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Axially chiral *N,N′*-dioxides ethers for catalysis in enantioselective allylation of aldehydes

Shijie Wu | Yongfei Xing | Jie Wang | Xingchen Guo | Huajie Zhu | Wan Li

College of Pharmacy, Hebei University, Baoding, China

Correspondence
Huajie Zhu and Wan Li, College of Pharmacy, Hebei University, Baoding 071002, China.
Email: hjzhu2017@163.com; liwanjingmin@163.com

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Abstract

A series of axially chiral ethers synthesized from biscarboline *N,N′*-dioxides, (*S*)-**1a** to (*S*)-**1n**, was investigated in enantioselectivity addition reactions of allyltrichlorosilane with a series of substituted aldehydes, including bulky substituted aldehydes. High enantioselectivities (up to 96%ee) were achieved using the catalyst (*S*)-**1k** at 1 mol % loading.

KEYWORDS

axially chiral biscarboline ethers, enantioselective allylation, *N,N′*-dioxides

1 | INTRODUCTION

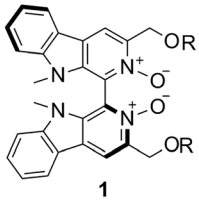
Chiral alcohols are indispensable for synthesis of pharmacological agents and other products; plenty of allylation methodologies have been developed over the last several decades using various chiral catalysts.[1-5] Various chiral Lewis bases have received increasing attention in recent years,[6-10] which were employed in enantioselective allylation of aldehydes and ketones, such as binaphthyl-derivatives,[11] chiral phosphoramides,[12] chiral formamides,[13-22] ureas,,[23] diamine, [24] Ti-complexes,[25,26] Ir-complexes,[27-29] *N,N′*-dioxides,[19,30] and sulfoxides.[31-35] Among these compounds, bipyridine *N,N′*-dioxides are particular groups that have been tested as potential catalysts for the allylation reaction of aldehydes.[36] Design and synthesis of novel chiral Lewis base catalysts have promoted the development of catalytic asymmetric allylations.

Over the last decade, we have been interested in developing chiral *N,N′*-dioxide biscarboline Lewis bases as catalysts for enantioselective allylation. For allylation of aldehydes with allyltrichlorosilane catalyzed by chiral Lewis bases (a.k.a. Sakurai-Hosomi-Denmark allylation) has been a testing ground for new chiral Lewis bases, the synthesized catalysis includes 1,1′-biscarboline *N,N′*-dioxide ester, amides and alcohol derivatives. [37,38] Those axially chiral Lewis bases showed their own advantages, a wide range of the substrate scope, including aliphatic, aromatic, heteroaromatic, and α,β-unsaturated aldehydes. In the present work, a series of axially chiral 1,1′-biscarboline *N,N′*-dioxide ethers (*S*)-**1a** to (*S*)-**1n** (Figure 1) were synthesized and used as catalysts in enantioselective allylation, which could catalyze a wide range of the substrates, even the bulky substituted aldehydes, with high enantioselectivity (up to 96%ee), were recorded.

2 | MATERIALS AND METHODS

2.1 | General methods

Thin layer chromatography was performed on TLC plates (GF254). Flash column chromatography was performed



(*S*)-**1a**: R=Et (*S*)-**1h**: R=*i*-pentyl
(*S*)-**1b**: R=*n*-Pr (*S*)-**1i**: R=3-amyl
(*S*)-**1c**: R=*n*-Bu (*S*)-**1j**: R=diisopropylmethyl
(*S*)-**1d**: R=*n*-pentyl (*S*)-**1k**: R=*c*-pentyl
(*S*)-**1e**: R=*n*-hexyl (*S*)-**1l**: R=*neo*-pentyl
(*S*)-**1f** : R=*i*-Pr (*S*)-**1m**: R=*c*-hexyl
(*S*)-**1g**: R=*i*-Bu (*S*)-**1n**: R=diphenylmethyl

FIGURE 1 Chiral ethers derived from biscarboline *N*,*N*-dioxide (*S*)-**1a** to (*S*)-**1n**

with silica gel (200-300 mesh). Enantiomeric excess was determined using a Waters HPLC with a 2695 pump and a 2996 diode array detector. Optical rotations were performed on an Optical Activity AA-55 polarimeter using a 10-cm cell with a Na 589 nm filter. ^{1}H NMR and ^{13}C NMR were recorded on a Bruker AV-400 or Bruker DRX-500 spectrometer. The mass spectra were measured on an API QSTAR Pulsar. All solvents for the reactions were reagent grade and were dried and/or distilled before use. Compounds **2** were prepared according to our reported method.

2.2 | General procedure for 3

$SOCl_2$ (25 mmol) was added dropwise to a solution of compound **2** (10 mmol) in CH_2Cl_2 (15 mL) at 0°C stirredly, then pyridine was added dropwise as catalysis. The reaction solution was stirred for 2 hours at room temperature. The reaction mixture was quenched by the addition of saturated aqueous $NaHCO_3$ and extracted with CH_2Cl_2. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude product was purified by column chromatography on silica gel eluted with dichloromethane/methanol (180: 1) to give chlorine compound **3** (92%). MS-ESI, *m/z* 481.09 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{26}H_{21}Cl_2N_4$ $[M + H]^+$ 459.1138, found 459.1143. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 8.26 (d, J = 7.9 Hz, 1 H), 7.65 (t, J = 7.6 Hz, 1 H), 7.44 (d, J = 8.2 Hz, 1 H), 7.37 (t, J = 7.5 Hz, 1 H), 5.00 (d, J = 22.4 Hz, 2 H), 3.39 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 144.37, 143.09, 139.95, 135.44, 131.28, 129.00, 121.68, 120.84, 120.16, 114.56, 109.83, 47.97, 32.20.

2.3 | General procedure for 4

Method 1, from compound **2** to compound **4**. To a suspension of NaH (3.75 mmol) in DMF (15 mL) at 0°C was added the DMF solution of compound **2** (1.5 mmol), stirred for 0.5 hour at room temperature, halogenated hydrocarbon was added dropwise, and a catalytic amount of KI were added. After 2 hours, TLC analysis showed the complete consumption of compound **2**. The reaction mixture was poured into ice water and extracted with EtOAc. The organic layers were washed with saturated brine, dried ($MgSO_4$), and evaporated to afford the crude product. The crude mixtures were purified using column chromatograph using silica gel to give compounds **4a** to **4e**, respectively.

Method 2, from compound **3** to compound **4**. The substituted sodium alkoxide (3.75 mmol) was added into a stirred solution of compound **3** (1.5 mmol) in anhydrous DMF (15 mL), and KI was added as phase-transferring catalyst. The reaction solution was stirred for 6 to 8 hours at room temperature. Then, the reaction mixture was poured into ice water. It was extracted with EtOAc three times. The combined organic layers were dried over Na_2SO_4 and concentrated. The crude mixtures were purified by column chromatography using silica gel eluted with petroleum ether:ethyl acetate = 10:1 to give compounds **4f** to **4n,** respectively.

3,3′-bis (ethoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4a) (yield of 95%) MS-ESI, *m/z* 501.22 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{30}H_{30}N_4O_2$ $[M + H]^+$ 479.2425, found: 479.2447. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (s, 1 H), 8.16 (d, J = 7.8 Hz, 1 H), 7.52 (t, J = 7.7 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 1 H), 7.24 (t, J = 7.5 Hz, 1 H), 4.83 (d, J = 4.7 Hz, 2 H), 3.66 (q, J = 6.9 Hz, 2 H), 3.17 (s, 3 H), 1.28 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.79, 142.93, 139.88, 135.40, 131.05, 128.59, 121.79, 121.11, 119.73, 112.47, 109.52, 73.97, 66.33, 31.78, 15.35.

3,3′-bis (propoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4b) (yield of 96%) MS-ESI, *m/z* 529.25 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{32}H_{34}N_4O_2$ $[M + H]^+$ 507.2738, found: 507.2760. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 8.24 (d, J = 7.9 Hz, 1 H), 7.59 (t, J = 8.0 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1 H), 7.31 (t, J = 7.5 Hz, 1 H), 4.90 (d, J = 3.6 Hz, 2 H), 3.63 (t, J = 6.7 Hz, 2 H), 3.24 (s, 3 H), 1.78 to 1.72 (m, 2 H), 1.02 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.91, 142.94, 139.86, 135.40, 131.06, 128.59, 121.77, 121.11, 119.71, 112.44, 109.52, 74.12, 72.73, 31.79, 23.09, 10.70.

3,3′-bis (butoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4c) (yield of 96%) MS-ESI, *m/z* 557.28 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{34}H_{38}N_4O_2$ $[M + H]^+$ 535.3051, found: 535.3073. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 8.24 (d, J = 7.9 Hz, 1 H), 7.59 (t, J = 7.7 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1 H), 7.31 (t, J = 7.5 Hz, 1 H), 4.89 (d, J = 3.1 Hz, 2 H), 3.66 (t, J = 6.6 Hz, 2 H), 3.24 (s, 3 H), 1.74 to 1.69 (m, 2 H), 1.51

to 1.44 (m, 2 H), 0.97 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.93, 142.93, 139.85, 135.39, 131.05, 128.58, 121.78, 121.12, 119.71, 112.40, 109.51, 74.15, 70.85, 31.98, 31.79, 19.44, 14.00.

3,3′-bis((pentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4d) (yield of 94%) MS-ESI, *m/z* 585.32 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_2$ $[M + H]^+$ 563.3359, found: 563.3386. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 8.24 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 7.7 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1 H), 7.31 (t, J = 7.5 Hz, 1 H), 4.89 (d, J = 3.4 Hz, 2 H), 3.66 (t, J = 6.7 Hz, 2 H), 3.24 (s, 3 H), 1.76 to 1.71 (m, 2 H), 1.45 to 1.40 (m, 2 H), 1.38 (dd, J = 14.2, 6.5 Hz, 2 H), 0.93 (t, J = 7.2 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.92, 142.93, 139.85, 135.39, 131.05, 128.58, 121.77, 121.12, 119.71, 112.41, 109.50, 74.15, 71.16, 31.80, 29.57, 28.45, 22.60, 14.08.

3,3′-bis((hexyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4e) (yield of 94%) MS-ESI, *m/z* 613.35 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{38}H_{46}N_4O_2$ $[M + H]^+$ 591.3672, found: 591.3699. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 8.23 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 7.2 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1 H), 7.31 (t, J = 7.5 Hz, 1 H), 4.89 (d, J = 3.6 Hz, 2 H), 3.66 (t, J = 6.7 Hz, 2 H), 3.24 (s, 3 H), 1.73 (dd, J = 14.6, 7.4 Hz, 2 H), 1.44 (dd, J = 14.9, 7.2 Hz, 2 H), 1.36 to 1.32 (m, 4 H), 0.90 (t, J = 6.9 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.92, 142.93, 139.85, 135.39, 131.05, 128.58, 121.77, 121.12, 119.71, 112.41, 109.50, 74.15, 71.18, 31.80, 31.76, 29.85, 25.95, 22.67, 14.06.

3,3′-bis (isopropoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4f) (yield of 87%) MS-ESI, *m/z* 529.25 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{32}H_{34}N_4O_2$ $[M + H]^+$ 507.2744, found: 507.2760. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 8.24 (d, J = 7.9 Hz, 1 H), 7.58 (t, J = 7.7 Hz, 1 H), 7.35 (d, J = 8.3 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 1 H), 4.91 (s, 2 H), 3.88 (dq, J = 12.2, 6.1 Hz, 1 H), 3.23 (s, 3 H), 1.33 (d, J = 4.0 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.43, 142.92, 139.78, 135.32, 131.07, 128.54, 121.82, 121.15, 119.66, 112.18, 109.48, 71.78, 71.49, 31.78, 22.32.

3,3′-bis (isobutoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4g) (yield of 87%) MS-ESI, *m/z* 557.28 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{34}H_{38}N_4O_2$ $[M + H]^+$ 535.3058, found: 535.3073. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.21 (s, 1 H), 8.16 (d, J = 7.9 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 1 H), 7.23 (t, J = 7.5 Hz, 1 H), 4.81 (d, J = 4.3 Hz, 2 H), 3.35 (d, J = 6.7 Hz, 2 H), 3.17 (s, 3 H), 1.95 (td, J = 13.4, 6.7 Hz, 1 H), 1.23 to 1.15 (m, 2 H), 0.93 (d, J = 6.7 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.98, 141.91, 138.78, 134.36, 130.04, 127.57, 120.74, 120.09, 118.68, 111.39, 108.49, 76.88, 73.24, 30.77, 27.62, 18.50.

3,3′-bis((isopentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4h) (yield of 85%) MS-ESI, *m/z* 585.32 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_2$ $[M + H]^+$ 563.3378, found: 563.3386. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.20 (s, 1 H), 8.16 (d, J = 7.9 Hz, 1 H), 7.51 (t, J = 8.2 Hz, 1 H), 7.28 (d, J = 8.3 Hz, 1 H), 7.23 (t, J = 7.5 Hz, 1 H), 4.81 (d, J = 3.1 Hz, 2 H), 3.61 (t, J = 6.8 Hz, 2 H), 3.16 (s, 3 H), 1.74 (td, J = 13.4, 6.7 Hz, 1 H), 1.55 (q, J = 6.8 Hz, 2 H), 0.88 (d, J = 6.7 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 145.89, 141.90, 138.80, 134.36, 130.03, 127.57, 120.75, 120.08, 118.69, 111.39, 108.48, 73.16, 68.50, 37.70, 30.76, 24.20, 21.72.

3,3′-bis((pentan-3-yloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4i) (yield of 74%) MS-ESI, *m/z* 585.32 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_2$ $[M + H]^+$ 563.3373, found: 563.3386. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.26 (s, 1 H), 8.17 (d, J = 7.8 Hz, 1 H), 7.52 (t, J = 7.7 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 1 H), 7.24 (t, J = 7.5 Hz, 1 H), 4.84 (s, 2 H), 3.38 (dd, J = 11.6, 5.8 Hz, 1 H), 3.16 (s, 3 H), 1.60 (dd, J = 13.3, 6.8 Hz, 4 H), 0.96 to 0.91 (m, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.71, 142.93, 139.66, 135.33, 131.08, 128.54, 121.82, 121.18, 119.65, 112.28, 109.48, 82.21, 71.99, 31.77, 26.02, 9.75.

3,3′-bis(((2,4-dimethylpentan-3-yl)oxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b] indole (4j) (yield of 71%) MS-ESI, *m/z* 641.38 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{40}H_{50}N_4O_2$ $[M + H]^+$ 619.4005, found: 619.4012. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1 H), 8.18 (d, J = 7.8 Hz, 1 H), 7.51 (t, J = 7.7 Hz, 1 H), 7.28 (d, J = 8.3 Hz, 1 H), 7.23 (t, J = 7.5 Hz, 1 H), 4.94 (s, 2 H), 3.16 (s, 3 H), 2.92 (t, J = 5.6 Hz, 1 H), 1.90 (dp, J = 13.2, 6.6 Hz, 2 H), 0.96 (dd, J = 40.1, 6.7 Hz, 12 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.81, 142.90, 139.61, 135.23, 131.00, 128.45, 121.82, 121.22, 119.54, 111.91, 109.44, 91.36, 76.77, 31.77, 30.98, 20.43.

3,3′-bis((cyclopentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4k) (yield of 62%) MS-ESI, *m/z* 581.28 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{38}N_4O_2$ $[M + H]^+$ 559.3063, found: 559.3073. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.27 (s, 1 H), 8.24 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 7.7 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1 H), 7.30 (d, J = 7.2 Hz, 1 H), 4.87 (s, 2 H), 4.19 to 4.17 (m, 1 H), 3.24 (s, 3 H), 1.81 (ddd, J = 6.7, 5.4, 4.8 Hz, 8 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.33, 142.91, 139.80, 135.31, 131.04, 128.52, 121.81, 121.14, 119.64, 112.26, 109.48, 81.62, 72.08, 32.48, 31.81, 23.70.

3,3′-bis((neopentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4l) (yield of 86%) MS-ESI, *m/z* 585.32 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_2$ $[M + H]^+$ 563.3368, found: 563.3386. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.28 (s, 1 H), 8.24 (d, J = 7.9 Hz, 1 H), 7.59 (t, J = 7.6 Hz, 1 H), 7.36 (d, J = 8.3 Hz, 1

H), 7.31 (t, J = 7.5 Hz, 1 H), 4.90 (d, J = 9.8 Hz, 2 H), 3.25 (s, 3 H), 1.03 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.27, 142.94, 139.80, 135.36, 131.05, 128.59, 121.72, 121.14, 119.67, 112.26, 109.51, 81.48, 74.72, 32.29, 31.82, 26.93.

3,3′-bis((cyclohexyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4m) (yield of 65%) MS-ESI, *m/z* 586.33 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{38}H_{42}N_4O_2$ $[M + H]^+$ 586.3291, found: 586.3308. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 8.24 (d, J = 7.8 Hz, 1 H), 7.61 to 7.56 (m, 1 H), 7.35 (d, J = 8.3 Hz, 1 H), 7.30 (t, J = 7.5 Hz, 1 H), 4.91 (s, 2 H), 3.60 to 3.55 (m, 1 H), 3.23 (s, 3 H), 1.71 to 1.23 (m, 10 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 147.71, 142.92, 139.66, 135.30, 131.06, 128.50, 121.82, 121.18, 119.62, 112.16, 109.45, 79.56, 71.94, 36.28, 31.76, 18.75, 14.37.

3,3′-bis((benzhydryloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-1,1′-bipyrido[3,4-b]indole (4n) (yield of 65%) MS-ESI, *m/z* 777.32 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{52}H_{42}N_4O_2$ $[M + H]^+$ 755.3369, found: 755.3386. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.34 (s, 1 H), 8.23 (d, J = 7.8 Hz, 1 H), 7.59 (t, J = 8.2 Hz, 1 H), 7.45 (d, J = 7.4 Hz, 4 H), 7.33 (dd, J = 14.4, 6.6 Hz, 6 H), 7.25 (t, J = 3.5 Hz, 2 H), 5.64 (s, 1 H), 4.91 (d, J = 5.3 Hz, 2 H), 3.21 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 146.55, 142.92, 142.21, 139.91, 135.32, 131.01, 128.51, 127.52, 127.18, 121.79, 121.11, 119.70, 112.53, 109.54, 83.57, 72.16, 31.90.

2.4 | General procedure for 1

m-CPBA (3 mmol) was added portion-wise to a stirred solution of 1,1′-biscarboline **4** (1 mmol) in CH_2Cl_2 (50 mL) at °C. The reaction was stirred at room temperature for 6 to 8 hours. Then, the mixtures were poured into saturated aqueous $NaHCO_3$ (50 mL). It was then extracted with CH_2Cl_2 three times. The combined organic layers were dried over Na_2SO_4 and concentrated under a reduced pressure. The residue was purified by chromatography (silica gel) eluting with PE/EA = 4:1 to give the corresponding compounds. The chiral separation of **1** was performed via HPLC with a chiralpak ID column.

3,3′-bis (ethoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1a) (yield of 62%) MS-ESI, *m/z* 533.21 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{30}H_{30}N_4O_4$ $[M + H]^+$ 511.2339, found: 511.2345. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 8.13 (d, J = 7.9 Hz, 1 H), 7.53 (t, J = 7.7 Hz, 1 H), 7.33 (d, J = 7.6 Hz, 1 H), 7.30 (d, J = 8.3 Hz, 1 H), 4.96 (dd, J = 34.2, 15.8 Hz, 2 H), 3.85 to 3.80 (m, 2 H), 3.24 (s, 3 H), 1.40 (t, J = 7.0 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.39, 141.14, 137.21, 127.89, 125.25, 121.11, 120.78, 114.31, 109.39, 100.14, 67.12, 29.49, 25.36, 15.32. HPLC resolution with a chiralpak ID column (THF/EtOH = 50/50, 2 mL/min), t_{R1} = 8.1 minutes (S); t_{R2} = 8.6 minutes (R) $[\alpha]_D = -245.8$ (c = 0.26, $CHCl_3$).

3,3′-bis (propoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole]2,2′ dioxide (1b) (yield of 61%) MS-ESI, *m/z* 561.24 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{32}H_{34}N_4O_4$ $[M + H]^+$ 539.2643, found: 539.2658. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 8.15 (d, J = 7.9 Hz, 1 H), 7.55 (t, J = 8.0 Hz, 1 H), 7.35 (d, J = 7.6 Hz, 1 H), 7.32 (d, J = 8.1 Hz, 1 H), 4.98 (q, J = 15.9 Hz, 2 H), 3.78 to 3.70 (m, 2 H), 3.26 (s, 3 H), 1.87 to 1.79 (m, 2 H), 1.09 (t, J = 7.4 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.37, 141.20, 137.19, 127.85, 125.24, 121.54, 121.28 to 121.08, 120.88, 114.25, 109.38, 100.00, 73.51, 67.28, 29.47, 23.04, 10.70. HPLC resolution with a chiralpak ID column (THF/EtOH = 50/50, 2 mL/min), t_{R1} = 7.8 minutes (S); t_{R2} = 8.3 minutes (R). $[\alpha]_D = -232.4$ (c 0.25, $CHCl_3$).

3,3′-bis (butoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1c) (yield of 64%) MS-ESI, *m/z* 589.27 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{34}H_{38}N_4O_4$ $[M + H]^+$ 567.2957, found: 567.2971. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 8.13 (d, J = 7.6 Hz, 1 H), 7.54 to 7.50 (m, 1 H), 7.33 (d, J = 7.5 Hz, 1 H), 7.30 (d, J = 2.9 Hz, 1 H), 4.98 (dd, J = 36.4, 16.0 Hz, 2 H), 3.77 to 3.71 (m, 2 H), 3.21 (s, 3 H), 1.74 (dd, J = 12.4, 8.0 Hz, 2 H), 1.52 (d, J = 11.2 Hz, 2 H), 1.00 (t, J = 5.9 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.38, 141.21, 137.22, 127.86, 125.26, 121.50, 121.18, 121.01, 120.75, 114.23, 109.40, 71.66, 67.34, 31.93, 29.49, 19.46, 14.02. HPLC resolution with a chiralpak ID column (THF/EtOH = 50/50, 2 mL/min), t_{R1} = 7.5 minutes (S); t_{R2} = 8.0 minutes (R). $[\alpha]_D = -285.6$ (c = 0.17, $CHCl_3$).

3,3′-bis((pentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1d) (yield of 68%) MS-ESI, *m/z* 617.31 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_4$ $[M + H]^+$ 595.3268, found: 595.3284. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1 H), 8.12 (d, J = 7.1 Hz, 1 H), 7.53 (t, J = 7.4 Hz, 1 H), 7.32 (d, J = 7.6 Hz, 1 H), 7.29 (d, J = 8.7 Hz, 1 H), 4.95 (dd, J = 32.1, 15.8 Hz, 2 H), 3.74 (s, 2 H), 3.23 (s, 3 H), 1.52 to 1.39 (m, 6 H), 0.88 (t, J = 6.8 Hz, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.38, 141.22, 137.22, 127.86, 125.26, 121.52, 121.18, 121.01, 120.76, 114.24, 109.39, 72.00, 67.33, 29.50, 28.44, 22.60,14.11. HPLC resolution with a chiralpak ID column (THF/EtOH = 60/40, 2 mL/min), t_{R1} = 7.2 minutes (S); t_{R2} = 7.7 minutes (R). $[\alpha]_D = -282.5$ (c = 0.16, $CHCl_3$).

3,3′-bis((hexyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1e) (yield of 58%) MS-ESI, *m/z* 645.34 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{38}H_{46}N_4O_4$ $[M + H]^+$ 623.3582, found:

623.3597. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.24 (s, 1 H), 8.05 (d, *J* = 7.3 Hz, 1 H), 7.46 (d, *J* = 8.7 Hz, 1 H), 7.25 (s, 1 H), 7.21 (d, *J* = 8.0 Hz, 1 H), 4.90 (dd, *J* = 32.9, 14.6 Hz, 2 H), 3.67 (s, 2 H), 3.17 (d, *J* = 31.8 Hz, 3 H), 1.42 to 1.27 (m, 8 H), 0.83 to 0.78 (m, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.40, 141.27,137.21, 127.90, 125.24, 121.64, 121.15, 121.02, 120.78, 114.26, 109.40, 72.02, 67.33, 31.76, 29.80, 29.51, 25.96, 22.68, 14.10. HPLC resolution with a chiralpak ID column (THF/EtOH = 70/30, 2 mL/min), t_{R1} = 7.0 minutes (S); t_{R2} = 7.5 minutes (R). $[\alpha]_D$ = −168.3 (c 0.17, $CHCl_3$).

3,3′-bis (isopropoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1f) (yield of 63%) MS-ESI, *m/z* 561.24 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{32}H_{34}N_4O_4$ $[M + H]^+$ 539.2641, found: 539.2658 ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 8.13 (d, *J* = 7.8 Hz, 1 H), 7.52 (t, *J* = 7.7 Hz, 1 H), 7.32 (t, *J* = 7.6 Hz, 1 H), 7.29 (d, *J* = 8.3 Hz, 1 H), 4.96 (q, *J* = 15.9 Hz, 2 H), 3.91 (dd, *J* = 17.3, 11.7 Hz, 1 H), 3.22 (s, 3 H), 1.36 (d, *J* = 9.5 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.41, 141.78, 137.14, 127.87, 125.17, 121.13, 120.74, 114.34, 109.37, 100.00, 72.75, 64.91, 29.54, 22.34. HPLC resolution with a chiralpak ID column (THF/EtOH = 50/50, 2 mL/min), t_{R1} = 6.6 minutes (S); t_{R2} = 7.2 minutes (R). $[\alpha]_D$ = −224.3 (c 0.23, $CHCl_3$).

3,3′-bis (isobutoxymethyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1 g) (yield of 66%) MS-ESI, *m/z* 589.27 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{34}H_{38}N_4O_4$ $[M + H]^+$ 567.2958, found: 567.2971. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 8.12 (d, *J* = 7.9 Hz, 1 H), 7.52 (t, *J* = 7.7 Hz, 1 H), 7.32 (t, *J* = 7.5 Hz, 1 H), 7.29 (d, *J* = 8.3 Hz, 1 H), 4.97 (q, *J* = 15.9 Hz, 2 H), 3.52 (d, *J* = 6.3 Hz, 2 H), 3.23 (s, 3 H), 2.13 to 2.05 (m, 1 H), 1.08 to 1.03 (m, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.44, 141.45, 137.16, 128.00, 125.18, 121.09, 120.81, 114.27, 109.40, 99.99, 78.63, 67.45, 29.59, 28.65, 19.47. HPLC resolution with a chiralpak ID column (THF/EtOH = 60/40, 2 mL/min), t_{R1} = 7.7 minutes (S); t_{R2} = 8.6 minutes (R). $[\alpha]_D$ = −326.4 (c = 0.17 $CHCl_3$).

3,3′-bis((isopentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1 h) (yield of 55%) MS-ESI, *m/z* 617.31 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{56}H_{42}N_4O_4$ $[M + H]^+$ 595.3253, found: 595.3284. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.29 (s, 1 H), 8.12 (d, *J* = 7.9 Hz, 1 H), 7.53 (t, *J* = 7.4 Hz, 1 H), 7.33 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.1 Hz, 1 H), 4.95 (q, *J* = 15.8 Hz, 2 H), 3.78 (dd, *J* = 11.8, 6.7 Hz, 2 H), 3.24 (s, 3 H), 1.86 (dt, *J* = 13.4, 6.7 Hz, 1 H), 1.71 to 1.64 (m, 2 H), 1.00 (d, *J* = 6.6 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.40, 141.23, 137.21, 127.89, 125.25, 121.59, 121.10, 120.78, 114.27, 109.39, 70.36, 67.35, 38.65, 29.48, 25.23, 22.73. HPLC resolution with a chiralpak ID column (THF/EtOH = 70/30, 2 mL/min), t_{R1} = 9.2 minutes (S); t_{R2} = 9.8 minutes (R). $[\alpha]_D$ = −286.7 (c = 0.24, $CHCl_3$).

3,3′-bis((pentan-3-yloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1i) (yield of 58%) MS-ESI, *m/z* 617.31 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_4$ $[M + H]^+$ 595.3267, found 595.3284. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.33 (s, 1 H), 8.06 (d, *J* = 7.1 Hz, 1 H), 7.56 (dd, *J* = 24.6, 7.7 Hz, 1 H), 7.39 to 7.33 (m, 1 H), 7.28 (s, 1 H), 4.96 to 4.87 (m, 2 H), 3.46 (d, *J* = 27.0 Hz, 1 H), 3.23 to 3.06 (m, 3 H), 1.20 (d, *J* = 14.0 Hz, 4 H), 0.83 to 0.76 (m, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.41, 141.95 , 137.16 , 127.84, 125.16 , 121.67, 121.22, 121.06, 120.70, 114.36, 109.35, 83.07, 65.28, 29.55, 26.03, 9.71. HPLC resolution with a chiralpak ID column (THF/EtOH = 70/30, 2 mL/min), t_{R1} = 9.7 minutes (S); t_{R2} = 10.4 minutes (R). $[\alpha]_D$ = −294.6 (c = 0.17, $CHCl_3$).

3,3′-bis(((2,4-dimethylpentan-3-yl)oxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1j) (yield of 58%) MS-ESI, *m/z* 673.37 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{40}H_{50}N_4O_4$ $[M + H]^+$ 651.3874, found: 651.3910. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.40 (s, 1 H), 8.15 (d, *J* = 7.8 Hz, 1 H), 7.52 (t, *J* = 8.1 Hz, 1 H), 7.32 (d, *J* = 7.6 Hz, 1 H), 7.30 (d, *J* = 8.2 Hz, 1 H), 5.04 (q, *J* = 15.8 Hz, 2 H), 3.24 (s, 3 H), 3.08 (t, *J* = 5.6 Hz, 1 H), 2.00 (dp, *J* = 13.0, 6.6 Hz, 2 H), 1.07 (d, *J* = 6.7 Hz, 6 H), 1.00 (d, *J* = 6.8 Hz, 6 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.37, 141.81, 137.12, 127.79, 125.10, 121.57, 121.23, 121.05, 120.65, 114.32, 109.33, 91.68, 69.81, 30.93, 29.49, 20.35, 17.94. HPLC resolution with a chiralpak ID column (THF/EtOH = 80/20, 2 mL/min), t_{R1} = 12.4 minutes (S); t_{R2} = 12.9 minutes (R). $[\alpha]_D$ = −423.8 (c = 0.24, $CHCl_3$).

3,3′-bis((cyclopentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1 k) (yield of 63%) MS-ESI, *m/z* 613.27 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{38}N_4O_4$ $[M + H]^+$ 591.2956, found: 591.2971. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.31 (s, 1 H), 8.14 (d, *J* = 7.6 Hz, 1 H), 7.54 to 7.50 (m, 1 H), 7.33 (d, *J* = 1.2 Hz, 1 H), 7.32 (d, *J* = 3.3 Hz, 1 H), 4.97 to 4.92 (m, 2 H), 4.27 to 4.19 (m, 1 H), 3.21 (s, 3 H), 1.85 (d, *J* = 27.2 Hz, 8 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.41, 141.66, 137.16, 130.88, 128.84, 121.69 , 121.17, 121.07, 120.73, 114.35, 109.37, 82.49, 65.55, 32.52, 30.59, 23.72. HPLC resolution with a chiralpak ID column (THF/EtOH = 80/20, 2 mL/min), t_{R1} = 13.6 minutes (S); t_{R2} = 14.2 minutes (R). $[\alpha]_D$ = −385.3 (c = 0.17, $CHCl_3$).

3,3′-bis((neopentyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1 l) (yield of 65%) MS-ESI, *m/z* 617.31 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{36}H_{42}N_4O_4$ $[M + H]^+$ 595.3268, found: 595.3284. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.32 (s, 1 H), 8.12 (d, *J* = 7.8 Hz, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.32

(t, J = 7.5 Hz, 1 H), 7.29 (d, J = 8.3 Hz, 1 H), 4.97 (q, J = 16.0 Hz, 2 H), 3.40 (s, 2 H), 3.23 (s, 3 H), 1.08 (s, 9 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.45, 141.62, 137.14, 132.24, 128.03, 125.17, 121.06, 120.80, 114.20, 109.41, 82.25, 67.96, 32.43, 29.61, 26.90. HPLC resolution with a chiralpak ID column (THF/EtOH = 80/20, 2 mL/min), t_{R1} = 15.1 minutes (S); t_{R2} = 15.7 minutes (R). $[\alpha]_D$ = −363.6 (c = 0.23, $CHCl_3$).

3,3′-bis((cyclohexyloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1 m) (yield of 54%) MS-ESI, *m/z* 641.31 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{38}H_{42}N_4O_4$ $[M + H]^+$ 619.3269, found: 619.3284. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.30 (s, 1 H), 8.06 (d, J = 7.9 Hz, 1 H), 7.44 (t, J = 7.6 Hz, 1 H), 7.24 (t, J = 7.5 Hz, 1 H), 7.20 (d, J = 8.3 Hz, 1 H), 4.91 (q, J = 15.8 Hz, 2 H), 3.60 to 3.53 (m, 1 H), 3.15 (s, 3 H), 1.73 to 1.29 (m, 10 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 143.47, 142.15, 137.06, 128.04, 125.04, 122.21, 121.14, 120.79, 114.42, 109.38, 80.40, 65.21, 36.19, 29.70, 18.72, 14.32. HPLC resolution with a chiralpak ID column (THF/EtOH = 85/15, 2 mL/min), t_{R1} = 15.6 minutes (S); t_{R2} = 16.3 minutes (R). $[\alpha]_D$ = −222.4 (c = 0.17, $CHCl_3$).

3,3′-bis((benzhydryloxy)methyl)-9,9′-dimethyl-9*H*,9′*H*-[1,1′-bipyrido[3,4-b]indole] 2,2′-dioxide (1n) (yield of 63%) MS-ESI, *m/z* 809.31 $[M + Na]^+$. HR-MS-EI *m/z* calcd for $C_{52}H_{42}N_4O_4$ $[M + H]^+$ 787.3267, found: 787.3284. ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.36 (s, 1 H), 8.04 (d, J = 8.5 Hz, 1 H), 7.47 to 7.43 (m, 1 H), 7.38 (dd, J = 21.3, 13.4 Hz, 5 H), 7.28 (s, 5 H), 7.25 (s, 1 H), 7.21 (s, 1 H), 5.62 (s, 1 H), 4.91 (q, J = 15.1 Hz, 2 H), 3.12 (s, 3 H). ^{13}C NMR (151 MHz, $CDCl_3$) δ 142.36, 140.81, 140.61, 140.05, 127.52, 126.96, 126.71, 126.13, 124.11, 119.94, 113.55, 108.39, 83.61, 65.04, 28.68. HPLC resolution with a chiralpak ID column (THF/EtOH = 90/10, 2 mL/min), t_{R1} = 16.8 minutes (S); t_{R2} = 17.9 minutes (R). $[\alpha]_D$ = −212.3 (c = 0.17, $CHCl_3$).

2.5 | General procedure for reaction of allyltrichlorosilanes with aldehydes

Allyltrichlorosilane **7** (0.6 mmol) was added to a solution of the catalyst (*S*)-**1** (1 mol%), diisopropylethylamine (1.5 mmol), and aldehyde **6** or **9** (0.5 mmol) in anhydrous CH_2Cl_2 (2 mL) under nitrogen at −80°C. The mixture was stirred at the same temperature for 16 hours and then quenched with aqueous saturated $NaHCO_3$ (1 mL). The aqueous layer was extracted with CH_2Cl_2, and the combined organic layer was washed with saturated NaCl, 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 alcohols **8** or **10.**

(*S*)-1-(9-methyl-1-phenyl-9H-pyrido[3,4-b]indol-3-yl)but-3-en-1-ol (10a) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.13 (d, J = 1.8 Hz, 1 H), 7.90 (s, 1 H), 7.64 (d, J = 6.6 Hz, 2 H), 7.60 to 7.41 (m, 5 H), 7.33 (d, J = 8.7 Hz, 1 H), 5.92 (ddt, J = 17.2, 10.2, 7.0 Hz, 1 H), 5.20 to 5.10 (m, 2 H), 5.03 (dd, J = 7.3, 4.9 Hz, 1 H), 3.45 (s, 3 H), 2.79 to 2.73 (m, 1 H), 2.62 (dt, J = 14.4, 7.3 Hz, 1 H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (PE/IPA/EtOH = 90/7/3, 2 mL/min), t_R (minor) = 34.1 minutes (*R*); t_R (major) = 34.7 minutes (*S*), ee = 84%. $[\alpha]_D$ = −15.8 (c = 0.46, $CHCl_3$). The reported value [39] for the R-enantiomer (90% ee) is $[\alpha]_D$ = +13.9 (c = 0.36, $CHCl_3$).

(*R*)-1-(1-(4-chlorophenyl)-9-methyl-9H-pyrido[3,4-b]indol-3-yl)but-3-en-1-ol (10b) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.10 (d, J = 7.8 Hz, 1 H), 7.89 (s, 1 H), 7.61 to 7.52 (m, 3 H), 7.45 (t, J = 7.2 Hz, 2 H), 7.35 (t, J = 6.9 Hz, 1 H), 7.25 (t, J = 7.5 Hz, 1 H), 5.86 (ddt, J = 17.2, 10.2, 7.1 Hz, 1 H), 5.07 (dd, J = 27.4, 13.6 Hz, 2 H), 4.98 to 4.94 (m, 1 H), 3.41 (d, J = 16.5 Hz, 3 H), 2.73 to 2.67 (m, 1 H), 2.55 (dt, J = 14.4, 7.3 Hz, 1 H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (PE/IPA/EtOH = 90/7/3, 2 mL/min), t_R (major) = 27.8 minutes (*R*); t_R (minor) = 28.3 minutes (*S*), ee = 92%. $[\alpha]_D$ + 26.7 (c = 0.44, $CHCl_3$). The reported value [39] for the R-enantiomer (94% ee) is $[\alpha]_D$ = +16.7 (c = 0.24, $CHCl_3$).

(*R*)-1-(1-(3-fluorophenyl)-9-methyl-9H-pyrido[3,4-b]indol-3-yl)but-3-en-1-ol (10c) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.17 (d, J = 7.8 Hz, 1 H), 7.96 (s, 1 H), 7.67 to 7.59 (m, 3 H), 7.42 (d, J = 8.3 Hz, 1 H), 7.32 (t, J = 7.5 Hz, 1 H), 7.23 (t, J = 8.6 Hz, 2 H), 5.93 (ddt, J = 17.2, 10.1, 7.0 Hz, 1 H), 5.14 (dd, J = 27.9, 13.7 Hz, 2 H), 5.03 (dd, J = 7.3, 4.8 Hz, 1 H), 3.48 (s, 3 H), 2.80 to 2.73 (m, 1 H), 2.62 (dt, J = 14.5, 7.3 Hz, 1 H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (PE/IPA/EtOH = 90/7/3, 2 mL/min), t_R (major) = 28.2 minutes (*R*); t_R (minor) = 28.7 minutes (*S*), ee = 94%. $[\alpha]_D$ = +46.3 (c = 0.42, $CHCl_3$). The reported value for the S-enantiomer (90% ee) is $[\alpha]_D$ = −33.3 (c = 0.24, $CHCl_3$).

(*R*)-1-(1-(3-methoxyphenyl)-9-methyl-9H-pyrido[3,4-b]indol-3-yl)but-3-en-1-ol (10d) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.18 (d, J = 7.8 Hz, 1 H), 7.96 (s, 1 H), 7.66 to 7.58 (m, 1 H), 7.46 to 7.39 (m, 2 H), 7.30 (dd, J = 18.7, 11.3 Hz, 1 H), 7.21 (dd, J = 8.0, 4.8 Hz, 2 H), 7.05 (dd, J = 8.3, 2.1 Hz, 1 H), 5.94 (ddt, J = 17.1, 10.1, 7.0 Hz, 1 H), 5.14 (dd, J = 29.4, 13.7 Hz, 2 H), 5.04 (dd, J = 7.4, 4.8 Hz, 1 H), 3.89 (s, 3 H), 3.49 (s, 3 H), 2.81 to 2.74 (m, 1 H), 2.62 (dt, J = 14.4, 7.4 Hz, 1 H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (PE/IPA/EtOH = 90/7/3, 2 mL/min), t_R (minor) = 41.2 minutes (*S*); t_R (major) = 41.6 minutes

(*R*), ee = 96%. $[\alpha]_D$ = +46.6 (c = 0.28, $CHCl_3$). The reported value for the S-enantiomer (92% ee) is $[\alpha]_D$ = −36.3 (c = 0.2, $CHCl_3$).

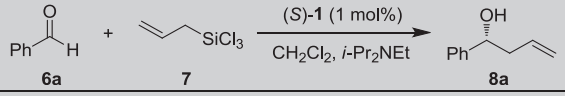
(*S*)-1-(9-methyl-1-(4-nitrophenyl)-9H-pyrido[3,4-b] indol-3-yl)but-3-en-1-ol (10e) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.41 (d, *J* = 8.6 Hz, 2 H), 8.19 (d, *J* = 7.8 Hz, 1 H), 8.03 (s, 1 H), 7.89-7.86 (m, 2 H), 7.67 to 7.63 (m, 1 H), 7.45 (d, *J* = 8.3 Hz, 1 H), 7.35 (t, *J* = 7.5 Hz, 1 H), 5.92 (ddt, *J* = 17.2, 10.2, 7.0 Hz, 1 H), 5.19 to 5.11 (m, 2 H), 5.05 (dd, *J* = 7.3, 4.8 Hz, 1 H), 3.50 (s, 3 H), 2.81 to 2.75 (m, 1 H), 2.63 (dt, *J* = 14.4, 7.3 Hz, 1 H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (PE/EtOH = 55/45, 2 mL/min), t_R (major) = 29.1 minutes (*S*); t_R (minor) = 29.8 minutes (*R*), ee = 91%. $[\alpha]_D$ = −36.6 (*c* = 0.38, $CHCl_3$). The reported value for the R-enantiomer (≥95% ee) is $[\alpha]_D$ = +46.4 (c = 0.28, $CHCl_3$)

(*S*)-1-(1-cyclohexyl-9-methyl-9H-pyrido[3,4-b] indol-3-yl)but-3-en-1-ol (10f) ^{1}H NMR (600 MHz, $CDCl_3$) δ 8.03 (d, *J* = 7.7 Hz, 1 H), 7.64 (s, 1 H), 7.52 (t, *J* = 7.6 Hz, 1 H), 7.37 (d, *J* = 8.3 Hz, 1 H), 7.22 to 7.16 (m, 2 H), 5.83 (ddt, *J* = 17.1, 10.2, 7.0 Hz, 1 H), 5.08 to 4.98 (m, 2 H), 4.90 to 4.85 (m, 1 H), 3.51 to 3.42 (m, 1 H), 2.67 to 2.59 (m, 1 H), 2.50 (dt, *J* = 13.8, 6.8 Hz, 1 H), 1.99 to 1.83 (m, 7 H), 1.76 (d, *J* = 12.7 Hz, 1 H), 1.46 to 1.41 (m, 2 H), 1.35 to 1.30 (m, 1 H). Enantiomeric excess was determined by HPLC with a Chiralpark ID column (PE/EtOH = 95/5, 2 mL/min), t_R (minor) = 20.8 minutes (*R*); t_R (major) = 21.6 minutes (*S*), ee = 91%. $[\alpha]_D$ = −34.3 (*c* = 0.36, $CHCl_3$). The reported value for the R-enantiomer (96% ee) is $[\alpha]_D$ = +21.7 (*c* = 0.23, $CHCl_3$).

3 | RESULTS AND DISCUSSION

In this research, the cheap L-tryptophane was used as starting material. By a series of reactions like esterification, Pictet-Spengler reaction, and reduction, new axially chiral ethers of biscarboline *N*,*N*′-dioxides, (*S*)-**1a** to (*S*)-**1n**, were obtained using the previously reported methods. [37] Their catalytic activity was then tested in additions of allyltrichlorosilane to aldehydes.

TABLE 1 Enantioselectivive addition of allyltrichlorosilane to benzaldehyde [a]



6a 7 8a

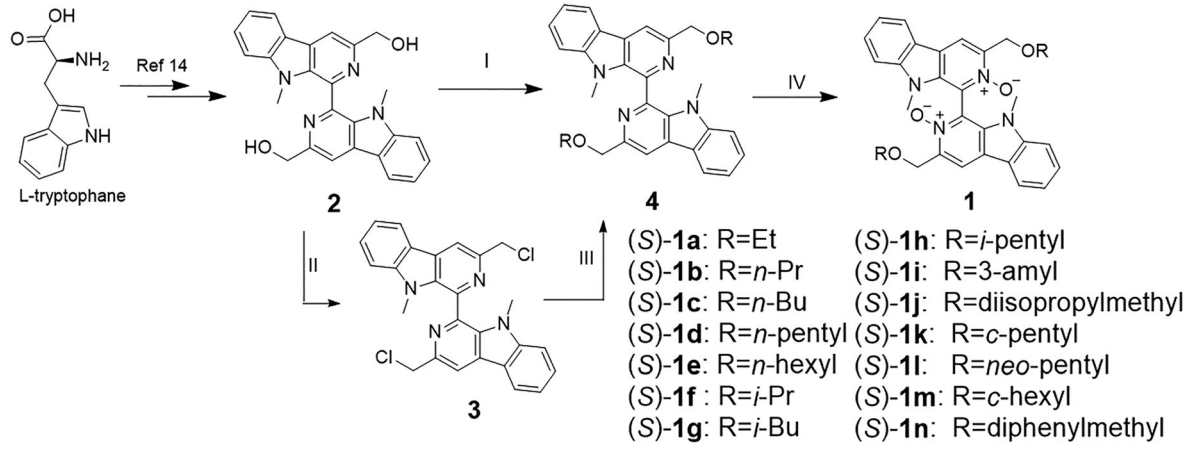
Entry	Cat.*	Yield (%)	Ee(%)[b]	Config.[c]
1	(*S*)-**1a**	96	78	*R*
2	(*S*)-**1b**	96	78	*R*
3	(*S*)-**1c**	94	77	*R*
4	(S)-**1d**	95	76	*R*
5	(*S*)-**1e**	97	76	*R*
6	(*S*)-**1f**	88	81	*R*
7	(*S*)-**1g**	86	82	*R*
8	(*S*)-**1h**	92	82	*R*
9	(*S*)-**1i**	93	64	*R*
10	(*S*)-**1j**	86	62	*R*
11	(*S*)-**1k**	96	84	*R*
12	(*S*)-**1l**	98	83	*R*
13	(*S*)-**1m**	81	81	*R*
14	(*S*)-**1n**	89	56	*R*

[a]Reaction condition: **6a** (0.5 mmol), **7** (0.6 mmol), (*S*)-**1** (1 mol%) as a catalyst.

[b]Determined by HPLC using a Chirapak IB column.

[c]The configuration was determined by comparing its optical rotation data and HPLC retention times with those reported in literatures. [37]

The synthetic routes of target compounds **1** and intermediate **2** are outlined in Scheme 1. Two routes via I and



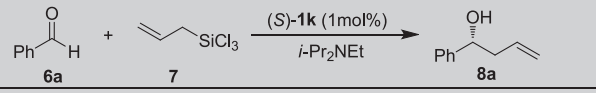
SCHEME 1 Synthesis of axially chiral biscarboline *N*,*N*′-dioxides ethers (*S*)-**1a** to (*S*)-**1n**. Conditions: (I) NaH, DMF, RX, rt, 2 h; (II) $SOCl_2$, DCM, rt, 2 h; (III) KI, RONa, DMF, rt, 6 h; (IV) m-CPBA, CH_2Cl_2, rt, 6 h

via II and III were employed for synthesis of ethers **4**, which were further oxidized by *m*-CPBA to afford biscarboline *N*,*N*-dioxides ethers **1**. Separation of (−)-**1a** to **(−)-1n** was performed via HPLC with a Chiralpak ID column. One of the enantiomer possessed negative optical rotation. According to our previous researches, biscarboline *N*,*N*-dioxides derivatives having negative optical rotation would have (*S*) configuration.[37]

Benzaldehyde was used as an initial substrate for enantioselective allylation in the presence of catalysts (*S*)-**1a to** (*S*)-**1n.**[39,40] The enantioselectivity (%ee) is listed in Table 1. It showed that most of the ethers of biscarboline *N*,*N*-dioxide **1** induce good enantioselectivities in the allylation. (*S*)-**1k** with cyclopentyl at C_3 and C_3' positions promoted the allylation product in 96% yield and 84%ee. The catalysts **1f**, **1g**, **1h**, **1l**, and **1m** almost had over 80%ee enantioselectivity. Catalysts **1a** to **1e** provided over 75%ee enantioselectivity.

Effects of solvents and temperatures on the enantioselectivities were investigated using (*S*)-**1k** as the catalyst. Solvents like dichloromethane (DCM), CH_3CN, THF, toluene (Tol), EtOAc, Et_2O, $CHCl_3$, and dichloroethane (DCE) were selected in the investigations. The results are summarized in Table 2. High yields up to 96% were obtained at −80°C to −40°C (entries 1-3) in CH_2Cl_2; however, the ee% decreased from 84% to 72%. Good yield of 94% and 81% ee were observed in CH_3CN. Poor yields and enantioselectivities were recorded using THF, toluene, ethyl acetate, or diethyl ether as the solvent

TABLE 2 Effects of solvents and temperatures on the enantioselective allylations [a]



Entry	Solvent	T, °C	Yield, %	Ee, %[b]
1	DCM	−80	96	84
2	DCM	−60	98	78
3	DCM	−40	99	72
4	CH_3CN	−40 [c]	94	81
5	THF	−80	5	76
6	Tol	−80	10	72
7	EtOAc	−80	10	65
8	Et_2O	−80	5	73
9	$CHCl_3$	−60 [d]	86	67
10	DCE	−30 [e]	88	63

[a]Reaction conditions: **6a** (0.5 mmol), **7** (0.6 mmol), (*S*)-**1 k** (1 mol%) as catalyst in DCM.

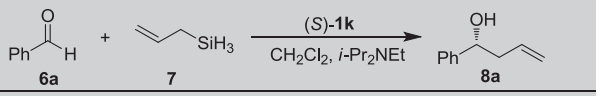
[b]Determined by HPLC on a Chirapak IB column.

[c]The melting point for acetonitrile is −45°C.

[d]The melting point of chloroform is −63°C.

[e]The melting point for DCE is −35°C. Thus, the lowest temperatures for the allylations listed in entries 4, 8 to 10 cannot be lower than those melting point temperatures.

TABLE 3 Effect of catalyst loading on enantioselectivity [a]

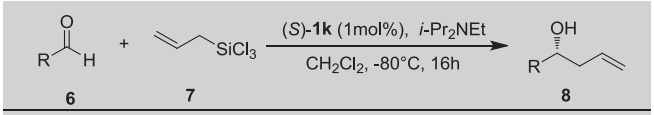


Entry	Cat., mol%	Yield, %	Ee [b] %
1	0.5	54	82
2	1	96	84
3	5	83	73
4	10	65	64

[a]Reaction condition: **6a** (0.5 mmol), **7** (0.6 mmol), (*S*)-**1k** as catalyst in DCM.

[b]Determined by HPLC using a Chirapak IB column.

TABLE 4 Asymmetric allylation to aldehydes 6 catalyzed by (*S*)-**1k**[a]



Entry	R	Yield, %[b]	Ee, %[c]	Config. [d]
1	Ph (**8a**)	96	84	(*R*)-(+)
2	4-MeO-C_6H_4 (**8b**)	94	91	(*R*)-(+)
3	3-MeO-C_6H_4 (**8c**)	88	88	(*R*)-(+)
4	3-Cl-C_6H_4 (**8d**)	82	89	(*R*)-(+)
5	4-Cl-C_6H_4 (**8e**)	85	83	(*R*)-(+)
6	3-NO_2-C_6H_4 (**8f**)	86	87	(*R*)-(+)
7	4-NO_2-C_6H_4 (**8g**)	74	84	(*R*)-(+)
8	3-F-C_6H_4 (**8h**)	86	86	(*R*)-(+)
9	4-F-C_6H_4 (**8i**)	85	84	(*R*)-(+)
10	4-Me-C_6H_4 (**8j**)	81	84	(*R*)-(+)
11	3.4-diMeO-C_6H_3 (**8k**)	84	86	(*R*)-(+)
12	2-Thiophenyl (**8l**)	94	88	(*R*)-(+)
13	2-Naphthyl (**8m**)	95	86	(*R*)-(+)
14	1-Naphthyl (**8n**)	84	84	(*R*)-(+)
15	(*E*)-PhCH═CH (**8o**)	93	83	(*R*)-(+)
16	PhCH-CH_2 (**8p**)	64	83	(*S*)-(+)

[a]Reaction condition: **6** (0.5 mmol), **7** (0.6 mmol), (*S*)-**1k** (1% mol).

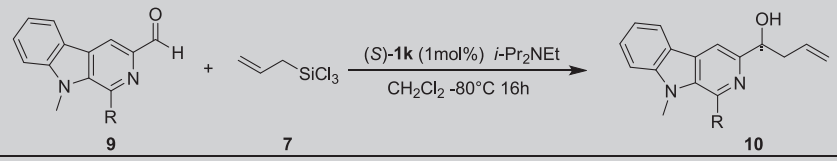
[b]Isolated yield. Some products are fairly volatile.

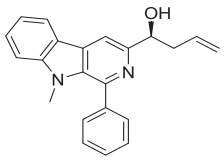
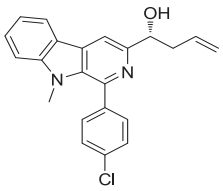
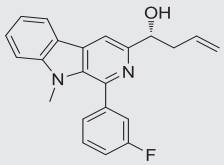
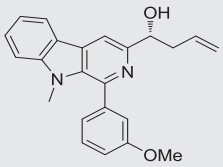
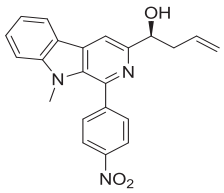
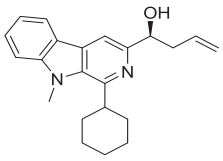
[c]The ee% was determined by HPLC.

[d]The configuration was determined by comparing their optical rotation data and HPLC retention times with those reported in literatures. See ref. 37 for details.

[e]Compound **8o** is levorotatory in $CHCl_3$ and dextrorotatory in Et_2O.

TABLE 5 Enantioselectivities in the addition of allyltrichlorosilane to bulky substituted aldehydes



Structure	Er	Structure	Er
 **10a**	92:8	 **10d**	
 **10b**	96:4	 **10e**	95.5:4.5
 **10c**	97:3	 **10f**	95.5:4.5

in the allylations. Thus, the best reaction conditions were at −80°C using DCM as the solvent.

Influence of the catalyst loading on the enantioselectivity was then examined. When the amount of catalyst (*S*)-**1k** increased from 0.5, 1, 5 to 10 mol%, both yields and ee% values exhibited nonlinear changes (Table 3). The highest yield and enantioselectivity were recorded when the amount of catalyst was 1 mol %.

A total of 16 aldehydes was investigated using (*S*)-**1k** as the catalyst (Table 4). Ee values of 83% to 91% were observed. Half of them had over 86%ee values. It exhibited that this catalyst gave good enantioselectivity in the allylations.

Subsequently, six bulky substituted aldehydes were used in the allylations (Table 5). When1 mol % (*S*)-**1k** was applied for the enantioselective allylations, the product **10d** was obtained with up to 96% ee, while other products **10b**, **10c**, **10e**, and **10f** had ee values of 92%, 94%, 91%, and 91%, respectively. All of these exhibited that the catalyst (*S*)-**1k** had quite good enantioselectivities for allylation of the bulky substituted aldehydes. Their configuration was determined by comparing its optical rotation data and HPLC retention times with those reported in literatures. [41]

4 | CONCLUSION

In summary, we have introduced a serials of new Lewis base catalysts derived from the L-tryptophan. The best catalyst **1k** gave high enantioselectivity up to 96%ee for the allylation using substrate **9d**. Further applications of this catalyst are being developed in our laboratory.

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ORCID

Huajie Zhu https://orcid.org/0000-0002-7263-2360

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of the article.

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