, 9H), 1.21 (t, \(J = 7.1\) Hz, 3H). \textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 166.25, 150.36, 142.70, 134.70, 134.53, 132.56, 132.26, 129.45, 128.85, 128.45, 128.32, 126.87, 124.06, 118.49, 117.59, 116.57, 84.55, 60.79, 40.34, 28.57, 28.42, 14.21. ESI-MS: calculated [C\textsubscript{26}H\textsubscript{25}ClNO\textsubscript{4} + H\textsuperscript{+}]: 452.1623, found: 452.1628. \([\alpha]\)\textsubscript{D}\textsuperscript{20} = 24.3 (c = 0.97, CH\textsubscript{2}Cl\textsubscript{2}). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH = 98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), \(t_1\) (minor) = 7.00 min, \(t_2\) (major) = 9.44 min.

9-(Tert-butyl) 3-ethyl (S)-6-bromo-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3e)
Step 1: 24 h; Step 2: 16 h (Silica gel 400 mg); Total yield: 30.3 mg (61%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.95 (d, J = 8.8 Hz, 1H), 7.35 (d, J = 1.8 Hz, 1H), 7.32 – 7.20 (m, 6H), 7.17 – 7.10 (m, 1H), 5.12 (t, J = 5.8 Hz, 1H), 4.21 – 3.99 (m, 4H), 1.70 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.24, 150.34, 142.68, 135.08, 134.51, 132.57, 132.13, 129.95, 128.83, 128.46, 126.88, 126.77, 121.52, 117.51, 116.99, 116.09, 84.59, 60.79, 40.31, 28.54, 28.42, 14.21. ESI-MS: calculated [C$_{26}$H$_{26}$BrNO$_4$ + H]$^+$: 496.1118, found: 496.1100. $[^{[\alpha]}]_{20}D =$ -38.3 (c = 1.01, CH$_2$Cl$_2$).

The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (CHIRALPAK IA, hexane/i-PrOH =98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), $t_1$(major) = 9.77 min, $t_2$(minor) =12.54 min.

9-(Tert-butyl) 3-ethyl 6-methyl (S)-4-phenyl-1,4-dihydro-9-carbazole-3,6,9-tricarboxylate (3f)

Step 1: 24 h; Step 2: 12 h (Silica gel 400 mg); Total yield: 23.8 mg (50%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.12 (d, J = 8.8 Hz, 1H), 7.99 (s, 1H), 7.89 (d, J = 8.8 Hz, 1H), 7.38 – 7.30 (m, 2H), 7.25 – 7.20 (m, 3H), 7.16 – 7.07 (m, 1H), 5.23 (t, J = 5.8 Hz, 1H), 4.19 – 4.02 (m, 4H), 3.88 (s, 3H), 1.71 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.51, 166.27, 150.36, 142.85, 139.11, 134.59, 132.65, 132.22, 128.82, 128.43, 128.04, 126.84, 125.39, 124.70, 120.97, 118.67, 115.23, 84.81, 60.81, 52.11, 40.32, 28.58, 28.42, 14.22. ESI-MS: calculated [C$_{28}$H$_{29}$NO$_6$ + H]$^+$: 476.2068, found:476.2068. $[^{[\alpha]}]_{20}D =$ -49.2 (c = 0.96, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH =90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), $t_1$(minor) =5.61 min, $t_2$(major) =6.62 min.

9-(Tert-butyl) 6-ethyl 2-methyl (S)-5-phenyl-5,8-dihydro-9-carbazole-2,6,9-tricarboxylate (3h)
Step 1: 24 h; Step 2: 6 h (Silica gel 400 mg); Total yield: 24.4 mg (51%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.81 (s, 1H), 7.77 (dd, J = 8.2, 1.2 Hz, 1H), 7.34 – 7.29 (m, 2H), 7.27 – 7.19 (m, 4H), 7.15 – 7.07 (m, 1H), 5.20 (t, J = 5.8 Hz, 1H), 4.19 – 4.06 (m, 4H), 3.89 (s, 3H), 1.74 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H).

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.84, 166.27, 150.33, 142.80, 135.68, 134.47, 134.28, 132.50, 131.86, 128.90, 128.39, 126.83, 125.51, 124.06, 118.50, 117.53, 84.80, 60.82, 52.16, 40.35, 28.56, 28.38, 14.21. ESI-MS: calculated [C$_{26}$H$_{26}$NO$_6$ + H]$^+$: 476.2068, found:476.2083. [α]$^D$ = 15.5 (c = 0.51, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 86% ee (CHIRALPAK IA, hexane/i-PrOH =95/5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(minor) = 7.49 min, t$_2$(major) = 8.38 min.

9-(Tert-butyl) 3-ethyl (S)-7-bromo-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3i)

Step 1: 24 h; Step 2: 6 h (Silica gel 200 mg); Total yield: 30.3 mg (61%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.29 (s, 1H), 7.32 – 7.27 (m, 2H), 7.24 – 7.15 (m, 4H), 7.15 – 7.09 (m, 1H), 7.09 – 7.04 (m, 1H), 5.14 (t, J = 5.8 Hz, 1H), 4.20 – 3.97 (m, 4H), 1.71 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.29, 150.29, 142.84, 137.00, 134.58, 132.48, 131.37, 128.88, 128.37, 127.06, 126.81, 125.94, 119.93, 118.81, 117.95, 117.68, 84.72, 60.78, 40.38, 28.51, 28.39, 14.22. ESI-MS: calculated [C$_{26}$H$_{26}$BrNO$_4$ + H]$^+$: 496.1118, found:496.1121. [α]$^D$ = -24.8 (c = 0.97, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(minor) = 5.87 min, t$_2$(major) = 7.63 min.

9-(Tert-butyl) 3-ethyl (S)-8-methyl-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3j)

Step 1: 18 h; Step 2: 6 h (Silica gel 400 mg); Total yield: 23.9 mg (55%); $^1$H NMR (400 MHz, CDCl$_3$) δ 7.33 – 7.28 (m, 2H), 7.24 – 7.17 (m, 3H), 7.13 – 7.06 (m, 2H), 7.00 – 6.95 (m, 2H), 5.17 (t, J = 5.9 Hz, 1H), 4.18 – 4.04 (m, 2H), 4.00 – 3.78 (m, 2H), 2.45 (s, 3H), 1.68 (s, 9H), 1.21 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.45, 150.35, 143.09, 135.84, 134.33, 133.16, 130.71, 129.23, 129.01, 128.26, 127.06, 126.60, 124.68, 122.90, 117.27, 116.65, 84.01, 77.48, 77.16, 76.84, 60.73, 40.70, 28.25, 27.97, 21.36, 14.22. ESI-MS: calculated [C$_{27}$H$_{25}$NO$_4$ + Na]$^+$:454.1989, found: 454.1993. [α]$^D$ = 21.5 (c = 0.51, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(major) = 7.25 min, t$_2$(minor) = 7.98 min.

9-(Tert-butyl) 3-ethyl (S)-4-(p-tolyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3k)

Step 1: 24 h; Step 2: 3 h (Silica gel 200 mg); Total yield: 33.2 mg (77%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, J = 8.3 Hz, 1H), 7.28 – 7.24 (m, 1H), 7.23 – 7.15 (m, 4H), 7.09 – 7.04 (m, 1H), 7.01 (d, J = 7.9 Hz, 2H), 5.15 (t, J = 5.8 Hz, 1H), 4.20 – 4.00 (m, 4H), 2.24 (s, 3H), 1.70 (s, 9H), 1.23 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100
9-(Tert-butyl) 3-ethyl (S)-4-(4-fluorophenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3l)

Step 1: 12 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 40.1 mg (92%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.32 – 7.26 (m, 2H), 7.24 – 7.16 (m, 3H), 7.11 – 7.05 (m, 1H), 6.93 – 6.86 (m, 2H), 5.18 (t, J = 5.9 Hz, 1H), 4.24 – 3.94 (m, 4H), 1.71 (s, 9H), 1.23 (t, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.32, 161.60 (J = 244.5 Hz), 150.71, 138.91 (J = 3.0 Hz), 136.26, 134.99, 132.44, 130.91, 130.41 (J = 8.0 Hz), 128.07, 124.04, 122.78, 118.79, 117.84, 115.60, 115.11 (J = 21.4 Hz), 84.17, 60.78, 39.72, 28.52, 28.45, 14.25. $^{19}$F NMR (376 MHz, CDCl$_3$) δ -116.42. 

ESI-MS: calculated [C$_{22}$H$_{24}$NO$_5$ + Na]$^+$. 458.1738, found: 458.1746. [α]$_D^{26}$ = 27.6 (c = 1.00, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH = 97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(minor) = 5.58 min, t$_2$(major) = 7.38 min.

9-(Tert-butyl) 3-ethyl (S)-4-(4-chlorophenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3m)

Step 1: 12 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 41.3 mg (91%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.28 – 7.16 (m, 7H), 7.11 – 7.03 (m, 1H), 5.16 (t, J = 5.9 Hz, 1H), 4.23 – 4.00 (m, 4H), 1.71 (s, 9H), 1.23 (d, J = 7.1 Hz, 3H). $^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.22, 150.69, 141.77, 136.25, 135.27, 132.31, 132.17, 130.98, 130.32, 128.47, 127.99, 124.10, 122.82, 118.74, 117.59, 115.61, 84.21, 60.83, 39.88, 28.53, 28.45, 14.26. 

ESI-MS: calculated [C$_{28}$H$_{26}$ClNO$_4$ + Na]$^+$. 474.1443, found: 474.1443. [α]$_D^{26}$ = 13.5 (c = 1.01, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH = 97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(minor) = 6.06 min, t$_2$(major) = 7.57 min.

9-(Tert-butyl) 3-ethyl (S)-4-(4-bromophenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3n)

Step 1: 18 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 34.6 mg (70%); $^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, J = 8.3 Hz, 1H), 7.36 – 7.30 (m, 2H), 7.26 – 7.15 (m, 5H), 7.11 – 7.03 (m, 1H), 5.16 (t, J = 5.9 Hz, 1H), 4.21 – 4.09 (m, 2H), 4.09 – 4.02 (m, 2H), 1.71 (s, 9H), 1.24 (t, J = 7.1 Hz, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.21, 150.69, 142.31, 136.25, 135.32, 132.10, 131.42, 130.99, 130.72, 127.98, 124.12, 122.84, 120.48, 118.74, 117.52, 115.62, 84.23, 60.85, 39.96, 28.54, 28.46, 14.27. 

ESI-MS:
calculated [C\textsubscript{2}H\textsubscript{32}BrNO\textsubscript{4} + H\textsuperscript{+}]: 496.1118, found: 496.1111. \([\alpha]^{20}_{D}= 9.0 \text{ (c = 1.01, CH}_2\text{Cl}_2)\). The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), \(t_1\) (minor) = 5.73 min, \(t_2\) (major) = 7.02 min.

**9-(Tert-butyl) 3-ethyl (S)-4-(4-(trifluoromethyl)phenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3o)**

Step 1: 10 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 38.7 mg (80%); \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 8.09 \text{ (d, } J = 8.3 \text{ Hz, 1H)}, 7.52 – 7.40 \text{ (m, 4H)}, 7.32 – 7.27 \text{ (m, 1H)}, 7.24 – 7.16 \text{ (m, 2H)}, 7.13 – 7.05 \text{ (m, 1H)}, 5.26 \text{ (t, } J = 5.9 \text{ Hz, 1H}), 4.21 – 3.98 \text{ (m, 4H)}, 1.71 \text{ (s, 9H)}, 1.23 \text{ (t, } J = 7.1 \text{ Hz, 3H}). \(^13\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 166.07, 150.67, 147.35, 136.27, 135.79, 131.88, 131.14, 129.29, 128.88 \text{ (} J = 32.2 \text{ Hz)}, 127.88, 125.21 \text{ (} J = 3.7 \text{ Hz)}, 124.30 \text{ (} J = 270.3 \text{ Hz)}, 124.19, 122.88, 118.62, 117.30, 115.68, 84.32, 60.91, 40.36, 28.59, 28.45, 14.23. ESI-MS: calculated [C\textsubscript{2}H\textsubscript{32}F\textsubscript{3}NO\textsubscript{4} + H\textsuperscript{+}]: 486.1887, found: 486.1896. \([\alpha]^{20}_{D}= 18.8 \text{ (c = 1.00, CH}_2\text{Cl}_2)\). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), \(t_1\) (minor) = 5.67 min, \(t_2\) (major) = 6.86 min.

**9-(Tert-butyl) 3-ethyl (S)-4-(4-(methoxycarbonyl)phenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3p)**

Step 1: 8 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 40.9 mg (86%); \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 8.08 \text{ (d, } J = 8.5 \text{ Hz, 1H)}, 7.90 \text{ (d, } J = 8.3 \text{ Hz, 2H}), 7.41 \text{ (d, } J = 8.3 \text{ Hz, 2H)}, 7.28 \text{ (t, } J = 3.5 \text{ Hz, 1H)}, 7.22 – 7.17 \text{ (m, 2H)}, 7.08 – 7.03 \text{ (m, 1H)}, 5.24 \text{ (t, } J = 5.9 \text{ Hz, 1H)}, 4.19 – 4.03 \text{ (m, 4H)}, 3.85 \text{ (s, 3H)}, 1.71 \text{ (s, 9H)}, 1.19 \text{ (d, } J = 4.9 \text{ Hz, 3H}). \(^13\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 167.09, 166.15, 150.68, 148.58, 136.24, 135.68, 131.87, 131.03, 129.72, 129.07, 128.59, 127.96, 124.11, 122.83, 118.68, 117.33, 115.61, 84.26, 60.86, 52.10, 40.56, 28.58, 28.45, 14.23. ESI-MS: calculated [C\textsubscript{2}H\textsubscript{32}NO\textsubscript{6} + H\textsuperscript{+}]: 476.2068, found: 476.2063. \([\alpha]^{20}_{D}= 15.2 \text{ (c = 1.02, CH}_2\text{Cl}_2)\). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), \(t_1\) (minor) = 10.97 min, \(t_2\) (major) = 15.22 min.

**9-(Tert-butyl) 3-ethyl (S)-4-(4-(cyanophenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3q)**

Step 1: 12 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 38.4 mg (87%); \(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta 8.09 \text{ (d, } J = 8.4 \text{ Hz, 1H)}, 7.52 \text{ (d, } J = 8.3 \text{ Hz, 2H}), 7.45 \text{ (d, } J = 8.3 \text{ Hz, 2H)}, 7.31 \text{ (t, } J = 3.4 \text{ Hz, 1H)}, 7.25 – 7.19 \text{ (m, 1H)}, 7.16 – 7.12 \text{ (m, 1H)}, 7.11 – 7.05 \text{ (m, 1H)}, 5.24 \text{ (t, } J = 5.9 \text{ Hz, 1H}), 4.20 – 3.99 \text{ (m, 4H)}, 1.71 \text{ (s, 9H)}, 1.23 \text{ (t, } J = 7.1 \text{ Hz, 3H}). \(^13\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta 165.89, 150.60, 148.84, 136.21, 132.23, 131.41, 131.23, 129.79, 127.69, 124.30, 124.08, 122.93, 119.04, 118.42, 116.79, 115.72, 110.54, 84.43, 60.98, 40.62, 28.56, 28.43, 14.24. ESI-MS: calculated
[C27H26N2O4 + H]+: 443.1965, found: 443.1966. [α]20D = 8.7 (c = 1.01, CH2Cl2). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 7.03 min, t2(major) = 8.21 min.

9-(Tert-butyl) 3-ethyl (S)-4-(m-tolyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3r)

Step 1: 20 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 25.0 mg (58%); 1H NMR (400 MHz, CDCl3) δ 8.07 (d, J = 8.3 Hz, 1H), 7.29 – 7.15 (m, 4H), 7.13 – 7.03 (m, 3H), 6.92 (d, J = 7.2 Hz, 1H), 5.15 (t, J = 5.8 Hz, 1H), 4.19 – 4.01 (m, 4H), 2.26 (s, 3H), 1.71 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 166.53, 150.80, 143.02, 137.73, 136.28, 134.79, 132.73, 130.80, 128.36, 128.07, 127.47, 126.20, 123.89, 118.99, 118.24, 115.51, 84.05, 60.70, 40.46, 28.59, 28.48, 21.62, 14.22. ESI-MS: calculated [C27H29N2O4 + Na]+: 454.1989, found: 454.2002. [α]20D = 8.7 (c = 1.01, CH2Cl2). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH = 98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 6.35 min, t2(major) = 10.35 min.

9-(Tert-butyl) 3-ethyl (S)-4-(3-chlorophenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3s)

Step 1: 12 h; Step 2: 2 h (Silica gel 100 mg); Total yield: 23.5 mg (52%); 1H NMR (400 MHz, CDCl3) δ 8.09 (d, J = 8.3 Hz, 1H), 7.29 – 7.18 (m, 5H), 7.18 – 7.06 (m, 3H), 5.16 (t, J = 5.8 Hz, 1H), 4.21 – 4.02 (m, 4H), 1.71 (s, 9H), 1.24 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 166.18, 150.69, 145.33, 136.29, 135.59, 134.09, 131.99, 131.07, 129.50, 128.99, 128.00, 127.42, 126.96, 124.11, 122.85, 118.73, 117.39, 115.63, 84.25, 60.87, 40.26, 28.57, 28.47, 14.24. ESI-MS: calculated [C26H26ClNO4 + H]+: 452.1623, found: 452.1616. [α]20D = 27.5 (c = 0.94, CH2Cl2). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH = 98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 6.35 min, t2(major) = 10.35 min.

9-(Tert-butyl) 3-ethyl (S)-4-(3-(methoxycarbonyl)phenyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3t)

Step 1: 12 h; Step 2: 2 h (Silica gel 100 mg); Total yield: 29.4 mg (62%); 1H NMR (400 MHz, CDCl3) δ 8.10 – 8.05 (m, 1H), 8.00 (t, J = 1.6 Hz, 1H), 7.85 – 7.78 (m, 1H), 7.23 – 7.18 (m, 5H), 7.18 – 7.06 (m, 3H), 5.16 (t, J = 5.8 Hz, 1H), 4.21 – 4.02 (m, 4H), 3.87 (s, 3H), 1.71 (s, 9H), 1.22 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 167.22, 166.21, 150.69, 143.76, 136.27, 135.66, 135.33, 135.59, 134.09, 131.99, 131.07, 129.50, 128.99, 128.00, 127.42, 126.96, 124.11, 122.85, 118.73, 117.39, 115.63, 84.25, 60.87, 40.26, 28.57, 28.47, 14.24. ESI-MS: calculated [C28H29NO6 + Na]+: 498.1887, found: 498.1890. [α]20D = 17.4 (c = 1.03, CH2Cl2). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH = 98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 5.39 min, t2(major) = 7.82 min.
(CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min),
t_1(minor) = 8.06 min, t_2(major) = 13.97 min.

9-(Tert-butyl) 3-ethyl (S)-4-(naphthalen-2-yl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3u)

Step 1: 36 h; Step 2: 3 h (Silica gel 200 mg); Total yield: 41.0 mg (88%); 1H NMR (400 MHz, CDCl_3) δ 8.06 (d, J = 8.3 Hz, 1H), 7.85 (s, 1H), 7.78 (d, J = 7.9 Hz, 1H), 7.72 (d, J = 7.8 Hz, 1H), 7.67 (d, J = 8.5 Hz, 1H), 7.44 – 7.32 (m, 3H), 7.29 – 7.22 (m, 2H), 7.15 (t, J = 7.7 Hz, 1H), 7.01 (t, J = 7.5 Hz, 1H), 5.37 (t, J = 6.0 Hz, 1H), 4.21 – 3.98 (m, 4H), 1.71 (s, 9H), 1.19 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl_3) δ 166.42, 150.79, 140.58, 136.26, 135.04, 133.48, 132.53, 132.50, 130.96, 128.25, 128.01, 127.93, 127.81, 127.69, 125.90, 125.55, 123.96, 122.77, 118.95, 117.97, 115.52, 84.12, 60.74, 40.64, 28.65, 28.47, 14.23. ESI-MS: calculated [C_{30}H_{29}NO_4]^+ = 490.1989, found: 490.1994. [α]_{20}^D = 48.3 (c = 0.99, CH_2Cl_2). The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t_1(minor) = 6.66 min, t_2(major) = 10.38 min.

9-(Tert-butyl) 3-ethyl (S)-4-((benzyloxy)methyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3v)

Step 1: 24 h; Step 2: 2 h (Silica gel 200 mg); Total yield: 30.2 mg (65%); 1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 8.2 Hz, 1H), 7.55 (d, J = 7.5 Hz, 1H), 7.28 – 7.17 (m, 6H), 7.14 – 7.07 (m, 2H), 4.38 – 4.31 (m, 3H), 4.23 (q, J = 7.1 Hz, 2H), 3.99 – 3.85 (m, 2H), 3.84 – 3.77 (m, 2H), 1.69 (s, 9H), 1.31 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl_3) δ 166.87, 150.65, 138.59, 137.69, 136.34, 132.35, 130.10, 128.44, 128.20, 123.86, 122.68, 118.85, 116.39, 115.67, 83.92, 73.17, 72.65, 60.78, 35.15, 28.77, 28.44, 14.39. ESI-MS: calculated [C_{28}H_{31}NO_5]^+ = 484.2094, found: 484.2103. [α]_{20}^D = -34.2 (c = 1.15, CH_2Cl_2). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t_1(minor) = 8.15 min, t_2(major) = 9.94 min.

9-(Tert-butyl) 3-ethyl (S)-4-propyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3w)

Step 1: 36 h; Step 2: 4 h (Silica gel 400 mg); Total yield: 28.9 mg (75%); 1H NMR (400 MHz, CDCl_3) δ 8.14 (d, J = 7.8 Hz, 1H), 7.54 (d, J = 7.1 Hz, 1H), 7.32 – 7.23 (m, 3H), 7.20 (s, 1H), 4.36 – 4.20 (m, 3H), 3.97 – 3.72 (m, 2H), 1.95 – 1.80 (m, 2H), 1.69 (s, 9H), 1.36 (t, J = 7.0 Hz, 3H), 1.17 – 1.04 (m, 1H), 1.00 – 0.87 (m, 1H), 0.74 (t, J = 7.2 Hz, 3H). 13C NMR (100 MHz, CDCl_3) δ 166.95, 150.69, 138.55, 136.36, 132.27, 131.83, 128.45, 123.80, 122.67, 118.63, 118.10, 115.70, 83.89, 60.72, 36.08, 33.27, 28.74, 28.45, 17.93, 14.45, 14.35. ESI-MS: calculated [C_{23}H_{29}NO_4]^+ = 384.2169, found: 384.2161. [α]_{20}^D = -71.1 (c = 0.39, CH_2Cl_2). The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (CHIRALPAK IA, hexane/i-PrOH =99/1, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t_1(minor) = 5.54 min, t_2(major) = 7.23 min.
**9-(Tert-butyl) 3-ethyl (S)-4-(3-ethoxy-3-oxopropyl)-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3x)**

Step 1: 36 h; Step 2: 4 h (Silica gel 400 mg); Total yield: 30.8 mg (70%); 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.14 (d, $J$ = 8.0 Hz, 1H), 7.55 (d, $J$ = 7.2 Hz, 1H), 7.35 – 7.18 (m, 3H), 4.41 – 4.34 (m, 1H), 4.32 – 4.22 (m, 2H), 3.98 – 3.88 (m, 3H), 3.87 – 3.77 (m, 1H), 2.37 – 2.27 (m, 2H), 2.12 – 2.01 (m, 1H), 1.98 – 1.88 (m, 1H), 1.70 (s, 9H), 1.37 (t, $J$ = 7.1 Hz, 3H), 1.12 (t, $J$ = 7.1 Hz, 3H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 173.65, 166.46, 150.57, 137.70, 136.40, 132.28, 130.99, 127.99, 124.06, 122.86, 118.53, 116.56, 115.75, 84.08, 60.88, 60.30, 32.42, 29.58, 28.71, 28.43, 28.08, 14.42, 14.19. 

ESI-MS: calculated [C$_{25}$H$_{31}$NO$_6$ + H]$^+$: 442.2224, found: 442.2208. 

[α]$^{20}_D$ = -47.5 (c = 0.51, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 81% ee (CHIRALPAK AS-H, hexane/i-PrOH =97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(major) = 5.74 min, t$_2$(minor) = 6.62 min.

**3-Benzyl 9-(tert-butyl) (S)-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3y)**

Step 1: 18 h; Step 2: 1.5 h (Silica gel 200 mg); Total yield: 32.9 mg (69%); 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $J$ = 8.3 Hz, 1H), 7.34 – 7.27 (m, 6H), 7.26 – 7.15 (m, 6H), 7.14 – 7.09 (m, 1H), 7.08 – 7.02 (m, 1H), 5.20 (t, $J$ = 5.9 Hz, 1H), 5.10 (dd, $J$ = 39.1, 12.4 Hz, 2H), 4.15 – 3.95 (m, 2H), 1.69 (s, 9H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 166.25, 150.71, 143.00, 136.26, 136.00, 135.59, 132.38, 130.69, 128.98, 128.60, 128.36, 128.26, 128.23, 128.19, 126.68, 123.95, 122.75, 118.91, 118.08, 115.53, 84.07, 66.57, 40.53, 28.64, 28.45. 

ESI-MS: calculated [C$_{31}$H$_{29}$NO$_4$ + Na]$^+$: 502.1989, found: 502.1987. 

[α]$^{20}_D$ = 24.5 (c = 0.97, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 93% ee (CHIRALPAK IA, hexane/i-PrOH = 97/3, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(minor) = 8.10 min, t$_2$(major) = 11.15 min.

**Di-tert-butyl (S)-4-phenyl-1,4-dihydro-9H-carbazole-3,9-dicarboxylate (3z)**

Step 1: 36 h; Step 2: 1.5 h (Silica gel 200 mg); Total yield: 33.7 mg (76%); 

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.07 (d, $J$ = 8.3 Hz, 1H), 7.34 – 7.27 (m, 3H), 7.26 – 7.17 (m, 3H), 7.17 – 7.10 (m, 2H), 7.09 – 7.04 (m, 1H), 5.12 (t, $J$ = 6.0 Hz, 1H), 4.12 – 3.93 (m, 2H), 1.70 (s, 9H), 1.36 (s, 9H). 

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 165.89, 150.76, 143.28, 136.29, 133.95, 133.89, 130.91, 129.02, 128.35, 128.18, 126.56, 123.85, 122.69, 118.95, 118.12, 115.52, 84.02, 80.92, 40.72, 28.53, 28.46, 28.10. 

ESI-MS: calculated [C$_{28}$H$_{31}$NO$_4$ + H]$^+$: 446.2326, found: 446.2318. 

[α]$^{20}_D$ = 26.9 (c = 2.0, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH = 98.5/1.5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t$_1$(minor) = 5.32 min, t$_2$(major) = 6.60 min.

**Ethyl (R)-1-(4-bromophenyl)-1,4-dihydropbenzo[b,d]thiophene-2-carboxylate (6a)**
Step 1: 48 h; Step 2: 5 h (Silica gel 300 mg); Total yield: 24.4 mg (59%); ¹H NMR (400 MHz, CDCl₃) δ 7.77 – 7.71 (m, 1H), 7.48 – 7.42 (m, 1H), 7.34 – 7.30 (m, 2H), 7.28 – 7.25 (m, 1H), 7.24 – 7.16 (m, 4H), 5.27 (t, J = 5.2 Hz, 1H), 4.26 – 4.06 (m, 2H), 4.02 – 3.89 (m, 1H), 3.87 – 3.74 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 166.04, 141.73, 139.23, 137.89, 134.40, 133.13, 132.89, 131.50, 130.77, 130.44, 124.30, 122.48, 121.78, 120.62, 60.97, 41.47, 28.07, 14.30. ESI-MS: calculated [C₂₁H₂₁BrN₂S + H]⁺: 413.0205, found: 413.0213. 

[α]²⁰D = -36.9 (c = 0.81, CH₂Cl₂).

The product was analyzed by HPLC to determine the enantiomeric excess: 95% ee (CHIRALPAK IA, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 7.53 min, t₂(major) = 8.22 min.

Ethyl (R)-1-(4-cyanophenyl)-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6b)

Step 1: 48 h; Step 2: 5 h (Silica gel 300 mg); Total yield: 25.7 mg (72%); ¹H NMR (400 MHz, CDCl₃) δ 7.79 – 7.74 (m, 1H), 7.53 – 7.48 (m, 2H), 7.45 – 7.38 (m, 3H), 7.36 – 7.32 (m, 1H), 7.29 – 7.19 (m, 2H), 5.36 (t, J = 5.1 Hz, 1H), 4.25 – 4.08 (m, 2H), 4.03 – 3.94 (m, 1H), 3.91 – 3.78 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 165.76, 148.20, 139.27, 137.64, 135.25, 133.55, 132.60, 129.86, 129.69, 124.47, 124.45, 122.49, 118.95, 110.68, 61.11, 42.09, 28.12, 14.29. ESI-MS: calculated [C₂₂H₁₇NO₂S + H]⁺: 360.1053, found: 360.1055. [α]²⁰D = -34.2 (c = 1.15, CH₂Cl₂).

The product was analyzed by HPLC to determine the enantiomeric excess: 90% ee (CHIRALPAK IA, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 15.32 min, t₂(major) = 18.83 min.

Ethyl (R)-8-bromo-1-(4-cyanophenyl)-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6c)

Step 1: 60 h; Step 2: 8 h (Silica gel 500 mg); Total yield: 23.7 mg (54%); ¹H NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 8.5 Hz, 1H), 7.56 – 7.50 (m, 3H), 7.41 (d, J = 8.3 Hz, 2H), 7.37 – 7.29 (m, 2H), 5.30 (t, J = 5.1 Hz, 1H), 4.30 – 4.08 (m, 2H), 4.04 – 3.91 (m, 1H), 3.90 – 3.77 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H).

¹³C NMR (100 MHz, CDCl₃) δ 165.55, 141.73, 139.30, 137.86, 135.38, 135.25, 133.35, 132.50, 132.30, 129.86, 129.69, 124.47, 124.45, 122.62, 121.49, 118.95, 110.68, 61.11, 42.09, 28.12, 14.29. ESI-MS: calculated [C₂₂H₁₆BrNO₂S + H]⁺: 438.0158, found: 438.0164. [α]²⁰D = -100.3 (c = 0.74, CH₂Cl₂).

The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (CHIRALPAK IA, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 18.98 min, t₂(major) = 21.56 min.

Ethyl (R)-8-chloro-1-(4-cyanophenyl)-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6d)

Step 1: 60 h; Step 2: 8 h (Silica gel 500 mg); Total yield: 24.2 mg (61%); ¹H NMR (400 MHz, CDCl₃) δ 7.66 (d, J = 8.5 Hz, 1H), 7.53 (d, J = 8.2 Hz, 2H), 7.42 (d, J = 8.2 Hz, 2H), 7.35 (d, J = 1.9 Hz, 1H), 7.34 – 7.30 (m, 1H), 7.21 (dd,
J = 8.5, 1.9 Hz, 1H), 5.30 (t, J = 5.1 Hz, 1H), 4.25 – 4.09 (m, 2H), 4.04 – 3.93 (m, 1H), 3.90 – 3.77 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.45, 147.57, 138.76, 137.24, 135.44, 132.34, 132.28, 130.68, 129.63, 129.13, 124.80, 123.48, 121.08, 118.75, 110.83, 61.09, 41.81, 28.02, 14.18. ESI-MS: calculated [C₂₂H₁₆ClNO₂S + H]⁺: 394.0663, found: 394.0667. [α]₂⁰D = -100.0 (c = 1.01, CH₂Cl₂). The product was analyzed by HPLC to determine the enantiomeric excess: 91% ee (CHIRALPAK IA, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 16.12 min, t₂(major) = 19.62 min.

Ethyl (R)-7-bromo-1-(4-cyanophenyl)-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6e)

Step 1: 60 h; Step 2: 5 h (Silica gel 600 mg); Total yield: 22.5 mg (51%); ¹H NMR (400 MHz, CDCl₃) δ 7.38 (d, J = 1.6 Hz, 1H), 7.51 (d, J = 8.2 Hz, 2H), 7.40 (d, J = 8.3 Hz, 2H), 7.34 – 7.28 (m, 2H), 7.23 (d, J = 8.5 Hz, 1H), 5.31 (t, J = 5.2 Hz, 1H), 4.27 – 4.07 (m, 2H), 4.03 – 3.89 (m, 1H), 3.89 – 3.75 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.59, 147.80, 140.74, 136.42, 134.91, 134.03, 132.35, 129.78, 129.48, 127.87, 125.16, 122.53, 118.80, 118.30, 110.89, 61.16, 41.97, 28.01, 14.27. ESI-MS: calculated [C₂₂H₁₆ClNO₂S + H]⁺: 438.0158, found: 438.0167. [α]₂⁰D = -11.8 (c = 0.49, CH₂Cl₂). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 18.73 min, t₂(major) = 23.81 min.

Ethyl (R)-8-bromo-1-(4-bromophenyl)-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6f)

Step 1: 60 h; Step 2: 24 h (Silica gel 600 mg); Total yield: 31.9 mg (65%); ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.52 (m, 2H), 7.37 – 7.29 (m, 3H), 7.25 – 7.23 (m, 1H), 7.19 – 7.14 (m, 2H), 7.25 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.35 – 7.27 (m, 2H), 5.21 (t, J = 5.1 Hz, 1H), 4.26 – 4.07 (m, 2H), 4.00 – 3.89 (m, 1H), 3.85 – 3.73 (m, 1H), 1.27 (t, J = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 165.83, 141.24, 139.57, 137.86, 134.91, 134.07, 133.08, 131.68, 130.61, 129.96, 127.34, 124.52, 123.79, 120.90, 118.45, 61.05, 41.31, 28.06, 14.30. ESI-MS: calculated [C₂₁H₁₆Br₂O₂S + H]⁺: 492.9290, found: 492.9296. [α]₂⁰D = -112.6 (c = 1.00, CH₂Cl₂). The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (CHIRALPAK AD-H, hexane/i-PrOH = 85/15, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(major) = 8.59 min, t₂(minor) = 9.49 min.

Ethyl (R)-8-bromo-1-(4-(trifluoromethyl)phenyl)-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6g)

Step 1: 60 h; Step 2: 24 h (Silica gel 600 mg); Total yield: 33.7 mg (70%); ¹H NMR (400 MHz, CDCl₃) δ 7.61 – 7.54 (m, 2H), 7.49 (d, J = 8.2 Hz, 2H), 7.41 (d, J = 8.2 Hz, 2H), 7.35 – 7.27 (m, 2H), 5.32 (t, J = 5.0 Hz, 1H), 4.28 – 4.07 (m, 2H), 4.05 – 3.92 (m, 1H), 3.89 – 3.75 (m, 1H), 1.26 (t, J = 7.1 Hz, 3H). ¹³C NMR (100 MHz, CDCl₃) δ 165.71, 146.27, 139.50, 137.92, 135.19, 134.52, 132.95, 129.74, 129.27
(d, J = 32.4 Hz), 129.23, 127.45, 125.59 (q, J = 3.8 Hz), 124.43, 123.85, 118.54, 61.12, 41.69, 28.13, 14.28. 19F NMR (377 MHz, CDCl3) δ -62.45. ESI-MS: calculated [C22H14BrF3O2S + H]+: 481.0079, found: 481.0090. [α]D20 = -57.1 (c = 0.99, CHCl3). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK AD-H, hexane/i-PrOH =85/15, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 6.41 min, t2(major) = 7.08 min.

Ethyl (R)-8-chloro-1-phenyl-1,4-dihydrodibenzo[b,d]thiophene-2-carboxylate (6h)

Step 1: 60 h; Step 2: 24 h (Silica gel 600 mg); Total yield: 16.7 mg (45%); 1H NMR (400 MHz, CDCl3) δ 7.62 (d, J = 8.5 Hz, 1H), 7.47 (d, J = 1.9 Hz, 1H), 7.32 – 7.27 (m, 2H), 7.26 – 7.10 (m, 5H), 5.24 (t, J = 5.1 Hz, 1H), 4.25 – 4.05 (m, 2H), 4.03 – 3.89 (m, 1H), 3.87 – 3.71 (m, 1H), 1.25 (t, J = 7.1 Hz, 3H). 13C NMR (100 MHz, CDCl3) δ 166.09, 142.16, 139.43, 137.37, 134.82, 133.67, 130.72, 130.54, 128.94, 128.55, 124.55, 123.35, 121.68, 60.92, 41.98, 28.15, 14.28. ESI-MS: calculated [C21H16ClO2S + H]+: 369.0711, found: 369.0712. [α]D20 = -109.0 (c = 0.52, CH2Cl2). The product was analyzed by HPLC to determine the enantiomeric excess: 97% ee (CHIRALPAK IA, hexane/i-PrOH =90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 7.33 min, t2(major) = 8.36 min.

Tert-butyl(3R,4R)-4-(hydroxymethyl)-3-(methylcarbamoyl)-1,2,3,4-tetrahydro-9H-carbazole-9-carboxylate (7)

1H NMR (400 MHz, CDCl3) δ 8.10 (d, J = 8.1 Hz, 1H), 7.47 (d, J = 7.3 Hz, 1H), 7.25 – 7.13 (m, 2H), 6.08 (brs, 1H), 4.01 (dd, J = 12.0, 8.1 Hz, 1H), 3.79 (d, J = 10.7 Hz, 1H), 3.70 (brs, 1H), 3.41 (s, 1H), 3.27 (dd, J = 18.4, 5.8 Hz, 1H), 2.95 – 2.82 (m, 4H), 2.65 – 2.56 (m, 1H), 2.42 – 2.27 (m, 1H), 2.08 – 1.99 (m, 1H), 1.66 (s, 9H). 13C NMR (100 MHz, CDCl3) δ 150.61, 136.11, 135.70, 128.41, 123.89, 122.83, 117.66, 116.02, 115.76, 83.91, 62.69, 44.39, 38.03, 28.40, 26.72, 25.55, 22.34. ESI-MS: calculated [C20H26N2O4S + H]+: 359.1965, found: 359.1966. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK IA, hexane/i-PrOH =95/5, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 17.88 min, t2(major) = 19.27 min.

(3aR,10cR)-2-methyl-1,3a,4,5,6,10c-hexahydropyrrolo[3,4-c]carbazol-3(2H)-one (8)

1H NMR (400 MHz, CDCl3) δ 8.39 (brs, 1H), 7.43 (d, J = 7.6 Hz, 1H), 7.30 (d, J = 7.8 Hz, 1H), 7.12 (m, 2H), 7.02 – 6.46 (m, 2H), 3.89 – 3.76 (m, 1H), 3.22 – 3.08 (m, 1H), 2.96 (s, 3H), 2.92 – 2.80 (m, 1H), 2.70 – 2.57 (m, 1H), 2.41 – 2.27 (m, 1H), 2.10 – 1.95 (m, 1H). 13C NMR (100 MHz, CDCl3) δ 165.58, 136.06, 135.49, 126.71, 121.58, 119.61, 117.60, 111.03, 107.64, 73.59, 39.37, 34.85, 34.12, 22.31, 19.60. ESI-MS: calculated [C15H16N2O + H]+: 235.1335, found: 235.1331. The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK AD-H, hexane/i-PrOH =85/15, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t1(minor) = 6.41 min, t2(major) = 7.08 min.
AD-H, hexane/i-PrOH = 90/10, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(minor) = 7.48 min, t₂(major) = 8.71 min.

(3aR,10cR)-2-methyl-1,2,3,3a,4,5,6,10c-octahydropyrrolo[3,4-c]carbazole (9)

$^1$H NMR (400 MHz, DMSO) δ 10.66 (s, 1H), 7.40 (d, $J = 7.6$ Hz, 1H), 7.23 (d, $J = 7.8$ Hz, 1H), 7.01 – 6.86 (m, 2H), 3.62 – 3.52 (m, 2H), 3.25 – 3.14 (m, 1H), 2.76 – 2.58 (m, 4H), 2.31 (s, 3H), 2.17 – 2.04 (m, 1H), 1.83 – 1.65 (m, 2H). $^{13}$C NMR (100 MHz, DMSO) δ 136.10, 135.00, 126.92, 120.01, 118.10, 117.29, 110.67, 109.71, 61.79, 54.49, 37.08, 35.72, 23.31, 22.69. ESI-MS: calculated [C$_{15}$H$_{18}$N$_2$]+ H$: 227.1543, found: 227.1541.

The product was analyzed by HPLC to determine the enantiomeric excess: 92% ee (CHIRALPAK AS-H, hexane/i-PrOH = 70/30, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(major) = 5.49 min, t₂(minor) = 9.67 min.

9-(Tert-butyl) 3-ethyl (4R)-4a-nitro-4-phenyl-1,4,4a,9a-tetrahydro-9H-carbazole-3,9-dicarboxylate (10)

Total yield: 34.6 mg (74%); $^1$H NMR (400 MHz, Acetone) δ 7.92 – 7.49 (m, 2H), 7.44 (t, $J = 7.7$ Hz, 1H), 7.40 – 7.26 (m, 5H), 7.19 – 7.12 (m, 2H), 5.86 (d, $J = 8.5$ Hz, 1H), 5.45 (s, 1H), 4.16 – 4.03 (m, 2H), 3.74 – 3.49 (m, 1H), 2.70 (d, $J = 18.6$ Hz, 1H), 1.61 (s, 9H), 1.17 (t, $J = 7.4$ Hz, 3H). $^{13}$C NMR (100 MHz, Acetone) δ 171.38, 165.60, 140.51, 138.62, 133.33, 131.59, 130.89, 129.90, 129.30, 126.01, 124.73, 116.84, 62.03, 61.02, 59.69, 45.78, 34.27, 28.94, 21.33, 14.98, 14.81. ESI-MS: calculated [C$_{26}$H$_{28}$N$_2$O$_6$]+ Na*: 487.1845, found: 487.1869. [α]$^2$D = -246.5 (c = 0.45, CH$_2$Cl$_2$). The product was analyzed by HPLC to determine the enantiomeric excess: 94% ee (CHIRALPAK IA, hexane/i-PrOH = 99/1, detector: 254 nm, T = 30 °C, flow rate: 1 mL/min), t₁(major) = 12.93 min, t₂(minor) = 19.06 min.

Supplemental References
1. Cheng, Q., Zhang, F., Cai, Y., Guo, Y.-L., and You, S.-L. (2018). Stereodivergent synthesis of tetrahydrofuroindoles through Pd-catalyzed asymmetric dearomative formal [3+2] cycloaddition. Angew. Chem. Int. Ed. 57, 2134-2138.
2. Cheng, Q., Zhang, H.-J., Yue, W.-J., You, S.-L. (2017). Palladium-catalyzed highly stereoselective dearomative [3 + 2] cycloaddition of nitrobenzofurans. Chem 3, 428-436.
3. Tran, Y. S., and Kwon, O. (2007). Phosphine-catalyzed [4 + 2] annulation: synthesis of cyclohexenes. J. Am. Chem. Soc. 129, 12632-12633.