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(Thiolan-2-yl)diphenylmethyl benzyl ether/*N*,*N*′-diarylurea cocatalyzed asymmetric aziridination of cinnamyl bromide and aryl aldimine

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ABSTRACT

A dual catalyst system using THT-based chiral sulfide **2a** and H-bond donor **10a** was developed for the asymmetric imino Corey–Chaykovsky reaction. Under the optimum reaction conditions, cinnamyl bromide reacted with a wide scope of *N*-diphenylphosphinic aldimines, to give the major *trans*-aryl cinnamyl aziridines with up to 98% ee. The role of H-bond donor **10a** was demonstrated empirically as well.

1. Introduction

Chiral sulfur ligands are becoming a versatile tool in organic chemistry due to the blossomed development achieved in the past years. These sulfur catalysts are being used less than the more developed phosphorus- or nitrogen-based ligands in view of electronic and steric considerations, but have proved to be as useful as other classical chiral ligands in a broad variety of asymmetric reactions.[1] We recently reported an efficient preparation of tetrahydrothiophene(THT)-based chiral sulfide **1a** (Fig. 1A) and its benzyl ether derivative **2a** that shows excellent activity in catalyzing different enantioselective transformations, thus allowing access to various synthetically useful compounds such as diaryl epoxides and diaryl aziridines.[2] In 2008, Connon et al. demonstrated that *N*,*N*′-diarylureas and thioureas are capable of the efficient catalysis of sulfonium ylide-mediated aldehyde epoxidation (Corey–Chaykovsky reaction[3]) through the stabilization of the rate-determining transition state.[4] In the present study, we have now evaluated the compatibility of the same family of chiral sulfides and *N*,*N*′-diaryl(thio)ureas in the asymmetric imino Corey–Chaykovsky reaction of cinnamyl bromide and aryl aldimines (Fig. 1B), the stereo control of which is more challenging than that of the diaryl aziridine formation.[5]

2. Results and discussions

2.1. Synthesis of chiral sulfide catalysts

A series of THT-based sulfides (**2a**–**2f**) were readily synthesized according to our previously reported procedure, as depicted in Scheme 1.[2] Commercially available ethyl 5-bromovalerate (**3**) was reacted with an excess amount of arylmagnesium bromide to afford diarylalcohols **4a**–**4c** that were dehydrated in hot toluene in the presence of PTSA. The resulting diphenylethylenes **5a**–**5c** were

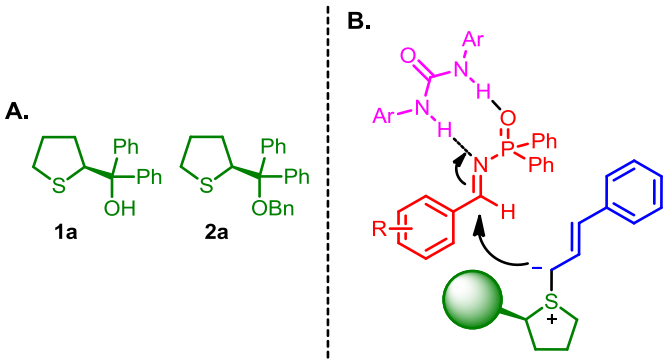

Fig. 1. A. Structures of THT-based chiral sulfides **1a** and **2a**. B. Concept of the dual catalysis in this work.

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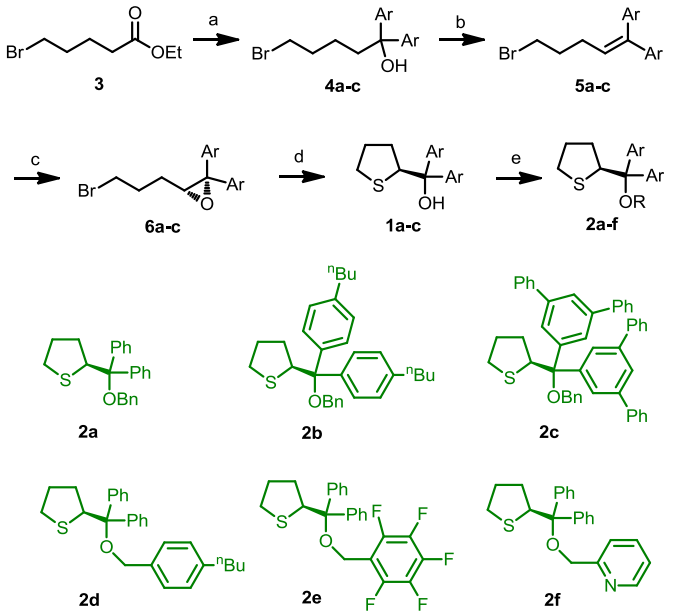
0040-4020/

then subjected to Shi epoxidation condition to furnish optically active epoxides **6a**–**6c**.[6] After THT-ring formation with Na_2S, the hydroxy groups were protected by benzyl bromide, 4-butylbenzyl bromide, pentafluorobenzyl bromide, and picolyl bromide respectively under basic conditions in DMF, yielding catalysts **2a**–**f** for the subsequent aziridination process.

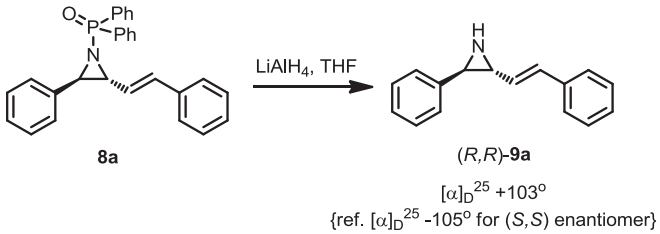


Scheme 1. Syntheses of chiral sulfide catalysts **2a**–**2f**. *Reagents and conditions*: a) ArMgBr, THF. b) PTSA(cat.) toluene, 70 °C. c) Shi epoxidation. d) $Na_2S{\cdot}9H_2O$, EtOH, sonication. e) NaH, RBr, DMF.

2.2. Screening of sulfide catalysts for imino Corey–Chaykovsky reaction and absolute configuration determination of the resulting aziridine 8a

We first compared the catalytic performance of THT-catalysts **2a**–**2f** in the imino Corey–Chaykovsky reaction of cinnamyl bromide and *N*-diphenylphosphinic aldimine **7a**. As shown in Table 1, **2a** was the best compound that catalyzed the aziridination smoothly in acetonitrile in the presence of K_2CO_3 (entry 1). The reaction was completed within 24 h, providing *trans*-aziridine **8a** (89% ee) and its *cis*-isomer in 82% yield, 66/33 dr. Catalyst **2b** (entry 2) was comparable to **2a** in terms of both the stereo-chemical outcome and catalytic activity. Sulfides **2c**–**2e** (entries 3–5) mediated the reaction with lower diastereoselectivity, while the enantioselectivity remained high. Apparently, the increase of the bulkiness on the side chain didn't supply a better chiral environment for the rate-determining transition state. Notably, the nitrogen atom on the picolyl group of sulfide **2f** even deteriorated the ee from 89% to 56%.

8a was then reduced with an excess amount of $LiAlH_4$ in THF to afford deprotected aziridine **9a** with dextrorotation ($[\alpha]_D^{25}$ +103°), of which the (*S*,*S*)-enantiomer has been reported to be levorotatory ($[\alpha]_D^{25}$ −105°).[7] Therefore, the absolute stereochemistry of **8a** was determined as (*R*,*R*) (Scheme 2).



Scheme 2. Deprotection of aziridine **8a** for absolute configuration determination.

The catalytic cycle is proposed in Fig. 2 to provide a mechanistic rationale for the high asymmetric induction observed in this aziridination. The sulfide is initially transformed to sulfonium salts **I**, which is then subsequently deprotonated by base to provide the corresponding ylide **II**. Intermediate **IIb** should be favored as the phenyl group pointing at equatorial position is located away from the bulky substituent of the sulfide. The ylide carbon of **IIb** then attacks the *Si* face of the imine with both diphenylphosphonyl and phenyl groups pointing away from the congested area to give the (*R*,*R*)-aziridine.

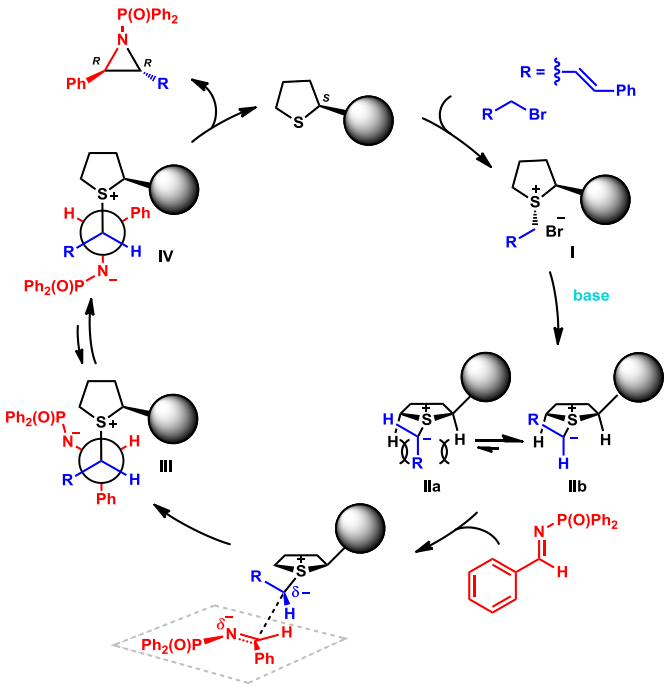
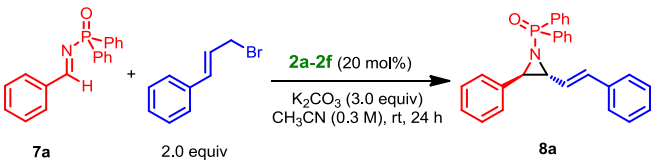


Fig. 2. Plausible mechanism of thiolane catalyzed asymmetric aziridination (arrows may be considered equilibria).

Table 1
Screening of sulfide catalysts



Entry	Sulfide	*trans*/*cis*[a]	ee %[b]	Yield %[c]
1	**2a**	66/34	89	82
2	**2b**	66/34	87	81
3	**2c**	55/45	87	63
4	**2d**	59/41	90	66
5	**2e**	61/39	89	64
6	**2f**	60/40	56	60

[a] Ratios were determined by ^1H NMR.
[b] ee of *trans* aziridine was determined by HPLC with a Chiralcel-OD column.
[c] Isolated yields of *trans* and *cis* isomers.

2.3. Screening of reaction solvents

Further optimization of **2a**-catalyzed aziridination of cinnamyl bromide and (*E*)-*N*-benzylidene-*P*,*P*-diphenylphosphinic amide (**7a**) showed that dichloromethane was a slightly better solvent

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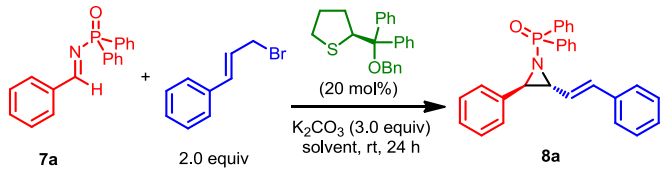
than acetonitrile (Table 2, entry 2). Reaction in THF and DMF resulted in much slower reaction rate, albeit DMF led to the highest stereoselectivity (entries 3 and 4). No reaction happened and the starting material was recovered when toluene was used (entry 5). Accordingly, dichloromethane was selected as the optimum solvent for the following experiments.

Table 2
Effect of solvent on the diastereoselectivity, enantioselectivity, and yield



Entry	Solvent	*trans*/*cis*[a]	ee (%)[b]	Yield (%)[c]
1	CH_3CN	66/34	89	82
2	CH_2Cl_2	68/32	90	78
3	THF	65/35	91	12
4	DMF	76/24	92	7
5	Toluene	N/A	N/A	0[d]

[a] Ratios were determined by ^1H NMR.
[b] ee of *trans* aziridine was determined by HPLC with a Chiralcel-OD column.
[c] Isolated yields of *trans* and *cis* isomers.
[d] No reaction.

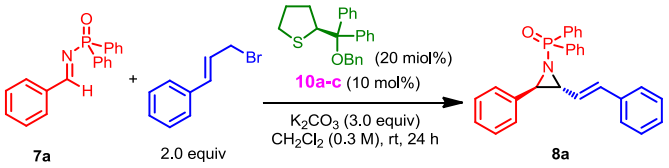
2.4. Screening of urea catalysts

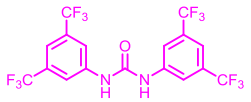
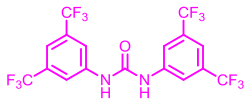
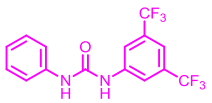
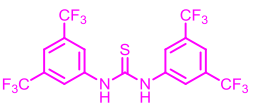
As mentioned above, Connon et al. has disclosed that *N*,*N*′-diaryl(thio)ureas, especially those incorporating electron deficient aromatic substituents, are good catalysts for the Corey–Chaykovsky reaction between trimethylsulfonium iodide and benzaldehyde. We therefore examined the compatibility of ureas **10a** and **10b**, and thiourea **10c** with the aziridination process. We were delighted to find that higher diastereoselectivity, enantioselectivity, and yield were obtained when 10–20 mol% of *N*,*N*′-bis(3,5-bis(trifluoromethyl)phenyl)urea (**10a**) was applied to the optimum protocol (Table 3, entries 2 and 3) whilst urea **10b** (entry 4), having a more electron rich phenyl group, showed a slightly negative effect to the reaction. In agreement with Connon's results, the more acidic thiourea **10c** (entry 5) was a less active catalyst than urea **10a**, which could be due to the high acidity of the thiourea derivatives relative to the sulfonium ion.

2.5. Substrate scope

Having developed a highly efficient process for asymmetric aziridination, we now turned our attention to the question of substrate scope. Gratifyingly, the dual-catalyst system catalyzed the reaction of cinnamyl bromide with various imines bearing electron deficient (**7b**–**7f**), neutral (**7a**, **7m**, **7n**), and electron rich (**7g**–**7l**, **7o**) aromatic substituents, giving diastereomer- and enantiomer-enriched aziridines in good to high yields (80–98%). Except for aziridines **8f**, **8g** and **8j** having moderate to good ee (70–80%), all other dominant *trans* products were obtained with high enantioselectivity (89–98%). Evidently, the steric effect of the *ortho* substituent of the aryl aldimines **7g** and **7j** eroded the enantioselectivity of the asymmetric aziridination. However, the reason why *para*-nitrile group was detrimental to the stereoselectivity is not clear. We have also inspected the substrate scope of the same reactions in the absence of urea **10a**. The results in Table 4 show that **10a** indeed universally promoted the asymmetric sulfonium ylide mediated aziridination in both reaction rate and stereochemical outcome. Notably, with the assistance of H-bonding catalyst **10a**, the reaction rate of the aziridination of *para*-

Table 3
Screening of urea catalysts



Entry	Urea catalyst	pK_a[a]	*trans*/*cis*[b]	ee%[c]	Yield%[d]
1	None	NA	68/32	90	78
2	 **10a**	13.8 (*Est.*)	71/29	92	80
3	 **10a** (20 mol%)	13.8 (*Est.*)	73/27	93	82
4	 **10b**	16.1	68/32	86	76
5	 **10c**	8.5	71/29	92	48

[a] Ref. 8.
[b] Ratios were determined by ^1H NMR.
[c] ee of *trans* aziridine was determined by HPLC with a Chiralcel-OD column.
[d] Isolated yields of *trans* and *cis* isomers.

substituted aryl imines **7f**, **7m**, and 2-naphthalenyl imine **7n** was doubled, and the ee of the resulting products **8f**, **8m**, and **8n** was improved by 15–22%.

3. Conclusions

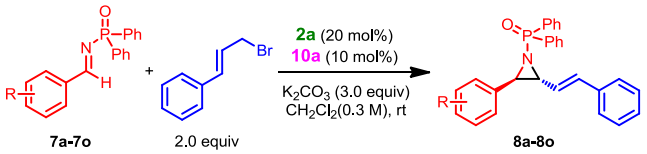
We have demonstrated that the dual catalytic system of chiral sulfide **2a** and urea **10a** is highly effective for the asymmetric imino Corey–Chaykovsky reaction of cinnamyl bromide and aryl *N*-diphenylphosphinic imines. We believe that this work should pave the way for the development of new strategies for sulfur-ylide chemistry.

4. Experimental section

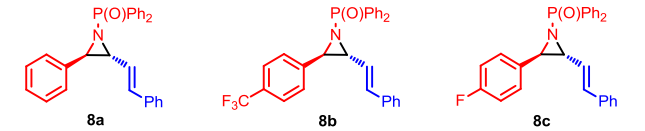
4.1. General

All reactions were carried out under an inert atmosphere unless mentioned otherwise, and standard syringe–septa techniques were followed. Solvents were freshly dried and purified by conventional methods prior to use. The progress of all the reactions were monitored by TLC, using TLC glass plates precoated with silica gel 60 F_{254} (Merck). Column chromatography was performed on silica gel Geduran® Si 60 (Merck). Optical rotation values were measured with Jasco P-2000 polarimeter, and IR spectra were recorded with Thermo Nicolet iS-5 FTIR spectrophotometer, λ_{max} in cm^{-1}. ^1H, ^{13}C and ^{31}P NMR spectra were recorded with Bruker AV-III 400 MHz, Bruker AV-400, or AV-500 MHz spectrometers and chemical shifts were measured in δ (parts per million) with residual solvent peaks as internal standards ($CDCl_3$, δ 7.26 ppm in ^1H NMR,

Table 4
Substrate scope of asymmetric aziridination



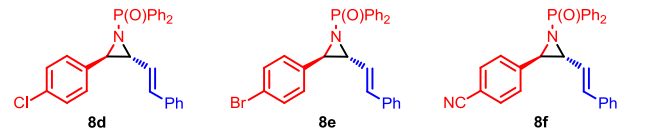
(without **10a**) yield[a], *trans/cis*[b], ee[c], reaction time
yield[a], *trans/cis*[b], ee[c], reaction time



78%, *68/32*, 90%, 1 d
80%, *71/29*, 92%, 1 d

74%, *58/42*, 87%, 2 d
80%, *65/35*, 89%, 1.5 d

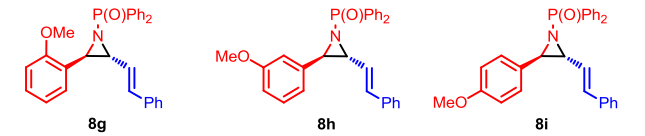
90%, *64/36*, 90%, 3.5 d
95%, *70/30*, 91%, 2 d



79%, *63/37*, 89%, 1.75 d
80%, *71/29*, 92%, 1.5 d

94%, *64/36*, 91%, 3 d
97%, *71/29*, 92%, 1 d

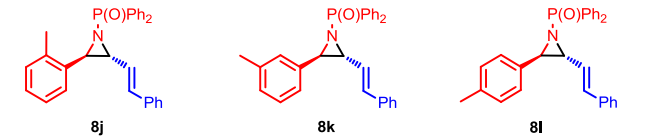
90%, *50/50*, 55%, 2 d
[d]93%, *60/40*, 70%, 17 hr



91%, *24/76*, 76%, 2.5 d
92%, *23/77*[e], 75%, 1.5 d

91%, *69/31*, 91%, 3 d
94%, *72/28*, 92%, 1.25 d

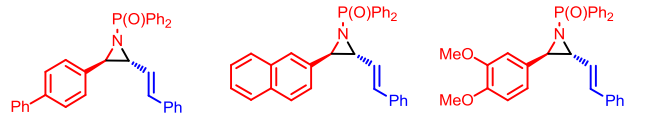
80%, *70/30*, 87%, 3 d
88%, *76/24*, 96%, 2 d



85%, *52/48*, 76%, 4 d
[d]98%, *57/43*, 80%, 1.5 d

86%, *67/33*, 92%, 3 d
92%, *72/28*, 93%, 2 d

82%, *71/29*, 90%, 2.5 d
88%, *74/26*, 91%, 1 d



73%, *65/35*, 66%, 2 d
[d]94%, *75/25*, 98%, 17 hr

86%, *68/32*, 83%, 3.5 d
88%, *76/24*, 93%, 1 d

80%, *69/31*, 91%, 8 d
95%, *77/23*, 92%, 1 d

[a] Isolated yields of *trans* and *cis* isomers.

[b] Ratios were determined by ^{1}H NMR.

[c] ee of *trans* aziridines was determined by HPLC with a Chiralcel-OD column.

[d] 20 mol% **10a** was used.

[e] 71% ee of the major *cis* isomer.

δ 77 ppm in ^{13}C NMR). Coupling constants *J*, measured in Hertz. MALDI-mass spectra were conducted on an Applied Biosystems 4800 Proteomics Analyzer (Applied Biosystem, Foster City) equipped with an Nd/YAG laser (335 nm) operating at a repetition rate of 200 Hz. HR EI (LR EI)-mass spectra were recorded on a JMS-700 double focusing mass spectrometer (JEOL, Tokyo, Japan) with a resolution of 8000(3000) (5% valley definition) and HR (LR) ESI (Electrospray)-mass spectra were recorded using dual ionization ESCi® (ESI/APCi) source options, Waters LCT premier XE (Waters Corp., Manchester, UK). Melting points were recorded on Buchi M-565 apparatus. The determination of ee was performed via chiral phase HPLC analysis using Agilent 1200 series HPLC workstation.

4.2. General procedure for the synthesis of (*S*)-2-((benzyloxy) diarylmethyl)tetrahydrothiophene 2a–2f

((*S*)-Thiolan-2-yl)diarylmethanol **1a**–**1c** were prepared according the procedures reported by our lab earlier.[2] To a stirred solution of ((*S*)-thiolan-2-yl)diarylmethanol (3.7 mmol) in DMF (7.4 mL) at 0 °C was added sodium hydride (296 mg, 7.4 mmol). The reaction mixture was warmed to room temperature and stirred for 1 h. The corresponding bromide (0.53 mL, 4.4 mmol) was then slowly added to the reaction mixture. After 16 h, the reaction mixture was quenched with satd NH_4Cl (5 mL) at 0 °C, extracted with Et_2O (5 mL×3), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (EtOAc/hexane, 1:49) to give pure product.

*4.2.1. (S)-2-((Benzyloxy)diphenylmethyl)tetrahydrothiophene (**2a**).*[2] White solid; Yield—92% (1.2 g); R_f (10% EtOAc/hexane) 0.5; Prepared as shown in general experimental procedure.; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57–7.55 (m, 2H), 7.44 (d, *J*=7.2 Hz, 2H), 7.34–7.16 (m,11H), 4.66 (t, *J*=7.2 Hz, 1H), 4.38 (d, *J*=11.6 Hz, 1H), 4.21 (d, *J*=11.5 Hz, 1H), 2.63 (m, 1H), 2.32 (ddd, *J*=10.1, 8.2, 6.1 Hz, 1H), 1.98 (td, *J*=12.7, 6.0 Hz, 1H), 1.84 (m, 1H), 1.64 (m, 1H), 1.34 (tt, *J*=11.9, 5.9 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 129.3, 128.8, 128.0, 127.4, 127.2, 127.1, 127.0, 126.9, 126.9, 85.9, 65.5, 53.8, 32.6, 31.6, 30.2.

*4.2.2. (S)-2-((Benzyloxy)bis(4-(tert-utyl)phenyl)methyl)tetrahydrothiophene (**2b**).* Colorless liquid; Yield—95% (1.7 g); R_f (2% EtOAc/hexane) 0.35; Prepared as shown in general experimental procedure; $[\alpha]_D^{30}$ 5.86 (*c* 1.0, $CHCl_3$); IR (neat): 3443, 1650, 1538, 1504, 1383, 1176, 1084, 727, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, *J*=8.3 Hz, 2H), 7.38–7.27 (m, 6H), 7.27–7.20 (m, 1H), 7.10 (dd, *J*=8.2, 5.1 Hz, 4H), 4.66 (t, *J*=7.1 Hz, 1H), 4.37 (d, *J*=11.7 Hz, 1H), 4.19 (d, *J*=11.7 Hz, 1H), 2.73–2.64 (m, 1H), 2.60 (dd, *J*=15.7, 8.0 Hz, 4H), 2.38 (ddd, *J*=10.2, 8.0, 6.2 Hz, 1H), 2.01 (td, *J*=12.9, 5.9 Hz, 1H), 1.85 (ddd, *J*=20.0, 12.9, 7.3 Hz, 1H), 1.76–1.65 (m, 1H), 1.60 (ddd, *J*=19.8, 10.3, 4.8 Hz, 4H), 1.37 (dtd, *J*=12.0, 7.4, 5.0 Hz, 5H), 0.93 (td, *J*=7.3, 3.8 Hz, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ141.9, 141.7, 140.5, 139.6, 138.7, 129.3, 128.9, 128.1, 127.4, 127.0, 127.0, 126.9, 85.9, 65.5, 54.4, 35.2, 35.2, 33.5, 33.4, 32.7, 31.8, 30.3, 29.7, 22.4, 14.0, 14.0; HRMS-ESI (*m/z*): Calcd for $C_{32}H_{40}OS$ [(M+Na)$^+$] 495.2698, found [(M+Na)$^+$] 495.2691.

*4.2.3. (S)-2-(Di([1,1′:3′,1″-terphenyl]-5′-yl) (benzyloxy)methyl)tetrahydrothiophene (**2c**).* White solid; Yield—93% (2.3 g); R_f (5% EtOAc/hexane) 0.38; Prepared as shown in general experimental procedure.; Mp 99–101 °C; $[\alpha]_D^{30}$ 7.44 (*c* 1.0, $CHCl_3$); IR (neat): 3424, 1658, 1594, 1496, 1383, 1180, 1028, 879, 758, 737, 696 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95 (d, *J*=1.6 Hz, 2H), 7.81 (dd, *J*=3.3, 1.6 Hz, 3H), 7.77 (t, *J*=1.6 Hz, 1H), 7.70–7.60 (m, 8H), 7.45 (dd, *J*=16.1, 8.6 Hz, 10H), 7.37 (dd, *J*=8.3, 6.6 Hz, 6H), 7.32–7.26 (m, 1H), 4.88 (t, *J*=7.2 Hz, 1H), 4.63 (d, *J*=11.9 Hz, 1H), 4.52 (d, *J*=11.9 Hz, 1H), 2.87–2.76 (m, 1H), 2.53 (ddd, *J*=10.2, 8.3, 6.0 Hz, 1H), 2.18 (td, *J*=12.7, 5.9 Hz, 1H), 2.10–1.98 (m, 1H), 1.87–1.73 (m, 1H), 1.64–1.53 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.3, 142.5, 141.2, 141.3, 141.1, 141.1, 140.4, 139.3, 128.7, 128.3, 127.3, 127.3, 127.1, 127.0, 126.9, 125.4, 125.1, 86.7, 66.1, 54.3, 33.1, 31.9, 30.4; MALDI (*m/z*): Calcd for $C_{48}H_{40}OS$ [(M+Na)$^+$] 687.2692, found [(M+Na)$^+$] 687.2694.

*4.2.4. (S)-2-(((4-(tert-Butyl)benzyl)oxy)diphenylmethyl)tetrahydrothiophene (**2d**).* Coloress liquid; Yield—66% (1.0 g); R_f (5% EtOAc/

hexane) 0.55; Prepared as shown in general experimental procedure.; $[\alpha]_D^{30}$ 5.41 (*c* 1.0, $CHCl_3$); IR (neat): 3441, 1650, 1540, 1443, 1383, 1077, 752, 699 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.66–7.60 (m, 2H), 7.54–7.47 (m, 2H), 7.40–7.26 (m, 8H), 7.19 (d, *J*=8.0 Hz, 2H), 4.74 (t, *J*=7.2 Hz, 1H), 4.41 (d, *J*=11.3 Hz, 1H), 4.25 (d, *J*=11.3 Hz, 1H), 2.79–2.69 (m, 1H), 2.68–2.61 (m, 2H), 2.43 (ddd, *J*=10.2, 8.1, 6.1 Hz, 1H), 2.09 (td, *J*=12.8, 5.8 Hz, 1H), 1.92 (dddd, *J*=13.0, 9.0, 7.1, 5.9 Hz, 1H), 1.83–1.69 (m, 1H), 1.69–1.59 (m, 2H), 1.51–1.34 (m, 3H), 0.98 (t, *J*=7.3 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 143.4, 142.2, 141.7, 141.7, 136.4, 135.5, 129.4, 129.0, 128.4, 128.2, 127.8, 127.5, 127.3, 127.1, 127.0, 85.9, 65.5, 53.9, 35.3, 33.6, 32.8, 31.7, 30.3, 22.3, 13.9; MALDI (*m*/*z*): Calcd for $C_{48}H_{40}OS$ [(M+Na)$^+$] 439.2066, found [(M+Na)$^+$] 439.2065.

*4.2.5. (S)-2-(((Perfluorophenyl)methoxy)diphenylmethyl)tetrahydrothiophene (**2e**).* White solid; Yield—64% (1.1 g); R_f (2% EtOAc/hexane) 0.48; Prepared as shown in general experimental procedure.; Mp 65–68 °C; $[\alpha]_D^{30}$ 6.07 (*c* 1.0, $CHCl_3$); IR (neat): 3439, 1642, 1504, 1445, 1383, 1129, 1056, 938, 755, 702 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (dt, *J*=4.5, 2.5 Hz, 2H), 7.41–7.23 (m, 8H), 4.62 (t, *J*=7.2 Hz, 1H), 4.52 (d, *J*=10.1 Hz, 1H), 4.31 (d, *J*=10.1 Hz, 1H), 2.79–2.67 (m, 1H), 2.44 (ddd, *J*=10.2, 8.3, 6.0 Hz, 1H), 1.98 (td, *J*=12.7, 5.7 Hz, 1H), 1.90–1.78 (m, 1H), 1.72 (dddd, *J*=15.1, 12.3, 8.6, 6.2 Hz, 1H), 1.48 (dt, *J*=11.6, 5.5 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 146.9, 144.4, 142.9, 141.0, 138.6, 136.2, 129.3, 128.6, 127.6, 127.6, 127.4, 127.2, 112.1, 86.5, 53.8, 53.5, 32.9, 31.5, 30.3; MALDI (*m*/*z*): Calcd for $C_{24}H_{19}OSF_5$ [(M+Na)$^+$] 473.0968, found [(M+Na)$^+$] 473.0957.

*4.2.6. (S)-2-((Diphenyl(tetrahydrothiophen-2-yl)methoxy)methyl) pyridine (**2f**).* Colorless liquid; Yield—71% (950 mg); R_f (10% EtOAc/hexane) 0.35; $[\alpha]_D^{30}$ 6.10 (*c* 1.0, $CHCl_3$); IR (neat): 3591, 3439, 1650, 1590, 1433, 1383, 1100, 756, 701 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.48 (d, *J*=4.9 Hz, 1H), 7.72 (td, *J*=7.7, 1.8 Hz, 1H), 7.64 (d, *J*=7.8 Hz, 1H), 7.58 (dt, *J*=4.6, 2.5 Hz, 2H), 7.51–7.43 (m, 2H), 7.38–7.24 (m, 6H), 7.20–7.13 (m, 1H), 4.73 (t, *J*=7.2 Hz, 1H), 4.51 (d, *J*=13.4 Hz, 1H), 4.40 (d, *J*=13.4 Hz, 1H), 2.77–2.66 (m, 1H), 2.41 (ddd, *J*=10.2, 8.1, 6.1 Hz, 1H), 2.08 (td, *J*=12.8, 5.8 Hz, 1H), 1.95–1.83 (m, 1H), 1.74 (tdd, *J*=8.7, 7.1, 4.3 Hz, 1H), 1.43 (dt, *J*=11.8, 5.7 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.4, 148.6, 142.8, 141.3, 136.5, 129.3, 129.0, 127.5, 127.5, 127.3, 127.1, 121.9, 120.8, 86.3, 66.7, 53.8, 32.7, 31.7, 30.2; MALDI (*m*/*z*): Calcd for $C_{23}H_{23}OS$ [(M+Na)$^+$] 384.1392, found [(M+Na)$^+$] 384.1396.

4.3. General procedure for the synthesis of aziridine 8a–8o

To a flame-dried Schlenk tube containing K_2CO_3(67.9 mg, 0.49 mmol), *O*-benzyl(Thiolan-2-yl)diphenylmethyl ether (11.8 mg, 0.03 mmol), 1,3-bis(3,5-bis(trifluoromethyl)phenyl)urea (7.9 mg, 0.02 mmol), corresponding imine (0.16 mmol) and dichloromethane (0.5 mL) were added at room temperature. To the resulting mixture, cinnamyl bromide (48.5 μL, 0.33 mmol) was added and the reaction was monitored by TLC. Upon completion, the reaction mixture was diluted with dichloromethane (5 mL) and filtered through Celite®. The filtrate was evaporated in vacuo to afford the crude product. The crude products were further purified by column chromatography (EtOAc/hexane, 1:3) to yield the pure corresponding aziridine.

*4.3.1. ((2R,3R)-2-Phenyl-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8a**).* White solid; Yield—80% (55 mg); R_f (30% EtOAc/hexane) 0.43; Prepared as shown in general experimental procedure.; Mp 151–152 °C; $[\alpha]_D^{26}$ −55.87 (*c* 1.0, $CHCl_3$); IR (neat): 3061, 1637, 1454, 1437, 1193, 1124, 1070, 967, 934, 752, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.87 (m, 4H), 7.44–7.20 (m, 16H), 6.73 (dd, *J*=16.0, 9.6 Hz, 1H), 6.50 (d, *J*=16.0 Hz, 1H), 4.03 (dd, *J*=16.0, 2.8 Hz, 1H), 3.31 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2 (d, J_{C-P}=3.4 Hz), 136.3, 134.8, 133.8 (d, J_{C-P}=48.1 Hz), 132.6 (d, J_{C-P}=42.6 Hz), 131.7, 131.6, 131.5, 131.4, 128.5 (d, J_{C-P}=2.2 Hz), 128.4, 128.3, 128.3, 128.2, 127.7 (d, J_{C-P}=1.8 Hz), 126.4, 126.1, 125.9 (d, J_{C-P}=7.4 Hz), 52.4 (d, J_{C-P}=7.8 Hz), 43.7 (d, J_{C-P}=5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.77; HRMS-ESI (*m*/*z*): Calcd for $C_{28}H_{24}NOP$ [(M+Na)$^+$] 444.1493, found [(M+Na)$^+$] 444.1499; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 20/1); retention time: 10.5 min (enantiomer) and 20.8 min (major).

*4.3.1.1. cis-**8a**.* White foam; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.93 (m, 4H), 7.52–7.16 (m, 16H), 6.63 (d, *J*=15.9 Hz, 1H), 5.78 (dd, *J*=15.9, 8.4 Hz, 1H), 4.17 (dd, *J*=16.5, 6.2 Hz, 1H), 3.76–3.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.4, 135.5, 134.8 (d, J_{C-P}=4.5 Hz), 133.0 (d, J_{C-P}=37.7 Hz), 132.0, 131.7, 131.6, 131.5, 128.6, 128.5, 128.5, 128.4, 128.2, 127.8, 127.6, 126.4, 123.7 (d, J_{C-P}=4.8 Hz), 43.5 (d, J_{C-P}=22.3 Hz), 42.7 (d, J_{C-P}=24.6 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.40; HRMS-MALDI (*m*/*z*): Calcd for $C_{28}H_{24}NOP$ [(M+H)$^+$] 422.1668, found [(M+H)$^+$] 422.1656.

*4.3.2. ((2R,3R)-2-((E)-Styryl)-3-(4-(trifluoromethyl)phenyl)aziridin-1-yl)diphenylphosphine oxide (**8b**).* White solid; Yield—80% (52 mg); R_f (50% EtOAc/hexane) 0.45; Prepared as shown in general experimental procedure.; Mp 152–156 °C; $[\alpha]_D^{26}$ −36.59 (*c* 1.0, $CHCl_3$); IR (neat): 3058, 1619, 1438, 1324, 1166, 1123, 932, 826, 728, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.95–7.87 (m, 4H), 7.60–7.58 (m, 2H), 7.47–7.26 (m, 13H), 6.71 (dd, *J*=16.0, 9.6 Hz, 1H), 6.52 (d, *J*=16.0 Hz, 1H), 4.06 (dd, *J*=15.6, 2.8 Hz, 1H), 3.30 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 141.4, 136.1, 135.3, 133.5 (d, J_{C-P}=60.3 Hz), 132.5, 131.9, 131.6, 131.5, 131.5, 131.4, 130.0 (q, J_{C-F}=32.1 Hz), 128.5, 128.4, 128.3, 128.0, 126.4 (d, J_{C-P}=2.1 Hz), 125.5 (d, J_{C-P}=3.3 Hz), 125.2 (d, J_{C-P}=7.2 Hz), 121.3 (d, J_{C-F}=270.4 Hz), 52.7 (d, J_{C-P}=7.6 Hz), 43.0 (d, J_{C-P}=4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.89; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{23}NOPF_3$ [(M+Na)$^+$] 512.1367, found [(M+Na)$^+$] 512.1372; enantioselectivity was determined by HPLC analysis (Chiralcel-AD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 4/1); retention time: 12.1 min (enantiomer) and 24.8 min (major).

*4.3.2.1. cis-**8b**.* White foam; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.92 (m, 4H), 7.59–7.45 (m, 9H), 7.26–7.17 (m, 6H), 6.66 (d, *J*=15.8 Hz, 1H), 5.72 (dd, *J*=15.8, 8.3 Hz, 1H), 4.19 (dd, *J*=16.2, 5.9 Hz, 1H), 3.81–3.74 (m, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.0, 136.2, 136.0, 132.5, 132.2, 131.7, 131.6, 131.5, 131.4, 129.8 (q, J_{C-F}=32.3 Hz), 128.6 (d, J_{C-P}=3.8 Hz), 128.5, 128.1, 127.9, 126.3, 125.2 (d, J_{C-P}=3.1 Hz), 122.6 (d, J_{C-P}=4.6 Hz), 43.7 (d, J_{C-P}=5.3 Hz), 42.1 (d, J_{C-P}=5.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.47; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{23}NOPF_3$ [(M+H)$^+$] 490.1542, found [(M+H)$^+$] 490.1539.

*4.3.3. ((2R,3R)-2-(4-Fluorophenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8c**).* White solid; Yield—95% (65 mg); R_f (30% EtOAc/hexane) 0.30; Prepared as shown in general experimental procedure.; Mp 147–150 °C; $[\alpha]_D^{23}$ −57.48 (*c* 1.0, $CHCl_3$); IR(neat): 3058, 1606, 1511, 1438, 1193, 1125, 932, 840, 753, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.85 (m, 4H), 7.43–7.22 (m, 13H), 7.02 (t, *J*=8.4 Hz, 2H), 6.68 (dd, *J*=16.0, 9.6 Hz, 1H), 6.50 (d, *J*=15.6 Hz, 1H), 3.98 (dd, *J*=16.0, 2.8 Hz, 1H), 3.27 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.4 (d, J_{C-F}=244.7 Hz), 136.2, 134.9, 133.7 (d, J_{C-P}=61.0 Hz), 132.9, 132.4 (d, J_{C-P}=55.5 Hz), 131.7, 131.6, 131.5 (d, J_{C-P}=6.8 Hz), 131.4, 128.5, 128.4, 128.3 (d, J_{C-P}=4.1 Hz), 128.2, 127.7, 127.6, 126.4, 125.6 (d, J_{C-P}=7.3 Hz), 115.4 (d, J_{C-P}=21.6 Hz), 52.3 (d, J_{C-P}=7.7 Hz), 43.0 (d, J_{C-P}=5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.81; HRMS-ESI (*m*/*z*): Calcd for $C_{28}H_{23}NOPF$ [(M+Na)$^+$] 462.1399, found [(M+Na)$^+$] 462.1400; enantioselectivity was

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determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 6.9 min (enantiomer) and 21.0 min (major).

*4.3.3.1. cis-**8c**.* White foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.91 (m, 4H), 7.51–7.40 (m, 6H), 7.35–7.31 (m, 2H), 7.27–7.17 (m, 5H), 7.02–6.98 (m, 2H), 6.63 (d, J=15.9 Hz, 1H), 5.75 (dd, J=15.9, 8.4 Hz, 1H), 4.13 (dd, J=16.6, 6.1 Hz, 1H), 3.75–3.67 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.2 (d, $J_{C\text{-}F}$=244.5 Hz), 136.2, 135.7, 132.8 (d, J_{C-P}=5.2 Hz), 132.0, 131.7, 131.6, 131.5, 131.4, 130.5, 129.1 (d, J_{C-P}=8.0 Hz), 128.6, 128.5, 128.5, 128.5, 128.4, 127.9, 126.3, 123.2, (d, J_{C-P}=4.7 Hz), 115.2 (d, J_{C-P}=21.5 Hz), 43.4 (d, J_{C-P}=5.5 Hz), 42.0 (d, J_{C-P}=6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.40; HRMS-MALDI (*m*/*z*): Calcd for $C_{28}H_{23}NOPF$ [(M+H)$^+$] 440.1574, found [(M+H)$^+$] 440.1554.

*4.3.4. ((2R,3R)-2-(4-Chlorophenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8d**).* White solid; Yield—90% (60 mg); R_f (50% EtOAc/hexane) 0.33; Prepared as shown in general experimental procedure.; Mp 141–145 °C; $[\alpha]_D^{27}$ −35.08 (*c* 1.0, $CHCl_3$); IR (neat): 3058, 1596, 1493, 1192, 1124, 932, 838, 753, 693, 539 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89–7.85 (m, 4H), 7.44–7.22 (m, 16H), 6.68 (dd, J=16.0, 9.6 Hz, 1H), 6.50 (d, J=16.0 Hz, 1H), 3.98 (dd, J=16.0, 2.8 Hz, 1H), 3.27 (ddd, J=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.8, 135.1, 133.6 (d, J_{C-P}=59.5 Hz), 133.5, 132.4 (d, J_{C-P}=54.1 Hz), 131.8, 131.7, 131.5 (d, J_{C-P}=4.6 Hz), 131.4, 128.5, 128.3, 128.2, 127.8, 127.5, 126.4, 125.5 (d, J_{C-P}=7.3 Hz), 52.4 (d, J_{C-P}=7.8 Hz), 43.0 (d, J_{C-P}=5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.87; HRMS-ESI (*m*/*z*): Calcd for $C_{28}H_{23}NOPCl$ [(M+H)$^+$] 456.1284, found [(M+H)$^+$] 456.1277; enantioselectivity was determined by HPLC analysis (Chiralcel-AD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 4/1); retention time: 15.7 min (enantiomer) and 33.4 min (major).

*4.3.4.1. cis-**8d**.* White foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02–7.92 (m, 4H), 7.51–7.39 (m, 6H), 7.33–7.18 (m, 9H), 6.64 (d, J=15.9 Hz, 1H), 5.76 (dd, J=16.1, 8.5 Hz, 1H), 4.13 (dd, J=16.2, 6.1 Hz, 1H), 3.78–3.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.8, 133.3, 132.0, 131.6, 131.5 (d, J_{C-P}=5.7 Hz), 131.4, 128.8, 128.5 (d, J_{C-P}=3.6 Hz), 128.4, 128.4, 128.4, 127.9, 126.3, 122.9, (d, J_{C-P}=4.4 Hz), 43.5 (d, J_{C-P}=5.4 Hz), 42.0 (d, J_{C-P}=5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.42; HRMS-MALDI (*m*/*z*): Calcd for $C_{28}H_{23}NOPCl$ [(M+H)$^+$] 456.1279, found [(M+H)$^+$] 456.1285.

*4.3.5. ((2R,3R)-2-(4-Bromophenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8e**).* White solid; Yield—97% (64 mg); R_f (30% EtOAc/hexane) 0.48 Prepared as shown in general experimental procedure.; Mp 150–153 °C; $[\alpha]_D^{26}$ −3.55 (*c* 1.0, $CHCl_3$); IR (neat): 3439, 1642, 1484, 1383, 1180, 1124, 923, 757, 729, 690, 593 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92–7.84 (m, 4H), 7.46–7.21 (m, 15H), 6.67 (dd, J=16.0, 9.6 Hz, 1H), 6.50 (d, J=15.6 Hz, 1H), 3.96 (dd, J=16.0, 2.8 Hz, 1H), 3.26 (ddd, J=12.0, 9.2, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 136.1, 135.0, 133.5 (d, J_{C-P}=61.0 Hz), 132.3 (d, J_{C-P}=55.7 Hz), 131.7, 131.6, 131.5 (d, J_{C-P}=3.7 Hz), 131.3, 128.4, 128.3, 128.2, 127.7, 126.4, 125.4 (d, J_{C-P}=7.3 Hz), 121.5, 52.3 (d, J_{C-P}=7.7 Hz), 43.0 (d, J_{C-P}=5.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.45; HRMS-MALDI (*m*/*z*): Calcd for $C_{28}H_{23}NOPBr$[(M+H)$^+$] 500.0773, found [(M+H)$^+$] 500.0771; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 6.8 min (enantiomer) and 26.9 min (major).

*4.3.5.1. cis-**8e**.* White foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01–7.91 (m, 4H), 7.50–7.39 (m, 8H), 7.26–7.17 (m, 7H), 6.64 (d, J=15.9 Hz, 1H), 5.75 (dd, J=15.9, 8.3 Hz, 1H), 4.11 (dd, J=16.4, 6.1 Hz, 1H), 3.78–3.70 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.1, 135.9, 133.9 (d, J_{C-P}=4.2 Hz), 132.7, 132.0, 131.6 (d, J_{C-P}=9.5 Hz), 131.4 (d, J_{C-P}=9.2 Hz), 131.3, 129.2, 128.4, 127.9, 126.3, 122.9, (d, J_{C-P}=4.4 Hz), 121.5, 43.4 (d, J_{C-P}=5.4 Hz), 42.0 (d, J_{C-P}=5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.46; HRMS-MALDI (*m*/*z*): Calcd for $C_{28}H_{23}NOPBr$ [(M+H)$^+$] 500.0773, found [(M+H)$^+$] 500.0772.

*4.3.6. 4-((2R,3R)-1-(Diphenylphosphoryl)-3-((E)-styryl)aziridin-2-yl)benzonitrile (**8f**).* White solid; Yield—93% (63 mg); R_f (30% EtOAc/hexane) 0.33 Prepared as shown in general experimental procedure.; Mp 181–182 °C; $[\alpha]_D^{29}$ −10.28 (*c* 1.0, $CHCl_3$); IR (neat): 3050, 2226, 1640, 1609, 1438, 1194, 1124, 930, 827, 754, 693, 597 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.90–7.84 (m, 4H), 7.63–7.61 (m, 2H), 7.46–7.41 (m, 4H),7.39–7.30 (m, 4H), 7.28–7.23 (m, 5H), 6.68 (dd, J=16.0, 9.6 Hz, 1H), 6.52 (d, J=16.0 Hz, 1H), 4.03 (dd, J=15.6, 2.8 Hz, 1H), 3.29 (ddd, J=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 142.8, 135.9, 135.6, 133.3 (d, J_{C-P}=67.8 Hz), 132.2, 132.0 (d, J_{C-P}=64.2 Hz), 131.9, 131.7, 131.4, 131.3, 128.5, 128.4 (d, J_{C-P}=2.4 Hz), 128.3, 128.0, 126.8, 126.4, 124.9 (d, J_{C-P}=7.1 Hz), 118.6, 111.5, 52.9 (d, J_{C-P}=7.6 Hz), 42.9 (d, J_{C-P}=4.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.89; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{23}N_2OP$ [(M+H)$^+$] 447.1620, found [(M+H)$^+$] 447.1628; enantioselectivity was determined by HPLC analysis (Chiralcel-AS, 0.7 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 19.8 min (major) and 24.8 min (enantiomer).

*4.3.6.1. cis-**8f**.* White solid; Mp 52–54 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.90 (m, 4H), 7.61–7.59 (m, 2H), 7.54–7.40 (m, 8H), 7.27–7.19 (m, 3H), 7.17–7.15 (m, 2H), 6.65 (d, J=15.9 Hz, 1H), 5.67 (dd, J=15.9, 8.3 Hz, 1H), 4.16 (dd, J=16.0, 6.1 Hz, 1H), 3.82–3.75 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5 (d, J_{C-P}=4.5 Hz),136.4, 135.9, 132.4 (d, J_{C-P}=10.5 Hz), 132.2, 132.0, 131.6, 131.5 (d, J_{C-P}=6.3 Hz), 131.4, 131.1 (d, J_{C-P}=11.8 Hz), 128.6, 128.5, 128.3, 128.1, 126.3, 122.2, (d, J_{C-P}=4.6 Hz), 118.6, 111.5, 43.8 (d, J_{C-P}=5.5 Hz), 42.1 (d, J_{C-P}=5.7 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.46; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{23}N_2OP$ [(M+H)$^+$] 447.1621, found [(M+H)$^+$] 447.1630.

*4.3.7. ((2R,3R)-2-(2-Methoxyphenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8g**).* Colorless liquid; Yield—92% (62 mg); R_f (30% EtOAc/hexane) 0.30; Prepared as shown in general experimental procedure.; $[\alpha]_D^{27}$ −62.34 (*c* 0.9, $CHCl_3$); IR (neat): 3056, 1587, 1494, 1438, 1247, 1194, 1124, 935, 754, 693 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95–7.91 (m, 4H), 7.41–7.20 (m, 13H), 6.94 (t, J=7.6 Hz, 1H), 6.81 (d, J=8.0 Hz, 1H), 6.73 (dd, J=16.0, 9.6 Hz, 1H), 6.49 (d, J=16.0 Hz, 1H), 4.41 (dd, J=16.0, 2.8 Hz, 1H), 3.69 (s, 3H), 3.25 (ddd, J=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.3, 136.5, 134.4, 134.2 (d, J_{C-P}=54.7 Hz), 132.9 (d, J_{C-P}=49.2 Hz), 131.8, 131.7, 131.6, 131.5, 128.5, 128.4, 128.3 (d, J_{C-P}=4.6 Hz), 128.1 (d, J_{C-P}=4.4 Hz), 127.6, 126.5, 126.4, 125.6, 120.4, 110.2, 55.2, 51.5 (d, J_{C-P}=7.6 Hz), 39.4 (d, J_{C-P}=5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.53; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{26}NO_2P$ [(M+H)$^+$] 452.1799, found [(M+H)$^+$] 452.1781; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 9.1 min (enantiomer) and 13.7 min (major).

*4.3.7.1. cis-**8g**.* White solid; Mp 53–56 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.04–7.94 (m, 4H), 7.49–7.39 (m, 7H), 7.26–7.16 (m, 6H), 6.93 (t, J=7.2 Hz, 1H), 6.80 (d, J=8.0 Hz, 1H), 6.63 (d, J=16.0 Hz, 1H), 5.76 (dd, J=15.9, 8.4 Hz, 1H), 4.37 (dd, J=16.4, 6.2 Hz, 1H), 3.82–3.74 (m, 1H), 3.18 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.4, 136.5, 135.0, 133.2 (d, J_{C-P}=42.0 Hz), 132.0, 131.9, 131.8 (d, J_{C-P}=4.4 Hz), 131.6 (d, J_{C-P}=3.3 Hz), 131.5, 128.5, 128.4, 128.3, 127.9, 127.6, 126.3, 124.0 (d, J_{C-P}=4.7 Hz), 123.3 (d, J_{C-P}=4.7 Hz), 119.9, 110.1, 55.2, 43.8 (d, J_{C-P}=5.5 Hz), 39.5 (d, J_{C-P}=5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.28; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{26}NO_2P$ [(M+H)$^+$] 452.1774, found [(M+H)$^+$] 452.1794.

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*4.3.8. ((2R,3R)-2-(3-Methoxyphenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8h**).* White solid; Yield—94% (63 mg); R_f (50% EtOAc/hexane) 0.50; Prepared as shown in general experimental procedure.; Mp 145–146 °C; $[\alpha]_D^{26}$ −48.63 (*c* 1.0, $CHCl_3$); IR (neat): 3056, 1601, 1491, 1438, 1198, 1124, 936, 753, 695 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.93–7.88 (m, 4H), 7.43–7.21 (m, 12H), 6.95 (d, *J*=7.6 Hz, 1H), 6.88 (s, 1H), 6.82 (dd, *J*=8.0, 2.4 Hz, 1H), 6.69 (dd, *J*=16.0, 9.6 Hz, 1H), 6.49 (d, *J*=16.0 Hz, 1H), 3.99 (dd, *J*=16.0, 2.8 Hz, 1H), 3.79 (s, 3H), 3.29 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.8, 138.9 (d, J_{C-P}=3.5 Hz), 136.2, 134.8, 133.8 (d, J_{C-P}=54.9 Hz), 132.5 (d, J_{C-P}=49.4 Hz), 131.7, 131.6, 131.5, 131.4, 129.5, 128.4, 128.4, 128.3 (d, J_{C-P}=2.7 Hz), 128.2, 127.7, 126.4, 125.8 (d, J_{C-P}=7.4 Hz), 118.5, 113.3, 111.5, 55.2, 52.2 (d, J_{C-P}=7.8 Hz), 43.6 (d, J_{C-P}=5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.81; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{26}NO_2P$ [(M+Na)$^+$] 474.1599, found [(M+Na)$^+$] 474.1598; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 7.8 min (enantiomer) and 12.5 min (major).

*4.3.8.1. cis-**8h**.* Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.93 (m, 4H), 7.50–7.39 (m, 6H), 7.26–7.18 (m, 6H), 6.98 (d, *J*=7.6 Hz, 1H), 6.91 (d, *J*=1.9 Hz, 1H), 6.80 (dd, *J*=8.1, 2.5 Hz, 1H), 6.64 (d, *J*=15.9 Hz, 1H), 5.81 (dd, *J*=15.8, 8.4 Hz, 1H), 4.15 (dd, *J*=16.3, 6.2 Hz, 1H), 3.76 (s, 3H), 3.74–3.68 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 136.5 (d, J_{C-P}=4.5 Hz), 136.4, 135.5, 133.0, 131.9, 131.7, 131.6, 131.5, 129.2, 128.5, 128.5, 128.4, 128.4, 127.8, 126.3, 123.7 (d, J_{C-P}=4.4 Hz), 119.9, 113.1 (d, J_{C-P}=4.9 Hz), 55.2, 43.5 (d, J_{C-P}=5.6 Hz), 42.6 (d, J_{C-P}=6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.28; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{26}NO_2P$ [(M+H)$^+$] 452.1774, found [(M+H)$^+$] 452.1782.

*4.3.9. ((2R,3R)-2-(4-Methoxyphenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphineoxide (**8i**).* White solid; Yield—88% (59 mg); R_f (50% EtOAc/hexane) 0.50; Prepared as shown in general experimental procedure.; Mp 149–152 °C; $[\alpha]_D^{26}$ −42.02 (*c* 0.8, $CHCl_3$); IR (neat): 3050, 1612, 1514, 1438, 1302, 1250, 933, 836, 752, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.86 (m, 4H), 7.42–7.21 (m, 13H), 6.88–6.86 (m, 2H), 6.70 (dd, *J*=16.0, 9.6 Hz, 1H), 6.49 (d, *J*=15.6 Hz, 1H), 3.97 (dd, *J*=16.0, 2.8 Hz, 1H), 3.80 (s, 3H), 3.28 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.3, 136.4, 134.6, 133.9 (d, J_{C-P}=53.2 Hz), 132.7 (d, J_{C-P}=47.7 Hz), 131.7, 131.6, 131.5, 131.4, 129.2 (d, J_{C-P}=3.6 Hz), 128.5, 128.4, 128.3 (d, J_{C-P}=3.2 Hz), 128.2, 127.7, 127.3, 126.4, 126.0 (d, J_{C-P}=7.4 Hz), 114.0, 55.3, 52.1 (d, J_{C-P}=7.8 Hz), 43.5 (d, J_{C-P}=5.3 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.79; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{26}NO_2P$ [(M+H)$^+$] 452.1779, found [(M+H)$^+$] 452.1782; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 7.5 min (enantiomer) and 22.7 min (major).

*4.3.9.1. cis-**8i**.* Colorless liquid; ^1H NMR (400 MHz, $CDCl_3$) δ 8.00–7.91 (m, 4H), 7.50–7.40 (m, 5H), 7.30–7.17 (m, 8H), 6.86–6.84 (m, 2H), 6.62 (d, *J*=16.0 Hz, 1H), 5.80 (dd, *J*=16.0, 8.4 Hz, 1H), 4.11 (dd, *J*=16.0, 6.8 Hz, 1H), 3.79 (s, 3H), 3.72–3.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 136.4, 135.4, 131.9, 131.7, 131.6 (d, J_{C-P}=4.5 Hz), 131.5, 128.6, 128.4, 127.8, 126.8 (d, J_{C-P}=5.3 Hz), 126.3, 123.8 (d, J_{C-P}=6.4 Hz), 113.7, 55.2, 43.5 (d, J_{C-P}=5.4 Hz), 42.3 (d, J_{C-P}=6.8 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.30; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{26}NO_2P$ [M$^+$] 451.1696, found [M$^+$] 451.1698.

*4.3.10. ((2R,3R)-2-((E)-Styryl)-3-(o-tolyl)aziridin-1-yl)diphenylphosphine oxide (**8j**).* White solid; Yield—95% (65 mg); R_f (30% EtOAc/hexane) 0.40 Prepared as shown in general experimental procedure.; Mp 144–146 °C; $[\alpha]_D^{26}$ −72.29 (*c* 1.0, $CHCl_3$); IR(neat): 3075, 3058, 1642, 1633, 1438, 1380, 1195, 1124, 951, 933, 751, 729, 693, 593 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.96 (m, 4H), 7.46–7.10 (m, 15H), 6.77 (dd, *J*=15.6, 9.6 Hz, 1H), 6.51 (d, *J*=16.0 Hz, 1H), 4.17 (dd, *J*=16.0, 2.8 Hz, 1H), 3.20 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.7, 136.3, 135.5 (d, J_{C-P}=3.4 Hz), 132.7, 133.8 (d, J_{C-P}=75.6 Hz), 132.6 (d, J_{C-P}=70.6 Hz), 131.7, 131.7, 131.6, 131.5, 129.8, 128.4, 128.4 (d, J_{C-P}=6.9 Hz), 128.2 (d, J_{C-P}=6.4 Hz), 127.7, 127.3, 126.4, 126.0 (d, J_{C-P}=7.7 Hz), 126.0, 124.7, 51.6 (d, J_{C-P}=7.6 Hz), 42.0 (d, J_{C-P}=5.0 Hz), 19.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.69; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{26}NOP$[(M+Na)$^+$] 458.1674, found [(M+Na)$^+$] 458.1665; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 5.2 min (enantiomer) and 7.9 min (major).

*4.3.10.1. cis-**8j**.* White foam; ^1H NMR (400 MHz, $CDCl_3$) δ 8.04–7.96 (m, 4H), 7.51–7.42 (m, 6H), 7.37–7.35 (m, 1H), 7.26–7.08 (m, 8H), 6.64 (d, *J*=16.0 Hz, 1H), 5.61 (dd, *J*=16.0, 8.7 Hz, 1H), 4.18 (dd, *J*=16.2, 6.1 Hz, 1H), 3.84–3.76 (m, 1H), 2.30 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.8, 136.3, 135.3, 133.1 (d, J_{C-P}=4.6 Hz), 132.9 (d, J_{C-P}=9.6 Hz), 132.0, 131.8, 131.7, 131.6, 131.5, 129.7, 128.5 (d, J_{C-P}=6.4 Hz), 128.4, 128.4, 127.8, 127.4, 126.3, 123.8 (d, J_{C-P}=4.8 Hz), 43.1 (d, J_{C-P}=5.5 Hz), 41.7 (d, J_{C-P}=6.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.60; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{26}NOP$ [(M+H)$^+$] 436.1825, found [(M+H)$^+$] 436.1823.

*4.3.11. ((2R,3R)-2-((E)-Styryl)-3-(m-tolyl)aziridin-1-yl)diphenylphosphine oxid (**8k**).* White solid; Yield—92% (63 mg); R_f (30% EtOAc/hexane) 0.38 Prepared as shown in general experimental procedure. Mp 144–146 °C; $[\alpha]_D^{29}$ −74.95 (*c* 1.0, $CHCl_3$); IR (neat): 3057, 1640, 1608, 1438, 1197, 1124, 937, 753, 716, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.88 (m, 4H), 7.43–7.20 (m, 12H), 7.15 (d, *J*=7.6 Hz, 2H), 7.09 (d, *J*=7.2 Hz, 1H), 6.70 (dd, *J*=16.0, 9.6 Hz, 1H), 6.49 (d, *J*=15.6 Hz, 1H), 3.98 (dd, *J*=15.6, 2.8 Hz, 1H), 3.29 (ddd, *J*=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.2, 137.2, 136.4, 134.7, 134.0 (d, J_{C-P}=50.0 Hz), 132.7 (d, J_{C-P}=44.1 Hz), 131.8, 131.6, 131.6, 131.5, 128.5, 128.3 (d, J_{C-P}=4.3 Hz), 128.2, 127.7, 127.0, 126.4, 126.0 (d, J_{C-P}=7.3 Hz), 121.1, 52.3 (d, J_{C-P}=7.8 Hz), 43.8, 21.4; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.79; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{26}NOP$ [(M+Na)$^+$] 458.1650, found [(M+Na)$^+$] 458.1653; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 6.3 min (enantiomer) and 12.1 min (major).

*4.3.11.1. cis-**8k**.* White foam; ^1H NMR (400 MHz, $CDCl_3$) δ 8.01–7.93 (m, 4H), 7.48–7.41 (m, 6H), 7.26–7.14 (m, 8H), 7.07–7.06 (m, 1H), 6.63 (d, *J*=15.9 Hz, 1H), 5.80 (dd, *J*=16.0, 8.6 Hz, 1H), 4.14 (dd, *J*=16.5, 6.1 Hz, 1H), 3.75–3.67 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.8, 136.4, 135.5, 134.7 (d, J_{C-P}=4.4 Hz), 132.9 (d, J_{C-P}=10.6 Hz), 131.9, 131.8, 131.7, 131.6, 131.5, 128.5, 128.4, 128.4, 128.3, 128.0, 127.8, 126.3, 124.4, 123.8 (d, J_{C-P}=4.8 Hz), 43.5 (d, J_{C-P}=5.5 Hz), 42.6 (d, J_{C-P}=6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.40; HRMS-MALDI (*m*/*z*): Calcd for $C_{29}H_{26}NOP$ [(M+H)$^+$] 436.1825, found [(M+H)$^+$] 436.1826.

*4.3.12. ((2R,3R)-2-((E)-Styryl)-3-(p-tolyl)aziridin-1-yl)diphenylphosphine oxide (**8l**).* White solid; Yield—88% (60 mg); R_f (30% EtOAc/hexane) 0.40 Prepared as shown in general experimental procedure.; Mp 146–148 °C; $[\alpha]_D^{26}$ −43.98 (*c* 1.0, $CHCl_3$); IR (neat): 3056, 3026, 1682, 1574, 1493, 1392, 1193, 932, 829, 751, 693 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 7.92–7.87 (m, 4H), 7.42–7.12 (m, 13H), 7.15–7.13 (m, 2H) 6.70 (dd, *J*=16.0, 9.6 Hz, 1H), 6.48 (d, *J*=15.6 Hz, 1H), 3.98 (dd, *J*=16.0, 2.8 Hz, 1H), 3.27 (ddd, *J*=12.3, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.4, 136.3, 134.6, 133.9 (d, J_{C-P}=48.4 Hz), 132.6 (d, J_{C-P}=42.8 Hz), 131.7, 131.6, 131.5, 131.4, 129.2, 128.4, 128.4, 128.4, 128.3, 128.2, 128.1, 127.6, 126.4, 126.0, 52.3 (d, J_{C-P}=7.8 Hz), 43.6 (d, J_{C-P}=5.2 Hz), 21.1; ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.79; HRMS-ESI (*m*/*z*): Calcd for $C_{29}H_{26}NOP$ [(M+H)$^+$] 436.1830, found [(M+H)$^+$] 436.1825; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm,

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hexane/*i*-PrOH 100/7); retention time: 7.2 min (enantiomer) and 20.2 min (major).

*4.3.12.1. cis-**8l**.* White foam; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.91 (m, 4H), 7.50–7.38 (m, 6H), 7.27–7.17 (m, 7H), 7.11 (d, J=7.9 Hz, 1H), 6.62 (d, J=16.0 Hz, 1H), 5.80 (dd, J=15.9, 8.5 Hz, 1H), 4.13 (dd, J=16.4, 6.2 Hz, 1H), 3.73–3.65 (m, 1H), 2.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 137.2, 136.4, 135.4, 133.0 (d, J_{C-P}=11.0 Hz), 131.9, 131.7, 131.6, 131.5, 128.9, 128.5, 128.5, 128.4, 128.3, 127.7, 127.4, 126.3, 123.8 (d, J_{C-P}=4.7 Hz), 43.5 (d, J_{C-P}=5.6 Hz), 42.5 (d, J_{C-P}=6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.36; HRMS-MALDI (m/z): Calcd for $C_{29}H_{26}NOP$ [(M+H)$^+$] 436.1825, found [(M+H)$^+$] 436.1831.

*4.3.13. ((2R,3R)-2-([1,1′-Biphenyl]-4-yl)-3-((E)-styryl)aziridin-1-yl) diphenylphosphine oxide (**8m**).* White solid; Yield—91% (59 mg); R_f (30% EtOAc/hexane) 0.35 Prepared as shown in general experimental procedure.; Mp 155–158 °C; $[\alpha]_D^{27}$ −6.16 (c 1.0, $CHCl_3$); IR (neat): 3052, 1642, 1492, 1439, 1194, 1124, 932, 845, 756, 692, 602 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ7.93–7.90 (m, 4H), 7.60–7.56 (m, 4H), 7.46–7.20 (m, 16H), 6.72 (dd, J=16.0, 9.6 Hz, 1H), 6.51 (d, J=15.6 Hz, 1H), 4.06 (dd, J=16.0, 2.8 Hz, 1H), 3.34 (ddd, J=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.6 (d, J_{C-P}=6.8 Hz), 136.3, 134.8, 133.8 (d, J_{C-P}=51.4 Hz), 132.5 (d, J_{C-P}=45.8 Hz), 131.7, 131.6 (d, J_{C-P}=3.7 Hz), 131.5, 131.4, 128.8, 128.4 (d, J_{C-P}=3.0 Hz), 128.3, 128.2, 127.7, 127.3, 127.2, 127.0, 126.5, 126.4, 125.8 (d, J_{C-P}=7.3 Hz), 52.4 (d, J_{C-P}=7.8 Hz), 43.5 (d, J_{C-P}=5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.85; HRMS-ESI (m/z): Calcd for $C_{34}H_{28}NOP$ [(M+Na)$^+$] 520.1806, found [(M+Na)$^+$] 520.1807; enantioselectivity was determined by HPLC analysis (Chiralcel-OD, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 4/1); retention time: 5.6 min (enantiomer) and 20.7 min (major).

*4.3.13.1. cis-**8m**.* White solid; Mp 56–60 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03–7.95 (m, 4H), 7.60–7.53 (m, 4H), 7.48–7.40 (m, 8H), 7.36–7.32 (m, 1H), 7.26–7.17 (m, 5H), 6.66 (d, J=15.9 Hz, 1H), 5.85 (dd, J=15.9, 8.5 Hz, 1H), 4.21 (dd, J=16.4, 6.1 Hz, 1H), 3.80–3.72 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 140.5 (d, J_{C-P}=22.3 Hz), 136.3, 135.6, 133.9 (d, J_{C-P}=4.7 Hz), 133.0 (d, J_{C-P}=7.5 Hz), 132.0, 131.7, 131.6, 131.5, 128.7, 128.6, 128.5, 128.0, 127.8, 127.3 (d, J_{C-P}=7.5 Hz), 126.3, 123.8 (d, J_{C-P}=4.7 Hz), 43.6 (d, J_{C-P}=5.6 Hz), 42.5 (d, J_{C-P}=6.0 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.41; HRMS-MALDI (m/z): Calcd for $C_{34}H_{28}NOP$ [(M+H)$^+$] 498.1981, found [(M+H)$^+$] 498.1968.

*4.3.14. ((2R,3R)-2-(Naphthalen-2-yl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8n**).* White solid; Yield—88% (58 mg); R_f (30% EtOAc/hexane) 0.45 Prepared as shown in general experimental procedure.; Mp 157–160 °C; $[\alpha]_D^{29}$ −18.78(c 1.0, $CHCl_3$); IR (neat): 3056, 1630, 1509, 1437, 1408, 1383, 1195, 1123, 959, 933, 751, 727, 692, 596, 537 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.91 (m, 4H), 7.90–7.80 (m, 4H), 7.51–7.21 (m, 14H), 6.79 (dd, J=16.0, 9.6 Hz, 1H), 6.54 (d, J=16.0 Hz, 1H), 4.20 (dd, J=16.0, 2.8 Hz, 1H), 3.20 (ddd, J=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.3, 134.9, 134.7 (d, J_{C-P}=3.4 Hz), 133.8 (d, J_{C-P}=49.9 Hz), 133.2, 133.0, 132.5 (d, J_{C-P}=44.3 Hz), 131.7, 131.6 (d, J_{C-P}=2.4 Hz), 131.5, 128.5, 128.4, 128.3, 128.3, 128.2, 127.7, 126.4, 126.3, 125.9, 125.9, 125.8, 125.7, 123.4, 52.3 (d, J_{C-P}=7.8 Hz), 43.9 (d, J_{C-P}=5.1 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.93; MALDI (m/z): Calcd for $C_{32}H_{26}NOP$ [(M+H)$^+$] 472.1824, found [(M+H)$^+$] 472.1831; enantioselectivity was determined by HPLC analysis (Chiralcel-ODH, 1.0 mL/min, 254 nm, hexane/*i*-PrOH 9/1); retention time: 9.4 min (enantiomer) and 26.7 min (major).

*4.3.14.1. cis-**8n**.* White solid; Mp 55–58 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.06–7.98 (m, 4H), 7.84–7.79 (m, 4H), 7.52–7.39 (m, 9H), 7.26–7.13 (m, 5H), 6.67 (d, J=15.9 Hz, 1H), 5.84 (dd, J=16.0, 8.6 Hz, 1H), 4.33 (dd, J=16.4, 6.1 Hz, 1H), 3.85–3.78 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 136.2, 135.7, 133.1, 132.9, 132.8, 132.4 (d, J_{C-P}=4.7 Hz), 132.0, 131.7, 131.7, 131.6, 131.5, 128.6, 128.5 (d, J_{C-P}=3.3 Hz), 128.4, 127.9, 127.8, 127.7, 126.7, 126.3, 126.2, 125.9, 125.3, 123.5 (d, J_{C-P}=4.6 Hz), 43.8 (d, J_{C-P}=5.4 Hz), 42.8 (d, J_{C-P}=5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.57; HRMS-MALDI (m/z): Calcd for $C_{32}H_{26}NOP$ [(M+H)$^+$] 472.1825, found [(M+H)$^+$] 472.1819.

*4.3.15. ((2R,3R)-2-(3,4-Dimethoxyphenyl)-3-((E)-styryl)aziridin-1-yl)diphenylphosphine oxide (**8o**).* White solid; Yield—95% (63 mg); R_f (50% EtOAc/hexane) 0.55 Prepared as shown in general experimental procedure.; Mp 48–60 °C; $[\alpha]_D^{28}$ −32.56(c 1.0, $CHCl_3$); IR (neat): 3050, 1640, 1515, 1438, 1124, 1026, 932, 754, 693, 534 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93–7.88 (m, 4H), 7.43–7.19 (m, 11H), 6.93–6.91 (m, 1H), 6.83–6.81 (m, 2H), 6.69 (dd, J=15.6, 9.2 Hz, 1H), 6.52 (d, J=16.0 Hz, 1H), 3.99 (dd, J=16.0, 2.8 Hz, 1H), 3.86 (s, 3H), 3.85 (s, 3H), 3.32 (ddd, J=12.4, 9.6, 2.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.0, 148.6, 136.2, 134.7, 133.8 (d, J_{C-P}=70.7 Hz), 132.5 (d, J_{C-P}=64.8 Hz), 131.7, 131.6, 131.5, 131.4, 129.6 (d, J_{C-P}=3.6 Hz), 128.4, 128.2 (d, J_{C-P}=3.3 Hz), 128.1, 127.7, 126.3, 125.9 (d, J_{C-P}=7.4 Hz), 118.6, 111.2, 109.3, 55.8 (d, J_{C-P}=6.0 Hz), 51.8 (d, J_{C-P}=7.8 Hz), 43.7 (d, J_{C-P}=5.2 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 30.89; MALDI (m/z): Calcd for $C_{30}H_{28}NO_3P$ [(M+H)$^+$] 482.1879, found [(M+H)$^+$] 482.1881; enantioselectivity was determined by HPLC analysis (Chiralcel-ODH, 1.0 mL/min, 254 nm, hexane/i-PrOH 9/1); retention time: 12.4 min (enantiomer) and 45.4 min (major).

*4.3.15.1. cis-**8o**.* Colorless liquid; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.00–7.93 (m, 4H), 7.50–7.39 (m, 7H), 7.27–7.18 (m, 5H), 6.93–6.90 (m, 1H), 6.82–6.80 (m, 1H), 6.64 (d, J=16.0 Hz, 1H), 5.80 (dd, J=16.0, 8.4 Hz, 1H), 4.12 (dd, J=16.5, 6.1 Hz, 1H), 3.86 (s,3H), 3.79 (s,1H), 3.72–3.64 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.6, 148.4, 136.3, 135.3, 132.8 (d, J_{C-P}=28.2 Hz), 132.5, 132.0, 131.7 (d, J_{C-P}=11.8 Hz), 131.6, 131.5, 128.9, 128.5, 128.5, 128.4, 127.8, 127.2 (d, J_{C-P}=4.5 Hz), 126.3, 123.9 (d, J_{C-P}=4.6 Hz), 119.8, 110.9 (d, J_{C-P}=13.4 Hz), 55.8 (d, J_{C-P}=5.9 Hz), 43.5 (d, J_{C-P}=5.6 Hz), 42.3 (d, J_{C-P}=5.9 Hz); ^{31}P NMR (162 MHz, $CDCl_3$) δ 33.40; HRMS-MALDI (m/z): Calcd for $C_{30}H_{28}NO_3P$ [(M+H)$^+$] 482.1880, found [(M+H)$^+$] 482.1870.

4.4. (2*R*,3*R*)-2-Phenyl-3-((*E*)-styryl)aziridine (9a)

To a suspension of $LiAlH_4$ (8.1 mg, 0.21 mmol) in THF (0.2 mL) under nitrogen at 0 °C, a solution of aziridine **8a** (30 mg, 0.07 mmol) in THF (0.7 mL) was added dropwise. The mixture was stirred at 0 °C and monitored by TLC. Upon completion (0.75 h), the reaction mixture was diluted with satd NH_4Cl (1 mL), extracted with EtOAc (5 mL×3), dried over Na_2SO_4, and concentrated in vacuo. The residue was purified by column chromatography (EtOAc/hexane, 1:9) to give **9a** as a colorless liquid (10.2 mg, 65% yield); R_f (30% EtOAc/hexane) 0.58; $[\alpha]_D^{25}$ +103.1 (c 0.6, $CHCl_3$); ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38–7.22 (m, 10H), 6.71–6.67 (d, J=16.0 Hz, 1H), 5.95–5.89 (dd, J=16.0, 8.0, 1H), 3.07–3.06 (d, J=2.0 Hz, 1H), 2.72–2.70 (d, J=7.2 Hz, 1H).

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Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.tet.2014.12.063.

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