Asymmetric Vinylogous Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

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HIGHLIGHTS
Asymmetric vinylogous aldol
Excellent regioselectivity
HWE and Julia olefinations
Asymmetric Vinylogous Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

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SUMMARY
Two catalytic asymmetric vinylogous aldol-type reactions of aldehydes with allyl phosphonate and allyl sulfone have been uncovered in good to high yields for the first time. The bulky ligand—(R)-DTBM-SEGPHOS—was found to be the key to perfectly control both regio- and enantioselectivities. Transformations of the vinylogous products (including Horner-Wadsworth-Emmons and Julia olefination) were successfully realized by virtue of the phosphonate and sulfone moieties. Moreover, the present methodology was successfully applied in the asymmetric synthesis of natural products.

INTRODUCTION
Asymmetric vinylogous aldol reaction (VAR) has been one of the most important reactions in the synthesis of complex natural products, especially in the synthesis of polyketides. In the past decades, catalytic asymmetric VAR of aldehydes or ketones has evolved from classical Mukaiyama vinylogous aldol reaction (Denmark et al., 2005; Casiraghi et al., 2011; Pansare and Paul, 2011; Bisai, 2012; Kalesse et al., 2014; Hosokawa, 2018a, 2018b) to direct vinylogous aldol reaction (DVAR) (Li and Yin, 2018; Otsuka et al., 2013; Zhu et al., 2013; Li et al., 2014; Han and Chang, 2016; Jing et al., 2016; Ray and Mukherjee, 2018), which enjoys the advantages of easy reaction protocol and high atom economy (Trost, 1991; Anastas and Crabbtree, 2009; Newhouse et al., 2010). However, the nuclophiles in DVAR were mainly limited to unsaturated carbonyl compounds and their close derivatives (FGrand et al., 2017). Unsaturated phosphonates or phosphine oxides, as well as unsaturated sulfones, have never been investigated as prenucleophiles in vinylogous aldol-type reactions.

In such reactions, synthetically versatile chiral vinylogous products containing α,β-unsaturated phosphonate or phosphine oxide moiety or α,β-unsaturated sulfone motif (Nishida et al., 2008; Xue et al., 2011; Konno et al., 2012; Lefevre et al., 2013; Hornillos et al., 2015; Lim and Hayashi, 2015, 2017; Wang and Hayashi, 2018; El-Awe et al., 2009; Alba et al., 2010; Nielsen et al., 2010; Zhu and Lu, 2010; Moteki et al., 2010; Quintard et al., 2011; Moure et al., 2011; Nishimura et al., 2012; Halskov et al., 2012; Zhou et al., 2012; Hernández-Toribio et al., 2012), would be produced. Furthermore, phosphonates and phosphine oxides had great applications in medicinal and agricultural chemistry (Mucha et al., 2011; Ordoñez et al., 2012; Corbridge, 2013; Horsman and Zechel, 2017). Sulfones, especially α,β-unsaturated sulfones, were widely distributed in biologically active compounds, even in the commercial pharmaceuticals (Meadows and Gervay-Hague, 2006; Dunny et al., 2013; Woo et al., 2014; Fang et al., 2016). Therefore it is highly desirable to achieve a vinylogous aldol-type reaction of unsaturated phosphonates or phosphine oxides, as well as unsaturated sulfones.

One inherent difficulty faced in the vinylogous aldol-type reaction of allyl phosphonate or allyl sulfone is the control of regioselectivity. The addition of allyl phosphonate to aldehyde was investigated by Yuan and co-workers in detail (Scheme 1A) (Yuan et al., 1990, 1991). Treating allyl phosphonate with “BuLi in tetrahydrofuran (THF) at −70°C afforded the corresponding delocalized allylic carbanion, which reacted with benzaldehyde to give a mixture of α- and γ-adducts. α-Addition was the natural tendency and thus dominated the addition pathways, which led to the vinylogous product (γ-adduct) in significantly low yield. Increasing the steric hindrance of the alkyl group in phosphonate only led to a slight improvement of the γ-selectivity.

Furthermore, the addition of allyl sulfone to benzaldehyde catalyzed by a phosphine-based strong base was studied by Verkade and co-workers, which delivered the α-adduct in 63% yield at −78°C (Scheme 1B) (Kisanga and Verkade, 2002). The same reaction promoted by stoichiometric “BuLi also afforded the...
A. Reported Addition of Allyl Phosphonate to Benzaldehyde Dominated by $\alpha$-Selectivity

$$
\begin{align*}
\text{PhCHO} & \quad \text{+} \quad \text{Ph} = \text{P(OEt)}_2 \\
& \quad \text{BuLi} \quad \text{THF, -70 °C, 0.5 h} \quad \rightarrow \\
& \quad \text{89%} \quad \text{Ph} \quad \text{OH} \quad \text{O} \quad \text{P(OEt)}_2 \\
& \quad \text{7%} \quad \text{Ph} \quad \text{OH} \quad \text{O} \quad \text{P(OEt)}_2
\end{align*}
$$

B. Reported Addition of Allyl Sulfone to Benzaldehyde Dominated by $\alpha$-Selectivity

$$
\begin{align*}
\text{PhCHO} & \quad \text{+} \quad \text{Ph} = \text{SO}_2 \text{Ph} \\
& \quad \text{P(RNCH}_2\text{CH}_2\text{)}_3\text{N} \quad \text{THF, -78 °C, 3 h} \quad \rightarrow \\
& \quad \text{63%} \quad \text{Ph} \quad \text{OH} \quad \text{SO}_2 \text{Ph} \\
& \quad \text{no data reported}
\end{align*}
$$

C. This Work: Catalytic Asymmetric Vinlogous Aldol-Type Reactions of Allyl Phosphonate and Allyl Sulfone ($\gamma$-Selectivity)

$$
\begin{align*}
\text{R'CHO} & \quad \text{+} \quad \text{PO(OEt)}_2 \quad \text{or} \quad \text{SO}_2\text{-2-Py} \\
& \quad \text{[Cu], base} \quad \text{THF} \quad \rightarrow \\
& \quad \text{3/5}
\end{align*}
$$

intermediates for

- HWE Olefination
- Julia Olefination

addressing points:

- reversing the natural regioselectivity
- first catalytic asymmetric example
- no elimination products
- synthetically versatile products

D. Selected Natural Products Synthesized with Horner-Wadsworth-Emmons (HWE) Olefination or Julia Olefination

- Callipellitosate A
- HWE Olefination
- HWE Olefination
- HWE Olefination
- (±)-Indolizomycin
- (±)-Ambruticin
- Julia Olefination
- Dictyostatin
- Julia Olefination

Scheme 1. Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone and Selected Natural Products Synthesized with Horner-Wadsworth-Emmons and Julia Olefinations
The α-carbanions of phosphate and sulfone have been employed as nucleophiles in Horner-Wadsworth-Emmons (HWE) and Julia olefinations, which were identified as two prominent synthetic tools to assemble the carbon-carbon double bond in organic synthesis, especially in the total synthesis of complex natural products (Kobayashi et al., 2018; Ma et al., 2010) (such as callipeltoside A, dicyostatin, indolizomycin and ambruticin) (Scheme 1D) (Trost et al., 2002; Ho et al., 2013; Kim et al., 1993; Liu and Jacobson, 2001). The products from the saturation of vinylogous aldol-type products (3/5) would be suitable substrates for HWE and Julia olefinations for further structure elaboration. Herein, we report two asymmetric vinylogous aldol-type reactions of aldehydes with allyl phosphonate and allyl sulfone catalyzed by a bulky chiral copper(I) complex and an organic base. The deprotonation of allyl phosphate or allyl sulfone would generate a nucleophilic allylcopper(I) species, which afforded the vinylogous product through an asymmetric allylation via a six-member ring transition state (Scheme 1C).

RESULTS AND DISCUSSION

The reaction of allyl sulfone 4′/4 and benzaldehyde (2a) was investigated as a model reaction in the presence of Cu(CH3CN)4PF6, phosphine ligand, and Barton’s base (Table 1). In all cases with 4′, the vinylogous product 5a′ was obtained with unsatisfactory regio- and enantioselectivities (entries 1–9). (R)-DTBM-SEGPHOS, an effective bulky ligand, led to good control of the enantioselectivity in our previously reported catalytic asymmetric aldol reaction of unsaturated esters and aldehydes (Zhang and Yin, 2018) and gave excellent control of the regioselectivity. The enantioselectivity was improved from 43% to 76% by switching phenyl to 2-pyridylin (entry 10). Lowering the temperature to −40 °C resulted in 97% enantiomeric excess (ee) for 5a (entry 11). The moderate yield was enhanced to 98% by changing the ratio of 2a/4, increasing the amount of Barton’s base to 30 mol %, and prolonging the reaction time to 36 h (entries 12–14). Finally, the catalyst loading was successfully decreased to 3 mol % without changing both regio- and enantioselectivities (entry 15).

By modifying the optimized reaction conditions for 4 (3 equiv. 1, 20 mol % Barton’s base, and −10 °C), the substrate scope of aldehydes 2 in the reaction with allyl phosphate 1 was studied (Table 2). Aromatic aldehydes with electron-withdrawing groups or electron-donating groups were competent substrates to generate the corresponding vinylogous products uniformly in good yields with both excellent regioselectivity (>20/1) and excellent enantioselectivity (≥95% ee) (3a–3o). Moreover, the reaction was not sensitive to the position of a substituent on the phenyl ring of the aromatic aldehydes. Even the sterically congested ortho-CF3-benzaldehyde afforded the product 3l in 91% yield with 95% ee. 1-Naphthaldehyde was also an excellent substrate (3p). Moreover, the present reaction conditions were applicable to various heteroaromatic aldehydes (3q–3x). Although the yields were moderate in some cases, both regio- and enantioselectivities were excellent. Particularly noteworthy are the aldehydes containing a pyridine motif (3t) and a carbazole motif (3x) as these functional groups potentially can coordinate to the metal center and thus deactivate the catalyst.

α,β-Unsaturated aldehydes also served as suitable substrates (3y–3a). Aryls, heteroaryls, alkyls, and vinyls with substituent were well tolerated at the β-position of the α,β-unsaturated aldehydes. Moreover, functional groups, such as alkyl chloride (3af), tert-butyldimethylsilyl (TBS)-ether (3ag), alkynyl (3ah), and prenyl (3ai), remained intact in the present reaction conditions. These functional groups offer the opportunity for further structure elaboration. It is noteworthy that acrolein (2ab), susceptible to conjugate addition, served as a suitable substrate to give the vinylogous product 3ab in moderate yield with excellent enantioselectivity. The chiral aldehydes, including α,β-unsaturated aldehyde 2aj derived from (−)-citronellal, (−)-perillaldehyde (2ak), and (−)-myrtenal (2al), were also investigated with both (R)-DTBM-SEGPHOS and (S)-DTBM-SEGPHOS. In both cases, the products (3aj, 3aj′, 3ak, 3ak′, 3al, and 3al′) were obtained in good yields with excellent diastereoselectivity, which indicated that the asymmetric
introduction was dominated by the copper(I)-catalyst. The absolute configuration of 3a was determined to be R by transforming it to a reported compound (for details, see Supplemental Information). The absolute configurations of other products were tentatively assigned by analogy.

### Table 1. Optimization of the Reaction Conditions

| Entry | Ar     | Ligand                | T (°C) | x     | Total yield | γ/α | ee of 5a/5a |
|-------|--------|-----------------------|--------|-------|-------------|-----|-------------|
| 1     | Ph     | (R)-BINAP             | rt     | 5     | 52%         | 1/1.5 | 45%         |
| 2     | Ph     | (R)-TOL-BINAP         | rt     | 5     | 43%         | 1/1  | 33%         |
| 3     | Ph     | (R)-SEGPHOS           | rt     | 5     | 42%         | 1/1.5| 8%          |
| 4     | Ph     | (R)-QUINAP            | rt     | 5     | 11%         | 1/1  | 40%         |
| 5     | Ph     | (R,R)-QUINOXP⁺        | rt     | 5     | 48%         | 1.5/1| 8%          |
| 6     | Ph     | (R)-(S)-JOSIPHOS      | rt     | 5     | 51%         | 1/1  | 58%         |
| 7     | Ph     | (R,R)-TANIAPHOS       | rt     | 5     | 47%         | 1/2  | 51%         |
| 8     | Ph     | (R,R)-Ph-BPE          | rt     | 5     | 37%         | 1/1  | 14%         |
| 9     | Ph     | (R)-DTBM-SEGPHOS      | rt     | 5     | 80%         | >20/1| 43%         |
| 10    | 2-Py   | (R)-DTBM-SEGPHOS      | rt     | 5     | 70%         | >20/1| 76%         |
| 11    | 2-Py   | (R)-DTBM-SEGPHOS      | −40    | 5     | 76%         | >20/1| 97%         |
| 12    | 2-Py   | (R)-DTBM-SEGPHOS      | −40    | 5     | 79%         | >20/1| 97%         |
| 13    | 2-Py   | (R)-DTBM-SEGPHOS      | −40    | 30    | 92%         | >20/1| 97%         |
| 14    | 2-Py   | (R)-DTBM-SEGPHOS      | −40    | 30    | 98%         | >20/1| 97%         |
| 15    | 2-Py   | (R)-DTBM-SEGPHOS      | −40    | 30    | 82%         | >20/1| 97%         |

HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance.

4/4, 0.1 mmol; 2a, 0.2 mmol.

* Determined by 1H NMR analysis of reaction crude mixture using mesitylene as an internal standard.

** Determined by chiral-stationary-phase HPLC analysis.

4 d, 0.2 mmol; 2a, 0.1 mmol.

36 h.

Cu(CH3CN)4PF6 and ligand, 3 mol %, Barton’s base = 2’-Bu-1,1,3,3-tetramethylguanidine.
| R      | Product | Yield | ee  |
|--------|---------|-------|-----|
| H      | 3a      | 85%   | 99% ee |
| F      | 3b      | 81%   | 99% ee |
| Cl     | 3c      | 74%   | 99% ee |
| Br     | 3d      | 77%   | 98% ee |
| I      | 3e      | 92%   | 99% ee |
| Me     | 3f      | 85%   | 99% ee |
| tBu    | 3g      | 81%   | 97% ee |
| CH3S   | 3h      | 83%   | 99% ee |
| CH3O   | 3i      | 81%   | 97% ee |
| CF3O   | 3j      | 83%   | 99% ee |

| R      | Product | Yield | ee  |
|--------|---------|-------|-----|
| F      | 3k      | 90%   | 98% ee |
| CF3    | 3l      | 91%   | 95% ee |
| OCH3   | 3m      | 91%   | 98% ee |
| Cl     | 3n      | 81%   | 98% ee |
| Br     | 3o      | 88%   | 97% ee |
| O      | 3p      | 94%   | 99% ee |
| S      | 3q      | 85%   | >99% ee |
| S      | 3r      | 91%   | >99% ee |
| H      | 3s      | 76%   | 98% ee |
| Me     | 3t      | 55%   | >99% ee |
|       | 3u      | 85%   | >99% ee |
| O      | 3v      | 81%   | 97% ee |
| S      | 3w      | 80%   | 97% ee |
| H      | 3x      | 81%   | >99% ee |
| Me     | 3y      | 78%   | 98% ee |
|       | 3z      | 78%   | 98% ee |
|       | 3aa     | 85%   | 98% ee |
|       | 3ab     | 68%   | 93% ee |
|       | 3ac     | 58%   | 97% ee |
|       | 3ad     | 68%   | 95% ee |
|       | 3ae     | 71%   | 93% ee |
|       | 3af     | 71%   | 97% ee |

Table 2. Substrate Scope of Aldehydes in the Reaction with 1a

(Continued on next page)
Moreover, the substrate scope of aldehydes in the reaction with allyl sulfone 4 was evaluated (Table 3). Various aromatic aldehydes with a substituent at ortho-, meta-, or para-position were suitable substrates. Both 1-naphthyl and 2-naphthyl aldehydes were well applicable. The vinylogous products (5a–5h, 5k–5l, 5n–5o, and 5p–5am–5aq) were isolated in moderate to excellent yields with excellent regio- and enantioselectivities. Heteroaromatic aldehydes also served as competent substrates without compromising enantioselectivity (5q–5u, 5x–5ar, and 5as). As for α,β-unsaturated aldehydes, aryls, heteroaryl, vinyls with substituent, and alkyls were accepted at β-position (5y–5z, 5aa–5ad, 5ae–5at, 5au, and 5ah). Moreover, the reaction conditions were successfully applied to chiral natural products bearing α,β-unsaturated aldehyde moieties, such as (−)-perillaldehyde (2ak) and (−)-myrtenal (2al). The corresponding vinylogous products (5ak, 5ak′, 5al, and 5al′) were obtained in moderate yields with high diastereoselectivity. It is evident that in the case of (−)-myrtenal with (S)-DTBM-SEGPHOS, mismatch phenomenon was observed. The absolute configuration of 5a was assigned to be R by its transformation to a known compound (for details, see Supplemental Information). Analogically, the stereochemistry of other products was dictated tentatively. It should be pointed out that the gram-scale syntheses of both 3a and 5a were successfully carried out with constant results. Moreover, it should be mentioned that aliphatic aldehydes afforded α-adducts mainly in low yields at the present reaction conditions, which is a limitation of the present reactions. However, the vinylogous products of aliphatic aldehydes could be potentially accessed by the transformations of vinylogous products of various α,β-unsaturated aldehydes by means of the carbon-carbon double bond.

### Table 2. Continued

| Reaction Conditions | 3ag, 47%, 98% ee; | 3ah, 85%, 98% ee; | 3ai, 68%, 99% ee; |
|--------------------|-----------------|-----------------|-----------------|
| THF (0.15 M), -10 °C, 48 h | 3aj, 52%, 15/1 dr; | 3aj′, 60%, >20/1 dr; | 3ak, 58%, >20/1 dr; |
| Cu(CH₂CN)₂PF₆ (5 mol %), (R)-DTBM-SEGPHOS (5 mol %), Barton’s Base (20 mol %) | 3ak′, 79%, >20/1 dr; | 3al, 88%, >20/1 dr; | 3al′, 61%, >20/1 dr; |

**Table 2. Continued**

HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance

*2*, 0.3 mmol; 1, 0.9 mmol. Isolated yield was reported. Regio- and diastereoselectivity were determined by 1H NMR analysis of reaction crude mixture. Enantioselectivity was determined by chiral-stationary-phase HPLC analysis.

*2* Gram-scale synthesis.

*2* (S)-DTBM-SEGPHOS was used.
| R  | 5a  | 95%, 97% ee; | 5b  | 88%, 97% ee; | 5c  | 93%, 97% ee; | 5d  | 85%, 92% ee; | 5e  | 82%, 91% ee; | 5f  | 89%, 92% ee; | 5g  | 91%, 95% ee; | 5h  | 90%, 97% ee; | 5i  | 76%, 98% ee; | 5j  | 95%, 97% ee; | 5k  | 85%, 92% ee; | 5l  | 98%, 99% ee; | 5m  | 91%, 95% ee; | 5n  | 97%, 95% ee; | 5o  | 76%, 98% ee; | 5p  | 95%, 97% ee; | 5q  | 81%, 98% ee; | 5r  | 98%, 98% ee; | 5s  | 76%, >99% ee; | 5t  | 85%, 95% ee; | 5u  | 85%, 95% ee; | 5v  | 87%, 97% ee; | 5w  | 84%, 94% ee; | 5x  | 51%, 95% ee; | 5y  | 70%, 95% ee; | 5z  | 56%, >20/1 dr; | 5aa | 80%, 92% ee; | 5ab | 50%, 93% ee; | 5ac | 50%, 93% ee; | 5ad | 50%, 93% ee; | 5ae | 70%, 97% ee; | 5af | 88%, 96% ee; | 5ag | 80%, 94% ee; | 5ah | 70%, 95% ee; | 5ai | 56%, >20/1 dr; |

Table 3. Substrate Scope of Aldehydes in the Reaction with 4a

(Continued on next page)
To get insights into the mechanism, rac-α-3a and rac-α-5a (racemic α-adducts) prepared according to a reported and a modified reaction procedure (for details, see Supplemental Information) were subjected to the standard reaction conditions, respectively (Scheme 2A). It was found that rac-α-3a was completely consumed and 3a was observed in 40% yield with 99% ee, together with benzaldehyde (2a), allyl phosphonate 1, and α,β-unsaturated phosphonate 6. These results clearly indicated that retro-aldol reaction of rac-α-3a proceeded to afford benzaldehyde (2a) and allyl phosphonate 1. One portion of allyl phosphonate 1 reacted with benzaldehyde (2a) to give the vinylogous product 3a in 40% yield with 99% ee in the presence of 5 mol % copper(I) catalyst and 20 mol % Barton’s base. One portion of allyl phosphonate 1 isomerized to α,β-unsaturated phosphonate 6, whereas the other portion of allyl phosphonate 1 remained. The same tendency was also observed in the retro-aldol reaction of rac-α-5a. This phenomenon indicated that significantly reversible α-addition led to the transformation of α-adducts to γ-adducts, which finally led to excellent control of the regioselectivity.

Rac-3a and rac-5a prepared by Cu(CH3CN)4PF6-rac-DTBM-SEGPHOS-catalyzed reactions were also submitted to the standard reaction conditions, respectively (Scheme 2B). Thin-layer chromatography, 1H nuclear magnetic resonance, and chiral high-performance liquid chromatographic analyses of the reaction crude mixtures indicated that slow and inefficient retro-vinylogous additions occurred, as 3a was obtained in 83% yield with 18% ee, whereas 5a was generated in 70% yield with ~8% ee. It was obvious that the retro-vinylogous aldol reactions of both (R)-3a and (R)-5a proceeded selectively, which resulted in the slight enrichment of (S)-3a and (S)-5a in the reaction mixtures. However, these retro-vinylogous aldol reactions were very slow and inefficient, which would not have detrimental effect on the enantioselectivity in the catalytic asymmetric vinylogous aldol-type reactions of allyl phosphonate 1 and allyl sulfone 4. Based on these important experimental observations and literatures (Bazán-Tejeda et al., 2006; Yamaguchi et al., 2007; Bouaouli et al., 2018), a possible reaction pathway was proposed in Supplemental Information.

The transformations of the vinylogous aldol products (3a and 5a) were carried out as shown in Scheme 3. The cleavage of unsaturated double bond in 3a was easily achieved through ozonolysis to deliver diol 8 in 67% yield after the reduction of generated aldehyde moiety with NaBH4. After being protected as TBS-ether, 3a was reduced to phosphonate 10 with H2 in the presence of Pd/C. 10 Was easily transformed to α,β-unsaturated compounds 11 and 12 via α-functionalization and subsequent HWE olefination. The sulfone moiety in 5a was successfully removed without touching the double bond to afford ester 13 in 52% yield after the protection of the alcohol motif. Sulfone 15 was easily accessed through the reduction of the unsaturated double bond and the protection of the hydroxyl group in 5a, which was transformed to olefin 16 in 67% yield with >20/1 E/Z ratio through modified Julia olefination. Ketone 17 was prepared from 15 in 68% yield in two steps by α-functionalization and the following removal of the sulfone group. Moreover, chiral diol 18 was synthesized from 5a in 74% yield with >20/1 diastereoisomeric ratio (dr) in two steps through intramolecular oxo-Michael addition and the

### Table 3. Continued

| Compound | Yield (%) | dr Ratio |
|----------|-----------|----------|
| 5a, 60%, >20/1 | 5a, 68%, >20/1 | 5a, 53%, 10/1 |

HPLC, high-performance liquid chromatography; NMR, nuclear magnetic resonance.

*2, 0.3 mmol; 4, 0.6 mmol. Isolated yield was reported. Regio- and diastereoselectivity were determined by 1H NMR analysis of reaction crude mixture. Enantioselectivity was determined by chiral-stationary-phase HPLC analysis.

*Gram-scale synthesis.

*(S)-DTBM-SEGPHOS was used.
cleavage of the generated acetal motif. Furthermore, the synthetic utilities of the present methodology were
showcased by its applications in the asymmetric synthesis of yashabushidiol B and the formal asymmetric synthe-
sis of (+)-cryptocaryalactone (for the details, see Supplemental Information). Moreover, our synthetic route pro-
vided a straightforward method for the asymmetric synthesis of various chiral diols. Some of the diols (both
natural and man-made) exhibited significant anti-proliferative activity on some human cancer cell lines (Narasim-
hulu et al., 2009; Yokosuka et al., 2002).

Limitations of Study
Aliphatic aldehydes were not applicable in the present reactions as α-adducts were obtained in low yields
and no vinylogous products were generated. Fortunately, α,β-unsaturated aldehydes served as competent
substrates and their vinylogous products could be potentially converted to the vinylogous products of
aliphatic aldehydes through the transformations of carbon-carbon double bond.

Conclusion
In summary, two copper(I)-(R)-DBTM-SEGPHOS complex-catalyzed asymmetric vinylogous aldol-type re-
actions of aldehydes with allyl phosphonate and allyl sulfone were disclosed. These two reactions enjoyed
advantages of 100% atomic economy, mild reaction conditions, easy reaction protocol, broad substrate
scope, excellent regioselectivity, and excellent enantioselectivity. The mechanistic studies revealed a
significantly reversible α-addition process and a slightly reversible γ-addition process, which accounted for the perfect control of the regioselectivity in these two vinylogous aldol-type reactions. Finally, various transformations of the vinylogous products (including HWE and Julia olefinations) were successfully carried out by means of phosphonate and sulfone. Application of the present methodology in the asymmetric synthesis of complex natural products is currently on the way in our laboratory.

METHODS

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

Supplemental Information can be found online at https://doi.org/10.1016/j.isci.2019.03.010.

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AUTHOR CONTRIBUTIONS

L.Y. conceived the project and designed the experiments. W.-J.Y. and C.-Y.Z. performed and analyzed the related materials. All the authors discussed the results and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

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Supplemental Information

Asymmetric Vinylogous Aldol-type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

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Supplement Information

Asymmetric Vinylogous Aldol-Type Reactions of Aldehydes with Allyl Phosphonate and Sulfone

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Copies of product NMR spectra

Figure S1. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 2ah, related to Table 2

Figure S2. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 2ah, related to Table 2
Figure S3. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3a, related to Table 2

Figure S4. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3a, related to Table 2
Figure S5. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3a, related to Table 2
Figure S6. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3b, related to Table 2

Figure S7. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3b, related to Table 2
Figure S8. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3b, related to Table 2

Figure S9. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 3b, related to Table 2
Figure S10. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3c, related to Table 2

Figure S11. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3c, related to Table 2
Figure S12. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3c, related to Table 2
Figure S13. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3d, related to Table 2

Figure S14. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3d, related to Table 2
Figure S15. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3d, related to Table 2.
Figure S16. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3e, related to Table 2

Figure S17. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3e, related to Table 2
Figure S18. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3e, related to Table 2
Figure S19. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3f, related to Table 2

Figure S20. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3f, related to Table 2
Figure S21. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3f, related to Table 2
Figure S22. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3g, related to Table 2

Figure S23. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3g, related to Table 2
Figure S24. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3g, related to Table 2
**Figure S25.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3h, related to Table 2

**Figure S26.** $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3h, related to Table 2
Figure S27. $^{31}\text{P}$ NMR (162 MHz, CDCl$_3$) spectrum of compound 3h, related to Table 2.
Figure S28. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3i, related to Table 2

Figure S29. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3i, related to Table 2
Figure S29. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3i, related to Table 2
Figure S30. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3j, related to Table 2

Figure S31. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3j, related to Table 2
Figure S32. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3j, related to Table 2

Figure S33. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 3j, related to Table 2
Figure S34. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3k, related to Table 2

Figure S35. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3k, related to Table 2
Figure S36. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3k, related to Table 2

Figure S37. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 3k, related to Table 2
Figure S38. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3l, related to Table 2

Figure S39. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3l, related to Table 2
Figure S40. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3l, related to Table 2

Figure S41. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 3l, related to Table 2
Figure S42. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3m, related to Table 2

Figure S43. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3m, related to Table 2
Figure S44. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3m, related to Table 2.
Figure S45. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3n, related to Table 2

Figure S46. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3n, related to Table 2
Figure S47. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3n, related to Table 2
Figure S48. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3o, related to Table 2

Figure S49. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3o, related to Table 2
Figure S50. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3o, related to Table 2.
Figure S51. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3p, related to Table 2

Figure S52. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3p, related to Table 2
Figure S53. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3p, related to Table 2.
Figure S54. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3q, related to Table 2

Figure S55. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3q, related to Table 2
Figure S56. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3q, related to Table 2
Figure S57. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3r, related to Table 2

Figure S58. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3r, related to Table 2
Figure S59. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3r, related to Table 2.
Figure S60. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3s, related to Table 2

Figure S61. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3s, related to Table 2
Figure S62. $^{31}$P NMR (162 MHz, CDCl₃) spectrum of compound 3s, related to Table 2
Figure S63. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3t, related to Table 2

Figure S64. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3t, related to Table 2
Figure S65. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3t, related to Table 2
Figure S66. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3u, related to Table 2

Figure S67. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3u, related to Table 2
Figure S68. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3u, related to Table 2
Figure S69. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3v, related to Table 2

Figure S70. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3v, related to Table 2
Figure S71. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3v, related to Table 2
Figure S72. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3w, related to Table 2

Figure S73. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3w, related to Table 2
Figure S74. $^{31}\text{P}$ NMR (162 MHz, CDCl$_3$) spectrum of compound 3w, related to Table 2
Figure S75. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3x, related to Table 2

Figure S76. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3x, related to Table 2
Figure S77. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3x, related to Table 2
Figure S78. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3y, related to Table 2

Figure S79. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3y, related to Table 2
Figure S80. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3y, related to Table 2
Figure S81. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3z, related to Table 2

Figure S82. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3z, related to Table 2
Figure S83. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3z, related to Table 2
Figure S84. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3aa, related to Table 2

Figure S85. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3aa, related to Table 2
Figure S86. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3aa, related to Table 2
Figure S87. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ab, related to Table 2

Figure S88. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ab, related to Table 2
Figure S89. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ab, related to Table 2
Figure S90. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ac, related to Table 2

Figure S91. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ac, related to Table 2
Figure S92. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ac, related to Table 2.
Figure S93. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ad, related to Table 2

Figure S94. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ad, related to Table 2
Figure S95. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ad, related to Table 2
Figure S96. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ae, related to Table 2

Figure S97. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ae, related to Table 2
Figure S98. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ae, related to Table 2
Figure S99. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3af, related to Table 2

Figure S100. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3af, related to Table 2
Figure S101. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3af, related to Table 2
Figure S102. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ag, related to Table 2

Figure S103. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ag, related to Table 2
Figure S104. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ag, related to Table 2.
Figure S105. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ah, related to Table 2

Figure S106. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ah, related to Table 2
Figure S107. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ah, related to Table 2
Figure S108. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ai, related to Table 2

Figure S109. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ai, related to Table 2
Figure S110. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ai, related to Table 2
Figure S111. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3aj, related to Table 2

Figure S112. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3aj, related to Table 2
Figure S113. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3aj, related to Table 2
Figure S114. $^1$H NMR (400 MHz, CDCl₃) spectrum of compound 3aj', related to Table 2

Figure S115. $^{13}$C NMR (100 MHz, CDCl₃) spectrum of compound 3aj', related to Table 2
Figure S116. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3aj', related to Table 2
Figure S117. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ak, related to Table 2

Figure S118. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ak, related to Table 2
Figure S119. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ak, related to Table 2
Figure S120. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3ak', related to Table 2

Figure S121. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3ak', related to Table 2
Figure S122. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3ak', related to Table 2.
Figure S123. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3al, related to Table 2

Figure S124. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3al, related to Table 2
Figure S125. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3al, related to Table 2
Figure S126. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 3af', related to Table 2.

![Figure S126: $^1$H NMR spectrum of compound 3af']

Figure S127. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 3af', related to Table 2.

![Figure S127: $^{13}$C NMR spectrum of compound 3af']
Figure S128. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 3al', related to Table 2
Figure S129. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5a, related to Table 3

Figure S130. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5a, related to Table 3
Figure S131. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5b, related to Table 3

Figure S132. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5b, related to Table 3
Figure S133. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 5b, related to Table 3
Figure S134. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5c, related to Table 3

Figure S135. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5c, related to Table 3
Figure S136. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5d, related to Table 3

Figure S137. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5d, related to Table 3
Figure S138. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5e, related to Table 3

Figure S139. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5e, related to Table 3
Figure S140. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5f, related to Table 3

Figure S141. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5f, related to Table 3
Figure S142. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5g, related to Table 3

Figure S143. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5g, related to Table 3
Figure S144. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5h, related to Table 3

Figure S145. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5h, related to Table 3
Figure S146. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5k, related to Table 3

Figure S147. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5k, related to Table 3
Figure S148. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 5k, related to Table 3
Figure S149. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5l, related to Table 3

Figure S150. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5l, related to Table 3
Figure S151. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 5l, related to Table 3
Figure S152. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5n, related to Table 3

Figure S153. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5n, related to Table 3
Figure S154. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5o, related to Table 3

Figure S155. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5o, related to Table 3
Figure S156. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5p, related to Table 3

Figure S157. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5p, related to Table 3
Figure S158. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5q, related to Table 3

Figure S159. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5q, related to Table 3
Figure S160. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5r, related to Table 3

Figure S161. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5r, related to Table 3
Figure S162. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5u, related to Table 3

Figure S163. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5u, related to Table 3
Figure S164. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5x, related to Table 3

Figure S165. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5x, related to Table 3
Figure S166. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5y, related to Table 3

Figure S167. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5y, related to Table 3
Figure S168. $^1$H NMR (400 MHz, CDCl₃) spectrum of compound 5z, related to Table 3

Figure S169. $^{13}$C NMR (100 MHz, CDCl₃) spectrum of compound 5z, related to Table 3
Figure S170. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5aa, related to Table 3

Figure S171. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5aa, related to Table 3
Figure S172. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ad, related to Table 3

Figure S173. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ad, related to Table 3
Figure S174. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ae, related to Table 3

Figure S175. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ae, related to Table 3
Figure S176. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ah, related to Table 3

Figure S177. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ah, related to Table 3
Figure S178. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ak, related to Table 3

Figure S179. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ak, related to Table 3
Figure S180. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ak', related to Table 3

Figure S181. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ak', related to Table 3
Figure S182. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5al, related to Table 3

Figure S183. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5al, related to Table 3
Figure S184. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5al', related to Table 3

Figure S185. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5al', related to Table 3
Figure S186. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5am, related to Table 3

Figure S187. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5am, related to Table 3
Figure S188. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5an, related to Table 3

Figure S189. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5an, related to Table 3
Figure S190. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ao, related to Table 3

Figure S191. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ao, related to Table 3
Figure S192. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ap, related to Table 3

Figure S193. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ap, related to Table 3
Figure S194. $^{19}$F NMR (376 MHz, CDCl$_3$) spectrum of compound 5ap, related to Table 3
Figure S195. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5aq, related to Table 3

Figure S196. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5aq, related to Table 3
Figure S197. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5ar, related to Table 3

Figure S198. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5ar, related to Table 3
Figure S199. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5as, related to Table 3

Figure S200. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5as, related to Table 3
Figure S201. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5at, related to Table 3

Figure S202. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5at, related to Table 3
Figure S203. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 5au, related to Table 3

Figure S204. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 5au, related to Table 3
Figure S205. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 9, related to Scheme 3

Figure S206. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 9, related to Scheme 3
**Figure S207.** $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 9, related to Scheme 3
Figure S208. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 10, related to Scheme 3

Figure S209. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 10, related to Scheme 3
Figure S210. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 10, related to Scheme 3
Figure S211. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 11, related to Scheme 3.

Figure S212. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 11, related to Scheme 3.
Figure S213. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 12, related to Scheme 3

Figure S214. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 12, related to Scheme 3
Figure S215. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 14, related to Scheme 3

Figure S216. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 14, related to Scheme 3
**Figure S217.** $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 15, related to Scheme 3

**Figure S218.** $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 15, related to Scheme 3
Figure S219. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 16, related to Scheme 3

Figure S220. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 16, related to Scheme 3
Figure S221. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 17, related to Scheme 3

Figure S222. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 17, related to Scheme 3
Figure S223. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 18, related to Scheme 3

Figure S224. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 18, related to Scheme 3
Figure S225. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 19, related to Scheme 3

Figure S226. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 19, related to Scheme 3
Figure S227. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 19, related to Scheme 3
Figure S228. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 20, related to Scheme 3

Figure S229. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 20, related to Scheme 3
Figure S230. $^{31}$P NMR (162 MHz, CDCl$_3$) spectrum of compound 20, related to Scheme 3.
Figure S231. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 21, related to Scheme 3

Figure S232. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 21, related to Scheme 3
Figure S233. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 22, related to Scheme 3

Figure S234. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 22, related to Scheme 3
Figure S235. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of compound 23, related to Scheme 3

Figure S236. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of compound 23, related to Scheme 3
Figure S237. $^1$H NMR (400 MHz, CDCl$_3$) spectrum of yashabushidiol B, related to Scheme 3

Figure S238. $^{13}$C NMR (100 MHz, CDCl$_3$) spectrum of yashabushidiol B, related to Scheme 3
Transparent Methods

All reagents were obtained commercially unless otherwise noted. Nuclear Magnetic Resonance (NMR) spectra were acquired on an Agilent 400 or Bruker 400 spectrometer. For $^1$H NMR, chemical shifts were reported in δ ppm referenced to an internal SiMe$_4$ standard. For $^{19}$F NMR, CFCl$_3$ was used as the reference with chemical shift at 0 ppm. For $^{13}$C NMR, chemical shifts were reported in the scale relative to NMR solvent (CDCl$_3$: 77.0 ppm) as an internal reference. $^{31}$P NMR spectra were referenced externally to phosphoric acid. Multiplicities are reported using the following abbreviations: br = broad, s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, m = multiplet. Mass spectra (EI) were measured on Agilent Technologies 5973N GC-MS. High-resolution mass spectra (EI) were measured on Waters Micromass GCT Premier spectrometer. Mass spectra (ESI) were measured on Agilent Technologies 1100 Series LC-MS. High-resolution mass spectra (ESI) were measured on Thermo Scientific LTQ FT Ultra FT-MS. Mass spectra (DART) and high-resolution mass spectra (DART) were measured on Thermo Fisher Scientific LTQ FTICR-MS. Infrared (IR) spectra were recorded on Thermo Scientific Nicolet iS5 FT-IR. Optical rotation was measured using a 1 mL cell with 1.0 dm path length on a JASCO P-1030 polarimeter. HPLC analysis was conducted on a Shimadzu HPLC system equipped with Daicel chiral-stationary-phase columns (4.6 mm×250 mm).

The procedure for preparation of 2ah: A solution of (triphenylphosphoranylidene)-acetaldehyde (3.04 g, 10 mmol, 1.0 equiv) and dec-5-ynal (1.52 g, 10 mmol, 1.0 equiv) in absolute chloroform (concentration of the aldehyde: 0.3 M) was refluxed until no further reaction progress was monitored by GC/MS. Then the reaction mixture was adsorbed on a small amount of silica gel and was purified by column chromatography (petroleum ether/ethyl acetate = 100/1 to 80/1) to afford the aldehyde 2ah (0.54 g, 3 mmol, 30% yield) as a pale green oil.

General procedure for catalytic asymmetric direct vinyllogous aldol-type reaction of aldehydes and allyl phosphonate:

Procedure A:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with [Cu(CH$_3$CN)$_4$]PF$_6$ (5.6 mg, 0.15 mmol, 0.05 equiv) and (R)-DTBM-SEGPHOS (17.7 mg, 0.15 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate 1 (160.4 mg, 0.9 mmol, 3.0 equiv) and aldehyde 2 (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton’s Base (12 μL, 0.06 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (300 μL, 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 °C. After solvent was removed under reduced pressure, the residue was purified by column chromatography (petroleum ether/ethyl acetate/methanol) to give the desired product.

Procedure B:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with [Cu(CH$_3$CN)$_4$]PF$_6$ (5.6 mg, 0.15 mmol, 0.05 equiv) and (S)-DTBM-SEGPHOS (17.7 mg, 0.15
mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate \( \textbf{1} \) (160.4 mg, 0.9 mmol, 3.0 equiv) and aldehyde \( \textbf{2} \) (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton’s Base (12 μL, 0.06 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 °C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol) to give the desired product.

**General procedure for catalytic asymmetric direct vinylogous aldol-type reaction of aldehydes and allyl sulfone:**

**Procedure A:**
A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with \([\text{Cu(CH_3CN)_4}]PF_6\) (5.6 mg, 0.15 mmol, 0.05 equiv) and \((R\text{-DTBM-SEGPHOS}\) (17.7 mg, 0.15 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl sulfone \( \textbf{4} \) (109.9 mg, 0.6 mmol, 2.0 equiv) and aldehyde \( \textbf{2} \) (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton’s Base (18 μL, 0.09 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 36 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -40 °C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired product.

**Procedure B:**
A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with \([\text{Cu(CH_3CN)_4}]PF_6\) (5.6 mg, 0.15 mmol, 0.05 equiv) and \((S\text{-DTBM-SEGPHOS}\) (17.7 mg, 0.15 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.15 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl sulfone \( \textbf{4} \) (109.9 mg, 0.6 mmol, 2.0 equiv) and aldehyde \( \textbf{2} \) (0.3 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton’s Base (18 μL, 0.09 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 36 hours. Then, the reaction mixture was quenched by acetic acid (300 μL (0.4 M in THF), 0.12 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -40 °C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate) to give the desired product.

**The procedure for determination of the absolute configuration of \( \textbf{3a} \)**
Absolute configuration of \( \textbf{3a} \) was determined by its transformation to \((R\text{-1-phenylpropane-1,3-diol}\) as shown below and the comparison of its optical rotation with the one reported in literature (Denmark et. al., 2004 ).
Ozone was bubbled into a solution of 3a (110 mg, 0.39 mmol, 1.0 equiv) in MeOH (5.0 mL) at -78 °C until the appearance of a persistent blue color (about 30 min). The reaction solution was then allowed to warm up to 0 °C and the mixture was subsequently treated with NaBH₄ (73.8 mg, 1.95 mmol, 5 equiv.) at 0°C. The reaction mixture was allowed to warm up to room temperature and was stirred for additional 2 hours. Then, the reaction was quenched by H₂O (5 mL) and extracted with DCM (15 mL×3). The combined organic layers were dried over Na₂SO₄. After removal of solvent under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford (R)-1-phenylpropane-1,3-diol (39 mg, colorless oil, 67% yield).

The procedure for determination of the absolute configuration of 5a

Absolute configuration of 5a was determined by its transformation to (R)-1-phenylpropane-1,3-diol as shown below and the comparison of its optical rotation with the one reported in literature (Denmark et. al., 2004).

Ozone was bubbled into a solution of 5a (94 mg, 0.33 mmol, 1.0 equiv) in MeOH (5.0 mL) at -78 °C until the appearance of a persistent blue color (about 30 min). The reaction solution was then allowed to warm up to 0 °C and the mixture was subsequently treated with NaBH₄ (62.4 mg, 1.65 mmol, 5 equiv.) at 0°C. The reaction mixture was allowed to warm up to room temperature and was stirred for additional 2 hours. Then, the reaction was quenched by H₂O (5 mL) and extracted with DCM (15 mL×3). The combined organic layers were dried over Na₂SO₄. After removal of solvent under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to afford (R)-1-phenylpropane-1,3-diol (21 mg, colorless oil, 42% yield).

The procedure for preparation of rac-3a:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with [Cu(CH₃CN)₄]PF₆ (9.3 mg, 0.025 mmol, 0.05 equiv) and rac-DTBM-SEGPHOS (29.5 mg, 0.025 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.25 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate 1 (267.3 mg, 1.5 mmol, 3.0 equiv) and
aldehyde 2a (53.1 mg, 0.5 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton’s Base (17.1 mg, 0.10 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (500 μL (0.4 M in THF), 0.20 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 °C. Then the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 30/15/1) to give rac-3a (128.0 mg, 90% yield) as a colorless oil.

The procedure for preparation of rac-5a:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with [Cu(CH3CN)4]PF6 (11.2 mg, 0.030 mmol, 0.05 equiv) and rac-DTBM-SEGPHOS (35.4 mg, 0.030 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (2.0 mL, 0.30 M) was added via a syringe. The mixture was stirred for 15 minutes to give a colorless catalyst solution. Then allyl sulfone 4 (220.0 mg, 1.2 mmol, 2.0 equiv) and aldehyde 2a (63.7 mg, 0.6 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton’s Base (30.8 mg, 0.18 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 12 hours. Then, the reaction mixture was quenched by acetic acid (600 μL (0.4 M in THF), 0.20 mmol, 0.40 equiv), and was stirred for additional 20 minutes at -40 °C. Then the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/2) to give rac-5a (110.0 mg, 63% yield) as pale green powders.

The procedure for preparation of rac-α-3a:

rac-3a was prepared according to a reported procedure (Yuan et al., 1991). A dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with allyl phosphonate 1 (534.5 mg, 3.0 mmol, 1.0 equiv) under N2 atmosphere. Anhydrous THF (10 mL) was added via a syringe. The mixture was cooled to -78 °C and was stirred for 10 minutes. Then "BuLi (1.3 mL (2.5 M solution in hexane), 3.15 mmol, 1.05 equiv) was added via a syringe. After 30 minutes, benzaldehyde 2a (318.4 mg, 3 mmol, 1.0 equiv) was added via a syringe and the mixture was stirred for 30 minutes. The reaction was quenched by saturated aqueous NH4Cl (5 mL) at -78 °C. The aqueous phase was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na2SO4 and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 14/7/1) to give rac-α-3a (724.9 mg, 85% yield, dr = 2.5/1) as a colorless oil.

The procedure for preparation of rac-α-5a:

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with LDA (1.0 mL (2 M solution in hexane/THF), 2 mmol, 1.0 equiv) under N2 atmosphere. Anhydrous THF (2 mL) was added via a syringe. The mixture was cooled to -78 °C and HMPA (358.4 mg, 2 mmol, 1.0 equiv) was added via a syringe. The resulting mixture was stirred at -78 °C for 30 minutes and then allyl sulfone 5 (439.8 mg, 2.4 mmol, 1.2 equiv) was added. After 30 minutes, benzaldehyde 2a (318.4 mg, 3 mmol, 1.5 equiv) was added and the resulting mixture was stirred for 20 minutes. The reaction was quenched by saturated aqueous NH4Cl (5 mL) at -78 °C. The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over
anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give rac-α-5a (101.0 mg, 15% yield, dr = 1/1) as pale green powders.

Proposed Mechanism for the Copper(I)-Catalyzed Asymmetric Aldol-Type Reaction:

![Figure S241, Proposed Mechanism, related to Scheme 2]

Based on these experimental observations and literature proposals, a postulated reaction pathway was given as shown above. In the presence of copper(I) complex U and Barton’s Base, the deprotonation of substrate 1/4 occurred smoothly to give allylcopper(I) species V, which might form an equilibrium with allylcopper(I) species W. The α-addition of V with aldehyde 2 produced copper(I) alkoxide complex X, which afforded α-adduct after protonation with substrate 1/4. As demonstrated by the experiments, the α-addition was a significantly reversible process. It was possible that the γ'-addition of W with aldehyde 2 also furnished copper(I) alkoxide complex X. The γ-addition of allylcopper(I) species V generated copper(I) alkoxide complex Y through a six-membered ring transition state, which was identified as a slightly reversible process. The protonation of Y with additional substrate 1/4 led to γ-adduct.

The procedure for gram-scale preparation of vinylogous product 3a:

A dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with [Cu(CH₃CN)₄]PF₆ (74.5 mg, 0.20 mmol, 0.05 equiv) and (R)-DTBM-SEGPHOS (235.9 mg, 0.20 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (40 mL, 0.2 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl phosphonate 1 (2.140 g, 12 mmol, 3.0 equiv) and benzaldehyde 2a (424.5 mg, 4.0 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -10 °C, Barton’s Base (137.0 mg, 0.80 mmol, 0.20 equiv) was added. The resulting reaction mixture was stirred at -10 °C for 48 hours. Then, the reaction mixture was quenched by acetic acid (4 mL (0.4 M in THF), 1.6 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -10 °C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate/methanol = 30/15/1) to give product 3a (0.990 g, 85% yield, 99% ee) as a colorless oil.

The procedure for gram-scale preparation of vinylogous product 5a:
A dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with [Cu(CH₃CN)₄]PF₆ (74.5 mg, 0.20 mmol, 0.05 equiv) and (R)-DTBM-SEGPHOS (235.9 mg, 0.20 mmol, 0.05 equiv) in a glove box under Ar atmosphere. Anhydrous THF (40 mL, 0.1 M) was added via a syringe. The mixture was stirred at room temperature for 15 minutes to give a colorless catalyst solution. Then allyl sulfone 4 (1.466 g, 12 mmol, 3.0 equiv) and benzaldehyde 2a (424.5 mg, 4.0 mmol, 1.0 equiv) were added sequentially. After the mixture was cooled to -40 °C, Barton’s Base (205.5 mg, 1.20 mmol, 0.30 equiv) was added. The resulting reaction mixture was stirred at -40 °C for 36 hours. Then, the reaction mixture was quenched by acetic acid (4 mL (0.4 M in THF), 1.6 mmol, 0.40 equiv) and was stirred for additional 20 minutes at -40 °C. After solvent was removed under reduced pressure, the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/2) to give product 5a (1.100 g, 95% yield, 97% ee) as pale green powders.

**Transformations of vinylogous product 3a:**

![Figure S242, Transformations, related to Scheme 3](image)

A dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with 3a (250 mg, 0.88 mmol, 1.0 equiv) and 2,6-lutidine (189 mg, 1.76 mmol, 2.0 equiv) under N₂ atmosphere. After the mixture was cooled to -10 °C, TBSOTf (465 mg, 1.76 mmol, 2.0 equiv) was added via a syringe. The resulting mixture was stirred at -10 °C for 7 hours. After removing the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product 9 (312 mg, 90% yield) as a colorless oil.

![Figure S243, Transformations, related to Scheme 3](image)

A dried 25 mL round bottom flask equipped with a magnetic stirring bar was charged with 9 (79.7 mg, 0.20 mmol, 1.0 equiv), Pd/C (16 mg, 5% w/w) and EtOH (4 mL). The resulting mixture was stirred at room temperature for 3 hours with a balloon filled with H₂. The black solids were filtered off and washed thoroughly with EtOH. The filtrate was concentrated under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product 10 (78.5 mg, 98% yield) as a colorless oil.

![Figure S244, Transformations, related to Scheme 3](image)

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with LDA
(0.1 mL (2 M solution in hexane/THF), 2 mmol, 1.0 equiv) under N₂ atmosphere. Anhydrous THF (0.2 mL) was added via a syringe. The mixture was cooled to -78 °C and 10 (38.1 mg, 0.095 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 5 minutes and then EtOOCOEt (11.8 mg, 0.10 mmol, 1.05 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 30 minutes and then was warmed to 0 °C. Benzaldehyde 2a (11.1 mg, 0.105 mmol, 1.1 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at room temperature overnight and then was quenched by saturated aqueous NH₄Cl (2 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give 11 (32.5 mg, 81% yield, E/Z > 20/1) as a colorless oil.

**Figure S245, Transformations, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with LDA (0.105 mL (2 M solution in hexane/THF), 2 mmol, 1.0 equiv) under N₂ atmosphere. Anhydrous THF (0.2 mL) was added via a syringe. The mixture was cooled to -78 °C and 10 (40.1 mg, 0.10 mmol, 1.0 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 5 minutes and then EtOOCOEt (13.0 mg, 0.105 mmol, 1.05 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at -78 °C for 30 minutes and then was warmed to 0 °C. Cinnamaldehyde 2y (14.5 mg, 0.11 mmol, 1.1 equiv) in THF (0.5 mL) was added dropwise via a syringe. The resulting mixture was stirred at room temperature overnight and then was quenched by saturated aqueous NH₄Cl (2 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give 11 (32 mg, 71% yield, E/Z = 5/1) as a colorless oil.

**Transformations of vinylogous product 5a:**

**Figure S246, Transformations, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 5a (57.9 mg, 0.2 mmol, 1.0 equiv) under N₂ atmosphere. SmI₂ (10 mL (0.1 M solution in THF), 1 mmol, 5.0 equiv) was added via a syringe. The mixture was cooled to -20 °C and HMPA (0.8 mL) was added dropwise via a syringe. The resulting mixture was stirred at -20 °C for 2 hours, Then the reaction mixture was concentrated under reduced pressure to give the crude which was used in next step without further purification.
To the solution of above crude (0.2 mmol, 1.0 equiv) in toluene (2 mL) were added DMAP (4.8 mg, 0.04 mmol, 0.10 equiv) and benzoic anhydride (136 mg, 0.6 mmol, 1.5 equiv). The resulting mixture was stirred at room temperature for 10 hours. Then the reaction mixture was concentrated under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 50/1) to give 13 (26 mg, 52% yield) as a pale yellow oil.

**Figure S247, Transformations, related to Scheme 3**

A dried 100 mL round bottom flask equipped with a magnetic stirring bar was charged with 5a (1.00 g, 3.46 mmol, 1.0 equiv) under N$_2$ atmosphere. THF (40 mL) was added via a syringe. The mixture was cooled to 0 °C and LiBH(Et)$_3$ (4.5 mL (1 M solution in THF), 4.50 mmol, 1.3 equiv) was added dropwise via a syringe. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction was quenched by saturated aqueous NH$_4$Cl (20 mL). The aqueous phase was extracted with ethyl acetate (50 mL × 3). The combined organic extracts were dried over anhydrous Na$_2$SO$_4$ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give 14 (932 mg, 92% yield) as white powders.

**Figure S248, Transformations, related to Scheme 3**

A dried 50 mL round bottom flask equipped with a magnetic stirring bar was charged with 14 (697 mg, 2.40 mmol, 1.0 equiv) and 2,6-lutidine (514 mg, 4.80 mmol, 2.0 equiv) under N$_2$ atmosphere. After cooling to -10 °C, TBSOTf (1.27 g, 4.80 mmol, 2.0 equiv) was added via a syringe. The resulting mixture was stirred at -10 °C for 12 hours. After removing the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give product 15 (908 mg, 93% yield) as a colorless oil.

**Figure S249, Transformations, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 15 (81.2 mg, 0.20 mmol, 1.0 equiv) under N$_2$ atmosphere. Anhydrous DME (5 mL) was added via a syringe. The mixture was cooled to -78 °C and KHMDS (0.40 mL (1 M solution in THF), 0.40 mmol, 2.0 equiv) was added via a syringe. After 3 minutes, benzaldehyde 2a (31.8 mg, 0.30 mmol, 1.5 equiv) was added via a syringe and the resulting mixture was stirred for 2 hours. Then the reaction mixture was warm to room temperature and stirred for 12 hours. The reaction was
quenched by saturated aqueous NH₄Cl (5 mL). The aqueous phase was extracted with ethyl acetate (20 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give 16 (47 mg, 67% yield) as a colorless oil.

**Figure S250, Transformations, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 15 (40.6 mg, 0.10 mmol, 1.0 equiv) under N₂ atmosphere. Anhydrous THF (3 mL) was added via a syringe. The mixture was cooled to -78 °C and was stirred for 10 minutes. Then nBuLi (0.20 mL (1 M solution in THF), 0.20 mmol, 2.0 equiv) was added via a syringe. After 30 minutes, PhCOCl (21.1 mg, 0.15 mmol, 1.5 equiv) was added and the resulting mixture was stirred for 2 hours. Then the reaction was quenched by saturated aqueous NH₄Cl (5 mL). The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure to give the crude which was used in next step without further purification.

The solution of above crude (0.1 mmol, 1.0 equiv) in THF (2 mL) was added to a mixture of activated Zn powder (180 mg), THF (4 mL) and H₂O(4 mL). The resulting mixture was stirred at room temperature for 4 hours. The solids were filtered off and washed thoroughly with DCM. The filtrate was dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 20/1) to give 17 (25 mg, 68% yield) as a colorless oil.

**Figure S251, Transformations, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 5a (63.1 mg, 0.20 mmol, 1.0 equiv) under N₂ atmosphere. Anhydrous THF (2 mL) was added via a syringe. The mixture was cooled to 0 °C and was stirred for 10 minutes. Then benzaldehyde 2a (23.4 mg, 0.22 mmol, 1.1 equiv) and LiHMDS (0.2 mL (1 M solution in THF), 0.20 mmol, 1.0 equiv) were added via a syringe. After 15 minutes, benzaldehyde 2a (23.4 mg, 0.22 mmol, 1.1 equiv) and LiHMDS (0.2 mL (1 M solution in THF), 0.20 mmol, 1.0 equiv) was added again. This procedure was repeated twice. Then the resulting reaction mixture was quenched by saturated aqueous NH₄Cl (5 mL). The aqueous phase was extracted with ethyl acetate (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure to give the crude which was used in next step without further purification.

The above crude (0.2 mmol, 1.0 equiv) was added to HOAc (4 mL, 80% in water). The resulting reaction mixture was heating to 80 °C and stirred at this temperature overnight. Then the
resulting reaction mixture was quenched by saturated aqueous NaHCO₃ (20 mL). The aqueous phase was extracted with diethyl ether (20 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure. The residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 1/2) to give 18 (45.5 mg, 74% yield) as white powders.

**Synthetic Application of the Methodology:**

\[
\begin{align*}
\text{Ph} & \quad \text{OH} & \quad \text{P(\text{OEt})₂} \\
\text{ent-3y} & \quad \xrightarrow{TBSOTf, 2,6-lutidine} \quad \text{DCM, -10 °C} \\
\text{Ph} & \quad \text{O} & \quad \text{OTBS} & \quad \text{P(\text{OEt})₂}
\end{align*}
\]

**Figure S252, Synthetic application, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with ent-3y (93.1 mg, 0.30 mmol, 1.0 equiv) and 2,6-lutidine (64.3 mg, 0.60 mmol, 2.0 equiv) under N₂ atmosphere. After the mixture was cooled to -10 °C, TBSOTf (158.6 mg, 0.60 mmol, 2.0 equiv) was added. The resulting mixture was stirred at -10 °C for 4 hours. After removing the volatiles under reduced pressure, the crude was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product 19 (105.7 mg, 83% yield) as a colorless oil.

\[
\begin{align*}
\text{Ph} & \quad \text{OTBS} & \quad \text{O} & \quad \text{P(\text{OEt})₂} \\
\text{19} & \quad \xrightarrow{\text{CuCl (10 mol%), rac-BINAP (15 mol%)}} \quad \text{Bz₂(Pin)₂ (2.0 equiv) (1.1 equiv)} \\
\text{Ph} & \quad \text{O} & \quad \text{OTBS} & \quad \text{P(\text{OEt})₂}
\end{align*}
\]

**Figure S253, Synthetic application, related to Scheme 3**

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with CuCl (3.0 mg, 0.03 mmol, 0.10 equiv), rac-BINAP (22.5 mg, 0.036 mmol, 0.12 equiv) and NaO'Bu (4.3 mg, 0.045 mmol, 0.15 equiv) in a glove box under Ar atmosphere. 19 (127.5 mg, 0.30 mmol, 1.0 equiv) and Bz₂(Pin)₂ (152.4 mg, 0.6 mmol, 2.0 equiv) were added under N₂ atmosphere. Anhydrous THF (3.0 mL) was added via a syringe. The mixture was stirred at room temperature for 15 minutes. Then MeOH (19.2 mg, 0.6 mmol, 2.0 equiv) was added. The resulting reaction mixture was stirred at room temperature for 24 hours. Then, water (3 mL) and NaBO₂·H₂O (138.6 mg, 0.90 mmol, 3.0 equiv) were added sequentially. The mixture was stirred at room temperature for additional 3 hours. Then the resulting reaction mixture was quenched by saturated aqueous NH₄Cl (5 mL). The aqueous phase was extracted with diethyl ether (10 mL × 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure to give the crude which was used in next step without further purification.

To the solution of above crude (0.30 mmol, 1.0 equiv) in DCM (18 mL) was added 4Å molecular sieves (350 mg) and PCC (516 mg, 2.40 mmol, 8.0 equiv). The resulting mixture was stirred at room temperature for 12 hours. The solids were filtered off and washed thoroughly with ethyl acetate. The filtrate was concentrated under reduced pressure to give the crude which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give product 20 (97.8 mg, 74% yield) as a colorless oil.
Figure S254, Synthetic application, related to Scheme 3

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 20 (61 mg, 0.14 mmol, 1.0 equiv) under N₂ atmosphere. THF (2.0 mL) was added via a syringe. Then Ba(OH)₂ (29.5 mg, 0.17 mmol, 1.25 equiv) was added. The resulting mixture was stirred for 30 minutes at room temperature and then benzaldehyde 2a (15.3 mg, 0.15 mmol, 1.05 equiv) in THF/H₂O (2 mL, 40/1) was added dropwise via a syringe. The resulting mixture was stirred at room temperature for 2 hours. Then the reaction was quenched by saturated aqueous NH₄Cl (3 mL). The aqueous phase was extracted with diethyl ether (10 mL x 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 100/1) to give product 21 (46.1 mg, 85% yield) as a colorless oil.

Figure S255, Synthetic application, related to Scheme 3

A 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with 21 (42 mg, 0.107 mmol, 1.0 equiv) and THF (2.0 mL). Then HCl (0.21 mL (3 M solution in water), 0.63 mmol, 6.0 equiv) was added. The resulting mixture was stirred at room temperature for 4 hours. Then the reaction was quenched by saturated aqueous NaHCO₃ (3 mL). The aqueous phase was extracted with diethyl ether (10 mL x 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 6/1) to give product 22 (21.1 mg, 71% yield) as white powders.

Figure S256, Synthetic application, related to Scheme 3

A dried 25 mL Schlenk tube equipped with a magnetic stirring bar was charged with MeBH(OAc)₃ (157.9 mg, 0.60 mmol, 6.0 equiv) under N₂ atmosphere. Anhydrous CH₃CN (0.5 mL) and HOAc (0.5 mL) were added via syringes. The resulting mixture was stirred at room temperature for 30 minutes. Then the resulting mixture was cooled to -20 °C. 22 (27.8 mg, 0.10 mmol, 1.0 equiv) in anhydrous CH₃CN (1 mL) was added dropwise via a syringe. The resulting mixture was stirred at -20 °C for 4 hours. Then the reaction was quenched by saturated aqueous sodium potassium tartarate and saturated aqueous NaHCO₃. The aqueous phase was extracted with diethyl ether (10 mL x 3). The combined organic extracts were dried over anhydrous Na₂SO₄ and the volatiles were removed under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product 23 (25.2 mg, 90% yield, dr = 8/1) as white powders (Diastereoselectivity was determined by ¹H NMR...
Figure S257, Synthetic application, related to Scheme 3

A dried 25 mL round bottom flask equipped with a magnetic stirring bar was charged with 23 (25 mg, 0.09 mmol, 1.0 equiv), Pd/C (27.4 mg, 5% w/w) and EtOH (2 mL). The resulting mixture was stirred for 2 hours at room temperature with a ballon filled with H₂. The black solids were filtered off and washed thoroughly with EtOH. The filtrate was concentrated under reduced pressure to give the crude, which was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 2/1) to give product yashabushidiol B (23 mg, 88% yield) as white powders.
Characterization of all compounds:

\[
\begin{align*}
\text{2ah} & \\
\end{align*}
\]

\(^1\text{H NMR (400 MHz, CDCl}_3\)) \delta 9.44 (d, J = 7.9 Hz, 1H), 6.80 (dt, J = 15.6, 6.8 Hz, 1H), 6.07 (dd, J = 15.6, 7.9 Hz, 1H), 2.44–2.34 (m, 2H), 2.19–2.12 (m, 2H), 2.10–2.06 (m, 2H), 1.72–1.55 (m, 2H), 1.47–1.24 (m, 4H), 0.84 (t, J = 7.1 Hz, 3H) ppm.

\(^{13}\text{C NMR (100 MHz, CDCl}_3\)) \delta 193.88, 157.83, 133.26, 81.35, 78.64, 31.59, 31.08, 27.11, 21.87, 18.32, 18.21, 13.54 ppm.

\text{MS(EI) m/z [M-H]}^+ : 177.00.

\text{HRMS(EI) m/z [M]}^+: \text{calcd. 178.1358, found 178.1359.}

\text{IR (film)}: 2933, 2320, 1698, 1652, 1286 cm\(^{-1}\).
3a: Procedure A, 78 mg, colorless liquid, 91\% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.42–7.12 (m, 5H), 6.76 (ddt, $J = 22.0, 17.1, 7.0$ Hz, 1H), 5.66 (dd, $J = 21.2, 17.1$ Hz, 1H), 4.81 (dd, $J = 7.4, 5.5$ Hz, 1H), 4.07–3.88 (m, 4H), 3.34 (s, 1H), 2.80–2.50 (m, 2H), 1.26 (td, $J = 7.0, 5.4$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.89 (d, $J = 4.9$ Hz), 143.80, 128.36, 127.50, 125.78, 119.28 (d, $J = 186.6$ Hz), 72.50, 61.68 (d, $J = 5.5$ Hz), 43.94 (d, $J = 22.0$ Hz), 16.24 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.05 ppm.

MS(ESI) m/z [M+H]$^+$: 285.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 285.1250, found 285.1250.

IR (film): 3361, 2984, 1632, 1259, 1020, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +19.72$ (c = 1.780, CHCl$_3$, 99\% ee).

HPLC: DAICEH CHIRALPAK ID, hexane/i-PrOH = 13/3, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 11.8 min, $t_R$(minor) = 13.4 min, ee = 99\%.

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 11.986    | 49.886|
| 2     | 13.551    | 50.114|

Figure S258, the HPLC spectrum of compound 3a, related to Table 2
3b: Procedure A, 73 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.32 (dd, $J$ = 8.6, 5.5 Hz, 2H), 7.01 (t, $J$ = 8.7 Hz, 2H), 6.75 (ddt, $J$ = 22.0, 17.1, 7.0 Hz, 1H), 5.66 (dd, $J$ = 21.1, 17.1 Hz, 1H), 4.81 (t, $J$ = 7.9 Hz, 1H), 4.23–3.82 (m, 4H), 3.62 (d, $J$ = 3.5 Hz, 1H), 2.77–2.52 (m, 2H), 1.26 (td, $J$ = 7.1, 3.7 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 162.09 (d, $J$ = 245.5 Hz), 149.55 (d, $J$ = 5.0 Hz), 139.59 (d, $J$ = 3.0 Hz), 127.42 (d, $J$ = 8.1 Hz), 119.58 (d, $J$ = 186.6 Hz), 115.17 (d, $J$ = 21.3 Hz), 71.88 (d, $J$ = 0.7 Hz), 61.70 (d, $J$ = 5.4 Hz), 4.01 (d, $J$ = 22.1 Hz), 16.24 (d, $J$ = 6.5 Hz) ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -115.10–115.18 (m) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.88 ppm.

MS(EI) m/z [M+H]$^+$: 303.10.

HRMS(EI) m/z [M+H]$^+$: calcd. 303.1154, found 303.1155.

IR (film): 3354, 2984, 1633, 1510, 1260, 1026 cm$^{-1}$.

Optical rotation: [α]$^D$ = +20.98 (c = 2.070, CHCl$_3$, 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t$_R$(major) = 18.5 min, t$_R$(minor) = 19.9 min, ee = 99%.

Figure S259, the HPLC spectrum of compound 3b, related to Table 2
3c: Procedure A, 71 mg, colorless liquid, 74% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.31–7.19 (m, 4H), 6.75 (ddt, $J = 22.0$, 17.1, 7.0 Hz, 1H), 5.65 (dd, $J = 21.1$, 17.1 Hz, 1H), 4.80 (t, $J = 7.4$ Hz, 1H), 4.06–3.89 (m, 4H), 3.78 (d, $J = 3.2$ Hz, 1H), 2.73–2.51 (m, 2H), 1.26 (td, $J = 7.1$, 2.7 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.49 (d, $J = 5.0$ Hz), 142.37, 133.11, 128.48, 127.19, 119.63 (d, $J = 186.6$ Hz), 71.81 (d, $J = 1.3$ Hz), 61.73 (d, $J = 5.5$ Hz), 43.93 (d, $J = 22.1$ Hz), 16.24 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.83 ppm.

MS(ESI) m/z [M+H]$^+$: 319.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 319.0860, found 319.0863.

IR (film): 3354, 2988, 1632, 1260, 1027, 750 cm$^{-1}$.

Optical rotation: [α]$^D_{28} = +18.26$ (c = 2.470, CHCl$_3$, 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t$_R$(major) = 18.5 min, t$_R$(minor) = 19.9 min, ee = 99%.

Figure S260, the HPLC spectrum of compound 3c, related to Table 2
3d: Procedure A, 84 mg, colorless liquid, 77% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.46 (d, $J = 8.4$ Hz, 2H), 7.23 (d, $J = 8.4$ Hz, 2H), 6.76 (ddt, $J = 22.0$, 17.1, 7.0 Hz, 1H), 5.66 (dd, $J = 21.0$, 17.1 Hz, 1H), 4.80 (t, $J = 6.3$ Hz, 1H), 4.03–3.84 (m, 4H), 3.43 (s, 1H), 2.72–2.54 (m, 2H), 1.27 (td, $J = 7.1$, 2.9 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.28 (d, $J = 5.2$ Hz), 142.76, 131.48, 127.52, 121.32, 119.84 (d, $J = 186.5$ Hz), 71.93 (d, $J = 1.2$ Hz), 61.74 (d, $J = 5.5$ Hz), 43.87 (d, $J = 22.0$ Hz), 16.27 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.75 ppm.

MS(ESI) m/z [M+H]$^+$: 363.00.
HRMS(ESI) m/z [M+H]$^+$: calcd. 363.0353, found 363.0353.
IR (film): 3352, 2988, 1630, 1260, 1027, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = +16.74$ (c = 1.450, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 19.4 min, $t_R$(minor) = 20.8 min, ee = 98%.

Figure S261, the HPLC spectrum of compound 3d, related to Table 2
3e: Procedure A, 113 mg, colorless liquid, 92% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.10 (d, $J = 8.2$ Hz, 2H), 6.75 (ddt, $J = 22.1$, 17.1, 7.0 Hz, 1H), 5.66 (dd, $J = 20.9$, 17.1 Hz, 1H), 4.79 (t, $J = 6.2$ Hz, 1H), 4.05–3.86 (m, 4H), 3.33 (s, 1H), 2.79–2.21 (m, 2H), 1.27 (td, $J = 7.1$, 2.8 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.27 (d, $J = 5.0$ Hz), 143.42, 137.46, 127.78, 119.86 (d, $J = 186.4$ Hz), 92.91, 72.02 (d, $J = 1.3$ Hz), 61.75 (d, $J = 5.4$ Hz), 43.85 (d, $J = 22.0$ Hz), 16.30 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.77 ppm.

MS(ESI) m/z [M+H]$^+$: 411.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 411.0217, found 411.0215.

IR (film): 3354, 2986, 1634, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = +16.00$ (c = 2.60, CHCl$_3$, 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 39/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, t$_R$(major) = 64.7 min, t$_R$(minor) = 70.9 min, ee = 99%.

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**Figure S262**, the HPLC spectrum of compound 3e, related to **Table 2**
**3f:** Procedure A, 72 mg, colorless liquid, 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (d, $J = 8.0$ Hz, 2H), 7.14 (d, $J = 8.0$ Hz, 2H), 6.74 (ddt, $J = 22.0$, 17.1, 7.0 Hz, 1H), 5.66 (dd, $J = 21.2$, 17.1 Hz, 1H), 4.77 (t, $J = 7.9$ Hz, 1H), 4.05–3.86 (m, 4H), 3.05 (d, $J = 3.4$ Hz, 1H), 2.80–2.51 (m, 2H), 2.33 (s, 3H), 1.26 (q, $J = 6.9$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.79 (d, $J = 4.9$ Hz), 140.69, 137.28, 129.09, 125.72, 119.41 (d, $J = 186.3$ Hz), 72.51 (d, $J = 1.2$ Hz), 61.64 (d, $J = 5.4$ Hz), 43.87 (d, $J = 21.9$ Hz), 21.06, 16.26 (d, $J = 6.6$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.01 ppm.

MS(ESI) m/z [M+H]$^+$: 341.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 341.1876, found 341.1879.

IR (film): 3371, 2985, 1635, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $\lbrack \alpha \rbrack_D^{27} = +15.25$ (c = 1.510, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 19.5 min, $t_R$(minor) = 23.9 min, ee = 98%.

### Table 2

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 18.865    | 49.578|
| 2     | 22.829    | 50.422|

**Figure S263,** the HPLC spectrum of compound 3f, related to Table 2
3g: Procedure A, 92 mg, colorless liquid, 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.35 (d, $J = 8.3$ Hz, 2H), 7.27 (d, $J = 8.3$ Hz, 2H), 6.77 (ddt, $J = 22.1$, 17.1, 6.9 Hz, 1H), 5.69 (dd, $J = 21.3$, 17.1 Hz, 1H), 4.79 (dd, $J = 7.3$, 5.6 Hz, 1H), 4.08–3.89 (m, 4H), 3.10 (s, 1H), 2.83–2.53 (m, 2H), 1.40–1.15 (m, 15H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 150.52, 149.98 (d, $J = 5.1$ Hz), 140.66, 125.52, 125.30, 119.26 (d, $J = 186.3$ Hz), 72.39, 61.65 (d, $J = 5.5$Hz), 43.77 (d, $J = 22.0$ Hz), 34.46, 31.31, 16.27 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.09 ppm.

MS(ESI) m/z [M+H]$^+$: 299.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 299.1407, found 299.1405.

IR (film): 3366, 2963, 1635, 1230, 1027, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +16.03$ (c = 3.325, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 37/3, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 23.6 min, $t_R$(minor) = 25.7 min, ee = > 99%.

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**Figure S264**, the HPLC spectrum of compound 3g, related to **Table 2**
3h: Procedure A, 84 mg, colorless liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.27 (d, J = 7.6 Hz, 2H), 7.22 (d, J = 8.4 Hz, 2H), 6.75 (ddt, J = 22.0, 17.1, 7.0 Hz, 1H), 5.67 (dd, J = 21.1, 17.1 Hz, 1H), 4.79 (t, J = 7.4 Hz, 1H), 4.20–3.66 (m, 4H), 3.09 (d, J = 3.1 Hz, 1H), 2.74–2.54 (m, 2H), 2.47 (s, 3H), 1.27 (td, J = 7.0, 5.0 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.52 (d, J = 5.2 Hz), 140.54, 137.75, 126.59, 126.33, 119.65 (d, J = 186.3 Hz), 72.26 (d, J = 1.4 Hz), 61.70 (d, J = 5.5 Hz), 43.82 (d, J = 22.0 Hz), 16.28 (d, J = 6.0 Hz), 15.83 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.88 ppm.

MS(ESI) m/z [M+H]+: 331.10.

HRMS(ESI) m/z [M+H]+: calcd. 331.1127, found 331.1126.

IR (film): 3366, 2988, 1635, 1260, 1025, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +15.85$ (c = 1.485, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-ProOH = 15/1, flow rate: 0.8 mL/min, λ = 207 nm, t$_R$(major) = 27.6 min, t$_R$(minor) = 30.4 min, ee = > 99%.

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**Figure S265**, the HPLC spectrum of compound 3h, related to Table 2
3i: Procedure A, 76 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.26 (d, $J = 8.7$ Hz, 2H), 6.87 (d, $J = 8.6$ Hz, 2H), 6.74 (ddt, $J = 22.0, 17.1, 7.0$ Hz, 1H), 5.68 (dd, $J = 21.1, 17.1$ Hz, 1H), 4.77 (t, $J = 7.9$ Hz, 1H), 4.17–3.86 (m, 4H), 3.79 (s, 3H), 2.79 (d, $J = 3.3$ Hz, 1H), 2.75–2.53 (m, 2H), 1.27 (q, $J = 7.0$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 159.11, 149.66 (d, $J = 5.1$ Hz), 135.73, 127.02, 119.53 (d, $J = 186.5$ Hz), 113.82, 72.34 (d, $J = 1.2$ Hz), 61.66 (d, $J = 5.4$ Hz), 55.25, 43.82 (d, $J = 21.9$ Hz), 16.27 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.95 ppm.

MS(ESI) $m/z$ [M+H]$^+$: 315.10.

HRMS(ESI) $m/z$ [M+H]$^+$: calcd. 315.1356, found 315.1355.

IR (film): 3368, 2988, 1612, 1260, 1028, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = +16.00$ (c = 1.600, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 29.2 min, $t_R$(minor) = 33.3 min, ee = 97%.

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**Figure S266**, the HPLC spectrum of compound 3i, related to Table 2
**Figure S267**, the HPLC spectrum of compound 3j, related to Table 2.
3k: Procedure A, 82 mg, colorless liquid, 90% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.52 (t, $J = 6.9$ Hz, 1H), 7.27–7.18 (m, 1H), 7.14 (t, $J = 7.4$ Hz, 1H), 7.05–6.95 (m, 1H), 6.81 (ddt, $J = 24.0$, 17.1, 6.9 Hz, 1H), 5.68 (dd, $J = 21.2$, 17.1 Hz, 1H), 5.16 (dd, $J = 10.7$, 5.6 Hz, 1H), 4.05–3.85 (m, 4H), 3.78 (d, $J = 4.3$ Hz, 1H), 2.78–2.58 (m, 2H), 1.25 (q, $J = 7.0$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 159.39 (d, $J = 245.2$ Hz), 149.63 (d, $J = 5.0$ Hz), 130.88 (d, $J = 13.4$ Hz), 128.79 (d, $J = 8.2$ Hz), 127.29 (d, $J = 4.4$ Hz), 124.23 (d, $J = 3.4$ Hz), 119.43 (d, $J = 186.4$ Hz), 115.06 (d, $J = 21.7$ Hz), 66.33, 61.69 (d, $J = 5.5$Hz), 42.72 (d, $J = 22.1$ Hz), 16.23 (d, $J = 6.5$ Hz) ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) δ -119.42~-119.56 (m) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.97 ppm.

MS(ESI) m/z [M+H]$^+$: 303.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 303.1156, found 303.1155.

IR (film): 3353, 2986, 1634, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: [α]$_D^{28} = +23.86$ (c = 2.480, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, $t_R$(major) = 12.7 min, $t_R$(minor) = 16.7 min, ee = 98%.

**Figure S268**, the HPLC spectrum of compound 3k, related to Table 2
3l: Procedure A, 96 mg, colorless liquid, 91% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.84 (d, \(J = 7.8\) Hz, 1H), 7.59 (dd, \(J = 14.9, 7.7\) Hz, 2H), 7.36 (t, \(J = 7.6\) Hz, 1H), 6.88 (ddt, \(J = 22.0, 17.1, 6.9\) Hz, 1H), 5.71 (dd, \(J = 21.1, 17.1\) Hz, 1H), 5.34–5.14 (m, 1H), 4.05–3.94 (m, 4H), 3.91 (d, \(J = 3.3\) Hz, 1H), 2.69–2.49 (m, 2H), 1.28 (td, \(J = 7.1, 2.3\) Hz, 6H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.81 (d, \(J = 5.0\) Hz), 143.29, 132.23, 127.63, 127.39, 126.42 (q, \(J = 30.6\) Hz), 125.32 (q, \(J = 5.9\) Hz), 124.30 (q, \(J = 273.9\) Hz), 119.39 (d, \(J = 186.8\) Hz), 67.86, 61.70 (d, \(J = 5.5\) Hz), 44.13 (d, \(J = 22.4\) Hz), 16.22 (d, \(J = 6.5\) Hz) ppm.

\(^{19}\)F NMR (376 MHz, CDCl\(_3\)) \(\delta\) -58.23 ppm.

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 19.97 ppm.

MS(ESI) \(m/z\) [M+Na]\(^+\): 375.10.

HRMS(ESI) \(m/z\) [M+H]\(^+\): calcd. 353.1124, found 353.1122.

IR (film): 3342, 2985, 1632, 1259, 1056, 750 cm\(^{-1}\).

Optical rotation: \([\alpha]_D^{28} = +28.63\) (c = 2.655, CHCl\(_3\), 95% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProH = 7/1, flow rate: 0.8 mL/min, \(\lambda = 207\) nm, \(t_R\) (major) = 9.5 min, \(t_R\) (minor) = 13.9 min, ee = 95%.

**Figure S269**, the HPLC spectrum of compound 3l, related to **Table 2**
3m: Procedure A, 86 mg, colorless liquid, 91% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.34 (dd, $J = 7.5, 1.4$ Hz, 1H), 7.29–7.21 (m, 1H), 6.95 (t, $J = 7.4$ Hz, 1H), 6.87 (d, $J = 8.2$ Hz, 1H), 6.85–6.71 (m, 1H), 5.69 (dd, $J = 21.4, 17.2$ Hz, 1H), 5.06 (dd, $J = 12.4, 6.0$ Hz, 1H), 4.10–3.90 (m, 4H), 3.84 (s, 3H), 3.05 (d, $J = 5.8$ Hz, 1H), 2.72–2.67 (m, 2H), 1.28 (td, $J = 7.1, 4.2$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 156.17, 150.25 (d, $J = 4.8$ Hz), 131.30, 128.49, 126.68, 120.72, 118.96 (d, $J = 186.4$ Hz), 110.35, 68.94 (d, $J = 1.1$ Hz), 61.59 (d, $J = 5.4$ Hz), 55.21, 42.08 (d, $J = 21.9$ Hz), 16.29 (d, $J = 6.6$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.20 ppm.

MS(ESI) m/z [M+Na]$^+$: 337.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 315.1356, found 315.1354.

IR (film): 3365, 2982, 1632, 1239, 1026, 756 cm$^{-1}$.

Optical rotation: [$\alpha$]$^D_{27}$ = +22.46 (c = 2.095, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK I, hexane/i-ProOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 27.3 min, $t_R$(minor) = 34.0 min, ee = 98%.

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**Figure S270**, the HPLC spectrum of compound 3m, related to Table 2
3n: Procedure A, 77 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.36 (s, 1H), 7.29–7.18 (m, 3H), 6.76 (ddt, $J = 22.0, 17.1, 7.0$ Hz, 1H), 5.66 (dd, $J = 21.1, 17.1$ Hz, 1H), 4.87–4.69 (m, 1H), 4.07–3.90 (m, 5H), 2.73–2.53 (m, 2H), 1.27 (td, $J = 7.1, 3.0$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.54 (d, $J = 4.9$ Hz), 146.12, 134.21, 129.65, 127.49, 125.97, 123.95, 119.53 (d, $J = 186.6$ Hz), 71.78 (d, $J = 1.0$ Hz), 61.78 (d, $J = 5.4$ Hz), 43.88 (d, $J = 22.1$ Hz), 16.23 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.89 ppm.

MS(ESI) m/z [M+H]$^+$: 319.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 319.0860, found 319.0863.

IR (film): 3346, 2984, 1635, 1259, 1027, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +18.19$ (c = 2.420, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, t$_R$(major) = 14.8 min, t$_R$(minor) = 18.4 min, ee = 98%.

**Figure S271**, the HPLC spectrum of compound 3n, related to Table 2
**3o**: Procedure A, 96 mg, colorless liquid, 88% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (s, 1H), 7.38 (d, $J$ = 7.8 Hz, 1H), 7.27 (d, $J$ = 7.1 Hz, 1H), 7.20 (t, $J$ = 7.7 Hz, 1H), 6.77 (ddt, $J$ = 22.0, 17.1, 7.0 Hz, 1H), 5.67 (dd, $J$ = 21.1, 17.1 Hz, 1H), 4.80 (t, $J$ = 7.9 Hz, 1H), 4.07–3.90 (m, 4H), 3.82 (d, $J$ = 3.7 Hz, 1H), 2.74–2.49 (m, 2H), 1.27 (td, $J$ = 7.1, 3.1 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.37 (d, $J$ = 5.1 Hz), 146.30, 130.51, 129.99, 128.89, 124.42, 122.52, 119.71 (d, $J$ = 186.5 Hz), 71.81 (d, $J$ = 1.3 Hz), 61.78 (d, $J$ = 5.5 Hz), 43.90 (d, $J$ = 22.1 Hz), 16.28 (d, $J$ = 6.5 Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.83 ppm.

MS(ESI) m/z [M+H]$^+$: 363.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 363.0355, found 363.0353.

IR (film): 3352, 2986, 1630, 1260, 1027, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28}$ = +14.69 (c = 2.265, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 15.8 min, $t_R$(minor) = 20.3 min, ee = 97%.

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**Figure S272**, the HPLC spectrum of compound 3o, related to Table 2
3p: Procedure A, 94 mg, pale yellow liquid, 94% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.03 (d, \(J = 8.1\) Hz, 1H), 7.89–7.79 (m, 1H), 7.76 (d, \(J = 8.2\) Hz, 1H), 7.68 (d, \(J = 7.1\) Hz, 1H), 7.56–7.42 (m, 3H), 6.89 (ddt, \(J = 22.0, 17.1, 6.9\) Hz, 1H), 5.69 (dd, \(J = 21.1, 17.1\) Hz, 1H), 5.62–5.56 (m, 1H), 4.05–3.77 (m, 4H), 3.21 (d, \(J = 3.4\) Hz, 1H), 2.91–2.58 (m, 2H), 1.24 (dt, \(J = 12.9, 7.1\) Hz, 6H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.95 (d, \(J = 5.0\) Hz), 139.28, 133.72, 130.04, 128.95, 128.05, 126.13, 125.55, 125.42, 123.00, 122.80, 119.34 (d, \(J = 186.5\) Hz), 69.39, 61.68 (d, \(J = 7.1\) Hz), 43.01 (d, \(J = 22.0\) Hz), 16.26 (d, \(J = 6.5\) Hz) ppm.

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 18.02 ppm.

MS(ESI) m/z [M+H]: 335.15.

HRMS(ESI) m/z [M+H]: calcd. 335.1407, found 335.1406.

IR (film): 3356, 2983, 1635, 1259, 1026, 750 cm\(^{-1}\).

Optical rotation: \([\alpha]_D^{29} = +38.34\) (c = 1.620, CHCl\(_3\), 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProH = 7/1, flow rate: 0.8 mL/min, \(\lambda = 207\) nm, \(t_R\) (major) = 22.2 min, \(t_R\) (minor) = 24.6 min, ee = 99%.

**Figure S273**, the HPLC spectrum of compound 3p, related to Table 2
3q: Procedure A, 70 mg, colorless liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.35 (d, $J = 1.0$ Hz, 1H), 6.76 (ddt, $J = 22.1, 17.2, 6.9$ Hz, 1H), 6.31 (dd, $J = 3.1, 1.8$ Hz, 1H), 6.25 (d, $J = 3.2$ Hz, 1H), 5.73 (dd, $J = 21.0, 17.2$ Hz, 1H), 4.83 (t, $J = 6.6$ Hz, 1H), 4.14–3.88 (m, 4H), 3.73 (s, 1H), 2.77 (t, $J = 6.7$ Hz, 2H), 1.28 (td, $J = 7.1, 1.4$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 155.87, 149.22 (d, $J = 5.1$ Hz), 141.84, 119.45 (d, $J = 186.7$ Hz), 110.09, 106.16, 66.01 (d, $J = 1.2$ Hz), 61.75 (d, $J = 5.6$ Hz), 40.39 (d, $J = 22.3$ Hz), 16.23 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.96 ppm.

MS(ESI) m/z [M+H]$^+$: 275.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 275.1043, found 275.1045.

IR (film): 3361, 2985, 1635, 1226, 1020, 750 cm$^{-1}$.

Optical rotation: [$\alpha$]$^D_{29} = +9.75$ (c = 3.005, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 37/3, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 34.0 min, $t_R$(minor) = 39.4 min, ee = > 99%.

**Figure S274**, the HPLC spectrum of compound 3q, related to Table 2
3r: Procedure A, 79 mg, colorless liquid, 91% yield. 

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.22 (dd, $J = 4.8, 1.2$ Hz, 1H), 6.94 (dd, $J = 7.9, 3.0$ Hz, 2H), 6.76 (ddt, $J = 22.1, 17.1, 6.9$ Hz, 1H), 5.71 (dd, $J = 21.1, 17.1$ Hz, 1H), 5.06 (t, $J = 6.4$ Hz, 1H), 4.22–3.70 (m, 5H), 2.91–2.59 (m, 2H), 1.27 (td, $J = 7.1, 3.9$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.34 (d, $J = 5.3$ Hz), 147.97, 126.54, 124.42, 123.59, 119.53 (d, $J = 186.4$ Hz), 68.40, 61.75 (d, $J = 5.4$ Hz), 44.02 (d, $J = 22.1$ Hz), 16.24 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.94 ppm.

MS(ESI) m/z [M+H]$^+$: 291.05. 
HRMS(ESI) m/z [M+H]$^+$: calcd. 291.0814, found 291.0813. 
IR (film): 3342, 2984, 1634, 1259, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +9.24$ (c = 2.640, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 18.3 min, $t_R$(minor) = 20.3 min, ee = > 99%.

Figure S275, the HPLC spectrum of compound 3r, related to Table 2.
3s: Procedure A, 63 mg, colorless liquid, 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.43–7.34 (m, 2H), 6.77 (ddt, $J = 22.0$, 17.2, 6.9 Hz, 1H), 6.40 (s, 1H), 5.81–5.68 (m, 1H), 4.82 (t, $J = 5.2$ Hz, 1H), 4.17–3.89 (m, 4H), 2.88 (d, $J = 2.5$ Hz, 1H), 2.76–2.57 (m, 2H), 1.30 (td, $J = 7.1$, 1.6 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.22 (d, $J = 5.2$ Hz), 143.39, 139.07, 128.25, 119.88 (d, $J = 186.6$ Hz), 108.37, 65.37 (d, $J = 1.4$ Hz), 61.71 (d, $J = 5.4$ Hz), 42.62 (d, $J = 22.1$ Hz), 16.28 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.97 ppm.

MS(ESI) m/z [M+H]$^+$: 275.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 275.1043, found 275.1041.

IR (film): 3368, 2989, 1631, 1260, 1027, 750 cm$^{-1}$.

Optical rotation: [α]$_{D}^{27}$ = +10.84 (c = 1.070, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 21.1 min, $t_R$(minor) = 25.1 min, ee = 98%.

Figure S276, the HPLC spectrum of compound 3s, related to Table 2.
3t: Procedure A, 47 mg, colorless liquid, 55% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.57 (s, 1H), 8.47 (d, $J = 3.4$ Hz, 1H), 7.74 (d, $J = 7.8$ Hz, 1H), 7.29 (t, $J = 6.2$ Hz, 1H), 6.81 (ddt, $J = 24.1$, 17.1, 6.9 Hz, 1H), 5.71 (dd, $J = 20.9$, 17.1 Hz, 1H), 4.90 (dd, $J = 7.4$, 5.3 Hz, 1H), 4.13–3.81 (m, 4H), 2.75–2.53 (m, 2H), 1.27 (t, $J = 7.1$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.17 (d, $J = 4.3$ Hz), 148.59, 147.55, 139.53, 133.73, 123.46, 120.00 (d, $J = 186.8$ Hz), 70.13, 61.77 (d, $J = 5.7$ Hz), 43.81 (d, $J = 22.1$ Hz), 16.25 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.62 ppm.

MS(ESI) m/z [M+Na]$^+$: 308.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 286.1203, found 286.1203.

IR (film): 3355, 2983, 1634, 1229, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +34.45$ (c = 4.000, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, tR(major) = 49.9 min, tR(minor) = 56.1 min, ee = > 99%.

**Figure S277**, the HPLC spectrum of compound 3t, related to Table 2.
3u: Procedure A, 87 mg, pale yellow liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.87–7.78 (m, 2H), 7.48–7.28 (m, 3H), 6.85 (ddt, $J = 22.0$, 17.1, 6.9 Hz, 1H), 5.69 (dd, $J = 21.0$, 17.1 Hz, 1H), 5.32–5.07 (m, 1H), 4.03–3.85 (m, 4H), 3.49 (d, $J = 3.9$ Hz, 1H), 2.93–2.66 (m, 2H), 1.30–1.18 (m, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.57 (d, $J = 4.9$ Hz), 140.92, 138.75, 136.93, 124.43, 124.07, 122.94, 122.51, 122.06, 119.56 (d, $J = 186.5$ Hz), 68.17 (d, $J = 1.3$ Hz), 61.72 (d, $J = 6.1$ Hz), 42.05 (d, $J = 22.1$ Hz), 16.27 (d, $J = 6.6$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.89 ppm.

MS(ESI) m/z [M+H]$^+$: 341.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 341.0971, found 341.0972.

IR (film): 3351, 2988, 1630, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $\left[\alpha\right]_D^{28} = +32.45$ (c = 1.465, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 21.2 min, $t_R$(minor) = 23.3 min, ee = > 99%.

Figure S278, the HPLC spectrum of compound 3u, related to Table 2
3v: Procedure A, 79 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.49 (d, $J$ = 7.4 Hz, 1H), 7.42 (d, $J$ = 8.0 Hz, 1H), 7.31–7.09 (m, 2H), 6.82 (ddt, $J$ = 24.0, 17.1, 6.9 Hz, 1H), 6.63 (s, 1H), 5.73 (dd, $J$ = 20.9, 17.1 Hz, 1H), 4.96 (t, $J$ = 6.2 Hz, 1H), 4.39 (s, 1H), 4.05–3.79 (m, 4H), 3.00–2.64 (m, 2H), 1.19 (td, $J$ = 7.0, 1.2 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.66 (d, $J$ = 5.4 Hz), 154.70, 149.02, 128.08, 124.08, 122.75, 120.99, 119.75 (d, $J$ = 181.9 Hz), 111.11, 102.88, 66.58, 61.78 (d, $J$ = 5.4 Hz), 40.45 (d, $J$ = 22.4 Hz), 16.17 (d, $J$ = 6.5 Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.85 ppm.

MS(ESI) m/z [M+H]$^+$: 325.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 325.1199, found 325.1200.

IR (film): 3341, 2988, 1632, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +16.59$ (c = 2.590, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 7/1, flow rate: 0.8 mL/min, $\lambda$ = 254 nm, $t_R$(major) = 19.1 min, $t_R$(minor) = 20.3 min, ee = 97%.

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 19.218    | 49.751|
| 2     | 20.346    | 50.249|

Figure S279, the HPLC spectrum of compound 3v, related to Table 2
3w: Procedure A, 92 mg, colorless liquid, 90% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.78 (d, \(J = 7.6\) Hz, 1H), 7.67 (d, \(J = 7.2\) Hz, 1H), 7.36–7.23 (m, 2H), 7.15 (s, 1H), 6.79 (ddt, \(J = 24.0, 17.1, 6.9\) Hz, 1H), 5.70 (dd, \(J = 21.0, 17.1\) Hz, 1H), 5.12 (t, \(J = 6.3\) Hz, 1H), 4.21 (s, 1H), 4.01–3.75 (m, 4H), 2.87–2.67 (m, 2H), 1.23–1.11 (m, 6H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 148.87 (d, \(J = 4.9\) Hz), 148.44, 139.39, 139.26, 124.27, 124.16, 123.43, 122.39, 120.18, 119.98 (d, \(J = 186.0\) Hz), 69.05, 61.77 (d, \(J = 5.2\) Hz), 43.67 (d, \(J = 22.3\) Hz), 16.17 (dd, \(J = 6.5, 3.6\) Hz) ppm.

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 17.78 ppm.

MS(ESI) m/z [M+H]+: 341.05.

HRMS(ESI) m/z [M+H]+: calcd. 341.0971, found 341.0972.

IR (film): 3336, 2988, 1635, 1260, 1026, 750 cm\(^{-1}\).

Optical rotation: \([\alpha]_D^{29} = +11.64\) (c = 1.760, CHCl\(_3\), > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, \(\lambda = 207\) nm, \(t_R\) (major) = 60.1 min, \(t_R\) (minor) = 64.5 min, ee = > 99%.

**Figure S280**, the HPLC spectrum of compound 3w, related to Table 2.
Figure S281, the HPLC spectrum of compound 3x, related to Table 2
3y: Procedure A, 71 mg, colorless liquid, 76% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42–7.17 (m, 5H), 6.82 (ddt, \(J = 22.0, 17.1, 7.0\) Hz, 1H), 6.60 (d, \(J = 15.9\) Hz, 1H), 6.21 (dd, \(J = 15.9, 6.6\) Hz, 1H), 5.77 (dd, \(J = 21.0, 17.1\) Hz, 1H), 4.55–4.35 (m, 1H), 4.11–3.92 (m, 4H), 2.69 (s, 1H), 2.66–2.46 (m, 2H), 1.27 (q, \(J = 7.1\) Hz, 6H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 149.33 (d, \(J = 5.1\) Hz), 136.33, 131.12, 130.78, 128.55, 127.78, 126.46, 119.82 (d, \(J = 186.4\) Hz), 71.16 (d, \(J = 1.2\) Hz), 61.74 (d, \(J = 5.3\) Hz), 42.18 (d, \(J = 22.0\) Hz), 16.27 (d, \(J = 6.6\) Hz) ppm.

\(^{31}\)P NMR (162 MHz, CDCl\(_3\)) \(\delta\) 17.89 ppm.

MS(ESI) \(m/z\) [M+Na]: 333.10.

HRMS(ESI) \(m/z\) [M+H]: calcd. 311.1407, found 311.1405.

IR (film): 3361, 2983, 1631, 1228, 1027, 750 cm\(^{-1}\).

Optical rotation: \([\alpha]\)^{28}_D = +1.10 (c = 1.150, CHCl\(_3\), 97% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, \(\lambda = 207\) nm, \(t_R\) (major) = 23.4 min, \(t_R\) (minor) = 25.6 min, ee = 97%.

**Figure S282**, the HPLC spectrum of compound 3y, related to Table 2.
3z: Procedure A, 76 mg, colorless liquid, 78% yield.

$^{1}$H NMR (400 MHz, CDCl$_3$) δ 7.32 (t, J = 7.5 Hz, 2H), 7.28–7.18 (m, 3H), 6.80 (ddt, J = 21.9, 17.1, 7.0 Hz, 1H), 6.52 (s, 1H), 5.77 (dd, J = 21.0, 17.1 Hz, 1H), 4.43–4.23 (m, 1H), 4.12–3.93 (m, 4H), 2.68–2.49 (m, 2H), 2.38 (d, J = 3.2 Hz, 1H), 1.88 (s, 3H), 1.28 (q, J = 7.2 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.58 (d, J = 4.9 Hz), 139.07, 137.15, 128.92, 128.10, 126.57, 126.19, 119.43 (d, J = 186.7 Hz), 76.11 (d, J = 1.2 Hz), 61.71 (d, J = 5.4 Hz), 40.13 (d, J = 22.0 Hz), 16.29 (d, J = 6.5 Hz), 13.49 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.90 ppm.

MS(ESI) m/z [M+Na]$^+$: 347.15.

HRMS(ESI) m/z [M+H]$^+$: calcld. 325.1562, found 325.1562.

IR (film): 3366, 2985, 1634, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{27}$ = -11.16 (c = 1.260, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IA, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 19.6 min, $t_R$(minor) = 22.4 min, ee = 98%.

Figure S283, the HPLC spectrum of compound 3z, related to Table 2.
3aa: Procedure A, 81 mg, colorless liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.19–7.13 (m, 1H), 6.98–6.93 (m, 2H), 6.89–6.68 (m, 2H), 6.05 (dd, $J$ = 15.7, 6.4 Hz, 1H), 5.77 (dd, $J$ = 21.0, 17.2 Hz, 1H), 4.51–4.31 (m, 1H), 4.10–3.98 (m, 4H), 2.65–2.45 (m, 2H), 2.34–2.10 (br, 1H), 1.29 (m, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.28 (d, $J$ = 4.8 Hz), 141.44, 130.61, 127.36, 126.09, 124.48, 123.97, 119.85 (d, $J$ = 186.4 Hz), 70.81 (d, $J$ = 1.2 Hz), 61.80 (d, $J$ = 5.4 Hz), 42.10 (d, $J$ = 22.0 Hz), 16.27 (d, $J$ = 6.5 Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.89 ppm.

MS(ESI) $m/z$ [M+H]$^+$: 317.05.

HRMS(ESI) $m/z$ [M+H]$^+$: calcld. 317.0971, found 317.0970.

IR (film): 3358, 2986, 1631, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +3.05$ (c = 0.680, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda$ = 254 nm, $t_R$ (major) = 22.6 min, $t_R$ (minor) = 27.4 min, ee = 98%.

Figure S284, the HPLC spectrum of compound 3aa, related to Table 2
3ab: Procedure A, 48 mg, colorless liquid, 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.78 (ddt, J = 22.0, 17.1, 7.0 Hz, 1H), 5.93–5.82 (m, 1H), 5.81–5.67 (m, 1H), 5.27 (d, J = 17.2 Hz, 1H), 5.15 (d, J = 10.4 Hz, 1H), 4.27 (q, J = 6.1 Hz, 1H), 4.17–3.97 (m, 4H), 2.64 (s, 1H), 2.58–2.38 (m, 2H), 1.32 (t, J = 7.1 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.33 (d, J = 5.0 Hz), 139.90, 119.66 (d, J = 186.9 Hz), 115.28, 71.22 (d, J = 1.2 Hz), 61.72 (d, J = 5.3 Hz), 41.78 (d, J = 22.0 Hz), 16.30 (d, J = 6.4 Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.96 ppm.

MS(ESI) m/z [M+Na]$^+$: 257.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 235.1094, found 235.1094.

IR (film): 3379, 2985, 1633, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = +2.52$ (c = 1.060, CHCl$_3$, 93% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, λ = 207 nm, t$_R$(major) = 13.7 min, t$_R$(minor) = 14.9 min, ee = 93%.

**Figure S285**, the HPLC spectrum of compound 3ab, related to Table 2
3ac: Procedure A, 48 mg, colorless liquid, 58% yield, E/Z = 6/1 (2ac was used as a mixture (E/Z = 6/1)).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.76 (ddt, $J$ = 21.9, 17.1, 7.0 Hz, 1H), 6.19 (dd, $J$ = 15.2, 10.4 Hz, 1H), 6.07–5.90 (m, 1H), 5.82–5.62 (m, 2H), 5.55 (dd, $J$ = 15.2, 6.8 Hz, 1H), 4.28 (q, $J$ = 6.4 Hz, 1H), 4.11–3.98 (m, 4H), 2.56 (s, 1H), 2.51–2.43 (m, 2H), 1.75 (d, $J$ = 7.0 Hz, 3H), 1.42–1.20 (m, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.56 (d, $J$ = 5.0 Hz), 131.88, 131.26, 130.53, 130.34, 119.46 (d, $J$ = 186.6 Hz), 70.87 (d, $J$ = 1.3 Hz), 61.71 (d, $J$ = 5.5 Hz), 42.15 (d, $J$ = 21.9 Hz), 18.05, 16.28 (d, $J$ = 6.5 Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.06 ppm.

MS(ESI) m/z [M+Na]$^+$: 297.10.

HRMS(ESI) m/z [M+H]$^+$: calc. 275.1407, found 275.1407.

IR (film): 3363, 2962, 1634, 1260, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{25}$ = +8.32 (c = 0.510, CHCl$_3$, 97% ee, E/Z = 6/1).

HPLC: DAICEL CHIRALPAK IC, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 16.8 min, $t_R$(minor) = 19.6 min, ee = 97%.

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Figure S286, the HPLC spectrum of compound 3ac, related to Table 2
3ad: Procedure A, 51 mg, colorless liquid, 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.76 (ddt, $J = 24.1, 17.1, 7.0$ Hz, 1H), 5.82–5.62 (m, 2H), 5.50 (dd, $J = 15.3, 5.9$ Hz, 1H), 4.21 (dd, $J = 12.8, 6.4$ Hz, 1H), 4.17–3.95 (m, 4H), 2.55–2.36 (m, 2H), 2.24 (s, 1H), 1.69 (d, $J = 6.3$ Hz, 3H), 1.32 (t, $J = 7.1$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.55 (d, $J = 4.5$ Hz), 132.95, 127.57, 119.50 (d, $J = 185.8$ Hz), 71.25, 61.69 (d, $J = 5.5$ Hz), 42.06 (d, $J = 21.9$ Hz), 17.61, 16.31 (d, $J = 6.4$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.02 ppm.

MS(ESI) m/z [M+H]$^+$: 249.10.

HRMS(ESI) m/z [M+H]$^+$: calcd. 249.1250, found 249.1251.

IR (film): 3386, 2985, 1633, 1259, 1020, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +5.38$ (c = 1.155, CHCl$_3$, 95% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 14.5 min, $t_R$(minor) = 15.9 min, ee = 95%.

![HPLC spectrum](image)

**Figure S287**, the HPLC spectrum of compound 3ad, related to **Table 2**
3ae: Procedure A, 59 mg, colorless liquid, 71% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.76 (ddt, $J = 24.1, 17.1, 7.0$ Hz, 1H), 5.83–5.61 (m, 2H), 5.48 (dd, $J = 15.4, 6.8$ Hz, 1H), 4.22 (q, $J = 6.4$ Hz, 1H), 4.17–3.96 (m, 4H), 2.52–2.41 (m, 2H), 2.32 (s, 1H), 2.10–1.89 (m, 2H), 1.45–1.33 (m, 2H), 1.32 (t, $J = 7.1$ Hz, 6H), 0.90 (t, $J = 7.4$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.59 (d, $J = 5.0$ Hz), 132.59, 131.81, 119.42 (d, $J = 187.0$ Hz), 71.24, 61.67 (d, $J = 5.2$ Hz), 42.17 (d, $J = 21.9$ Hz), 34.16, 22.17, 16.29 (d, $J = 6.5$ Hz), 13.61 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.03 ppm.

MS(ESI) m/z [M+H]$^+$: 277.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 277.1563, found 277.1563.

IR (film): 3384, 2960, 1635, 1230, 1098, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = +5.67$ (c = 1.510, CHCl$_3$, 93% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 12.8 min, $t_R$(minor) = 13.8 min, ee = 93%.

![HPLC spectrum of 3ae](image)

Figure S288, the HPLC spectrum of compound 3ae, related to Table 2
3af: Procedure A, 69 mg, colorless liquid, 71% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.76 (ddt, $J = 24.1, 17.1, 7.0$ Hz, 1H), 5.81–5.61 (m, 2H), 5.51 (dd, $J = 15.4, 6.6$ Hz, 1H), 4.22 (q, $J = 6.3$ Hz, 1H), 4.17–3.09 (m, 4H), 3.54 (t, $J = 6.6$ Hz, 2H), 2.46 (t, $J = 6.5$ Hz, 2H), 2.25 (s, 1H), 2.17–1.96 (m, 2H), 1.85–1.72 (m, 2H), 1.57–1.45 (m, 2H), 1.32 (t, $J = 7.1$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.41 (d, $J = 5.0$ Hz), 132.29, 131.79, 119.62 (d, $J = 187.1$ Hz), 71.10 (d, $J = 1.1$ Hz), 61.73 (d, $J = 5.4$ Hz), 44.83, 42.14 (d, $J = 22.0$ Hz), 31.94, 31.28, 26.20, 16.32 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.97 ppm.

MS(ESI) m/z [M+Na]$^+$: 347.05.

HRMS(ESI) m/z [M+H]+$^+$: calcld. 325.1330, found 325.1332.

IR (film): 3379, 2987, 1635, 1260, 1028, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = +5.66$ (c = 0.940, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 18.1 min, $t_R$(minor) = 20.0 min, ee = 97%.

**Figure S289**, the HPLC spectrum of compound 3af, related to **Table 2**.
3ag: Procedure A, 59 mg, colorless liquid, 47% yield.

1H NMR (400 MHz, CDCl3) δ 6.76 (ddt, $J = 24.1, 17.2, 7.0$ Hz, 1H), 5.81–5.61 (m, 2H), 5.48 (dd, $J = 15.4, 6.8$ Hz, 1H), 4.21 (q, $J = 6.4$ Hz, 1H), 4.17–3.96 (m, 4H), 3.60 (t, $J = 6.3$ Hz, 2H), 2.45 (t, $J = 6.4$ Hz, 2H), 2.22 (s, 1H), 2.14–1.96 (m, 2H), 1.57–1.47 (m, 2H), 1.46–1.36 (m, 2H), 1.32 (t, $J = 7.1$ Hz, 6H), 0.89 (s, 9H), 0.05 (s, 6H) ppm.

13C NMR (100 MHz, CDCl3) δ 149.55 (d, $J = 5.1$ Hz), 132.62, 131.80, 119.51 (d, $J = 186.9$ Hz), 71.23 (d, $J = 1.3$ Hz), 62.94, 61.70 (d, $J = 5.5$ Hz), 42.15 (d, $J = 21.9$ Hz), 32.26, 31.86, 29.66, 25.93, 25.29, 18.33, 16.31 (d, $J = 6.4$ Hz), -5.31 ppm.

31P NMR (162 MHz, CDCl3) δ 18.03 ppm.

MS(ESI) m/z [M+Na]+: 443.15.

HRMS(ESI) m/z [M+H]+: calcd. 421.2534, found 421.2534.

IR (film): 3381, 2930, 1633, 1255, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{27} = +3.45$ (c = 1.100, CHCl3, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 7/1, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 19.1 min, $t_R$(minor) = 20.9 min, ee = 98%.

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Figure S290, the HPLC spectrum of compound 3ag, related to Table 2
3ah: Procedure A, 91 mg, colorless liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.76 (ddt, $J$ = 22.1, 17.1, 7.0 Hz, 1H), 5.81–5.61 (m, 2H), 5.51 (dd, $J$ = 15.4, 6.7 Hz, 1H), 4.22 (q, $J$ = 6.4 Hz, 1H), 4.17–3.98 (m, 4H), 2.56–2.44 (m, 2H), 2.23–2.01 (m, 7H), 1.62–1.49 (m, 2H), 1.54–1.33 (m, 4H), 1.32 (t, $J$ = 7.1 Hz, 6H), 0.91 (t, $J$ = 7.1 Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.43, 132.29, 131.85 (d, $J$ = 2.6 Hz), 119.58 (d, $J$ = 187.0 Hz), 80.66, 79.47, 71.19, 61.71 (d, $J$ = 5.6 Hz), 42.11 (d, $J$ = 21.9 Hz), 31.18, 31.13, 28.42, 21.89, 18.38, 18.18, 16.32 (d, $J$ = 6.4 Hz), 13.59 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 17.97 ppm.

MS(ESI) m/z [M+H]$^+$: 357.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 357.2189, found 357.2191.

IR (film): 3379, 2932, 1634, 1275, 1027, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29}$ = +3.32 (c = 1.110, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 15/1, flow rate: 0.8 mL/min, $\lambda$ = 207 nm, $t_R$(major) = 28.5 min, $t_R$(minor) = 30.6 min, ee = 98%.

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**Figure S291**, the HPLC spectrum of compound 3ah, related to **Table 2**
3ai: Procedure A, 80 mg, colorless liquid, 68% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.76 (ddt, $J = 22.0, 17.1, 7.0$ Hz, 1H), 5.74 (dd, $J = 21.3, 17.1$ Hz, 1H), 5.21 (dd, $J = 8.6, 0.7$ Hz, 1H), 5.19–5.00 (m, 2H), 4.51 (dd, $J = 14.4, 6.7$ Hz, 1H), 4.17–4.00 (m, 4H), 2.55–2.33 (m, 2H), 2.28 (s, 1H), 2.13–1.93 (m, 8H), 1.68 (s, 6H), 1.60 (s, 6H), 1.32 (s, 6H, 7.1 Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.74 (d, $J = 4.7$ Hz), 139.24, 135.37, 131.29, 126.56, 124.21, 123.58, 119.31 (d, $J = 187.0$ Hz), 67.04 (d, $J = 1.0$ Hz), 61.66 (d, $J = 5.6$ Hz), 42.42 (d, $J = 21.7$ Hz), 39.62, 39.45, 26.66, 26.29, 25.64, 17.63, 16.68, 16.29 (d, $J = 6.5$ Hz), 15.96 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.11 ppm.

MS(ESI) m/z [M+Na]$^+$: 421.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 399.2659, found 399.2659.

IR (film): 3385, 2927, 1633, 1270, 1028, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{27} = +2.53$ (c = 2.675, CHCl$_3$, 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 37/3, flow rate: 0.8 mL/min, $\lambda = 207$ nm, $t_R$(major) = 19.3 min, $t_R$(minor) = 23.1 min, ee = 99%.

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**Figure S292**, the HPLC spectrum of compound 3ai, related to Table 2
3aj: Procedure A, 56 mg, colorless liquid, 52% yield, 15/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl₃) δ 6.77 (ddt, $J$ = 22.1, 17.1, 7.0 Hz, 1H), 5.80–5.60 (m, 2H), 5.48 (dd, $J$ = 15.3, 6.7 Hz, 1H), 5.09 (t, $J$ = 7.1 Hz, 1H), 4.32–4.16 (m, 1H), 4.17–3.95 (m, 4H), 2.56–2.40 (m, 2H), 2.40 (s, 1H), 2.11–1.81 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.45 (m, 1H), 1.40–1.23 (m, 7H), 1.22–1.07 (m, 1H), 0.87 (d, $J$ = 6.6 Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl₃) δ 149.58 (d, $J$ = 4.8 Hz), 132.97, 131.15, 124.64, 119.47 (d, $J$ = 187.1 Hz), 109.99, 71.20 (d, $J$ = 1.2 Hz), 61.69 (d, $J$ = 6.4 Hz), 42.21 (d, $J$ = 21.9 Hz), 39.48, 36.62, 32.43, 25.67, 25.48, 19.32, 17.61, 16.31 (d, $J$ = 6.4 Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl₃) δ 18.04 ppm.

MS(ESI) m/z [M+Na]$^+$: 381.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 359.2346, found 359.2346.

IR (film): 3381, 2912, 1633, 1231, 1028, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{28} = +6.51$ (c = 2.205, CHCl₃, 15/1 dr).
3aj': Procedure B, 65 mg, colorless liquid, 60% yield, > 20/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.77 (ddt, $J = 22.1, 17.1, 7.0$ Hz, 1H), 5.79–5.58 (m, 2H), 5.48 (dd, $J = 15.3, 6.8$ Hz, 1H), 5.09 (t, $J = 7.1$ Hz, 1H), 4.29–4.16 (m, 1H), 4.17–4.00 (m, 4H), 2.56–2.36 (m, 2H), 2.38 (s, 1H), 2.12–1.75 (m, 4H), 1.68 (s, 3H), 1.60 (s, 3H), 1.55–1.41 (m, 1H), 1.38–1.24 (m, 7H), 1.22–1.08 (m, 1H), 0.86 (d, $J = 6.6$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.56 (d, $J = 5.0$ Hz), 132.96, 131.30, 131.18, 124.64, 119.46 (d, $J = 187.1$ Hz), 71.27 (d, $J = 1.3$ Hz), 61.69 (d, $J = 5.2$ Hz), 42.22 (d, $J = 21.9$ Hz), 39.53, 36.67, 32.40, 25.67, 25.48, 19.30, 17.61, 16.31 (d, $J = 6.4$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.03 ppm.

MS(ESI) m/z [M+H]$^+$: 381.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 359.2346, found 359.2347.

IR (film): 3380, 2964, 1633, 1231, 1028 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = -5.73$ (c = 1.875, CHCl$_3$, > 20/1 dr).
3ak: Procedure A, 57 mg, colorless liquid, 58% yield, > 20/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.73 (ddt, $J = 24.1$, 17.1, 6.9 Hz, 1H), 5.83–5.64 (m, 2H), 4.71 (d, $J = 9.3$ Hz, 2H), 4.15 (t, $J = 6.6$ Hz, 1H), 4.12–4.00 (m, 4H), 2.57–2.35 (m, 2H), 2.30–1.91 (m, 5H), 1.91–1.82 (m, 1H), 1.73 (s, 3H), 1.55–1.37 (m, 1H), 1.38–1.21 (m, 7H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.92 (d, $J = 4.5$ Hz), 149.54, 138.71, 123.61, 119.09 (d, $J = 186.7$ Hz), 108.71, 74.40, 61.68 (d, $J = 5.4$ Hz), 41.19, 39.82 (d, $J = 21.9$ Hz), 30.39, 27.42, 23.81, 20.69, 16.32 (d, $J = 6.4$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.06 ppm.

MS(ESI) m/z [M+H]$^+$: 329.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 329.1876, found 329.1877.

IR (film): 3379, 2988, 1636, 1260, 1028, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = -25.80$ (c = 1.330, CHCl$_3$, > 20/1 dr).
3ak': Procedure B, 78 mg, colorless liquid, 79% yield, > 20/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) δ 6.74 (ddt, $J = 24.1, 7.0$ Hz, 1H), 5.82–5.65 (m, 2H), 4.71 (d, $J = 12.2$ Hz, 2H), 4.14 (t, $J = 6.2$ Hz, 1H), 4.16–4.00 (m, 4H), 2.59–2.39 (m, 3H), 2.21–2.05 (m, 3H), 2.02–1.90 (m, 1H), 1.89–1.75 (m, 1H), 1.73 (s, 3H), 1.56–1.49 (m, 1H), 1.36–1.20 (m, 7H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 150.03 (d, $J = 4.9$ Hz), 149.5, 138.49, 122.37, 119.08 (d, $J = 178.0$ Hz), 108.68, 74.10 (d, $J = 1.0$ Hz), 61.68 (d, $J = 5.4$ Hz), 41.05, 40.12 (d, $J = 22.0$ Hz), 30.27, 27.30, 24.50, 20.73, 16.31 (d, $J = 6.3$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 18.10 ppm.

MS(ESI) m/z [M+H$^+$]: 329.15.

HRMS(ESI) m/z [M+H$^+$]: calcd. 329.1876, found 329.1876.

IR (film): 3379, 2985, 1642, 1260, 1028, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = -38.08$ (c = 1.735, CHCl$_3$, > 20/1 dr).
3aI: Procedure A, 87 mg, colorless liquid, 88% yield, > 20/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 6.78 (ddt, $J = 23.9, 17.1, 6.8$ Hz, 1H), 5.74 (dd, $J = 21.1, 17.1$ Hz, 1H), 5.48 (s, 1H), 4.14 (t, $J = 6.0$ Hz, 1H), 4.16–3.96 (m, 4H), 2.52–2.35 (m, 3H), 2.32–2.19 (m, 3H), 2.16–2.00 (m, 2H), 1.37–1.24 (m, 9H), 1.16 (d, $J = 8.6$ Hz, 1H), 0.82 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 149.97 (d, $J = 4.9$ Hz), 149.51, 119.20 (d, $J = 187.0$ Hz), 118.07, 73.05 (d, $J = 1.1$ Hz), 61.63 (d, $J = 3.8$ Hz), 42.05, 40.83, 39.64 (d, $J = 22.0$ Hz), 37.79, 31.66, 31.01, 26.11, 21.39, 16.31 (d, $J = 6.5$ Hz) ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) $\delta$ 18.03 ppm.

MS(ESI) m/z [M+H]$^+$: 329.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 329.1876, found 329.1876.

IR (film): 3384, 2914, 1635, 1260, 1027, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{29} = -9.99$ (c = 1.540, CHCl$_3$, > 20/1 dr).
3a\textsuperscript{I}: Procedure B, 60 mg, colorless liquid, 61% yield, > 20/1 dr (Diastereoselectivity was determined by \textsuperscript{1}H NMR analysis of reaction crude mixture).

\textbf{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \(\delta 6.74 \) (ddt, \(J = 24.0, 17.1, 6.9\) Hz, 1H), \(5.72 \) (dd, \(J = 21.2, 17.1\) Hz, 1H), \(5.48 \) (s, 1H), \(4.14 \) (t, \(J = 6.5\) Hz, 1H), \(4.16–4.00 \) (m, 4H), \(2.48–2.34 \) (m, 3H), \(2.31–2.18 \) (m, 3H), \(2.15–2.00 \) (m, 2H), \(1.37–1.24 \) (m, 9H), \(1.12 \) (d, \(J = 8.6\) Hz, 1H), 0.84 (s, 3H) ppm.

\textbf{\textsuperscript{13}C NMR (100 MHz, CDCl\textsubscript{3})} \(\delta 150.00 \) (d, \(J = 4.8\) Hz), 149.02, 119.10 (d, \(J = 187.0\) Hz), 118.53, 72.99 (d, \(J = 0.9\) Hz), 61.64 (d, \(J = 5.4\) Hz), 41.82, 40.84, 39.57 (d, \(J = 22.0\) Hz), 37.77, 31.60, 31.03, 26.04, 21.35, 16.30 (d, \(J = 6.5\) Hz) ppm.

\textbf{\textsuperscript{31}P NMR (162 MHz, CDCl\textsubscript{3})} \(\delta 18.11 \) ppm.

\textbf{MS(ESI) m/z [M+H]^+}: 329.15.

\textbf{HRMS(ESI) m/z [M+H]^+}: calcd. 329.1876, found 329.1875.

\textbf{IR (film)}: 3379, 2988, 1631, 1260, 1028, 750 cm\textsuperscript{-1}.

\textbf{Optical rotation}: \([\alpha]_D^{29} = -24.74 \) (c = 1.870, CHCl\textsubscript{3}, > 20/1 dr).
5a: Procedure A, 83 mg, pale green solid, 96% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.66 (s, 1H), 8.06 (d, \(J = 7.5\) Hz, 1H), 7.94 (t, \(J = 7.7\) Hz, 1H), 7.57–7.47 (m, 1H), 7.36–7.24 (m, 5H), 7.15 (dt, \(J = 15.2, 7.2\) Hz, 1H), 6.60 (d, \(J = 15.2\) Hz, 1H), 5.24–4.49 (m, 1H), 2.78 (d, \(J = 3.2\) Hz, 1H), 2.76–2.66 (m, 2H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.21, 150.15, 146.36, 142.95, 138.25, 129.96, 128.61, 127.96, 127.13, 125.63, 121.91, 72.36, 41.34 ppm.

MS(ESI) m/z [M+H]\(^+\): 290.00.

HRMS(ESI) m/z [M+H]\(^+\): calcd. 290.0845, found 290.0846.

IR (film): 3502, 2914, 1630, 1428, 1170, 750 cm\(^{-1}\).

Optical rotation: [\(\alpha\)]\(_D\)\(^{27}\) = +32.29 (c = 1.050, CHCl\(_3\), 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, \(\lambda = 254\) nm, \(t_R\) (major) = 31.9 min, \(t_R\) (minor) = 36.1 min, ee = 97%.

![HPLC Spectrum](image)

**Figure S293**, the HPLC spectrum of compound 5a, related to **Table 3**
5b: Procedure A, 81 mg, colorless crystal, 88% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 4.1$ Hz, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.99–7.85 (m, 1H), 7.53 (dd, $J = 7.1$, 5.2 Hz, 1H), 7.30 (dd, $J = 8.5$, 5.4 Hz, 2H), 7.13 (dt, $J = 15.2$, 7.3 Hz, 1H), 7.00 (t, $J = 8.7$ Hz, 2H), 6.60 (d, $J = 15.2$ Hz, 1H), 4.89 (t, $J = 6.2$ Hz, 1H), 2.81–2.62 (m, 2H), 2.49 (s, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.31 (d, $J = 246.2$ Hz), 158.24, 150.15, 145.86, 138.61 (d, $J = 3.2$ Hz), 138.25, 130.25, 127.31 (d, $J = 8.1$ Hz), 127.13, 121.81, 115.48 (d, $J = 21.4$ Hz), 71.78, 41.43 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.86 ~ -117.88 (m) ppm.

MS(ESI) m/z [M+Na]$^+$: 329.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 308.0751, found 308.0752.

IR (film): 3405, 2921, 1428, 1276 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{27} = +21.10$ (c = 0.250, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda$ = 254 nm, $t_R$(major) = 41.4 min, $t_R$(minor) = 47.7 min, ee = 97%.

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**Figure S294**, the HPLC spectrum of compound 5b, related to Table 3
5c: Procedure A, 90 mg, colorless crystal, 93% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.68 (d, $J = 4.6$ Hz, 1H), 8.06 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8, 1.6$ Hz, 1H), 7.53 (dd, $J = 7.1, 5.2$ Hz, 1H), 7.31–7.21 (m, 4H), 7.12 (dt, $J = 15.2, 7.3$ Hz, 1H), 6.58 (d, $J = 15.2$ Hz, 1H), 4.89 (t, $J = 6.3$ Hz, 1H), 2.78 (s, 1H), 2.69 (t, $J = 6.6$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.14, 150.15, 145.78, 141.34, 138.28, 133.59, 130.31, 128.73, 127.18, 127.01, 121.84, 71.69, 41.34 ppm.

MS(ESI) m/z [M+Na]$^+$: 345.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 324.0456, found 324.0455.

IR (film): 3494, 2919, 1630, 1453, 1163 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{26} = +27.84$ (c = 0.625, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 27.5 min, $t_R$(minor) = 29.7 min, ee = 97%.

![HPLC spectrum](image)

**Figure S295**, the HPLC spectrum of compound 5c, related to Table 3
5d: Procedure A, 94 mg, white powder, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 4.1$ Hz, 1H), 8.07 (d, $J = 7.8$ Hz, 1H), 7.96 (td, $J = 7.8$, 1.6 Hz, 1H), 7.54 (dd, $J = 6.6$, 4.8 Hz, 1H), 7.43 (d, $J = 8.4$ Hz, 2H), 7.20 (d, $J = 8.3$ Hz, 2H), 7.12 (dt, $J = 15.2$, 7.3 Hz, 1H), 6.59 (d, $J = 15.2$ Hz, 1H), 4.87 (t, $J = 6.2$ Hz, 1H), 2.69 (t, $J = 7.0$ Hz, 2H), 2.55 (s, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.21, 150.16, 145.61, 141.80, 138.25, 131.69, 130.41, 127.33, 127.15, 121.79, 121.76, 71.78, 41.27 ppm.

MS(ESI) m/z [M+Na]$^+$: 389.90.

HRMS(ESI) m/z [M+H]$^+$: calcld. 367.9951, found 367.9951.

IR (film): 3490, 2924, 1428, 1262 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{25} = +30.84$ (c = 0.335, CHCl$_3$, 92% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 3/1, flow rate: 0.8 mL/min, $\lambda$ = 254 nm, $t_R$ (major) = 29.8 min, $t_R$ (minor) = 31.7 min, ee = 92%.

**Figure S296**, the HPLC spectrum of compound 5d, related to Table 3.
5e: Procedure A, 102 mg, white powder, 82% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (d, $J = 4.5$ Hz, 1H), 8.04 (d, $J = 7.8$ Hz, 1H), 7.95 (td, $J = 7.7$, 1.6 Hz, 1H), 7.61 (d, $J = 8.3$ Hz, 2H), 7.54 (ddd, $J = 7.5$, 4.7, 0.9 Hz, 1H), 7.19–6.99 (m, 3H), 6.56 (d, $J = 15.2$ Hz, 1H), 4.85 (t, $J = 6.2$ Hz, 1H), 3.20 (s, 1H), 2.77–2.56 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 157.99, 150.18, 145.93, 142.67, 138.35, 137.55, 130.21, 127.63, 127.26, 121.92, 93.26, 71.69, 41.25 ppm.

MS(ESI) m/z [M+Na]$^+$: 437.70.

HRMS(ESI) m/z [M+H]$^+$: calcd. 415.9812, found 415.9812.

IR (film): 3493, 2919, 1630, 1427, 1163 cm$^{-1}$.

Optical rotation: [$\alpha$]$_D^{26} = +28.57$ ($c = 1.835$, CHCl$_3$, 91% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 5/1, flow rate: 0.72 mL/min, $\lambda = 254$ nm, $t_R$(major) = 70.4 min, $t_R$(minor) = 75.0 min, ee = 91%.

Figure S297, the HPLC spectrum of compound 5e, related to Table 3
5f: Procedure A, 87 mg, white powder, 96% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.67 (d, \(J = 4.2\) Hz, 1H), 8.05 (d, \(J = 7.9\) Hz, 1H), 7.93 (td, \(J = 7.8, 1.6\) Hz, 1H), 7.51 (ddd, \(J = 7.5, 4.7, 0.9\) Hz, 1H), 7.25–7.05 (m, 5H), 6.59 (d, \(J = 15.2\) Hz, 1H), 4.93–4.75 (m, 1H), 2.84–2.58 (m, 3H), 2.32 (s, 3H) ppm.

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.20, 150.16, 146.53, 140.00, 138.25, 129.84, 129.25, 127.11, 125.57, 121.90, 72.21, 41.32, 21.09 ppm.

**MS(ESI) m/z [M+Na]**: 326.00.

**HRMS(ESI) m/z [M+H]**: calcd. 304.1002, found 304.1002.

**IR (film)**: 3514, 2921, 1630, 1442, 1270 cm\(^{-1}\).

**Optical rotation**: \([\alpha]\)\(\text{D}^{26}\) = +35.05 (c = 1.165, CHCl\(_3\), 97% ee).

**HPLC**: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, \(\lambda = 254\) nm, \(t_\alpha\) (major) = 36.0 min, \(t_\alpha\) (minor) = 39.0 min, ee = 97%.

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**Figure S298**, the HPLC spectrum of compound 5f, related to **Table 3**
5g: Procedure A, 94 mg, colorless liquid, 91% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.67 (d, $J = 4.6$ Hz, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.94 (td, $J = 7.8, 1.6$ Hz, 1H), 7.51 (ddd, $J = 7.6, 4.8, 0.9$ Hz, 1H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.25 (d, $J = 8.3$ Hz, 2H), 7.22–7.06 (m, 1H), 6.62 (d, $J = 15.2$ Hz, 1H), 4.89–4.78 (m, 1H), 2.91–2.59 (m, 3H), 1.30 (s, 9H). ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.19, 150.92, 150.18, 146.67, 139.99, 138.28, 129.78, 127.14, 125.50, 125.40, 121.94, 72.13, 41.24, 34.52, 31.30 ppm.

MS(ESI) m/z [M+Na]$^+$: 368.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 346.1471, found 346.1469.

IR (film): 3507, 2989, 1461, 1260, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{26} = +28.35$ ($c = 1.790$, CHCl$_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/i-PrOH = 3/1, flow rate: 0.6 mL/min, $\lambda = 254$ nm, $t_R$(major) = 41.0 min, $t_R$(minor) = 38.7 min, ee = 95%.

![HPLC spectrum](image_url)

**Figure S299**, the HPLC spectrum of compound 5g, related to Table 3
5h: Procedure A, 91 mg, pale green liquid, 90% yield.

\(^1\)H NMR (400 MHz, CDCl\textsubscript{3}) \(\delta\) 8.70 (d, \(J = 4.6\) Hz, 1H), 8.07 (d, \(J = 7.9\) Hz, 1H), 7.95 (td, \(J = 7.8, 1.6\) Hz, 1H), 7.56–7.49 (m, 1H), 7.31–7.18 (m, 4H), 7.19–7.06 (m, 1H), 6.60 (d, \(J = 15.2\) Hz, 1H), 4.86 (t, \(J = 6.2\) Hz, 1H), 2.76–2.63 (m, 2H), 2.47 (s, 3H), 2.43 (s, 1H) ppm.

\(^13\)C NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 157.86, 150.15, 146.45, 139.97, 138.40, 137.82, 129.86, 127.29, 126.45, 126.27, 121.97, 71.73, 41.16, 15.68 ppm.

MS(ESI) m/z [M+Na]+: 357.95.

HRMS(ESI) m/z [M+H]+: calcd. 336.0723, found 336.0723.

IR (film): 3393, 2921, 1428, 1270 cm\textsuperscript{-1}.

Optical rotation: \([\alpha]_D^{26} = +23.63\) (c = 0.420, CHCl\textsubscript{3}, 97% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-PrOH = 11/5, flow rate: 0.8 mL/min, \(\lambda = 254\) nm, t\textsubscript{R}(major) = 48.7 min, t\textsubscript{R}(minor) = 52.8 min, ee = 97%.

**Figure S300**, the HPLC spectrum of compound 5h, related to **Table 3**
5am: Procedure A, 79 mg, colorless liquid, 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.62 (d, $J = 4.3$ Hz, 1H), 8.02 (d, $J = 7.8$ Hz, 1H), 7.97–7.87 (m, 3H), 7.51 (dd, $J = 6.9$, 4.9 Hz, 1H), 7.38 (d, $J = 8.2$ Hz, 2H), 7.13 (dt, $J = 15.2$, 7.2 Hz, 1H), 6.56 (d, $J = 15.2$ Hz, 1H), 4.96 (t, $J = 6.1$ Hz, 1H), 3.89 (s, 3H), 3.65 (s, 1H), 2.70 (t, $J = 6.7$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 166.81, 157.87, 150.13, 148.20, 146.01, 138.39, 130.15, 129.76, 129.35, 127.28, 125.62, 121.96, 71.68, 52.14, 41.21 ppm.

MS(ESI) m/z [M+Na]$^+$: 369.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 348.0900, found 348.0900.

IR (film): 3493, 2952, 1717, 1429, 1026, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{26} = +28.54$ (c = 0.289, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 53.8 min, $t_R$(minor) = 59.7 min, ee = 98%.

**Figure S301**, the HPLC spectrum of compound 5am, related to Table 3
5k: Procedure A, 88 mg, colorless liquid, 95% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.70 (d, $J = 4.4$ Hz, 1H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.5 Hz, 1H), 7.60–7.48 (m, 1H), 7.46 (td, $J = 7.5$, 1.2 Hz, 1H), 7.29–7.09 (m, 3H), 7.03–6.96 (m, 1H), 6.63 (d, $J = 15.2$ Hz, 1H), 5.24–5.18 (m, 1H), 2.86–2.66 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 160.59, 158.18 (d, $J = 8.1$ Hz), 150.16, 145.98, 138.26, 130.20, 129.87 (d, $J = 13.2$ Hz), 129.31 (d, $J = 8.3$ Hz), 127.13, 127.00 (d, $J = 4.2$ Hz), 124.43 (d, $J = 3.5$ Hz), 121.87, 115.34 (d, $J = 21.6$ Hz), 66.42 (d, $J = 2.5$ Hz), 40.03 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -119.29~119.40 (m) ppm.

MS(ESI) m/z [M+Na]$^+$: 329.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 308.0751, found 308.0751.

IR (film): 3490, 2989, 1456, 1275, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{26} = +35.66$ (c = 0.670, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-PrOH = 11/5, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 30.0 min, $t_R$(minor) = 28.7 min, ee = 98%.

**Figure S302**, the HPLC spectrum of compound 5k, related to Table 3
**5an**: Procedure A, 94 mg, colorless liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.69 (d, $J = 4.1$ Hz, 1H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8, 1.6$ Hz, 1H), 7.58–7.43 (m, 3H), 7.36–7.16 (m, 2H), 7.13 (td, $J = 7.8, 1.6$ Hz, 1H), 6.63 (d, $J = 15.2$ Hz, 1H), 5.33–5.18 (m, 1H), 2.96 (s, 1H), 2.86–2.77 (m, 1H), 2.66–2.55 (m, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.21, 150.17, 146.21, 141.85, 138.28, 132.68, 130.08, 129.20, 127.84, 127.18, 127.15, 121.91, 121.47, 71.07, 39.61 ppm.

MS(ESI) m/z [M+Na]$^+$: 389.85.

HRMS(ESI) m/z [M+H]$^+$: cacld. 367.9951, found 367.9951.

IR (film): 3493, 2960, 1632, 1428, 1198 cm$^{-1}$.

Optical rotation: [α]$^D_{25} = +69.81$ (c = 1.070, CHCl$_3$, 92% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, $t_R$(major) = 28.3 min, $t_R$(minor) = 30.3 min, ee = 92%.

**Figure S303**, the HPLC spectrum of compound 5an, related to Table 3
Sao: Procedure A, 89 mg, colorless liquid, 98% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.71 (d, \(J = 4.3\) Hz, 1H), 8.09 (d, \(J = 7.8\) Hz, 1H), 7.95 (td, \(J = 7.8, 1.4\) Hz, 1H), 7.53 (dd, \(J = 7.0, 4.8\) Hz, 1H), 7.46 (d, \(J = 6.9\) Hz, 1H), 7.24–7.09 (m, 4H), 6.64 (d, \(J = 15.2\) Hz, 1H), 5.12 (t, \(J = 6.2\) Hz, 1H), 2.68 (s, 1H), 2.36 (s, 1H), 2.31 (s, 3H) ppm.

\(^13\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.30, 150.18, 146.49, 140.97, 138.23, 134.13, 130.55, 129.94, 127.71, 127.10, 126.48, 124.99, 121.84, 68.79, 40.16, 18.99 ppm.

MS(ESI) m/z [M+Na]: 326.00.

HRMS(ESI) m/z [M+H]: calcd. 304.1002, found 304.1003.

IR (film): 3405, 2918, 1462, 1276 cm\(^{-1}\).

Optical rotation: \([\alpha]_D^{27} = +40.80\) (c = 0.345, CHCl\(_3\), 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, \(\lambda = 254\) nm, \(t_R\) (major) = 32.2 min, \(t_R\) (minor) = 40.8 min, ee = 99%.

**Figure S304**, the HPLC spectrum of compound Sao, related toTable 3
5l: Procedure A, 87 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J = 4.2$ Hz, 1H), 8.10 (d, $J = 7.9$ Hz, 1H), 7.96 (td, $J = 7.8$, 1.6 Hz, 1H), 7.78 (d, $J = 7.9$ Hz, 1H), 7.67–7.49 (m, 3H), 7.39 (t, $J = 7.6$ Hz, 1H), 7.21 (dt, $J = 15.2$, 7.4 Hz, 1H), 6.65 (d, $J = 15.2$ Hz, 1H), 5.35–5.25 (m, 1H), 2.77–2.56 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.29, 150.16, 145.91, 141.98, 138.25, 132.42, 130.28, 127.93, 127.40, 127.13, 125.61, 125.55, 122.82, 121.83, 67.73, 41.33 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -58.23 ppm.

MS(ESI) m/z [M+Na]$^+$: 379.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 358.0719, found 358.0718.

IR (film): 3494, 2925, 1132 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +54.75$ (c = 2.750, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 19.9 min, $t_R$(minor) = 21.4 min, ee = 97%.

Figure S305, the HPLC spectrum of compound 5l, related to Table 3
5ap: Procedure A, 74 mg, colorless liquid, 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.65 (d, $J = 4.2$ Hz, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.6 Hz, 1H), 7.57–7.47 (m, 1H), 7.32–7.22 (m, 1H), 7.19–7.01 (m, 3H), 6.93 (td, $J = 8.3$, 2.2 Hz, 1H), 6.58 (d, $J = 15.2$ Hz, 1H), 4.96–4.86 (m, 1H), 3.20 (d, $J = 3.7$ Hz, 1H), 2.80–2.62 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 162.87 (d, $J = 246.5$ Hz), 158.09, 150.15, 145.91, 145.66 (d, $J = 6.8$ Hz), 138.32, 130.24, 130.13 (d, $J = 8.2$ Hz), 127.19, 121.89, 121.22 (d, $J = 2.9$ Hz), 114.69 (d, $J = 21.1$ Hz), 112.60 (d, $J = 22.0$ Hz), 71.66, 41.27 ppm.

$^{19}$F NMR (376 MHz, CDCl$_3$) $\delta$ -112.27~ -112.39 (m) ppm.

MS(ESI) m/z [M+Na]$^+$: 330.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 308.0751, found 308.0751.

IR (film): 3316, 2915, 1428, 1232, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +36.50$ (c = 1.355, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 40.2 min, $t_R$(minor) = 43.0 min, ee = 97%.

Figure S306, the HPLC spectrum of compound 5ap, related to Table 3
5n: Procedure A, 79 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.70 (d, $J = 4.6$ Hz, 1H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.96 (td, $J = 7.8$, 1.5 Hz, 1H), 7.59–7.50 (m, 1H), 7.34 (s, 1H), 7.29–7.08 (m, 4H), 6.62 (d, $J = 15.2$ Hz, 1H), 4.96–4.85 (m, 1H), 2.71 (t, $J = 6.7$ Hz, 2H), 2.63 (d, $J = 3.5$ Hz, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.21, 150.16, 145.67, 144.92, 138.28, 134.56, 130.39, 129.91, 128.09, 127.14, 125.79, 123.77, 121.81, 71.75, 41.28 ppm.

MS(ESI) m/z [M+H]$^+$: 323.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 324.0456, found 324.0457.

IR (film): 3396, 2924, 1428, 1270 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{25} = +37.10$ (c = 0.300, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_{R}$(major) = 26.8 min, $t_{R}$(minor) = 31.1 min, ee = 98%.

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 27.093    | 50.782|
| 2     | 31.010    | 49.218|

Figure S307, the HPLC spectrum of compound 5n, related to Table 3
5o: Procedure A, 84 mg, colorless liquid, 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (d, J = 4.6 Hz, 1H), 8.09 (d, J = 7.9 Hz, 1H), 7.96 (td, J = 7.8, 1.6 Hz, 1H), 7.59–7.46 (m, 2H), 7.40 (d, J = 7.7 Hz, 1H), 7.27–7.05 (m, 3H), 6.62 (d, J = 15.3 Hz, 1H), 4.87 (t, J = 6.3 Hz, 1H), 2.71 (t, J = 6.8 Hz, 2H), 2.53 (s, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.23, 150.16, 145.63, 145.15, 138.28, 131.05, 130.41, 130.20, 128.71, 127.14, 124.25, 122.76, 121.80, 71.71, 41.30 ppm.

MS(ESI) m/z [M+H]$^+$: 367.90.

HRMS(ESI) m/z [M+H]$^+$: calcd. 367.9951, found 367.9951.

IR (film): 3485, 2961, 1428, 1261, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +33.07$ (c = 1.850, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK I D, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_\alpha$(major) = 30.0 min, $t_\alpha$(minor) = 35.5 min, ee = 98%.

Figure S308, the HPLC spectrum of compound 5o, related to Table 3
5aq: Procedure A, 90 mg, colorless liquid, 88% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (d, $J = 4.7$ Hz, 1H), 8.01 (d, $J = 7.9$ Hz, 1H), 7.90–7.74 (m, 5H), 7.52–7.38 (m, 4H), 7.19 (dt, $J = 15.2$, 7.3 Hz, 1H), 6.61 (d, $J = 15.2$ Hz, 1H), 5.10–4.99 (m, 1H), 2.91–2.73 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.24, 150.08, 146.04, 140.15, 138.10, 133.15, 133.05, 130.18, 128.57, 127.98, 127.67, 127.00, 126.33, 126.10, 124.51, 123.45, 121.70, 72.59, 41.23 ppm.

MS(ESI) m/z [M+Na]$^+$: 361.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 340.1002, found 340.1002.

IR (film): 3494, 2925, 1427, 1162 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +30.68$ (c = 2.200, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_\alpha$(major) = 46.5 min, $t_\alpha$(minor) = 50.4 min, ee = 97%.

**Figure S309**, the HPLC spectrum of compound 5aq, related to Table 3.
5p: Procedure A, 99 mg, colorless liquid, 97% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.61 (d, $J = 4.6$ Hz, 1H), 8.04–7.94 (m, 2H), 7.92–7.80 (m, 2H), 7.73 (d, $J = 8.2$ Hz, 1H), 7.61 (d, $J = 7.1$ Hz, 1H), 7.50–7.43 (m, 3H), 7.40 (t, $J = 7.7$ Hz, 1H), 7.25 (dt, $J = 15.2$, 7.2 Hz, 1H), 6.60 (d, $J = 15.2$ Hz, 1H), 5.69–5.58 (m, 1H), 3.24 (s, 1H), 2.93–2.67 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.06, 150.14, 146.79, 138.58, 138.29, 133.69, 129.83, 129.74, 129.00, 128.27, 127.16, 126.30, 125.66, 125.42, 122.96, 122.62, 121.92, 69.02, 40.37 ppm.

MS(ESI) m/z [M+Na]$^+$: 362.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 340.1002, found 340.1003.

IR (film): $3493$, $2989$, $1427$, $1275$ cm$^{-1}$.

Optical rotation: $\lbrack \alpha \rbrack_26^D = +60.65$ (c = 2.035, CHCl$_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 108.8 min, $t_R$(minor) = 92.3 min, ee = 95%.

**Figure S310**, the HPLC spectrum of compound 5p, related to Table 3
5q: Procedure A, 70 mg, colorless liquid, 81% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.70 (d, $J = 4.2$ Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.5 Hz, 1H), 7.53 (dd, $J = 7.2$, 5.0 Hz, 1H), 7.35 (s, 1H), 7.21–6.98 (m, 1H), 6.65 (d, $J = 15.3$ Hz, 1H), 6.39–6.00 (m, 2H), 4.90 (t, $J = 6.0$ Hz, 1H), 2.85 (t, $J = 6.8$ Hz, 2H), 2.65 (s, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.18, 154.82, 150.15, 145.47, 142.28, 138.26, 130.22, 127.15, 121.89, 110.27, 106.62, 65.89, 37.80 ppm.

MS (ESI) m/z [M+Na]$^+$: 301.95.
HRMS (ESI) m/z [M+H]$^+$: calcld. 280.0638, found 280.0639.

 IR (film): 3349, 2924, 1631, 1429, 1163 cm$^{-1}$.

Optical rotation: [α]$^D_{15}$ = +21.31 (c = 0.535, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_\alpha$(major) = 61.1 min, $t_\alpha$(minor) = 67.4 min, ee = 98%.

![Figure S311](image_url), the HPLC spectrum of compound 5q, related to Table 3.
5r: Procedure A, 74 mg, colorless liquid, 84% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.68 (d, $J = 4.4$ Hz, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.5 Hz, 1H), 7.56–7.45 (m, 1H), 7.25–7.20 (m, 1H), 7.15 (dt, $J = 15.2$, 7.2 Hz, 1H), 7.00–6.88 (m, 2H), 6.64 (d, $J = 15.2$ Hz, 1H), 5.14 (t, $J = 6.3$ Hz, 1H), 2.99 (s, 1H), 2.89–2.71 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.13, 150.16, 146.71, 145.61, 138.29, 130.30, 127.16, 126.79, 124.96, 124.03, 121.91, 68.34, 41.39 ppm.

MS(ESI) m/z [M+Na]$^+$: 317.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 296.0410, found 296.0410.

IR (film): 3392, 2922, 1630, 1428, 1238 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{26} = +21.45$ (c = 0.735, CHCl$_3$, 98% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 60.7 min, $t_R$(minor) = 70.8 min, ee = 98%.

Figure S312, the HPLC spectrum of compound 5r, related to Table 3.
5ar: Procedure A, 67 mg, colorless liquid, 76% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (d, $J = 4.4$ Hz, 1H), 8.06 (d, $J = 7.8$ Hz, 1H), 7.94 (td, $J = 7.8$, 1.5 Hz, 1H), 7.60–7.44 (m, 1H), 7.38–7.18 (m, 1H), 7.23–7.10 (m, 2H), 7.05 (d, $J = 4.9$ Hz, 1H), 6.60 (d, $J = 15.2$ Hz, 1H), 4.98 (t, $J = 6.0$ Hz, 1H), 2.99 (s, 1H), 2.75 (t, $J = 6.5$ Hz, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.14, 150.16, 146.19, 144.41, 138.30, 130.03, 127.18, 126.52, 125.30, 121.91, 121.20, 68.56, 40.64 ppm.

MS(ESI) m/z [M+Na]$^+$: 317.95.

HRMS(ESI) m/z [M+H]$^+$: calcd. 296.0410, found 296.0410.

IR (film): 3493, 3005, 1427, 1276 cm$^{-1}$.

Optical rotation: [α]$_{D}^{26}$ = +30.34 ($c = 1.115$, CHCl$_3$, > 99% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, λ = 254 nm, t$_R$(major) = 40.5 min, t$_R$(minor) = 48.1 min, ee = > 99%.

### Table 3

| Peak# | Ret. Time | Area%  |
|-------|-----------|--------|
| 1     | 40.957    | 49.677 |
| 2     | 47.480    | 50.323 |

Figure S313, the HPLC spectrum of compound 5ar, related to Table 3
5u: Procedure A, 88 mg, colorless liquid, 85% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.63 (d, $J = 4.6$ Hz, 1H), 8.02 (d, $J = 7.9$ Hz, 1H), 7.90 (td, $J = 7.8, 1.5$ Hz, 1H), 7.86–7.76 (m, 2H), 7.50–7.45 (m, 1H), 7.39–7.30 (m, 3H), 7.28–7.16 (m, 1H), 6.60 (d, $J = 15.2$ Hz, 1H), 5.31–5.20 (m, 1H), 3.25 (s, 1H), 2.96–2.76 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.04, 150.14, 146.24, 140.89, 138.30, 137.95, 136.68, 130.04, 127.18, 124.56, 124.20, 122.99, 122.85, 121.95, 121.91, 67.87, 39.40 ppm.

MS(ESI) $m/z$ [M+Na]$^+$: 367.95.

HRMS(ESI) $m/z$ [M+H]$^+$: calcd. 346.0566, found 346.0568.

IR (film): 3493, 3054, 1428, 1276, 750 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{26} = +44.56$ ($c = 1.435$, CHCl$_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IE, hexane/i-ProH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_{R}$ (major) = 76.5 min, $t_{R}$ (minor) = 72.0 min, $ee = 95\%$.

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 71.518    | 49.940|
| 2     | 77.347    | 50.060|

Figure S314, the HPLC spectrum of compound 5u, related to Table 3
5as: Procedure A, 100 mg, colorless liquid, 78% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.66 (d, $J$ = 4.5 Hz, 1H), 8.13 (d, $J$ = 7.7 Hz, 1H), 8.03 (d, $J$ = 7.8 Hz, 1H), 7.91 (t, $J$ = 7.7 Hz, 1H), 7.60 (d, $J$ = 7.8 Hz, 1H), 7.54 (s, 1H), 7.49 (dd, $J$ = 7.5, 4.7 Hz, 1H), 7.32 (t, $J$ = 7.7 Hz, 1H), 7.27–7.14 (m, 2H), 6.66 (d, $J$ = 15.2 Hz, 1H), 5.16 (t, $J$ = 6.2 Hz, 1H), 2.91 (t, $J$ = 6.7 Hz, 2H), 2.77 (s, 1H), 1.66 (s, 9H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.16, 150.15, 149.52, 146.18, 138.23, 135.79, 130.03, 127.98, 127.11, 124.70, 122.70, 122.67, 122.46, 121.80, 119.48, 115.44, 83.96, 66.21, 39.56, 28.16 ppm.

MS(ESI) m/z [M+Na]$^+$: 451.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 429.1479, found 429.1479.

IR (film): 3507, 2979, 1731, 1428, 1254 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{27} = +23.31$ (c = 1.225, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda$ = 254 nm, $t_R$(major) = 82.7 min, $t_R$(minor) = 67.5 min, ee = 97%.

Figure S315, the HPLC spectrum of compound 5as, related to Table 3.
5x: Procedure A, 56 mg, colorless liquid, 46% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.52 (d, $J$ = 4.6 Hz, 1H), 8.06–7.97 (m, 2H), 7.94 (d, $J$ = 7.9 Hz, 1H), 7.72 (td, $J$ = 7.8, 1.6 Hz, 1H), 7.46 (t, $J$ = 7.6 Hz, 1H), 7.40–7.35 (m, 2H), 7.35–7.28 (m, 2H), 7.27–7.10 (m, 2H), 6.57 (d, $J$ = 15.2 Hz, 1H), 5.11–4.92 (m, 1H), 4.31 (q, $J$ = 7.2 Hz, 2H), 2.97 (s, 1H), 2.88–2.68 (m, 2H), 1.39 (t, $J$ = 7.2 Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.09, 150.01, 146.73, 140.22, 139.56, 138.09, 133.57, 129.76, 126.94, 125.84, 123.49, 122.78, 122.69, 121.76, 120.48, 118.91, 117.67, 109.99, 108.55, 72.93, 41.76, 37.56, 13.82 ppm.

MS(ESI) m/z [M+Na]$^+$: 429.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 407.1351, found 407.1352.

IR (film): 3506, 2977, 1427, 1233, 750 cm$^{-1}$.

Optical rotation: [$\alpha$]$_D^{26}$ = +29.12 (c = 2.140, CHCl$_3$, 93% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda$ = 254 nm, $t_R$(major) = 98.2 min, $t_R$(minor) = 89.8 min, ee = 93%.

Figure S316, the HPLC spectrum of compound 5x, related to Table 3
$5y$: Procedure A, 79 mg, pale green solid, 84% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.63 (d, $J = 4.1$ Hz, 1H), 8.05 (d, $J = 7.9$ Hz, 1H), 7.88 (td, $J = 7.8$, 1.6 Hz, 1H), 7.45 (ddd, $J = 7.6$, 4.7, 0.9 Hz, 1H), 7.35–7.09 (m, 6H), 6.71–6.51 (m, 2H), 6.18 (dd, $J = 15.9$, 6.5 Hz, 1H), 4.55–4.45 (m, 1H), 2.92 (s, 1H), 2.68–2.52 (m, 2H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.09, 150.15, 146.29, 138.28, 136.17, 131.10, 130.50, 129.97, 128.56, 127.87, 127.16, 126.53, 121.90, 70.75, 39.59 ppm.

MS(ESI) m/z [M+Na]$^+$: 338.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 316.1002, found 316.1003.

IR (film): 3494, 2922, 1428, 1276 cm$^{-1}$.

Optical rotation: $[\alpha]_{D}^{26} = +14.38$ (c = 1.910, CHCl$_3$, 94% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_{R}$(major) = 37.6 min, $t_{R}$(minor) = 42.1 min, ee = 94%.

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 37.674    | 50.013|
| 2     | 42.033    | 49.987|

Figure S317, the HPLC spectrum of compound $5y$, related to Table 3.
5z: Procedure A, 50 mg, pale green solid, 51% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.66 (d, $J = 4.4$ Hz, 1H), 8.07 (d, $J = 7.9$ Hz, 1H), 7.89 (td, $J = 7.8$, 1.6 Hz, 1H), 7.47 (dd, $J = 6.8$, 4.8 Hz, 1H), 7.41–7.25 (m, 2H), 7.23–7.13 (m, 4H), 6.68 (d, $J = 15.2$ Hz, 1H), 6.52 (s, 1H), 4.38 (t, $J = 6.0$ Hz, 1H), 2.75–2.55 (m, 2H), 2.10 (s, 1H), 1.85 (d, $J = 1.1$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.35, 150.15, 146.37, 138.47, 138.15, 136.92, 129.80, 128.92, 128.12, 127.03, 126.69, 126.58, 121.77, 75.69, 37.65, 13.54 ppm.

MS(ESI) m/z [M+Na]$^+$: 352.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 330.1158, found 330.1159.

IR (film): 3305, 2921, 1427, 1163 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{28} = -1.98$ (c = 0.250, CHCl$_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 48.5 min, $t_R$(minor) = 39.7 min, ee = 95%.

![Figure S318](image)

Table 3

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 39.820    | 50.022|
| 2     | 48.830    | 49.978|

Table 3

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 39.730    | 2.355 |
| 2     | 48.475    | 97.645|

Figure S318, the HPLC spectrum of compound 5z, related to Table 3.
5aa: Procedure A, 77 mg, yellow liquid, 80% yield.

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.65 (d, \(J = 4.3\) Hz, 1H), 8.06 (d, \(J = 7.8\) Hz, 1H), 7.89 (td, \(J = 7.8, 1.5\) Hz, 1H), 7.47 (dd, \(J = 7.2, 5.0\) Hz, 1H), 7.23–7.07 (m, 2H), 7.02–6.86 (m, 2H), 6.75–6.59 (m, 2H), 6.00 (dd, \(J = 15.7, 6.4\) Hz, 1H), 4.55–4.35 (m, 1H), 2.93 (s, 1H), 2.66–2.47 (m, 2H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.07, 150.17, 146.13, 141.22, 138.28, 130.03, 129.93, 127.40, 127.17, 126.32, 124.64, 124.32, 121.91, 70.47, 39.50 ppm.

MS(ESI) \(m/z\) [M+Na]\(^{+}\): 343.95.

HRMS(ESI) \(m/z\) [M+H]\(^{+}\): calcd. 322.0566, found 322.0566.

IR (film): 3494, 2923, 1428, 1249 cm\(^{-1}\).

Optical rotation: \([\alpha]\)\(_D^{28}\) = +14.19 (\(c = 1.445\), CHCl\(_3\), 92% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-ProH = 3/1, flow rate: 0.8 mL/min, \(\lambda = 254\) nm, \(t_{R}\)(major) = 39.6 min, \(t_{R}\)(minor) = 49.5 min, ee = 92%.

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**Figure S319**, the HPLC spectrum of compound **5aa**, related to **Table 3**
5ad: Procedure A, 38 mg, colorless liquid, 50% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.0$ Hz, 1H), 8.10 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8, 1.6$ Hz, 1H), 7.53 (dd, $J = 6.7, 4.8$ Hz, 1H), 7.13 (dt, $J = 15.2, 7.3$ Hz, 1H), 6.63 (d, $J = 15.2$ Hz, 1H), 5.82–5.62 (m, 1H), 5.55–5.46 (m, 1H), 4.35–4.20 (m, 1H), 2.63–2.43 (m, 2H), 2.06 (s, 1H), 1.68 (d, $J = 5.7$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.33, 150.17, 146.40, 138.24, 132.37, 129.73, 128.19, 127.10, 121.83, 70.91, 39.50, 17.61 ppm.

MS(ESI) m/z [M+Na]$^+$: 276.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 254.0845, found 254.0846.

IR (film): 3514, 2918, 1428, 1276, 750 cm$^{-1}$.

Optical rotation: $\lbrack \alpha \rbrack_d^{27} = +10.63$ (c = 0.600, CHCl$_3$, 93% ee).

HPLC: DAICEL CHIRALPAK ID, hexano/i-PrOH = 3/1, flow rate: 0.6 mL/min, $\lambda$ = 254 nm, t$_R$(major) = 37.1 min, t$_R$(minor) = 43.2 min, ee = 93%.

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 37.301    | 50.200|
| 2     | 42.823    | 49.800|

| Peak# | Ret. Time | Area% |
|-------|-----------|-------|
| 1     | 37.131    | 96.563|
| 2     | 43.164    | 3.437|
5ae: Procedure A, 59 mg, colorless liquid, 70% yield.

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.72 (d, $J = 4.7$ Hz, 1H), 8.10 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.7 Hz, 1H), 7.52 (ddd, $J = 7.6$, 4.7, 1.0 Hz, 1H), 7.13 (dt, $J = 15.2$, 7.3 Hz, 1H), 6.63 (d, $J = 15.2$ Hz, 1H), 5.78–5.62 (m, 1H), 5.47 (dd, $J = 15.4$, 6.9 Hz, 1H), 4.37–4.17 (m, 1H), 2.57–2.49 (m, 2H), 2.06–1.93 (m, 3H), 1.42–1.32 (m, 2H), 0.88 (t, $J = 7.4$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.38, 150.17, 146.34, 138.21, 133.31, 131.20, 129.73, 127.07, 121.80, 70.97, 39.57, 34.12, 22.11, 13.61 ppm.

MS(ESI) m/z [M+Na]$^+$: 304.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 282.1158, found 282.1160.

IR (film): 3405, 2957, 1428, 1170, 750 cm$^{-1}$.

Optical rotation: [α]$^D_{27} = +8.41$ (c = 0.560, CHCl$_3$, 97% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.6 mL/min, $\lambda = 254$ nm, t$_R$(major) = 30.6 min, t$_R$(minor) = 34.8 min, ee = 97%.

Figure S321, the HPLC spectrum of compound 5ae, related to Table 3
\[ \text{5at: Procedure A, 90 mg, colorless liquid, 88% yield.} \]

\[ ^1H \text{ NMR (400 MHz, } \text{CDCl}_3) \delta 8.70 (d, J = 4.1 \text{ Hz, } 1\text{H}), 8.09 (d, J = 7.9 \text{ Hz, } 1\text{H}), 7.92 (td, J = 7.8, 1.6 \text{ Hz, } 1\text{H}), 7.51–7.45 (m, 1\text{H}), 7.42–7.36 (m, 2\text{H}), 7.34–7.30 (m, 2\text{H}), 7.28–7.21 (m, 1\text{H}), 7.16 (dt, J = 15.2, 7.3 \text{ Hz, } 1\text{H}), 6.77–6.60 (m, 2\text{H}), 6.54 (d, J = 15.7 \text{ Hz, } 1\text{H}), 6.41 (dd, J = 15.2, 10.4 \text{ Hz, } 1\text{H}), 5.80 (dd, J = 15.2, 6.6 \text{ Hz, } 1\text{H}), 4.54–4.36 (m, 1\text{H}), 2.66–2.50 (m, 2\text{H}), 2.21 (s, 1\text{H}) \text{ ppm.} \]

\[ ^13C \text{ NMR (100 MHz, } \text{CDCl}_3) \delta 158.29, 150.18, 145.97, 138.24, 136.85, 134.13, 133.61, 131.70, 130.09, 128.62, 127.79, 127.58, 127.10, 126.41, 121.84, 70.59, 39.53 \text{ ppm.} \]

\[ \text{MS(ESI) } m/z \ [\text{M+Na}]^+: 364.00. \]

\[ \text{HRMS(ESI) } m/z \ [\text{M+H}]^+: \text{ calcd. 342.1158, found 342.1158.} \]

\[ \text{IR (film): 3492, 2924, 1630, 1450, 1162 \text{ cm}^{-1}.} \]

\[ \text{Optical rotation: } [\alpha]_D^{28} = +13.92 \ (c = 1.930, \text{ CHCl}_3, 96\% \text{ ee).} \]

\[ \text{HPLC: DAICEL CHIRALPAK IBN-3, hexane/PrOH = 3/1, flow rate: 0.8 mL/min, } \lambda = 254 \text{ nm,} \]

\[ t_R(\text{major}) = 44.2 \text{ min, } t_R(\text{minor}) = 80.0 \text{ min, ee = 96\%.} \]

**Figure S322**, the HPLC spectrum of compound 5at, related to Table 3
5au: Procedure A, 88 mg, colorless liquid, 80% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.1$ Hz, 1H), 8.10 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8, 1.6$ Hz, 1H), 7.53 (ddd, $J = 7.6, 4.7, 1.0$ Hz, 1H), 7.47–7.37 (m, 2H), 7.36–7.29 (m, 3H), 7.14 (dt, $J = 15.2, 7.3$ Hz, 1H), 6.71–6.53 (m, 2H), 6.34 (dd, $J = 15.2, 10.9$ Hz, 1H), 5.81 (dd, $J = 15.3, 7.8$ Hz, 2H), 4.53–4.36 (m, 1H), 2.66–2.20 (m, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.17, 150.20, 145.89, 140.28, 138.33, 136.38, 131.44, 130.40, 130.15, 128.33, 128.27, 127.21, 123.17, 121.90, 112.41, 92.64, 88.51, 70.17, 39.41 ppm.

MS(ESI) m/z [M+Na]$^+$: 388.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 366.1158, found 366.1158.

IR (film): 3493, 2989, 1428, 1275, 750 cm$^{-1}$.

Optical rotation: $[^{[\alpha]}]_D = +33.73$ (c = 0.900, CHCl$_3$, 94% ee).

HPLC: DAICEL CHIRALPAK ID, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, t$_R$(major) = 35.2 min, t$_R$(minor) = 38.9 min, ee = 94%.

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Figure S323, the HPLC spectrum of compound 5au, related to Table 3
5ah: Procedure A, 76 mg, colorless liquid, 70% yield.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.5$ Hz, 1H), 8.10 (d, $J = 7.8$ Hz, 1H), 7.96 (td, $J = 7.8$, 1.6 Hz, 1H), 7.53 (dd, $J = 7.0$, 4.8 Hz, 1H), 7.13 (dt, $J = 15.2$, 7.2 Hz, 1H), 6.63 (d, $J = 15.2$ Hz, 1H), 5.77–5.62 (m, 1H), 5.50 (dd, $J = 15.4$, 6.7 Hz, 1H), 4.36–4.28 (m, 1H), 2.52 (t, $J = 6.5$ Hz, 2H), 2.38 (s, 1H), 2.20–2.05 (m, 6H), 1.61–1.32 (m, 6H), 0.90 (t, $J = 7.1$ Hz, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.27, 150.17, 146.42, 138.27, 132.30, 131.76, 129.69, 127.13, 121.85, 80.71, 79.46, 70.80, 39.57, 31.17, 31.08, 28.31, 21.89, 18.38, 18.16, 13.60 ppm.

MS(ESI) m/z [M+Na]$^+$: 384.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 362.1784, found 362.1784.

IR (film): 3514, 2931, 1428, 1276 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{26} = +7.74$ (c = 1.625, CHCl$_3$, 95% ee).

HPLC: DAICEL CHIRALPAK IG-3, hexane/i-PrOH = 3/1, flow rate: 0.8 mL/min, $\lambda = 254$ nm, $t_R$(major) = 22.8 min, $t_R$(minor) = 21.8 min, ee = 95%.

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**Figure S324**, the HPLC spectrum of compound 5ah, related to Table 3
**5ak**: Procedure A, 56 mg, colorless liquid, 56% yield, > 20/1 dr (Diastereoselectivity was determined by \(^1\)H NMR analysis of reaction crude mixture).

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 8.72 (d, \(J = 4.1\) Hz, 1H), 8.09 (d, \(J = 7.9\) Hz, 1H), 7.95 (td, \(J = 7.8, 1.6\) Hz, 1H), 7.52 (ddd, \(J = 7.6, 4.7, 0.9\) Hz, 1H), 7.10 (dt, \(J = 15.2, 7.2\) Hz, 1H), 6.63 (d, \(J = 15.2\) Hz, 1H), 5.72 (d, \(J = 4.0\) Hz, 1H), 4.70 (d, \(J = 15.9\) Hz, 2H), 4.20 (t, \(J = 6.4\) Hz, 1H), 2.65–2.44 (m, 2H), 2.21–1.80 (m, 7H), 1.72 (s, 3H), 1.41 (m, 1H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 158.37, 150.17, 149.42, 146.76, 138.28, 138.22, 129.40, 127.09, 123.97, 121.81, 108.78, 73.91, 41.00, 37.40, 30.28, 27.32, 23.87, 20.73 ppm.

MS(ESI) m/z [M+Na]+: 356.05.

HRMS(ESI) m/z [M+H]+: calcd. 334.1471, found 334.1471.

IR (film): 3513, 2920, 1642, 1453, 1163 cm\(^{-1}\).

Optical rotation: \([\alpha]_D^{26} = -25.34\) (c = 1.025, CHCl\(_3\), > 20/1 dr).
Sak': Procedure B, 60 mg, colorless liquid, 60% yield, > 20/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.72 (d, $J = 4.6$ Hz, 1H), 8.10 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.6 Hz, 1H), 7.56–7.44 (m, 1H), 7.10 (dt, $J = 14.9$, 7.3 Hz, 1H), 6.63 (d, $J = 15.2$ Hz, 1H), 5.72 (s, 1H), 4.80–4.61 (m, 2H), 4.20 (t, $J = 5.9$ Hz, 1H), 2.59–2.49 (m, 2H), 2.21–1.79 (m, 7H), 1.72 (s, 3H), 1.50–1.35 (m, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 158.43, 150.17, 149.31, 146.67, 138.20, 137.98, 129.55, 127.06, 123.02, 121.78, 108.80, 73.84, 40.89, 37.64, 30.17, 27.17, 24.50, 20.79 ppm.

MS(ESI) m/z [M+Na]$^+$: 356.00.

HRMS(ESI) m/z [M+H]$^+$: calcd. 334.1471, found 334.1472.

IR (film): 3514, 2921, 1642, 1428, 1270 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = -33.51$ (c = 0.480, CHCl$_3$, > 20/1 dr).
Sal: Procedure A, 68 mg, colorless liquid, 68% yield, > 20/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.71 (d, $J = 4.4$ Hz, 1H), 8.08 (d, $J = 7.9$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.6 Hz, 1H), 7.55–7.50 (m, 1H), 7.18–7.09 (m, 1H), 6.63 (d, $J = 15.3$ Hz, 1H), 5.49 (d, $J = 1.0$ Hz, 1H), 4.20 (t, $J = 6.0$ Hz, 1H), 2.53–2.44 (m, 2H), 2.43–2.33 (m, 1H), 2.29–2.14 (m, 4H), 2.08 (s, 1H), 1.27 (s, 3H), 1.10 (d, $J = 8.7$ Hz, 1H), 0.76 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.34, 150.16, 148.99, 146.89, 138.23, 129.46, 127.08, 121.81, 118.62, 72.66, 41.96, 40.77, 37.78, 37.18, 31.61, 30.98, 26.07, 21.34 ppm.

MS(ESI) m/z [M+H]$^+$: 334.05.
HRMS(ESI) m/z [M+H]$^+$: calcd. 334.1473, found 334.1473.
IR (film): 3508, 2984, 1630, 1428, 1204 cm$^{-1}$.
Optical rotation: $[\alpha]_D^{27} = -9.72$ (c = 1.995, CHCl$_3$, > 20/1 dr).
Sal': Procedure B, 53 mg, colorless liquid, 53% yield, 10/1 dr (Diastereoselectivity was determined by $^1$H NMR analysis of reaction crude mixture).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.72 (d, $J = 4.5$ Hz, 1H), 8.08 (d, $J = 7.8$ Hz, 1H), 7.95 (td, $J = 7.8$, 1.5 Hz, 1H), 7.52 (dd, $J = 7.0$, 4.9 Hz, 1H), 7.10 (dt, $J = 14.7$, 7.2 Hz, 1H), 6.62 (d, $J = 15.3$ Hz, 1H), 5.49 (s, 1H), 4.20 (t, $J = 6.3$ Hz, 1H), 2.58--2.42 (m, 2H), 2.39--2.30 (m, 1H), 2.27--2.21 (m, 2H), 2.18 (t, $J = 5.1$ Hz, 1H), 2.08 (s, 1H), 2.02--1.92 (m, 1H), 1.28 (s, 3H), 1.05 (d, $J = 8.7$ Hz, 1H), 0.80 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 158.32, 150.18, 148.56, 146.72, 138.22, 129.47, 129.47, 127.08, 121.83, 119.00, 72.56, 41.84, 40.77, 37.77, 37.08, 31.56, 31.00, 26.01, 21.35 ppm.

MS(ESI) m/z [M+Na]$^+$: 356.05.

HRMS(ESI) m/z [M+H]$^+$: calcd. 334.1471, found 334.1472.

IR (film): 3515, 2986, 1428, 1276 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{27} = -31.50$ (c = 1.470, CHCl$_3$, 10/1 dr).
**1H NMR (400 MHz, CDCl₃)** δ 7.43–7.28 (m, 5H), 4.97 (dd, J = 8.8, 3.6 Hz, 1H), 3.87 (t, J = 5.6 Hz, 2H), 2.77 (s, 1H), 2.32 (s, 1H), 2.11–1.87 (m, 2H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 144.4, 128.6, 127.7, 125.7, 74.6, 61.6, 40.5 ppm.

**Optical rotation:** [α]D²⁵ = +64.7 (c = 1.000, CHCl₃, 99% ee).

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**1H NMR (400 MHz, CDCl₃)** δ 7.35–7.19 (m, 5H), 6.71 (ddt, J = 21.9, 17.1, 7.1 Hz, 1H), 5.61 (dd, J = 21.5, 17.1 Hz, 1H), 4.80 (dd, J = 6.5, 5.4 Hz, 1H), 4.07–3.91 (m, 4H), 2.71–2.45 (m, 2H), 1.28 (td, J = 7.1, 3.6 Hz, 6H), 0.88 (s, 9H), 0.04 (s, 3H), -0.13 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 149.54 (d, J = 4.7 Hz), 144.08, 128.14, 127.23, 125.69, 119.41 (d, J = 186.8 Hz), 73.72 (d, J = 1.4 Hz), 61.53 (d, J = 5.4 Hz), 45.62 (d, J = 21.9 Hz), 25.75, 18.13, 16.29 (d, J = 6.8 Hz), -4.74, -5.04 ppm.

**31P NMR (162 MHz, CDCl₃)** δ 17.79 ppm.

**MS(ESI) m/z [M+H]+**: 399.20.

**HRMS(ESI) m/z [M+H]+**: calcd. 399.2115, found 399.2116.

**IR (film)**: 2982, 1634, 1259, 1029, 750 cm⁻¹.

**Optical rotation**: [α]D²⁵ = +28.54 (c = 1.580, CHCl₃).

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**1H NMR (400 MHz, CDCl₃)** δ 7.32–7.27 (m, 4H), 7.25–7.17 (m, 1H), 4.64 (dd, J = 7.3, 3.6 Hz, 1H), 4.15–3.94 (m, 4H), 1.84–1.62 (m, 6H), 1.29 (td, J = 7.0, 4.4 Hz, 6H), 0.88 (s, 9H), 0.02 (s, 3H), -0.16 (s, 3H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 145.17, 128.02, 126.92, 125.75, 74.48 (d, J = 1.6 Hz), 61.34 (d, J = 6.5 Hz), 41.63 (d, J = 16.1 Hz), 25.80, 25.61 (d, J = 140.6 Hz), 18.65 (d, J = 5.0 Hz), 18.15, 16.41 (d, J = 6.1 Hz), -4.65, -5.04 ppm.

**31P NMR (162 MHz, CDCl₃)** δ 32.07 ppm.

**MS(ESI) m/z [M+H]+**: 401.20.

**HRMS(ESI) m/z [M+H]+**: calcd. 401.2271, found 401.2271.

**IR (film)**: 2929, 1454, 1270, 1030, 836 cm⁻¹.

**Optical rotation**: [α]D²⁵ = +38.26 (c = 0.855, CHCl₃).
OTBS

\[
\begin{align*}
\text{Ph} & & \text{CO}_2\text{Et} \\
\end{align*}
\]

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$^1$H NMR (400 MHz, CDCl$_3$) δ 7.60 (s, 1H), 7.34–7.27 (m, 8H), 7.26–7.17 (m, 2H), 4.76 (t, $J = 5.8$ Hz, 1H), 4.23 (q, $J = 7.1$ Hz, 2H), 2.78–2.62 (m, 1H), 2.58–2.39 (m, 1H), 2.01–1.86 (m, 2H), 1.31 (t, $J = 7.1$ Hz, 3H), 0.89 (s, 9H), 0.03 (s, 3H), -0.12 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 168.38, 145.06, 138.65, 135.47, 132.85, 129.45, 128.42, 128.26, 128.00, 126.93, 125.89, 74.96, 60.70, 39.68, 25.86, 23.83, 18.20, 14.29, -4.70, -4.96 ppm.

MS(ESI) m/z [M+Na]$^+$: 447.20.

HRMS(ESI) m/z [M+Na]$^+$: calcd. 447.2332, found 447.2332.

IR (film): 2956, 1709, 1630 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +106.96$ (c = 0.915, CHCl$_3$).

OTBS

\[
\begin{align*}
\text{Ph} & & \text{CO}_2\text{Et} \\
\end{align*}
\]

12

$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45–7.17 (m, 11H), 6.90–6.75 (m, 2H), 4.77 (t, $J = 5.7$ Hz, 1H), 4.33–4.09 (m, 2H), 2.63–2.38 (m, 2H), 1.98–1.71 (m, 2H), 1.34–1.25 (m, 3H), 0.95 (s, 9H), 0.09 (s, 3H), -0.10 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 167.97, 145.09, 139.06, 138.18, 136.51, 132.12, 128.65, 128.63, 128.05, 127.08, 126.97, 125.92, 123.61, 74.67, 60.50, 40.65, 25.89, 23.19, 18.24, 14.31, -4.65, -4.94 ppm.

MS(ESI) m/z [M+Na]$^+$: 473.25.

HRMS(ESI) m/z [M+Na]$^+$: calcd. 473.2488, found 473.2488.

IR (film): 2927, 1704, 1621, 1452, 1228 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +102.52$ (c = 0.890, CHCl$_3$).

OTBS

\[
\begin{align*}
\text{Ph} & & \text{CO}_2\text{Et} \\
\end{align*}
\]

13

$^1$H NMR (400 MHz, CDCl$_3$) δ 8.08 (d, $J = 7.2$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 1H), 7.48–7.39 (m, 4H), 7.37–7.32 (m, 2H), 7.30–7.24 (m, 1H), 6.05 (dd, $J = 7.5$, 6.0 Hz, 1H), 5.79 (ddt, $J = 17.1$, 10.2, 7.0 Hz, 1H), 5.12 (dd, $J = 17.1$, 1.4 Hz, 1H), 5.07 (d, $J = 10.7$ Hz, 1H), 2.89–2.76 (m, 1H), 2.74–2.60 (m, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 181.42, 165.68, 133.21, 132.92, 129.61, 128.43, 128.32, 127.93, 126.43,
118.18 ppm.

**MS(EI) m/z [M+NH₄]⁺**: 270.10.

**HRMS(EI) m/z [M+NH₄]⁺**: calcd. 270.1489, found 270.1488.

**IR (film)**: 2960, 1723, 1494, 1270, 1026 cm⁻¹.

**Optical rotation**: $[\alpha]_D^{25} = -2.676$ ($c = 0.275$, CHCl₃).

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl₃)} & \delta 8.72 (d, J = 4.2 \text{ Hz}, 1\text{H}), 8.05 (d, J = 7.8 \text{ Hz}, 1\text{H}), 7.95 (td, J = 7.7, 1.6 \text{ Hz}, 1\text{H}), 7.58–7.48 \text{ (m, 1H)}, 7.35–7.22 \text{ (m, 5H)}, 4.77–4.58 \text{ (m, 1H)}, 3.55–3.31 \text{ (m, 2H)}, 2.20 \text{ (d, J = 3.4 \text{ Hz}, 1\text{H})}, 1.95–1.77 \text{ (m, 4H) ppm.}
\end{align*}
\]

**MS(EI) m/z [M+Na]⁺**: 314.00.

**HRMS(EI) m/z [M+Na]⁺**: calcd. 314.0821, found 314.0821.

**IR (film)**: 3506, 2997, 1579, 1428, 1270, 750 cm⁻¹.

**Optical rotation**: $[\alpha]_D^{25} = +27.68$ ($c = 1.210$, CHCl₃).

\[
\begin{align*}
\text{1H NMR (400 MHz, CDCl₃)} & \delta 8.73 (d, J = 4.6 \text{ Hz}, 1\text{H}), 8.05 (d, J = 7.8 \text{ Hz}, 1\text{H}), 7.94 (td, J = 7.7, 1.2 \text{ Hz}, 1\text{H}), 7.54 \text{ (dd, J = 7.6, 4.7 \text{ Hz}, 1\text{H})}, 7.35–7.03 \text{ (m, 5H)}, 4.64 \text{ (t, J = 5.0 \text{ Hz}, 1\text{H})}, 3.47–3.28 \text{ (m, 2H)}, 1.85–1.65 \text{ (m, 4H)}, 0.82 \text{ (s, 9H)}, -0.04 \text{ (s, 3H)}, -0.20 \text{ (s, 3H) ppm.}
\end{align*}
\]

**MS(EI) m/z [M+Na]⁺**: 428.15.

**HRMS(EI) m/z [M+Na]⁺**: calcd. 428.1686, found 428.1686.

**IR (film)**: 3506, 2997, 1578, 1257, 1164, 777 cm⁻¹.

**Optical rotation**: $[\alpha]_D^{25} = +52.64$ ($c = 1.520$, CHCl₃).
(s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 145.46, 137.81, 130.58, 129.91, 128.43, 128.01, 126.89, 126.77, 125.88, 125.86, 74.45, 40.41, 29.03, 25.86, 18.22, -4.59, -4.92 ppm.

MS(DART) m/z [M+NH$_4$]$^+$: 370.20.

HRMS(DART) m/z [M+NH$_4$]$^+$: calcd. 370.2561, found 370.2557.

IR (film): 2928, 1600, 1257, 1092, 777 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +27.29$ (c = 0.920, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97–7.86 (m, 2H), 7.54 (t, $J$ = 7.4 Hz, 1H), 7.49–7.35 (m, 2H), 7.32–7.23 (m, 4H), 7.22–7.18 (m, 1H), 4.75–4.63 (m, 1H), 2.94 (t, $J$ = 6.5 Hz, 2H), 1.88–1.65 (m, 4H), 0.88 (s, 9H), 0.03 (s, 3H), -0.15 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 200.17, 145.38, 136.97, 132.83, 128.49, 128.00, 127.97, 126.86, 125.82, 74.87, 40.37, 38.48, 25.83, 20.44, 18.19, -4.65, -4.97 ppm.

MS(ESI) m/z [M+Na]$^+$: 391.15.

HRMS(ESI) m/z [M+Na]$^+$: calcd. 391.2070, found 391.2072.

IR (film): 3444, 2924, 1580, 1428, 1308, 793 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +36.41$ (c = 0.425, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.73 (d, $J$ = 4.4 Hz, 1H), 8.12 (d, $J$ = 7.9 Hz, 1H), 8.01 (td, $J$ = 7.8, 1.6 Hz, 1H), 7.60 (ddd, $J$ = 7.6, 4.7, 0.9 Hz, 1H), 7.39–7.22 (m, 5H), 4.98 (dd, $J$ = 9.5, 3.0 Hz, 1H), 4.68 (s, 1H), 4.61 (t, $J$ = 9.3 Hz, 1H), 3.60 (dd, $J$ = 14.9, 9.0 Hz, 1H), 3.53 (s, 1H), 3.49 (dd, $J$ = 14.9, 2.3 Hz, 1H), 2.08–1.95 (m, 1H), 1.86 (dt, $J$ = 14.3, 3.0 Hz, 1H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 157.43, 149.89, 143.71, 138.70, 128.50, 127.74, 127.69, 125.64, 122.04, 73.74, 66.54, 59.66, 44.67 ppm.

MS(ESI) m/z [M+H]$^+$: 308.15.

HRMS(ESI) m/z [M+H]$^+$: calcd. 308.0951, found 308.0953.

IR (film): 3444, 2924, 1580, 1428, 1308, 793 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = +27.58$ (c = 0.710, CHCl$_3$).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.38–7.18 (m, 5H), 6.77 (ddt, $J$ = 21.8, 17.1, 7.1 Hz, 1H), 6.52 (d, $J$ = 15.8
Hz, 1H), 6.15 (dd, J = 15.9, 6.4 Hz, 1H), 5.71 (dd, J = 21.3, 17.1 Hz, 1H), 4.43 (q, J = 5.9 Hz, 1H), 4.11–3.87 (m, 2H), 2.62–2.42 (m, 2H), 1.27 (q, J = 7.2 Hz, 6H), 0.91 (s, 9H), 0.09 (s, 3H), 0.06 (s, 3H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) δ 149.41 (d, J = 4.9 Hz), 136.57, 131.83, 129.88, 128.53, 127.57, 126.38, 119.54 (d, J = 186.7 Hz), 72.22 (d, J = 13.5 Hz), 61.59 (d, J = 5.6 Hz), 43.39 (d, J = 21.8 Hz), 25.82, 18.18, 16.28 (d, J = 6.5 Hz), -4.33, -4.84 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 17.83 ppm.

MS (ESI) m/z [M+Na]$^+$: 447.15.

HRMS (ESI) m/z [M+H]$^+$: calcd. 425.2271, found 425.2273.

IR (film): 2958, 1635, 1252, 1029 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = -19.61$ (c = 1.145, CHCl$_3$).

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$^1$H NMR (400 MHz, CDCl$_3$) δ 7.45–7.18 (m, 5H), 6.56 (d, J = 15.9 Hz, 1H), 6.18 (dd, J = 15.9, 6.5 Hz, 1H), 4.79 (dd, J = 12.2, 6.4 Hz, 1H), 4.20–4.03 (m, 4H), 3.13 (dq, J = 22.6, 13.5 Hz, 2H), 2.99 (dd, J = 15.6, 7.5 Hz, 1H), 2.79 (dd, J = 15.6, 5.1 Hz, 1H), 1.41–1.23 (m, 6H), 0.89 (s, 9H), 0.08 (s, 3H), 0.06 (s, 3H) ppm.

13C NMR (100 MHz, CDCl$_3$) δ 200.29, 136.55, 131.53, 129.86, 128.53, 127.60, 126.42, 70.16, 62.50 (d, J = 6.4 Hz), 52.13, 43.81 (d, J = 12.6 Hz), 25.82, 18.09, 16.27 (d, J = 6.2 Hz), -4.29, -4.99 ppm.

$^{31}$P NMR (162 MHz, CDCl$_3$) δ 19.63 ppm.

MS (ESI) m/z [M+Na]$^+$: 463.20.

HRMS (ESI) m/z [M+H]$^+$: calcd. 441.2221, found 441.2223.

IR (film): 2929, 1716, 1472, 1249, 780 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = -46.06$ (c = 1.000, CHCl$_3$).

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$^1$H NMR (400 MHz, CDCl$_3$) δ 7.65–7.45 (m, 3H), 7.40–7.28 (m, 7H), 7.26–7.20 (m, 1H), 6.78 (d, J = 16.2 Hz, 1H), 6.61 (d, J = 15.9 Hz, 1H), 6.26 (dd, J = 15.9, 6.2 Hz, 1H), 4.90 (dt, J = 6.5, 5.5 Hz, 1H), 3.09 (dd, J = 14.7, 7.8 Hz, 1H), 2.76 (dd, J = 14.7, 4.9 Hz, 1H), 0.87 (s, 9H), 0.06 (s, 3H), 0.06 (s, 3H) ppm.

13C NMR (100 MHz, CDCl$_3$) δ 198.50, 143.22, 136.74, 134.52, 132.19, 130.46, 129.50, 128.91, 128.54, 128.31, 127.53, 127.30, 126.44, 70.75, 49.25, 25.83, 18.15, -4.34, -4.94 ppm.

MS (ESI) m/z [M+Na]$^+$: 415.15.

HRMS (ESI) m/z [M+Na]$^+$: calcd. 415.2064, found 415.2061.

IR (film): 2955, 1689, 1471, 1249, 836, 779 cm$^{-1}$.

Optical rotation: $[\alpha]_D^{25} = -104.50$ (c = 1.000, CHCl$_3$).
**1H NMR (400 MHz, CDCl₃)** δ 7.61–7.41 (m, 3H), 7.38–7.04 (m, 8H), 6.70–6.50 (m, 2H), 6.21 (dd, J = 15.9, 5.9 Hz, 1H), 4.90–4.73 (m, 1H), 3.33 (s, 1H), 3.07–2.77 (m, 2H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 200.00, 143.92, 136.56, 134.12, 130.85, 130.40, 130.27, 129.01, 128.55, 128.43, 127.69, 126.49, 126.23, 68.74, 46.88 ppm.

**MS(ESI) m/z [M+Li]⁺:** 285.10.

**HRMS(ESI) m/z [M+Li]⁺:** calcd. 285.1463, found 285.1462.

**IR (film):** 3385, 2924, 1458, 1275, 1260, 749 cm⁻¹.

**Optical rotation:** [α]₀²⁵ = -10.78 (c = 0.615, CHCl₃).

**1H NMR (400 MHz, CDCl₃)** δ 7.48–7.20 (m, 10H), 6.65 (d, J = 15.8 Hz, 2H), 6.31 (dd, J = 15.8, 5.9 Hz, 2H), 4.79–4.58 (m, 2H), 2.60 (s, 2H), 1.98 (t, J = 5.3 Hz, 2H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 136.55, 131.62, 130.21, 128.59, 127.70, 126.47, 70.47, 42.64 ppm.

**MS(ESI) m/z [M+Na]⁺:** 303.10.

**HRMS(ESI) m/z [M+Na]⁺:** calcd. 303.1356, found 303.1356.

**IR (film):** 3358, 2954, 2924, 1260, 963, 750 cm⁻¹.

**Optical rotation:** [α]₀²⁵ = +46.20 (c = 0.260, CHCl₃).

**1H NMR (400 MHz, CDCl₃)** δ 7.32–7.26 (m, 4H), 7.23–7.13 (m, 6H), 4.05–3.92 (m, 2H), 2.83–2.73 (m, 2H), 2.71–2.58 (m, 2H), 2.30 (d, J = 4.2 Hz, 2H), 1.92–1.71 (m, 4H), 1.67 (t, J = 5.6 Hz, 2H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 141.82, 128.43, 128.35, 125.89, 68.93, 42.52, 39.08, 32.16 ppm.

**MS(ESI) m/z [M+Na]⁺:** 307.10.

**HRMS(ESI) m/z [M+Na]⁺:** calcd. 307.1674, found 307.1672.

**IR (film):** 3285, 2923, 1453, 1061, 919, 727 cm⁻¹.

**Optical rotation:** [α]₀²⁵ = +5.66 (c = 0.250, CHCl₃). (literature (Hashimoto et. al., 1986), [α]₀ = +7.2 (CHCl₃)).
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