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SYNTHESIS OF A NEW CHIRAL C_2-SYMMETRIC NHC-AuCl COMPLEX

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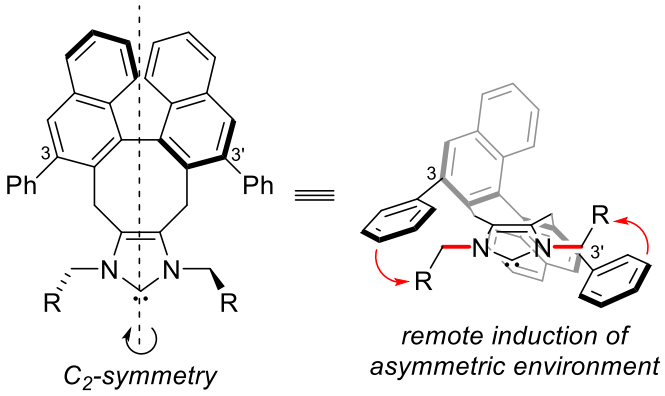
Abstract – A New chiral C_2 symmetric NHC ligand with two binaphthyl units has been synthesized. The new NHC ligand features two seven-membered rings that link the imidazolylidene with the binaphthyl units. X-Ray crystallographic analysis of the new NHC-AuCl complex indicates that the Au-Cl bond is located between the phenyl groups of the binaphthyl units and suggests that this arrangement could induce enantioselectivity in reactions. Indeed, catalytic asymmetric ene-yne cyclization of **2b** in the presence of a catalytic amount (5 mol%) of cationic complex of **13** quantitatively afforded the cyclized product with 78% *ee*.

N-Heterocyclic carbenes (NHCs) were first isolated as stable crystals in 1991 by Arduengo and co-workers,[1] but metal complexes of NHCs are known since the independent works of Öfele[2] and Wanzlick[3] in 1968. NHCs have attracted attention because of their unique structures and properties, which result from the strong coordination with late-transition metals owing to their strong σ-donor and weak π-accepter characteristics.[4] NHCs have been studied as a new class of ligands in organometallic chemistry and have been developed as privileged ligands in terms of their coordinating properties and stability. They have been used as organocatalysts,[5] and their use is expected to increase in future.

Chiral ligands play a pivotal role in asymmetric catalysis, and a number of chiral phosphine ligands have been developed to achieve high enantioselectivity.[6] While chiral phosphine[7] and phosphoramidite ligands,[8] and chiral counter ions,[9] have been developed to achieve high enantioselectivity in Au(I)-catalyzed reactions, very few successful examples of chiral NHC-Au(I) have been documented.[10] This is attributed to the linear geometry of Au(I) complexes, which naturally places the captured substrate *trans* to the chiral ligand. We have been studying the design and synthesis of chiral NHC ligands,[11] and

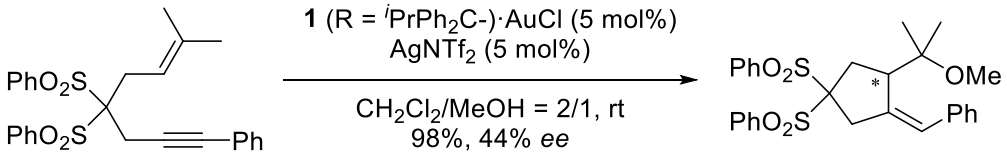
report herein a new chiral C_2-symmetric NHC ligand-Au(I) complex that catalyzes the enantioselective cyclization of a 1,6-ene-yne with high % *ee*.

Recently, we reported new NHC ligands **1** with chiral binaphthyl units linked at the C4 and C5 positions by a carbocyclic eight-membered ring (Figure 1).[11c] A cationic Au(I) complex of **1** (R = ^{i}PrPh$_2$C-) showed catalytic activity toward the enantioselective cyclization of 1,6-ene-yne **2a** to afford the product **3a** (98%, 44% *ee*, Scheme 1). The marginal enantioselectivity was attributed to unhindered (or free) rotation of the substituents (R) that were located at a sterically less hindered position to avoid steric repulsion from the phenyl groups at C3 and C3′. The enantioselectivity depends on the steric bulkiness of these substituents, and free rotation about the carbon-nitrogen bond allows them to move to positions less conducive for enantioselective discrimination.



1: R = ^{t}Bu-, MePh$_2$C-, EtPh$_2$C-, ^{i}PrPh$_2$C-, (CH$_2$)$_5$PhC-

Figure 1. Previously reported chiral C_2-symmetric NHC ligands with a binaphthyl unit



2a **3a**

Scheme 1. Catalytic asymmetric ene-yne cyclization of **2a** catalyzed by cationic **1** (R = ^{i}PrPh$_2$C-)-Au(I) complex

To overcome the limitations due to the stability and rigid structure of NHC ligands possessing fixed nitrogen substituents, we designed a new chiral C_2-symmetric NHC ligand using rigid nitrogen substituents **4** (Figure 2). This ligand features two chiral binaphthyl units that are bound to either side of the imidazolylidene moiety as part of the seven-membered rings. Although the phenyl groups on the binaphthyl groups rotate about the carbon-carbon bond, their fixed orientation would be expected to induce good enantioselectivity in the ene-yne cyclization.

Scheme 2 shows our retrosynthetic analysis of imidazolium salt **5**, which would be the precursor of the new chiral ligand **4**. Based on the previously reported procedure, diimine **6** was selected as the precursor of **5**. Diimine **6** could be prepared by the intramolecular reaction of the corresponding diamino-diketone

formed by the removal of the protective group on nitrogen in diketone **7**. Diketone **7** could be prepared by the pinacol coupling of aldehyde **8**, which itself could be prepared from **9**, a derivative of (*S*)-BINOL reported by Page and co-workers.[12]

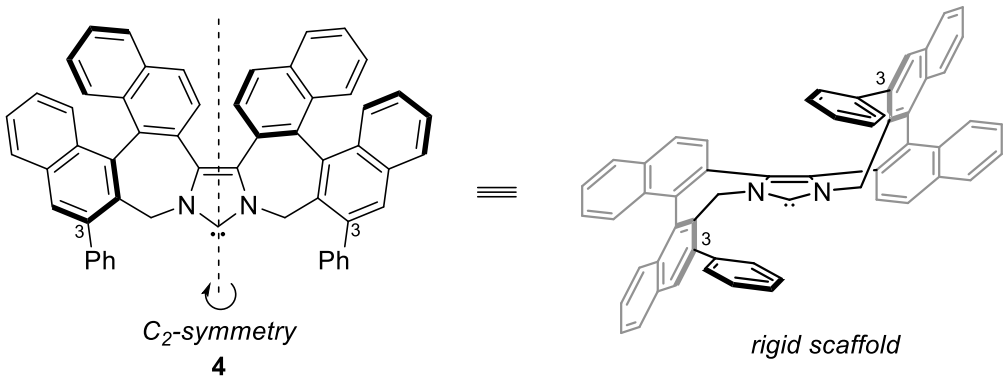
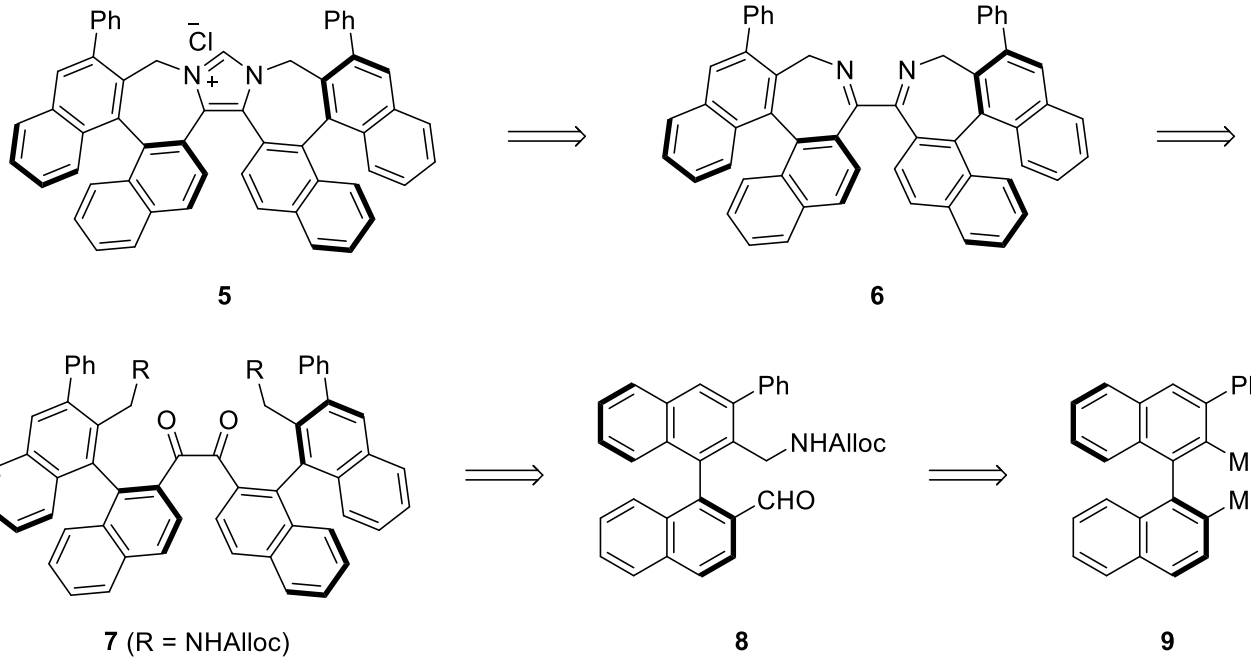


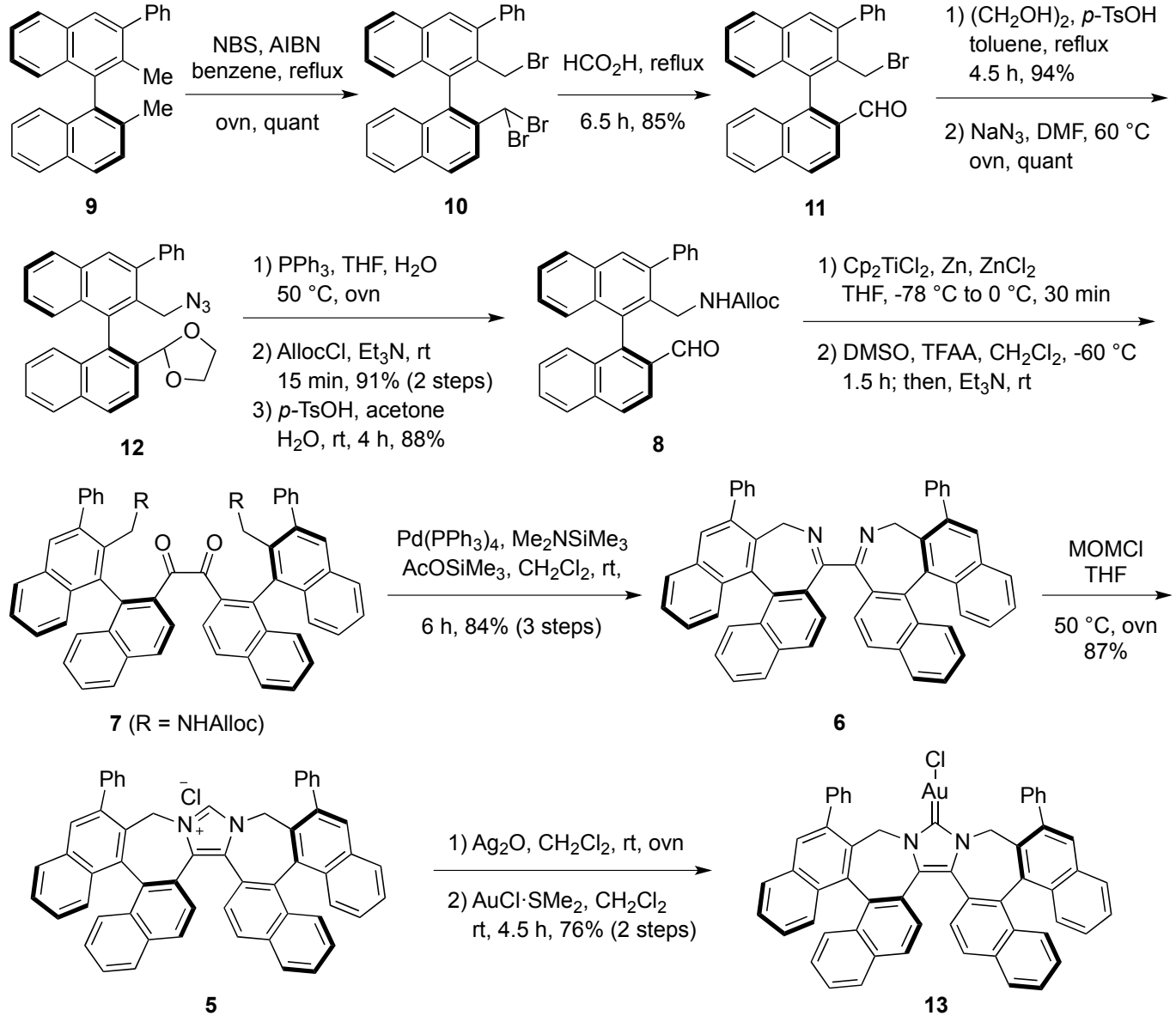
Figure 2. New chiral C_2 symmetric NHC ligand **4**



Scheme 2. Retrosynthetic analysis of chiral C_2-symmetric imidazolium salt **5**

The synthesis of the new chiral C_2-symmetric imidazolium salt **5** is summarized in Scheme 3. The synthesis commenced with the benzylic bromination of **9** with a slight excess of NBS (4 equiv), in the presence of AIBN in refluxing benzene, to afford **10** quantitatively. The sterically hindered methyl group (adjacent to the phenyl group) was mono-brominated, and the less-hindered methyl group was di-brominated. The two methyl groups were thus successfully converted to different oxidation levels. Treatment of compound **10** with formic acid under reflux afforded aldehyde **11** in 85% yield. Aldehyde **11** was converted to the corresponding ethylene acetal (94% yield), which was reacted with sodium azide to generate azide **12** (quantitative yield). Azide **12** was subjected to Staudinger reaction to afford the corresponding amine. Subsequent reaction of this amine with allyl chloroformate and hydrolysis of the

ethylene acetal under acidic conditions afforded aldehyde **8**, the key intermediate in Scheme 2. The reaction of **8** with a low-valent titanium reagent which was in situ generated by Cp_2ZrCl_2 and Zn lead to pinacol coupling,[13] producing a mixture of diastereomeric 1,2-diols. Although Swern oxidation of the 1,2-diols was not reproducible, oxidation using DMSO and TFAA successfully afforded 1,2-diketone **7**. Following the removal of the Alloc groups from **7**,[14] the obtained diamino-diketone underwent spontaneous cyclization to diimine **6** (84%, three steps). Treatment of **6** with MOMCl in THF at 50 °C produced the desired chiral C_2-symmetric imidazolium salt **5** in 87% yield. Compound **5** was stable, and was purified by silica gel column chromatography.



Scheme 3. Retrosynthetic analysis of chiral C_2 symmetric imidazolium salt **5**

Recrystallization of NHC-AuCl complex **13** from benzene-hexane gave a single crystal suitable for X-ray crystallographic analysis.[15] Figure 3 shows the X-ray crystal structure of **13**. The seven-membered rings

lack flexibility because they include four atoms of the binaphthyl unit, and two of the imidazolylidene group. Although the two phenyl groups can rotate around the carbon-carbon bonds attaching them to the binaphthyl units, their axial direction is constrained due to the rigid conformation of the seven-membered rings. Moreover, the side view (b) of the crystal structure of **13** shows that the two phenyl groups are located near the Au-Cl bond. Reactions catalyzed by the Au(I) complex **13** would therefore be expected to experience an asymmetric steric interaction between the phenyl groups and the substrate, and display enantioselectivity.

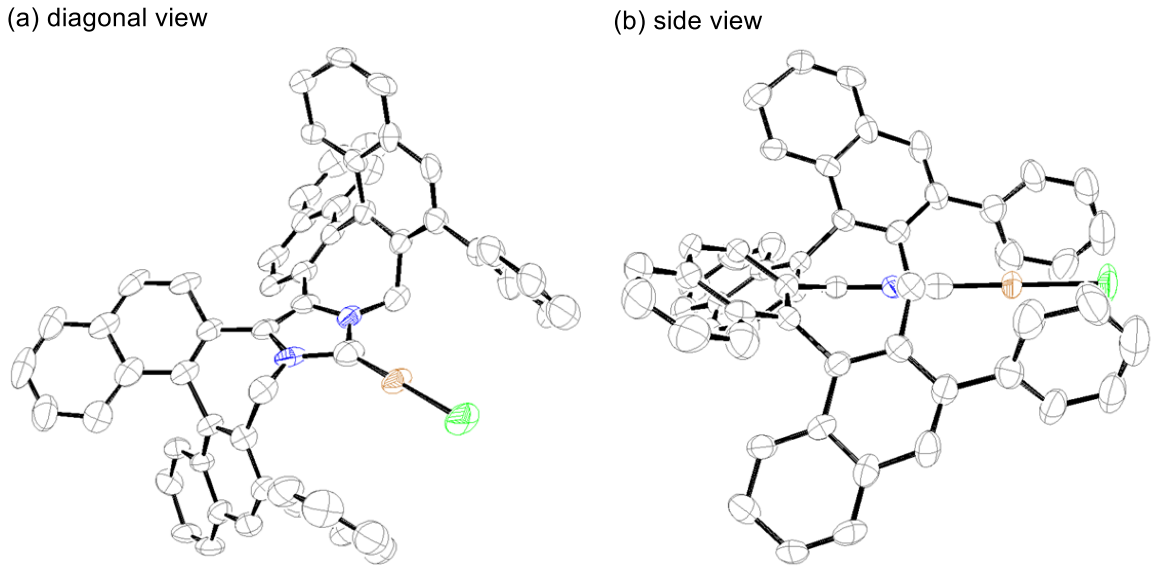
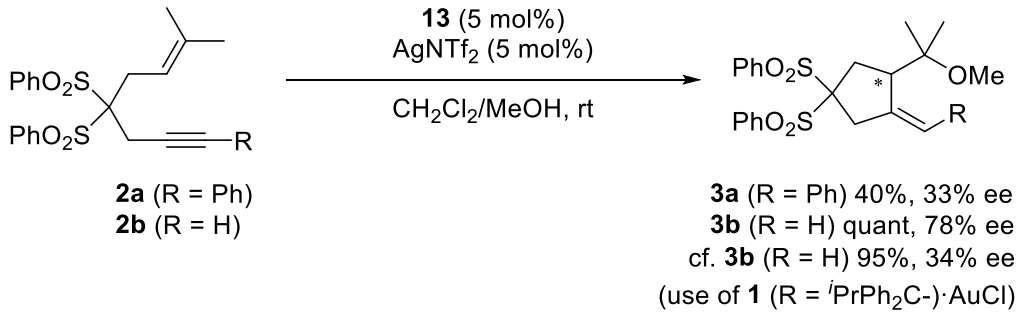


Figure 3. X-Ray crystal structure of NHC-complex **13** (hydrogen atoms and co-crystallized hexane are omitted for clarity).

The catalytic asymmetric ene-yne cyclization of **2a** in the presence of 5 mol% of cationic complex of **13** afforded **3a** with 33% *ee* in 40% yield (Scheme 4). When compared with the reaction of **2a** with cationic **1** (R = ^{i}PrPh$_2$C-)-Au(I) complex, the *ee* and yield decreased. However, the reaction of less-bulky substrate **2b** with a catalytic amount of cationic **13** quantitatively afforded **3b** with 78% *ee*, which surpassed those of the reaction of **2b** using cationic **1** (R = ^{i}PrPh$_2$C-)-Au(I) complex (95% yield and 34% *ee*). Therefore, further structural modification of **13**, selection of the substrate and optimization of the reaction conditions could improve the *ee* and yield of the product.



Scheme 4. Catalytic asymmetric ene-yne cyclizations of **2a** and **2b** catalyzed by cationic complex of **13**

In summary, a new chiral C_2-symmetric NHC ligand with two binaphthyl units has been synthesized. The new NHC ligand features two seven-membered rings that link the imidazolylidene with the binaphthyl units. X-Ray crystallographic analysis of the new NHC-AuCl complex indicates that the Au-Cl bond is located between the phenyl groups of the binaphthyl units and suggests that this arrangement could induce enantioselectivity in the catalytic reactions. Indeed, although the catalytic asymmetric ene-yne cyclization of **2a** in the presence of 5 mol% of cationic complex of **13** afforded **3a** with 33% *ee* in 40% yield, the reaction of less-bulky substrate **2b** quantitatively afforded **3b** with 78% *ee*. Further modifications of the ligand and asymmetric catalysis utilizing the cationic complex of **13** and its derivatives will be reported in due course.

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were recorded on a JEOL AL-400 spectrometer. Chemical shifts are reported in ppm with the residual solvent resonance as internal standard ($CDCl_3$ ^{1}H, δ = 7.26 ppm, ^{13}C, δ = 77.16 ppm; $(CD_3)_2SO$ ^{1}H, δ = 2.50 ppm, ^{13}C, δ = 39.52 ppm). The following abbreviations were used to explain the multiplicities: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; band, several overlapping signals; br, broad. IR spectra were recorded on a JASCO FT/IR-8300. Optical rotations were measured using a 2 mL cell with a 1 dm path length on a JASCO DIP-1000. Mass spectra and elemental analyses were provided at the Materials Characterization Central Laboratory, Waseda University. All reactions were carried out under an argon atmosphere with dry, freshly distilled solvents under anhydrous conditions, unless otherwise noted. Melting point (mp) is uncorrected and recorded on a Yamato capillary melting point apparatus. Chiral HPLC analysis was performed on a JASCO PU-980 and UV-970 detector. X-Ray crystallographic analysis was performed with a Rigaku R-AXIS RAPID-II. All reactions were monitored by thin-layer chromatography carried out on 0.25 mm E. Merck silica gel plates (60F-254) using UV light as visualizing agent and phosphomolybdic acid and heat as developing agents. Kanto Chemical Silica Gel 60N (spherical, neutral, 63-210 μm or 40-50 μm partial size) was used for flash chromatography. Preparative thin-layer chromatography (PTLC) separations were carried out on self-made 0.3 mm E. Merck silica gel plates (60F-254). In general, reactions were carried out in dry solvents under an argon atmosphere. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Dichloromethane (CH_2Cl_2) and *N*,*N*-dimethylformamide (DMF) was distilled from calcium hydride. Tetrahydrofuran (THF) was distilled from sodium/benzophenone ketyl. Toluene was distilled from sodium.

(*S*)-2-Bromomethyl-2'-dibromomethyl-3-phenyl-1,1'-binaphthyl (10). A stirred suspension of (*S*)-3-phenyl-2,2'-dimethyl-1,1'-binaphthyl **9** (3.40 g, 9.48 mmol), NBS (5.91 g, 33.2 mmol), and AIBN (156 mg, 0.95 mmol) in benzene (32 mL) was refluxed overnight. To the reaction mixture was added

Et_2O (20 mL) and water (20 mL), and the aqueous layer was extracted with Et_2O (15 mL × 2). Combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 20/1) to afford **10** (5.64 g, quant) as a white solid: R_f = 0.49 (hexane/EtOH = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.23 (d, *J* = 8.7 Hz, 1H), 8.13 (d, *J* = 8.7 Hz, 1H), 7.96–7.90 (m, 3H), 7.64–7.59 (m, 2H), 7.55–7.43 (m, 5H), 7.35–7.27 (m, 2H),7.16 (d, *J* = 8.7 Hz, 1H), 7.01 (d, *J* = 8.2 Hz, 1H), 6.29 (s, 1H), 4.33 (d, *J* = 10.3 Hz, 1H), 4.14 (d, *J* = 10.3 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 141.1, 140.3, 137.3, 134.3, 133.9, 133.2, 133.1, 131.8, 131.3, 131.0, 130.5, 130.3, 129.7, 128.4, 128.2, 128.1, 127.8, 127.7, 127.6, 127.1, 127.0, 126.3, 40.2, 30.4; IR (ATR): 3057.6, 1493.7, 1220.2, 902.2, 747.3, 701.4, 590.5 cm^{-1}; HRMS (DART) [M–Br$^-$] calcd for $C_{28}H_{19}Br_2$: 512.9848, found 512.9838; mp 208 °C; $[\alpha]_D^{24}$ –59 (*c* 0.40, $CHCl_3$).

(*S*)-2-Bromomethyl-2'-oxomethyl-3-phenyl-1,1'-binaphthyl (11). A solution of **9** (894 mg, 1.50 mmol) in formic acid (15 mL) was refluxed for 6.5 h. To the reaction mixture were added CH_2Cl_2 (10 mL) and water (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (15 mL × 2). Combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2/EtOAc = 100/1 to 75/1) to afford **11** (579 mg, 85%) as an yellow solid: R_f = 0.29 (hexane/EtOAc = 10/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.65 (s, 1H), 8.24 (d, *J* = 8.7 Hz, 1H), 8.11 (d, *J* = 8.7 Hz, 1H), 8.01 (d, *J* = 8.2 Hz, 1H), 7.95 (s, 1H), 7.93 (d, *J* = 8.2 Hz, 1H), 7.66–7.60 (m, 3H), 7.55–7.43 (m, 4H), 7.40–7.34 (m, 1H), 7.31–7.27 (m, 2H), 7.02 (d, *J* = 8.2 Hz, 1H), 4.30 (d, *J* = 9.8 Hz, 1H), 3.99 (d, *J* = 9.8 Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.2, 141.8, 140.7, 140.1, 136.5, 134.4, 133.2, 132.9, 132.8, 132.5, 130.8, 129.7, 129.5, 129.2, 128.7, 128.4, 128.2, 127.9, 127.5, 127.5, 127.4, 126.8, 126.5, 122.5, 30.7; IR (ATR): 3055.3, 2843.3, 1678.2, 1225.1, 788.8, 750.4, 698.0, 586.2 cm^{-1}; HRMS (ESI) [M+Na$^+$] calcd for $C_{28}H_{19}BrONa$: 473.0511, found 473.0513; mp 218 °C; $[\alpha]_D^{24}$ –125 (*c* 0.40, $CHCl_3$).

(*S*)-2-Bromomethyl-2'-(1,3-dioxolanyl)-3-phenyl-1,1'-binaphthyl (11a). A solution of **11** (1.20 g, 2.65 mmol), ethylene glycol (0.89 mL, 16.0 mmol), and TsOH·H_2O (50.4 mg, 0.27 mmol) in toluene (27 mL) was refluxed using Dean-Stark apparatus for 2.5 h. Then, ethylene glycol (0.30 mL, 5.32 mmol) was added to the reaction mixture and reflux was continued for 2 h. To the reaction mixture was added saturated aqueous $NaHCO_3$ (20 mL) and Et_2O (15 mL), and the aqueous layer was extracted with Et_2O (15 mL × 2). Combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 50/1 to 30/1) to afford **11a** (1.23 g, 94%) as a white solid: R_f = 0.41 (hexane/EtOAc = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 1H), 7.94 (d, *J* = 8.2 Hz, 1H), 7.91–7.86 (m, 3H), 7.64–7.60 (m, 2H), 7.52–7.42 (m, 5H), 7.31–7.22 (m, 2H), 7.14 (d, *J* = 7.8 Hz, 1H), 7.08 (d, *J* = 9.2 Hz, 1H), 5.38 (s, 1H), 4.32 (d, *J* = 10.1 Hz, 1H), 4.25 (d, *J* = 10.1 Hz, 1H), 4.15–4.07 (m, 2H), 3.87–3.74 (m,

2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.7, 140.7, 136.1, 135.0, 134.3, 134.2, 133.0, 132.8, 132.7, 132.5, 130.2, 129.7, 129.2, 128.3, 128.1, 127.8, 127.6, 127.4, 127.3, 127.1, 126.8, 126.8, 126.3, 123.7, 101.9, 65.6, 31.1; IR (ATR): 3058.9, 2889.1, 1213.4, 1062.6, 942.0, 813.4, 754.6, 723.5 cm^{-1}; HRMS (ESI) [M+Na$^+$] calcd for $C_{30}H_{23}BrO_2Na$: 517.0774, found 517.0776; mp 204 °C; $[\alpha]_D^{24}$ –58 (*c* 0.40, $CHCl_3$).

(*S*)-2-Azidomethyl-2'-(1,3-dioxolanyl)-3-phenyl-1,1'-binaphthyl (12). A suspension of **11a** (643 mg, 1.30 mmol) and NaN_3 (211 mg, 3.24 mmol) in DMF (13 mL) was heated at 60 °C overnight. To the reaction mixture was added Et_2O (10 mL) and water (10 mL), and the aqueous layer was extracted with Et_2O (5 mL × 2). Combined organic layers were washed with brine (5 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 40/1 to 30/1) to afford **11** (592 mg, 100%) as a white solid: R_f = 0.41 (hexane/EtOAc = 4/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, *J* = 8.7 Hz, 1H), 7.97–7.86 (m, 4H), 7.56–7.47 (m, 6H), 7.46–7.40 (m, 1H), 7.33–7.27 (m, 2H), 7.14 (d, *J* = 8.9 Hz, 1H), 7.11 (d, *J* = 8.7 Hz, 1H), 5.36 (s, 1H), 4.20–4.07 (m, 4H), 3.85–3.76 (m, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 140.9, 140.7, 136.4, 135.2, 134.3, 134.1, 132.8, 132.8, 132.6, 131.5, 129.9, 129.6, 129.2, 128.4, 128.2, 127.9, 127.6, 127.1, 127.0, 126.8, 126.8, 126.7, 123.7, 101.9, 65.7, 50.8; IR (ATR): 3057.2, 2890.1, 2074.7, 1240.6, 1098.8, 817.1, 748.1, 701.6 cm^{-1}; HRMS (ESI) [M+Na$^+$] calcd for $C_{30}H_{23}N_3O_2Na$: 480.1682, found 480.1684; mp 76 °C $[\alpha]_D^{24}$ –87 (*c* 0.33, $CHCl_3$).

(*S*)-2-(*N*-Allyloxycarbonylaminomethyl)-2'-(1,3-dioxolanyl)-3-phenyl-1,1'-binaphthyl (12a). A suspension of **11** (927 mg, 2.03 mmol) and PPh_3 (797 mg, 3.04 mmol) in THF (20 mL) and water (2 mL) was heated at 50 °C overnight. The reaction mixture was concentrated under reduced pressure and a phosphine oxide was removed by short silica gel column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 20/1) to afford a crude amine. To the crude amine dissolved in THF (20 mL) were added Et_3N (0.56 mL, 4.05 mmol) and AllocCl (0.29 mL, 2.43 mmol) at room temperature. After stirring at room temperature for 15 min, to the reaction mixture was added water (15 mL) and the aqueous layer was extracted with Et_2O (10 mL × 2). Combined organic layers were washed with brine (10 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1 to 5/1) to afford **12a** (956 mg, 91%) as a white solid: R_f = 0.36 (hexane/EtOAc = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.03 (d, *J* = 8.7 Hz, 1H), 7.96–7.84 (m, 4H), 7.53–7.26 (m, 9H), 7.12 (d, *J* = 8.2 Hz, 2H), 5.83–5.45 (m, 2H), 5.41 (s, 1H), 5.20–4.88 (m, 2H), 4.34–3.58 (m, 8H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 155.1, 141.6, 140.9, 135.7, 135.5, 134.1, 134.0, 133.9, 133.5, 132.7, 132.6, 132.2, 130.0, 129.5, 128.9, 128.3, 128.2, 127.9, 127.5, 127.0, 126.9, 126.9, 126.8, 126.4, 126.1, 123.5, 116.5, 101.8, 66.0, 65.2, 64.9, 41.0; IR (ATR): 3306.7, 3060.3, 2884.9, 1681.7, 1541.1, 1249.2, 1097.8, 703.7 cm^{-1}; HRMS (ESI) [M+Na$^+$] calcd for $C_{34}H_{29}NO_4Na$: 538.1989, found 538.1989; mp 108 °C; $[\alpha]_D^{24}$ –168 (*c* 0.33, $CHCl_3$).

(*S*)-2-(*N*-Allyloxycarbonylaminomethyl)-2'-oxomethyl-3-phenyl-1,1'-binaphthyl (8). A suspension of **12a** (1.78 g, 3.46 mmol) and $TsOH \cdot H_2O$ (328 mg, 1.73 mmol) in acetone/water (35mL/2.3mL) was stirred at room temperature for 4 h. To the reaction mixture was added saturated aqueous $NaHCO_3$ (20 mL) and Et_2O (20 mL), and the aqueous layer was extracted with Et_2O (15 mL × 2). Combined organic layers were washed with brine (15 mL), dried over Na_2SO_4, and concentrated under reduced pressure. The residue was purified by recrystallization (CH_2Cl_2/EtOAc) to afford **8** (1.43g, 88%) as a white solid: R_f = 0.49 (hexane/EtOAc = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 9.68 (s, 1H), 8.18 (d, *J* = 8.7 Hz, 1H), 8.08 (d, *J* = 8.7 Hz, 1H), 7.99 (d, *J* = 8.2 Hz, 1H), 7.94 (s, 1H), 7.93 (d, *J* = 10.5 Hz, 1H), 7.62 (dd, *J* = 7.3, 7.3 Hz, 1H), 7.54–7.27 (m, 9H), 7.04 (d, *J* = 8.2 Hz, 1H), 5.66 (br, 1H), 5.13–5.07 (m, 2H), 4.23–3.92 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 192.0, 154.7, 142.7, 140.7, 140.6, 136.4, 133.1, 133.0, 132.9, 132.5, 132.4, 130.5, 129.3, 129.1, 128.7, 128.7, 128.1, 127.8, 127.2, 127.0, 126.9, 126.6, 122.6, 117.5, 65.4, 41.2; IR (ATR): 3304.3, 3060.7, 1682.4, 1540.8, 1254.3, 749.9, 700.8, 652.6 cm^{-1}; HRMS (ESI) [M+Na$^+$] calcd for $C_{32}H_{25}NO_3Na$: 494.1727, found 494.1727; mp 180 °C; $[\alpha]_D^{24}$ –40 (*c* 0.33, $CHCl_3$).

(*S*,*S*)-1,2-Bis(2'-*N*-allyloxycarbonylaminomethyl-3'-phenyl-1,1'-binaphthyl-2-yl)ethan-1,2-dione (7). To a stirred suspension of Cp_2TiCl_2 (323 mg, 1.30 mmol), activated zinc dust (255 mg, 3.89 mmol) and $ZnCl_2$ (1 M solution in Et_2O, 0.66 mL, 0.66 mmol) in THF (4 mL) was added a solution of **8** (583 mg, 1.24 mmol) in THF (8 mL) at –78 °C. After stirring the reaction mixture at 0 °C for 30 min, to the mixture was added CH_2Cl_2 (20 mL) and saturated aqueous $NaHCO_3$ (10 mL), and the aqueous layer was extracted with CH_2Cl_2 (20 mL × 2). Combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 8/1 to 6/1 to 2/1) to afford a mixture of 1,2-diol diastereomers. To a solution of TFAA (1.02 mL, 7.42 mmol) and DMSO (0.70 mL, 9.89 mmol) in CH_2Cl_2 (4 mL) was added a solution of the mixture of 1,2-diol diastereomers in CH_2Cl_2 (8 mL) at –60 °C. After stirring the reaction mixture at –60 °C for 1.5 h, to the mixture was added Et_3N (1.38 mL, 9.89 mmol) at –60 °C and 1 M-HCl (10 mL) after warming the mixture to room temperature. The aqueous layer was extracted with CH_2Cl_2 (5 mL × 2) and combined organic layers were dried over Na_2SO_4 and concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 10/1 to 4/1) to afford **6** with inseparable impurities as an yellow solid. Pure **7** was obtained by preparative TLC to collect the spectroscopic data: R_f = 0.28 (hexane/EtOAc = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): 7.92–7.81 (m, 6H), 7.76–7.62 (m, 2H), 7.57–7.08 (m, 20H), 7.03–6.92 (m, 2H), 6.78 (d, *J* = 8.7 Hz, 2H), 5.69 (br, 2H), 5.50–4.77 (m, 6H), 4.26–3.68 (m, 8H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 155.0, 141.1, 140.9, 139.2, 135.4, 135.3, 133.4, 133.3, 132.9, 132.9, 131.9, 131.1, 130.2, 129.4, 129.0, 128.5, 128.3, 128.2, 128.1, 127.6, 127.5, 127.4, 126.6, 126.4, 126.0, 125.7, 117.1, 65.2, 41.7; IR (ATR): 3342.6, 3055.3, 1712.2, 1494.0, 1218.3, 1027.8,

746.2, 701.4 cm^{-1}; HRMS (ESI) [M+Na^+] calcd for $C_{64}H_{48}N_2O_6Na$: 963.3405, found 963.3402; mp 108 °C; $[\alpha]_D^{24}$ –15 (*c* 0.25, $CHCl_3$).

(*S*,*S*)- 6,6'-Diphenyl-5*H*,5'*H*-3,3'-bidinaphtho[2,1-*c*:1',2'-*e*]azepine (6). To a stirred solution of crude **7** (568 mg, 0.60 mmol) and $Pd(PPh_3)_4$ (34.9 mg, 0.030 mmol) in CH_2Cl_2 (12 mL) was added Me_2NSiMe_3 (0.29 mL, 1.81 mmol) and $AcOSiMe_3$ (0.27 mL, 1.81 mmol) at room temperature. After stirring the reaction mixture for 6 h, the solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (hexane/EtOAc = 30/1 to 15/1 to 8/1) to afford **6** (374.3 mg, 84% for 3 steps from aldehyde **8**) as a white solid: R_f = 0.57 (hexane/EtOAc = 2/1); ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.00 (s, 2H), 7.99 (d, *J* = 8.7 Hz, 2H), 7.76 (br, 4H), 7.68 (d, *J* = 7.8 Hz, 2H), 7.53 (d, *J* = 6.9 Hz, 4H), 7.49 (d, *J* = 8.2 Hz, 4H), 7.44 (d, *J* = 7.3 Hz, 2H), 7.40 (d, *J* = 6.9 Hz, 2H), 7.28–7.10 (m, 8H), 6.51 (d, *J* = 8.2 Hz, 2H), 5.33 (d, *J* = 10.1 Hz, 2H), 3.79 (d, *J* = 10.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$): δ 168.0, 140.9, 140.8, 139.0, 137.4, 133.4, 132.9, 132.5, 131.9, 131.8, 131.4, 130.2, 129.9, 128.9, 128.5, 128.4, 128.1, 127.9, 127.6, 127.4, 127.0, 126.3, 125.9, 125.8, 123.9, 52.9; IR (ATR): 3054.1, 2855.7, 1586.0, 1492.5, 1206.7, 1044.8, 807.8, 749.8, 703.4 cm^{-1}; HRMS (ESI) [M+H^+] calcd for $C_{56}H_{37}N_2$: 737.2951, found 737.2947; mp 233 °C; $[\alpha]_D^{24}$ +695 (*c* 0.33, $CHCl_3$).

(*S*,*S*)-Imidazolium salt 5. To a stirred solution of **6** (810 mg, 1.10 mmol) in THF (22 mL) was added MOMCl (0.83 mL, 11.0 mmol) at room temperature. After stirring the reaction mixture at 50 °C overnight, the solution was concentrated under reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2 to CH_2Cl_2/MeOH = 20/1) to afford **5** (755 mg, 87%) as a white solid: R_f = 0.34 (CH_2Cl_2/MeOH = 10/1); ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.98 (s, 1H), 8.18–8.07 (m, 8H), 7.69–7.53 (m, 14H), 7.44–7.35 (m, 6H), 7.18 (d, *J* = 6.0 Hz, 2H), 7.16 (d, *J* = 6.0 Hz, 2H), 5.55 (d, *J* = 14.7 Hz, 2H), 5.07 (d, *J* = 14.7 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 139.3, 138.8, 135.1, 134.0, 133.6, 133.6, 133.2, 132.8, 132.3, 130.9, 130.2, 129.9, 129.7, 129.7, 128.6, 128.5, 128.4, 127.9, 127.3, 127.3, 127.1, 126.9, 126.4, 124.2, 47.9; IR (ATR): 3307.0, 3052.0, 1589.6, 1493.1, 1446.4, 1179.5, 819.6, 749.7, 703.9 cm^{-1}; HRMS (ESI) [M–Cl^-] calcd for $C_{57}H_{37}N_2$: 749.2951, found 749.2946; mp 307 °C (decomposition); $[\alpha]_D^{24}$ +394 (*c* 0.33, $CHCl_3$).

(*S*,*S*)-NHC-Au(I) complex 13. To a mixture of **5** (158 mg, 0.20 mmol) and Ag_2O (46.5 mg, 0.20 mmol) was added CH_2Cl_2 (4 mL). After stirring the reaction mixture in the absence of light at room temperature overnight, the resulting mixture was filtered through a pad of Celite and concentrated under reduced pressure. To a solution of the crude NHC-silver (I) complex in CH_2Cl_2 (4 mL) was added $AuCl{\cdot}SMe_2$ (59.3 mg 0.20 mmol). After stirring the reaction mixture at room temperature for 4.5 h, the mixture was filtered through a pad of Celite and concentrated at reduced pressure. The residue was purified by silica gel column chromatography (CH_2Cl_2) to afford the corresponding NHC-Au (I) complex **13** (149 mg, 76% (2 steps)) as a yellowish to white solid: R_f = 0.59 (benzene/EtOAc = 20/1); ^{1}H NMR (400 MHz,

$CDCl_3$): δ 7.93–7.87 (m, 6H), 8.07 (d, *J* = 8.2 Hz, 2H), 7.63–7.19 (m, 24H), 5.98 (d, *J* = 14.0 Hz, 2H), 4.59 (d, *J* = 14.0 Hz, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): δ 166.4, 139.9, 138.9, 135.2, 134.6, 133.9, 133.1, 133.0, 132.3, 130.2, 129.8, 129.3, 128.7, 128.5, 128.4, 127.4, 127.2, 126.9, 126.8, 126.6, 126.5, 48.8; IR (ATR): 3054.0, 1493.6, 1398.7, 899.0, 819.3, 745.7, 694.1 cm^{-1}; HRMS (ESI) [M–Cl^-] calcd for $C_{57}H_{36}N_2Au$: 945.2539, found 945.2522, [M–Cl^-+NH_3] calcd for $C_{57}H_{39}N_3Au$: 962.2804, found 962.2803; mp 319 °C (decomposition); $[\alpha]_D^{24}$ +207 (*c* 0.33, $CHCl_3$).

(*Z*)-3-Benzylidene-4-(2-methoxypropan-2-yl)-1,1-bis(phenylsulfonyl)cyclopentane (3a). A suspension of $AgNTf_2$ (0.679 mg, 1.75×10^{-3} mmol) and NHC-AuCl complex **13** (1.7 mg, 1.75×10^{-3} mmol) in CH_2Cl_2 (0.20 mL) was stirred for 30 min at room temperature in the absence of light. To the stirred suspension was added MeOH (0.28 mL) and a solution of **2a**[16] (16.8 mg, 0.035 mmol) in CH_2Cl_2 (0.22 mL). After stirring at room temperature for 88 h in the absence of light, the reaction mixture was diluted with CH_2Cl_2, filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **3a** (7.1 mg, 40%): Spectroscopic data were in agreement with those previously reported[16]). *Ee* was determined by chiral HPLC analysis (Daicel ID-3 column, hexane/2-propanol = 9/1, 1 mL/ min, 254 nm, t_R = 21.1 min (minor) and 26.8 min (major), 33% *ee*): R_f = 0.28 (hexane/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.15–8.08 (m, 4H), 7.75–7.66 (m, 2H), 7.64–7.58 (m, 2H), 7.58–7.52 (m, 2H), 7.34–7.31 (m, 4H), 7.25–7.19 (m, 1H), 6.41 (s, 1H), 3.77 (dd, J = 6.0, 8.7 Hz, 1H), 3.68 (d, J = 15.6 Hz, 1H), 2.94 (s, 3H), 2.87 (dd, J = 6.0, 15.6 Hz, 1H), 2.79 (dd, J = 8.7, 15.6 Hz, 1H), 2.55 (d, J = 15.6 Hz, 1H), 0.89 (s, 3H), 0.80 (s, 3H); $[\alpha]_D^{24}$ +60 (*c* 0.42, $CHCl_3$, 33% *ee*).

4-(2-Methoxypropan-2-yl)-3-methylidene-1,1-bis(phenylsulfonyl)cyclopentane (3b). A suspension of $AgNTf_2$ (0.679 mg, 1.75×10^{-3} mmol) and NHC-AuCl complex **13** (1.7 mg, 1.75×10^{-3} mmol) in CH_2Cl_2 (0.22 mL) was stirred for 30 min at room temperature in the absence of light. To the stirred suspension was added MeOH (0.28 mL) and a solution of **2b**[16] (14.1 mg, 0.035 mmol) in CH_2Cl_2 (0.20 mL). After stirring at room temperature for 20 min in the absence of light, the reaction mixture was diluted with CH_2Cl_2, filtered through a pad of Celite and concentrated under reduced pressure. The residue was purified by silica gel column chromatography to afford **3b** (15.2 mg, quant): Spectroscopic data were in agreement with those previously reported[16]). *Ee* was determined by chiral HPLC analysis (Daicel ID-3 column, hexane/2-propanol = 2/1, 1 mL/ min, 254 nm, t_R = 15.8 min (major) and 18.2 min (minor), 78% *ee*): R_f = 0.22 (hexane/EtOAc = 3/1); ^1H NMR (400 MHz, $CDCl_3$): δ 8.07 (d, 7.8 Hz, 2H), 8.05 (d, 7.8 Hz, 2H), 7.71 (t, 7.8 Hz, 1H), 7.71 (t, 7.8 Hz, 1H), 7.60 (dd, *J* = 7.8, 7.8 Hz, 2H), 7.58 (dd, *J* = 7.8, 7.8 Hz, 2H), 5.03–4.97 (m, 2H), 3.46 (ddd, 16.9, 6.0, 3.2 Hz, 1H), 3.13 (s, 3H), 3.05–2.98 (m, 1H), 2.77 (d, 16.9 Hz, 1H), 2.73 (dd, *J* = 15.6, 8.2 Hz, 1H), 2.64 (dd, *J* = 15.6, 9.2 Hz, 1H), 1.19 (s, 3H), 1.10 (s, 3H); $[\alpha]_D^{18}$ –20 (*c* 0.24, $CHCl_3$, 78% *ee*).[17]

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17. The absolute value of the specific rotation of **3b** ($[\alpha]_D^{18}$ –20 (*c* 0.24, $CHCl_3$, 78% *ee*)) was inconsistent with those reported by other research groups ($[\alpha]_D^{25}$ +21.2 (*c* 0.4, $CHCl_3$, 53% *ee*)[7a]; $[\alpha]_D^{25}$ –20.5 (*c* 0.97, $CHCl_3$, 52% *ee*)[10e]) when compared their *ee* values with that of **3b**, but the *ee* of **3b** was confirmed by independent HPLC analyses using different chiral columns, Daicel ID-3 and AD-H (see Supporting Information).