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Addition of aldehydes with allyltrichlorosilane catalyzed by chiral bis-N–O secondary amides

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ABSTRACT

New axially *N*-oxide amides derived from L-tryptophan were prepared and used as organocatalysts in enantioselective allylation of aromatic aldehydes with allyltrichlorosilanes. The corresponding addition adducts homoallylic chiral alcohols obtained high enantioselectivities (up to 96% ee) when 1 mol % of catalyst was used. The unexpected result is the addition product's absolute configuration is *R* when (*R*)-chiral amides was used, in contrast, it was (*S*) when (*R*)-chiral methyl ester were used in allylation. It exhibited that the N atoms of amides take part in the transition state procedure.

1. Introduction

Asymmetric additions of aldehydes with allylic reagents represent an important method to prepare highly useful chiral building blocks in organic synthesis due to synthetic versatility of propylene unit.[1] In 1994, Denmark reported the first example of asymmetric allylation utilizing chiral phosphoramides as chiral Lewis basic ligands.[2] Following this report, a series of chiral Lewis bases have been designed and investigated in the asymmetric allylation with allytrichlorosilanes.[3–6] Among these Lewis bases, *N*-oxide compounds, for their strong dipole and high nucleophilicity, serving as organocatalysts to catalyze asymmetric allylations have attracted considerable attention in the past two decades.[7] Since Nakajima first reported the axially chiral biquinoline *N*,*N*′-dioxide was an excellent catalyst for Sakurai–Hosomi reaction in 1998,[5a] several kinds of *N*-oxides derivatives from pyridines and tertiary amines have been synthesized and used for the asymmetric allylation by Malkov and Kocovsky,[8] Hayashi,[9] Kotora,[10] Zhu,[11] and others.[12] Some axially chiral *N*,*N*′-dioxide have shown modest to good enantioselectivities, and these catalysts were effective for aromatic aldehydes but stranded in aliphatic aldehydes.[7] On basis of aforementioned results and intrigued by the unique properties of *N*-oxides, a type of new axial Lewis bases embracing biscarboline moiety were developed for enantioselective allylation in our study recently.[11] We have found that 1,1′-biscarboline-*N*,*N*′-dioxide was useful for allylation of aldehydes. Inexpensive material, low catalytic amount (1 mol %) and convenient to manipulate of this catalysts promote us to study it profoundly and we continued to synthesize axial amides using the similar methods.

The unexpected result reported in this study is the addition products had (*R*) configuration using (*R*)-axially chiral 1,1′-biscarboline *N*,*N*′-dioxide amides (e.g., (*R*)-(+)-**5a**). In contrast, the absolute configuration of addition product was all (*S*) configuration when (*R*)-axially chiral 1,1′-biscarboline *N*,*N*′-dioxide methyl ester (like (*R*)-(+)-**9**) was used.

2. Results and discussion

Tryptophan **1** was converted to the corresponding methyl ester using $SOCl_2$ in methanol. After Pictet–Spengler reactions and hydrolysis, **1** was transferred to **2** based on our recent report. Seven secondary amines (**3a**–**g**) and carboxylic acid **2** were condensed to form the corresponding amides, which were further oxidized by MCPBA or UHP. The specific route to amides **5a**–**g** is illustrated in Scheme 1.

The chiral separation of (+)-**5** from (−)-**5** was performed via chiral column with the eluent DCM/MeOH (v/v=90/10 to 95/5) at a rate of 2 or 2.5 mL/min. Optical rotation of (*R*)-**5g** was computed using density functional theory (DFT) at the B3LYP/6-311+G(d)

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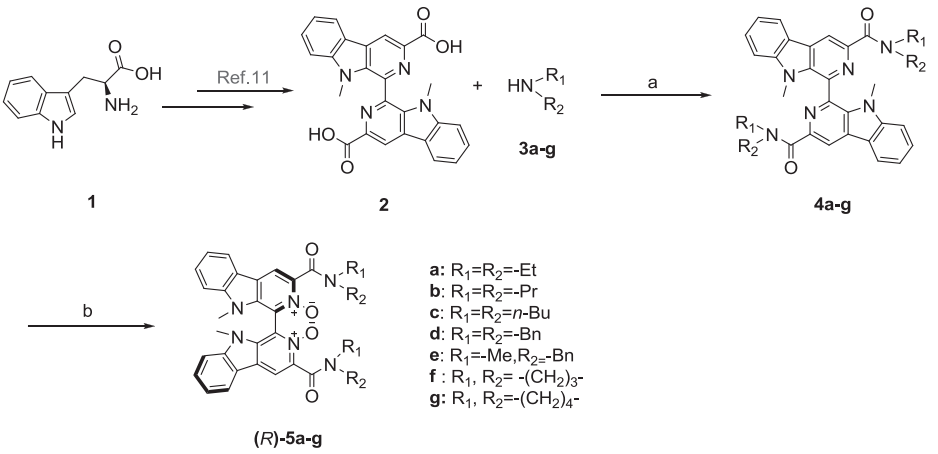
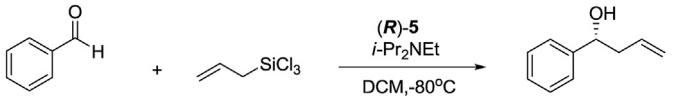


Scheme 1. Preparation of axially chiral catalysts (*R*)-**5a**–**g**. Reaction conditions: (a) (i) **2**, isobutyl-chloroformate (2.2 equiv), Et_3N (4 equiv), DCM, 0 °C, 15–20 min; (ii) amine (2.2 equiv), rt, 10 h. (**b**) (i) Unless otherwise noted, the reaction was carried out in DCM and MCPBA (6 equiv) at rt for 12 h; (ii) **5f** was oxidized by UHP (6 equiv) and TFA (6 equiv) in DCM at rt for 12 h. (iii) The racemic products were resolutioned by chiral HPLC on a CHIRALPAK ID column.

level in the gas phase.[13] The predicted optical rotation for (*R*)-**5g** should have positive optical rotations. The experimental data was +697.0 in $CHCl_3$. Obviously, (+)-**5g** owns (*R*) configuration.

The enantioselectivity of the catalysts is listed in Table 1. It was found that the higher ee% values were obtained by catalyst (*R*)-**5f**,**g** with cyclic amides (entries 10–15) at the C-3 and C-3′ positions. Among these ligands, (*R*)-**5g** with pyrrolidine moiety (entry 13) presented the best result (100% conv., 87%ee). *N*,*N*′-Dioxide catalysts with aliphatic amides (entries 1–9) at the C-3 and C-3′ positions (*R*)-**5a**–**e** were found to possess high conversion but low enantioselectivity. As illustrated in entries 1–9, a change in the amide substituent resulted in little or no difference in enantioselectivity. An interesting phenomenon was that the enantioselectivity was higher in the presence of 1 mol % of catalyst (*R*)-**5g** than using 10 mol % and 5 mol % in the catalytic reaction. However, the enantioselectivity was not improved with lower catalytic amount (0.5 mol % and 0.1 mol %) of (*R*)-**5g** and the conversion was poor in the reactions. The catalysts with aliphatic amides did exhibit low ee% values in the reaction.[14] The unexpected discovery is that the obtained addition products had (*R*) configuration using axially chiral 1,1′-biscarboline *N*,*N*′-dioxide amide, (*R*)-**5g**. This is different from what we obtained recently. In our recent report, it was found that the addition product had the (*S*)-configuration when using axially chiral (*R*)-1,1′-biscarboline *N*,*N*′-dioxide methyl ester. The problem of reverse configuration of product would be discussed later according to mechanism analysis.

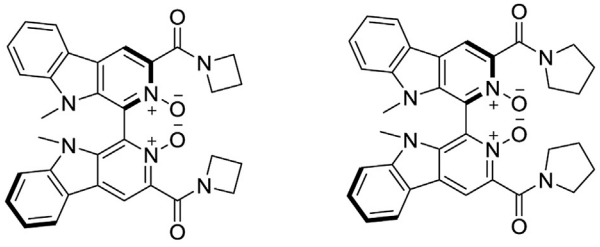
Table 1
Enantioselectivity of ligands (*R*)-**5a**–**g** in addition of aldehydes with allytrichlorosilane[a]



6a **7** **(*R*)-8a**

Entry	Cat.*	Amount (mol %)	ee[b,c] (%)
1	**5a**	1	17
2	**5a**	10	24
3	**5b**	1	22
4	**5b**	10	40
5	**5c**	1	11
6	**5c**	10	28
7	**5d**	10	31
8	**5e**	1	16
9	**5e**	10	19
10	**5f**	1	84
11	**5g**	0.1	78
12	**5g**	0.5	84
13	**5g**	1	87
14	**5g**	5	77
15	**5g**	10	69

[a] Reaction condition: **6a**, **7** (1.5 equiv), *i*-Pr_2NEt (3 equiv), 20 h.
[b] Determined by chiral HPLC on a CHIRAPAK IB column, see Experimental section for details.
[c] The absolute configuration of the major product was (*R*), which was determined by comparison with the reported value of optical rotation, see Ref. 11.

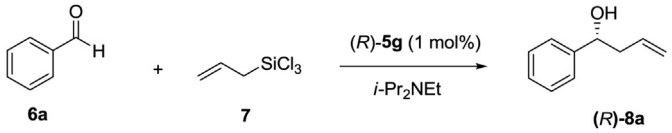


(*R*)-**5f** (*R*)-**5g**

Effects from solvent and temperature on the enantioselectivity were investigated. DCM, CH_3CN, toluene, THF, and other aprotic solvent were employed.[1,2] It was found that DCM was the suitable solvent. The results are summarized in Table 2. Temperature had great effect on ee% values, e.g., the 87% of ee% observed at −80 °C decreased to 56% while the temperature increased to −60 °C, and this magnitude decreased to 30% once the temperature raised to −40 °C (Table 2, entries 1–3).

It was found that (*R*)-**5g** could catalyze the reaction in a high enantioselectivity. Therefore, catalyst (*R*)-**5g** was used in the additions for other aldehydes (Table 3). Aldehydes with electron-donating groups, e.g., MeO at C-3 and C-4 catalyzed by (*R*)-**5g** exhibited good enantioselectivity (entries 3 and 4). Those aldehydes with strong electron-withdrawing group, e.g., 4-cyanobenzaldehyde, 3-nitrobenzaldehyde, and 4-nitrobenzaldehyde were catalyzed to give good enantioselectivities (entries 8, 11, and 12). Some aldehydes with electron-donating group, for example, 2-methoxyben zaldehyde present unsatisfied ee% value (67%ee, entry 2). The aliphatic aldehydes, e.g., cyclohexanecarboxaldehyde and phenylpropyl aldehyde were investigated to test the catalytic activity of (*R*)-**5g**. However, the resolution result showed that (*R*)-**5g** was not very effective for aliphatic aldehydes. The ee% value of the above two aliphatic aldehydes was 40% and 41%, respectively.

Table 2
Investigation of effects from solvents and temperatures on the allylation[a]

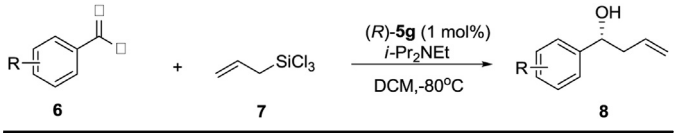


6a **7** **(*R*)-8a**

Entry	Solvent	*T* (°C)	ee[b,c] (%)
1	DCM	−80	87
2	DCM	−60	56
3	DCM	−40	30
4	DCM	20	17
5	DCM/$CHCl_3$ (1:10)	−80	68
6	$CHCl_3$	−60	42
7	CH_3CN	−45	34
8	THF	−80	33
9	Toluene	−80	31
10	$(CH_2)_2Cl_2$	−40	29

[a] Reaction condition: **6a**, **7** (1.5 equiv), *i*-Pr_2NEt (3 equiv), 20 h.
[b] Determined by chiral HPLC on a CHIRAPAK IB column.
[c] The absolute configuration of the major product was *R*, which was determined by comparison with the reported value of optical rotation, see Ref. 11.

Table 3
Asymmetric addition of aldehydes **6** with allytrichlorosilane catalyzed by (*R*)-**5g**[a]

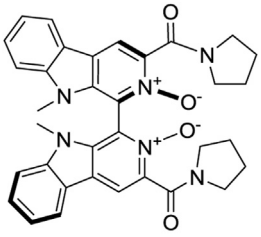


6 **7** **8**

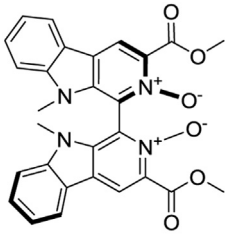
Entry	R	Yield[b] (%)	ee[c] (%)	Config.[d]	$[\alpha]_D$[e]
1	H	85	87	*R*	+45.6
2	2-OMe	86	67	*R*	+63.0
3	3-OMe	90	83	*R*	+56.1
4	4-OMe	88	94	*R*	+69.1
5	4-Me	90	76	*R*	+54.6
6	3-Cl	80	82	*R*	+58.3
7	4-Cl	85	76	*R*	+48.6
8	4-CN	80	82	*R*	+101.5
9	3-F	86	81	*R*	+45.6
10	4-F	88	73	*R*	+57.6
11	3-NO_2	97	96	*R*	+57.9
12	4-NO_2	95	86	*R*	+80.0
13	2-Naphth	87	76	*R*	+178.6

[a] Reaction condition: **6**, **7** (1.5 equiv), *i*-Pr_2NEt (3 equiv), 20 h.
[b] Isolated yield.
[c] Determined by HPLC using chiral column.
[d] The configuration was determined by comparing the recorded optical rotation with the reported data.
[e] Determined using enantiomeric pure enantiomer (100%ee), see Experimental section for details.

As mentioned above, the unexpected results are the obtained addition products had (*R*) configuration based on its positive optical rotation value. The absolute configuration of addition product is all (*S*) configuration with negative optical rotation values when axially chiral 1,1′-biscarboline *N*,*N*′-dioxide methyl ester (*R*)-**9** were used. The interesting result is exhibited here: why did (*R*)-**5g** give (*R*) configuration for the product in this report while (*R*)-**9** displayed (*S*) configuration in our previous study?



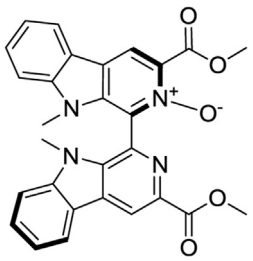
(*R*)-**5g**



(*R*)-**9**

Theoretically, the fundamental reason is that the transition state barriers using the (*R*)-**5** and (*R*)-**9** are different. However, to investigate such a big chiral catalyst to explore their barriers is currently out of our expectation due to the huge computational time. Based on the distribution of free ligand in solution has a large effect on the enantioselectivity,[15] we carefully investigated the structures of (*R*)-(+)-**5g** and (*R*)-(+)-**9** at the B3LYP/6-311++G(2d,p) level, respectively. It is unexpected that the two catalysts had total different stable conformations. For example, in (*R*)-(+)-**9**, the −OMe toward the outside resulted in the two O atoms of N−O in a close distance; thus leading to the normal bis-N−O structure TS structure formation (Fig. 1, up). However, it could not form the similar structure in (*R*)-(+)-**5g**. The two >C=O(NC_4H_8) tended to be close each other, which isolated the two O atoms of N−O groups (Fig. 1). Hence, two molecules of $SiCl_3CH_2CH{=}CH_2$ easily chelated with the two O atom of N−O groups in (*R*)-(+)-**5g**. Therefore, it formed two catalytic centers other than one. Once two Si atoms chelated with two O of N−O groups, the amide group may change their conformation, the O of C=O may chelate with the Si atom again. This new conformation may be kept until the reaction finished. Finally it catalyzed the addition to give the (*S*)-product.

Since bis N−O (*R*)-(+)-**9** catalyzed the addition to afford product (−)-**8a** and if the hypothesis above is correct, mono N−O catalyst like (*R*)-(+)-**10** should catalyze the addition to afford (+)-**8a**. To confirm the hypothesis, a mono N−O catalyst (*R*)-(+)-**10** was synthesized and used in the addition reactions. The product **8a** obtained had optical rotation of +15° in chloroform, the ee% was 33%. This addition product **8a** has (*R*)-configuration. Now, the whole mechanism for (*R*)-(+)-**5g** catalyzing the addition to afford (+)-**8a** is clear.



(*R*)-(+)-**10**

3. Conclusion

In summary, new axially chiral *N*,*N*′-dioxide catalysts bearing secondary amides at the C-3 and C-3′ positions were developed. The preliminary study of structure−activity indicated that catalysts possessing cyclic amides were more effective than the catalysts bearing acyclic amides for the asymmetric allylation of aromatic and aliphatic aldehydes. One unexpected and interesting result was the absolute configuration of the products provided by the catalyst (+)-(*R*)-**5g** were (*R*), which were reverse to the outcomes offered by (+)-(*R*)-**9**. The mechanism for the difference was well investigated using quantum methods and experimental results. Investigation of more reaction scope and better catalyst is in progress and will be reported in future.

4. Experimental section

4.1. General methods

GF_{254} thin layer chromatography was used. Flash column chromatography was performed with silica gel (200−300 mesh). Enantiomeric excess was determined by HPLC using chiral column and also compared with the corresponding pure enantiomers' optical rotation values, respectively. Optical rotations were performed on an

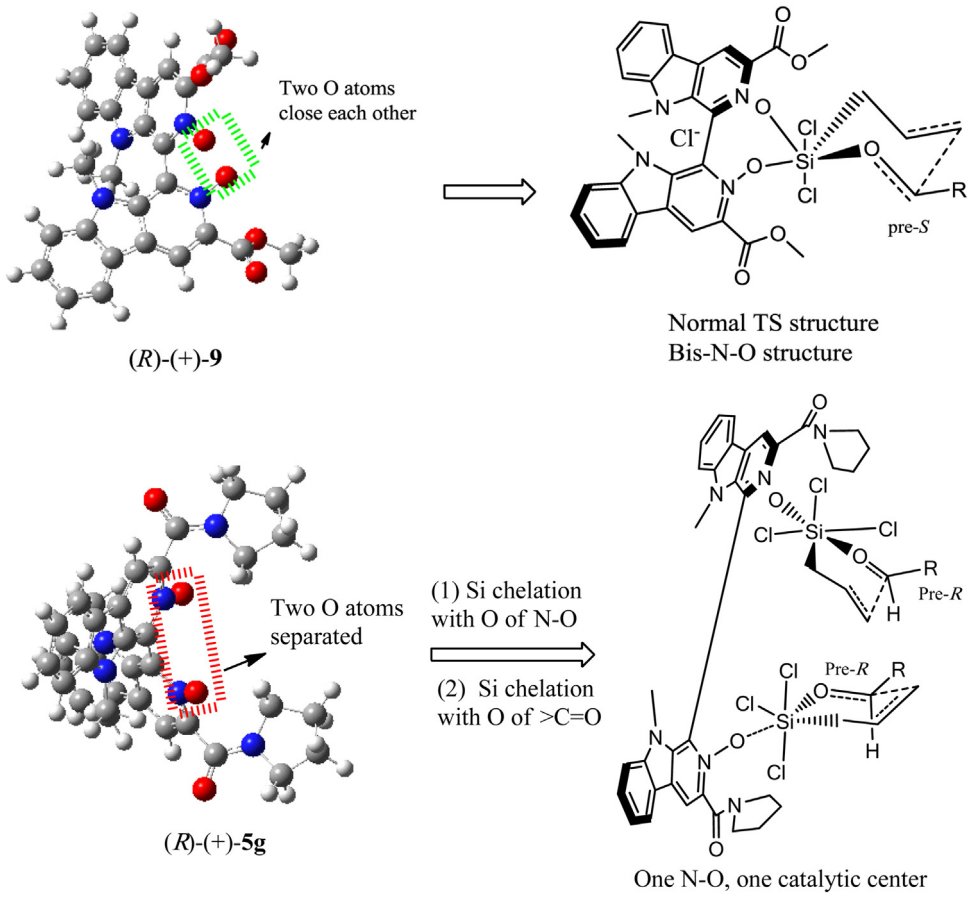


Fig. 1. The proposed TS structure for the procedure using (*R*)-(+)-**5g** (down) and the normal TS structure for bis-N–O catalyst (*R*)-(+)-**9** (up).

Optical Activity AA-55 polarimeter using a 10 cm cell with a Na 589 nm filter. IR spectra were obtained with an FT-IR spectrometer (Bruker Tensor 27). ^{1}H NMR and C NMR were recorded on a Bruker AV-400 spectrometer. The mass spectra were measured on an API QSTAR Pulsar. All solvents for the reactions were of reagent grade and were dried and distilled before used. Compound **2** was synthesized according to our former reported method.[11]

4.2. General procedure for preparation of 4a–g

To a dried DCM (50 mL) solution of **2** (0.45 g, 1 mmol) were added drop-wise isobutyl-chloroformate (2.2 equiv) and Et_3N (4 equiv) at ice-bath stirred. The mixture was kept at this temperature for 15 min. Then amines (2.2 equiv) were added and the mixture was stirred at rt for 12 h. The reaction was quenched by dilute HCl (1 mol/L), and the pH of the solution was adjusted to 7–8 by using saturated $NaHCO_3$. The solution was washed with saturated brine two times and was dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The residue was purified by chromatography (silica gel) eluting with petroleum ether/EtOAc.

*4.2.1. N,N,N′,N′-Tetraethyl-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-dicarboxamide (**4a**).* Following the general procedure mentioned above, **4a** was obtained as yellow solid, yield 75%. IR (KBr) ν=3431, 2961, 1639, 1450, 1391, 1336, 1235, 1132, 1008, 747 cm^{-1}. MS-ESI, *m*/*z* 560 [M+H]$^+$. HRMS *m*/*z* calcd for $C_{34}H_{36}N_6O_2$ 560.2900, Found 560.2899. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H×2), 8.07 (d, *J*=7.2 Hz, 1H×2), 7.58 (d, *J*=7.2 Hz, 1H×2), 7.36 (d, *J*=5.3 Hz, 2H×2), 3.39 (d, *J*=50.7 Hz, 7H×2), 1.30–1.15 (m, 6H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.99, 143.50, 138.25, 128.35, 124.75, 121.23, 120.86, 115.58, 109.77, 42.66, 39.43, 29.58, 14.18, 12.61.

*4.2.2. 9,9′-Dimethyl-N,N,N′,N′-tetrapropyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-dicarboxamide (**4b**).* Following the general procedure, **4b** was obtained as yellow solid, yield of 70%. IR (KBr) ν=3436, 2962, 1619, 1408, 1254, 1130, 1039, 743 cm^{-1}. MS-ESI, *m*/*z* 617[M+H]$^+$. HRMS *m*/*z* calcd for $C_{34}H_{44}N_6O_2$ 616.3526, Found 616.3530. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.56 (s, 1H×2), 8.33–8.13 (d, 1H×2), 7.49 (ddd, *J*=28.1, 14.8, 7.4 Hz, 3H×2), 3.66–3.12 (m, 4H×2), 3.35 (s, 3H×2), 1.86–1.16 (m, 4H×2), 1.11–0.82 (m, 3H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ168.57, 143.11, 135.81, 130.98, 129.38, 121.97, 120.98, 120.59, 115.77, 109.92, 51.21, 48.26, 32.24, 22.26, 20.82, 11.58, 10.82.

*4.2.3. N,N,N′,N′-Tetrabutyl-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-dicarboxamide (**4c**).* Following the general procedure, **4c** was obtained as yellow solid, yield of 80%. IR (KBr) ν=3425, 2954, 1614, 1450, 1409, 1287, 1245, 1131, 1040, 745 cm^{-1}. MS-ESI, *m*/*z* 672 [M+H]$^+$. HRMS *m*/*z* calcd for $C_{42}H_{52}N_6O_2$ 672.4152, Found 672.4156. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.57 (s, 1H×2), 8.25 (d, *J*=7.8 Hz, 1H×2), 7.50 (ddd, *J*=31.1, 14.9, 7.5 Hz, 3H×2), 3.45 (m, 4H×2), 3.40 (s, 3H×2), 1.69–1.41 (m, 8H×2), 0.94 (dd, *J*=24.2, 17.0 Hz, 4H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ168.25, 143.14, 135.83, 131.10, 129.40, 121.98, 121.03, 120.63, 115.98, 109.95, 49.53, 46.50, 31.28, 29.76, 20.44, 19.75, 13.94, 13.55.

*4.2.4. N,N,N′,N′-Tetrabenzyl-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-dicarboxamide (**4d**).* Following the general procedure, **4d** was obtained as yellow solid, yield of 74%. IR (KBr) ν=3430, 1627,

1544, 1492, 1472, 1445, 1407, 1325, 1251, 1154, 1041, 745 cm^{-1}. MS-ESI, *m/z* 808$[M+H]^+$. HRMS *m/z* calcd for $C_{54}H_{44}N_6O_2$ 808.3526, Found 808.3514. ^1H NMR (400 MHz, $CDCl_3$) δ 8.68 (s, 1H×2), 8.25 (d, *J*=12.6 Hz, 1H×2), 7.66 (m, 1H×2), 7.28 (m, 6H×2), 6.92 (d, *J*=3.9 Hz, 2H×2), 6.72 (d, *J*=3.2 Hz, 2H×2), 4.76 (dd, *J*=198.6, 64.4 Hz, 1H×2), 3.26 (s, 1H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 169.16, 142.95, 137.05, 135.75, 130.93, 129.30, 128.47, 127.76, 127.28, 126.72, 121.90, 120.65, 116.38, 109.90, 51.72. 48.66, 32.09.

*4.2.5. N,N′-Dibenzyl-N,N′,9,9′-tetramethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-dicarboxamide (**4e**).* Following the general procedure, **4e** was obtained as yellow solid, yield of 76%. IR (KBr) ν=3425, 2922, 1620, 1544, 1488, 1443, 1393, 1247, 1131, 1041, 745 cm^{-1}. MS-ESI, *m/z* 656$[M+H]^+$. HRMS *m/z* calcd for $C_{42}H_{36}N_6O_2$ 656.2900, Found 656.2894. ^1H NMR (400 MHz, $CDCl_3$) δ 8.59 (s, 1H×2), 8.18 (d, *J*=7.7 Hz, 1H×2), 7.58–7.25 (m, 3H×2), 7.20–6.79 (m, 5H×2), 4.25 (m, 2H×2), 3.31–2.72 (m, 6H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 166.55, 142.90, 137.20, 129.57, 128.57, 128.12, 127.98, 127.38, 126.94, 122.04, 121.93, 120.79, 116.36, 109.87, 55.13, 51.61, 34.19, 31.95.

*4.2.6. (9,9′-Dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-diyl)bis(azetidin-1-ylmethanone) (**4f**).* Following the general procedure, **4f** was obtained as yellow solid, yield of 85%. IR (KBr) ν=3430, 2946, 1617, 1542, 1469, 1434, 1399, 1243, 1129, 1039, 734 cm^{-1}. MS-ESI, *m/z* 528$[M+H]^+$. HRMS *m/z* calcd for $C_{32}H_{28}N_6O_2$ 528.2274, Found 528.2278. ^1H NMR (400 MHz, $CDCl_3$) δ 9.02 (s, 1H×2), 8.30 (d, *J*=13.5 Hz, 1H×2), 7.83–6.99 (m, 3H×2), 4.76–3.98 (t, 4H×2), 3.30 (s, 3H×2), 2.53–1.88 (m, 3H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.67, 142.73, 138.43, 129.16, 122.02, 121.36, 120.83, 116.07, 109.85, 55.29, 49.19, 31.87, 16.44.

*4.2.7. (9,9′-Dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole-3,3′-diyl) bis(pyrrolidin-1-ylmethanone) (**4g**).* Following the general procedure, **4g** was obtained as yellow solid, yield of 78%. IR (KBr) ν=3431, 2870, 1612, 1544, 1437, 1400, 1244, 1044, 747 cm^{-1}. MS-ESI, *m/z* 556$[M+H]^+$. HRMS *m/z* calcd for $C_{34}H_{32}N_6O_2$ 556.2587, Found 556.2578. ^1H NMR (400 MHz, $CDCl_3$) δ 8.83 (s, 1H×2), 8.25 (t, *J*=13.0 Hz, 1H×2), 7.65 (t, *J*=7.6 Hz, 1H×2), 7.38 (t, *J*=7.9 Hz, 2H×2), 4.03–3.58 (m, 4H×2), 3.19 (s, 3H×2), 1.86 (m, 4H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ166.58, 142.97, 136.09, 129.40, 122.11, 121.16, 120.75, 116.52, 109.86, 49.54, 47.15, 31.56, 26.66, 24.02.

4.3. General procedure for preparation of 5a–e, g

To a stirring solution of **4a**–**e** and **4g** (0.5 mmol) in DCM (25 mL) was added MCPBA (85%, 6 equiv), the reaction mixture was stirred at rt for 12 h. Then reaction was quenched by saturated $NaHCO_3$ and the pH was adjusted to 7–8. Then the solution was washed with saturated brine three times and was dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The residue was purified by chromatography (silica gel) eluting with DCM/MeOH.

*4.3.1. 3,3′-Bis(diethylcarbamoyl)-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5a**).* Following the general procedure, **5a** was obtained as brown solid, yield 60%. IR (KBr) ν=3426, 2961, 1639, 1450, 1391, 1336, 1235, 1132, 1008, 747 cm^{-1}. MS-ESI, *m/z* 593 $[M+H]^+$. HRMS *m/z* calcd for $C_{34}H_{36}N_6O_4$ 592.2798, Found 592.2796. ^1H NMR (400 MHz, $CDCl_3$) δ 8.08 (s, 1H×2), 7.99 (d, *J*=7.4 Hz, 1H×2), 7.50 (t, *J*=7.3 Hz, 1H×2), 7.35–7.22 (m, 3H×2), 3.76–3.01 (m, 11H×2), 1.30–1.13 (m, 6H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.82, 143.61, 138.19, 128.58, 124.70, 121.33, 120.98, 120.79, 115.66, 109.87, 42.92, 39.45, 14.23, 12.60, 11.81. $[\alpha]_D$ +435 (*c* 0.31, $CHCl_3$).

*4.3.2. 3,3′-Bis(dipropylcarbamoyl)-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5b**).* Following the general procedure, **5b** was obtained as yellow solid, yield 65%. IR (KBr) ν=3431, 1636, 1456, 1392, 1314, 1234, 1131, 1007, 749 cm^{-1}. MS-ESI, *m/z* 649 $[M+H]^+$. HRMS *m/z* calcd for $C_{38}H_{44}N_6O_4$ 648.3424, Found 648.3444. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H×2), 8.08 (d, *J*=7.7 Hz, 1H×2), 7.59 (t, *J*=7.3 Hz, 1H×2), 7.37 (t, *J*=7.5 Hz, 2H×2), 3.41 (s, 3H×2), 3.39–3.11 (m, 4H×2), 1.69 (m, 4H×2), 0.99 (t, *J*=7.4 Hz, 3H×2), 0.81 (t, *J*=7.3 Hz, 3H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.46, 143.57, 138.22, 128.45, 121.26, 120.93, 115.99, 109.76, 49.89, 46.63, 21.86, 20.45, 11.49, 11.23. $[\alpha]_D$ +459 (*c* 0.255, $CHCl_3$).

*4.3.3. 3,3′-Bis(dibutylcarbamoyl)-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5c**).* Following the general procedure, **5c** was obtained as yellow solid, yield 60%. IR (KBr) ν=3432, 2956, 1640, 1491, 1454, 1391, 1336, 1233, 1132, 1008, 748 cm^{-1}. MS-ESI, *m/z*705 $[M+H]^+$. HRMS *m/z* calcd for $C_{42}H_{52}N_6O_4$ 704.4050, Found 704.4056. ^1H NMR (400 MHz, $CDCl_3$) δ 8.17 (s, 1H×2), 8.07 (d, *J*=7.8 Hz, 1H×2), 7.58 (t, *J*=7.6 Hz, 1H×2), 7.35 (m, 2H×2), 3.42 (s, 3H×2), 3.25 (m, 4H×2), 1.74–1.40 (m, 2H×2), 1.39–1.10 (m, 2H×2), 0.93 (t, *J*=7.3 Hz, 3H×2), 0.80 (t, *J*=7.3 Hz, 3H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.16, 143.67, 138.16, 128.62, 121.34, 121.01, 120.80, 116.01, 109.82, 47.98, 44.79, 30.75, 29.86, 29.21, 20.26, 19.91, 13.96. $[\alpha]_D$ +377 (*c* 0.215, $CHCl_3$).

*4.3.4. 3,3′-Bis(dibenzylcarbamoyl)-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5d**).* Following the general procedure, **5d** was obtained as yellow solid, yield 56%. IR (KBr) ν=3432, 1643, 1603, 1493, 1449, 1391, 1315, 1234, 1019, 746 cm^{-1}. MS-ESI, *m/z* 841 $[M+H]^+$. HRMS *m/z* calcd for $C_{54}H_{54}N_6O_4$ 840.3424, Found 840.3425. ^1H NMR (400 MHz, $CDCl_3$) δ 8.10 (s, 1H×2), 8.01 (d, *J*=7.7 Hz, 1H×2), 7.58 (t, *J*=7.6 Hz, 1H×2), 7.37–7.37 (m, 2H×2), 7.25–7.15 (m, 10H×2), 4.56 (d, 2H×2), 4.25 (d, 2H×2), 3.44 (s, 3H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ164.27, 143.69, 137.69, 135.90, 128.81, 128.62, 128.52, 127.79, 127.72, 127.41, 127.12, 121.56, 121.12, 120.82, 116.48, 109.86, 50.81, 47.94, 30.52. $[\alpha]_D$ +269 (*c* 0.275, $CHCl_3$).

*4.3.5. 9,9′-Dimethyl-3,3′-bis(2-methyl-3-phenylpropanoyl)-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5e**).* Following the general procedure, **5e** was obtained as yellow solid, yield 60%. IR (KBr) ν=3440, 2992, 1640, 1491, 1454, 1391, 1336, 1233, 1132, 1008, 748 cm^{-1}. MS-ESI, *m/z*689 $[M+H]^+$. HRMS *m/z* calcd for $C_{42}H_{36}N_6O_4$ 688.2769, Found 688.2769. ^1H NMR (400 MHz, $CDCl_3$) δ 8.25 (s, 1H×2), 8.08 (ddd, *J*=29.1, 14.3, 8.6 Hz, 1H×2), 7.59 (m, 1H×2), 7.36–7.40 (m, 2H×2), 7.33–7.23 (m, 5H×2), 4.73 (m, 2H×2), 3.45 (s, 3H×2), 3.01 (m, 3H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ163.70, 143.66, 138.37,136.22,128.70, 127.90, 127.82, 127.34, 121.52, 121.09, 116.32, 109.86, 54.33, 50.75, 35.09, 33.05, 29.98, 29.92. $[\alpha]_D$ +447 (*c* 0.275, $CHCl_3$).

*4.3.6. 9,9′-Dimethyl-3,3′-di(pyrrolidine-1-carbonyl)-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5g**).* Following the general procedure, **5g** was obtained as yellow solid, yield 70%. IR (KBr) ν=3440, 2874, 1635, 1490, 1443, 1334, 1234, 1007, 749 cm^{-1}. MS-ESI, *m/z* 589 $[M+H]^+$. HRMS *m/z* calcd for $C_{34}H_{32}N_6O_4$ 588.2485, Found 588.2479. ^1H NMR (400 MHz, $CDCl_3$) δ 8.26 (s, 1H×2), 8.07 (d, *J*=7.8 Hz, 1H×2), 7.58 (t, *J*=7.7 Hz, 1H×2), 7.37 (dd, *J*=12.7, 5.3 Hz, 2H×2), 3.84–3.58 (m, 4H×2), 3.43 (s, 3H×2), 1.93 (m, 4H×2). ^{13}C NMR (101 MHz, $CDCl_3$) δ 161.61, 143.66, 138.37, 128.71, 124.78, 121.98, 121.50, 121.05, 120.81, 116.25, 109.88, 46.69, 46.08, 29.81, 25.74, 24.42. $[\alpha]_D$ +697 (*c* 0.185, $CHCl_3$).

4.4. Procedure for preparation of 5f

UHP (6 equiv) was added portion-wise to the stirred solution of **4** (0.5 mmol) in DCM (25 mL) at ice-bath, stirring for 15 min and to the mixture was added TFA (6 equiv). The reaction was then transferred to rt for 10 h. After finished, the mixture was washed with water, dried over anhydrous Na_2SO_4. The solvents were evaporated under reduced pressure. The residue was purified by chromatography

(silica gel) eluting with DCM/MeOH=70:1 to give *N*,*N*′-dioxides as yellow solid 182 mg, yield 37%. The racemic mixtures of **5f** were resolved by HPLC on a Chiral-park ID column (250×10 mm, DCM/MeOH=90:10) and (+)-**5f**, (−)-**5f** yields 45%, 43%, respectively.

*4.4.1. 3,3′-Di(azetidine-1-carbonyl)-9,9′-dimethyl-9H,9′H-1,1′-bipyrido[3,4-b]indole 2,2′-dioxide (**5f**).* Following the general procedure, **5f** was obtained as yellow solid, yield 65%. IR (KBr) ν=3441, 1633, 1442, 1449, 1198, 1020, 749 cm^{-1}. MS-ESI, *m*/*z* $[M+H]^+$. HRMS *m*/*z* calcd for $C_{32}H_{28}N_6O_4$ 560.2172, Found 560.2155. ^1H NMR (400 MHz, $CDCl_3$) δ 8.31 (s, 1H×2), 8.03 (d, *J*=7.9 Hz, 1H×2), 7.53 (t, *J*=7.6 Hz, 1H×2), 7.31 (t, *J*=7.2 Hz, 2H×2), 4.48–4.17 (d, 2H×2), 4.16–4.05 (d, *J*=59.5 Hz, 2H×2), 3.31 (s, 3H×2), 2.37 (m, 2H×2). ^{13}C NMR (100 MHz, $CDCl_3$) δ 162.90, 143.57, 138.68, 128.58, 124.96, 121.58, 121.37, 121.05, 120.93, 117.70, 109.81, 50.70, 48.98, 29.68, 16.04. $[\alpha]_D$ +657 (*c* 0.20, $CHCl_3$).

4.5. General procedure for reaction of allyltrichlorosilane with aldehydes

Allyltrichlorosilane **7** (0.3 mmol) was added to a solution of the catalyst **5** (1 mol %), diisopropylethylamine (0.6 mmol), and aldehyde **6** (0.2 mmol) in dichloromethane (1 mL) under nitrogen at −80 °C. The mixture was stirred at the same temperature for 20 h and then quenched with aqueous saturated $NaHCO_3$ (0.5 mL). The aqueous layer was extracted with dichloromethane. The combined organic layer was washed with saturated sodium chloride, dried over Na_2SO_4, and evaporated under reduced pressure. The residue was purified by flash chromatography on silica gel (petroleum ether/EtOAc) to give alcohol **8**.

*4.5.1. (R)-1-Phenylbut-3-en-1-ol (**8a**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (br s, 1H), 2.45–2.56 (m, 2H), 4.74 (dd, *J*=7.3, 5.5 Hz, 1H), 5.13–5.19 (m, 2H), 5.76–5.86 (m, 1H), 7.28–7.36 (m, 5H). Enantiomeric excess was determined by HPLC with a Chiralpark IB column (hexane/2-propanol=95:5, 1.5 mL/min), t_1=20.7 min (*R*); t_2=22.8 min (*S*), ee=87%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +45.6 (*c* 0.56, $CHCl_3$). The reported value for the *S*-enantiomer (92% ee) is $[\alpha]_D$ −61.2 (*c* 1.05, $CHCl_3$).[16]

*4.5.2. (R)-1-(2-Methoxyphenyl)proene-2-en-1-ol (**8b**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.55 (m, 2H), 2.70 (br s, 1H), 3.84 (s, 3H), 4.98 (m, 1H), 5.14 (m, 2H), 5.85 (m, 1H), 6.88 (d, *J*=8.2 Hz, 1H), 6.97 (m, 1H), 7.25 (m, 1H), 7.34 (m, 1H). Enantiomeric excess was determined by HPLC with a Chiralpark IB column (hexane/2-propanol=95:5, 2.5 mL/min), t_1=15.6 min (*S*); t_2=16.7 min (*R*), ee=67%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +63 (*c* 0.86, $CHCl_3$).

*4.5.3. (R)-1-(3-Methoxyphenyl)proene-2-en-1-ol (**8c**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.09 (d, *J*=3.0 Hz, 1H), 2.52 (m, 2H), 3.82 (s, 3H), 4.71 (m, 1H), 5.13–5.19 (m, 2H), 5.76–5.86 (m, 1H), 6.82 (ddd, *J*=8.0, 2.4, 0.8 Hz, 1H), 6.93 (m, 2H), 7.26 (dd, *J*=9.1, 7.1 Hz, 1H). Enantiomeric excess was determined by HPLC with a Chiralpark IA column (hexane/2-propanol=96:4, 3 mL/min), t_1=23.3 min (*R*); t_2=24.5 min (*S*), ee=83%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +56.1 (*c* 0.76, $CHCl_3$). The reported value for the *R*-enantiomer (97% ee) is $[\alpha]_D$ +53.8 (*c* 0.9,benzene).

*4.5.4. (R)-1-(4-Methoxyphenyl)proene-2-en-1-ol (**8d**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.04 (br s, 1H), 2.50 (t, *J*=6.8 Hz, 2H), 3.80 (s, 3H), 4.68 (t, *J*=6.4 Hz, 1H), 5.11–5.18 (m, 2H), 5.76–5.83 (m, 1H), 6.88 (d, *J*=8.6 Hz, 2H), 7.28 (d, *J*=8.6 Hz, 2H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (hexane/2-propanol=95:5, 3 mL/min), t_1=18.4 min (*R*); t_2=17.6 min (*S*), ee=93%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +69.1 (*c* 0.66, $CHCl_3$). The reported value for the *S*-enantiomer (92% ee) is $[\alpha]_D$ −48.0 (*c* 1.0, $CHCl_3$).[16]

*4.5.5. (R)-1-p-Tolylbut-3-en-1-ol (**8e**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (d, *J*=2.6 Hz, 1H), 2.36 (s, 3H), 2.49–2.53 (m, 2H), 4.72 (m, 1H), 5.14–5.19 (m, 2H), 5.77–5.87 (m, 1H), 7.18 (d, *J*=7.9 Hz, 2H), 7.26 (d, *J*=7.9 Hz, 2H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (hexane/2-propanol=95:5, 2 mL/min), t_1=16.0 min (*R*); t_2=17.3 min (*S*), ee=76%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +54.6 (*c* 0.48, $CHCl_3$). The reported value for the *S*-enantiomer (89% ee) is $[\alpha]_D$ −43.4 (*c* 1.1, $CHCl_3$).[9a]

*4.5.6. (R)-1-(3-Chlorophenyl)but-3-en-1-ol (**8f**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.17 (s, 1H), 2.41–2.55 (m, 2H), 4.71 (m, 1H), 5.15–5.20 (m, 2H), 5.73–5.84 (m, 1H), 7.21–7.30 (m, 3H), 7.37 (s, 1H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (hexane/2-propanol=95:5, 3 mL/min), t_1=9.7 min (*R*); t_2=10.3 min (*S*), ee=82%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +58.3 (*c* 0.60, $CHCl_3$).

*4.5.7. (R)-1-(4-Chlorophenyl)but-3-en-1-ol (**8g**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (d, *J*=2.7 Hz, 1H), 2.41–2.54 (m, 2H), 4.71 (m, 1H), 5.14–5.18 (m, 2H), 5.74–5.81 (m, 1H), 7.26–7.33 (m, 4H). Enantiomeric excess was determined by HPLC with a Chiralpark IA column (hexane/2-propanol=95:5, 1.5 mL/min), t_1=26.1 min (*R*); t_2=27.5 min (*S*), ee=76%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +48.6 (*c* 0.70, $CHCl_3$). The reported value for the *S*-enantiomer (89% ee) is $[\alpha]_D$ −60.6 (*c* 1.5, $CHCl_3$).[16]

*4.5.8. (R)-4-(1-Hydroxybut-3′-enyl)benzonitrile (**8h**).* ^1H NMR (400 MHz, $CDCl_3$) 2.23 (br s, 1H), 2.31–2.53 (m, 2H), 4.54 (m, 1H), 5.07–5.21 (m, 2m), 5.82 (m, 1H), 7.44–7.54 (m, 4H) Enantiomeric excess was determined by HPLC with a Chiralpark ID column (hexane/2-propanol=95:5, 3 mL/min), t_1=19.9 min (*R*); t_2=20.7 min (*S*), ee=82%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +101.5 (*c* 0.34, $CHCl_3$).

*4.5.9. (R)-1-(3-Fluorophenyl)but-3-en-1-ol (**8i**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.13 (d, *J*=3.0 Hz, 1H), 2.45–2.56 (m, 2H), 4.75 (m, 1H), 5.16–5.21 (m, 2H), 5.76–5.82 (m, 1H), 6.95–6.99 (m, 1H), 7.08–7.14 (m, 2H), 7.30–7.34 (m, 1H). Enantiomeric excess was determined by HPLC with a Chiralpark IA column (hexane/2-propanol=95:5, 1.5 mL/min), t_1=24.0 min (*R*); t_2=25.8 min (*S*), ee=81%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +45.6 (*c* 0.50, $CHCl_3$). The reported value for the *S*-enantiomer (99% ee) is $[\alpha]_D$ −14.1 (*c* 3.58, $CHCl_3$).[16]

*4.5.10. (R)-1-(4-Fluorophenyl)but-3-en-1-ol (**8j**).* ^1H NMR (400 MHz, $CDCl_3$) δ=2.13 (s, 1H), 2.43–2.55 (m, 2H), 4.73 (m, 1H), 5.15–5.19 (m, 2H), 5.74–5.83 (m, 1H), 7.02–7.06 (m, 2H), 7.27–7.35 (m, 2H). Enantiomeric excess was determined by HPLC with a Chiralpark IA column (hexane/2-propanol=95:5, 1.5 mL/min), t_1=22.6 min (*R*); t_2=23.5 min (*S*), ee=73%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +57.6 (*c* 0.58, $CHCl_3$).

*4.5.11. (R)-1-(3-Nitrophenyl)but-3-en-1-ol (**8k**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.33 (d, *J*=3.1 Hz, 1H), 2.43–2.52 (m, 1H), 2.53–2.62 (m, 1H), 4.87 (m, 1H), 5.18–5.22 (m, 2H), 5.75–5.85 (m, 1H), 7.53 (t, *J*=7.9 Hz, 1H), 7.71 (d, *J*=7.6 Hz, 1H), 8.14 (d, *J*=8.0 Hz, 1H), 8.25 (s, 1H). Enantiomeric excess was determined by HPLC with a Chiralpark IB column (hexane/2-propanol=95:5, 2 mL/min), t_1=27.3 min (*S*); t_2=27.8 min (*R*), ee=96%. Pure *R*-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +57.9 (*c* 0.38, $CHCl_3$).

*4.5.12. (R)-1-(4-Nitrophenyl)but-3-en-1-ol (**8l**).* ^1H NMR (400 MHz, $CDCl_3$) δ 2.30 (d, *J*=3.2 Hz, 1H), 2.44–2.49 (m, 1H), 2.54–2.60 (m,

1H), 4.87 (m, 1H), 5.17–5.22 (m, 2H), 5.76–5.80 (m, 1H), 7.53 (d, J=10.7 Hz, 2H), 8.22 (d, J=10.4 Hz, 2H). Enantiomeric excess was determined by HPLC with a Chiralpark IA column (hexane/2-propanol=95:5, 2 mL/min), t_1=25.8 min (R); t_2=27.0 min (S), ee=85%. Pure R-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +80.0 (c 0.25, $CHCl_3$). The reported value for the S-enantiomer (65% ee) is $[\alpha]_D$ −33.2 (c 0.50, $CHCl_3$).[9b]

*4.5.13. (R)-1-(Naphthalen-2-yl)but-3-en-1-ol (**8m**).* ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (br s, 1H), 2.57–2.66 (m, 2H), 4.92 (m, 1H), 5.15–5.23 (2H,m), 5.79–5.90 (1H, m), 7.48–7.51 (3H, m), 7.82–7.86 (4H, m). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (hexane/2-propanol=95:5, 3 mL/min), t_1=14.1 min (R); t_2=15.1 min (S), ee=76%. Pure R-enantiomer (100%) was used for $[\alpha]_D$ determination. $[\alpha]_D$ +178.6 (c 0.14, $CHCl_3$). The reported value for the S-enantiomer (81% ee) is $[\alpha]_D$ −84.1 (c 1.0, $CHCl_3$).[9a]

*4.5.14. 3,3′-Bis(methoxycarbonyl)-9,9′-dimethyl-9H,9′H-[1,1′-bipyrido[3,4-b]indole] 2-oxide (**10**).* IR (KBr) ν=3440, 1729, 1251, 748 cm^{-1}. MS-ESI, m/z 507 $[M+Na]^+$. HRMS m/z calcd for $C_{28}H_{22}N_4O_5Na$ $[M+Na]^+$ 511.1487, found 517.1479. ^{1}H NMR (400 MHz, $CDCl_3$) δ 3.16 (3H, s, NCH_3), 3.62 (3H, s, NCH_3), 4.00 (3H, s, $COOCH_3$), 4.03 (3H, s, $COOCH_3$), 7.34–7.47 (4H, m), 7.57 (1H, t, J=7.4 Hz), 7.68 (1H, t, J=7.4 Hz), 8.11 (1H, d, J=7.8 Hz), 8.28 (1H, d, J=7.8 Hz), 8.49 (1H, s), 9.08 (1H, s). ^{13}C NMR (100 MHz, $CDCl_3$) δ 29.5, 31.9, 52.8, 53.1, 109.8, 110.1, 118.2, 118.9, 120.8, 120.9, 121.1, 121.1, 121.6, 121.8, 128.4, 129.3, 129.8, 132.1, 133.0, 133.2, 136.9, 136.9, 138.1, 138.8, 142.7, 143.6, 163.3, 166.4. $[\alpha]_D$ +605.3 (c 0.25, $CHCl_3$).

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References and notes

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