有机化学 DOI: 10.6023/cjoc202204058 研究论文
Chinese Journal of Organic Chemistry ARTICLE

钯催化的不对称碳氢键烯基化动力学拆分 2-(芳基亚磺酰基)吡啶

范铃洁[†,a] 周 涛[†,*,b] 杨 旭[c] 江梦雪[c] 胡信全[a] 史炳锋[*,b]
([a]浙江工业大学化学工程学院 杭州 310032)
([b]浙江大学化学系前瞻技术研究中心 杭州 310027)
([c]五邑大学生物科技与大健康学院 广东江门 529020)

摘要 通过发展钯催化的不对称碳氢键烯基化, 实现了 2-(芳基亚磺酰基)吡啶的动力学拆分. 利用该方法, 在温和条件下用廉价商业化的 *L*-焦谷氨酸作为手性配体, 以较高到优异的产率和对映选择性实现了一系列手性亚砜的合成, 对映选择性高达 99%, 拆分因子 *s* 大于 200. 该方法对于天然产物衍生的丙烯酸酯以及克级制备反应都有很好的兼容性.
关键词 动力学拆分; 碳氢键活化; 不对称; 手性亚砜

Pd(II)-Catalyzed Enantioselective C—H Olefination of 2-(Arylsulfinyl)pyridines through Kinetic Resolution

Fan, Lingjie[†,a] Zhou, Tao[†,*,b] Yang, Xu[c] Jiang, Mengxue[c]
Hu, Xinquan[a] Shi, Bingfeng[*,b]
([a] *College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310032*)
([b] *Center of Chemistry for Frontier Technologies, Department of Chemistry, Zhejiang University, Hangzhou 310027*)
([c] *School of Biotechnology and Health Sciences, Wuyi University, Jiangmen, Guangdong 529020*)

Abstract A Pd(II)-catalyzed enantioselective C—H olefination of 2-(arylsulfinyl)pyridines through kinetic resolution is developed. A wide range of chiral sulfoxides were prepared in good to high yields and selectivity (up to 99% *ee*, *s*-factor of up to 200) under mild conditions using cheap and commercially available *L*-*p*Glu-OH as chiral ligand. This protocol is easy to scale-up and compatible with various acrylates bearing core structures of natural products.
Keywords kinetic resolution; C—H activation; enantioselective; chiral sulfoxide

1 Introduction

Chiral sulfoxides are important motifs in pharmaceuticals and bioactive compounds,[1] and they also have been widely used as efficient and versatile auxiliaries or ligands in asymmetric synthesis (Figure 1a).[2] Traditional approaches for the synthesis of chiral sulfoxides mainly rely on resolution techniques, diastereoselective and/or biocatalytic transformations.[3] Meanwhile, despite catalytic asymmetric strategies are more appealing, the development is still rare and the established strategies are generally limited to asymmetric oxidation, and enantioselective arylation or alkylation of sulfenate anions.[3c,4] Therefore, the development of alternative strategy to enable the highly efficient synthesis of these chiral motifs is highly demanding.

In the past two decades, transition metal-catalyzed asymmetric C—H functionalization has been recognized as a highly atom- and step-economic approach to the synthesis of diverse chiral molecules.[5] However, the synthesis of chiral sulfoxides via asymmetric C—H activation was still very limited.[6-7] In 2018, Wang and co-workers[8-9] achieved the first synthesis of chiral sulfoxides via Pd(II)-catalyzed enantioselective C—H olefination of diarylsulfoxides using a mono-*N*-protected amino acid,

* Corresponding authors. E-mail: taozhou@zju.edu.cn; bfshi@zju.edu.cn
Received April 24, 2022; revised May 8, 2022; published online May 17, 2022.
Project supported by the National Natural Science Foundation of China (Nos. 21925109, 21801223), the Zhejiang Provincial Natural Science Foundation of China (No. LD22B030003), the Open Research Fund of School of Chemistry and Chemical Engineering of Henan Normal University and Center of Chemistry for Frontier Technologies of Zhejiang University.
国家自然科学金(Nos. 21925109, 21801223)、浙江省自然科学基金(No. LD22B030003)、河南师范大学化学化工学院开放基金和浙江大学化学前瞻技术研究中心资助项目.
† 共同第一作者(These authors contributed equally to this work).

Ac-Leu-OH, as the chiral ligand (Figure 1b). The He group reported an Ir(III)-catalyzed asymmetric C—H amidation to synthesize chiral sulfoxides via desymmetrization and parallel kinetic resolution (PKR).[10] Very recently, our group successfully achieved the synthesis of chiral sulfoxides via Pd(II)-catalyzed enantioselective C—H alkynylation using cheap and commercially available *L*-pyroglutamic acid (*L*-*p*Glu-OH) as chiral ligand.[11]

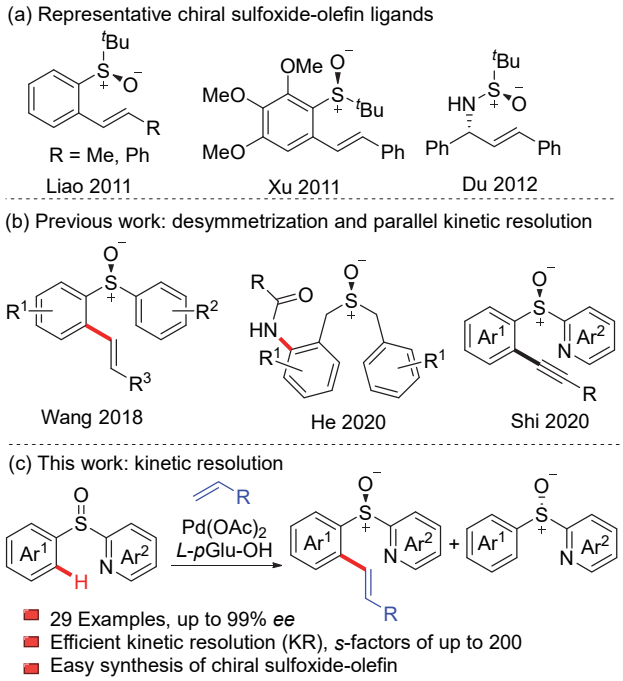


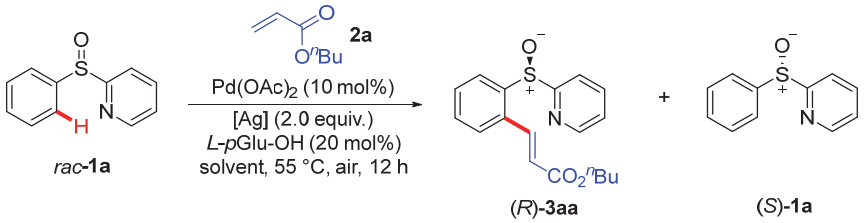
Figure 1 Representative chiral sulfoxide-olefin ligands and synthesis of chiral sulfoxide via Pd(II)-catalyzed enantioselective C—H olefination

Chiral sulfoxide-olefins have emerged as a class of efficient chiral ligands in asymmetric metal catalysis with outstanding performance.[12] We envisioned that enantioselective C—H olefination would be a powerful strategy to construct these chiral skeletons. In our continuous efforts to develop efficient transition-metal-catalyzed asymmetric C—H activation protocol using readily available chiral ligands.[13] Herein, we reported the Pd(II)-catalyzed enantioselective C—H olefination of 2-(arylsulfinyl)pyridines using *L*-*p*Glu-OH as the chiral ligand through kinetic resolution. This transformation exhibited excellent stereocontrol, broad scope, and mild conditions.

2 Results and discussion

We initiated our research by investigating the coupling reaction of *rac*-**1a** with butyl acrylate **2a**. When using 10 mol% $Pd(OAc)_2$ as the catalyst, 20 mol% *L*-*p*Glu-OH as the chiral ligand,[14] and 2.0 equiv. of Ag_3PO_4 as the additive in ^{i}PrOH/toluene (1.8 mL/0.2 mL) at 55 ℃ for 12 h under air (Table 1, Entry 1, standard conditions). The desired olefination product **3aa** was obtained in 38% isolated yield with 90% *ee* and the residual resolved (*S*)-**1a** was recovered in 49% yield with 91% *ee*. The silver salts were first screened (Table 1, Entries 2～4), Ag_2CO_3, $AgNO_3$, and AgOAc afforded **3aa** in high enantioselectivities (91%～95% *ee*), but the (*S*)-**1a** was recovered in only 34% to 56% *ee*. Other solvents such as toluene, ^{t}BuOH, ^{i}PrOH, MeOH also led the olefination product **3aa** in high *ee* values and the (*S*)-**1a** in moderate to good enantioselectivities (Table 1, Entries 5～8). A higher *ee* of **3aa** and a lower *ee* of (*S*)-**1a**

Table 1 Optimization of reaction conditions[a,b,c]



Entry	Deviation from standard conditions	*ee* (Yield)/%		*S*[e]
		3aa	**1a**	
1	None	90 (38)[d]	91 (49)[d]	60
2	Ag_2CO_3 instead of Ag_3PO_4	95 (34)	56 (60)	68
3	$AgNO_3$ instead of Ag_3PO_4	92 (44)	34 (28)	33
4	AgOAc instead of Ag_3PO_4	91 (26)	52 (70)	36
5	Toluene instead of ^{i}PrOH/toluene	90 (34)	34 (63)	26
6	^{t}BuOH instead of ^{i}PrOH/toluene	92 (39)	84 (51)	64
7	^{i}PrOH instead of ^{i}PrOH/toluene	94 (43)	78 (52)	77
8	MeOH instead of ^{i}PrOH/toluene	95 (32)	43 (63)	60
9	50 ℃ instead of 55 ℃	95 (48)	80 (50)	96
10	No *L*-*p*Glu-OH	n.r.		

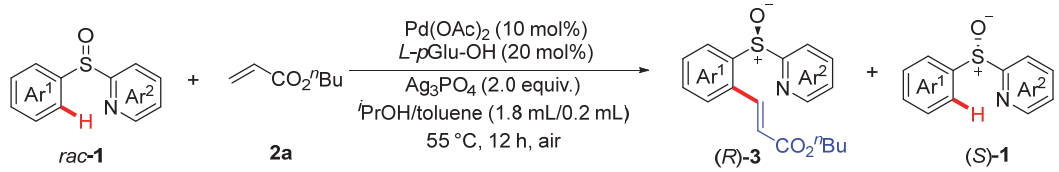
[a] Standard conditions: *rac*-**1a** (0.2 mmol), **2a** (1.0 equiv.), $Pd(OAc)_2$ (10 mol%), *L*-*p*Glu-OH (0.2 equiv.), Ag_3PO_3 (2.0 equiv.), ^{i}PrOH/toluene (1.8 mL/0.2 mL), 55 ℃, 12 h under air. [b] Determined by ^{1}H NMR spectroscopy using 1,3,5-trimethoxybenzene as the internal standard. [c] Determined by chiral HPLC. [d] Isolated yield. [e] Selectivity factors: $s=\ln[(1-C)(1-ee_{1a})]/\ln[(1-C)(1+ee_{1a})]$, $C=(ee_{1a})/(ee_{1a}+ee_{3aa})$

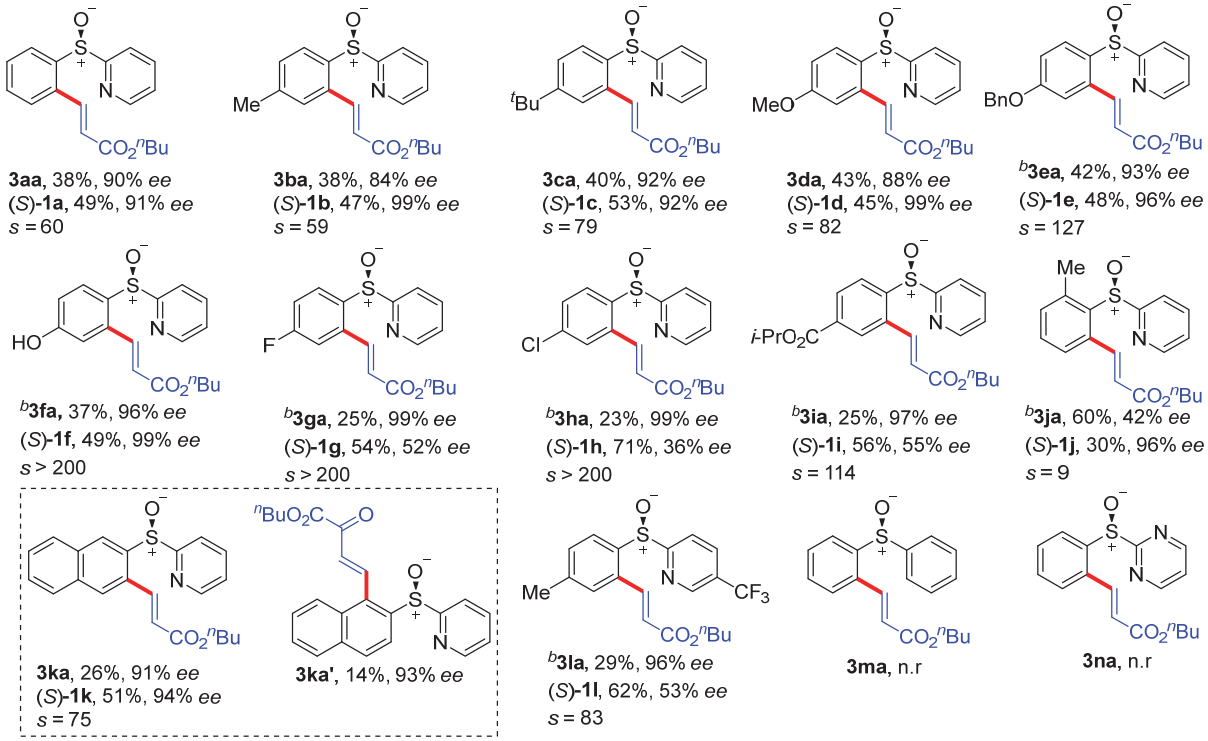
with the *s*-value increased to 96 were obtained when the reaction temperature was reduced to 50 ℃ (Table 1, Entry 9, (*R*)-**3aa**, 48%, 95% *ee*; (*S*)-**1a**, 50%, 80% *ee*). No product **3aa** was observed when the reaction was carried out in the absence of *L*-*p*Glu-OH.

With the optimized reaction conditions in hand, the scope of 2-(arylsulfinyl)pyridines with different substituents to investigate the generality of this Pd(II)-catalyzed enantioselective C—H olefination was then investigated (Table 2). 2-(Arylsulfinyl)pyridines bearing electron-donating groups (**1b**～**1f**) on the *para*-position of the benzene ring were well tolerated, giving the desired products **3ba**～**3ea** and the residual resolved (*S*)-**1b**～(*S*)-**1e** in good to excellent enantioselectivities (**3ba** ～ **3ea**, 84% ～ 96% *ee*; (*S*)-**1a**～(*S*)-**1e**, 91%～99% *ee*). To our delight, 2-(arylsulfinyl)pyridine with free hydroxyl group (**1f**) was also compatible, affording **3fa** in 37% yield with 96% *ee* and (*S*)-**1f** in 49% yield with 99% *ee*. Aryl ring with electron-withdrawing groups on the *para*-position were less reactive (**1g**～**1i**), giving the olefination product in only 23% ～ 25% yields with excellent enantioselectivities (**3ga**～**3ia**, 97%～99% *ee*), and the residual **1** were recovered in 54%～71% yield with only moderate enantioselectivities [(*S*)-**1g**～(*S*)-**1i**, 27%～75% *ee*]. It should be noted that all **1f**, **1g** and **1h** gave *s*-values of more than 200. *ortho*-Me substituted substrate **1j** resulted in excess desired product **3ja** in 60% yield with low *ee* value (44% *ee*), probably duo to the steric effect. The residual **1j** was obtained still in high enantioselectivity (96% *ee*). A mixture of products **3ka** and **3ka'**, which react at both the less hindered *ortho*-position and hindered *ortho*-position, were isolated in excellent *ee* values when 2-naphthyl **1k** was used (**3ka**, 26%, 91% *ee*; **3ka'**, 14%, 93% *ee*; (*S*)-**1k**: 51%, 94% *ee*). In addition, trifluoromethyl substituted at the 5-postion of the pyridine ring was also well tolerated (**1l**). In sharp contrast to Wang's protocol that sulfoxide itself is the directing group,[8] diphenyl sulfoxide **1m** did not react in our protocol, indicating that pyridine is the directing group. No olefination product was detected when changing 2-pyridyl to 2-pyrimidine (**1n**). However, the total yields of the olefination products and the recovered chiral materials were relatively low when some 2-(arylsulfinyl)pyridines were used, which might cause by the trace amount of diolefination products or the coordination between 2-(arylsulfinyl)-pyridines with Pd catalyst.

The scope of olefins was then investigated (Table 3).

Table 2 Scope of 2-(arylsulfinyl)pyridines[a]

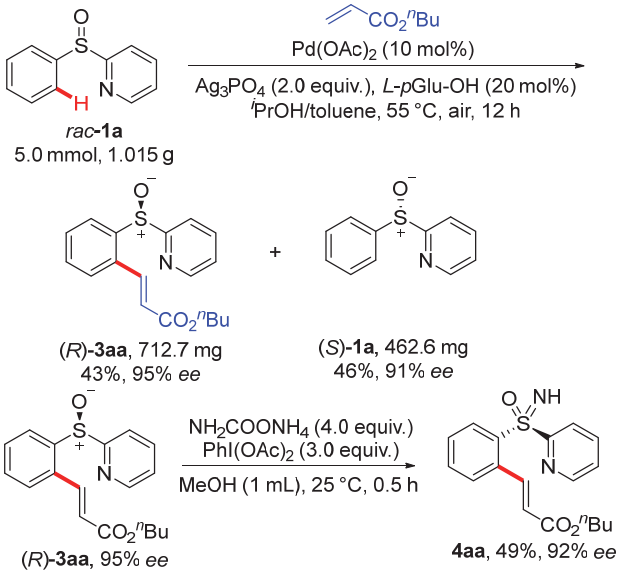




[a] Standard conditions, isolated yield. [b] Benzoquinone (BQ) (0.5 equiv.), *t*-AmylOH/toluene (1.0 mL/1.0 mL) at 60 ℃.

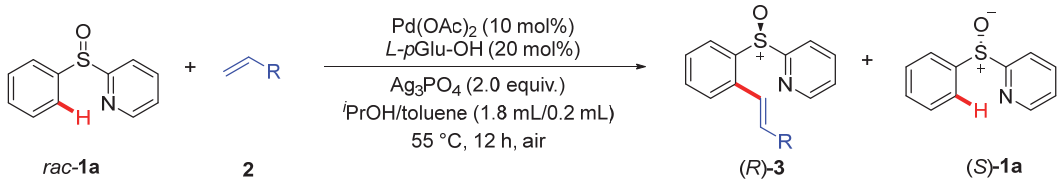
Acrylates bearing ^{t}Bu, allyl, hydroxyethyl, phenoxyethyl, phenyl and Bn worked well, giving the desired products **3** and residual **1a** with good results (**3ab**～**3ag**, 82%～95% *ee*; (*S*)-**1a**, 92%～99% *ee*). Racemic **2h** and **2i** afforded the coupling products in good enantioselectivities with *dr*＝1∶1. To demonstrate the utility of this protocol, the acrylates derived from the core structures of natural products (*L*-menthol, **2j**; tyrosine, **2k**; estrone, **2l**) were examined. The desired olefinated products and unreacted (*S*)-**1a** were obtained in high diastereomeric excess and enantioseletivities (**3aj**～**3al**, 90%～91% *de*; (*S*)-**1a**, 89%～99% *ee*). Various styrenes were also compatible with this reaction using $AgVO_3$ as the oxidant, giving the desired products in good to high enantioselectivities (**3am**～**3aq**, 84%～95% *ee*). Notably, electronically biased *α*,*β*-unsaturated ketone (**2r**) was also tolerated. The absolute configuration of the product **3ao** was unambiguously determined by the X-ray analysis.[15]

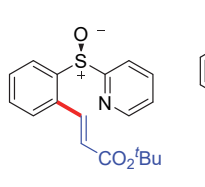
The synthetic applications to prove the practicality of this



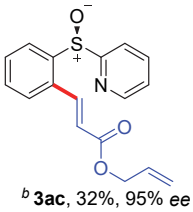
Scheme 1 Gram-scale kinetic resolution and derivatizations

Table 3 Scope of olefins[a]

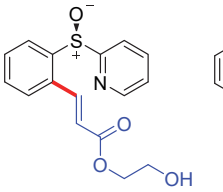




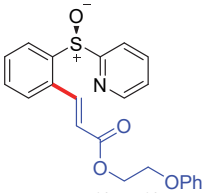
3ab 37%, 82% *ee*
(*S*)-**1a**, 42%, 98% *ee*
s = 46



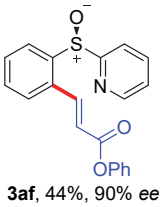
[b] **3ac**, 32%, 95% *ee*
(*S*)-**1a**, 50%, 97% *ee*
s = 165



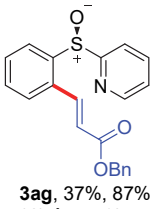
3ad, 49%, 88% *ee*
(*S*)-**1a**, 50%, 97% *ee*
s = 65



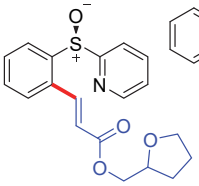
3ae, 30%, 88% *ee*
(*S*)-**1a**, 42%, 91% *ee*
s = 50



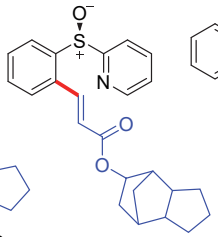
3af, 44%, 90% *ee*
(*S*)-**1a**, 51%, 92% *ee*
s = 62



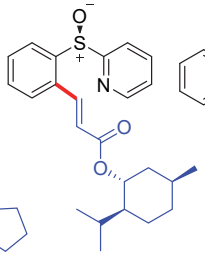
3ag, 37%, 87% *ee*
(*S*)-**1a**, 47%, 98% *ee*
s = 65



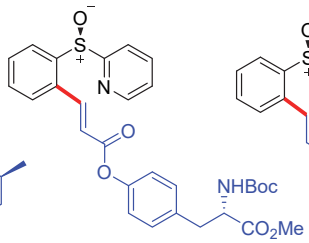
3ah, 39%, 90% *ee*, *dr* = 1:1
(*S*)-**1a**, 45%, 98% *ee*
s = 87



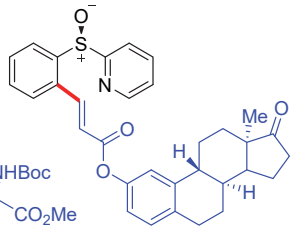
3ai, 41%, 86% *ee*, *dr* = 1:1
(*S*)-**1a**, 47%, 98% *ee*
s = 60



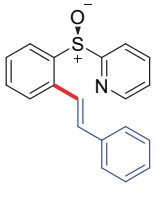
3aj, 37%, 90% *ee*
(*S*)-**1a**, 46%, 99% *ee*
s = 99



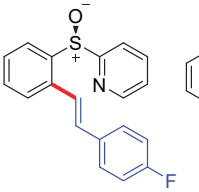
3ak, 40%, 91% *de*
(*S*)-**1a**, 51%, 89% *ee*
s = 63



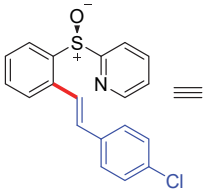
3al, 36%, 90% *de*
(*S*)-**1a**, 53%, 91% *ee*
s = 60



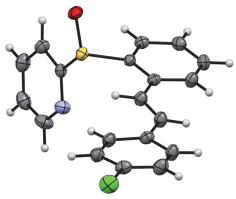
[c] **3am**, 31%, 91% *ee*
(*S*)-**1a**, 49%, 93% *ee*
s = 72



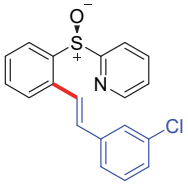
[c] **3an**, 29%, 84% *ee*
(*S*)-**1a**, 47%, 99% *ee*
s = 59



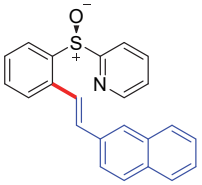
[c] **3ao**, 33%, 90% *ee*
(*S*)-**1a**, 48%, 93% *ee*
s = 65



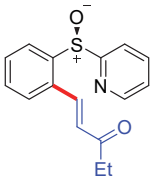
3ao (CCDC 2125440)



[c] **3ap**, 37%, 90% *ee*
(*S*)-**1a**, 53%, 80% *ee*
s = 47



[c] **3aq**, 29%, 95% *ee*
(*S*)-**1a**, 51%, 72% *ee*
s = 84



3ar, 35%, 88% *ee*
(*S*)-**1a**, 62%, 73% *ee*
s = 34

[a] Standard conditions, isolated yield. [b] Benzoquinone (0.5 equiv.), ^{t}AmylOH/toluene (1.0 mL/1.0 mL) at 60 ℃. [c] $AgVO_3$ (2.0 equiv.) at 60 ℃.

strategy were then investigated. The resolution of *rac*-**1b** was first performed on a 5.0 mmol (1.015 g) scale. To our delight, the scale-up reaction gave a better result than the mode reaction (Scheme 1, **3aa**, 43%, 95% *ee*). The olefination product **3aa** could be easily oxidized to chiral sulfoximine **4aa** without significant loss of enantiopurity.

3 Conclusions

In summary, we have reported a Pd(II)-catalyzed enantioselective C—H olefination/kinetic resolution of 2-(arylsulfinyl)pyridines enabled by the use of cheap and commercially available *L*-*p*Glu-OH as the chiral ligand. A wide range of chiral sulfoxides were prepared with high enantioselectivity. This protocol was also compatible with various acrylates bearing core structures of natural products. Scale-up reactions gave a better result, proving that this strategy may offer an efficient synthetic route to chiral sulfoxides. Further studies on the application of this protocol are in progress in our laboratory.

4 Experimental section

4.1 General information

All the materials and solvent were purchased from commercial suppliers and used without additional purification. $Pd(OAc)_2$ was purchased from Strem. NMR spectra were recorded on a Bruke Avance operating for ^1H NMR at 400 MHz, ^{13}C NMR at 101 MHz, and ^{19}F NMR at 376 MHz using TMS as internal standard. The peaks were internally referenced to residual undeuterated chloroform in $CDCl_3$ (δ_H 7.26, δ_C 77.16). Melting points were determined using a INESA WRS-1B melting point apparatus. Mass spectroscopy data of the products were collected on an HRMS-TOF instrument. The *ee* value was determined on a Shimadzu HPLC using CHIRALPAK column with hexane and 2-propanol as eluent, λ=254 nm. A suitable crystal was selected on a 'Bruker APEX-II CCD' diffractometer. The crystal was kept at 170.0 K during data collection. Using Olex2, the structure was solved with the ShelXT structure solution program using Intrinsic Phasing and refined with the ShelXL refinement package using Least Squares minimisation. 2-(Arylsulfinyl)pyridines **1a**～**1l** were known compounds and prepared according to the reported procedures.[11]

4.2 Representative produce for the kinetic resolution

4.2.1 General procedure A

To a 50 mL Schlenk tube was added substrate **1** (0.20 mmol), **2** (0.20 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), *L*-*p*Glu-OH (5.2 mg, 0.04 mmol), Ag_3PO_4 (167.4 mg, 0.4 mmol), *i*-PrOH/toluene (1.8 mL∶0.2 mL). The mixture was stirred for 12 h at 55 ℃ under air followed by cooling. The resulting mixture was filtered through a celite pad and concentrated *in vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the alkynylation product **3** and the residual **1**.

4.2.2 General procedure B

To a 50 mL Schlenk tube was added substrate **1** (0.20 mmol), **2** (0.20 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), *L*-*p*Glu-OH (5.2 mg, 0.04 mmol), Ag_3PO_4 (167.4 mg, 0.4 mmol), BQ (10.8 mg, 0.1 mmol), *t*-AmylOH/toluene (1 mL∶1 mL). The mixture was stirred for 12 h at 60 ℃ under air followed by cooling. The resulting mixture was filtered through a celite pad and concentrated *in vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the alkynylation product **3** and the residual **1**.

4.2.3 General procedure C

To a 50 mL Schlenk tube were added substrate **1** (0.20 mmol), **2** (0.20 mmol), $Pd(OAc)_2$ (4.4 mg, 0.02 mmol), *L*-*p*Glu-OH (5.2 mg, 0.04 mmol), $AgVO_3$ (82.8 mg, 0.4 mmol), *i*-PrOH/toluene (1.8 mL∶0.2 mL). The mixture was stirred for 12 h at 60 ℃ under air followed by cooling. The resulting mixture was filtered through a celite pad and concentrated *in vacuo*. The residue was purified by preparative TLC using hexane/EtOAc as the eluent to afford the alkynylation product **3** and the residual **1**.

4.3 Gram-scale kinetic resolution

To a 250 mL Schlenk tube were added substrate *rac*-**1b** (1012.5 mg, 5.0 mmol), **2a** (0.75 mL, 5.0 mmol), $Pd(OAc)_2$ (112.0 mg, 0.5 mmol), *L*-*p*Glu-OH (129.1 mg, 1.0 mmol), Ag_3PO_4 (4185.8 mg, 10.0 mmol), *i*-PrOH/toluene (V∶V=1.8∶0.2, 50 mL). The mixture was stirred for 12 h at 55 ℃ under air followed by cooling to room temperature. The mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by flash chromatography in petroleum ether/ethyl acetate (V∶V=4∶1) to give (*R*)-**3aa** as white solid (712.7 mg, 43%, 95% *ee*) and (*S*)-**1a** as white solid (462.6 mg, 46%, 91% *ee*).

4.4 Derivatizations

Compound **3aa** (65.8 mg, 0.2 mmol), NH_2COONH_4 (46.8 mg, 3.0 equiv.), PhI (193.2 mg, 3.0 equiv.) were dissolved in MeOH (2 mL) and stirred for 0.5 h at 25 ℃ under air, then added NH_2COONH_4 (23.4 mg, 1.5 equiv.), PhI (96.6 mg, 1.5 equiv.) under air followed by cooling. The mixture was diluted with ethyl acetate, filtrated through celite. After concentration, the resulting residue was purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=1∶1) to give **4aa** as white foam (33.5 mg, 49%).

Butyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl)acrylate (**3aa**) was prepared following GP (general procedure) A and was given by preparative TLC purification in petroleum ether/ethyl acetate (V∶V=4∶1) as white solid (25.0 mg, 38% yield). The *ee* value was determined by HPLC analysis on a Chiralcel IJ column (hexane/isopropanol, (V∶V=80∶20, flow=1.2 mL/min) with t_r=9.3 min (major), 12.0 min (minor): 90% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 46.7～47.4 ℃; ^1H NMR (400 MHz, $CDCl_3$) δ: 8.53～8.42

(m, 2H), 8.05 (d, J=7.9 Hz, 1H), 7.94～7.82 (m, 2H), 7.65 (d, J=7.4 Hz, 1H), 7.54～7.39 (m, 2H), 7.28 (d, J=4.4 Hz, 1H), 6.43 (dd, J=15.8, 1.2 Hz, 1H), 4.24 (t, J=6.6 Hz, 2H), 1.78～1.66 (m, 2H), 1.51～1.42 (m, 2H), 0.98 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 165.6, 150.0, 144.0, 139.8, 138.1, 134.5, 131.6, 130.8, 127.1, 125.6, 124.7, 121.8, 119.2, 64.8, 30.9, 19.3, 13.9. HRMS (ESI) calcd for $C_{18}H_{19}NNaO_3S$ $[M+Na]^+$ 352.0979, found 352.0983.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1a** as a white solid (19.9 mg, 49%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=20.0 min (major), 21.2 min (minor): 91% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (dt, J=4.4, 1.5 Hz, 1H), 8.04 (dt, J=8.0, 1.1 Hz, 1H), 7.87 (td, J=7.8, 1.8 Hz, 1H), 7.83～7.75 (m, 2H), 7.51～7.39 (m, 3H), 7.31～7.27 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.9, 149.9, 144.2, 138.3, 131.3, 129.3, 125.0, 124.8, 118.5.

Butyl (*R*,*E*)-3-(5-methyl-2-(pyridin-2-ylsulfinyl)phenyl) acrylate (**3ba**) was prepared following GP A and purified by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give as a yellow solid (26.1 mg, 38%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=70∶30, flow=1.0 mL/min) with t_r=6.7 min (major), 7.9 min (minor): 84% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 52.3～54.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52～8.37 (m, 2H), 8.05 (dt, J=8.0, 1.1 Hz, 1H), 7.86 (td, J=7.8, 1.8 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H), 7.44 (s, 1H), 7.34～7.21 (m, 2H), 6.41 (d, J=15.8 Hz, 1H), 4.22 (t, J=6.6 Hz, 2H), 2.37 (s, 3H), 1.70 (dq, J=8.6, 6.7 Hz, 2H), 1.52～1.39 (m, 2H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 165.7, 149.9, 142.1, 140.8, 139.9, 138.0, 134.4, 131.7, 127.7, 125.9, 124.5, 121.6, 119.2, 64.7, 30.8, 21.5, 19.3, 13.9. HRMS (ESI) calcd for $C_{19}H_{21}NNaO_3S$ $[M+Na]^+$ 366.1136, found 366.1140.

(*S*)-2-(*p*-Tolylsulfinyl)pyridine (*S*)-**1b**: A purification by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give **1b** as a white solid (20.4 mg, 47%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=9.0 min (minor), 10.4 min (major): 99% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.58～8.48 (m, 1H), 8.05 (dt, J=7.9, 1.1 Hz, 1H), 7.87 (td, J=7.8, 1.8 Hz, 1H), 7.76～7.59 (m, 2H), 7.39～7.12 (m, 3H), 2.35 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 149.9, 141.9, 141.0, 138.2, 130.0, 125.2, 124.7, 118.5, 21.5.

Butyl (*R*,*E*)-3-(5-(*tert*-butyl)-2-(pyridin-2-ylsulfinyl)-phenyl) acrylate (**3ca**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give as a yellow foam (31.3 mg, 40%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=19.6 min (major), 27.8 min (minor): 92% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59～8.30 (m, 2H), 8.07 (dt, J=8.0, 1.1 Hz, 1H), 7.87 (td, J=7.8, 1.7 Hz, 1H), 7.77 (d, J=8.4 Hz, 1H), 7.63 (d, J=2.0 Hz, 1H), 7.50 (dd, J=8.4, 2.0 Hz, 1H), 7.32～7.18 (m, 1H), 6.44 (d, J=15.8 Hz, 1H), 4.24 (t, J=6.7 Hz, 2H), 1.82～1.64 (m, 2H), 1.57～1.37 (m, 2H), 1.30 (s, 9H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.9, 166.0, 155.4, 150.3, 141.1, 140.7, 138.4, 134.4, 128.7, 126.1, 124.9, 124.5, 121.8, 119.6, 65.1, 35.5, 31.5, 31.2, 19.6, 14.2. HRMS (ESI) calcd for $C_{22}H_{27}NNaO_3S$ $[M+Na]^+$ 408.1606, found 408.1609.

Butyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl)acrylate (**3aa**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1c** as a white solid (36.1 mg, 53%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=11.6 min (minor), 13.4 min (major): 92% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60～8.51 (m, 1H), 8.07 (dt, J=7.9, 1.1 Hz, 1H), 7.88 (td, J=7.7, 1.8 Hz, 1H), 7.75～7.63 (m, 2H), 7.52～7.39 (m, 2H), 7.32～7.27 (m, 1H), 1.28 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 154.9, 149.9, 140.8, 138.2, 126.4, 125.1, 124.7, 118.7, 35.1, 31.2.

Butyl (*R*,*E*)-3-(5-methoxy-2-(pyridin-2-ylsulfinyl) phenyl)acrylate (**3da**) was prepared following GP A and purified by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) as a white foam (30.8 mg, 43%).The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=9.9 min (major), 11.9 min (minor): 88% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (d, J=4.8 Hz, 1H), 8.44 (d, J=15.8 Hz, 1H), 8.07 (d, J=7.9 Hz, 1H), 7.87 (td, J=7.7, 1.5 Hz, 1H), 7.74 (d, J=8.8 Hz, 1H), 7.30～7.22 (m, 1H), 7.10 (d, J=2.6 Hz, 1H), 6.99 (dd, J=8.7, 2.6 Hz, 1H), 6.40 (d, J=15.8 Hz, 1H), 4.23 (t, J=6.7 Hz, 2H), 3.84 (s, 3H), 1.71 (dq, J=8.4, 6.7 Hz, 2H), 1.54～1.36 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.4, 165.8, 162.1, 150.0, 139.7, 138.0, 136.5, 135.3, 128.3, 124.5, 122.2, 119.3, 116.8, 112.0, 64.8, 55.7, 30.9, 19.3, 13.9. HRMS (ESI) calcd for $C_{19}H_{21}NNaO_4S$ $[M+Na]^+$ 382.1083, found 382.1089.

(*S*)-2-((4-Methoxyphenyl)sulfinyl)pyridine [(*S*)-**1d**]: A purification by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give **1d** as a white solid (20.9 mg, 45%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=26.4 min (major), 32.6 min (minor): 99% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400

MHz, $CDCl_3$) δ: 8.53 (dt, J=4.6, 1.5 Hz, 1H), 8.07 (dt, J=7.9, 1.1 Hz, 1H), 7.89 (td, J=7.7, 1.8 Hz, 1H), 7.75～7.63 (m, 2H), 7.32～7.27 (m, 1H), 7.03～6.88 (m, 2H), 3.80 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 162.2, 149.9, 138.2, 135.2, 127.4, 124.6, 118.6, 114.9, 55.6.

Butyl (*R*,*E*)-3-(5-(benzyloxy)-2-(pyridin-2-ylsulfinyl) phenyl)acrylate (**3ea**) was prepared following GP B and purified by preparative TLC in toluene/ethyl acetate (V∶V=5∶1) as a yellow solid (36.7 mg, 42%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol, V∶V=70∶30, flow=1.2 mL/min) with t_r=6.5 min (major), 8.4 min (minor): 93% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 173.0～173.7 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56～8.33 (m, 2H), 8.07 (dt, J=7.9, 1.1 Hz, 1H), 7.88 (td, J=7.7, 1.8 Hz, 1H), 7.75 (d, J=8.8 Hz, 1H), 7.43～7.31 (m, 5H), 7.30～7.24 (m, 1H), 7.20 (d, J=2.6 Hz, 1H), 7.06 (dd, J=8.8, 2.6 Hz, 1H), 6.38 (d, J=15.8 Hz, 1H), 5.08 (s, 2H), 4.23 (t, J=6.7 Hz, 2H), 1.71 (dq, J=8.4, 6.7 Hz, 2H), 1.52～1.40 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.7, 166.1, 161.6, 150.3, 140.0, 138.4, 136.8, 136.3, 135.8, 129.2, 128.8, 128.7, 128.0, 124.9, 122.5, 119.6, 117.7, 113.3, 70.8, 65.1, 31.2, 30.2, 19.6, 14.2. HRMS (ESI) calcd for $C_{25}H_{25}NNaO_4S$ $[M+Na]^+$ 458.1400, found 458.1402.

(*S*)-2-((4-(Benzyloxy)phenyl)sulfinyl)pyridine [(*S*)-**1e**]: A purification by preparative TLC in toluene/ethyl acetate V∶V=5∶1) to give **1e** as a white solid (29.7 mg, 48%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=12.1 min (minor), 13.6 min (major): 96% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (dt, J=4.4, 1.4 Hz, 1H), 8.07 (dt, J=7.9, 1.1 Hz, 1H), 7.89 (td, J=7.7, 1.8 Hz, 1H), 7.69 (d, J=8.9 Hz, 2H), 7.43～7.21 (m, 6H), 7.03 (d, J=8.8 Hz, 2H), 5.05 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 161.4, 149.9, 138.2, 136.2, 135.6, 128.8, 128.4, 127.6, 127.4, 124.6, 118.6, 115.7, 70.3.

Butyl (*R,E*)-3-(5-hydroxy-2-(pyridin-2-ylsulfinyl) phenyl)acrylate **(3fa**) was prepared following GP B and purified by preparative TLC in dichloromethane/ethyl acetate (V∶V=2∶1) to give as a white solid (25.8 mg, 37%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=7.2 min (major), 35.0 min (minor): 96% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 95.6～96.5 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (dd, J=4.9, 1.7 Hz, 1H), 8.32 (d, J=15.7 Hz, 1H), 8.09 (d, J=7.9 Hz, 1H), 7.92 (td, J=7.8, 1.7 Hz, 1H), 7.47 (d, J=8.6 Hz, 1H), 7.35～7.29 (m, 1H), 6.93 (d, J=2.4 Hz, 1H), 6.77 (dd, J=8.6, 2.4 Hz, 1H), 6.24 (d, J=15.8 Hz, 1H), 4.20 (t, J=6.7 Hz, 2H), 1.76～1.64 (m, 2H), 1.52～1.35 (m, 2H), 0.95 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 164.7, 160.4, 149.9, 139.3, 138.4, 136.9, 132.9, 129.3, 124.9, 122.2, 119.9, 118.7, 114.1, 64.9, 30.8, 19.3, 13.9. HRMS (ESI) calcd for $C_{18}H_{19}NNaO_4S$ $[M+Na]^+$ 368.0928, found 368.0932.

(*S*)-4-(Pyridin-2-ylsulfinyl)phenol [(*S*)-**1f**]: A purification by preparative TLC in dichloromethane/ethyl acetate (V∶V=2∶1) to give **1f** as a white solid (21.6 mg, 49%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=7.5 min (major), 11.5 min (minor): 99% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60～8.51 (m, 1H), 8.13 (dt, J=7.9, 1.1 Hz, 1H), 7.95 (td, J=7.8, 1.7 Hz, 1H), 7.55～7.45 (m, 2H), 7.44～7.27 (m, 1H), 6.80～6.71 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.1, 159.4, 149.5, 138.3, 133.8, 128.1, 124.6, 118.8, 116.4.

Butyl (*R*,*E*)-3-(5-fluoro-2-(pyridin-2-ylsulfinyl) phenyl)acrylate (**3ga**) was prepared following GP B and purified by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give as a white solid (17.2 mg, 25%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=12.0 min (major), 48.3 min (minor): 99% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 85.6～86.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.48 (dd, J=4.9, 1.6 Hz, 1H), 8.43 (dd, J=15.7, 1.5 Hz, 1H), 8.05 (d, J=8.0 Hz, 1H), 7.94～7.81 (m, 2H), 7.37～7.24 (m, 2H), 7.14～7.19 (m, 1H), 6.42 (d, J=15.8 Hz, 1H), 4.24 (t, J=6.6 Hz, 2H), 1.70 (dq, J=8.5, 6.7 Hz, 2H), 1.57～1.33 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 165.7, 164.3 (d, $^1J_{C\text{-}F}$=227.0 Hz), 150.0, 139.6, 138.6, 138.2, 137.0 (d, $^2J_{C\text{-}F}$=8.7 Hz), 128.3 (d, $^3J_{C\text{-}F}$=9.5 Hz), 124.8, 122.9, 119.1, 118.1 (d, $^2J_{C\text{-}F}$=22.6 Hz), 113.9 (d, $^2J_{C\text{-}F}$=23.1 Hz), 65.0, 30.8, 19.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −107.78. HRMS (ESI) calcd for $C_{18}H_{18}FNNaO_3S$ $[M+Na]^+$ 370.0886, found 370.0889.

(*S*)-2-((4-Fluorophenyl)sulfinyl)pyridine [(*S*)-**1g**]: A purification by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give **1g** as a white solid (23.7 mg, 54%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=7.2 min (minor), 7.8 min (major): 52% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59～8.47 (m, 1H), 8.04 (dt, J=7.9, 1.1 Hz, 1H), 7.88 (td, J=7.7, 1.8 Hz, 1H), 7.82～7.74 (m, 2H), 7.35～7.28 (m, 1H), 7.18～7.10 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.4, 164.2 (d, $^1J_{C\text{-}F}$=252.6 Hz), 149.6, 139.3 (d, $^4J_{C\text{-}F}$=2.9 Hz), 138.0, 127.1 (d, $^3J_{C\text{-}F}$=8.9 Hz), 124.6, 118.1, 116.3 (d, $^2J_{C\text{-}F}$=22.7 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −108.39.

Butyl (*R*,*E*)-3-(5-chloro-2-(pyridin-2-ylsulfinyl) phenyl)acrylate (**3ha**) was prepared following GP B and purified by preparative TLC in ethyl acetate/acetone/dichloromethane (V∶V∶V=10∶1∶1) to give as a white solid (16.7 mg, 23%). The *ee* value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol,

V∶V=90∶10, flow=0.8 mL/min) with t_r=48.0 min (minor), 61.2 min (major): 99% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 66.5～67.4 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (dt, J=4.2, 1.2 Hz, 1H), 8.40 (d, J=15.8 Hz, 1H), 8.03 (dt, J=8.0, 1.0 Hz, 1H), 7.88 (td, J=7.7, 1.7 Hz, 1H), 7.84 (d, J=8.5 Hz, 1H), 7.61 (d, J=2.0 Hz, 1H), 7.44 (dd, J=8.5, 2.1 Hz, 1H), 7.30～7.26 (m, 1H), 6.43 (d, J=15.8 Hz, 1H), 4.24 (td, J=6.7, 1.3 Hz, 2H), 1.74～1.68 (m, 2H), 1.51～1.39 (m, 2H), 0.97 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 165.3, 150.1, 142.4, 138.6, 138.3, 137.9, 136.0, 130.8, 127.0, 127.0, 124.8, 122.9, 119.1, 64.9, 30.8, 19.3, 13.9. HRMS (ESI) calcd for $C_{18}H_{18}ClNNaO_3S$ $[M+Na]^+$ 386.0592, found 386.0594.

(*S*)-2-((4-Chlorophenyl)sulfinyl)pyridine [(*S*)-**1h**]: A purification by preparative TLC in ethyl acetate/acetone/dichloromethane (V∶V∶V=10∶1∶1) to give **1h** as a white solid (33.8 mg, 71%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=7.2 min (minor), 8.5 min (major): 36% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.59～8.50 (m, 1H), 8.02 (dt, J=7.9, 1.1 Hz, 1H), 7.88 (td, J=7.8, 1.8 Hz, 1H), 7.78～7.70 (m, 2H), 7.46～7.39 (m, 2H), 7.34～7.29 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.5, 150.0, 142.6, 138.4, 137.5, 129.5, 126.3, 125.0, 118.5.

Isopropyl (*R*,*E*)-3-(3-butoxy-3-oxoprop-1-en-1-yl)-4-(pyridin-2-ylsulfinyl)benzoate (**3ia**) was prepared following GP B and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=8∶1) to give as a white solid (20.4 mg, 25%). The *ee* value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=31.2 min (minor), 37.6 min (major): 97% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 110.1～111.6 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.56～8.40 (m, 2H), 8.27 (d, J=1.9 Hz, 1H), 8.10 (dt, J=8.2, 1.6 Hz, 1H), 8.07～7.93 (m, 2H), 7.93～7.74 (m, 1H), 7.26 (dd, J=8.5, 3.8 Hz, 1H), 6.53 (dd, J=15.8, 1.4 Hz, 1H), 5.39～4.95 (m, 1H), 4.25 (tt, J=6.7, 1.7 Hz, 2H), 1.72 (dd, J=15.5, 8.1 Hz, 3H), 1.50～1.41 (m, 2H), 1.35 (d, J=6.3 Hz, 6H), 0.97 (td, J=7.4, 1.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.3, 165.2, 164.7, 150.0, 148.2, 139.1, 138.3, 134.4, 133.7, 131.2, 128.1, 125.2, 124.9, 122.6, 119.2, 69.5, 64.9, 30.8, 22.0, 19.3, 13.9. HRMS (ESI) calcd for $C_{22}H_{25}NNaO_5S$ $[M+Na]^+$ 438.1348, found 438.1351.

Isopropyl (*R*)-4-(pyridin-2-ylsulfinyl)benzoate [(*S*)-**1i**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=3∶1) to give **3ia** as a yellow solid (32.3 mg, 56%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=11.5 min (minor), 15.0 min (major): 55% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.57～8.52 (m, 1H), 8.15～8.06 (m, 2H), 8.01 (dt, J=7.9, 1.1 Hz, 1H), 7.92～7.77 (m, 3H), 7.34～7.28 (m, 1H), 5.30～5.03 (m, 1H), 1.33 (d, J=6.2 Hz, 6H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.5, 165.2, 150.0, 148.9, 138.4, 133.5, 130.3, 125.0, 124.7, 118.6, 69.1, 22.0.

Butyl (*R*,*E*)-3-(3-methyl-2-(pyridin-2-ylsulfinyl) phenyl)acrylate (**3ja**) was prepared following GP B and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give as a white foam (41.5 mg, 60%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=60∶40, flow=1.4 mL/min) with t_r=13.9 min (major), 36.5 min (minor): 42% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, J=15.8 Hz, 1H), 8.48～8.41 (m, 1H), 8.18 (dt, J=8.0, 1.0 Hz, 1H), 7.87 (td, J=7.7, 1.8 Hz, 1H), 7.42～7.32 (m, 2H), 7.29～7.20 (m, 2H), 6.11 (d, J=15.8 Hz, 1H), 4.16 (td, J=6.7, 4.4 Hz, 2H), 2.63 (s, 3H), 1.76～1.56 (m, 2H), 1.50～1.34 (m, 2H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 164.4, 149.6, 140.5, 140.5, 139.7, 136.9, 136.8, 132.8, 131.7, 126.0, 123.7, 121.5, 120.4, 64.2, 30.5, 19.8, 18.9, 13.6. HRMS (ESI) calcd for $C_{19}H_{21}NNaO_3S$ $[M+Na]^+$ 366.1136, found 366.1140.

(*S*)-2-(*o*-Tolylsulfinyl)pyridine [(*S*)-**1j**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1j** as a white solid (13.0 mg, 30%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=24.1 min (minor), 25.6 min (major): 96% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51～8.41 (m, 1H), 7.99 (dt, J=8.0, 1.1 Hz, 1H), 7.82 (td, J=7.8, 1.8 Hz, 1H), 7.76～7.69 (m, 1H), 7.30～7.20 (m, 3H), 7.15 (dd, J=6.7, 2.2 Hz, 1H), 2.61 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.4, 149.7, 142.9, 138.2, 137.7, 131.2, 131.1, 127.1, 124.7, 119.1, 19.5.

Butyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl) naphthalen-2-yl)-acrylate (**3ka**), butyl (*R*,*E*)-3-(3-(pyridin-2-ylsulfinyl)-naphthalen-1-yl)acrylate (**3ka'**): **3ka** and **3ka'** was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give as a white foam (30.5 mg, **3ka**, 26%, **3ka'**, 14%). The *ee* value was determined by HPLC analysis on a Chiralcel AD-H column (hexane/isopropanol, V∶V=90∶10, flow=1.2 mL/min) with t_r=53.5 min (major), 69.9 min (minor); 32.0 min (major), 48.1 min (minor): **3ka**, 91%; **3ka'**, 93% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, J=15.7 Hz, 1H), 8.49～8.38 (m, 3H), 8.24～8.03 (m, 3H), 7.96～7.89 (m, 2H), 7.88～7.81 (m, 3H), 7.75 (d, J=8.8 Hz, 1H), 7.62～7.51 (m, 3H), 7.31～7.20 (m, 2H), 6.83 (d, J=16.0 Hz, 1H), 6.46 (d, J=15.7 Hz, 1H), 4.49～4.06 (m, 3H), 1.81～1.62 (m, 3H), 1.52～1.43 (m, 3H), 0.98 (t, J=7.4 Hz, 5H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 166.1, 166.0, 165.5, 150.0, 149.8, 140.9, 140.6, 140.5, 138.7, 138.1, 138.1, 134.8, 134.4, 134.2, 133.3, 131.0, 130.8, 130.6, 129.8, 128.7, 128.6, 128.4, 128.3, 128.1, 127.8,

127.6, 126.9, 125.9, 124.7, 124.5, 121.4, 120.9, 119.5, 119.5, 65.0, 64.7, 30.9, 30.8, 19.3, 19.3, 13.9. HRMS (ESI) calcd for $C_{22}H_{21}NNaO_3S$ $[M+Na]^+$ 402.1134, found 402.1140.

(*S*)-2-(Naphthalen-2-ylsulfinyl)pyridine [(*S*)-**1k**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1k** as a white solid (26.0 mg, 51%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=10.8 min (major), 12.6 min (minor): 94% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (dt, J=4.5, 1.5 Hz, 1H), 8.38 (d, J=1.7 Hz, 1H), 8.11 (dt, J=7.9, 1.1 Hz, 1H), 7.97～7.80 (m, 4H), 7.76 (dd, J=8.7, 1.8 Hz, 1H), 7.55 (dd, J=6.3, 3.2 Hz, 2H), 7.32～7.26 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.8, 149.9, 141.2, 138.3, 134.6, 132.9, 129.6, 128.8, 128.1, 128.0, 127.3, 125.7, 124.8, 120.9, 118.7.

Butyl (*R*,*E*)-3-(5-methyl-2-((5-(trifluoromethyl) pyridin-2-yl)sulfinyl)phenyl)acrylate (**3la**) was prepared following GP B and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=12∶1) to give as a white foam (23.7 mg, 29%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=24.9 min (minor), 30.0 min (major): 96% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.72 (d, J=2.2 Hz, 1H), 8.42 (d, J=15.8 Hz, 1H), 8.23 (d, J=8.2 Hz, 1H), 8.11 (dd, J=8.2, 2.2 Hz, 1H), 7.74 (d, J=8.1 Hz, 1H), 7.47 (d, J=1.8 Hz, 1H), 7.29 (dd, J=8.2, 1.8 Hz, 1H), 6.44 (d, J=15.7 Hz, 1H), 4.24 (t, J=6.6 Hz, 2H), 2.38 (s, 3H), 1.69 (dt, J=8.5, 6.8 Hz, 2H), 1.50～1.40 (m, 2H), 0.96 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.3, 166.5, 146.9 (q, $^3J_{C\text{-}F}$=4.0 Hz), 142.6, 140.0, 139.6, 135.4 (q, $^3J_{C\text{-}F}$=3.7 Hz), 134.4, 131.8, 127.9, 127.3 (q, $^2J_{C\text{-}F}$=33.7 Hz), 125.6, 121.8, 123.0 (q, $^1J_{C\text{-}F}$=273.9 Hz), 118.9, 64.8, 30.8, 21.5, 19.3, 13.9; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −64.40. HRMS (ESI) calcd for $C_{20}H_{20}F_3NNaO_3S$ $[M+Na]^+$ 434.1011, found 434.1014.

(*S*)-2-(*p*-Tolylsulfinyl)-5-(trifluoromethyl)pyridine [(*S*)-**1l**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=12∶1) to give **1l** as a white solid (35.1 mg, 62%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=10.9 min (minor), 12.3 min (major): 53% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.86～8.70 (m, 1H), 8.22 (d, J=8.2 Hz, 1H), 8.11 (dd, J=8.3, 2.2 Hz, 1H), 7.78～7.59 (m, 2H), 7.27 (d, J=9.5 Hz, 1H), 2.36 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 170.5, 146.8 (q, $^3J_{C\text{-}F}$=3.9 Hz), 142.4, 140.1, 135.5 (q, $^3J_{C\text{-}F}$=3.5 Hz), 130.2, 127.8 (q, $^2J_{C\text{-}F}$=33.6 Hz), 125.2, 123.0 (q, $^1J_{C\text{-}F}$=274.0 Hz), 118.4, 21.6; ^{19}F NMR (376 MHz, $CDCl_3$) δ: −62.35.

tert-Butyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl) acrylate (**3ab**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give as a yellow foam (24.3 mg, 37%). The *ee* value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol, V∶V=60∶40, flow=1.0 mL/min) with t_r=9.3 min (minor), 11.2 min (major): 82% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, J=4.7 Hz, 1H), 8.39 (d, J=15.7 Hz, 1H), 8.05 (d, J=7.9 Hz, 1H), 7.93～7.80 (m, 2H), 7.62 (dd, J=7.4, 1.7 Hz, 1H), 7.52～7.39 (m, 2H), 7.31～7.21 (m, 1H), 6.34 (d, J=15.7 Hz, 1H), 1.55 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.3, 149.7, 138.5, 137.8, 134.4, 131.2, 130.3, 126.8, 125.3, 124.4, 123.5, 119.0, 102.3, 80.7, 59.7, 28.0. HRMS (ESI) calcd for $C_{18}H_{19}NNaO_3S$ $[M+Na]^+$ 352.0978, found 352.0983.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1a** as a white solid (17.1 mg, 42%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=21.3 min (minor), 23.0 min (major): 98% *ee*.

Allyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl)acrylate (**3ac**) was prepared following GP B and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give as a yellow foam (20.0 mg, 32%). The *ee* value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol, V∶V=60/40, flow=1.0 mL/min) with t_r=16.8 min (minor), 18.7 min (major): 95% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.52 (d, J=15.8 Hz, 1H), 8.48 (d, J=4.8 Hz, 1H), 8.05 (d, J=7.9 Hz, 1H), 7.93～7.88 (m, 1H), 7.86 (dd, J=7.8, 1.7 Hz, 1H), 7.65 (d, J=7.2 Hz, 1H), 7.54～7.48 (m, 1H), 7.48～7.41 (m, 1H), 7.30～7.20 (m, 1H), 6.46 (d, J=15.8 Hz, 1H), 6.07～5.96 (m, 1H), 5.41 (dt, J=17.2, 1.6 Hz, 1H), 5.29 (d, J=10.4 Hz, 1H), 4.75 (d, J=5.6 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 150.0, 144.0, 140.3, 138.2, 134.4, 132.3, 131.6, 130.9, 127.2, 125.6, 124.7, 121.4, 119.2, 118.4, 65.5, 29.8. HRMS (ESI) calcd for $C_{17}H_{15}NNaO_3S$ $[M+Na]^+$ 336.0664, found 336.0670.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1a** as a white solid (20.3 mg, 50%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=20.3 min (minor), 22.0 min (major): 97% *ee*.

2-Hydroxyethyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl) acrylate (**3ad**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=1∶1) to give as a yellow solid (30.9 mg, 49%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=60∶40, flow=1.0 mL/min) with t_r=8.5 min (major), 14.7 min (minor): 88% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 121.0～

122.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.55～8.41 (m, 2H), 8.02 (dt, J=7.9, 1.1 Hz, 1H), 7.95～7.81 (m, 2H), 7.62 (dd, J=7.7, 1.5 Hz, 1H), 7.53～7.42 (m, 2H), 7.31～7.23 (m, 1H), 6.43 (d, J=15.8 Hz, 1H), 4.42～4.31 (m, 2H), 3.92 (d, J=4.7 Hz, 2H), 2.70 (s, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 165.5, 149.9, 143.9, 140.4, 138.3, 134.0, 131.6, 131.1, 127.1, 125.4, 124.9, 121.0, 119.3, 66.5, 61.3. HRMS (ESI) calcd for $C_{16}H_{15}NNaO_4S$ $[M+Na]^+$ 340.0615, found 340.0619.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=1∶1) to give **1a** as a white solid (20.1 mg, 50%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=21.2 min (minor), 22.9 min (major): 97% *ee*.

2-Phenoxyethyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl) phenyl)acrylate (**3ae**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=3∶1) to give as a white foam (23.6 mg, 30%). The *ee* value was determined by HPLC analysis on a Chiralcel AS-H column (hexane/isopropanol, V∶V=60∶40, flow=1.4 mL/min) with t_r=34.2 min (major), 54.5 min (minor): 88% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53 (d, J=15.8 Hz, 1H), 8.44 (d, J=4.7 Hz, 1H), 8.04 (d, J=7.9 Hz, 1H), 7.91 (dd, J=7.7, 1.6 Hz, 1H), 7.83 (td, J=7.7, 1.6 Hz, 1H), 7.64 (d, J=7.4 Hz, 1H), 7.55～7.48 (m, 1H), 7.48～7.40 (m, 1H), 7.30 (t, J=7.8 Hz, 2H), 7.23 (dd, J=7.6, 4.8 Hz, 1H), 6.97 (dd, J=11.6, 7.7 Hz, 3H), 6.47 (d, J=15.8 Hz, 1H), 4.60 (t, J=4.7 Hz, 2H), 4.28 (t, J=4.7 Hz, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.6, 165.8, 159.0, 150.3, 144.4, 140.9, 138.4, 134.6, 131.9, 131.3, 130.0, 127.5, 126.0, 125.0, 121.7, 121.4, 119.6, 115.1, 66.4, 63.6. HRMS (ESI) calcd for $C_{22}H_{19}NNaO_4S$ $[M+Na]^+$ 416.0930, found 416.0932.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=3∶1) to give **1a** as a white solid (17.0 mg, 42%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=21.6 min (minor), 23.5 min (major): 90% *ee*.

Phenyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl) acrylate (**3af**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give as a white solid (30.7 mg, 44%). The *ee* value was determined by HPLC analysis on a Chiralcel IA column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=51.0 min (major), 61.4 min (minor): 90% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 165.4～167.1 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.69 (d, J=15.8 Hz, 1H), 8.52～8.48 (m, 1H), 8.08 (dt, J=8.0, 1.0 Hz, 1H), 7.97～7.91 (m, 1H), 7.89 (td, J=7.7, 1.8 Hz, 1H), 7.73 (dd, J=7.4, 1.7 Hz, 1H), 7.54 (dd, J=7.4, 5.7 Hz, 1H), 7.49 (dd, J=7.4, 1.7 Hz, 1H), 7.46～7.38 (m, 2H), 7.33～7.23 (m, 2H), 7.23～7.17 (m, 2H), 6.63 (d, J=15.8 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.5, 164.8, 150.9, 150.0, 144.2, 141.8, 138.2, 134.1, 131.7, 131.2, 129.6, 127.3, 126.0, 125.8, 124.7, 121.7, 120.8, 119.2. HRMS (ESI) calcd for $C_{20}H_{15}NNaO_3S$ $[M+Na]^+$: 372.0668, found 372.0670.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1a** as a white solid (20.7 mg, 51%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=21.1 min (minor), 22.9 min (major): 92% *ee*.

Benzyl (*R*,*E*)-3-(2-(pyridin-2-ylsulfinyl)phenyl) acrylate (**3ag**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethylacetate (V∶V=4∶1) to give as a white foam (26.8 mg, 37%). The *ee* value was determined by HPLC analysis on a Chiralcel IJ column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=43.1 min (major), 53.9 min (minor): 87% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54 (d, J=15.8 Hz, 1H), 8.49～8.37 (m, 1H), 8.05～7.98 (m, 1H), 7.91 (dd, J=7.7, 1.6 Hz, 1H), 7.80 (td, J=7.8, 1.8 Hz, 1H), 7.63 (dd, J=7.5, 1.6 Hz, 1H), 7.51～7.43 (m, 4H), 7.42～7.32 (m, 3H), 7.20～7.25 (m, 1H), 6.47 (d, J=15.8 Hz, 1H), 5.28 (s, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 165.5, 149.9, 143.9, 140.4, 138.1, 136.1, 134.2, 131.5, 130.9, 128.7, 128.4, 128.4, 127.1, 125.6, 124.6, 121.3, 119.2, 66.6. HRMS (ESI) calcd for $C_{21}H_{17}NNaO_3S$ $[M+Na]^+$ 386.0824, found 386.0827.

(*S*)-2-(Phenylsulfinyl)pyridine (*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1a** as a white solid (19.0 mg, 47%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=21.1 min (minor), 22.9 min (major): 98% *ee*.

(Tetrahydrofuran-2-yl)methyl (*E*)-3-(2-((*R*)-pyridin-2-ylsulfinyl)phenyl)acrylate (**3ah**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=2∶1) to give as a yellow foam (27.8 mg, 39%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=85∶15, flow=1.0 mL/min) with t_r=49.3 min (major), 87.8 min (minor); 56.8 min (major), 67.9 min (minor): 90% *ee*; 90% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (d, J=15.9 Hz, 1H), 8.47 (d, J=4.5 Hz, 1H), 8.04 (d, J=7.9 Hz, 1H), 7.95～7.80 (m, 2H), 7.63 (d, J=7.4 Hz, 1H), 7.56～7.40 (m, 2H), 7.31～7.21 (m, 1H), 6.48 (dd, J=15.8, 2.6 Hz, 1H), 4.31 (dd, J=10.9, 3.0 Hz, 1H), 4.26～4.10 (m, 2H), 4.02～3.88 (m, 1H), 3.82 (q, J=7.2 Hz, 1H), 2.10～2.02 (m, 1H), 2.03～1.77 (m, 2H), 1.81～1.56 (m, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.3, 165.5, 150.0, 144.0, 140.3, 138.1, 134.3, 131.5, 130.9, 127.1, 125.5, 124.7, 121.3, 121.3, 119.2, 76.7, 68.7,

66.9, 66.9, 28.1, 28.1, 25.9, 25.8. HRMS (ESI) calcd for $C_{19}H_{19}NNaO_4S$ $[M+Na]^+$ 380.0928, found 380.0932.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=2∶1) to give **1a** as a white solid (18.2 mg, 45%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=21.8 min (minor), 23.5 min (major): 98% *ee*.

Octahydro-1*H*-4,7-methanoinden-5-yl (*E*)-3-(2-((*R*)-pyridin-2-ylsulfinyl)phenyl) acrylate (**3ai**) was prepared following GP A and purified by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give as a white foam (33.4 mg, 41%). The *ee* value was determined by HPLC analysis on a Chiralcel IG-ID column (hexane/isopropanol, *V*∶*V*=60∶40, flow=0.8 mL/min) with t_r=56.0 min (major), 61.9 min (minor); 66.6 min (minor), 76.7 min (major): 86% *ee*; 87% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.54～8.36 (m, 2H), 8.04 (d, *J*=8.0 Hz, 1H), 7.95～7.76 (m, 2H), 7.63 (d, *J*=7.4 Hz, 1H), 7.53～7.39 (m, 2H), 7.26 (d, *J*=11.5 Hz, 1H), 6.38 (d, *J*=15.6 Hz, 1H), 4.72 (d, *J*=6.8 Hz, 1H), 2.17 (s, 1H), 2.07 (d, *J*=4.4 Hz, 1H),1.96～1.63 (m, 7H), 1.51 (dt, *J*=13.4, 2.9 Hz, 1H), 1.39 (s, 2H), 1.04～1.90 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.5, 165.9, 150.3, 144.2, 139.8, 138.4, 134.8, 131.8, 131.0, 127.4, 126.0, 125.0, 122.6, 119.6, 47.7, 46.7, 43.4, 40.1, 39.6, 39.5, 32.5, 32.1, 29.9, 29.9, 28.2. HRMS (ESI) calcd for $C_{24}H_{25}NNaO_3S$ $[M+Na]^+$ 430.1449, found 430.1453.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give **1a** as a white solid (19.1 mg, 47%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90/10, flow=0.8 mL/min) with t_r=22.0 min (minor), 23.0 min (major): 98% *ee*.

2-((*R*)-(2-(((1*R*,3*R*)-2-((*tert*-Butyldimethylsilyl)oxy)-adamantan-2-yl)ethynyl)-4-methylphenyl)sulfinyl) pyridine (**3aj**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=3∶1) to give as a yellow foam (30.4 mg, 37%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, *V*∶*V*=70∶30, flow=1.0 mL/min) with t_r=6.4 min (major), 9.5 min (minor): 90% *de*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.53～8.39 (m, 2H), 8.04 (dt, *J*=7.9, 1.1 Hz, 1H), 7.92～7.83 (m, 2H), 7.64 (dd, *J*=7.5, 1.7 Hz, 1H), 7.54～7.39 (m, 2H), 7.32～7.21 (m, 1H), 6.40 (d, *J*=15.7 Hz, 1H), 4.82 (td, *J*=10.9, 4.4 Hz, 1H), 2.12～2.05 (m, 1H), 1.94 (pd, *J*=6.9, 2.6 Hz, 1H), 1.79 (s, 1H), 1.75～1.66 (m, 2H), 1.60～1.43 (m, 2H),1.15～1.04 (m, 2H), 0.97～0.92 (m, 3H), 0.91 (d, *J*=1.5 Hz, 3H), 0.80 (d, *J*=7.0 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.6, 165.2, 149.6, 143.5, 139.2, 137.8, 134.2, 131.2, 130.4, 126.8, 125.3, 124.4, 122.0, 119.0, 74.4, 46.9, 40.7, 34.1, 31.2, 26.2, 23.4, 21.9, 20.6, 16.3. HRMS (ESI) calcd for $C_{24}H_{29}NNaO_3S$ $[M+Na]^+$ 434.1763, found 434.1766.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=3∶1) to give **1a** as a white solid (18.6 mg, 46%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=21.9 min (minor), 23.4 min (major): 99% *ee*.

4-((*S*)-2-((*tert*-Butoxycarbonyl)amino)-3-methoxy-3-oxopropyl)phenyl (*E*)-3-(2-((*R*)-pyridin-2-ylsulfinyl) phenyl)acrylate (**3ak**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=2∶1) to give as a white foam (44.0 mg, 40%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, *V*∶*V*=55∶45, flow=1.5 mL/min) with t_r=7.9 min (major), 11.7 min (minor): 91% *de*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.67 (d, *J*=15.8 Hz, 1H), 8.49 (d, *J*=4.6 Hz, 1H), 8.08 (d, *J*=7.9 Hz, 1H), 7.98～7.90 (m, 1H), 7.91～7.85 (m, 1H), 7.72 (dd, *J*=7.3, 1.8 Hz, 1H), 7.52 (pd, *J*=7.4, 1.6 Hz, 2H), 7.33～7.24 (m, 1H), 7.16 (q, *J*=8.5 Hz, 4H), 6.61 (d, *J*=15.8 Hz, 1H), 5.02 (d, *J*=8.2 Hz, 1H), 4.59 (q, *J*=6.8 Hz, 1H), 3.72 (s, 3H), 3.21～3.00 (m, 2H), 1.43 (s, 9H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 172.4, 165.5, 164.7, 155.2, 150.0, 149.9, 144.2, 141.8, 138.2, 134.1, 133.8, 131.6, 131.2, 130.4, 127.3, 125.7, 124.7, 121.8, 120.7, 119.2, 80.2, 54.5, 52.4, 37.8, 29.8, 28.4. HRMS (ESI) calcd for $C_{29}H_{30}N_2NaO_7S$ $[M+Na]^+$ 573.1663, found 573.1671.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=2∶1) to give **1a** as a white solid (20.8 mg, 51%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=21.7 min (minor), 23.4 min (major): 89% *ee*.

(8S,9*R*,13*R*)-13-Methyl-17-*oxo*-7,8,9,11,12,13,14,15,16,17-decahydro-6*H*-cyclopenta[*a*]phenanthren-2-yl (*E*)-3-(2-((*R*)-pyridin-2-ylsulfinyl)phenyl)acrylate (**3al**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=2∶1) to give as a yellow foam (37.8 mg, 36%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, *V*∶*V*=60∶40, flow=1.5 mL/min) with t_r=22.5 min (major), 28.9 min (minor): 90% *de*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.66 (d, *J*=15.8 Hz, 1H), 8.49 (dd, *J*=5.1, 1.6 Hz, 1H), 8.07 (dt, *J*=7.9, 1.1 Hz, 1H), 7.97～7.84 (m, 2H), 7.72 (dd, *J*=7.3, 1.8 Hz, 1H), 7.51 (td, *J*=7.0, 1.7 Hz, 2H), 7.38～7.27 (m, 2H), 6.99～6.89 (m, 2H), 6.62 (d, *J*=15.8 Hz, 1H), 2.94 (dd, *J*=9.0, 4.2 Hz, 2H), 2.51 (dd, *J*=18.8, 8.6 Hz, 1H), 2.47～2.38 (m, 1H), 2.31 (td, *J*=10.9, 4.1 Hz, 1H), 2.22～1.92 (m, 4H), 1.69～1.41 (m, 6H), 0.92 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 165.5, 165.1, 150.0, 148.7,

144.2, 141.6, 138.2, 137.6, 134.1, 131.6, 131.2, 127.3, 126.6, 125.8, 124.7, 121.7, 120.8, 119.2, 118.9, 50.5, 48.1, 44.3, 38.1, 36.0, 31.6, 29.5, 26.4, 25.9, 21.7, 13.9. HRMS (ESI) calcd for $C_{32}H_{31}NNaO_4S$ $[M+Na]^+$ 548.1870, found 548.1871.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (*V*∶*V*=2∶1) to give **1a** as a white solid (21.5 mg, 53%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=21.5 min (minor), 23.4 min (major): 91% *ee*.

(*R*,*E*)-2-((2-Styrylphenyl)sulfinyl)pyridine (**3am**) was prepared following GP C and purified by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give as a yellow foam (18.9 mg, 31%). The *ee* value was determined by HPLC analysis on a Chiralcel IJ column (hexane/isopropanol, *V*∶*V*=80∶20, flow=1.0 mL/min) with t_r=19.2 min (minor), 21.1 min (major): 91% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (d, *J*=4.6 Hz, 1H), 8.02 (d, *J*=7.9 Hz, 1H), 7.94 (d, *J*=16.1 Hz, 1H), 7.89 (dd, *J*=7.7, 1.6 Hz, 1H), 7.83 (td, *J*=7.7, 1.7 Hz, 1H), 7.70 (d, *J*=7.6 Hz, 1H), 7.58 (d, *J*=7.5 Hz, 2H), 7.48～7.43 (m, 1H), 7.40 (dd, *J*=8.3, 6.7 Hz, 3H), 7.34～7.28 (m, 1H), 7.28～7.20 (m, 1H), 7.06 (d, *J*=16.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 149.8, 142.1, 138.1, 137.4, 137.1, 132.3, 131.5, 128.9, 128.5, 128.4, 127.2, 126.1, 125.4, 124.7, 124.1, 119.4, 109.3. HRMS (ESI) calcd for $C_{19}H_{15}NNaOS$ $[M+Na]^+$ 328.0766, found 328.0772.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give **1a** as a white solid (19.9 mg, 49%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=70∶30, flow=1.0 mL/min) with t_r=21.0 min (minor), 22.7 min (major): 93% *ee*.

(*R*,*E*)-2-((2-(4-Fluorostyryl)phenyl)sulfinyl)pyridine (**3an**) was prepared following GP C and purified by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give as a white solid (18.7 mg, 29%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, *V*∶*V*=80∶20, flow=1.0 mL/min) with t_r=10.5 min (major), 16.0 min (minor): 84% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 124.0～124.9 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.50 (dd, *J*=4.7, 1.7 Hz, 1H), 8.04 (d, *J*=7.9 Hz, 1H), 7.94～7.79 (m, 3H), 7.69 (dd, *J*=7.6, 1.5 Hz, 1H), 7.61～7.53 (m, 2H), 7.51～7.37 (m, 2H), 7.28 (t, *J*=2.7 Hz, 1H), 7.16～6.92 (m, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 162.8 (d, $^1J_{C\text{-}F}$=249.2 Hz), 149.7, 142.0, 138.1, 137.2, 133.2 (d, $^4J_{C\text{-}F}$=3.4 Hz), 131.5, 131.0, 128.7 (d, $^3J_{C\text{-}F}$=8.2 Hz), 128.5, 126.0, 125.3, 124.7, 123.9 (d, $^5J_{C\text{-}F}$=2.6 Hz), 119.3, 115.9 (d, $^2J_{C\text{-}F}$=21.9 Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ: −113.10. HRMS (ESI) calcd for $C_{19}H_{14}FNNaOS$ $[M+Na]^+$ 346.0671, found 346.0678.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give **1a** as a white solid (19.0 mg, 47%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=22.8 min (minor), 24.8 min (major): 99% *ee*.

(*R*,*E*)-2-((2-(4-chlorostyryl)phenyl)sulfinyl)pyridine (**3ao**) was prepared following GP C and purified by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give as a white solid (14.4 mg, 33%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, *V*∶*V*=80∶20, flow=1.0 mL/min) with t_r=11.2 min (major), 17.5 min (minor): 90% *ee*. The absolute stereochemistry was assigned by X-ray diffraction analysis. m.p. 145.9～147.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.47 (dd, *J*=4.7, 1.6 Hz, 1H), 8.02 (d, *J*=7.9 Hz, 1H), 7.96～7.78 (m, 3H), 7.67 (dd, *J*=7.6, 1.6 Hz, 1H), 7.53～7.32 (m, 6H), 7.30～7.21 (m, 1H), 6.99 (d, *J*=16.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.4, 150.0, 142.4, 138.4, 137.3, 135.8, 134.3, 131.8, 131.2, 129.4, 129.0, 128.6, 126.4, 125.7, 125.0, 119.6. HRMS (ESI) calcd for $C_{19}H_{14}ClNNaOS$ $[M+Na]^+$ 362.0379, found 362.0382.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give **1a** as a white solid (19.5 mg, 48%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=22.7 min (minor), 24.7 min (major): 93% *ee*.

(*R*,*E*)-2-((2-(3-Chlorostyryl)phenyl)sulfinyl)pyridine (**3ap**) was prepared following GP C and purified by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give as a white foam (25.1 mg, 37%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, *V*∶*V*=80∶20, flow=1.0 mL/min) with t_r=10.6 min (major), 14.5 min (minor): 90% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.51 (dd, *J*=4.8, 1.7 Hz, 1H), 8.05 (d, *J*=7.9 Hz, 1H), 8.00～7.82 (m, 3H), 7.69 (dd, *J*=7.5, 1.7 Hz, 1H), 7.55 (d, *J*=1.9 Hz, 1H), 7.51～7.41 (m, 3H), 7.38～7.24 (m, 3H), 7.00 (d, *J*=16.1 Hz, 1H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.3, 150.0, 142.5, 139.2, 138.5, 137.1, 135.1, 131.8, 131.0, 130.4, 129.2, 128.5, 127.4, 126.5, 125.9, 125.7, 125.5, 125.0, 119.6. HRMS (ESI) calcd for $C_{19}H_{14}ClNNaOS$ $[M+Na]^+$ 362.0377, found 362.0382.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in toluene/ethyl acetate (*V*∶*V*=10∶1) to give **1a** as a white solid (21.5 mg, 53%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, *V*∶*V*=90∶10, flow=0.8 mL/min) with t_r=21.8 min (minor), 23.8 min (major): 80% *ee*.

(*R*,*E*)-2-((2-(2-(naphthalen-2-yl)vinyl)phenyl)sulfinyl)-

pyridine (**3aq**) was prepared following GP C and purified by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give as a white foam (20.6 mg, 29%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=80∶20, flow=1.0 mL/min) with t_r=15.0 min (major), 20.6 min (minor): 95% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.49 (dd, J=4.9, 1.7 Hz, 1H), 8.11～7.99 (m, 2H), 7.94～7.79 (m, 7H), 7.75 (dd, J=7.7, 1.4 Hz, 1H), 7.54～7.36 (m, 4H), 7.29～7.15 (m, 2H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.0, 149.8, 141.9, 138.1, 137.3, 134.5, 133.7, 133.4, 132.3, 131.5, 128.6, 128.5, 128.3, 127.9, 127.6, 126.6, 126.4, 126.0, 125.4, 124.7, 124.3, 123.8, 119.4. HRMS (ESI) calcd for $C_{23}H_{17}NNaOS$ $[M+Na]^+$ 378.0924, found 378.0929.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in toluene/ethyl acetate (V∶V=10∶1) to give **1a** as a white solid (20.8 mg, 51%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=21.7 min (minor), 23.7 min (major): 72% *ee*.

(*R*,*E*)-1-(2-(Pyridin-2-ylsulfinyl)phenyl)pent-1-en-3-onee (**3ar**) was prepared following GP A and purified by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **3ab** as a white solid (19.7 mg, 35%). The *ee* value was determined by HPLC analysis on a Chiralcel OD-H column (hexane/isopropanol, V∶V=55∶45, flow=1.5 mL/min) with t_r=4.5 min (major), 14.2 min (minor): 88% *ee*. The absolute stereochemistry was assigned by analogy to compound **3ao**. m.p. 106.0～107.3 ℃; ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.46 (d, J=4.7 Hz, 1H), 8.39 (d, J=16.2 Hz, 1H), 8.04 (d, J=7.9 Hz, 1H), 7.97～7.91 (m, 1H), 7.91～7.83 (m, 1H), 7.66 (dd, J=7.6, 1.5 Hz, 1H), 7.55～7.48 (m, 1H), 7.46 (t, J=7.4 Hz, 1H), 7.33～7.20 (m, 1H), 6.65 (d, J=16.2 Hz, 1H), 2.80 (p, J=7.6 Hz, 2H), 1.20 (t, J=7.3 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 201.6, 150.2, 144.3, 138.6, 138.1, 134.8, 131.9, 131.2, 129.8, 127.4, 125.7, 125.1, 119.4, 33.7, 8.7. HRMS (ESI) calcd for $C_{16}H_{15}NNaO_2S$ $[M+Na]^+$ 308.0716, found 308.0721.

(*S*)-2-(Phenylsulfinyl)pyridine [(*S*)-**1a**]: A purification by preparative TLC in petroleum ether/ethyl acetate (V∶V=4∶1) to give **1a** as a white solid (25.0 mg, 62%). The *ee* value was determined by HPLC analysis on a Chiralcel OJ-H column (hexane/isopropanol, V∶V=90∶10, flow=0.8 mL/min) with t_r=20.4 min (minor), 22.0 min (major): 73% *ee*.

(*R*)-2-((2-Ethynylphenyl)sulfinyl)pyridine **4aa**: The *ee* value was determined by HPLC analysis on a Chiralcel IB N-5 column (hexane/isopropanol, V∶V=60∶40, flow=1.2 mL/min) with t_r=17.7 min (minor), flow=28.1 min (major): 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.60 (dt, J=4.8, 1.4 Hz, 1H), 8.53 (d, J=15.8 Hz, 1H), 8.47～8.41 (m, 1H), 8.29 (d, J=7.9 Hz, 1H), 7.88 (td, J=7.8, 1.8 Hz, 1H), 7.61～7.51 (m, 3H), 7.43～7.39 (m, 1H), 6.06 (d, J=15.8 Hz, 1H), 4.16 (t, J=6.6 Hz, 2H), 3.55 (s, 1H), 1.72～1.58 (m, 2H), 1.47～1.37 (m, 2H), 0.95 (t, J=7.4 Hz, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ: 166.1, 159.8, 150.1, 141.7, 139.4, 138.0, 135.1, 133.6, 130.7, 129.9, 128.8, 126.7, 122.7, 122.0, 64.6, 30.8, 19.2, 13.9. HRMS (ESI) calcd for $C_{18}H_{20}N_2NaO_3S$ $[M+Na]^+$ 367.1087, found 367.1089.

Supporting Information X-Ray crystallographic data, ^{1}H NMR, ^{13}C NMR, ^{19}F NMR spectra and HPLC charts for compounds. The Supporting Information is available free of charge via the Internet at http://sioc-journal.cn.

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[15] CCDC 2125440 (**3ao**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

(Lu, Y.)

