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Catalytic asymmetric synthesis of axially chiral 2-amino-1,1′-biaryl compounds by phase-transfer-catalyzed kinetic resolution and desymmetrization

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ABSTRACT

An efficient methodology for kinetic resolution of axially chiral 2-amino-1,1′-biaryl compounds as useful chiral building blocks was developed by means of binaphthyl-modified chiral quaternary ammonium salt-catalyzed *N*-allylations under phase-transfer conditions. The catalyst structure and reaction conditions were carefully optimized to achieve the highly selective kinetic resolutions. Various types of 2-amino-1,1′-biaryls were submitted to the kinetic resolution under the phase-transfer conditions to resolve the enantiomers with high selectivities. The synthetic utility of this method could be extended to the asymmetric desymmetrization of diamino biaryl compounds to obtain the corresponding axially chiral biaryls with high enantioselectivities.

1. Introduction

Axially chiral biaryl compounds are indispensable building blocks in modern organic synthesis. A wide variety of chiral ligands and catalysts were designed based on the biaryl scaffolds, and these chiral ligands and catalysts were utilized for various catalytic asymmetric transformations to produce important chiral compounds in optically enriched form.[1] Furthermore, axially chiral biaryl skeletons are observed in the structure of biologically active natural products.[2] Thus, the development of efficient enantioselective methods for the synthesis of axially chiral biaryls is an important task in the field of organic chemistry.[3] Among the enantioselective synthesis of axially chiral biaryls, we are interested in the catalytic asymmetric synthesis of 2-amino-1,1′-biaryls, owing to their high synthetic utility as chiral building blocks for the synthesis of important chiral ligands, catalysts, and biologically active compounds (Fig. 1).[4,5] Herein, we report our approach for the catalytic asymmetric synthesis of 2-amino-1,1′-biaryl compounds[6,7] via kinetic resolution[8,9] and desymmetrization[10] by chiral phase-transfer-catalyzed *N*-allylations (Scheme 1).[11,12]

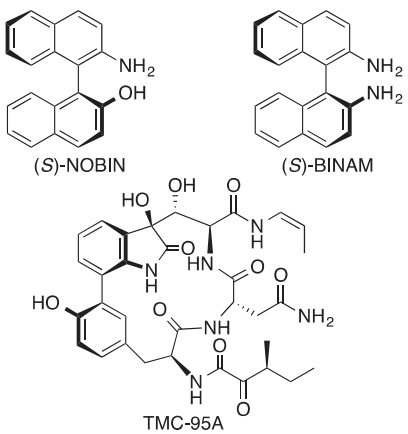

Fig. 1. Representative axially chiral 2-amino-1,1′-biaryls.

2. Results and discussion

We first investigated the effect of binaphthyl-modified chiral quaternary ammonium salts **3**–**5** in the kinetic resolution of 2-amino-2′-hydroxy-1,1′-binaphthyl (NOBIN) derivative (±)-**1a**, as a useful chiral building block,[4] through *N*-allylation under the

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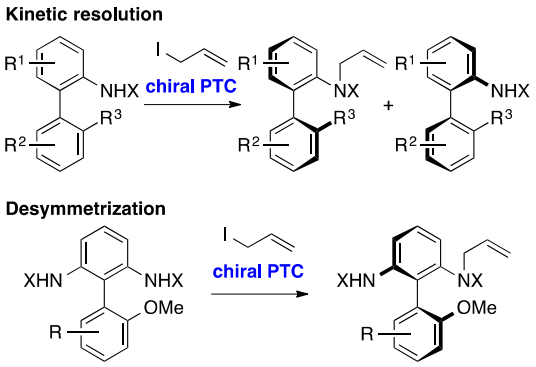


Scheme 1. Our approach for catalytic asymmetric synthesis of 2-amino-1,1′-biaryls.

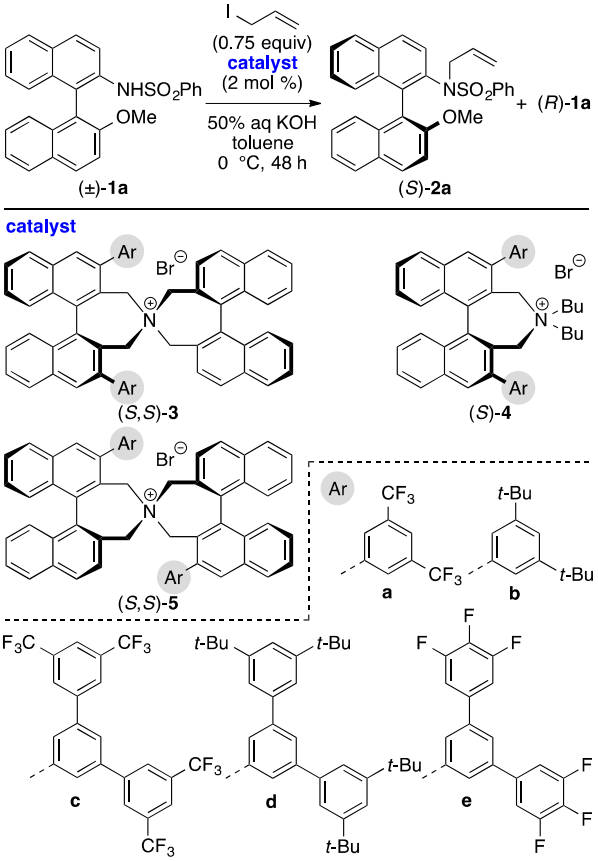
phase-transfer conditions (Table 1). The reaction of (±)-**1a** possessing a benzenesulfonamide moiety with allyl iodide (0.75 equiv) in aqueous KOH/toluene biphasic solution catalyzed by (*S*,*S*)-**3a** or **3c**, which were some of most reliable phase-transfer catalysts,[13] at 0 °C for 48 h afforded the allylation product **2a** with low to moderate selectivities (*s*=1.6–6.4, entries 1 and 2). The simplified-type catalysts (*S*)-**4a** and **4c**, which were also reliable catalysts,[14] does not improve the results (entries 3 and 4). We next employed symmetrical catalysts of the type (*S*,*S*)-**5**[15] to improve the selectivity of the kinetic resolution. Although symmetrical catalysts (*S*,*S*)-**5a** and **5b** did not show significant improvement of the results (entries 5 and 6), switching the 3,3′-aromatic substituents (Ar) of the catalyst (*S*,*S*)-**5** to radially extended substituents (**5c**–**e**) resulted in improved selectivities (*s*=11–35, entries 7–10). The best selectivity was achieved by employment of the catalyst (*S*,*S*)-**5c** (*s*=32, entry 7), and the product (*S*)-**2a** was obtained in 81% ee (53% yield) with recovery of the unreacted (*R*)-**1a** in 93% ee (43% yield). It should be noted that the further high enantioselectivity of the allylation product (*S*)-**2a** (90% ee) was obtained in the lower conversion (entry 8).

We next examined the effect of protecting groups (X) on the nitrogen of **1** in the kinetic resolution under the phase-transfer conditions (Scheme 2). Although the kinetic resolutions catalyzed by (*S*,*S*)-**5c** with substrates possessing sulfonyl groups, such as methanesulfonyl (**1b**) and *p*-nitrobenzenesulfonyl (**1c**) groups, gave the allylation products **2b** and **2c** with good selectivities (*s*=18–23), the reaction with amide-type substrates **1d** and **1e** showed low reactivities and gave only trace amount of allylation products **2d** and **2e**. The substrate **1a** possessing benzenesulfonyl group on the nitrogen was most appropriate substrate in terms of both reactivity and selectivity for the kinetic resolution under the phase-transfer conditions.

We also investigated the effect of electrophiles for the kinetic resolution of (±)-**1a** in the presence of catalyst (*S*,*S*)-**5c** (Scheme 3). The reactions with relatively reactive alkyl iodides, such as benzyl iodide and methyl iodide, gave alkylation products **2f** and **2g** in moderate conversion with good selectivities (*s*=13–19). On the other hand, Michael acceptors, such as methyl vinyl ketone and phenyl vinyl sulfone, were not appropriate electrophiles for the kinetic resolution under the phase-transfer conditions.[16] The best electrophile was allyl iodide in these trials.

With optimal phase-transfer catalyst and reaction conditions in hand, we studied the generality of the kinetic resolution of 2-amino-1,1′-biaryls (±)-**6** (Scheme 4). Although 2-amino-1,1′-binaphthyls **6a** and **6b** showed low reactivities for the phase-transfer-catalyzed *N*-allylations,[16] the kinetic resolutions with substrates **6c** and **6d** possessing a methylthio group and a dimethylamino group, respectively, were efficiently promoted by

Table 1
Effect of chiral phase-transfer catalysts[a]



Entry	Catalyst	Yield of 2a[b] (%)	ee of 2a[c] (%)	Yield of 1a[b] (%)	ee of 1a[c] (%)	*s*[d]
1	(*S*,*S*)-**3a**	15	−70	82	−12	6.4
2	(*S*,*S*)-**3c**	39	−20	57	−8	1.6
3	(*S*)-**4a**	44	−17	53	−12	1.6
4	(*S*)-**4c**	68	22	30	40	2.2
5	(*S*,*S*)-**5a**	26	60	69	22	4.9
6	(*S*,*S*)-**5b**	65	8	33	12	1.3
7	(*S*,*S*)-**5c**	53	81	43	93	32
8[e]	(*S*,*S*)-**5c**	38	90	60	61	35
9[f]	(*S*,*S*)-**5d**	47	70	50	64	11
10	(*S*,*S*)-**5e**	29	84	67	38	17

[a] Reaction conditions: (±)-**1a** (0.050 mmol), allyl iodide (0.038 mmol) in the presence of chiral phase-transfer catalyst (2 mol %) in 50% aqueous KOH (2.0 mL)/toluene (1.0 mL) at 0 °C for 48 h.
[b] Isolated yield.
[c] Enantiomeric excess (ee) was determined by HPLC analysis using a chiral stationary phase.
[d] The selectivity factor (*s*) was calculated as follows.[8] $s=k_{fast}/k_{slow}=\ln[1-C(1+ee\mathbf{2})]/\ln[1-C(1-ee\mathbf{2})]=\ln[(1-C)(1-ee\mathbf{1})]/\ln[(1-C)(1+ee\mathbf{1})]$; $C=ee\mathbf{1}/(ee\mathbf{1}+ee\mathbf{2})$.
[e] The reaction was performed for 16 h.
[f] Allyl iodide (0.028 mmol) was used.

catalyst (*S*,*S*)-**5c** to provide allylation products **7c** and **7d** in moderate to high selectivities (*s*=4.7–27). These results indicate that the heteroatoms at 2′-position of the binaphthyl core are important for efficient promotion of the present kinetic resolution.[17] Substrate **6e** possessing tetraline backbone, which was also useful building block,[18] was resolved with high selectivity (*s*=37). Other 2-amino-1,1′-biaryls **6f**–**j** possessing different biaryl skeletons were also resolved with moderate to high selectivities (*s*=5.7–43). Notably, introduction of an additional methoxy group onto the phenylamino moiety improved the selectivities (substrates **6g**, **6h** vs **6f**).

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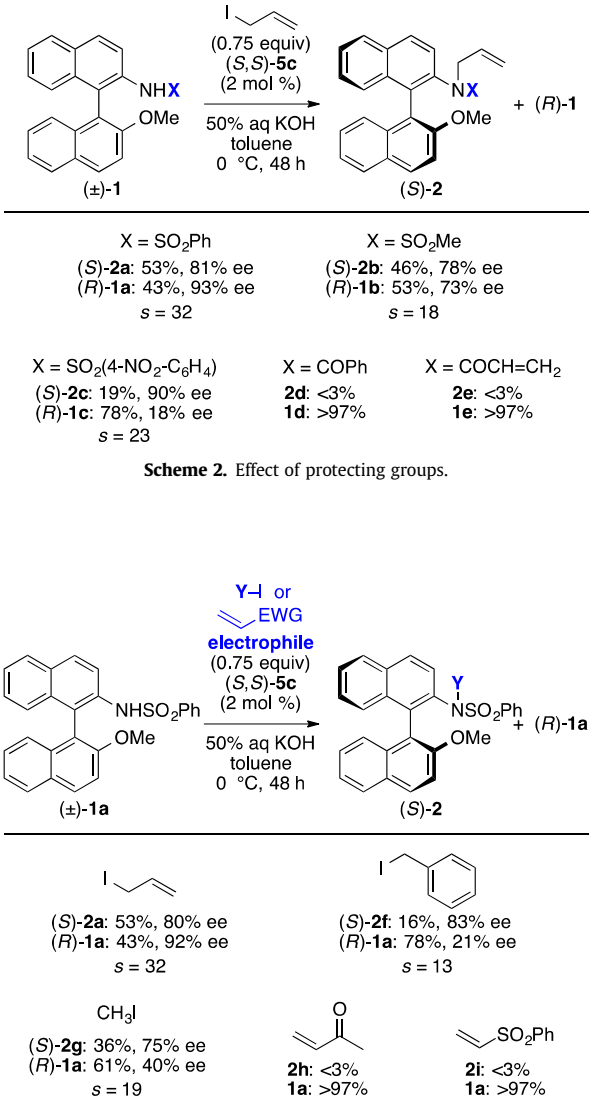
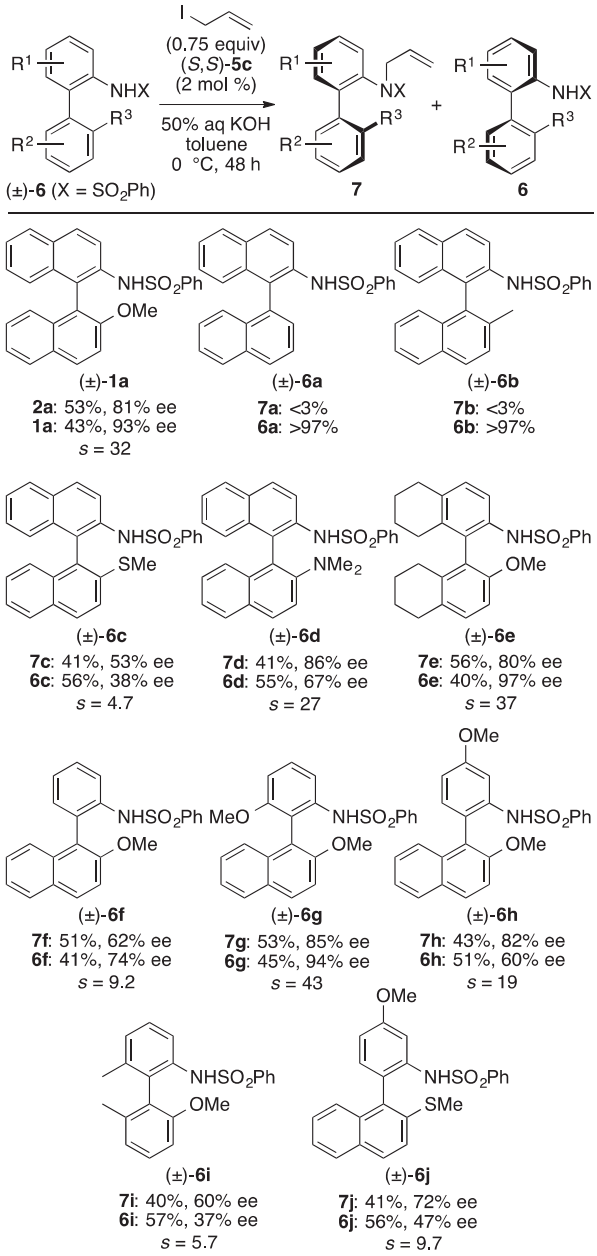


Scheme 2. Effect of protecting groups.

Scheme 3. Effect of electrophiles.

The protecting groups of the resulting optically enriched starting materials (**1a**, **6**) and allylation products (**2a**, **7**) could be readily deprotected (Scheme 5). For example, the benzenesulfonyl group of (*R*)-**1a** was removed by treatment with low-valent titanium reagent, which was generated in situ from titanium(IV) isopropoxide, trimethylsilyl chloride, and magnesium powder.[19] Subsequent treatment of the resulting 2-amino-2′-methoxy-1,1′-binaphthyl with boron tribromide gave (*R*)-NOBIN without any loss of enantioselectivity. Furthermore, (*S*)-NOBIN was obtained from allylation product (*S*)-**2a** by treatment with diisobutylaluminum hydride (DIBAL-H) in the presence of a nickel catalyst for cleavage of allyl group on nitrogen and methyl group on oxygen,[20] followed by reaction with low-valent titanium reagent.

The synthetic utility of this catalytic method for the asymmetric synthesis of 2-amino-1,1′-biaryls were further expanded in the enantioselective desymmetrization of the diamino compounds **8** (Scheme 6). Attempted reaction of **8a** with allyl iodide in aqueous KOH/toluene under the influence of catalyst (*S*,*S*)-**5c** (2 mol %) at −5 °C for 120 h afforded monoallylation product **9a** in moderate yield with high enantioselectivity (93% ee). Other substrates **8b** and **8c** were also employable for the catalytic asymmetric desymmetrizations to give axially chiral biaryls **9b** and **9c**, respectively, in moderate to good enantioselectivities.



Scheme 4. Kinetic resolution of 2-amino-1,1′-biaryls.

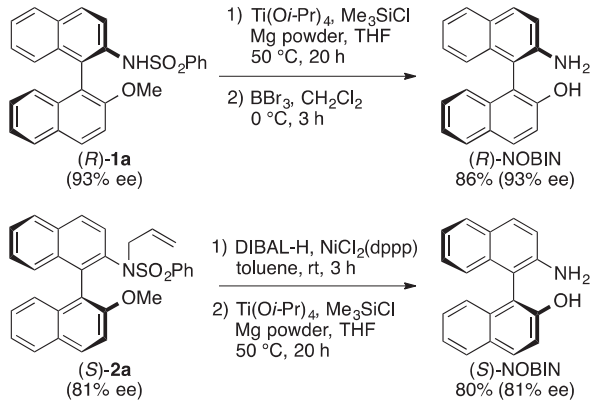
3. Conclusions

In summary, we have successfully developed an efficient methodology for the kinetic resolution of 2-amino-1,1′-biaryl compounds via asymmetric *N*-allylation promoted by binaphthyl-modified chiral quaternary ammonium salts under the phase-transfer conditions. Furthermore, this synthetic method could be extended to the asymmetric desymmetrization of diamino biaryl compounds. These are valuable examples of catalytic asymmetric synthesis of axially chiral 2-amino-1,1′-biaryls as important chiral building blocks.

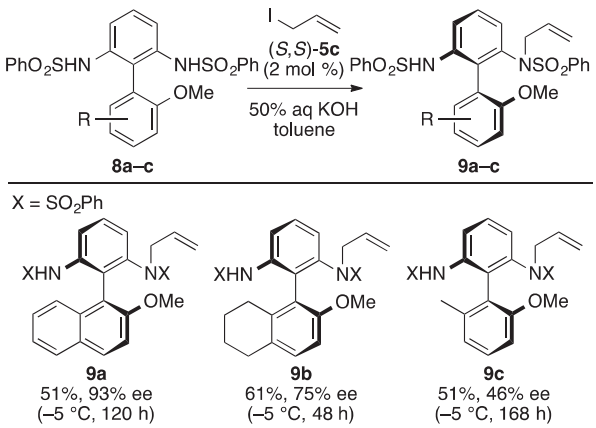
4. Experimental section

4.1. General

^{1}H NMR spectra were measured on JEOL JNM-FX 400 NMR, JEOL JNM-AL 400 NMR, and JEOL JNM-ECA 500 NMR instruments (400



Scheme 5. Deprotection of **1a** and **2a**.



Scheme 6. Catalytic enantioselective desymmetrization of biaryl compounds.

and 500 MHz for ^{1}H NMR). ^{13}C NMR spectra were measured on JEOL JNM-FX 400 NMR, JEOL JNM-AL 400 NMR, and JEOL JNM-ECA 500 NMR instruments (100 and 125 MHz for ^{13}C NMR). Tetramethylsilane (TMS) served as the internal standard (0 ppm) for ^{1}H NMR, and $CDCl_3$ served as the internal standard (77.0 ppm) for ^{13}C NMR. The following abbreviations were used to express the multiplicities: s=singlet; d=doublet; t=triplet; q=quartet; m=multiplet; br=broad. High performance liquid chromatography (HPLC) was performed on Shimadzu 10A instruments using Daicel Chiralpak IA-3 or IB-3 (4.6 mm×250 mm) columns. High-resolution mass spectra (HRMS) were performed on BRUKER microTOF focus–KR and JEOL JMS-700N. Optical rotations were measured on a JASCO DIP-1000 and P-2200 digital polarimeters. All reactions were monitored by thin-layer chromatography using Merck precoated TLC plates (silica gel 60GF-254, 0.25 mm), with visualization by using UV (254 nm), or dyes such as $KMnO_4$. The products were purified by flash column chromatography on silica gel 60N [Kanto Chemical Co., Inc. (spherical, neutral)] or Merck preparative thin layer chromatography on silica gel (PLC 60 F254, 0.5 mm). All simple chemicals were purchased and used as received.

4.2. Synthesis of chiral phase-transfer catalysts

Catalysts (*S*,*S*)-**3**,[13] (*S*)-**4**,[14] and (*S*,*S*)-**5**[15] were prepared according to the literature.

4.3. General procedure for synthesis of starting materials 1a and 6[7]

A solution of benzenesulfonyl chloride (0.36 mmol) in dichloromethane (2 mL) was added dropwise to a solution of corresponding primary 2-amino-1,1′-biaryl compound (0.30 mmol) and pyridine (4.5 mmol) in dichloromethane (8 mL), and the reaction mixture was stirred for 24 h at room temperature. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (dichloromethane/ethyl acetate/hexane as eluent) to give a starting material **1a** or **6** (81–93% yield).

4.4. General procedure for kinetic resolution of 1a and 6

To a solution of starting material **1a** or **6** (0.050 mmol) and chiral phase-transfer catalyst (*S*,*S*)-**5c** (2 mol %, 0.001 mmol) in toluene (1 mL)–50% aqueous KOH (2 mL) was added allyl iodide (0.038 mmol) at 0 °C. The reaction mixture was vigorously stirred for 48 h at 0 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (3×5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography or preparative thin layer chromatography on silica gel (ethyl acetate/hexane as eluent) to give allylation product **2a** or **7** and unreacted starting material **1a** or **6**.

*4.4.1. Recovered starting material **1a**.* $[\alpha]_D^{28}$=−26.2 (*c* 0.30, $CHCl_3$, 93% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 231 nm; retention time: 14.6 min (minor) and 21.0 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.11 (d, *J*=9.0 Hz, 1H), 8.01 (d, *J*=9.5 Hz, 1H), 7.92 (d, *J*=9.0 Hz, 1H), 7.82–7.84 (m, 2H), 7.44 (d, *J*=8.0 Hz, 2H), 7.40 (d, *J*=9.0 Hz, 1H), 7.26–7.35 (m, 3H), 7.09–7.15 (m, 3H), 6.95 (t, *J*=7.5 Hz, 1H), 6.88 (d, *J*=8.5 Hz, 1H), 6.56 (s, 1H), 6.46 (d, *J*=8.5 Hz, 1H), 3.67 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 139.2, 133.5, 133.1, 132.9, 132.6, 131.2, 131.0, 129.1, 129.0, 128.6, 128.0, 127.3, 126.9, 126.6, 125.9, 125.0, 124.4, 123.8, 122.6, 119.7, 115.9, 113.2, 56.4; IR (neat) 1592, 1508, 1399, 1316, 1268, 1254, 1167, 1148, 1089, 983, 811, 746, 720, 687, 582 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{21}NO_3SNa^+$: 462.1134 ($[M+Na]^+$), found 462.1115.

*4.4.2. Allylation product **2a**.* $[\alpha]_D^{28}$=−24.4 (*c* 0.60, $CHCl_3$, 81% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 225 nm; retention time: 26.6 min (major) and 36.9 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.99 (d, *J*=9.5 Hz, 1H), 7.91–7.95 (m, 2H), 7.88 (d, *J*=8.0 Hz, 1H), 7.48–7.62 (br, 1H), 7.44–7.48 (t, *J*=7.5 Hz, 1H), 7.38 (d, *J*=9.5 Hz, 2H), 7.33 (t, *J*=7.5 Hz, 2H), 7.22–7.26 (m, 3H), 6.96–7.18 (m, 4H), 5.49–5.96 (br, 1H), 4.78–4.90 (m, 2H), 3.77–3.81 (m, 2H), 3.72 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 140.0, 136.7, 134.5, 134.2, 133.9, 133.2, 133.0, 132.2, 129.9, 128.9, 128.4, 128.3, 128.0, 127.8, 127.7, 126.7, 126.38, 126.35, 123.8, 119.4, 118.9, 112.9, 55.9, 53.6; IR (neat) 1592, 1507, 1462, 1446, 1355, 1328, 1270, 1262, 1251, 1158, 1088, 1054, 1020, 809, 751, 721, 688, 633, 585 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{25}NO_3SNa^+$: 502.1447 ($[M+Na]^+$), found 502.1431.

*4.4.3. Recovered starting material **1b**.* $[\alpha]_D^{30}$=−16.6 (*c* 0.20, $CHCl_3$, 73% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=5:1, flow rate=0.5 mL/min, 230 nm; retention time: 18.3 min (minor) and 21.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.07 (d, *J*=9.2 Hz, 1H), 7.98–8.04 (m, 2H), 7.91 (d, *J*=8.4 Hz, 2H), 7.48 (d, *J*=9.2 Hz, 1H), 7.35–7.44 (m, 2H), 7.23–7.27 (m, 2H), 7.04 (d, *J*=8.4 Hz, 1H), 6.98 (d, *J*=8.4 Hz, 1H), 6.17 (s, 1H), 3.79 (s, 3H), 2.67 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 133.5, 133.18, 133.15, 131.41, 131.38, 129.5, 129.3, 128.5, 128.1, 127.6, 126.8, 125.9, 125.4, 124.4, 124.3, 123.5, 120.3, 116.2, 113.3, 56.3, 39.7; IR (neat) 1508, 1396, 1353, 1315, 1268, 1253, 1158, 1084, 985, 812, 752 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{22}H_{19}NO_3SNa^+$: 400.0978 ($[M+Na]^+$), found 400.0961.

*4.4.4. Allylation product **2b**.* $[\alpha]_D^{29}$=−19.9 (*c* 0.50, $CHCl_3$, 78% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=5:1, flow

rate=0.5 mL/min, 254 nm; retention time: 17.9 min (major) and 22.3 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.02 (d, J=8.8 Hz, 1H), 7.94 (t, J=8.8 Hz, 2H), 7.87 (d, J=8.4 Hz, 1H), 7.56 (d, J=8.8 Hz, 1H), 7.45–7.49 (m, 2H), 7.33 (t, J=8.0 Hz, 1H), 7.23–7.27 (m, 2H), 7.17 (d, J=8.8 Hz, 1H), 7.05–7.12 (br m, 1H), 5.58–5.77 (br, 1H), 4.99–5.06 (m, 2H), 3.86–3.97 (br m, 2H), 3.78 (s, 3H), 1.81–2.24 (br, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.4, 137.4, 134.1, 133.8, 133.7, 133.6, 132.9, 130.2, 129.9, 128.8, 128.4, 128.0, 127.8, 126.9, 126.5, 126.41, 126.36, 125.8, 124.0, 119.7, 119.4, 113.0, 56.1, 53.9, 41.1; IR (neat) 1506, 1331, 1271, 1262, 1250, 1147, 1088, 1054, 811, 753 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{25}H_{23}NO_3SNa^+$: 440.1291 ([M+Na]$^+$), found 440.1290.

4.4.5. Recovered starting material ***1c***. $[\alpha]_D^{29}$=−23.3 (*c* 0.40, $CHCl_3$, 18% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 18.2 min (minor) and 23.9 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.05 (d, J=8.8 Hz, 1H), 8.00 (d, J=8.8 Hz, 2H), 7.89 (d, J=8.4 Hz, 1H), 7.74 (d, J=8.0 Hz, 1H), 7.62 (d, J=8.8 Hz, 2H), 7.44 (d, J=9.6 Hz, 1H), 7.40 (t, J=7.6 Hz, 1H), 7.32 (d, J=9.2 Hz, 2H), 7.12–7.19 (m, 2H), 6.93 (s, 1H), 6.87 (d, J=8.8 Hz, 1H), 6.81 (t, J=7.6 Hz, 1H), 6.23 (d, J=8.8 Hz, 1H), 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 149.4, 144.8, 133.3, 132.9, 132.0, 131.6, 131.2, 129.5, 128.9, 128.1, 128.0, 127.4, 126.8, 126.7, 126.5, 126.0, 125.9, 124.8, 123.9, 123.6, 123.4, 116.8, 113.4, 56.9; IR (neat) 1528, 1348, 1313, 1268, 1169, 1089, 813, 743, 685 cm^{-1}; HRMS (FAB) calcd for $C_{27}H_{20}N_2O_5S$: 484.1093 ([M]$^+$), found 484.1105.

4.4.6. Allylation product ***2c***. $[\alpha]_D^{29}$=−12.9 (*c* 0.23, $CHCl_3$, 90% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 20.6 min (major) and 25.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J=8.8 Hz, 1H), 7.94 (d, J=7.6 Hz, 2H), 7.79 (br, 1H), 7.60–7.72 (br m, 2H), 7.49 (t, J=7.6 Hz, 1H), 7.37 (d, J=9.6 Hz, 1H), 7.22–7.31 (m, 4H), 7.15 (t, J=8.0 Hz, 1H), 7.06 (br, 2H), 6.94 (d, J=8.4 Hz, 1H), 5.85 (br, 1H), 4.93–5.07 (br m, 2H), 4.05 (br, 2H), 3.74 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.2, 149.2, 146.1, 136.0, 134.1, 133.8, 133.1, 130.1, 129.8, 128.8, 128.6, 128.0, 127.6, 126.9, 126.71, 126.68, 126.6, 126.1, 124.0, 123.2, 119.9, 119.3, 113.0, 56.0, 54.8; IR (neat) 1528, 1346, 1261, 1251, 1161, 1088, 1053, 1019, 808, 747, 736, 686 cm^{-1}; HRMS (FAB) calcd for $C_{30}H_{24}N_2O_5S$: 524.1406 ([M]$^+$), found 524.1406.

4.4.7. Recovered starting material ***1d***. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.79–8.82 (m, 1H), 8.02–8.10 (m, 2H), 7.92 (d, J=8.0 Hz, 2H), 7.75–7.76 (br, 1H), 7.13–7.60 (m, 12H), 3.77 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.1, 155.1, 135.0, 134.5, 133.5, 133.0, 131.5, 131.05, 130.99, 129.3, 128.9, 128.5, 128.2, 128.1, 127.6, 126.6, 126.3, 125.7, 124.9, 124.8, 124.3, 121.5, 120.3, 117.0, 113.6, 56.7; IR (neat) 1677, 1596, 1502, 1488, 1428, 1332, 1263, 1250, 1082, 812, 750, 709 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{28}H_{22}NO_2^+$: 404.1645 ([M+H]$^+$), found 404.1628.

4.4.8. Recovered starting material ***1e***. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.70 (br, 1H), 8.04 (d, J=9.2 Hz, 1H), 7.98 (d, J=9.2 Hz, 1H), 7.88 (d, J=8.0 Hz, 2H), 7.46 (d, J=9.2 Hz, 1H), 7.32–7.38 (m, 2H), 7.17–7.24 (m, 2H), 7.04–7.08 (m, 3H), 6.02 (d, J=16.8 Hz, 1H), 5.72–5.78 (br m, 1H), 5.46 (d, J=10.4 Hz, 1H), 3.73 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 163.3, 155.1, 134.2, 133.4, 132.9, 131.5, 131.0, 129.2, 128.7, 128.1, 128.0, 127.4, 126.7, 126.3, 125.7, 124.8, 124.7, 124.2, 121.5, 120.4, 116.7, 113.5, 56.5; IR (neat) 1682, 1592, 1495, 1427, 1260, 1247, 1084, 812, 747 cm^{-1}; HRMS (FAB) calcd for $C_{24}H_{20}NO_2$: 354.1494 ([M+H]$^+$), found 354.1498.

4.4.9. Benzylation product ***2f***. $[\alpha]_D^{28}$=−86.8 (*c* 0.70, $CHCl_3$, 83% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 227 nm; retention time: 24.3 min (major) and 33.3 min (minor). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.02 (d, J=9.0 Hz, 1H), 7.89–7.90 (m, 2H), 7.82 (d, J=9.0 Hz, 1H), 7.46 (t, J=7.5 Hz, 1H), 7.40 (d, J=9.5 Hz, 1H), 7.33 (t, J=7.5 Hz, 1H), 7.31 (d, J=9.0 Hz, 1H), 6.80–7.26 (m, 14H), 4.45 (br d, J=14.5 Hz, 1H), 4.28–4.36 (br, 1H), 3.69 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 140.6, 137.1, 135.2, 134.4, 134.3, 133.9, 133.0, 131.8, 130.0, 129.7, 129.4, 129.0, 128.2, 128.1, 128.0, 127.8, 127.6, 127.5, 127.4, 126.8, 126.7, 126.4, 126.3, 123.9, 119.6, 113.0, 55.9, 54.9; IR (neat) 1325, 1262, 1250, 1155, 1086, 1055, 808, 746, 720, 700, 686 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{34}H_{27}NO_3SNa^+$: 552.1604 ([M+Na]$^+$), found 552.1616.

4.4.10. Methylation product ***2g***. $[\alpha]_D^{30}$=+20.5 (*c* 0.50, $CHCl_3$, 75% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 227 nm; retention time: 23.8 min (major) and 35.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86–8.00 (m, 4H), 7.53 (d, J=8.8 Hz, 1H), 7.48 (t, J=7.4 Hz, 1H), 7.15–7.39 (m, 11H), 3.73 (s, 3H), 2.87 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.4, 138.7, 138.5, 134.5, 134.1, 133.8, 133.0, 132.3, 129.8, 129.3, 128.9, 128.4, 128.0, 127.8, 127.6, 126.9, 126.5, 126.45, 126.39, 126.30, 125.9, 123.7, 119.6, 113.0, 56.0, 38.4; IR (neat) 1593, 1507, 1446, 1353, 1328, 1264, 1248, 1179, 1152, 1088, 1052, 827, 809, 752, 721, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{28}H_{24}NO_3S^+$: 454.1471 ([M+H]$^+$), found 454.1457.

4.4.11. Recovered starting material ***6a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.14 (d, J=9.2 Hz, 1H), 7.93–7.98 (m, 3H), 7.87 (d, J=8.4 Hz, 1H), 7.36–7.51 (m, 6H), 7.30 (t, J=8.4 Hz, 2H), 7.13–7.20 (m, 2H), 6.90 (d, J=8.8 Hz, 1H), 6.84 (d, J=8.8 Hz, 1H), 6.66 (d, J=7.2 Hz, 1H), 6.24 (s, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 138.7, 133.8, 133.2, 132.9, 132.4, 132.2, 131.7, 131.0, 129.3, 129.2, 128.9, 128.5, 128.4, 127.9, 127.15, 127.11, 126.8, 126.7, 126.5, 126.1, 125.7, 125.3, 125.0, 120.2; IR (neat) 1447, 1401, 1367, 1323, 1168, 1091, 978, 867, 843, 804, 794, 782, 773, 748, 721, 687, 609, 581, 562 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{19}NO_2SNa^+$: 432.1029 ([M+Na]$^+$), found 432.1017.

4.4.12. Recovered starting material ***6b***. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.17 (d, J=8.8 Hz, 1H), 7.85–7.96 (m, 4H), 7.54 (d, J=7.2 Hz, 2H), 7.46–7.48 (m, 2H), 7.35–7.42 (m, 2H), 7.29 (t, J=8.0 Hz, 2H), 7.18 (t, J=7.6 Hz, 1H), 7.02 (t, J=7.4 Hz, 1H), 6.83 (d, J=8.4 Hz, 1H), 6.62 (d, J=8.8 Hz, 1H), 6.26 (s, 1H), 1.78 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.3, 136.3, 133.0, 132.6, 132.4, 132.3, 130.8, 129.3, 129.2, 129.1, 129.0, 128.9, 128.2, 128.0, 127.1, 127.0, 125.42, 125.39, 125.1, 124.6, 124.1, 118.3, 19.6; IR (neat) 1404, 1313, 1167, 1091, 979, 841, 814, 740, 719, 686, 611, 580, 563 cm^{-1}; HRMS (FAB) calcd for $C_{27}H_{21}NO_2S$: 423.1293 ([M]$^+$), found 423.1308.

4.4.13. Recovered starting material ***6c***. $[\alpha]_D^{29}$=+4.1 (*c* 0.60, $CHCl_3$, 38% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 15.0 min (minor) and 18.6 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J=9.2 Hz, 1H), 7.97 (t, J=9.8 Hz, 2H), 7.84 (d, J=8.0 Hz, 2H), 7.49–7.54 (m, 3H), 7.32–7.40 (m, 3H), 7.14–7.23 (m, 3H), 6.95 (t, J=7.6 Hz, 1H), 6.82 (d, J=8.8 Hz, 1H), 6.47 (d, J=8.4 Hz, 1H), 6.41 (s, 1H), 2.33 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 139.4, 138.0, 132.80, 132.75, 132.69, 132.5, 131.1, 130.9, 129.97, 129.95, 129.8, 128.7, 128.1, 127.5, 127.1, 127.0, 125.21, 125.18, 125.16, 124.0, 122.8, 122.3, 118.6, 15.2; IR (neat) 1405, 1306, 1165, 1090, 979, 864, 842, 810, 744, 719, 686, 617, 581 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{21}NO_2S_2Na^+$: 478.0906 ([M+Na]$^+$), found 478.0919.

4.4.14. Allylation product ***7c***. $[\alpha]_D^{29}$=−68.0 (*c* 0.60, $CHCl_3$, 53% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 16.3 min (major) and 41.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94–8.01 (m, 3H), 7.90 (d, J=8.4 Hz, 1H), 7.69 (d, J=8.8 Hz, 1H), 7.42–7.53 (m, 3H), 7.27–7.35 (m, 4H), 7.15 (d, J=8.4 Hz, 1H), 7.00–7.12 (m, 4H), 5.66–5.76 (m, 1H), 4.89–4.93 (m, 2H), 3.90 (dd, J=7.8, 15.8 Hz, 1H),

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3.65 (dd, J=4.4, 15.6 Hz, 1H), 2.37 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 139.5, 136.4, 135.4, 133.3, 133.25, 133.18, 133.0, 132.3, 131.9, 131.3, 129.2, 128.88, 128.85, 128.4, 128.2, 128.0, 127.6, 127.0, 126.8, 126.7, 126.6, 126.3, 125.6, 123.1, 119.1, 53.2, 15.8; IR (neat) 1350, 1325, 1158, 1089, 809, 749, 720, 687, 625, 582, 576, 569 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{25}NO_2S_2Na^+$: 518.1219 ([M+Na]$^+$), found 518.1198.

4.4.15. Recovered starting material ***6d***. $[\alpha]_D^{25}$=−141.6 (c 0.40, $CHCl_3$, 67% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 10.3 min (minor) and 11.0 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 8.06 (d, J=8.5 Hz, 1H), 8.01 (s, 1H), 7.93 (d, J=9.0 Hz, 1H), 7.88 (d, J=9.5 Hz, 1H), 7.86 (d, J=8.0 Hz, 1H), 7.70 (d, J=8.5 Hz, 1H), 7.46 (d, J=9.0 Hz, 1H), 7.36 (t, J=7.5 Hz, 1H), 7.11−7.19 (m, 4H), 6.99 (d, J=8.5 Hz, 1H), 6.89 (t, J=7.8 Hz, 1H), 6.78 (t, J=7.8 Hz, 1H), 6.70 (t, J=7.8 Hz, 2H), 6.21 (d, J=9.0 Hz, 1H), 2.58 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.0, 139.2, 133.8, 133.6, 132.0, 131.9, 131.6, 130.2, 129.4, 129.0, 128.1, 128.0, 127.5, 127.4, 126.9, 126.6, 126.4, 126.0, 125.5, 125.3, 123.6, 123.4, 121.9, 118.0, 43.4; IR (neat) 1352, 1306, 1161, 1091, 993, 816, 745, 719, 686, 586 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{28}H_{25}N_2O_2S$: 453.1631 ([M+H]$^+$), found 453.1619.

4.4.16. Allylation product ***7d***. $[\alpha]_D^{25}$=−8.3 (c 0.40, $CHCl_3$, 86% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 217 nm; retention time: 13.6 min (major) and 22.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78−7.94 (m, 4H), 6.79−7.66 (m, 13H), 5.55−6.13 (br, 1H), 4.56−5.18 (br, 2H), 3.62−4.35 (br, 2H), 2.50 (s, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.6, 140.1 (br), 137.1, 136.2, 135.0, 134.4, 133.9 (br), 133.0, 132.1, 129.2, 128.8 (br), 128.4, 128.2, 128.0, 127.7, 127.6, 127.5, 126.5, 126.3, 126.2, 123.7 (br), 119.0, 118.9, 53.1, 43.3; IR (neat) 1505, 1446, 1330, 1158, 1089, 812, 751, 720, 688, 579 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{31}H_{29}N_2O_2S$: 493.1944 ([M+H]$^+$), found 493.1934.

4.4.17. Recovered starting material ***6e***. $[\alpha]_D^{29}$=+5.9 (c 0.50, $CHCl_3$, 97% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 218 nm; retention time: 9.4 min (minor) and 11.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, J=8.4 Hz, 2H), 7.49−7.52 (m, 2H), 7.39−7.43 (m, 2H), 7.09 (d, J=8.8 Hz, 1H), 6.99 (d, J=8.4 Hz, 1H), 6.73 (d, J=8.4 Hz, 1H), 6.12 (s, 1H), 3.51 (s, 3H), 2.70−2.75 (m, 4H), 1.50−2.11 (m, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.5, 139.9, 137.0, 136.2, 133.1, 132.6, 131.8, 130.49, 130.45, 128.9, 128.8, 127.2, 126.6, 122.4, 115.0, 108.7, 55.4, 29.4, 29.2, 27.2, 26.7, 22.99, 22.98, 22.8, 22.7; IR (neat) 2930, 1474, 1447, 1384, 1331, 1313, 1260, 1164, 1088, 718, 688, 584 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{29}NO_3SNa^+$: 470.1760 ([M+Na]$^+$), found 470.1761.

4.4.18. Allylation product ***7e***. $[\alpha]_D^{30}$=−7.3 (c 0.60, $CHCl_3$, 80% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 207 nm; retention time: 11.0 min (major) and 23.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.44−7.49 (m, 3H), 7.29−7.33 (m, 2H), 7.05−7.14 (m, 3H), 6.76 (d, J=8.4 Hz, 1H), 5.63−5.73 (m, 1H), 4.84−4.92 (m, 2H), 3.70−3.72 (m, 2H), 3.64 (s, 3H), 2.57−2.84 (m, 5H), 2.01−2.22 (m, 3H), 1.55−1.79 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.1, 140.8, 137.60, 137.58, 137.4, 135.0, 133.51, 133.48, 132.2, 130.2, 129.0, 128.6, 128.5, 128.2, 127.8, 126.0, 118.4, 107.9, 54.9, 53.8, 29.9, 29.4, 27.4, 27.0, 23.04, 22.96, 22.7; IR (neat) 2930, 1482, 1474, 1446, 1351, 1324, 1262, 1157, 1088, 1039, 803, 757, 720, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{30}H_{33}NO_3SNa^+$: 510.2073 ([M+Na]$^+$), found 510.2058.

4.4.19. Recovered starting material ***6f***. $[\alpha]_D^{26}$=−1.3 (c 0.40, $CHCl_3$, 74% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 14.3 min (minor) and 18.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, J=9.6 Hz, 1H), 7.83 (d, J=8.4 Hz, 1H), 7.77 (d, J=8.0 Hz, 1H), 7.41 (dt, J=1.6, 7.8 Hz, 1H), 7.27−7.34 (m, 4H), 7.22 (dt, J=1.2, 7.6 Hz, 1H), 7.16 (t, J=7.6 Hz, 1H), 7.08−7.12 (m, 2H), 6.98 (t, J=8.0 Hz, 2H), 6.81 (d, J=8.8 Hz, 1H), 6.68 (s, 1H), 3.81 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 153.3, 139.1, 135.1, 133.3, 132.3, 132.2, 130.7, 129.2, 128.7, 128.5, 128.4, 127.8, 127.0, 126.7, 125.0, 124.5, 123.8, 122.7, 119.1, 113.0, 56.7; IR (neat) 1447, 1330, 1256, 1159, 1091, 1065, 916, 900, 808, 747, 717, 686, 631, 587 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{23}H_{19}NO_3SNa^+$: 412.0978 ([M+Na]$^+$), found 412.0957.

4.4.20. Allylation product ***7f***. $[\alpha]_D^{26}$=−9.2 (c 0.50, $CHCl_3$, 62% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 228 nm; retention time: 16.6 min (minor) and 22.1 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.90 (d, J=9.0 Hz, 1H), 7.80−7.84 (m, 1H), 7.13−7.48 (m, 13H), 5.43−5.70 (br, 1H), 4.81−4.92 (m, 2H), 3.80 (s, 3H), 3.58−3.82 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 153.6, 140.0, 139.2, 137.0, 133.9, 133.3, 132.9, 132.1, 131.2, 129.6, 128.8, 128.4, 128.1, 128.0, 127.7, 127.6, 126.4, 125.9, 123.6, 122.0, 118.7, 112.8, 56.0, 53.5; IR (neat) 1509, 1446, 1331, 1267, 1254, 1159, 1090, 1067, 860, 809, 756, 739, 689, 589 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{26}H_{23}NO_3SNa^+$: 452.1291 ([M+Na]$^+$), found 452.1281.

4.4.21. Recovered starting material ***6g***. $[\alpha]_D^{24}$=−38.8 (c 0.50, $CHCl_3$, 94% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 228 nm; retention time: 15.6 min (minor) and 20.2 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J=9.2 Hz, 1H), 7.78 (d, J=8.0 Hz, 1H), 7.47 (d, J=8.4 Hz, 1H), 7.25−7.41 (m, 6H), 7.07−7.14 (m, 3H), 6.72−6.79 (m, 2H), 6.39 (s, 1H), 3.78 (s, 3H) 3.52 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.9, 154.3, 139.1, 136.2, 133.1, 132.5, 130.8, 129.4, 129.1, 128.5, 128.0, 126.9, 124.2, 123.7, 116.1, 115.0, 113.3, 112.9, 107.5, 56.6, 55.8; IR (neat) 1585, 1466, 1447, 1393, 1328, 1268, 1252, 1164, 1090, 1074, 809, 735, 718, 686, 636, 585 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{21}NO_4SNa^+$: 442.1084 ([M+Na]$^+$), found 442.1071.

4.4.22. Allylation product ***7g***. $[\alpha]_D^{26}$=+3.0 (c 0.50, $CHCl_3$, 85% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 228 nm; retention time: 19.5 min (minor) and 23.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J=9.2 Hz, 1H), 7.81−7.84 (m, 1H), 7.30−7.45 (m, 7H), 7.05−7.12 (m, 5H), 5.47−5.58 (br, 1H), 4.78−4.89 (br m, 2H), 3.80 (s, 3H), 3.64 (s, 3H), 3.44−3.71 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 158.8, 154.1, 140.0, 133.8, 133.2, 132.1, 129.4, 128.9, 128.5, 128.3, 127.8, 127.6, 126.3, 126.0, 125.7, 123.6, 118.6, 118.2, 113.3, 111.0, 56.10, 56.07, 53.4; IR (neat) 1465, 1329, 1254, 1159, 1088, 1065, 809, 747, 730 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{25}NO_4SNa^+$: 482.1397 ([M+Na]$^+$), found 482.1383.

4.4.23. Recovered starting material ***6h***. $[\alpha]_D^{28}$=+29.6 (c 0.60, $CHCl_3$, 60% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 230 nm; retention time: 15.0 min (minor) and 18.7 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.88 (d, J=9.2 Hz, 1H), 7.76 (d, J=8.4 Hz, 1H), 7.24−7.41 (m, 5H), 7.13 (t, J=7.6 Hz, 1H), 7.10 (dt, J=1.2, 7.8 Hz, 1H), 6.98−7.01 (m, 3H), 6.85 (d, J=8.4 Hz, 1H), 6.78 (dd, J=2.4, 8.8 Hz, 1H), 6.67 (s, 1H), 3.88 (s, 3H) 3.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.7, 153.6, 139.0, 136.0, 133.7, 132.8, 132.3, 130.4, 129.2, 128.4, 127.8, 126.9, 126.7, 124.6, 123.7, 120.2, 118.9, 113.0, 111.3, 107.6, 56.7, 55.4; IR (neat) 1614, 1506, 1331, 1291, 1259, 1171, 1158, 1091, 1067, 809, 730, 686 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{21}NO_4SNa^+$: 442.1084 ([M+Na]$^+$), found 442.1070.

4.4.24. Allylation product ***7h***. $[\alpha]_D^{29}$=−2.2 (c 0.45, $CHCl_3$, 82% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 230 nm; retention time: 16.6 min (minor) and 18.5 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, J=9.2 Hz, 1H), 7.80−7.83 (m, 1H), 6.94−7.45 (m, 12H), 5.52−5.69 (br, 1H),

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4.83–4.93 (m, 2H), 3.86 (s, 3H), 3.81 (s, 3H), 3.59–3.84 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.0, 154.0, 140.2, 140.1, 134.3, 133.3, 132.2, 129.4, 128.9, 128.8, 128.4, 127.8, 127.6, 126.4, 125.9, 123.6, 121.8, 118.6, 116.6, 114.1, 112.8, 56.0, 55.4, 53.6; IR (neat) 1607, 1505, 1446, 1329, 1286, 1260, 1239, 1163, 1090, 1068, 1038, 910, 809, 751, 723, 689 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{25}NO_4SNa^+$: 482.1397 ([M+Na]$^+$), found 482.1382.

4.4.25. Recovered starting material ***6i***. $[\alpha]_D^{31}$=−4.1 (*c* 0.50, $CHCl_3$, 37% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=20:1, flow rate=0.5 mL/min, 219 nm; retention time: 21.1 min (major) and 21.9 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.70 (d, *J*=8.4 Hz, 2H), 7.58 (d, *J*=8.4 Hz, 1H), 7.51 (t, *J*=7.2 Hz, 1H), 7.37–7.41 (m, 2H), 7.29 (t, *J*=7.6 Hz, 1H), 7.19 (t, *J*=7.6 Hz, 1H), 6.99 (d, *J*=7.6 Hz, 1H), 6.87 (d, *J*=7.6 Hz, 1H), 6.80 (d, *J*=8.4 Hz, 1H), 6.20 (s, 1H), 3.56 (s, 3H), 1.83 (s, 3H), 1.59 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.7, 139.8, 138.8, 137.7, 134.4, 132.7, 129.7, 128.8, 128.0, 127.4, 127.2, 125.7, 123.12, 123.06, 116.0, 108.5, 55.5, 19.8, 18.9; IR (neat) 1579, 1465, 1447, 1383, 1327, 1290, 1256, 1161, 1090, 1081, 962, 856, 778, 750, 718, 687, 587 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{21}H_{21}NO_3SNa^+$: 390.1134 ([M+Na]$^+$), found 390.1123.

4.4.26. Allylation product ***7i***. $[\alpha]_D^{30}$=+22.9 (*c* 0.40, $CHCl_3$, 60% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=20:1, flow rate=0.5 mL/min, 250 nm; retention time: 26.2 min (minor) and 27.0 min (major). ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.46–7.53 (m, 3H), 7.23–7.36 (m, 5H), 7.15 (d, *J*=7.5 Hz, 1H), 6.96 (d, *J*=7.5 Hz, 1H), 6.80 (d, *J*=8.5 Hz, 1H), 5.59–5.67 (m, 1H), 4.84–4.92 (m, 2H), 3.74–3.76 (m, 2H), 3.65 (s, 3H), 2.06 (s, 3H), 1.98 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.3, 140.5, 138.8, 138.1, 137.9, 133.3, 132.3, 129.7, 128.6, 128.4, 128.0, 127.3, 126.6, 122.9, 118.4, 107.7, 55.0, 53.8, 20.0, 19.7; IR (neat) 1466, 1446, 1350, 1324, 1309, 1293, 1254, 1157, 1082, 822, 774, 755, 725, 689, 596 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{25}NO_3SNa^+$: 430.1447 ([M+Na]$^+$), found 430.1438.

4.4.27. Recovered starting material ***6j***. $[\alpha]_D^{29}$=+26.8 (*c* 0.50, $CHCl_3$, 47% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 258 nm; retention time: 17.0 min (minor) and 23.3 min (major). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.89 (d, *J*=8.8 Hz, 1H), 7.80 (d, *J*=8.0 Hz, 1H), 7.54 (d, *J*=8.0 Hz, 2H), 7.34–7.46 (m, 4H), 7.23–7.26 (m, 2H), 7.12 (t, *J*=8.0 Hz, 1H), 6.95 (d, *J*=8.4 Hz, 1H), 6.75–6.80 (m, 2H), 6.27 (s, 1H) 3.88 (s, 3H), 2.41 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 160.4, 139.2, 137.3, 135.8, 133.0, 132.8, 132.3, 131.1, 129.6, 129.5, 128.7, 128.0, 127.3, 127.2, 125.1, 124.2, 122.1, 120.2, 110.8, 105.1, 55.4, 15.4; IR (neat) 1612, 1509, 1500, 1396, 1333, 1293, 1158, 1123, 1091, 884, 806, 741, 719, 687, 595 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{24}H_{21}NO_3S_2Na^+$: 458.0855 ([M+Na]$^+$), found 458.0845.

4.4.28. Allylation product ***7j***. $[\alpha]_D^{29}$=−26.7 (*c* 0.50, $CHCl_3$, 72% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 254 nm; retention time: 18.2 min (major) and 20.0 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85 (t, *J*=8.0 Hz, 2H), 7.04–7.55 (m, 12H), 5.58–5.69 (m, 1H), 4.90–4.95 (m, 2H), 3.88 (s, 3H), 3.61–3.84 (m, 2H), 2.43 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 159.5, 139.7, 139.5, 135.5, 133.9, 133.4, 133.1, 132.3, 131.1, 129.9, 128.5, 128.4, 128.0, 127.5, 126.9, 126.7, 125.3, 122.7, 118.9, 116.9, 114.3, 55.4, 53.5, 15.9; IR (neat) 1605, 1509, 1498, 1446, 1325, 1288, 1159, 1089, 1036, 829, 808, 750, 722, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{27}H_{25}NO_3S_2Na^+$: 498.1168 ([M+Na]$^+$), found 498.1159.

4.5. Deprotection of 1a and 2a[19,20]

4.5.1. Deprotection of ***1a***. To a mixture of (*R*)-**1a** (0.025 mmol) and magnesium powder (0.25 mmol) in THF (0.30 mL) was added titanium(IV) isopropoxide (0.05 mmol) and trimethylsilyl chloride (0.075 mmol) under argon atmosphere, and the resulting mixture was stirred for 20 h at 50 °C. The reaction mixture was quenched with 1M aqueous NaOH (0.50 mL), and the mixture was stirred for 30 min. The resulting solution was filtered over Celite, and the filtrate was diluted with water. The solution was extracted with ethyl acetate (3×5 mL). The combined extracts were dried over Na_2SO_4, and concentrated to give crude 2-amino-2′-methoxy-1,1′-binaphthyl. To a solution of crude 2-amino-2′-methoxy-1,1′-binaphthyl in dichloromethane (3 mL) was added dropwise boron tribromide (0.70 mmol) at 0 °C under argon atmosphere, and the resulting mixture was stirred for 3 h at 0 °C. The mixture was quenched with water, and extracted with ethyl acetate (3×5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by preparative thin layer chromatography on silica gel (hexane/ethyl acetate=3/1 as eluent) to give (*R*)-NOBIN (0.22 mmol, 86% yield). The enantiomeric excess of (*R*)-NOBIN was determined by HPLC analysis.

4.5.2. Deprotection of ***2a***. To a solution of (*S*)-**2a** (0.020 mmol) and $NiCl_2$(dppp) (5 mol %, 0.001 mmol) in toluene (0.20 mL) was added a 1M solution of diisobutylaluminum hydride in toluene (0.10 mL, 0.10 mmol) at 0 °C, and the reaction mixture was stirred for 3 h at room temperature. The mixture was quenched with 1M aqueous NaOH (0.20 mL), and the mixture was diluted with water. The solution was extracted with ethyl acetate (3×5 mL). The combined extracts were dried over Na_2SO_4, and concentrated to give a crude *N*-benzenesulfonyl-protected NOBIN. Deprotection of benzenesulfonyl group was carried out as described in the deprotection of (*R*)-**1a**.[19] The resulting crude material was purified by thin layer chromatography on silica gel (hexane/ethyl acetate=3/1 as eluent) to give (*S*)-NOBIN (0.016 mmol, 80% yield). The enantiomeric excess of (*S*)-NOBIN was determined by HPLC analysis.

4.5.3. (R)- and (S)-NOBIN.[21] (*R*)-NOBIN: $[\alpha]_D^{30}$=+96.0 (*c* 0.45, THF, 93% ee) {lit.[21b] $[\alpha]_D^{19}$=+122 [*c* 1.0, THF, 99% ee (*R*)]}. (*S*)-NOBIN: $[\alpha]_D^{30}$=−77.6 (*c* 0.45, THF, 81% ee) {lit.[21a] $[\alpha]_D$=−117 [*c* 1.0, THF, >98% ee (*S*)]}. HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=3:1, flow rate=0.5 mL/min, 228 nm; retention time: 15.9 min (*R*) and 24.5 min (*S*). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J*=9.2 Hz, 1H), 7.84–7.87 (m, 2H), 7.79–7.81 (m, 1H), 7.04–7.39 (m, 8H), 5.15 (br s, 1H), 3.75 (br s, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 151.8, 143.7, 134.1, 133.2, 130.6, 130.3, 129.5, 128.4, 128.3, 128.2, 127.3, 126.9, 124.5, 123.7, 123.6, 122.7, 118.2, 117.7, 114.3, 108.5; IR (neat) 1617, 1595, 1381, 1216, 1175, 1146, 823, 750 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{20}H_{16}NO$: 286.1226 ([M+H]$^+$), found 286.1221.

4.6. Synthesis of starting materials 8[7,22]

To a mixture of 1-bromo-2-methoxynaphthalene (2.3 mmol) and magnesium turnings (9.0 mmol) in diethyl ether (10 mL) was stirred at room temperature under argon atmosphere until white slurry was formed. To the resulting mixture was added benzene (10 mL) to dissolve the material, and the mixture was stirred for 2 h at room temperature under argon atmosphere. The solution of resulting Grignard reagent was added dropwise to a solution of 2-methoxy-1,3-dinitrobenzene (1.5 mmol) in benzene (15 mL), and the mixture was stirred for 8 h at 50 °C. The reaction mixture was quenched with water and extracted with ethyl acetate (3×15 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by column chromatography on silica gel (ethyl acetate/hexane as eluent) to give a precursor of the starting material, which was the corresponding dinitro compound (1.1 mmol, 73% yield). A mixture of the corresponding dinitro compound (1.0 mmol) and Pd/C (80 mg; 10 wt %) in ethanol (10 mL) was stirred for 12 h at room temperature under hydrogen atmosphere (H_2 balloon). The reaction mixture was filtered over Celite

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and concentrated to give a diamino compound. To a solution of the resulting diamino compound and pyridine (30 mmol) in dichloromethane (20 mL) was added dropwise a solution of benzenesulfonyl chloride (3.0 mmol) in dichloromethane (10 mL), and the reaction mixture was stirred for 24 h at room temperature. The mixture was concentrated, and the residue was purified by column chromatography on silica gel (dichloromethane/ethyl acetate/hexane as eluent) to give starting material **8a** (0.98 mmol, 98% yield). Compounds **8b** and **8c** were synthesized by the same procedure.

*4.6.1. Starting material **8a**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.01 (d, J=8.8 Hz, 1H), 7.83 (d, J=8.4 Hz, 1H), 7.53 (d, J=8.4 Hz, 2H), 7.40–7.44 (m, 6H), 7.30–7.36 (m, 3H), 7.20–7.24 (m, 4H), 7.01 (t, J=8.0 Hz, 1H), 6.38 (d, J=8.8 Hz, 1H), 6.01 (s, 2H), 3.65 (s, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.9, 139.1, 135.9, 132.8, 132.6, 132.2, 129.5, 129.1, 128.7, 128.5, 127.0, 124.4, 122.6, 117.3, 115.7, 112.8, 111.4, 56.3; IR (neat) 1464, 1397, 1321, 1269, 1252, 1165, 1090, 748, 688 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{29}H_{24}N_2O_5S_2Na$: 567.1019 ([M+Na]$^+$), found 567.1034.

*4.6.2. Starting material **8b**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68–7.70 (m, 4H), 7.50–7.55 (m, 2H), 7.39–7.44 (m, 6H), 7.17–7.22 (m, 2H), 7.75 (d, J=8.8 Hz, 1H), 6.03 (s, 2H), 3.41 (s, 3H), 2.73 (t, J=6.2 Hz, 2H), 1.51–1.64 (m, 4H), 1.37–1.41 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 154.9, 139.3, 138.3, 135.3, 133.0, 132.6, 131.5, 129.1, 128.9, 127.1, 117.6, 116.7, 113.3, 109.2, 55.5, 29.0, 26.2, 22.7, 22.4; IR (neat) 1463, 1395, 1333, 1317, 1261, 1164, 1089, 1018, 748, 736, 686, 582 cm^{-1}; HRMS (FAB) calcd for $C_{29}H_{29}N_2O_5S_2$: 549.1518 ([M+H]$^+$), found 549.1519.

*4.6.3. Starting material **8c**.* ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62–7.65 (m, 4H), 7.53 (dt, J=1.6, 7.4 Hz, 2H), 7.34–7.44 (m, 7H), 7.24 (t, J=8.0 Hz, 1H), 6.86 (d, J=7.6 Hz, 1H), 6.81 (d, J=8.8 Hz, 1H), 6.03 (s, 2H), 3.47 (s, 3H), 1.32 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 157.0, 140.0, 139.5, 135.2, 133.0, 131.4, 129.2, 129.0, 127.1, 123.8, 117.84, 117.79, 114.6, 109.0, 55.6, 18.6; IR (neat) 1467, 1397, 1382, 1326, 1260, 1165, 1089, 1021, 718, 686, 584 cm^{-1}; HRMS (FAB) calcd for $C_{26}H_{25}N_2O_5S_2$: 509.1205 ([M+H]$^+$), found 509.1208.

4.7. General procedure for catalytic enantioselective desymmetrization of 8

To a solution of starting material **8** (0.026 mmol) and chiral phase-transfer catalyst (*S*,*S*)-**5c** (2 mol %, 0.0004 mmol) in toluene (0.5 mL)–50% aqueous KOH (0.5 mL) was added allyl iodide (0.020 mmol) at −5 °C. The reaction mixture was vigorously stirred for 48–168 h at −5 °C. The reaction mixture was quenched with saturated aqueous NH_4Cl and extracted with ethyl acetate (3×5 mL). The combined extracts were dried over Na_2SO_4, and concentrated. The residue was purified by preparative thin layer chromatography on silica gel (ethyl acetate/hexane as eluent) to give allylation product **9**. Yield of **9** was determined on the basis of amount of allyl iodide.

*4.7.1. Allylation product **9a**.* $[\alpha]_D^{33}$=−34.8 (*c* 0.40, THF, 93% ee); HPLC analysis: Daicel Chiralpak IB-3, hexane/2-propanol=2:1, flow rate=0.4 mL/min, 231 nm; retention time: 22.2 min (major) and 27.7 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.98 (d, J=8.8 Hz, 1H), 7.84 (t, J=7.0 Hz, 2H), 7.24–7.50 (m, 9H), 6.81–7.19 (br m, 7H), 6.30 (br s, 1H), 5.28–5.53 (br, 1H), 4.70–4.86 (br m, 2H), 3.77 (s, 3H), 3.38–3.57 (br m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 154.3, 140.1, 139.4, 139.0, 136.9, 133.1, 133.0, 132.7, 132.4, 131.4, 129.0, 128.9, 128.8, 128.4, 127.9, 127.6, 127.2, 126.8, 124.7, 124.2, 118.8, 118.5, 114.8, 112.5, 55.9, 53.6; IR (neat) 2957, 2923, 2853, 2361, 1460, 1447, 1326, 1258, 1161, 1089, 1064, 1023, 807, 749, 737, 687 cm^{-1}; HRMS (ESI-TOF) calcd for $C_{32}H_{28}N_2O_5S_2Na$: 607.1332 ([M+Na]$^+$), found 607.1335.

*4.7.2. Allylation product **9b**.* $[\alpha]_D^{29}$=+21.7 (*c* 0.20, $CHCl_3$, 75% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=5:1, flow rate=0.5 mL/min, 254 nm; retention time: 22.9 min (major) and 33.6 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.80 (m, 3H), 7.26–7.55 (m, 9H), 7.20 (d, J=8.8 Hz, 1H), 7.03 (d, J=7.6 Hz, 1H), 6.76 (d, J=8.8 Hz, 1H), 6.30 (s, 1H), 5.40–5.59 (br m, 1H), 4.76–4.89 (m, 2H), 3.59–3.69 (br m, 2H), 3.52 (s, 3H), 2.73–2.86 (m, 2H), 2.41–2.51 (br m, 1H), 1.52–1.71 (m, 3H), 1.44–1.50 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.3, 140.1, 139.4, 138.9, 136.3, 133.1, 132.8, 132.5, 131.2, 129.0, 128.8, 128.7, 128.6, 128.4, 127.8, 127.2, 126.5, 121.2, 120.0, 118.8, 116.8, 108.5, 55.0, 53.8, 29.3, 26.5, 22.7, 22.6; IR (neat) 1458, 1447, 1353, 1325, 1229, 1217, 1164, 1091, 581 cm^{-1}; HRMS (FAB) calcd for $C_{32}H_{33}N_2O_5S_2$: 589.1831 ([M+H]$^+$), found 589.1832.

*4.7.3. Allylation product **9c**.* $[\alpha]_D^{29}$=−2.4 (*c* 0.12, $CHCl_3$, 46% ee); HPLC analysis: Daicel Chiralpak IA-3, hexane/2-propanol=5:1, flow rate=0.5 mL/min, 254 nm; retention time: 44.7 min (major) and 55.8 min (minor). ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75–7.77 (m, 3H), 7.27–7.58 (m, 10H), 6.95–7.00 (m, 2H), 6.81 (d, J=8.0 Hz, 1H), 6.28 (s, 1H), 5.50 (br, 1H), 4.77–4.91 (m, 2H), 3.60–3.75 (m, 2H), 3.55 (s, 3H), 1.80 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.9, 140.0, 139.5, 139.3, 136.3, 133.1, 132.8, 132.6, 130.3, 129.0, 128.8, 128.7, 128.5, 128.0, 127.2, 126.1, 123.5, 120.8, 118.6, 117.7, 111.7, 108.3, 55.1, 53.9, 19.4; IR (neat) 1459, 1447, 1327, 1257, 1160, 1089, 752, 688, 584 cm^{-1}; HRMS (FAB) calcd for $C_{29}H_{29}N_2O_5S_2$: 549.1518 ([M+H]$^+$), found 549.1525.

4.8. Determination of absolute configurations of 1, 2, 6, 7, and 9

The absolute configurations of compounds **1a** and **2a** were confirmed after the transformation to NOBIN as shown in Scheme 5 and Experimental section 4, by comparison of the optical rotation with the literature value.[21] The absolute configurations of **6d** and **7d** were confirmed by comparison of the optical rotation and the retention time of HPLC with authentic samples, which were prepared from commercially available (*R*)-BINAM.[23] The absolute configuration of compound **6e** was confirmed after the transformation to H_8-NOBIN, by comparison of the retention time of HPLC with the literature value.[24] The absolute configuration of compound **6f** was assigned after the cleavage of benzenesulfonyl group, by comparison of the retention time of HPLC with the literature value.[6b] The absolute configurations of other compounds **1**, **2**, **6**, and **7** were assigned by analogy. The absolute configurations of compounds **9** were also tentatively assigned by analogy.

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Supplementary data

Supplementary data associated with this article can be found in the online version, at http://dx.doi.org/10.1016/j.tet.2015.10.074.

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