

Supporting Information

Enantioselective Oxidative Biaryl Coupling Reactions Catalyzed by 1,5-Diazadecalin Metal Complexes: Efficient Formation of Chiral Functionalized BINOL Derivatives

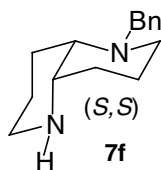
Xiaolin Li, J. Brian Hewgley, Carol A. Mulrooney, Jaemoon Yang, and Marisa C. Kozlowski*

Department of Chemistry, Roy and Diana Vagelos Laboratories, University of Pennsylvania, Philadelphia, Pennsylvania 19104, USA

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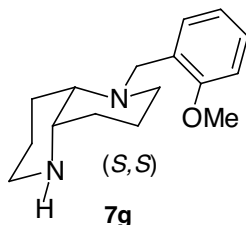
General Considerations. Unless otherwise noted, all non-aqueous reactions were carried out under an atmosphere of dry N₂ in dried glassware. When necessary, solvents and reagents were dried prior to use. Toluene, Et₂O, CH₂Cl₂, and THF were de-oxygenated by purging with N₂ and then dried by passing through activated alumina. CH₃CN, MeOH, TMEDA, Et₃N, iPr₂NH, and hexanes were distilled from CaH₂. Benzene was distilled from sodium. Solvents for the preparation of the catalyst complexes and for the oxidative coupling reactions were usually used without purification although acid-free halogenated solvents are required (if necessary, trace acid can be removed by filtering through basic Al₂O₃). Diamines **7a-7d** were prepared as described previously.¹ Naphthols **8b** and **8c** as well as phenanthrol **8d** were purchased from Acros and used without further purification while **8a**² and **8e**³ were prepared following known procedures. 4-Methoxybenzenesulfonyl fluoride was prepared from 4-methoxybenzenesulfonyl chloride and aqueous potassium fluoride.⁴ The Cu(TMEDA)Cl(OH) catalyst was prepared⁵ and used in the oxidative biaryl coupling reactions as described in the General Procedure (see below) to prepare racemic samples of the biaryl products.

Analytical thin layer chromatography (TLC) was performed on EM Reagents 0.25 mm silica gel 60-F plates. Preparative thin layer chromatography was performed on EM Reagents 1.00 mm silica-gel plates. Visualization was accomplished with UV light. Chromatography on silica gel was performed using a forced flow of the indicated solvent system on EM Reagents Silica Gel 60 (230-400 mesh).⁶ HPLC analyses were performed using a Waters Delta 600 system ($\lambda = 254$ nm) connected to Chiralpak AD or AS column (4.6 x 150 mm) from Daicel. Mass spectra were obtained on a low resonance Micromass Platform LC in electrospray mode. Optical rotations were measured on a Perkin Elmer 341 Polarimeter using a sodium lamp and are reported as follows: $[\alpha]_D^{25}$ (c g/100 mL, solvent).

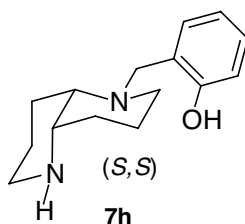


***N*-Benzyl-*cis*-decahydro-1,5-naphthyridine (7f).** Diamine **7a** (100 mg, 0.714 mmol) and KOH (40 mg, 0.714 mmol) were dissolved in MeOH (35 mL) and heated to reflux. Benzyl bromide (85 μ L, 0.714 mmol) was added. After heating 4 h, the mixture was acidified with AcOH (1.0 mL) and cooled to room temperature. The solvent was removed *in vacuo* and the crude product was suspended in H₂O (2 mL), made basic (pH > 14) with NaOH, and rapidly extracted with CHCl₃. After drying over K₂CO₃, the extracts were filtered and concentrated to afford a crude oil. Chromatography (10% MeOH/CH₂Cl₂, 0.5% NH₄OH) afforded *N*-benzyl ligand **7f** as a solid (91 mg, 55%): IR (thin film) 3419, 3026, 2937, 2796 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) (mixture of conformers) δ 7.20-7.34 (m, 5 H),

3.18-1.18 (m, 17 H); ^{13}C NMR (125 MHz, CDCl_3) δ (mixture of conformers) 20.5, 21.9, 24.1, 25.8, 26.1, 27.5, 29.1, 30.3, 31.9, 46.1, 46.5, 53.0, 53.3, 54.6, 56.9, 59.0, 60.0, 65.8, 68.2, 126.35, 126.41, 127.8, 127.9, 128.5, 128.7, 139.4; HRMS (ES) calcd for $\text{C}_{15}\text{H}_{23}\text{N}_2$ (MH^+) 231.1861, found 231.1857. In addition, *N,N*-dibenzylidiamine **7d** was obtained as a yellow oil (36 mg, 16%).

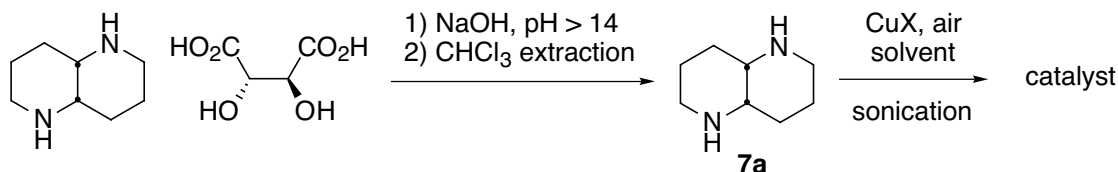


***N*-(2-Methoxybenzyl)-*cis*-decahydro-1,5-naphthyridine (7g).** Diamine **7a** (198 mg, 1.41 mmol) and KOH (118 mg, 2.1 mmol) were dissolved in MeOH (40 mL) and heated to reflux. A solution of 2-methoxybenzyl bromide (428 mg, 2.1 mmol) in MeOH (30 mL) was added. After heating for 24 h, the mixture was cooled to room temperature. The solvent was removed *in vacuo* and the crude product was suspended in H_2O (2 mL), made basic ($\text{pH} > 14$) with NaOH, and rapidly extracted with CHCl_3 . After drying over K_2CO_3 , the extracts were filtered and concentrated to afford a crude oil. Chromatography (10% MeOH/ CH_2Cl_2 , 0.5% NH_4OH) of the crude product yielded *N*-(2-methoxybenzyl)diamine (**7g**) as a white solid (105 mg, 29%): IR (thin film) 2942, 2834, 1241 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) (mixture of conformers) δ 8.0 (br, 1H), 7.64 (s, 1H), 7.19-7.22 (t, $J = 7.5$ Hz, 1H), 6.97-7.0 (t, $J = 7.2$ Hz, 1H), 6.82-6.84 (d, $J = 8.0$ Hz, 1H), 3.81 (s, 3H), 1.53-3.90 (m, 16H); ^{13}C NMR (125 MHz, CDCl_3) (mixture of conformers) δ 17.5 (m), 21.0 (m), 21.7, 23.4, 25.3, 27.4, 28.6, 29.3, 44.0 (m), 49.6, 50.0, 52.4, 55.0, 55.1, 57.3, 59.0, 62.2, 67.8, 109.8, 120.0, 120.5, 125.9, 127.0, 127.6, 129.6, 130.0, 157.1; HRMS (ES) calcd for $\text{C}_{16}\text{H}_{24}\text{N}_2\text{O}$ (MH^+) 261.1967, found 261.1967. In addition, *N,N*-di(2-methoxybenzyl)diamine product was obtained as an oil (152 mg, 28%).



***N*-(2-Hydroxybenzyl)-*cis*-decahydro-1,5-naphthyridine (7h).** Diamine **7g** (65 mg, 0.25 mmol) was dissolved in CH_2Cl_2 (10 mL) and BBr_3 (30 μL , 0.32 mmol) was added. After 24 h, aqueous NaHCO_3 was added and the product was extracted with CH_2Cl_2 . After drying over Na_2SO_4 , the extracts were filtered and concentrated to afford a crude oil. Chromatography (5% MeOH/ CH_2Cl_2 , 0.5% NH_4OH) provided **7h** as a solid (18 mg, 29%): ^1H NMR (500 MHz, CDCl_3) (mixture of conformers) δ 7.12-7.16 (q, $J = 7.6$ Hz, 1H), 6.93-6.96 (t, $J = 7.9$ Hz, 1H), 6.80-6.82 (d, $J = 8.1$ Hz, 1H), 6.75-6.77 (q, $J = 8.1$ Hz, 1H), 1.26-4.41 (m, 17H); ^{13}C NMR (125 MHz, CDCl_3) (mixture of conformers) δ 22.3, 24.0, 25.6, 28.2,

29.6, 31.4, 53.5, 54.0, 56.0, 56.7, 59.0, 59.9, 66.0, 116.1, 119.0, 121.7, 122.4, 128.0, 128.5, 157.6, 157.9; HRMS (ES) calcd for C₁₅H₂₂N₂O (MH⁺) 247.1810, found 247.1801.



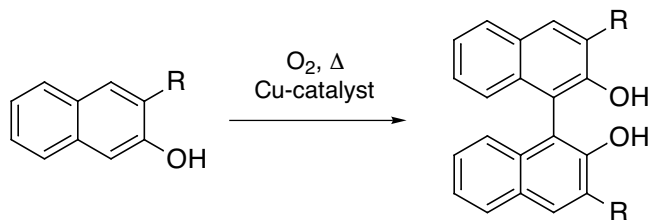
[(*S,S*)-1,5-Diaza-*cis*-decalin]Cu(OH)X(H₂O). The tartrate salt of (*S,S*)-**7a** was dissolved in a minimum volume of water and NaOH was added until pH > 14. This solution was then extracted with CHCl₃ (3-4 equal volumes) and the combined CHCl₃ extracts were dried over K₂CO₃, filtered, and concentrated to afford a crude oil. Application of vacuum for a short time (< 1 min) afforded the chiral diamine as a waxy white solid which was weighed and used directly in the next step.

Method A: The diamine was dissolved in the reaction solvent (0.1 M) to yield a clear solution. 0.9-1.0 equivalents of the copper source (CuCl, CuOTf, CuI) were added and the mixture was sonicated open to the atmosphere for 10-15 min until no solids were visible. The clear solution was used directly in the reaction.

Method B: The diamine was dissolved in CH₂Cl₂ (for CuCl) or CH₃CN (for CuI) to yield a clear solution (~0.1 M). A clear solution of CuCl or CuI (0.9-1.0 equiv) in CH₃CN (~0.1 M) was then added and the mixture was stirred for 15-20 min. The solution was filtered through a short plug of Celite in order to remove any insoluble components. The solvent was removed to yield the CuCl complex as a blue powder and the CuI complex as a black/gray powder in quantitative yield. Depending on the scale and ambient conditions, the catalyst may form as the hydrate. The presence of such small amounts of water were not found to substantially alter the activity. Molecular sieves could be employed in the reactions to remove larger amounts of water without any detrimental effect.

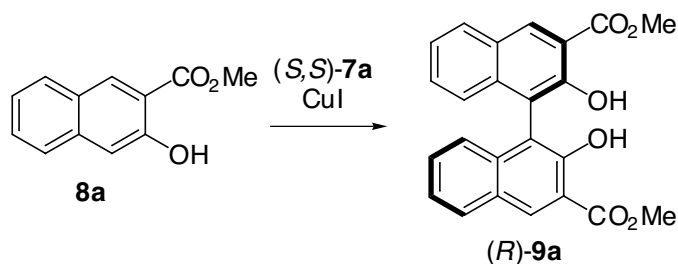
Slightly better reactivity was observed for the CuCl complex prepared using Method B, both methods for preparing the CuI complex yielded similar results.

General Procedure for Preparation of Chiral 1,5-Diaza-*cis*-decalin Metal Complexes. Method A described above for the copper(I) derived catalysts was employed using the indicated metal salt.



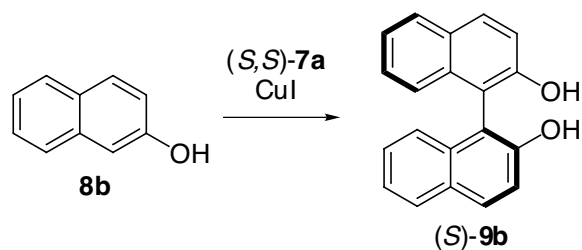
General Procedure for the Oxidative Biaryl Coupling. To a solution of the 2-naphthol substrate dissolved in the appropriate solvent (see Tables in the main text for solvents and concentrations) was added the catalyst (0.1-0.2 equiv) to yield a clear green, blue, purple, or red solution. (Sonication was occasionally necessary to dissolve all the compounds.) The solution was actively purged with air or O₂ (1 atm) for a short time (~1 min) and then placed under an air or O₂ atmosphere at the indicated temperature. After the indicated time (see Tables in the main text), the reaction mixture was diluted with CH₂Cl₂ and was washed with 1 N HCl. The aqueous phase was back extracted with CH₂Cl₂ and the combined organic solutions were dried over Na₂SO₄. Filtration and concentration afford the crude product. Purification was accomplished by chromatography.

For the 3-sulfonyl and 3-nitro substrates, the combined organic solutions after extraction were washed with brine and dried over Na₂SO₄. Filtration through a plug of SiO₂, rinsing with 10% MeOH/CH₂Cl₂, and concentration provided the crude product. Purification was then accomplished by chromatography.

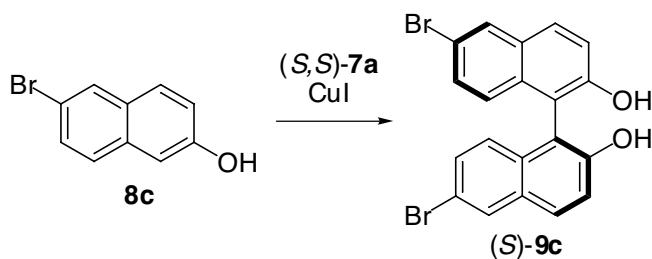


Dimethyl 2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (9a). Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-**7a**] and 0.5 mmol substrate in ClCH₂CH₂Cl (5 mL) at 40 °C for 48 h with O₂ to give the product as a solid in 85% (85 mg, 0.21 mmol) isolated yield and 92% ee. Purification by chromatography (10% EtOAc/hexanes to remove starting naphthol followed by CH₂Cl₂ to elute the product) yielded the pure biaryl product identical to that previously reported.⁵ Enantioselectivity was assayed by dissolving a small portion in MeOH completely (heating or sonicating as necessary) and analyzing by CSP (chiral stationary phase) HPLC: (Chiralpak AD, 1.0 mL/min, 90:10 hexanes:*i*PrOH) t_R(SM) = 5.3 min, t_R(*S*) = 10.7 min, t_R(*R*) = 16.6 min.

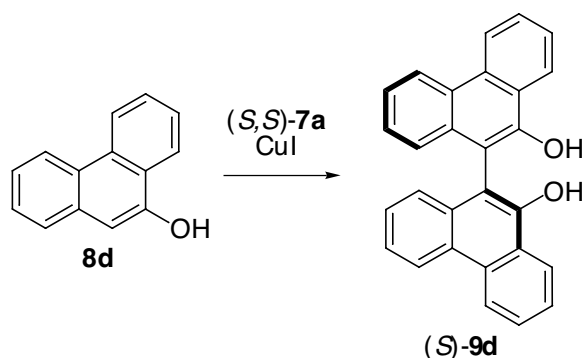
The reaction course could be monitored directly by removing small aliquots (50-200 μL) and filtering through a short SiO₂ plug (5 x 20 mm) with CH₂Cl₂. The CH₂Cl₂ was removed *in vacuo* and the residue was completely dissolved in MeOH (heating or sonicating as necessary) to yield a clear solution. After filtering through a 0.22 μm filter, the sample was then subjected to CSP HPLC as described above. Conversion could also be monitored by HPLC (the integration values of **8a** were multiplied by 1.2 to account for different UV absorption values of **8a** and **9a**).



1,1'-Binaphthalen-2,2'-diol (9b). Biaryl coupling was carried out according to the General Procedure using either air or O₂ as indicated in the equations and tables of the main text. The material obtained was identical to that commercially available (Aldrich). CSP HPLC: (Chiralpak AS; 1.0 mL/min, 90:10 hexanes:*i*PrOH) $t_{R(S)} = 10.4$ min, $t_{R(R)} = 14.7$ min.

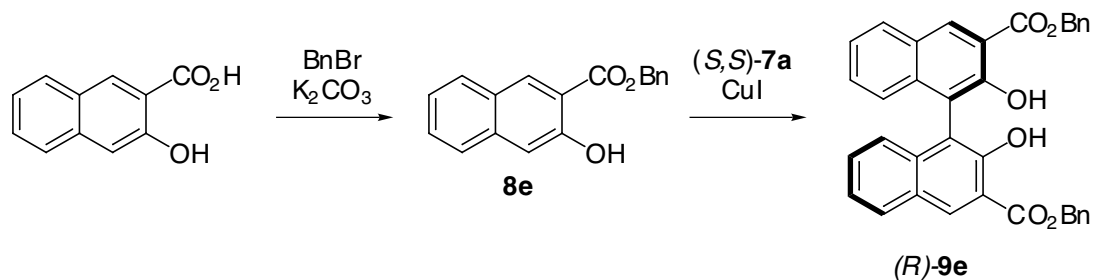


6,6'-Dibromo-1,1'-binaphthalen-2,2'-diol (9c). Biaryl coupling was carried out according to the General Procedure using O₂. The material obtained was identical to that described previously.⁷ CSP HPLC (Chiralpak AS; 1.0 mL/min, 95:5 hexanes:*i*PrOH) $t_{R(S)} = 20.7$ min, $t_{R(R)} = 33.2$ min.



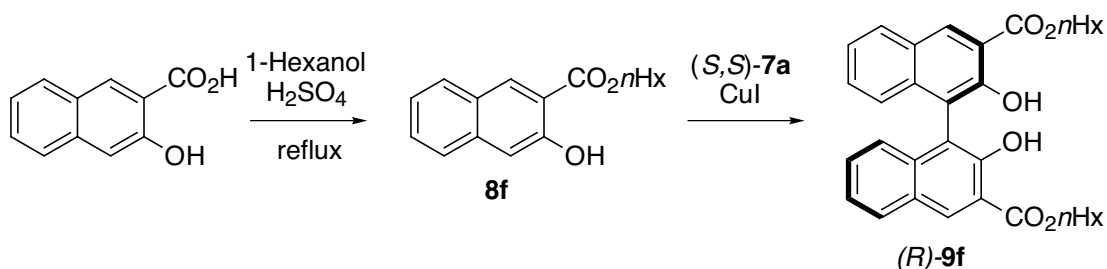
(S)-9,9'-Dihydroxy-2,2'-biphenanthryl (9d). The reaction of 9-phenanthrol (193 mg, 1 mmol) was carried out according to General Procedure with CuCl-[(S,S)-7a] catalyst in ClCH₂CH₂Cl at room temperature either under air (6 h) or O₂ (3 h) to give biphenanthryl **9d**⁸ (63% yield, 10% ee, air; 53% yield, 11% ee, O₂): $[\alpha]_D^{23} = -4.5$ (c 1.0, 11% ee, CHCl₃), lit.⁹ $[\alpha]_D^{23} = +58$ (c 1.0, CHCl₃) for pure (*R*)-isomer; ¹H NMR (200 MHz, CDCl₃) δ 8.82 (d, *J* = 8.2 Hz, 4 H), 8.76 (d, *J* = 8.6 Hz, 2 H), 7.87-7.29 (m, 10 H), 5.57 (s, 2 H); CSP HPLC (Chiralpak AS; 1.0 mL/min, 95:5 hexanes:*i*PrOH) $t_{R(S)} = 13.1$ min, $t_{R(R)} = 17.8$ min. Phenanthrenequinone was obtained as a byproduct in 32% yield (air) and in 44% yield

(oxygen): ^1H NMR (200 MHz, CDCl_3) δ 8.18 (d, $J = 7.8$ Hz, 2H), 8.02 (d, $J = 8.2$ Hz, 2H), 7.72 (t, $J = 7.7$ Hz, 2H), 7.47 (t, $J = 7.4$ Hz, 2H).



Dibenzyl 2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (9e). A solution of 3-hydroxy-naphthalene-2-carboxylic acid (9.4 g, 50 mmol) in DMF (30 mL) was treated with K_2CO_3 (3.45 g, 25 mmol) and stirred for 1 h at room temperature. Benzyl bromide (10.26 g, 60 mmol) was added and the mixture stirred at room temperature for 12 h. The product was extracted with EtOAc (3 x 50 mL), washed with brine (3 x 50 mL), dried (Na_2SO_4), and concentrated *in vacuo*. Chromatography (50-60% CH_2Cl_2 /hexane) gave the benzyl ester (11.2 g, 81%) as a pale yellow solid identical to that previously reported:¹⁰ ^1H NMR (500 MHz, CDCl_3) δ 10.40 (s, 1H), 8.50 (s, 1H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.65 (d, $J = 8.3$ Hz, 1H), 7.48-7.30 (m, 8H), 5.44 (s, 2H).

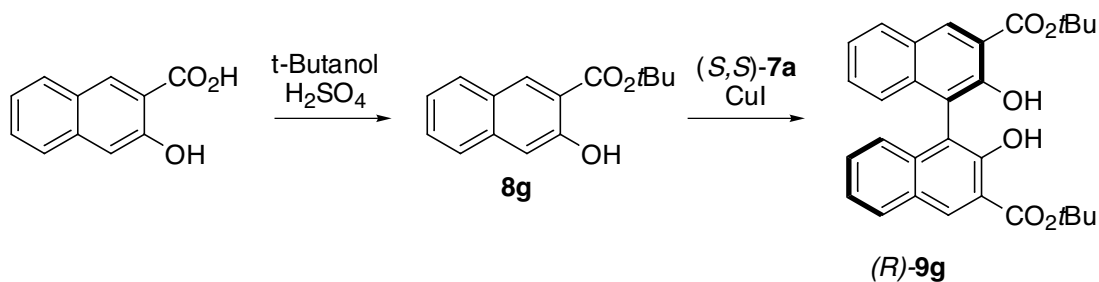
Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-7a] and 1.0 mmol substrate in $\text{ClCH}_2\text{CH}_2\text{Cl}$ (10 mL) at 40 °C using O_2 for 24 h to give the product as a solid in 79% (218 mg, 0.39 mmol) isolated yield and 90% ee. The material obtained was identical to that previously reported:⁵ $[\alpha]_{\text{D}}^{25} = +96.4$ (c 1.0, 93% ee, THF); ^1H NMR (200 MHz, CDCl_3) δ 10.71 (s, 2H), 8.71 (s, 2H), 7.93-7.89 (m, 2H), 7.55-7.31 (m, 14H), 7.16-7.12 (m, 2H), 5.48 (s, 4H); CSP HPLC (Chiralpak AD; 1.0 mL/min, 90:10 hexanes:*i*PrOH) $t_{\text{R}}(\text{S}) = 13.1$ min, $t_{\text{R}}(\text{R}) = 18.1$ min.



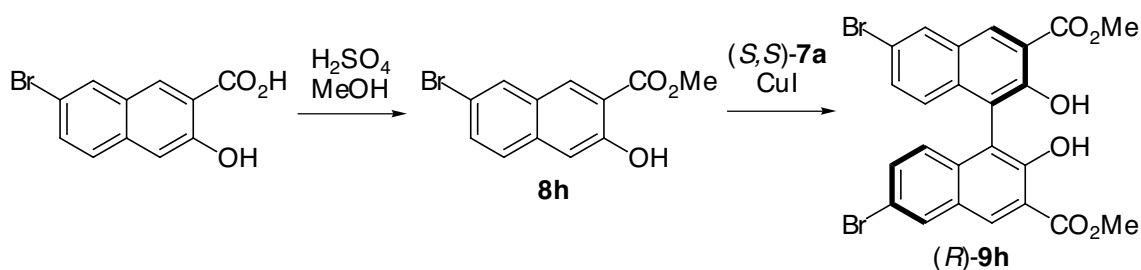
Bis(*n*-hexyl) 2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (9f). *n*-Hexyl-2-hydroxy-naphthalene-3-carboxylate (8f) was prepared following a similar procedure as for the methyl ester:² IR (thin film) 3227, 3192, 2957, 2934, 2860, 1683, 1212 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 0.92 (t, $J = 6.8$ Hz, 3H), 1.38 (m, 4H), 1.48 (m, 2H), 1.84 (quintet, $J = 7.1$ Hz, 2H), 4.41 (t, $J = 6.7$ Hz, 2H), 7.31 (m, 2H), 7.49 (t, $J = 7.5$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 1H), 7.8 (d, $J = 8.2$ Hz, 1H), 8.47 (s, 1H), 10.5 (s, 1 OH); ^{13}C

NMR (125 MHz, CDCl₃) δ 14.0, 22.5, 25.6, 28.5, 31.4, 65.9, 111.6, 114.5, 123.8, 126.3, 127, 129, 129.2, 132.2, 137.8, 156.4, 169.9; HRMS (ES) calcd for C₁₇H₂₀O₃ (M⁺) 272.1412, found 272.1411.

Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-7a] and 0.3 mmol substrate in ClCH₂CH₂Cl (3 mL) at 40 °C using O₂ for 48 h to give the product as a solid in 70% (0.056 g, 0.11 mmol) isolated yield and 87% ee: [α]_D²³ = +89 (c 1.08, 87% ee, CHCl₃); IR (thin film) 3412, 3022, 1675, 1220, 787, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 0.93 (t, *J* = 6.7 Hz, 6H), 1.38 (m, 8H), 1.5 (m, 4H), 1.86 (quintet, *J* = 7.1 Hz, 4H), 4.44 (m, 4H), 7.16 (t, *J* = 4.7 Hz, 2H), 7.32 (m, 4H), 7.91 (t, *J* = 4.6 Hz, 2H), 8.67 (s, 2H), 10.8 (s, 2 OH); ¹³C NMR (125 MHz, CDCl₃) δ 14.0, 22.5, 25.6, 28.5, 31.4, 66, 114.4, 117, 123.8, 124.6, 127.1, 129.3, 129.7, 132.6, 137.1, 154.1, 170.2; HRMS (ES) calcd for C₃₄H₃₈O₆Na (MNa⁺) 565.2566, found 565.2584; CSP HPLC (Chiralpak AD; 1.0 mL/min, 98:2 hexanes:*i*PrOH) t_R (*S*) = 7.5 min, t_R (*R*) = 12.5 min.



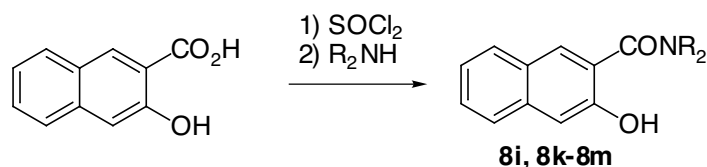
Bis(*tert*-butyl) 2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-dicarboxylate (9g). Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-7a] and 0.5 mmol substrate¹¹ in ClCH₂CH₂Cl (5 mL) at 40 °C using O₂ for 48 h to give the product as a solid in 70% (0.085 g, 0.18 mmol) isolated yield and 80% ee. The material obtained was identical to that previously reported;⁵ [α]_D²³ = +110 (c 1.0, 80% ee, THF); CSP HPLC (Chiralpak AD; 1.0 mL/min, 95.5:0.5 hexanes:*i*PrOH) t_R(*S*) = 13.9 min, t_R(*R*) = 17.3 min.



Dimethyl 6,6'-dibromo-2,2'-dihydroxy-1,1'-binaphthalenyl-3,3'-dicarboxylate (9h). 7-Bromo-3-hydroxy-2-naphthoic acid¹² was treated with 10% conc H₂SO₄ in MeOH overnight. Recrystallization of the crude product from MeOH/CH₂Cl₂ provided methyl 7-bromo-3-hydroxy-2-naphthoate **8h** in 50% yield: IR (thin film) 3208, 1683, 1282 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 4.01 (s, 3H), 7.25 (s, 1H), 7.52 (s, 2H), 7.90 (s, 1H), 8.33 (s, 1H), 10.4 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 52.7, 111.9, 115.0,

117.3, 127.90, 127.94, 130.9, 131.3, 132.3, 136.2, 156.7, 169.9; HRMS (ES) calcd for C₁₂H₁₀O₂Br (M⁺) 279.9735, found 279.9747; Anal. calcd for C₁₂H₉O₃Br: C, 51.25; H, 3.23. Found: C, 51.28; H, 3.01.

Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-**7a**] and 0.5 mmol substrate in ClCH₂CH₂Cl (5 mL) at 40 °C using O₂ for 48 h to give the product as a solid in 27% (38 mg, 0.068 mmol) isolated yield and 92% ee: [α]_D²³ = +112 (c 1.0, 92% ee, THF); IR (thin film) 3018, 3016, 2979, 1685, 1282 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 4.05 (s, 6H), 6.99 (d, *J* = 9.0 Hz, 2H), 7.37-7.39 (dd, *J* = 9.0, 1.3 Hz, 2H), 8.06 (s, 2H), 8.57 (s, 2H), 10.7 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 52.9, 115.1, 116.9, 117.7, 126.4, 128.2, 131.5, 131.9, 132.7, 135.5, 154.4, 170.2; HRMS (ES) calcd for C₂₄H₁₆O₄Br₂Na (MNa⁺) 580.9211, found 580.9238; CSP HPLC (Chiralpak AD; 1.0 mL/min, 70:30 hexanes:*i*PrOH) t_R(*S*) = 24.5 min, t_R(*R*) = 42.4 min.



General procedure for the preparation of amides **8i and **8k-8m**.**¹³ 3-Hydroxynaphthalene-2-carboxylic acid was treated with SOCl₂ for 4 h under reflux. Removal of excess SOCl₂ *in vacuo* afforded the crude acid chloride as a dark brown oil. A solution of the crude acid chloride in CH₂Cl₂ was then added dropwise to a solution of the amine (5 equiv) and DMAP (0.1 equiv) at 0 °C. The reaction mixture was stirred overnight at room temperature and poured into 1 N HCl. Extraction with CH₂Cl₂, drying with Na₂SO₄, filtration, and concentration gave the crude product. Recrystallization from acetone-hexanes provided pure amides **8i** and **8k-8m** as off-white solids:

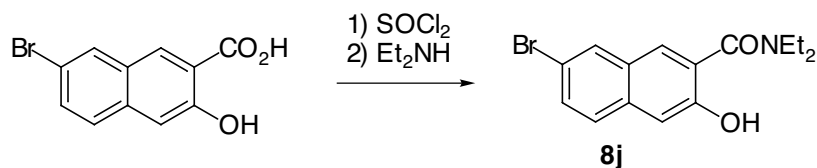
3-Hydroxy-2-naphthoic acid-*N,N*-diethylamide (8i**).** IR (thin film) 3059, 2979, 2938, 1646, 1615, 1582, 1480, 1466 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.02 (s, 1H), 7.75 (d, *J* = 6.3 Hz, 2H), 7.63 (d, *J* = 7.9 Hz, 1H), 7.42 (t, *J* = 6.9 Hz, 1H), 7.29 (t, *J* = 7.2 Hz, 1H), 7.25 (s, 1H), 3.52 (4H), 1.25 (6H); HRMS (ES) calcd for C₁₅H₁₇NO₂ (M⁺) 243.1259, found 243.1256.

3-Hydroxy-2-naphthoic acid-*N*-pyrrolidinylamide (8k**).** IR (thin film) 3062, 2980, 1649, 1580, 1470, 1449 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.95 (s, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.46 (t, *J* = 7.5 Hz, 1H), 7.31 (t, *J* = 5.9 Hz, 2H), 7.25 (s, 1H), 3.52 (br 4H), 1.25 (br 6H); HRMS (ES) calcd for C₁₅H₁₅NO₂ (M⁺) 241.1103, found 241.1104.

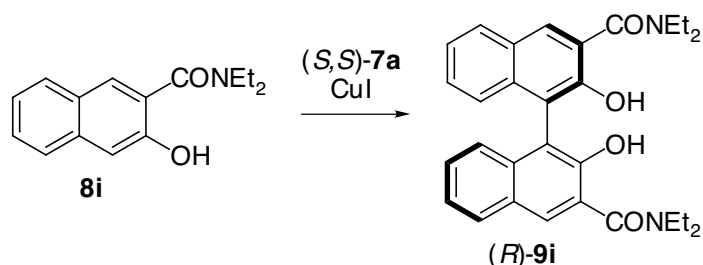
3-Hydroxy-2-naphthoic acid-*N*-piperidinylamide (8l**).** IR (thin film) 3052, 2945, 2861, 1646, 1615, 1583, 1475, 1445 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.09 (s, 1H), 7.76 (s, 2H), 7.65 (d, *J* = 7.6 Hz, 1H), 7.42 (m, 1H), 7.30 (t, *J* = 6.3 Hz, 1H), 7.25 (s, 1H), 3.65 (br 4H), 1.71 (br 2H), 1.66 (br 4H); HRMS (ES) calcd for C₁₆H₁₈NO₂ (MH⁺) 256.1338, found 256.1330.

3-Hydroxy-2-naphthoic acid-*N*-morpholinylamide (8m**).** IR (thin film) 3686, 3059, 2862, 1646, 1616, 1586, 1472, 1267, 1257 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 8.88 (s, 1H), 7.74 (d, *J* = 5.4 Hz, 2H), 7.69 (d,

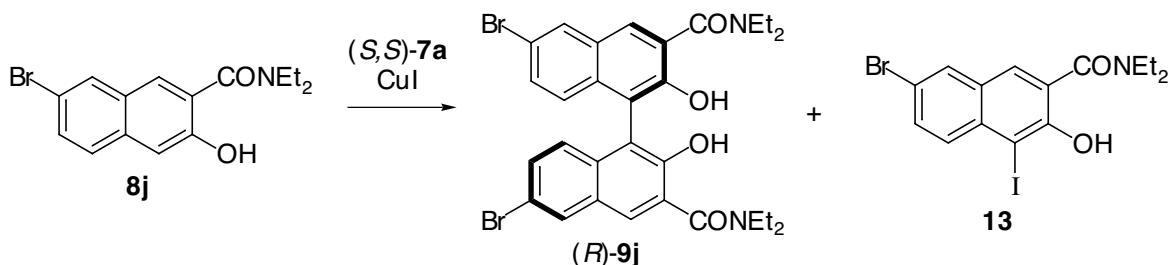
$J = 8.3$ Hz, 1H), 7.48 (t, $J = 7.5$ Hz, 1H), 7.34 (t, $J = 7.0$ Hz, 1H), 7.26 (s, 1H), 3.83 (t, $J = 4.5$ Hz, 2H), 3.76 (t, $J = 4.4$ Hz, 2H); HRMS (ES) calcd for $C_{15}H_{15}NO_3$ (M^+) 257.1052, found 257.1058.



7-Bromo-3-hydroxy-2-naphthoic acid-*N,N*-diethylamide (8j). 7-Bromo-3-hydroxy-2-naphthoic acid was treated with $SOCl_2$ at reflux to give the corresponding acid chloride, which was then subjected to Et_2NH in the presence of a catalytic amount of DMAP to afford **8j** in 44% yield after recrystallization: IR (thin film) 3138, 2980, 1590 cm^{-1} ; 1H NMR (500 MHz, $CDCl_3$) δ 7.87 (s, 1H), 7.64 (s, 1H), 7.48 (s, 2H), 7.23 (s, 1H), 3.55 (q, $J = 7.1$ Hz, 4H), 1.29 (t, $J = 7.1$ Hz, 6H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 170.4, 154.1, 133.9, 130.9, 130.1, 128.04, 128.02, 126.3, 122.9, 117.3, 112.2, 42.2, 13.5; HRMS (ES) calcd for $C_{15}H_{16}BrNO_2Na$ (MNa^+) 344.0262, found 344.0264.



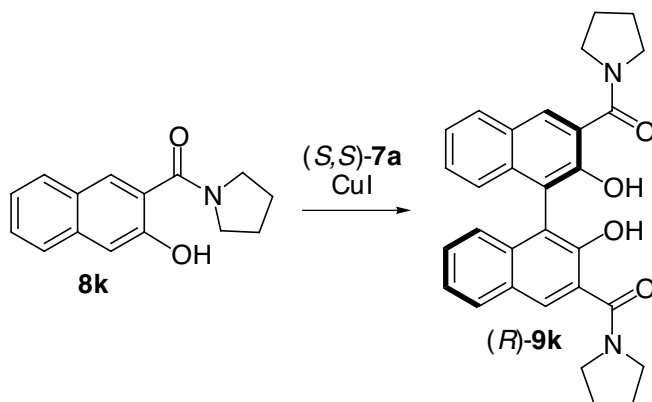
***N,N,N',N'*-Tetraethyl-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide (9i).** Biaryl coupling was carried out according to the General Procedure with 10 mol% $CuI-[(S,S)-7a]$ and 0.5 mmol substrate in $ClCH_2CH_2Cl$ (5 mL) at 40 °C for 48 h using O_2 to give the product¹⁴ as a solid in 48% yield (0.058 g, 0.12 mmol) and 72% ee: 1H NMR (500 MHz, $CDCl_3$) δ 1.28 (t, $J = 6.2$ Hz, 12H), 3.55 (m, 8H), 7.15 (d, $J = 8.3$ Hz, 2H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.33 (t, $J = 7.2$ Hz, 2H), 7.84 (d, $J = 8.0$ Hz, 2H), 7.93 (s, 2H), 8.17 (br, 2 H); ^{13}C NMR (125 MHz, $CDCl_3$) 13.3 (m), 41.9 (m), 115.8, 122.8, 122.8, 124.0, 124.7, 127.5, 127.9, 128.2, 128.7, 134.5, 151.0, 170.1; CSP HPLC (Chiralpak AD; 1.0 mL/min, 95:5 hexanes:*i*PrOH) $t_R(R) = 16.8$ min, $t_R(S) = 33.8$ min.



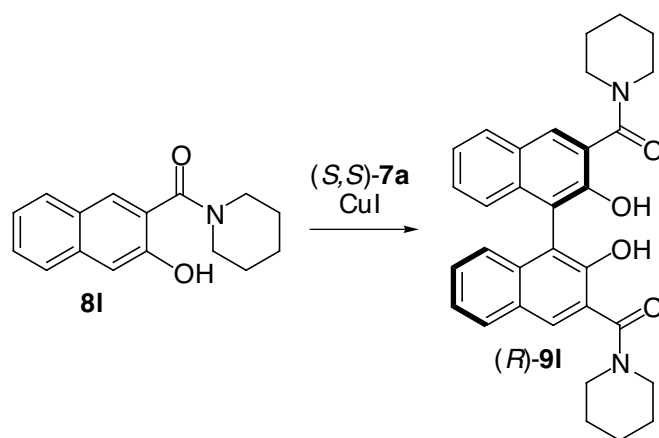
6,6'-Dibromo-2,2'-dihydroxy-1,1'-binaphthalenyl-3,3'-dicarboxylic acid bis-diethylamide (9j).

Biaryl coupling was carried out according to the General Procedure using CuI-[(*S,S*)-7a] as the catalyst at 40 °C for 48 h to give the product in 47% yield: $[\alpha]_{\text{D}}^{23} = +42.7$ (*c* 0.73, 53% ee, THF); IR (thin film) 3223 (br), 2976, 2937, 1630, 1590 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.63 (m, 2H), 8.0 (d, *J* = 1.3 Hz, 2H), 7.83 (s, 2H), 7.35 (dd, *J* = 8.8, 1.7 Hz, 2H), 6.98 (d, *J* = 9.0 Hz, 2H), 3.58 (m, 8H), 1.31 (t, *J* = 7.0 Hz, 12H); ^{13}C NMR (125 MHz, CDCl_3) δ 170.0, 151.8, 133.0, 131.3, 130.6, 128.5, 127.3, 126.5, 123.2, 117.8, 116.2, 42.0, 13.4; HRMS (ES) calcd for $\text{C}_{30}\text{H}_{30}\text{Br}_2\text{N}_2\text{O}_4\text{Na}$ (MNa^+) 663.0470, found 663.0486; CSP HPLC (Chiralpak AD; 1.0 mL/min, 92:8 hexanes:*i*PrOH) $t_{\text{R}}(\text{R}) = 7.1$ min, $t_{\text{R}}(\text{S}) = 30.4$ min.

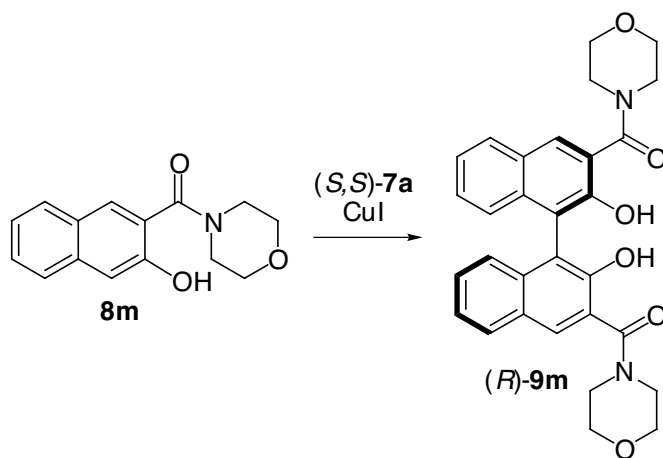
When the reaction was carried out with 20 mol% CuI-[(*S,S*)-7a] catalyst at 40 °C using O_2 for 24 h, the product was obtained in 28% yield along with 18% yield of 7-bromo-3-hydroxy-4-iodo-2-naphthoic acid-*N,N*-diethylamide (13): IR (thin film) 2974, 2934, 1633, 1592, 1477, 1462, 1281 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 9.60 (br s, 1H), 7.85 (s, 1H), 7.83 (d, *J* = 9.0 Hz, 1H), 7.62 (s, 1H), 7.56 (d, *J* = 8.0 Hz, 1H), 3.52 (d, *J* = 6.5 Hz, 4H), 1.28 (t, *J* = 7.0 Hz, 6H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.4, 153.4, 134.7, 132.5, 132.3, 130.5, 128.7, 127.2, 122.5, 118.4, 87.4, 29.2, 13.3; HRMS (ES) calcd for $\text{C}_{15}\text{H}_{16}\text{BrINO}_2$ (MH^+) 447.9409, found 447.9417.



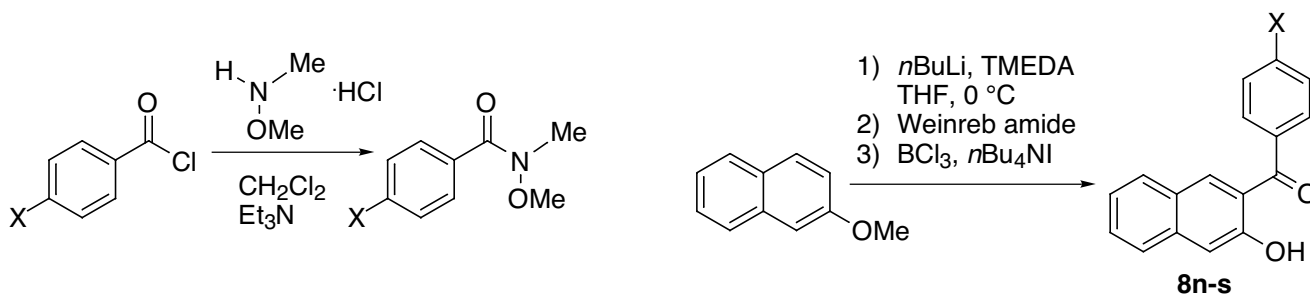
***N, N'*-Dipyrrolidinyl-2, 2'-Dihydroxy-1, 1'-binaphthalenyl-3, 3'-dicarboxamide (9k).** Biaryl coupling was carried out according to the General Procedure using CuI-[(*S,S*)-7a] as the catalyst at 40 °C using O_2 for 48 h to give the product in 47% yield and 73 % ee (assigned by optical rotation): $[\alpha]_{\text{D}}^{23} = +74.6$ (*c* 0.80, 73% ee, THF); IR (thin film) 3142 (br), 2941, 1602 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 8.09 (s, 2H), 7.80-7.81 (m, 2H), 7.26-7.30 (m, 4H), 7.15-7.17 (m, 2H), 3.77 (br, 8H), 1.96 (br, 8H), 1.50 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 169.7, 153.0, 135.2, 129.5, 128.8, 128.2, 126.8, 124.7, 123.6, 120.3, 117.0, 50.8, 47.2, 26.7, 24.0; HRMS (ES) calcd for $\text{C}_{30}\text{H}_{28}\text{N}_2\text{O}_4\text{Na}$ (MNa^+) 503.1947, found 503.2061.



***N,N'*-Dipiperidinyl-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-dicarboxamide (9l).** Biaryl coupling was carried out according to the General Procedure using CuI-[(*S,S*)-7a] as the catalyst at 40 °C using O₂ for 48 h to give the product in 47% yield and 70% ee (assigned by optical rotation): $[\alpha]_{\text{D}}^{23} = +58.0$ (*c* 0.50, 70% ee, CH₂Cl₂); IR (thin film) 3212 (br), 2972, 1633, 1567, 1455 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.93 (s, 2H), 7.84-7.85 (m, 2H), 7.26-7.34 (m, 4H), 7.14-7.16 (m, 2H), 3.74 (m, 8H), 0.70 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 170.0, 151.9, 135.1, 129.6, 129.2, 128.0, 125.2, 124.5, 122.1, 116.5, 47.0, 26.5, 25.0; HRMS (ES) calcd for C₃₂H₃₂N₂O₄Na (MNa⁺) 531.2260, found 531.2263.



***N,N'*-Dimorpholinyl-2, 2'-dihydroxy-1, 1'-binaphthyl-3, 3'-dicarboxamide (9m).** Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-7a] and 0.5 mmol substrate in ClCH₂CH₂Cl (5 mL) at 40 °C using O₂ for 48 h to give the product in 61% yield and 75 % ee (assigned by optical rotation): $[\alpha]_{\text{D}}^{23} = +73.6$ (*c* 0.40, 75% ee, THF); IR (thin film) 3258 (br), 2922, 1621, 1598 cm⁻¹; ¹H NMR (500 MHz, acetone *d*-₆) δ 8.53 (s, 2H), 7.96 (s, 2H), 7.94 (d, *J* = 7.2 Hz, 2H), 7.35 (t, *J* = 7.3 Hz, 2H), 7.28 (t, *J* = 7.5 Hz, 2H), 7.06 (d, *J* = 8.3 Hz, 2H), 3.66 (m, 16H); ¹³C NMR (125 MHz, acetone *d*-₆) δ 168.5, 151.8, 135.6, 129.9, 129.5, 129.3, 128.3, 126.7, 125.1, 124.6, 115.2, 67.4, 29.6; HRMS (ES) calcd for C₃₀H₂₉N₂O₆ (MH⁺) 513.2026, found 513.2016.



General procedure for the preparation of phenyl ketone substrates 8n-8s. To a 0.1 M solution of the requisite benzoyl chloride (1.0 equiv) in CH_2Cl_2 was added *N,O*-dimethylhydroxylamine hydrochloride (1.1 equiv). The stirred solution was cooled to 0 °C and Et_3N (2.2 equiv) was added dropwise over 5 min. The resulting solution was allowed to warm to room temperature and was stirred for 24 h. After washing twice with 1 N HCl, the organic layer was dried over Na_2SO_4 . When necessary the crude product was chromatographed using $\text{MeOH}/\text{CH}_2\text{Cl}_2$ to afford the pure *N*-methoxy-*N*-methyl-benzamide.^{15,16,17}

To a 0.5 M solution of 2-methoxynaphthalene (1.0 equiv) in THF and TMEDA (2.0 equiv) at 0 °C, was added *n*-BuLi (1.2 equiv, 2.5 M in hexanes). The resulting solution was stirred for 3 h at room temperature then cooled to 0 °C. The corresponding *para*-substituted *N*-methoxy-*N*-methylbenzamide (0.9 equiv) was then transferred via cannula to this mixture and the resulting solution was stirred overnight at room temperature. 1 N HCl (1 mL) was then added and the solution was stirred further for 1 h. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 . The combined organic layers were washed with brine, dried over Na_2SO_4 , and concentrated. If necessary the product was chromatographed with $\text{EtOAc}/\text{hexanes}$ to afford the pure methoxy protected derivative. Otherwise the product (1.0 equiv) was added directly to a 0.2 M stirred solution of *n*-Bu₄NI (1.0 equiv) in CH_2Cl_2 at -78 °C. The resultant mixture was treated with BCl_3 (2.5 equiv, 1 M in hexanes), stirred for 10 min, and then warmed to room temperature for 1 h. The reaction mixture was then diluted with water and stirred for 10 min. A solution of saturated aqueous NaHCO_3 was added dropwise until evolution of CO_2 ceased. The organic layer was separated and the aqueous layer was extracted twice with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 and concentrated. The residue was crystallized from EtOH to afford the substituted phenyl naphthylketone.¹⁸

(3-Hydroxy-naphthalen-2-yl)-(4-nitro-phenyl)-methanone (8n). Afforded an orange solid. $R_f = 0.48$ (20% $\text{EtOAc}/\text{hexanes}$); mp >280 °C; IR (thin film) 3389, 1633, 1519 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 11.25 (s, 1H), 8.47 (d, $J = 8.5$ Hz, 2H), 8.25 (s, 1H), 8.02 (d, $J = 8.6$ Hz, 2H), 7.86 (d, $J = 8.1$ Hz, 1H), 7.46-7.43 (m, 1H), 7.40-7.37 (m, 1H), 7.26-7.24 (m, 2H); ^{13}C NMR (500 MHz, CDCl_3) δ 200.3, 155.1, 150.1, 143.5, 137.9, 137.5, 131.1, 130.5, 130.5, 127.2, 124.9, 124.9, 124.1, 120.5, 118.0.

4-(3-hydroxy-naphthalen-2-carbonyl)-benzotrile (8o). Afforded an orange solid: $R_f = 0.65$ (30% $\text{EtOAc}/\text{hexanes}$); mp 165-170 °C; IR (thin film) 3095, 2231, 1642 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ

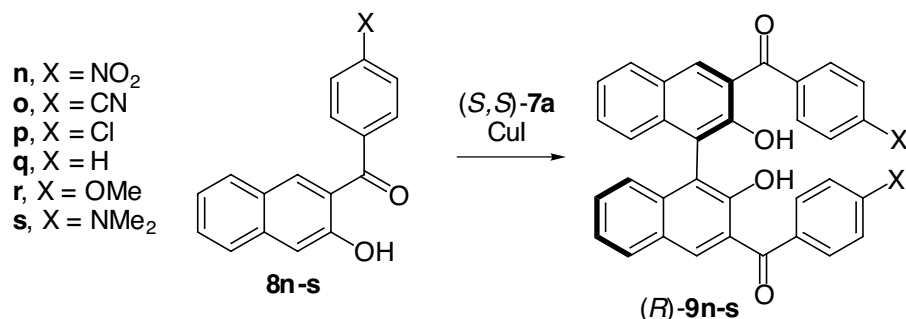
10.86 (s, 1H), 8.03 (s, 1H), 7.88-7.84 (m, 4H), 7.73-7.71 (m, 2H), 7.58-7.55 (m, 1H), 7.41 (s, 1H), 7.36-7.33 (m, 1H); ^{13}C NMR (500 MHz, CDCl_3) δ 200.2, 157.4, 141.9, 138.6, 136.7, 132.6, 130.6, 130.0, 129.8, 127.0, 126.6, 124.7, 120.7, 118.0, 116.0, 113.1; HRMS (CI) calcd for $\text{C}_{18}\text{H}_{11}\text{NO}_2$ (M^+) 273.0790, found 273.0796.

(4-Chloro-phenyl)-(3-hydroxy-naphthalen-2-yl)-methanone (8p). Afforded a yellow solid: $R_f = 0.61$ (20% EtOAc/hexanes); mp 135-139 °C; IR (thin film) 3360, 1639 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 10.95 (s, 1H), 8.12 (s, 1H), 7.34-7.71 (m, 4H), 7.56-7.53 (m, 3H), 7.39 (s, 1H), 7.35-7.32 (m, 1H); ^{13}C NMR (500 MHz, CDCl_3) δ 200.5, 157.4, 139.1, 138.2, 136.5, 131.2, 130.2, 129.7, 129.1, 127.0, 126.6, 124.5, 121.1, 112.8; HRMS (CI) calcd for $\text{C}_{17}\text{H}_{11}\text{ClO}_2$ (M^+) 282.0448, found 282.0445.

(3-Hydroxy-naphthalen-2-yl)-phenyl-methanone (8q). Afforded a yellow solid: $R_f = 0.38$ (10% EtOAc/hexanes); mp 156-158 °C; IR (thin film) 3416, 1639 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 11.13 (s, 1H), 8.17 (s, 1H), 7.78 (d, $J = 7.3$ Hz, 2H), 7.74-7.52 (m, 6H), 7.39 (s, 1H), 7.33-7.30 (m, 1H); ^{13}C NMR (500 MHz, CDCl_3) δ 202.0, 157.6, 138.3, 138.2, 136.9, 132.6, 130.1, 129.8, 129.8, 128.8, 127.0, 126.6, 124.3, 121.3, 112.7; HRMS (CI) calcd for $\text{C}_{17}\text{H}_{12}\text{O}_2$ (M^+) 248.0837, found 248.0837.

(3-Hydroxy-naphthalen-2-yl)-(4-methoxy-phenyl)-methanone (8r). Afforded a yellow solid: $R_f = 0.41$ (20% EtOAc/hexanes); mp 132-133 °C; IR (thin film) 3055, 2927, 1603 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 11.03 (s, 1H), 8.18 (s, 1H), 7.82 (d, $J = 8.7$ Hz, 2H), 7.75 (d, $J = 8.3$ Hz, 1H), 7.72 (d, $J = 8.4$ Hz, 1H), 7.53 (dd, $J = 7.5, 7.4$ Hz, 1H), 7.38 (s, 1H), 7.32 (dd, $J = 7.5, 7.5$ Hz, 1H), 7.04 (d, $J = 8.7$ Hz, 2H), 3.94 (s, 3H); ^{13}C NMR (500 MHz, CDCl_3) δ 200.2, 163.5, 157.4, 137.9, 136.2, 132.5, 130.7, 129.7, 129.6, 126.9, 126.5, 124.2, 121.7, 114.1, 112.5, 55.8; HRMS (CI) calcd for $\text{C}_{18}\text{H}_{14}\text{O}_3$ (M^+) 278.0943, found 278.0938.

(4-Dimethylamino-phenyl)-(3-hydroxy-naphthalen-2-yl)-methanone (8s). Afforded a yellow solid in 30% yield: $R_f = 0.50$ (30% EtOAc/hexanes); mp 156-158 °C; IR (thin film) 2904, 1639 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 11.06 (s, 1H), 8.21 (s, 1H), 7.82 (d, $J = 9.9$ Hz, 2H), 7.76 (d, $J = 8.2$ Hz, 1H), 7.71 (d, $J = 8.4$ Hz, 6H), 7.51 (m, 1H), 7.36 (s, 1H), 7.31 (m, 1H), 6.76 (d, $J = 8.9$ Hz, 2H), 3.12 (s, 6H); ^{13}C NMR (500 MHz, CDCl_3) δ 199.0, 157.5, 153.7, 137.6, 135.5, 133.1, 129.6, 129.3, 127.1, 126.6, 125.5, 124.1, 122.5, 112.3, 111.2, 40.5; HRMS (CI) calcd for $\text{C}_{19}\text{H}_{17}\text{NO}_2$ (M^+) 291.1259, found 291.1266.



General Procedure for Oxidative Biaryl Coupling of phenyl ketone substrates 8n-s To a solution of the 2-naphthol substrate (**8n-s**) dissolved in CH_2Cl_2 :MeCN (3:2) was added 10 mol% of the CuI -[(*S,S*)-**7a**] catalyst to give a 0.1 M solution in substrate. The mixture was sonicated to yield a clear

greenish solution which was purged with a stream of O₂ for 1-2 min and then stirred under O₂ at 40 °C. After cooling, the reaction mixture was extracted with 10% aqueous NH₄OH (to decompose the copper complexes) until the extracts were no longer blue. The combined NH₄OH layers were back-extracted with copious amounts of CH₂Cl₂ and the combined organic solutions were dried over Na₂SO₄. Filtration and concentration afford the crude product. Purification was accomplished by chromatography.

[2,2'-Dihydroxy-3'-(4-nitro-benzoyl)-1,1'-binaphthalenyl-3-yl]-(4-nitro-phenyl)-methanone (9n) Afforded an orange solid in 80% ee: R_f = 0.29 (20% EtOAc/hexanes); mp >280 °C; IR (thin film) 3685, 3107, 1632, 1523, 1349 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.26 (s, 2H), 8.47 (d, *J* = 8.4 Hz, 4H), 8.25 (s, 2H), 8.02 (d, *J* = 8.3 Hz, 4H), 7.86 (d, *J* = 8.2 Hz, 2H), 7.46-7.43 (m, 2H), 7.40-7.37 (m, 2H), 7.25 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 200.3, 155.1, 150.1, 143.5, 137.9, 131.1, 130.5, 130.5, 127.2, 124.9, 124.9, 124.1, 120.5, 118.0. In one trial, **9n** was recrystallized from a 0.1 M (substrate) reaction mixture in CH₂Cl₂ upon slow evaporation. These crystals allowed confirmation of the structure by X-ray diffraction (see below for x-ray methods and tables).

Enantiomeric excess was determined by methylation of **9n**. A solution of **9n** (5.8 mg, 0.1 mmol) in DMF (1 mL) was treated with K₂CO₃ (6 mg, 0.04 mmol) and iodomethane (5 mL, 0.04 mmol). After 48 h at 40 °C the solution was diluted with water (5 mL) and extracted twice with diethyl ether. The organic layer was dried over Na₂SO₄ and concentrated. The residue was isolated by preparative TLC (20% EtOAc/hexanes) to afford methylated **9n** (2.8 mg) in 47% yield and 80% ee: [α]_D²³ = +30 (*c* 0.25, 80% ee, CH₂Cl₂); R_f = 0.27 (20% EtOAc/hexanes); ¹H NMR (500 MHz, CDCl₃) δ 8.26 (d, *J* = 8.5 Hz, 4H), 8.17 (s, 2H), 8.04 (d, *J* = 8.6 Hz, 4H), 7.99 (d, *J* = 8.1 Hz, 2H), 7.54-7.51 (m, 2H), 7.46-7.43 (m, 2H), 7.27 (d, *J* = 8.5 Hz, 2H), 3.26 (s, 6H); ¹³C NMR (500 MHz, CDCl₃) δ 194.7, 153.7, 150.5, 142.5, 135.7, 132.2, 131.9, 130.8, 130.1, 129.5, 129.0, 126.4, 125.7, 124.9, 123.8, 62.3; CSP HPLC (Chiralpak AD; 1.0 mL/min, 70:30 hexanes:*i*PrOH) t_R(S) = 34.4 min, t_R(R) = 245.2 min.

[3'-(4-Cyano-benzoyl)-2,2'-dihydroxy-1,1'-binaphthalenyl-3-yl]-(4-cyano-phenyl)-methanone (9o). Afforded an orange solid in 83% ee: [α]_D²³ = +41 (*c* 0.41, 83% ee, CHCl₃); R_f = 0.42 (30% EtOAc/hexanes); mp >292 °C; IR (thin film) 3060, 2230, 1632 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.25 (s, 2H), 8.25 (s, 2H), 7.95 (d, *J* = 8.2 Hz, 4H), 7.91 (d, *J* = 8.3 Hz, 4H), 7.86 (d, *J* = 8.1 Hz, 2H), 7.45-7.42 (m, 2H), 7.39-7.37 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 200.4, 155.1, 141.9, 137.8, 137.4, 132.6, 131.0, 130.5, 130.0, 127.2, 124.9, 124.8, 120.5, 118.0, 118.0, 116.0; CSP HPLC (Chiralpak AD; 1.0 mL/min, 70:30 hexanes:*i*PrOH) t_R(S) = 35.8 min, t_R(R) = 98.4 min.

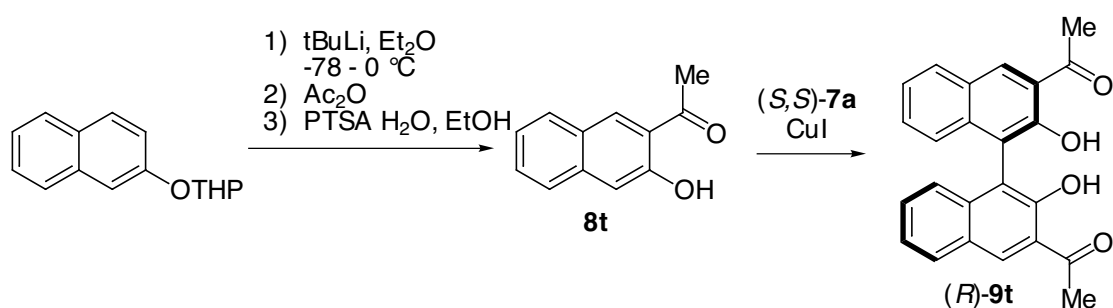
[3'-(4-Chloro-benzoyl)-2,2'-dihydroxy-1,1'-binaphthalenyl-3-yl]-(4-chloro-phenyl)-methanone (9p). Afforded an orange solid in 90% ee (enrichment during standard workup): [α]_D²³ +46 (*c* 0.56, 90% ee, CHCl₃); R_f = 0.49 (20% EtOAc/hexanes); mp 264-266 °C; IR (thin film): 3061, 1630 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.35 (s, 2H), 8.33 (s, 2H), 7.87 (d, *J* = 8.1 Hz, 2H), 7.83 (d, *J* = 8.3 Hz, 4H), 7.59 (d, *J* = 8.3 Hz, 4H), 7.43-7.40 (m, 2H), 7.38-7.35 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 200.8, 155.2, 139.1, 137.6, 137.2, 136.5, 131.3, 130.6, 130.4, 129.1, 127.1, 124.9, 124.5, 120.9,

117.9; CSP HPLC (Chiralpak AD; 1.0 mL/min, 90:10 hexanes:*i*PrOH) $t_R(S) = 19.2$ min, $t_R(R) = 122.4$ min.

[3'-Benzoyl-2,2'-dihydroxy-1,1'-binaphthalenyl-3-yl]-phenyl-methanone (9q). Afforded a yellow solid in 88% ee: $[\alpha]_D^{23} = +56$ (*c* 0.58, 88% ee, CHCl₃); $R_f = 0.12$ (10% EtOAc/hexanes); mp = 130-138 °C; IR (thin film) 3058, 1632 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.55 (s, 2H), 8.39 (s, 2H), 7.88-7.86 (m, 6H), 7.71-7.68 (m, 2H), 7.62-7.59 (m, 4H), 7.42-7.49 (m, 2H), 7.39-7.37 (m, 2H), 7.24 (d, *J* = 8.5 Hz, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 200.4, 155.1, 141.9, 137.8, 137.4, 132.6, 131.0, 130.5, 130.0, 127.2, 124.9, 124.8, 120.5, 118.0, 116.0; CSP HPLC (Chiralpak AD; 1.0 mL/min, 90:10 hexanes:*i*PrOH) $t_R(S) = 11.4$ min, $t_R(R) = 27.0$ min.

(3-Hydroxy-naphthalen-2-yl)-(4-methoxy-phenyl)-methanone (9r). Afforded a yellow solid. $R_f = 0.41$ (20% EtOAc/hexanes); mp = 132-133°C; IR (thin film) 3055, 2927, 1603 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.03 (s, 1H), 8.18 (s, 1H), 7.82 (d, *J* = 8.7 Hz, 2H), 7.75 (d, *J* = 8.3 Hz, 1H), 7.72 (d, *J* = 8.4 Hz, 1H), 7.53 (dd, *J* = 7.5, 7.4 Hz, 1H), 7.38 (s, 1H), 7.32 (dd, *J* = 7.5, 7.5 Hz, 1H), 7.04 (d, *J* = 8.7 Hz, 2H), 3.94 (s, 3H); ¹³C NMR (500 MHz, CDCl₃) δ 200.2, 163.5, 157.4, 137.9, 136.2, 132.5, 130.7, 129.7, 129.6, 126.9, 126.5, 124.2, 121.7, 114.1, 112.5, 55.8; HRMS (CI) calcd for C₁₈H₁₄O₃ (M⁺) 278.0943 found 278.0938.

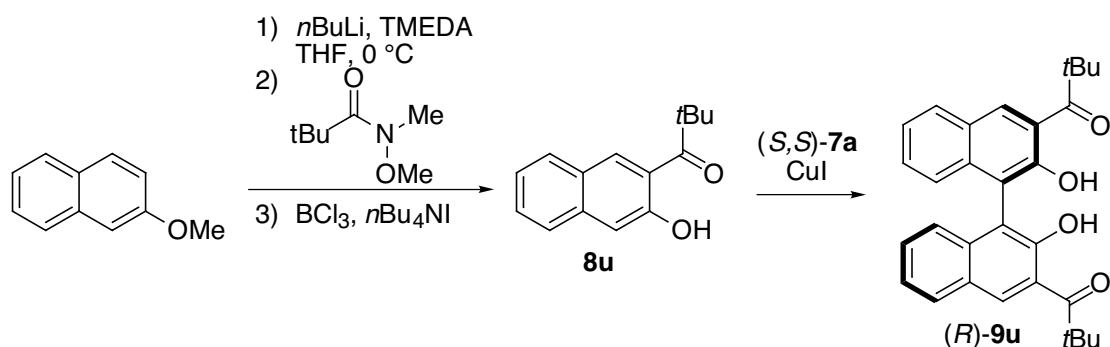
[3'-(4-Dimethylamino-benzoyl)-2,2'-dihydroxy-1,1'-binaphthalenyl-3-yl]-(4-dimethylamino-phenyl)-methanone (9s). Afforded a yellow solid in 94% ee: $[\alpha]_D^{23} = +111$ (*c* 0.50, 94% ee, CHCl₃); $R_f = 0.17$ (30% EtOAc/hexanes); mp 258-260 °C; IR (thin film) 2917, 1627 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.44 (s, 2H), 8.41 (s, 2H), 7.91 (d, *J* = 14.2 Hz, 4H), 7.87 (d, *J* = 7.7 Hz, 2H), 7.33 (m, 4H), 7.26 (d, *J* = 8.0 Hz, 4H), 6.79 (d, *J* = 14.5 Hz, 4H), 3.14 (s, 12H); ¹³C NMR (500 MHz, CDCl₃) δ 199.4, 155.3, 153.8, 136.9, 136.1, 133.2, 130.1, 129.6, 127.3, 125.5, 125.2, 124.1, 122.3, 117.8, 111.1, 40.4; HRMS (ES) calcd for C₃₈H₃₂N₂O₄ (M⁺) 581.2440, found 581.2438; CSP HPLC (Chiralpak AD; 1.0 mL/min, 50:50 hexanes:*i*PrOH) $t_R(S) = 14.8$ min, $t_R(R) = 147.6$ min.



3,3'-Diacetyl-1,1'-binaphthalene-2,2'-diol (9t). A stirred solution of THP protected 2-naphthol (1.19 g, 5.2 mmol)¹⁹ in Et₂O (10 mL) was cooled to -78 °C and treated with *t*-BuLi (6.6 mL, 1.2 M). The solution was warmed to room temperature, stirred for 3 h, and then cooled to 0 °C. Acetic anhydride (0.55 mL, 5.73 mmol) was added. After 1 h at room temperature, water (15 mL) was added and the aqueous layer was washed twice with Et₂O. The organic layer was dried over Mg₂SO₄ and concentrated. The crude material was dissolved in EtOH (10 mL) and treated with *p*-toluenesulfonic

acid monohydrate (99 mg, 0.5 mmol). The resulting solution was concentrated and the product was crystallized from EtOH to give **8t** (266 mg) in 27% yield. The spectroscopic properties for **8t** were identical to that reported by Wallace *et al.*²⁰

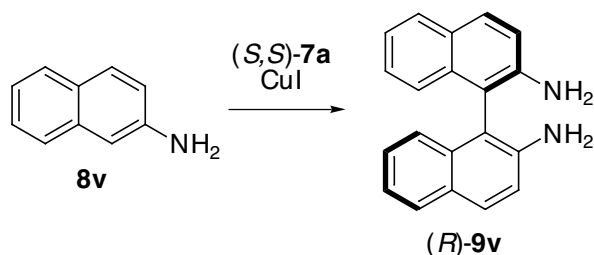
To a solution of **8t** (24.6 mg, 0.13 mmol) in CH₂Cl₂:MeCN (3:2, 1.3 mL) was added the CuI-[(*S,S*)-**7a**] catalyst (4.5 mg, 0.013 mmol). The mixture was sonicated to yield a clear brownish solution which was purged with a stream of O₂ for 1-2 min and then stirred under O₂ at 40 °C for 24 h. After cooling, the reaction mixture was extracted with 10% aqueous NH₄OH to decompose the copper complexes until the extracts were no longer blue. The combined NH₄OH layers were back-extracted with copious amounts of CH₂Cl₂ and the combined organic solutions were dried over Na₂SO₄. After filtration and concentration, the residue was purified by flash chromatography (10% EtOAc/hexanes) to afford **9t** (1.6 mg) in 7% yield and 72% ee: [α]_D²³ = +93 (*c* 0.22, 72% ee, CH₂Cl₂). The spectroscopic data of **9t** was identical to that reported by Nakajima *et al.*⁵



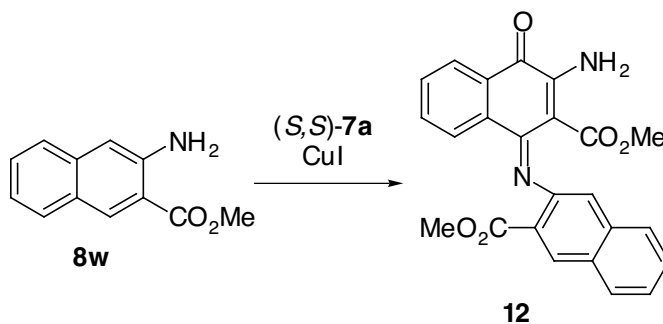
1-[3'-(2,2-Dimethyl-propionyl)-2,2'-dihydroxy-1,1'-binaphthalenyl-3-yl]-2,2-dimethyl-propan-1-one (9u**)**. The procedure outlined above for the phenyl ketone substrates using *N*-methoxy-*N*-methylpivalamide²¹ afforded a yellow resin: R_f = 0.40 (10% acetone/hexanes); IR (thin film) 3057, 2930, 1631 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.70 (s, 1H), 8.60 (s, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.52-7.49 (m, 1H), 7.34-7.31 (m, 2H), 1.56 (s, 9H); ¹³C NMR (500 MHz, CDCl₃) δ 212.8, 158.1, 137.5, 133.5, 129.7, 129.6, 126.4, 126.2, 124.1, 119.5, 113.0, 45.4, 29.4.

To a solution of **8u** (42.4 mg, 0.185 mmol) in CH₂Cl₂:MeCN (3:2, 1.9 mL) was added the CuI-[(*S,S*)-**7a**] catalyst (6.4 mg, 0.0185 mmol). The mixture was sonicated to yield a clear brownish solution and was purged with a stream of O₂ for 1-2 min and then stirred under O₂ at 40 °C for 48 h. After cooling, the reaction mixture was extracted with 10% aqueous NH₄OH to decompose the copper complexes until the extracts were no longer blue. The combined NH₄OH layers were back-extracted with copious amounts of CH₂Cl₂ and the combined organic solutions were dried over Na₂SO₄, filtered, and concentrated. The residue was chromatographed (10% EtOAc/Hexanes) to afford **9u** (13.4 mg) as a yellow residue in 58% yield and 56% ee: [α]_D²³ = +81 (*c* 0.67, 56% ee, CHCl₃); R_f = 0.15 (10% EtOAc/hexanes); IR (thin film) 3445, 2973, 1633 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 11.82 (s, 2H), 8.76 (s, 2H), 7.92-7.90 (m, 2H), 7.36-7.32 (m, 4H), 7.14-7.12 (m, 2H), 1.61 (s, 18H); ¹³C NMR (500 MHz,

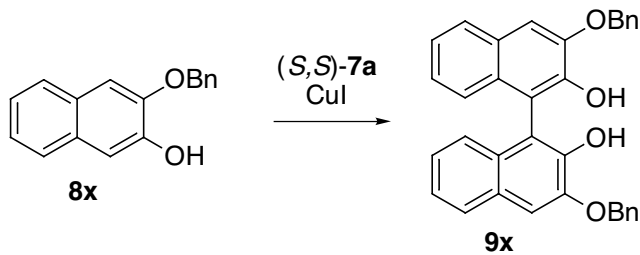
CDCl₃) δ 212.9, 155.5, 136.7, 133.8, 130.2, 129.8, 126.6, 124.7, 124.1, 119.7, 118.2, 45.6, 29.5; HRMS (ES) calcd for C₃₀H₃₀O₄Na (MNa⁺) 477.2042, found 477.2031; CSP HPLC (Chiralpak AD; 1.0 mL/min, 92:8 hexanes:*i*PrOH) $t_R(S)$ = 8.7 min, $t_R(R)$ = 9.8 min.



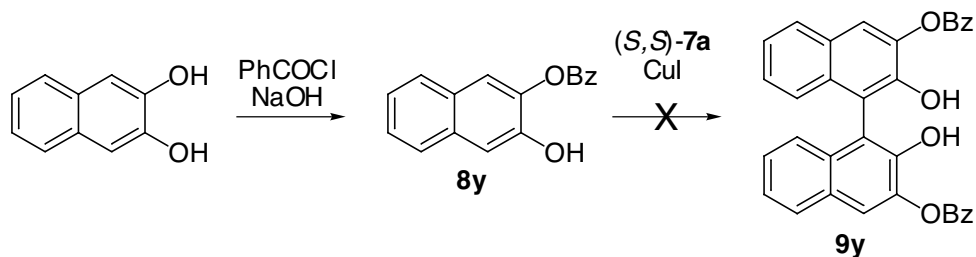
(R)-1,1'-Binaphthyl -2,2'-diamine (9v). The reaction of 2-naphthylamine (140 mg, 1 mmol) was carried out according to General Procedure with CuI-[(S,S)-7a] catalyst in ClCH₂CH₂Cl/CH₃CN at 40 °C using O₂ for 24 h to give **9h**²² (37 mg, 26% yield): $[\alpha]_D^{23} = +20$ (*c* 0.05, 6% ee, THF), Lit.²² $[\alpha]_D^{23} = +164$ (*c* 1.75, THF) for pure (*R*)-isomer; ¹H NMR (500 MHz, acetone-*d*₆) δ 7.70-7.75 (m, 4H), 7.26 (d, *J* = 8.8 Hz, 2H), 7.15-7.10 (m, 4H), 6.95-6.93 (m, 2H), 4.34 (br, 4H); CSP HPLC (Chiralpak AD; 1.0 mL/min, 85:15 hexanes:*i*PrOH) $t_R(R)$ = 13.7 min, $t_R(S)$ = 43.5 min.



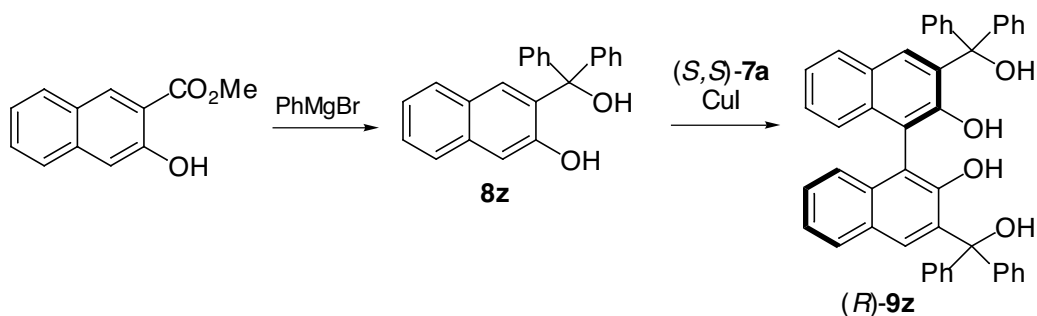
3-(3-Amino-2-methoxycarbonyl-4-oxo-4H-naphthalen-1-ylideneamino)-naphthalene-2-carboxylic acid methyl ester (12). Product obtained from the failed biaryl coupling of **8w** following the General Procedure using O₂. IR (thin film) 3460, 3345, 1724, 1674, 1594, 1573, 1288 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.81(s, 3H), 3.96(s, 3H), 6.88(br, 2H), 6.94(s, 1H), 7.38(t, *J* = 7.3 Hz, 1H), 7.47(t, *J* = 7.3Hz, 1H), 7.58(t, *J* = 5.3Hz, 1H), 7.69(d, *J* = 8.0Hz, 1H), 7.74 (t, *J* = 7.3Hz, 1H), 7.87(d, *J* = 8.0Hz, 1H), 8.13(d, *J* = 7.6Hz, 1H), 8.56(s, 1H), 8.58(s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 50.9, 52.2, 99.5, 113.9, 123.0, 125.3, 126.1, 126.9, 127.5, 128.6, 128.8, 129.2, 129.4, 130.3, 132.6, 134.4, 135.5, 138.4, 148.3, 148.5, 150.8, 166.8, 167.7, 180.8; HRMS (ES) calcd for C₂₄H₁₉N₂O₅ (MH⁺) 415.1294, found 415.1292. See below for the X-ray crystal structure.



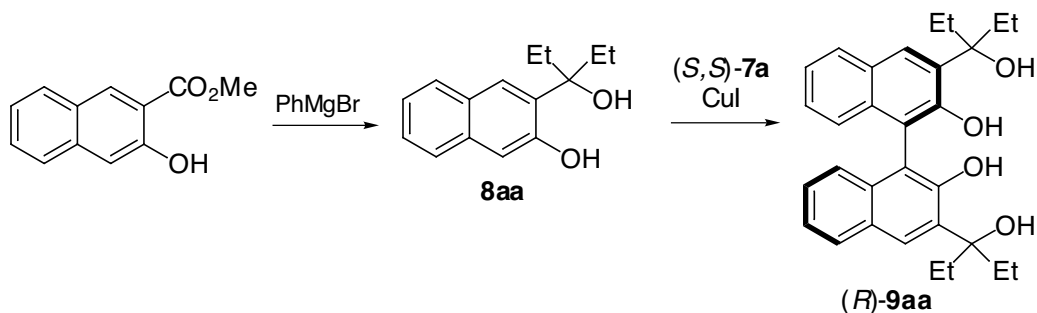
3,3'-Dibenzoyloxy-1,1'-binaphthalen-2,2'-diol (9x). The reaction of **8x** was carried out according to General Procedure with $\text{CuCl}[(S,S)\text{-7a}]$ and $\text{CuBr}_2[(S,S)\text{-7a}]$ catalysts using either air or O_2 as indicated in the equations and tables of the main text. The material obtained was identical to that previously reported.⁵ $^1\text{H NMR}$ (200 MHz, CDCl_3) δ 7.75 (d, $J = 8.0$ Hz, 2H), 7.53-7.25 (m, 14H), 7.16 (d, $J = 3.6$ Hz, 4H), 6.00 (s, 2H), 5.33 (s, 4H); $[\alpha]_{\text{D}}^{23} +22.0$ (c 0.80, 38% ee, THF), Lit.⁵ $[\alpha]_{\text{D}}^{24} -8.2$ (c 0.80, 24% ee (S) THF); CSP HPLC (Chiralpak AS; 1.0 mL/min, 85:15 hexanes:*i*PrOH) $t_{\text{R}}(\text{S}) = 32.8$ min, $t_{\text{R}}(\text{R}) = 39.3$ min.



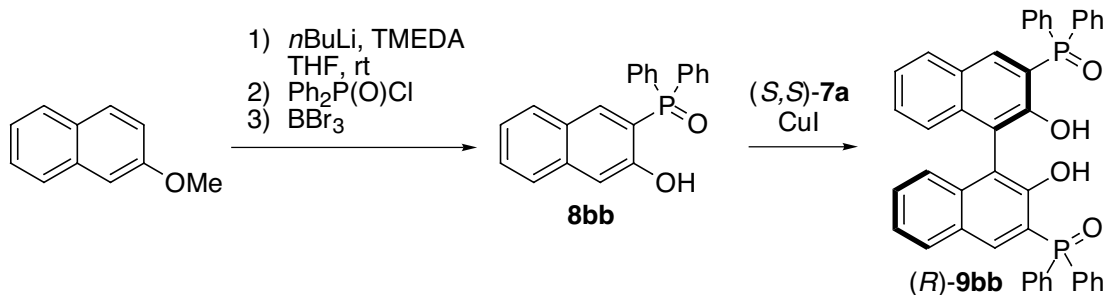
3-Hydroxy-naphthalen-2-yl Benzoate (8y). Compound **8y** was prepared following the procedure for catechol monobenzoate.²³ A suspension of 2,3-dihydroxynaphthalene (16.0 g, 0.10 mol) in H_2O (260 mL) was mechanically stirred, while the mixture was made basic (pH =10) with 10% NaOH. Benzoyl chloride (15.4 g, 0.11 mol) and 10% NaOH (40 mL) were simultaneously added over 30 min maintaining pH 10.5 - 11.5. After stirring at room temperature for 20 min further, the solid was collected, washed with water, and dried to give the monobenzoate (5.3 g, 20%) as an off-white solid: $R_{\text{f}} = 0.14$ (10% EtOAc/hexanes); mp 220-222 °C; $^1\text{H NMR}$ (200 MHz, $\text{DMSO-}d_6$) δ 10.21 (s, 1H), 8.17 (d, $J = 7.6$ Hz, 2H), 7.81-7.32 (m, 9H); $^{13}\text{C NMR}$ (125 MHz, $\text{DMSO-}d_6$) δ 164.3, 148.3, 140.2, 133.9, 132.5, 129.8, 128.9, 127.5, 127.1, 125.9, 125.8, 123.4, 120.4, 110.6; IR (KBr) 3387, 1718, 1527, 1400, 1278, 1152, 1114 cm^{-1} ; HRMS (ES) calcd for $\text{C}_{17}\text{H}_{12}\text{O}_3$ (M^+) 264.0786, found 264.0784.



3,3'-Bis-(diphenyl-hydroxymethyl)-1,1'-binaphthyl-2,2'-diol (9z). The reaction of **8z** was carried out according to General Procedure with 0.5 mmol substrate and 10 mol% CuCl-[(*S,S*)-**7a**] catalyst in CH₂Cl₂ at 40 °C for 24 h to give the product in 32% yield and 38% ee. The reaction was also carried out according to the General Procedure at room temperature using O₂ gave the product in 22% yield and 54% ee: $[\alpha]_{\text{D}}^{23} = +41.6$ (*c* 0.82, 38% ee, THF) for reaction at 40 °C and $[\alpha]_{\text{D}}^{23} = +58.8$ (*c* 0.60, 54% ee, CH₂Cl₂) for reaction at room temperature; IR (thin film) 3489, 3312 (br), 3061, 1447 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.62 (d, *J* = 7.0 Hz, 2H), 7.27-7.35 (m, 24H), 7.16 (s, 2H), 7.07 (d, *J* = 7.6 Hz, 2H), 7.02 (s, 2H), 4.59 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 151.8, 146.0, 145.6, 134.1, 133.8, 131.1, 129.2, 128.6, 128.5, 128.4, 128.3, 128.1, 128.0, 127.95, 127.6, 127.4, 124.4, 124.3, 115.3, 83.6; HRMS (ES) calcd for C₄₆H₃₄O₄Na (MNa⁺) 673.2355, found 673.2373.

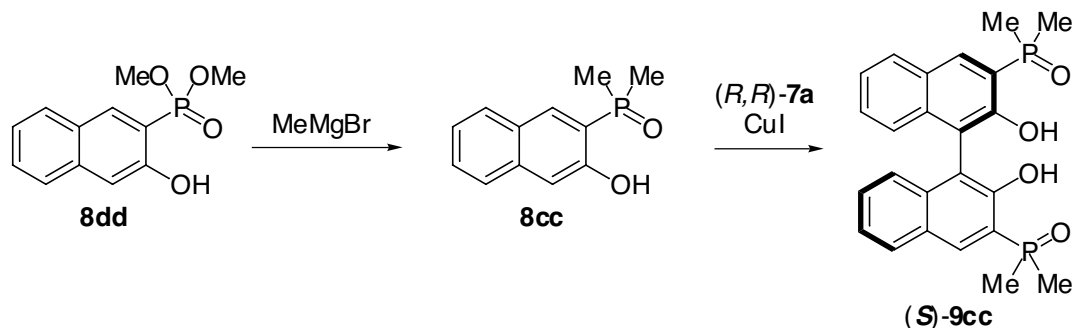


3,3'-Di(3-hydroxy-3-pentyl)-1,1'-binaphthyl-2,2'-diol (9aa). The reaction of **8aa** was carried out according to General Procedure with 0.5 mmol substrate and 10 mol% CuCl-[(*S,S*)-**7a**] catalyst in CH₂Cl₂ at room temperature using O₂ for 24 h to give the product in 25% yield and 21% ee: $[\alpha]_{\text{D}}^{23} = +20.5$ (*c* 1.4, 21% ee, THF); IR (thin film) 3420, 3145 (br), 2972, 1424 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 9.64 (s, 2H), 7.82 (m, 4H), 7.21 (m, 2H), 7.13 (m, 2H), 7.02 (m, 2H), 5.06 (s, 2H), 2.24 (m, 4H), 2.04 (m, 4H), 0.96 (m, 12H); ¹³C NMR (125 MHz, CDCl₃) δ 154.5, 134.6, 131.8, 129.1, 129.0, 127.3, 126.3, 125.2, 123.3, 117.7, 81.8, 81.7, 35.0, 34.5, 8.55; HRMS (ES) calcd for C₃₀H₃₄O₄Na (MNa⁺) 481.2355, found 481.2355.



2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-bis-diphenylphosphine oxide (9bb). *n*-BuLi (15 mmol, 2.5 M in hexanes) was added to TMEDA (15 mmol) in dry THF (15 mL) at 0 °C. After 30 min, 2-methoxynaphthalene (1.6 g, 10 mmol) in dry THF (5 mL) was added. The red solution was stirred at room temperature for an additional 2 h. Diphenylphosphinyl chloride was then added and the resultant brown solution was stirred overnight. MeOH was added to quench the reaction. The mixture was diluted with EtOAc and washed with 1 N HCl. The aqueous phase was extracted with EtOAc. The combined organic layers were dried with Na₂SO₄. Filtration and concentration gave the crude product as an oil: ¹H NMR (500 MHz, CDCl₃) δ 8.45 (d, 1H), 7.62-7.74 (m, 6H), 7.23-7.38 (m, 9H), 3.51 (s, 3H). This material was dissolved in dry CH₂Cl₂ (10 mL), cooled to -78 °C, and BBr₃ (1.0 equiv) was added. The reaction mixture was allowed to warm to room temperature overnight. After dilution with CH₂Cl₂, the mixture was washed with 1 N HCl. Extraction with CH₂Cl₂, drying with Na₂SO₄, filtration, and concentration gave an oil. Chromatography (1.5 % MeOH/CH₂Cl₂) provided the pure diphenyl (3-hydroxy-2-naphthyl)phosphine oxide²⁴ **8bb** (1.18 g, 34% yield) as a white solid: IR (thin film) 3397, 3022, 1216, 741 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 7.82 (d, 2H), 7.67-7.74 (m, 6H), 7.58-7.59 (m, 2H), 7.45-7.51 (m, 5H), 7.24-7.35 (m, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 157.6, 137.8, 136.1 (d, *J* = 8.8 Hz), 132.9 (d, *J* = 2.5 Hz), 132.4 (d, *J* = 11.3 Hz), 132.0 (d, *J* = 105 Hz), 129.12, 129.07, 129.03, 127.8 (d, *J* = 13.1 Hz), 126.5, 124.4, 117.9 (d, *J* = 102 Hz), 111.7 (d, *J* = 6.3 Hz); HRMS (ES) calcd for C₂₂H₁₈O₂P (MH⁺) 345.1044, found 345.1058.

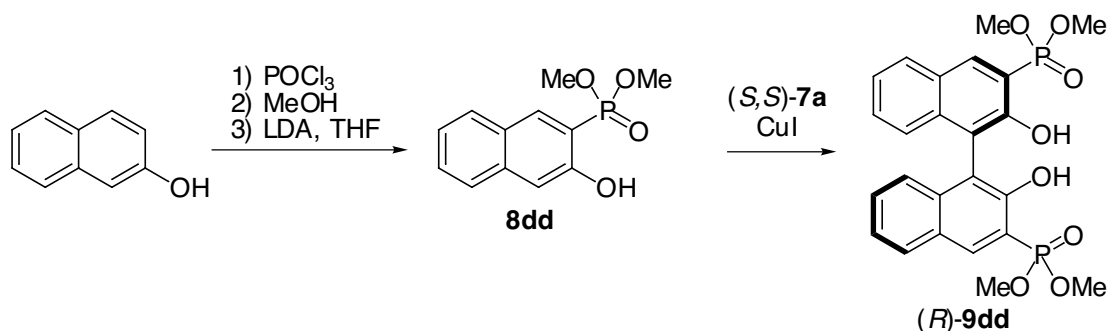
Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-7a] and 0.3 mmol substrate in ClCH₂CH₂Cl (3 mL) and MeCN (2 mL) at 40 °C using O₂ for 48 h to give the product as a solid in 25% (0.025 g, 0.0038 mmol) isolated yield and 96% ee: [α]_D²³ = +92.1 (*c* 1.0, 96% ee, CHCl₃); IR (thin film) 3420, 3022, 1216, 741 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 10.5 (s, 2 OH), 7.72-7.81 (m, 12H), 7.51-7.61 (m, 12H), 7.23-7.28 (m, 6H); ¹³C NMR (125 MHz, CDCl₃) δ 156.2, 136.4, 134.9 (d, *J* = 8.8 Hz), 132.6, 132.2 (d, *J* = 10 Hz), 131.9 (d, *J* = 105 Hz), 131.6 (d, *J* = 105 Hz), 129.0, 128.8, 128.7, 127.2 (d, *J* = 15 Hz), 125.0, 123.8, 117.5 (d, *J* = 6.3 Hz), 115.4 (d, *J* = 100 Hz); HRMS (ES) calcd for C₄₄H₃₃O₄P₂ (MH⁺) 687.1854, found 687.1844; CSP HPLC (Chiralpak AD, 1.0 mL/min, 80:20 hexanes:*i*PrOH) t_R(*S*) = 13.2 min, t_R(*R*) = 49.0 min.



2,2'-Dihydroxy-1,1'-binaphthalene-3,3'-bis-dimethylphosphine oxide (9cc). A solution of dimethyl (3-hydroxy-2-naphthyl)phosphite (**8dd**) (600 mg, 2.4 mmol) in benzene (10 mL) was treated with ethereal MeMgBr (10 equiv, 1.5 M) and heated to reflux overnight. The reaction mixture was quenched with 1 N HCl (pH < 1). Extraction with CH₂Cl₂, drying over Na₂SO₄, filtration, and concentration gave the crude product. Chromatography (4% MeOH/CH₂Cl₂) provided the pure dimethyl (3-hydroxy-2-naphthyl)phosphine oxide **8cc** (166 mg, 31% yield) as a white solid: IR (thin film) 3482, 3455, 3435, 3022, 1216, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.92 (d, *J* = 13.4 Hz, 6H), 7.3 (m, 2H), 7.47 (t, *J* = 7.5 Hz, 1H), 7.68 (d, *J* = 8.3 Hz, 1H), 7.73 (d, *J* = 8.2 Hz, 1H), 7.8 (d, *J* = 15 Hz, 1H), 10.6 (s, 1 OH); ¹³C NMR (125 MHz, CDCl₃) 18.9 (d, *J* = 70.9 Hz), 111.9 (d, *J* = 6.5 Hz), 118 (d, *J* = 95 Hz), 124, 126.4, 127.3 (d, *J* = 13 Hz), 128.2, 128.4, 131.8, 137.1, 157.6; HRMS (ES) calcd for C₁₂H₁₃O₂P (M⁺) 220.0653, found 220.0649.

Biaryl coupling was carried out according to General Procedure with 10 mol% CuI-[(R,R)-7a] and 0.3 mmol substrate in ClCH₂CH₂Cl (5 mL) at 40 °C using O₂ for 48 h to give the product as a solid in 40% (0.026 g, 0.006 mmol) isolated yield after preparative TLC (5-10% MeOH/CH₂Cl₂) purification: [α]_D²³ = -30 (c 0.05, CHCl₃); IR (thin film) 3455, 3428, 3022, 1216, 741 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) 1.96 (d, *J* = 13.1 Hz, 6H), 1.99 (d, *J* = 13.1 Hz, 6H), 7.16 (d, *J* = 8.1 Hz, 2H), 7.35 (m, 4H), 7.88 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 14.9 Hz, 2H), 9.68 (s, 2OH); ¹³C NMR (125 MHz, CDCl₃) 18.9 (d, *J* = 70.9 Hz), 19.0 (d, *J* = 70.8 Hz), 116.7 (d, *J* = 163 Hz), 118.6 (d, *J* = 95 Hz), 124.2, 124.9, 127.8 (d, *J* = 12.6 Hz), 128.8, 128.9, 133.2 (d, *J* = 9.3 Hz), 136.1, 154.6; HRMS (ES) calcd for C₂₄H₂₄O₄P₂Na (MNa⁺) 461.1048, found 461.1058.

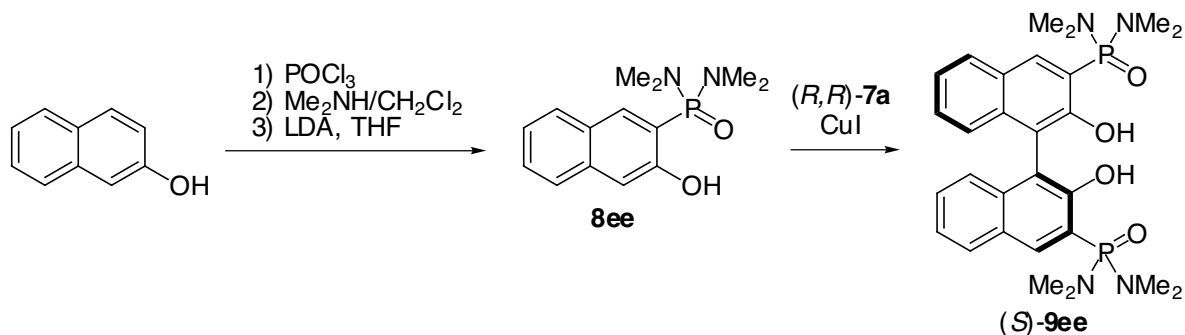
Racemic or (S)-9cc and 2.0 equiv (-)-quinine were dissolved in CDCl₃ to form the chiral solvates. The enantioselectivity was determined from the ¹H NMR spectra of these complexes. A doublet at 8.08 ppm splits into two sets of doublets upon the addition of (-)-quinine. The integrations of these peaks (doublet at 8.15 and 8.08 ppm) were used to calculate the ratio of the diastereomeric solvates. The (S)-9cc obtained from the above reaction was thus measured to be 46% ee.



Dimethyl-2, 2'-dihydroxy-1, 1'-binaphthyl-3, 3'-diphosphate (9dd). Dimethyl (3-hydroxy-2-naphthyl)phosphate (**8dd**) was prepared via phosphorylation and rearrangement following a procedure reported for analogous compounds.²⁵ 2-Naphthol (8.1 g, 0.056 mol) was mixed with POCl₃ (33 mL) at room temperature. After Cs₂CO₃ (0.9 g, 2.8 mmol) was added, the mixture was heated at reflux overnight. Removal of excess POCl₃ afforded a crude oil which was cooled to 0 °C. MeOH (80 mL) was then added slowly and the solution was stirred at room temperature overnight. Removal of the solvent *in vacuo* afforded the product as an oil. Chromatography (1% MeOH/CH₂Cl₂) provided pure dimethyl 2-naphthylphosphate (10.8 g, 76% yield) as a colorless oil: IR (thin film) 3401, 3022, 1216, 741 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.89 (d, *J* = 11.3 Hz, 6H), 7.36 (d, *J* = 8.9 Hz, 1H), 7.43-7.5 (m, 2H), 7.68 (s, 1H), 7.79-7.83 (m, 3H); ¹³C NMR (125 MHz, CDCl₃) δ 54.9 (d, *J* = 5 Hz), 116.3 (d, *J* = 5 Hz), 119.8 (d, *J* = 6.3 Hz), 125.5, 126.7, 127.5, 127.7, 129.9, 130.9, 133.8, 148.2 (d, *J* = 7.5 Hz); ; HRMS (ES) calcd for C₁₂H₁₄O₄P (MH⁺) 253.0630, found 253.0632. *i*-Pr₂NH (3.5 mL, 25 mmol) was dissolved in dry THF (40 mL) and was treated with *n*-BuLi (25 mmol, 2.5 M in hexanes) at -78 °C. A solution of dimethyl 2-naphthylphosphate (2.5 g, 10 mmol) in dry THF was added. After 2 h, MeOH was added slowly to quench the reaction. The mixture was diluted with CH₂Cl₂ and washed with 1 N HCl. The aqueous phase was extracted with CH₂Cl₂. The combined organic extracts were dried with Na₂SO₄. Filtration and concentration gave an oil which was chromatographed (1% MeOH/CH₂Cl₂) to provide pure dimethyl (3-hydroxy-2-naphthyl)phosphate **8dd** (1.4 g, 56% yield) as a white solid: IR (thin film) 3424, 3022, 1216, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.8 (d, *J* = 11.4 Hz, 6H), 7.32 (t, *J* = 7.2 Hz, 2H), 7.48 (t, *J* = 7.5 Hz, 1H), 7.69 (d, *J* = 8.4 Hz, 1H), 7.76 (d, *J* = 8.2 Hz, 1H), 8.0 (d, *J* = 16.2 Hz, 1H), 9.79 (s, 1 OH); ¹³C NMR (125 MHz, CDCl₃) δ 53.1 (d, *J* = 5 Hz), 110.9 (d, *J* = 178.8 Hz), 111.7 (d, *J* = 11.3 Hz), 124.0, 126.5, 127.3 (d, *J* = 15 Hz), 128.5, 128.8, 134.3 (d, *J* = 6.3 Hz), 137.8 (d, *J* = 1.3 Hz), 156.8 (d, *J* = 7.5 Hz); HRMS (ES) calcd for C₁₂H₁₃O₄P (MH⁺) 252.0551, found 252.0546.

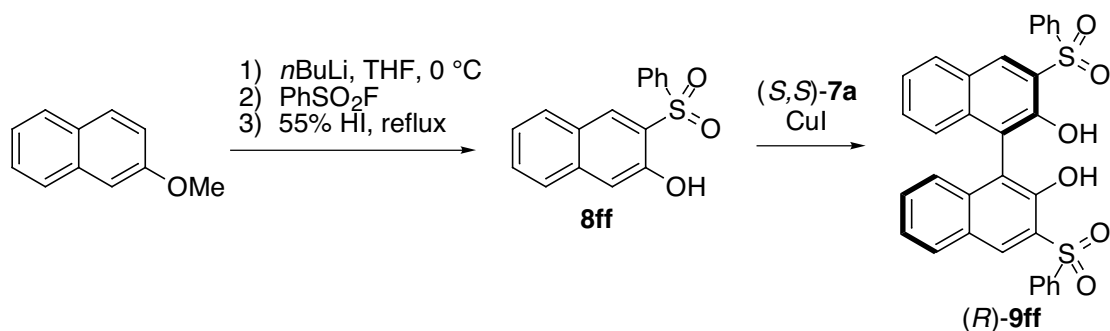
Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*S,S*)-7a] and 0.4 mmol substrate in ClCH₂CH₂Cl (4 mL) at 40 °C using O₂ for 48 h to give the product as a white solid in 76% (0.076 g, 0.15 mmol) isolated yield and 92% ee after preparative TLC (3% MeOH/CH₂Cl₂) purification: [α]_D²⁵ = +84.8 (*c* 1.0, 92% ee, CHCl₃); IR (thin film) 3161, 3069, 3015, 2957, 1625, 1216, 1027 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.86 (q, *J* = 9.1 Hz, 12H), 7.17 (q, *J* = 3.2 Hz, 2H), 7.33 (q, *J* = 3.2 Hz, 4H), 7.87 (q, *J* = 3.1 Hz, 2H), 8.2 (d, *J* = 16.3 Hz, 2H), 9.72 (s, 2 OH); ¹³C NMR (125

MHz, CDCl₃) δ 53.1 (d, *J* = 5 Hz), 53.3 (d, *J* = 5 Hz), 111.1 (d, *J* = 178.8 Hz), 116.9 (dd, *J* = 2.5 Hz, 11.3 Hz), 123.9, 124.8, 127.5 (d, *J* = 16.3 Hz), 129.05, 129.07, 134.9 (d, *J* = 5 Hz), 136.9 (d, *J* = 2.5 Hz), 154.3 (d, *J* = 7.5 Hz); HRMS (ES) calcd for C₂₄H₂₄O₈P₂Na (MNa⁺) 525.0844, found 525.0854; CSP HPLC (Chiralpak AD, 1.0 mL/min, 90:10 hexanes:*i*PrOH) t_R(*R*) = 12.9 min, t_R(*S*) = 26.9 min.



***N,N,N',N'*-Tetramethyl-2,2'-dihydroxy-1,1'-binaphthyl-3,3'-bis-phosphinic diamide (9ee).** *N,N,N',N'*-Tetramethyl 3-(2-hydroxynaphthyl)phosphonic amide (8ee) was prepared as previously reported.²⁶

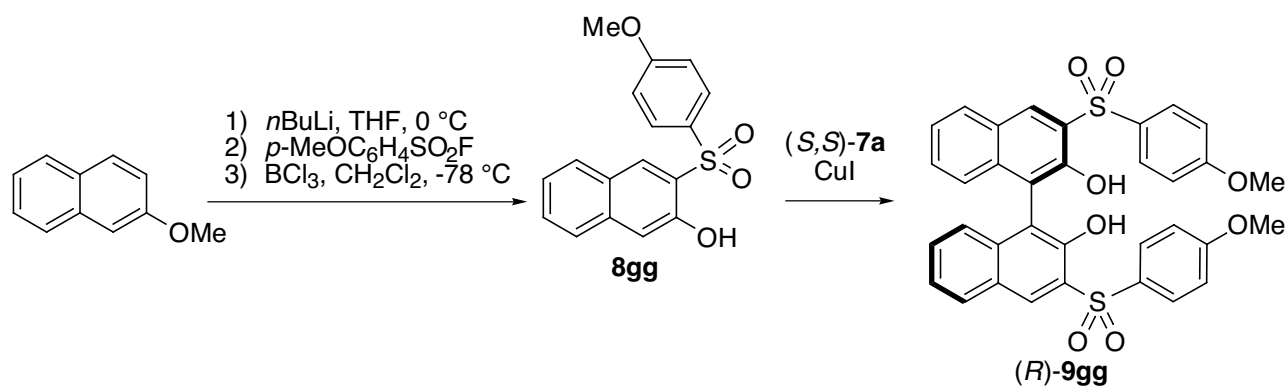
Biaryl coupling was carried out according to the General Procedure with 10 mol% CuI-[(*R,R*)-7a] and 0.36 mmol substrate in ClCH₂CH₂Cl (4 mL) at 40 °C using O₂ for 48 h to give the product as a yellow solid residue in 30% (0.03 g, 0.054 mmol) isolated yield and 90% ee after preparative TLC (5% MeOH/CH₂Cl₂) purification: [α]_D²³ = -121 (*c* 0.67, 90% ee, CHCl₃); IR (thin film) 3412, 3022, 1220, 787, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 2.78 (d, *J* = 10.2 Hz, 12H), 7.12 (d, *J* = 3.0 Hz, 2H), 7.28 (m, 4H), 7.83 (q, *J* = 2.9 Hz, 2H), 7.98 (d, *J* = 14.5 Hz, 2H), 11.23 (s, 2OH); ¹³C NMR (125 MHz, CDCl₃) δ 36.5 (d, *J* = 3.8 Hz), 114.0 (d, *J* = 146.3 Hz), 117.4, 123.2, 124.8, 127.2 (d, *J* = 13.8 Hz), 128.1, 128.8, 133.2 (d, *J* = 5 Hz), 136.2 (d, *J* = 2.5 Hz), 155.8 (d, *J* = 6.3 Hz); HRMS (ES) calcd for C₂₈H₃₆O₄N₄P₂Na (MNa⁺) 577.2110, found 577.2125; CSP HPLC (Chiralpak AD, 1.0 mL/min, 95:5 hexanes:*i*PrOH) t_R(*S*) = 20.5 min, t_R(*R*) = 37.1 min.



3,3'-Bis-benzenesulfonyl-1,1'-binaphthalenyl-2,2'-diol (9ff). To a solution of 2-methoxynaphthalene (322 mg, 2.04 mmol) in dry THF (5 mL) chilled in an ice bath was added 2.5 M *n*-BuLi in hexanes (1.6 mL, 4 mmol). After stirring at room temperature for 1 h, this solution was

cooled in an ice bath and benzenesulfonyl fluoride (0.29 mL, 2.41 mmol) was added dropwise. The bath was removed and this mixture was stirred for 16 h. The resultant red-brown mixture was poured into ice and saturated NH_4Cl and diluted with EtOAc. The aqueous layer was extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na_2SO_4 , and evaporated to yield a yellow oil. Chromatography (15% EtOAc/hexanes) afforded 2-benzenesulfonyl-3-methoxy-naphthalene in 58% yield. A mixture of this product (123 mg, 0.412 mmol) and 55% aqueous HI (2 mL) was heated in a 180 °C oil bath under an Ar atmosphere for 2.5 h. The mixture was cooled and ice/ H_2O (5 mL) was added. The resultant white solid was filtered. After washing with water, the solid was dried to afford 3-benzenesulfonyl-naphthalen-2-ol (**8ff**) (113 mg) in 96% yield: mp 140-142 °C; IR (thin film) 3366, 3061, 3026, 1629, 1289, 1146, 749 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.36 (s, 1H), 7.38 (t, $J = 7.2$ Hz, 1H), 7.52 (m, 3H), 7.58 (t, $J = 7.4$ Hz, 1H), 7.69 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 8.00 (d, $J = 7.3$ Hz, 2H), 8.38 (s, 1H), 8.70 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 114.14, 125.25, 126.29, 126.76, 127.18, 127.80, 129.34, 129.73, 129.94, 131.82, 134.01, 138.03, 141.69, 150.91; HRMS (CI) calcd for $\text{C}_{16}\text{H}_{12}\text{O}_3\text{S}$ (M^+) 284.0507, found 284.0500.

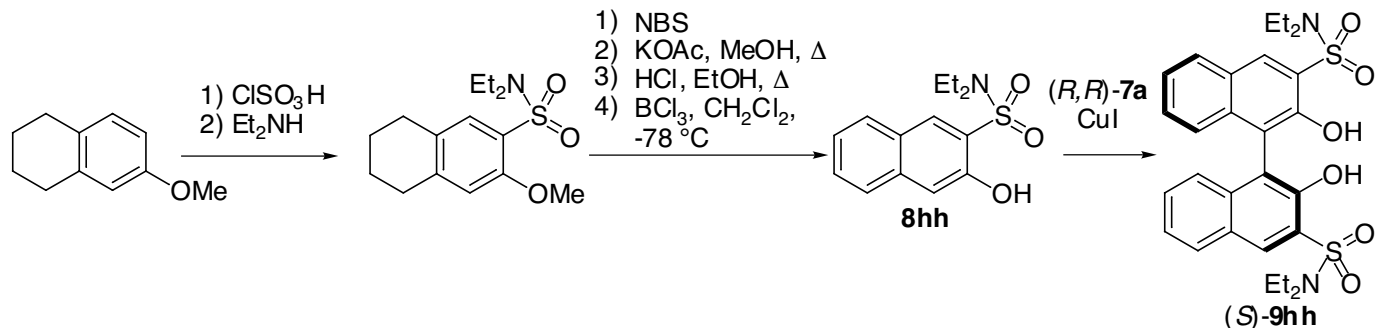
Biaryl coupling was carried out according to the General Procedure with 20 mol% $\text{CuI}[(S,S)\text{-7a}]$ and 0.239 mmol substrate in 0.24 mL 1:3:1 MeCN: $\text{ClCH}_2\text{CH}_2\text{Cl}$:DMF at 80 °C using O_2 for 16 h to give the product as a resin in 65% (44 mg, 0.078 mmol) isolated yield and 45% ee. The enantiomeric excess could be raised by trituration with EtOAc, followed by chromatography (25-50% Et_2O /hexane) to provided the product in 90% ee: $[\alpha]_{\text{D}}^{23} = +91$ (c 1.0, 90% ee, CHCl_3); IR (thin film) 3366, 3069, 1621, 1586, 1285, 1131, 749 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 7.05 (d, $J = 8.5$ Hz, 2H), 7.35 (t, $J = 6.9$ Hz, 2H) 7.40 (t, $J = 6.8$ Hz, 2H), 7.56 (t, $J = 7.4$ Hz, 4H), 7.62 (t, $J = 7.4$ Hz, 2H), 7.95 (d, $J = 8.2$ Hz, 2H), 8.03 (d, $J = 7.4$ Hz, 4H), 8.59 (s, 2H), 8.60 (s, 2H); ^{13}C NMR (125 MHz, CDCl_3) δ 118.22, 124.95, 125.36, 126.54, 127.28, 127.83, 129.73, 130.00, 130.36, 132.58, 134.08, 136.94, 141.65, 148.75; HRMS (ES) calcd for $\text{C}_{32}\text{H}_{22}\text{O}_6\text{S}_2$ (Na^+) 589.0756, found 589.0749; CSP HPLC (Chiralpak AD, 1.0 mL/min, 70:30:0.1 hexanes: i PrOH:TFA) $t_{\text{R}}(S) = 18.5$ min, $t_{\text{R}}(R) = 24.4$ min.



3,3'-Bis-(4-methoxy-benzenesulfonyl)-1,1'-binaphthalenyl-2,2'-diol (9gg). To a solution of 2-methoxynaphthalene (646 mg, 4.08 mmol) in dry THF (8 mL) chilled in an ice-salt bath was added

2.5M *n*-BuLi in hexanes (2.0 mL, 5.0 mmol) dropwise. The red solution was stirred for 1 h and a solution of 4-methoxybenzenesulfonyl fluoride (1.00 g, 5.26 mmol) in dry THF (5 mL) was added dropwise. The bath was removed and the reaction mixture was stirred for 2.5 h. The red-brown mixture was poured into ice/saturated NH₄Cl and was diluted with EtOAc. The phases were partitioned and the aqueous phase was extracted with EtOAc. The combined organic phases were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Chromatography (0-50% EtOAc/hexanes) gave the product 2-methoxy-3-(4-methoxybenzenesulfonyl)-naphthalene (520 mg, 39%) as a yellow solid. A mixture of this material (117 mg, 0.357 mmol) and *n*-Bu₄NI (143 mg, 0.386 mmol) was dissolved in CH₂Cl₂ (4 mL) and chilled to -72 °C in a dry ice-acetone bath under an Ar atmosphere. To this solution was added a solution of BCl₃ in hexanes (1 M, 0.70 mL, 0.70 mmol). After warming to room temperature and stirring for 16 h, the reaction mixture was poured over H₂O. The aqueous phase was extracted with CH₂Cl₂. The combined organic phases were washed with H₂O, brine, dried over Na₂SO₄, and concentrated *in vacuo*. Chromatography (CH₂Cl₂) gave a **8gg** (60 mg, 54%) as a white powder: mp 160-162 °C; IR (thin film) 3358, 3061, 3022, 2968, 1629, 1594, 1289, 1131, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.83 (s, 3H), 6.96 (d, *J* = 8.0 Hz, 2H), 7.34 (s, 1H), 7.36 (t, *J* = 6.9 Hz, 1H), 7.51 (t, *J* = 7.0 Hz, 1H), 7.67 (d, *J* = 8.4 Hz, 1H), 7.80 (d, *J* = 8.3 Hz, 1H), 7.93 (d, *J* = 6.9 Hz, 2H), 8.35 (s, 1H), 8.73 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 55.89, 113.98, 114.91, 125.12, 126.68, 127.13, 127.77, 129.24, 129.48, 129.70, 131.25, 133.09, 137.79, 150.73, 164.03; HRMS (CI) calcd for C₁₇H₁₄O₄S (M⁺) 314.0613, found 314.0599.

Biaryl coupling was carried out according to the General Procedure with 20 mol% CuI-[(*S,S*)-**7a**] and 0.224 mmol substrate in 0.22 mL 1:3:1 MeCN:ClCH₂CH₂Cl:DMF at 80 °C using O₂ for 16 h to give the product as a resin in 76% (53 mg, 0.085 mmol) isolated yield and 57% ee. The enantiomeric excess could be raised by trituration with EtOAc followed by chromatography (25-50% Et₂O/hexane) to provide the product in 98% ee: [α]_D²⁵ = +34 (*c* 1.0, 98% ee, CHCl₃); IR (thin film) 3339, 3069, 3022, 1594, 1262, 1131, 753 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.87 (s, 6H), 7.00 (d, *J* = 9.0 Hz, 4H), 7.03 (d, *J* = 8.5 Hz, 2H), 7.33 (t, *J* = 8.4 Hz, 2H), 7.40 (t, *J* = 8.4 Hz, 2H), 7.93 (d, *J* = 8.2 Hz, 2H), 7.97 (d, *J* = 9.0 Hz, 4H); 8.55 (s, 2H), 8.62 (s, 2H); ¹³C NMR (500 MHz, CDCl₃) δ 55.97, 114.95, 118.24, 124.99, 125.24, 127.41, 127.84, 129.65, 129.92, 130.12, 132.02, 133.14, 136.78, 148.67, 164.14; HRMS (ES) calcd for C₃₄H₂₆O₈S₂ (MNa⁺) 649.0967, found 649.0986; CSP HPLC (Chiralpak AD, 1.0 mL/min, 70:30:0.1 hexanes:*i*PrOH:TFA) t_R(*R*) = 54.0 min, t_R(*S*) = 62.7 min.

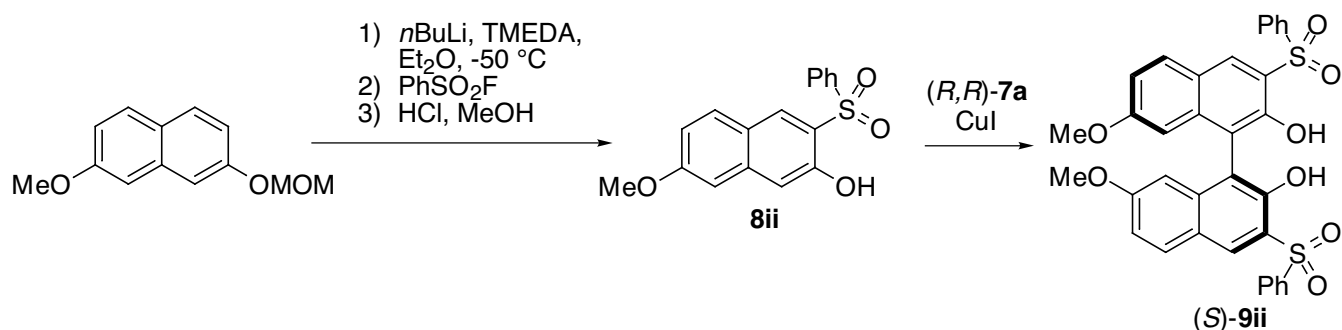


2,2'-Dihydroxy-1,1'-binaphthalenyl-3,3'-disulfonic acid bis-diethylamide (9hh) To a chilled (ice- H_2O bath) solution of 5,6,7,8-tetrahydro-2-methoxynaphthalene (2.00 g, 12.3 mmol) in CH_2Cl_2 (30 mL) was added chlorosulfonic acid (2.5 mL, 37.5 mmol). The reaction mixture was stirred for 10 min, then carefully poured onto ice- H_2O . The aqueous phase was extracted with CH_2Cl_2 . The organic phase was washed with H_2O and brine, dried (Na_2SO_4), and concentrated *in vacuo* to yield 3-methoxy-5,6,7,8-tetrahydro-2-naphthalene-2-sulfonyl chloride (2.09 g, 75%). To a solution of this substrate (0.760 g, 2.92 mmol) in CH_2Cl_2 (3 mL) was added Et_2NH (1 mL, 9.67 mmol) and the reaction was stirred for 30 min. The mixture was diluted with CH_2Cl_2 , washed with 1 N HCl and brine, dried over Na_2SO_4 , and concentrated *in vacuo* to yield 3-methoxy-5,6,7,8-tetrahydro-naphthalene-2-sulfonic acid diethyl amide (757 mg, 87%).

A mixture of 3-methoxy-5,6,7,8-tetrahydro-naphthalene-2-sulfonic acid diethyl amide (695 mg, 2.34 mmol), *N*-bromosuccinimide (830 mg, 4.66 mmol), and benzoyl peroxide (51 mg, 0.21 mmol) in CCl_4 (12 mL) under Ar was heated to reflux. After 2 h, the solvent was evaporated. KOAc (457 mg, 4.66 mmol) and MeOH (8 mL) were added to the reaction mixture. The mixture was heated to reflux for 1 h. After the MeOH was evaporated *in vacuo*, the residue was suspended in H_2O and extracted with EtOAc. The combined organic layers were washed with H_2O and brine and concentrated *in vacuo*. The residue was taken up in 95% EtOH (9 mL) and 12 N HCl (3 mL) was added. The reaction mixture was heated to reflux for 1 h. The resultant suspension was cooled, poured into ice- H_2O , and extracted with EtOAc. The organic extracts were dried over Na_2SO_4 and purified by chromatography (0-20% EtOAc/hexanes) to yield 3-methoxynaphthalene-2-sulfonic acid diethylamide (230 mg, 34%). A mixture of this product (45 mg, 0.153 mmol) and *n*- Bu_4NI (62 mg, 0.169 mmol) was dissolved in CH_2Cl_2 (2 mL) and chilled to -72°C in a dry ice-acetone bath under an Ar atmosphere. To this mixture was added a solution of BCl_3 in hexanes (1 M, 0.35 mL, 0.35 mmol). After warming to room temperature and stirring for 16 h, the reaction mixture was poured onto H_2O and the aqueous phase was extracted with CH_2Cl_2 . The combined organic phases were washed with H_2O , brine, dried (Na_2SO_4), and concentrated *in vacuo*. The resultant orange oil was triturated with hexanes to provide 3-hydroxy-naphthalene-2-sulfonic acid diethylamide (**8hh**) in 80% yield ((34 mg): mp $94\text{--}95^\circ\text{C}$; IR (thin film) 3347, 3061, 2980, 2937, 1633, 1320, 1143, 706 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 1.17 (t, $J = 7.1$ Hz, 6H), 3.33 (q, $J = 7.1$ Hz, 4H), 7.38-7.41(m, 2H), 7.54 (t, $J = 7.1$ Hz, 1H), 7.72 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 1H), 8.24 (s, 1H), 8.62 (s, 1H); ^{13}C NMR (125 MHz, CDCl_3) δ 150.63, 137.29, 130.12,

129.29, 129.04, 127.56, 126.66, 125.83, 124.98, 113.65, 42.20, 14.03; HRMS (CI) calcd for C₁₄H₁₇NO₃S (M⁺) 279.0929, found 279.0923.

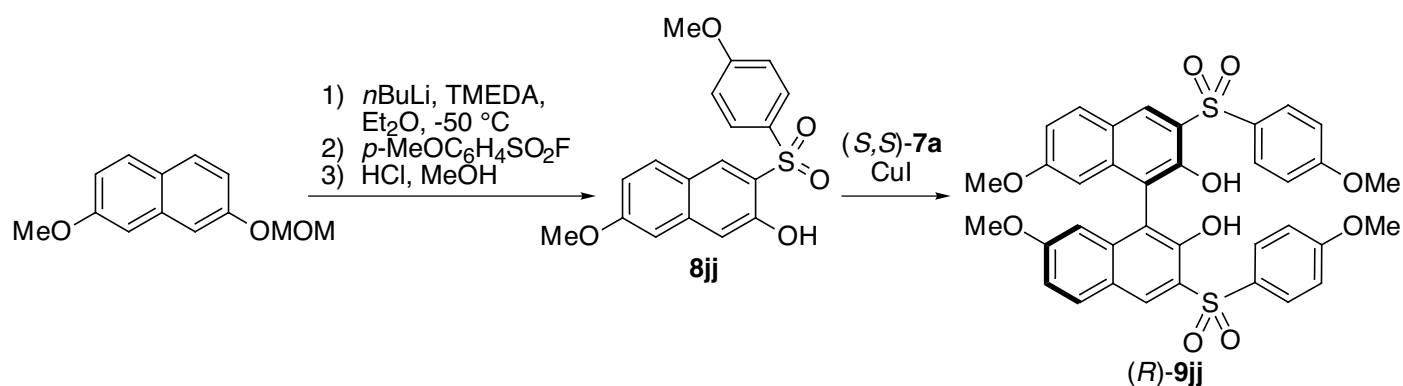
Biaryl coupling was carried out according to the modified general procedure with 20 mol% CuI-[(*R,R*)-**7a**] and 0.104 mmol substrate in 0.22 mL 1:3:1 MeCN:ClCH₂CH₂Cl:DMF at 80 °C using O₂ for 16 h to give the product as a resin in 46% (13 mg, 0.046 mmol) isolated yield and 44% ee: [α]_D²³ = -3.7 (c 1.0, 44% ee, CHCl₃); IR (thin film) 3335, 3069, 3022, 2980, 2937, 1625, 1320, 1127, 753 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 1.17 (t, *J* = 7.1 Hz, 12H), 3.38 (m, 8H), 7.11 (d, *J* = 8.4 Hz, 2H), 7.37 (t, *J* = 7.5 Hz, 2H), 7.41 (t, *J* = 8.0 Hz, 2H), 7.93 (d, *J* = 8.0 Hz, 2H), 8.43 (s, 2H), 8.53 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 13.89, 42.11, 118.54, 124.97, 125.12, 126.19, 129.69, 129.73, 130.72, 136.48, 148.48; HRMS (ES) calcd for C₂₈H₃₂N₂O₆S₂ (MNa⁺) 579.1600, found 579.1623; CSP HPLC (Chiralpak AD, 1.0 mL/min, 70:30:0.1 hexanes:*i*PrOH:TFA) t_R(*R*) = 7.7 min, t_R(*S*) = 9.3 min.



3,3'-Bis-benzenesulfonyl-7,7'-dimethoxy-1,1'-binaphthalenyl-2,2'-diol (9ii) 7-Methoxy-2-methoxymethylenenaphthalene was prepared from 2,7-dihydroxynaphthalene:²⁷ ¹H NMR (200 MHz, CDCl₃) δ 3.54 (s, 3H), 3.92 (s, 3H), 5.30 (s, 2H), 7.07 (m, 3H), 7.33 (s, 1H), 7.68 (m, 2H). A solution of 7-methoxy-2-methoxymethylenenaphthalene (2.90 g, 13.2 mmol) and TMEDA (2.0 mL, 13.3 mmol) in dry Et₂O (25 mL) was chilled to -15 °C in an ice-acetone bath and was treated with 2.4 M *n*-BuLi in hexanes (6.0 mL, 14.4 mmol) dropwise. After stirring at -15 °C for 1.5 h, this solution was transferred via cannula to a solution of benzenesulfonyl fluoride (1.91 mL, 15.9 mmol) in dry Et₂O (50 mL). After stirring 30 min at room temperature, the resultant mixture was poured onto ice-saturated NH₄Cl and extracted with EtOAc. The combined organic extracts were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Chromatography (20-50% EtOAc/hexane) afforded an oil which was dissolved in methanol (40 mL) and treated with 12 N HCl (10 mL). The suspension was stirred overnight, poured onto ice-H₂O, and extracted with CH₂Cl₂. The organic layers were washed with water and brine, dried over Na₂SO₄, and concentrated *in vacuo*. Chromatography (CH₂Cl₂) gave 3-benzenesulfonyl-7-methoxy-naphthalen-2-ol (**8ii**) in 38% overall yield (1.6 g): mp 174-175 °C; IR (thin film) 3370, 3022, 1633, 1289, 1216, 1143, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.94 (s, 3H), 6.97 (s, 1H), 7.06 (d, *J* = 9.0 Hz, 1H), 7.54 (t, *J* = 7.8 Hz, 2H), 7.60 (t, *J* = 7.3 Hz, 1H), 7.73 (d, *J* = 9.0 Hz, 1H), 8.02 (d, *J* = 8.4 Hz, 2H), 8.30 (s, 1H), 8.79 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 55.65, 104.20,

112.81, 118.78, 123.24, 123.37, 127.00, 129.66, 130.95, 131.45, 133.79, 140.05, 142.05, 151.67, 160.95; HRMS (CI) calcd for C₁₇H₁₄O₄S (M⁺) 314.0613, found 314.0604.

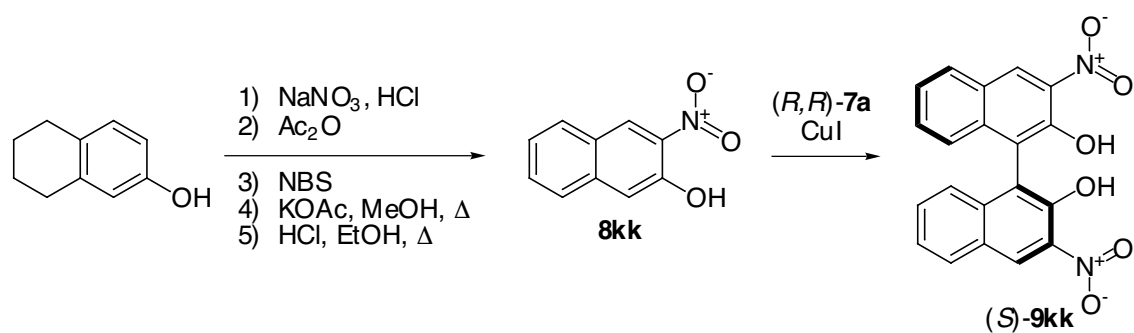
Biaryl coupling was carried out according to the General Procedure with 20 mol% CuI-[(*R,R*)-7a] and 0.097 mmol substrate in 0.2 mL 1:3:1 MeCN:ClCH₂CH₂Cl:DMF at 40 °C using O₂ for 22 h to give the product as a residue in 67% (21 mg, 0.034 mmol) isolated yield and 68% ee: [α]_D²³ = -112 (c 1.0, 68% ee, CHCl₃); IR (thin film) 3389, 3022, 1621, 1285, 1216, 1139, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.40 (s, 6H), 6.27 (s, 2H), 7.04 (d, *J* = 9.0 Hz, 2H), 7.52 (t, *J* = 7.9 Hz, 4H), 7.59 (t, *J* = 7.4 Hz, 2H), 7.82 (d, *J* = 9.0 Hz, 2H), 8.00 (d, *J* = 7.5 Hz, 4H), 8.49 (s, 2H), 8.52 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 55.30, 102.96, 116.82, 118.49, 123.38, 123.54, 127.19, 129.63, 131.74, 132.15, 133.80, 138.83, 142.04, 149.31, 161.39; HRMS (ES) calcd for C₃₄H₂₆O₈S₂ (MNa⁺) 649.0967, found 649.0982.; CSP HPLC (Chiralpak AD, 1.0 mL/min, 70:30:0.1 hexanes:*i*PrOH:TFA) t_R(*S*) = 25.0 min, t_R(*R*) = 45.5 min.



7,7'-Dimethoxy-3,3'-bis(4-methoxybenzenesulfonyl)-1,1'-binaphthalenyl-2,2'-diol (9jj). A solution of 7-methoxy-2-methoxymethylenephthalene²⁷ (3.04 g, 13.7 mmol) and TMEDA (2.0 mL, 13.3 mmol) in dry Et₂O (60 mL) was chilled to -15 °C in an ice-acetone bath and was treated with *n*-BuLi (2.4 M, 6.0 mL, 14.4 mmol) dropwise. The reaction mixture was stirred at -15 °C for 1.5 h and a solution of 4-methoxybenzenesulfonyl fluoride (3.13 g, 16.5 mmol) in dry Et₂O (30 mL) was added. After warming to room temperature, the mixture was stirred for 16 h. The resultant mixture was poured onto ice-H₂O and the aqueous phase was extracted with EtOAc. The combined organic layers were washed with brine, dried over Na₂SO₄, and concentrated *in vacuo*. Chromatography (20-50% EtOAc/hexanes) afforded a clear oil which was dissolved in MeOH (20 mL) and treated with 12 N HCl (5 mL). The pink suspension was stirred overnight, poured onto ice-H₂O and extracted with CH₂Cl₂. The combined organic extracts were washed with H₂O, brine, dried over Na₂SO₄ and concentrated *in vacuo*. Chromatography (CH₂Cl₂) provided 7-methoxy-3-(4-methoxybenzenesulfonyl)naphthalen-2-ol (8jj) in 10% overall yield (472 mg): mp 154.5-155 °C; IR (thin film) 3358, 3019, 2945, 1629, 1293, 1139, 1089, 834, 753 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.84 (s, 3H), 3.91 (s, 3H), 6.94 (s, 1H), 6.97 (d, *J* = 9.0 Hz, 2H), 7.02 (d, *J* = 9.0 Hz, 1H), 7.21 (s, 1H), 7.69 (d, *J* = 9.0 Hz, 1H), 7.92 (d, *J* = 9.0 Hz, 1H), 8.22 (s, 1H), 8.79 (s, 1H); ¹³C NMR (125 MHz, CDCl₃) δ 55.58, 55.85,

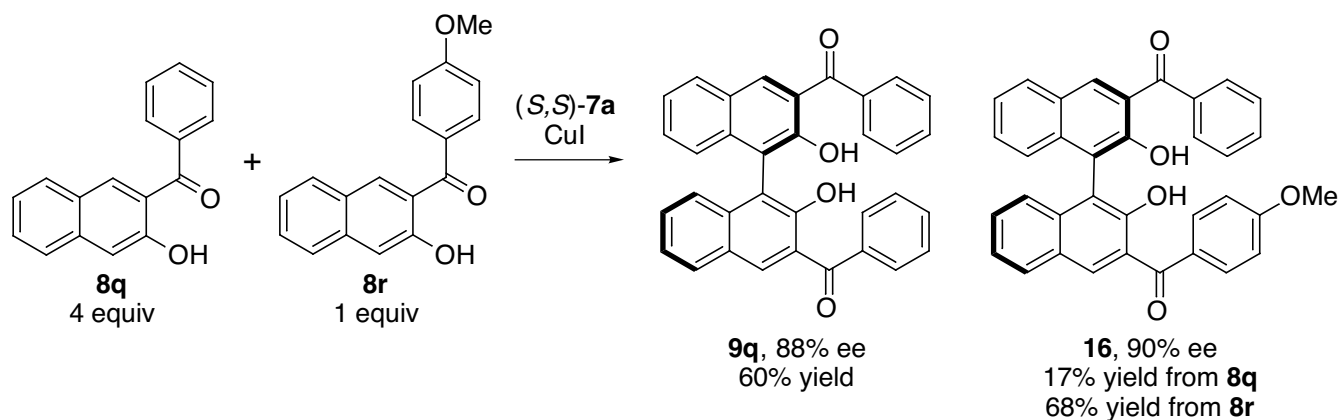
104.16, 112.66, 114.82, 118.60, 123.31, 124.13, 129.28, 130.83, 130.91, 133.47, 139.76, 151.47, 160.74, 163.84; HRMS (CI) calcd for C₁₈H₁₆O₅S (M⁺) 344.0718, found 344.0706.

Biaryl coupling was carried out according to the General Procedure with 20 mol% CuI-[(*S,S*)-7a] and 0.56 mmol substrate in 0.56 mL 1:3:1 MeCN:ClCH₂CH₂Cl:DMF at 40 °C using O₂ for 24 h. Chromatography (0-2% MeOH/CH₂Cl₂) gave the product in 57% (110 mg, 0.160 mmol) isolated yield and 75% ee: [α]_D²⁵ = +141.5 (c 1.0, 75% ee, CHCl₃); IR (thin film) 3412, 3022, 1621, 1262, 1216, 1135, 1089, 749 cm⁻¹; ¹H NMR (500 MHz, CDCl₃) δ 3.42 (s, 6H), 3.85 (s, 6H), 6.28 (s, 2H), 6.96 (d, *J* = 8.9 Hz, 4H), 7.04 (d, *J* = 6.7 Hz, 2H), 7.81 (d, *J* = 9.0 Hz, 2H), 7.93 (d, *J* = 8.9 Hz, 4H), 8.45 (s, 2H), 8.53 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 55.23, 55.92, 103.02, 114.80, 116.79, 118.31, 123.36, 124.42, 129.51, 131.63, 133.46, 138.58, 149.15, 161.18, 163.91; HRMS (ES) calcd for C₃₆H₃₀O₁₀S₂ (MNa⁺) 709.1178, found 709.1166; CSP HPLC (Chiralpak AD, 1.0 mL/min, 70:30:0.1 hexanes:*i*PrOH:TFA) t_R(*S*) = 38.5 min, t_R(*R*) = 70.7 min.



3,3'-Dinitro-[1,1']binaphthalenyl-2,2'-diol (9kk). 3-Nitro-2-naphthol (9kk) was prepared as described previously:²⁸ ¹H NMR (200 MHz, CDCl₃) δ 7.44 (t, *J* = 8.0 Hz, 1H), 7.57 (s, 1H), 7.62 (t, *J* = 8.40 Hz, 1H), 7.75 (d, *J* = 8.40 Hz, 1H), 7.90 (d, *J* = 8.20 Hz, 1H), 8.78 (s, 1H), 9.99 (s, 1H).

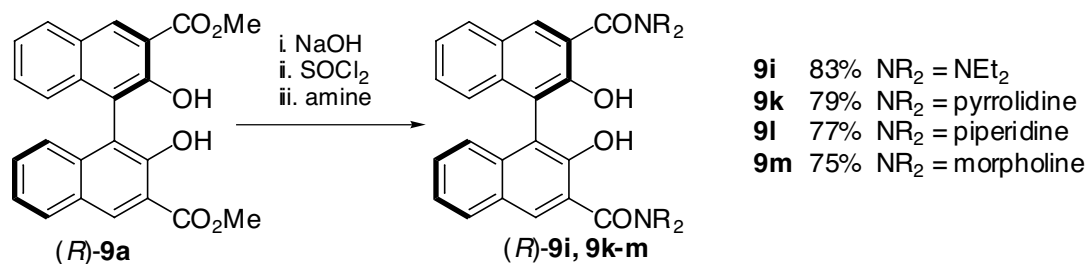
Biaryl coupling was carried out according to the General Procedure with 20 mol% CuI-[(*R,R*)-7a] and 0.520 mmol substrate in 0.52 mL 1:3:1 MeCN:ClCH₂CH₂Cl:DMF at 80 °C using O₂ for 48 h to give the product in 38% (37 mg) isolated yield and 10% ee: ¹H NMR (500 MHz, CDCl₃) δ 7.26 (m, 2H), 7.48 (m, 4H), 8.04 (M, 2H), 9.00 (s, 2H), 10.26 (s, 2H); ¹³C NMR (125 MHz, CDCl₃) δ 147.58, 138.05, 134.90, 131.66, 130.80, 128.06, 126.84, 125.95, 124.81, 119.08; HRMS (ES) calcd for C₂₀H₁₁N₂O₆ (MH⁻) 375.0617 found 375.0604; CSP HPLC (Chiralpak AD, 1.0 mL/min, 70:30:0.1 hexanes:*i*PrOH:TFA) t_R(*S*) = 13.9 min, t_R(*R*) = 19.8 min.



Phenyl ketone cross-coupling. A solution of $\mathbf{8q}$ (21.3 mg, 0.086 mmol) and $\mathbf{8r}$ (5.8 mg, 0.021 mmol) in 3:2 CH_2Cl_2 :MeCN (1 mL) was added via syringe pump (0.6 mL/h) to a stirred solution of CuI -[(*S,S*)- $\mathbf{7a}$] catalyst (0.41 mL, 0.021 M) in CH_2Cl_2 :MeCN (3:2) at 40 °C under O_2 . The reaction mixture was monitored by TLC and after 1 h the pump was turned off. After 4 h, addition was resumed at 0.1 mL/h. After 32 h, 1 N HCl (1 mL) was added, the organic layer was separated and the aqueous layer was extracted three times with CH_2Cl_2 . The combined organic layers were dried over Na_2SO_4 . Preparative TLC (20% EtOAc/hexanes) afforded $\mathbf{8q}$ (3.6 mg), $\mathbf{8r}$ (0.8 mg), $\mathbf{9q}$ (12.8 mg, 88% ee), $\mathbf{9r}$ (0.8 mg, 91% ee), and $\mathbf{16}$ (7.5 mg, 90% ee) as a yellow solid in 68% overall yield from $\mathbf{8r}$ and 17% overall yield from $\mathbf{8q}$: [$\alpha_{\text{D}}^{23} = +47$ (*c* 0.28, 90% ee, CHCl_3); $R_f = 0.17$ (20% EtOAc/hexanes); mp 122-132 °C; IR (thin film) 2917, 1627 cm^{-1} ; ^1H NMR (500 MHz, CDCl_3) δ 11.54 (s, 1H), 11.46 (s, 1H), 8.40 (s, 1H), 8.38 (s, 1H), 7.91 (d, *J* = 8.7 Hz, 2H), 7.89-7.85 (m, 4H), 7.71-7.68 (m, 1H) 7.62-7.59 (m, 2H), 7.42-7.33 (m, 2H), 7.26-7.25 (m, 2H), 7.09 (d, *J* = 8.7 Hz, 2H); ^{13}C NMR (500 MHz, CDCl_3) δ 199.4, 155.3, 153.8, 136.9, 136.1, 133.2, 130.1, 129.6, 127.3, 125.5, 125.2, 124.1, 122.3, 117.8, 111.1, 40.4; HRMS (ES) calcd for $\text{C}_{38}\text{H}_{32}\text{N}_2\text{O}_4$ (M^+) 581.2440, found 581.2438; CSP HPLC (Chiralpak AD; 1.0 mL/min, 70:30 hexanes:*i*PrOH) $t_{\text{R}}(\text{S}) = 11.5$ min, $t_{\text{R}}(\text{R}) = 39.8$ min.

Preparative Synthesis of $\mathbf{9a}$. The catalyst derived from CuI and (*S,S*)- $\mathbf{7a}$ (0.44 g, 1.26 mmol) was dissolved in 2:1 $\text{ClCH}_2\text{CH}_2\text{Cl}$: CH_3CN (100 mL) by sonicating for 5 min. Methyl ester $\mathbf{8a}$ (10.0 g, 50 mmol) and powdered 4Å molecular sieves (5.0 g) were added. After purging with a stream of O_2 for ~5 min, the mixture was stirred for 3 d at 40-45 °C (temperature control is required; at higher temperatures the selectivity decreases slightly) under an O_2 atmosphere. After decanting, the molecular sieve residue was stirred for 30 min with 2:1 CH_2Cl_2 : CH_3CN (50 mL) and the molecular sieves were filtered away. The resultant filtrate was combined with the reaction mixture and was washed with 1 N HCl (20 mL). The aqueous layer was back-extracted with CH_2Cl_2 (2 x 50 mL). The combined organic layers were washed with 1 N HCl (2 x 20 mL), water, and then brine. After drying over Na_2SO_4 , the solvent was removed to provide the crude product (13.4 g) as a reddish brown solid. This material was treated with MeOH (100 mL). Removal of the undissolved $\mathbf{9a}$ by filtration and rinsing with further MeOH (2 x 10 mL) afforded pure $\mathbf{9a}$ (8.06 g, 81%, 93% ee) as a light-brown

solid. Additional product (0.21 g, 2%, 98% ee) was obtained from the filtrate after chromatography (20-80% CH₂Cl₂:hexanes).



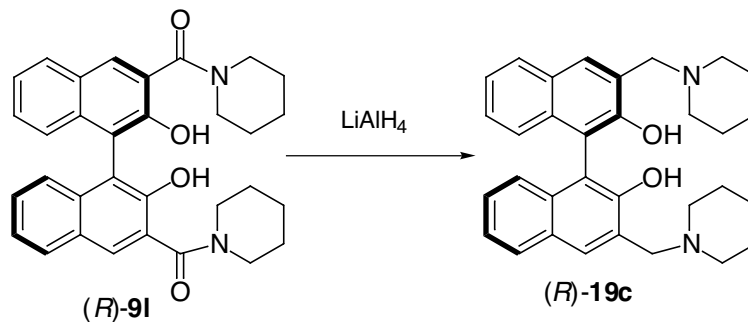
General procedure for the preparation of diamides 9i,k-m from 9a. Ester **9a** (99% ee) was stirred with a mixture of concentrated aqueous NaOH and MeOH (1:1) at room temperature for 4 h. The reaction mixture was acidified (pH < 1), extracted with EtOAc, and concentrated *in vacuo* to give the acid as a yellow solid. The crude acid was treated with SOCl₂ for 4 h at reflux. Removal of the excess SOCl₂ *in vacuo* afforded the crude acyl chloride as a dark brown oil. A solution of this acid chloride in CH₂Cl₂ was then added dropwise to a solution of amine (10 equiv) and DMAP (0.1 equiv) at 0 °C. The reaction mixture was stirred overnight and poured into 1 N HCl. Extraction with CH₂Cl₂, drying with Na₂SO₄, filtration, and concentration gave a crude product. Chromatography (2 % MeOH/CH₂Cl₂) provided the pure amides:

***N, N, N', N'*-Tetraethyl-2, 2'-dihydroxy-1, 1'-binaphthyl-3, 3'-dicarboxamide (9i).** (0.32 g, 83%) The spectral data are identical to that described above from direct biaryl coupling of the corresponding naphthol amide.

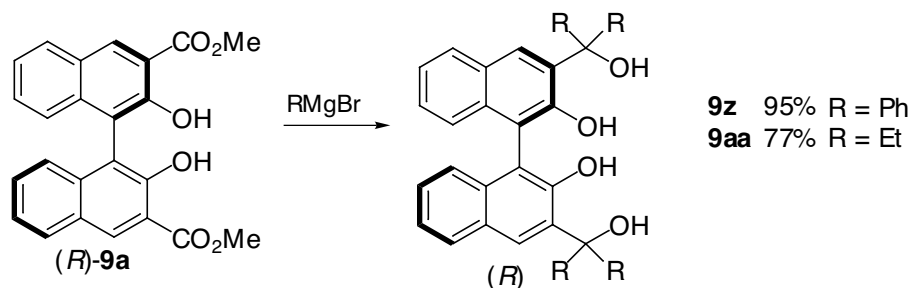
***N, N'*-Dipyrrolidinyl-2, 2'-Dihydroxy-1, 1'-binaphthalenyl-3, 3'-dicarboxamide (9k).** (0.30 g, 79%): $[\alpha]_{\text{D}}^{23} = +102.7$ (*c* 1.0, 99% ee, THF) The spectral data are identical to that described above from direct biaryl coupling of the corresponding naphthol amide.

***N, N'*-Dipiperidinyl-2, 2'-dihydroxy-1, 1'-binaphthyl-3, 3'-dicarboxamide (9l).** (0.31 g, 77%): $[\alpha]_{\text{D}}^{23} = +122.0$ (*c* 1.0, 99% ee, THF) The spectral data are identical to that described above from direct biaryl coupling of the corresponding naphthol amide.

***N, N'*-Dimorpholinyl-2, 2'-dihydroxy-1, 1'-binaphthyl-3, 3'-dicarboxamide (9m).** (0.31 g, 75%): $[\alpha]_{\text{D}}^{23} = +102.5$ (*c* 0.4, 99% ee, THF) The spectral data are identical to that described above from direct biaryl coupling of the corresponding naphthol amide.



3,3'-Bis-(*N,N*-dipiperidinomethyl)-2,2'-dihydroxy-1,1'-binaphthyl (19c). To a solution of (*R*)-**9l** (60 mg, 0.12 mmol) in dry THF (5 mL) at 0 °C was added LiAlH₄ (18 mg, 0.48 mmol). The mixture was heated at reflux for 4 h, cooled to 0 °C, quenched with saturated KF solution (0.10 mL), filtered through Celite, and concentrated. The residue was recrystallized from EtOAc to afford **19c** (34 mg) in 60% yield: ¹H NMR (500 MHz, CDCl₃) δ 7.75 (d, *J* = 8.0 Hz, 2H), 7.61 (s, 2H), 7.25-7.15 (m, 6H), 4.06 (d, *J* = 13.5 Hz, 2H), 3.83 (d, *J* = 13.5 Hz, 2H), 2.58 (m, 8H), 1.57 (m, 8H), 1.45 (m, 4H).



General procedure for the preparation of tetrols 9z and 9aa from 9a. A solution of ester **9a** (99% ee) in benzene was treated with either PhMgBr or EtMgBr (10 equiv) at reflux overnight. The reaction mixture was quenched with 1 N HCl (pH < 1). Extraction with CH₂Cl₂, drying with Na₂SO₄, filtration, and concentration gave a crude product. Chromatography (15-20% EtOAc/hexane) provided the pure alcohols as solids.

3,3'-Bis-(diphenyl-hydroxymethyl)-1,1'-binaphthyl-2,2'-diol (9z). (0.62 g, 95%): [α]_D²³ = +109.0 (*c* 1.0, 99% ee, CH₂Cl₂) The spectral data are identical to that described above from direct biaryl coupling of the corresponding naphthol benzyl alcohols.

3,3'-Di(3-hydroxy-3-pentyl)-1,1'-binaphthyl-2,2'-diol (9aa). (0.35 g, 77%): [α]_D²³ = +96.0 (*c* 1.0, 99% ee, THF) The spectral data are identical to that described above from direct biaryl coupling of the corresponding naphthol benzyl alcohols.

X-Ray structure determination of 9a dimethyl ether. Compound **9a dimethyl ether**, C₂₆H₂₂O₆, crystallizes in the triclinic space group P $\bar{1}$ with a=11.9793(4) Å, b=16.0953(5) Å, c=11.9541(3) Å, α =105.138(2)°, β =97.878(3)°, γ =99.038(2)°, V=2158.59(11) Å³, Z=4 and d_{calc} =1.324 g/cm³. X-ray intensity data were collected on a Rigaku R-Axis IIC area detector employing graphite-monochromated Mo-K α radiation (λ =0.71069 Å) at a temperature of 200 K. Indexing was performed from a series of 1° oscillation images with exposures of 120 seconds per frame. A hemisphere of data was collected using 6° oscillation angles with exposures of 200 seconds per frame and a crystal-to-detector distance of 82 mm. Oscillation images were processed using *bioteX*,²⁹ producing a listing of unaveraged F² and σ (F²) values which were then passed to the *teXsan*³⁰ program package for further processing and structure solution on a Silicon Graphics Indigo R4000 computer. A total of 17223 reflections were measured over the ranges $5.06 \leq 2\theta \leq 50.7^\circ$, $-14 \leq h \leq 14$, $-19 \leq k \leq 19$, $-13 \leq l \leq 14$ yielding 7225 unique reflections ($R_{\text{int}} = 0.0306$). The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (SIR92³¹). Refinement was by full-matrix least squares based on F² using SHELXL-93.³² All reflections were used during refinement (F²'s that were experimentally negative were replaced by F² = 0). The weighting scheme used was $w=1/[\sigma^2(F_o^2) + 0.0722P^2 + 1.1473P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to $R_1=0.0576$ and $wR_2=0.1458$ for 6370 reflections for which $F > 4\sigma(F)$ and $R_1=0.0653$, $wR_2=0.1539$ and GOF = 1.097 for all 7225 unique, non-zero reflections and 586 variables.³³ The maximum Δ/σ in the final cycle of least squares was -0.004 and the two most prominent peaks in the final difference Fourier were +0.425 and -0.259 e/Å³.

Table S1 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S2. Anisotropic thermal parameters are in Table S3. Tables S4 and S5 list bond distances and bond angles. Figures S1 and S2 are ORTEP³⁴ representations of the molecule with 30% probability thermal ellipsoids displayed.

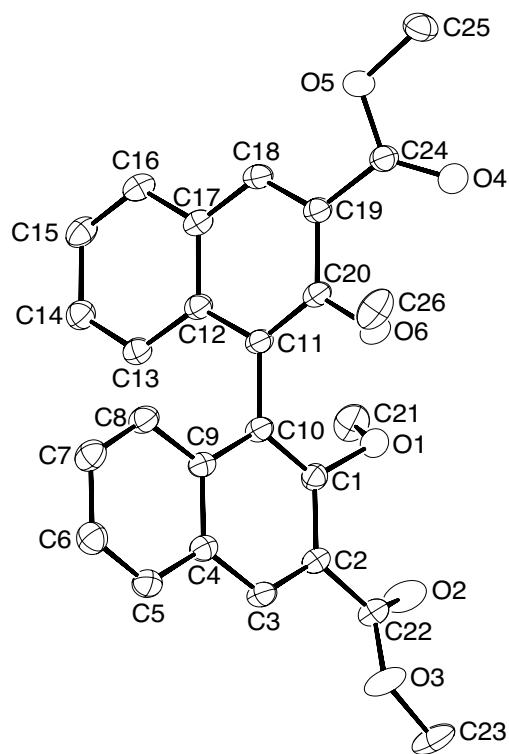


Figure S1. ORTEP drawing of molecule no. 1 of the asymmetric unit with 30% probability thermal ellipsoids.

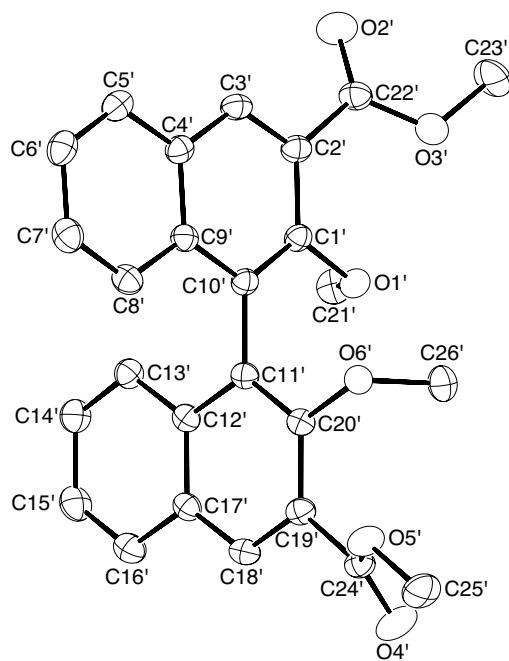


Figure S2. ORTEP drawing of molecule no. 2 of the asymmetric unit with 30% probability thermal ellipsoids.

Table S1. Summary of structure determination of (*R*)-**9a dimethyl ether**.

Formula:	C ₂₆ H ₂₂ O ₆
Formula weight:	430.44
Crystal class:	triclinic
Space group:	PI (#2)
Z	4
Cell constants:	
a	11.9793(4)Å
b	16.0953(5)Å
c	11.9541(3)Å
α	105.138(2)°
β	97.878(3)°
γ	99.038(2)°
V	2158.59(11)Å ³
μ	0.94 cm ⁻¹
crystal size, mm	0.35 x 0.20 x 0.15
D _{calc}	1.324 g/cm ³
F(000)	904
Radiation:	Mo-K _α (λ=0.71069Å)
2θ range	5.06 – 50.7 °
hkl collected:	-14 ≤ h ≤ 14; -19 ≤ k ≤ 19; -13 ≤ l ≤ 14
No. reflections measured:	17223
No. unique reflections:	7225 (R _{int} =0.0306)
No. observed reflections	6370 (F>4σ)
No. reflections used in refinement	7225
No. parameters	586
R indices (F>4σ)	R ₁ =0.0576 wR ₂ =0.1458
R indices (all data)	R ₁ =0.0653 wR ₂ =0.1539
GOF:	1.097
Final Difference Peaks, e/Å ³	+0.425, -0.259

Table S2. Refined positional parameters for **9a dimethyl ether**.

Atom	x	y	z	U_{eq} Å ²
C1	0.2775(2)	0.84891(14)	0.5152(2)	0.0350(5)
C2	0.3626(2)	0.8588(2)	0.4446(2)	0.0362(5)
C3	0.4404(2)	0.8046(2)	0.4358(2)	0.0382(5)
H3	0.4969(2)	0.8116(2)	0.3909(2)	0.051
C4	0.4368(2)	0.7382(2)	0.4935(2)	0.0373(5)
C5	0.5172(2)	0.6818(2)	0.4837(2)	0.0444(6)
H5	0.5730(2)	0.6880(2)	0.4379(2)	0.059
C6	0.5133(2)	0.6188(2)	0.5406(2)	0.0486(6)
H6	0.5663(2)	0.5821(2)	0.5336(2)	0.065
C7	0.4293(2)	0.6092(2)	0.6102(2)	0.0478(6)
H7	0.4272(2)	0.5660(2)	0.6489(2)	0.064
C8	0.3508(2)	0.6623(2)	0.6218(2)	0.0419(6)
H8	0.2963(2)	0.6550(2)	0.6687(2)	0.056
C9	0.3513(2)	0.7284(2)	0.5633(2)	0.0354(5)
C10	0.2714(2)	0.7858(2)	0.5738(2)	0.0356(5)
C11	0.1806(2)	0.7771(2)	0.6471(2)	0.0347(5)
C12	0.0810(2)	0.7082(2)	0.6024(2)	0.0357(5)
C13	0.0601(2)	0.6467(2)	0.4886(2)	0.0399(5)
H13	0.1135(2)	0.6505(2)	0.4395(2)	0.053
C14	-0.0367(2)	0.5823(2)	0.4499(2)	0.0438(6)
H14	-0.0481(2)	0.5427(2)	0.3752(2)	0.058
C15	-0.1195(2)	0.5750(2)	0.5214(2)	0.0464(6)
H15	-0.1856(2)	0.5311(2)	0.4939(2)	0.062
C16	-0.1024(2)	0.6324(2)	0.6311(2)	0.0442(6)
H16	-0.1573(2)	0.6274(2)	0.6783(2)	0.059
C17	-0.0025(2)	0.6996(2)	0.6748(2)	0.0369(5)
C18	0.0154(2)	0.7596(2)	0.7887(2)	0.0371(5)
H18	-0.0382(2)	0.7530(2)	0.8367(2)	0.049
C19	0.1092(2)	0.8271(2)	0.8303(2)	0.0354(5)
C20	0.1941(2)	0.8347(2)	0.7581(2)	0.0355(5)
C21	0.0946(2)	0.8822(2)	0.4634(3)	0.0595(8)
H21a	0.0505(6)	0.9262(7)	0.4886(13)	0.089
H21b	0.0581(7)	0.8276(8)	0.473(2)	0.089
H21c	0.0990(2)	0.8746(14)	0.3818(4)	0.089
C22	0.3657(2)	0.9247(2)	0.3767(2)	0.0403(5)
C23	0.4772(3)	1.0009(2)	0.2738(3)	0.0662(9)
H23a	0.5543(6)	1.0109(13)	0.259(2)	0.099
H23b	0.458(2)	1.0560(6)	0.3116(9)	0.099

H23c	0.425(2)	0.9735(7)	0.2003(8)	0.099
C24	0.1149(2)	0.8934(2)	0.9452(2)	0.0379(5)
C25	0.0469(2)	0.9201(2)	1.1243(2)	0.0509(6)
H25a	0.1205(4)	0.9387(10)	1.1761(7)	0.076
H25b	-0.0079(13)	0.8918(4)	1.1611(9)	0.076
H25c	0.022(2)	0.9703(6)	1.1084(3)	0.076
C26	0.3661(2)	0.8994(2)	0.8987(3)	0.0606(8)
H26a	0.389(2)	0.9577(3)	0.9521(9)	0.091
H26b	0.4326(9)	0.8784(14)	0.8757(4)	0.091
H26c	0.3273(6)	0.8611(11)	0.9370(11)	0.091
O1	0.20778(13)	0.90924(10)	0.5329(2)	0.0419(4)
O2	0.2862(2)	0.9558(2)	0.3462(2)	0.0656(6)
O3	0.4685(2)	0.94407(14)	0.3496(2)	0.0608(6)
O4	0.1606(2)	0.96929(12)	0.9719(2)	0.0656(6)
O5	0.0563(2)	0.85938(12)	1.0154(2)	0.0482(4)
O6	0.29007(13)	0.90086(11)	0.7967(2)	0.0418(4)
C1'	0.2380(2)	0.46148(14)	0.9133(2)	0.0329(5)
C2'	0.2069(2)	0.5429(2)	0.9115(2)	0.0366(5)
C3'	0.0924(2)	0.5442(2)	0.8805(2)	0.0377(5)
H3'	0.0716(2)	0.5967(2)	0.8761(2)	0.050
C4'	0.0059(2)	0.4683(2)	0.8552(2)	0.0357(5)
C5'	-0.1119(2)	0.4699(2)	0.8222(2)	0.0427(6)
H5'	-0.1332(2)	0.5224(2)	0.8180(2)	0.057
C6'	-0.1942(2)	0.3954(2)	0.7965(2)	0.0471(6)
H6'	-0.2710(2)	0.3969(2)	0.7731(2)	0.063
C7'	-0.1633(2)	0.3167(2)	0.8053(2)	0.0473(6)
H7'	-0.2201(2)	0.2663(2)	0.7888(2)	0.063
C8'	-0.0506(2)	0.3128(2)	0.8378(2)	0.0409(5)
H8'	-0.0318(2)	0.2600(2)	0.8438(2)	0.054
C9'	0.0378(2)	0.38827(14)	0.8624(2)	0.0336(5)
C10'	0.1567(2)	0.38605(14)	0.8907(2)	0.0322(5)
C11'	0.1938(2)	0.30077(14)	0.8852(2)	0.0317(5)
C12'	0.2023(2)	0.24464(14)	0.7732(2)	0.0331(5)
C13'	0.1783(2)	0.2682(2)	0.6676(2)	0.0381(5)
H13'	0.1538(2)	0.3206(2)	0.6697(2)	0.051
C14'	0.1908(2)	0.2144(2)	0.5619(2)	0.0439(6)
H14'	0.1755(2)	0.2310(2)	0.4934(2)	0.058
C15'	0.2264(2)	0.1348(2)	0.5562(2)	0.0474(6)
H15'	0.2339(2)	0.0988(2)	0.4841(2)	0.063
C16'	0.2501(2)	0.1101(2)	0.6560(2)	0.0439(6)
H16'	0.2734(2)	0.0570(2)	0.6513(2)	0.058

C17'	0.2398(2)	0.16447(14)	0.7675(2)	0.0341(5)
C18'	0.2665(2)	0.14082(14)	0.8717(2)	0.0367(5)
H18'	0.2903(2)	0.08803(14)	0.8678(2)	0.049
C19'	0.2580(2)	0.19431(14)	0.9791(2)	0.0348(5)
C20'	0.2224(2)	0.27557(14)	0.9850(2)	0.0315(5)
C21'	0.4137(2)	0.4603(2)	0.8451(2)	0.0489(6)
H21a'	0.4917(5)	0.4552(13)	0.8682(7)	0.073
H21b'	0.4131(14)	0.5155(5)	0.8286(11)	0.073
H21c'	0.3774(10)	0.4131(8)	0.7758(5)	0.073
C22'	0.2884(2)	0.6290(2)	0.9429(2)	0.0420(6)
C23'	0.4605(3)	0.7202(2)	1.0604(3)	0.0667(9)
H23a'	0.5293(9)	0.7160(5)	1.108(2)	0.100
H23b'	0.4257(8)	0.7644(4)	1.105(2)	0.100
H23c'	0.479(2)	0.7359(8)	0.9921(3)	0.100
C24'	0.2893(2)	0.1642(2)	1.0844(2)	0.0378(5)
C25'	0.2381(3)	0.1433(2)	1.2592(2)	0.0591(7)
H25a'	0.1722(7)	0.1416(14)	1.2967(11)	0.089
H25b'	0.3030(12)	0.1832(8)	1.3131(9)	0.089
H25c'	0.255(2)	0.0856(6)	1.2364(3)	0.089
C26'	0.3267(2)	0.3742(2)	1.1645(2)	0.0465(6)
H26a'	0.3626(7)	0.3316(3)	1.1909(14)	0.070
H26b'	0.3175(2)	0.4190(8)	1.2316(9)	0.070
H26Fc'	0.3741(6)	0.4004(10)	1.1192(5)	0.070
O1'	0.35247(13)	0.45594(10)	0.93881(14)	0.0385(4)
O2'	0.2713(2)	0.68754(13)	0.9015(2)	0.0683(6)
O3'	0.3806(2)	0.63617(11)	1.0235(2)	0.0503(5)
O4'	0.3731(2)	0.13309(14)	1.1010(2)	0.0595(5)
O5'	0.2139(2)	0.17265(12)	1.1559(2)	0.0469(4)
O6'	0.21641(13)	0.33193(10)	1.09281(13)	0.0357(4)
$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^* \cos g + 2U_{13}aa^*cc^* \cos b + 2U_{23}bb^*cc^* \cos a]$				

Table S3. Refined thermal parameters (U's) for **9a dimethyl ether**.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.0331(11)	0.0316(11)	0.0398(13)	0.0103(10)	0.0070(9)	0.0048(9)
C2	0.0348(11)	0.0360(12)	0.0389(12)	0.0146(10)	0.0090(9)	0.0026(9)
C3	0.0349(12)	0.0414(12)	0.0418(13)	0.0169(11)	0.0123(9)	0.0053(10)
C4	0.0356(12)	0.0372(12)	0.0401(13)	0.0128(10)	0.0096(9)	0.0051(9)
C5	0.0416(13)	0.0433(13)	0.053(2)	0.0160(12)	0.0162(11)	0.0107(10)
C6	0.0472(14)	0.0456(14)	0.057(2)	0.0181(13)	0.0106(12)	0.0164(11)

C7	0.0499(14)	0.0452(14)	0.055(2)	0.0249(13)	0.0098(12)	0.0109(11)
C8	0.0427(13)	0.0423(13)	0.0461(14)	0.0201(11)	0.0123(10)	0.0082(10)
C9	0.0346(11)	0.0355(12)	0.0381(12)	0.0126(10)	0.0109(9)	0.0057(9)
C10	0.0338(11)	0.0364(12)	0.0387(13)	0.0145(10)	0.0100(9)	0.0042(9)
C11	0.0334(11)	0.0359(12)	0.0397(13)	0.0166(10)	0.0120(9)	0.0066(9)
C12	0.0363(12)	0.0364(12)	0.0382(13)	0.0159(10)	0.0098(9)	0.0074(9)
C13	0.0459(13)	0.0385(12)	0.0377(13)	0.0146(11)	0.0107(10)	0.0069(10)
C14	0.0511(14)	0.0397(13)	0.0384(13)	0.0107(11)	0.0074(11)	0.0041(11)
C15	0.0423(13)	0.0435(14)	0.048(2)	0.0155(12)	0.0034(11)	-0.0051(11)
C16	0.0396(13)	0.0462(14)	0.049(2)	0.0193(12)	0.0116(11)	0.0015(10)
C17	0.0341(11)	0.0397(12)	0.0403(13)	0.0182(11)	0.0080(9)	0.0050(9)
C18	0.0365(12)	0.0420(13)	0.0380(13)	0.0173(11)	0.0124(9)	0.0086(10)
C19	0.0348(11)	0.0376(12)	0.0378(12)	0.0155(10)	0.0098(9)	0.0085(9)
C20	0.0328(11)	0.0362(12)	0.0420(13)	0.0184(11)	0.0097(9)	0.0055(9)
C21	0.0373(14)	0.058(2)	0.087(2)	0.028(2)	0.0084(13)	0.0126(12)
C22	0.0365(12)	0.0426(13)	0.0448(14)	0.0196(11)	0.0088(10)	0.0040(10)
C23	0.059(2)	0.080(2)	0.083(2)	0.060(2)	0.025(2)	0.010(2)
C24	0.0366(12)	0.0387(13)	0.0421(14)	0.0154(11)	0.0116(10)	0.0082(10)
C25	0.054(2)	0.058(2)	0.0379(14)	0.0081(12)	0.0139(11)	0.0083(12)
C26	0.043(2)	0.058(2)	0.079(2)	0.034(2)	-0.0096(14)	-0.0023(12)
O1	0.0382(9)	0.0374(9)	0.0540(11)	0.0163(8)	0.0129(7)	0.0098(7)
O2	0.0534(11)	0.084(2)	0.085(2)	0.0586(13)	0.0227(10)	0.0227(11)
O3	0.0465(10)	0.0762(14)	0.085(2)	0.0583(12)	0.0266(10)	0.0145(9)
O4	0.087(2)	0.0411(11)	0.0669(14)	0.0085(10)	0.0382(11)	-0.0005(10)
O5	0.0547(10)	0.0477(10)	0.0394(10)	0.0085(8)	0.0185(8)	0.0010(8)
O6	0.0378(9)	0.0418(9)	0.0442(10)	0.0156(8)	0.0083(7)	-0.0025(7)
C1'	0.0341(11)	0.0343(11)	0.0328(12)	0.0143(10)	0.0058(9)	0.0065(9)
C2'	0.0415(12)	0.0349(12)	0.0377(13)	0.0161(10)	0.0098(9)	0.0084(9)
C3'	0.0461(13)	0.0337(12)	0.0389(13)	0.0158(10)	0.0109(10)	0.0127(10)
C4'	0.0388(12)	0.0393(12)	0.0317(12)	0.0121(10)	0.0082(9)	0.0112(10)
C5'	0.0416(13)	0.0499(14)	0.0414(14)	0.0170(12)	0.0084(10)	0.0160(11)
C6'	0.0356(13)	0.061(2)	0.045(2)	0.0149(13)	0.0058(10)	0.0128(11)
C7'	0.0369(13)	0.0485(14)	0.052(2)	0.0093(12)	0.0086(11)	0.0026(11)
C8'	0.0398(13)	0.0363(12)	0.0449(14)	0.0089(11)	0.0101(10)	0.0052(10)
C9'	0.0384(12)	0.0329(11)	0.0302(11)	0.0088(9)	0.0075(9)	0.0083(9)
C10'	0.0336(11)	0.0322(11)	0.0323(11)	0.0125(9)	0.0061(9)	0.0058(9)
C11'	0.0309(11)	0.0304(11)	0.0350(12)	0.0111(9)	0.0084(8)	0.0046(8)
C12'	0.0315(11)	0.0321(11)	0.0355(12)	0.0097(10)	0.0088(9)	0.0039(9)
C13'	0.0403(12)	0.0391(12)	0.0353(13)	0.0113(10)	0.0079(9)	0.0075(10)
C14'	0.0453(13)	0.0489(14)	0.0378(13)	0.0121(12)	0.0102(10)	0.0089(11)
C15'	0.0505(14)	0.052(2)	0.0368(14)	0.0028(12)	0.0146(11)	0.0120(12)

C16'	0.0447(13)	0.0378(12)	0.048(2)	0.0077(11)	0.0124(11)	0.0090(10)
C17'	0.0319(11)	0.0313(11)	0.0374(12)	0.0068(10)	0.0094(9)	0.0042(9)
C18'	0.0375(12)	0.0298(11)	0.0447(14)	0.0108(10)	0.0122(10)	0.0085(9)
C19'	0.0323(11)	0.0334(11)	0.0418(13)	0.0157(10)	0.0091(9)	0.0053(9)
C20'	0.0308(11)	0.0318(11)	0.0332(12)	0.0092(9)	0.0101(8)	0.0065(8)
C21'	0.0405(13)	0.056(2)	0.054(2)	0.0175(13)	0.0178(11)	0.0096(11)
C22'	0.0445(13)	0.0355(12)	0.049(2)	0.0174(11)	0.0110(11)	0.0075(10)
C23'	0.055(2)	0.040(2)	0.092(2)	0.015(2)	0.004(2)	-0.0120(12)
C24'	0.0371(12)	0.0351(12)	0.0439(14)	0.0154(11)	0.0081(10)	0.0077(9)
C25'	0.080(2)	0.061(2)	0.048(2)	0.0318(14)	0.0135(14)	0.020(2)
C26'	0.0412(13)	0.0497(14)	0.0429(14)	0.0105(12)	0.0052(10)	-0.0004(11)
O1'	0.0330(8)	0.0400(9)	0.0458(10)	0.0192(8)	0.0070(7)	0.0059(7)
O2'	0.0732(14)	0.0446(11)	0.092(2)	0.0397(11)	0.0028(12)	0.0022(10)
O3'	0.0451(10)	0.0357(9)	0.0656(12)	0.0180(9)	0.0019(8)	-0.0028(7)
O4'	0.0485(11)	0.0767(14)	0.0740(14)	0.0462(12)	0.0161(9)	0.0273(10)
O5'	0.0585(11)	0.0555(11)	0.0414(10)	0.0258(9)	0.0196(8)	0.0253(9)
O6'	0.0378(8)	0.0365(8)	0.0327(8)	0.0091(7)	0.0080(6)	0.0080(6)

The form of the anisotropic displacement parameter is:

$$\exp[-2p^2(a^*U_{11}h^2+b^*U_{22}k^2+c^*U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)].$$

Table S4. Bond distances (Å) in **9a dimethyl ether**.

C1-O1	1.372(3)	C1-C10	1.374(3)	C1-C2	1.425(3)
C2-C3	1.370(3)	C2-C22	1.493(3)	C3-C4	1.414(3)
C4-C5	1.419(3)	C4-C9	1.423(3)	C5-C6	1.359(4)
C6-C7	1.406(4)	C7-C8	1.363(3)	C8-C9	1.417(3)
C9-C10	1.427(3)	C10-C11	1.500(3)	C11-C20	1.378(3)
C11-C12	1.427(3)	C12-C13	1.421(3)	C12-C17	1.424(3)
C13-C14	1.363(3)	C14-C15	1.407(4)	C15-C16	1.360(4)
C16-C17	1.415(3)	C17-C18	1.414(3)	C18-C19	1.367(3)
C19-C20	1.432(3)	C19-C24	1.489(3)	C20-O6	1.371(3)
C21-O1	1.427(3)	C22-O2	1.200(3)	C22-O3	1.328(3)
C23-O3	1.448(3)	C24-O4	1.196(3)	C24-O5	1.334(3)
C25-O5	1.440(3)	C26-O6	1.427(3)	C1'-C10'	1.371(3)
C1'-O1'	1.386(3)	C1'-C2'	1.422(3)	C2'-C3'	1.375(3)
C2'-C22'	1.490(3)	C3'-C4'	1.408(3)	C4'-C9'	1.419(3)
C4'-C5'	1.419(3)	C5'-C6'	1.363(4)	C6'-C7'	1.401(4)
C7'-C8'	1.368(3)	C8'-C9'	1.417(3)	C9'-C10'	1.427(3)
C10'-C11'	1.496(3)	C11'-C20'	1.375(3)	C11'-C12'	1.433(3)

C12'-C13'	1.417(3)	C12'-C17'	1.419(3)	C13'-C14'	1.375(3)
C14'-C15'	1.400(4)	C15'-C16'	1.360(4)	C16'-C17'	1.424(3)
C17'-C18'	1.406(3)	C18'-C19'	1.373(3)	C19'-C20'	1.426(3)
C19'-C24'	1.485(3)	C20'-O6'	1.387(3)	C21'-O1'	1.431(3)
C22'-O2'	1.205(3)	C22'-O3'	1.331(3)	C23'-O3'	1.451(3)
C24'-O4'	1.205(3)	C24'-O5'	1.325(3)	C25'-O5'	1.443(3)
C26'-O6'	1.431(3)				

Table S5. Bond angles (deg) in **9a** dimethyl ether.

O1-C1-C10	119.8(2)	O1-C1-C2	118.4(2)	C10-C1-C2	121.5(2)
C3-C2-C1	119.1(2)	C3-C2-C22	119.5(2)	C1-C2-C22	121.3(2)
C2-C3-C4	121.4(2)	C3-C4-C5	121.3(2)	C3-C4-C9	119.1(2)
C5-C4-C9	119.6(2)	C6-C5-C4	120.6(2)	C5-C6-C7	120.0(2)
C8-C7-C6	121.0(2)	C7-C8-C9	120.9(2)	C8-C9-C4	117.9(2)
C8-C9-C10	122.7(2)	C4-C9-C10	119.3(2)	C1-C10-C9	119.5(2)
C1-C10-C11	120.1(2)	C9-C10-C11	120.4(2)	C20-C11-C12	120.1(2)
C20-C11-C10	120.0(2)	C12-C11-C10	119.9(2)	C13-C12-C17	117.5(2)
C13-C12-C11	123.6(2)	C17-C12-C11	118.9(2)	C14-C13-C12	121.3(2)
C13-C14-C15	120.9(2)	C16-C15-C14	119.6(2)	C15-C16-C17	121.1(2)
C18-C17-C16	121.3(2)	C18-C17-C12	119.1(2)	C16-C17-C12	119.6(2)
C19-C18-C17	122.0(2)	C18-C19-C20	118.8(2)	C18-C19-C24	118.6(2)
C20-C19-C24	122.4(2)	O6-C20-C11	118.1(2)	O6-C20-C19	120.9(2)
C11-C20-C19	121.0(2)	O2-C22-O3	122.5(2)	O2-C22-C2	126.0(2)
O3-C22-C2	111.5(2)	O4-C24-O5	122.5(2)	O4-C24-C19	125.8(2)
O5-C24-C19	111.6(2)	C1-O1-C21	116.2(2)	C22-O3-C23	115.7(2)
C24-O5-C25	116.1(2)	C20-O6-C26	115.7(2)	C10'-C1'-O1'	117.5(2)
C10'-C1'-C2'	121.7(2)	O1'-C1'-C2'	120.8(2)	C3'-C2'-C1'	118.5(2)
C3'-C2'-C22'	116.1(2)	C1'-C2'-C22'	125.3(2)	C2'-C3'-C4'	121.8(2)
C3'-C4'-C9'	119.1(2)	C3'-C4'-C5'	121.5(2)	C9'-C4'-C5'	119.5(2)
C6'-C5'-C4'	120.6(2)	C5'-C6'-C7'	120.1(2)	C8'-C7'-C6'	120.9(2)
C7'-C8'-C9'	120.7(2)	C8'-C9'-C4'	118.2(2)	C8'-C9'-C10'	122.5(2)
C4'-C9'-C10'	119.2(2)	C1'-C10'-C9'	119.6(2)	C1'-C10'-C11'	119.7(2)
C9'-C10'-C11'	120.5(2)	C20'-C11'-C12'	119.0(2)	C20'-C11'-C10'	121.8(2)
C12'-C11'-C10'	119.2(2)	C13'-C12'-C17'	118.5(2)	C13'-C12'-C11'	121.8(2)
C17'-C12'-C11'	119.6(2)	C14'-C13'-C12'	120.6(2)	C13'-C14'-C15'	120.8(2)
C16'-C15'-C14'	120.2(2)	C15'-C16'-C17'	120.9(2)	C18'-C17'-C12'	119.4(2)
C18'-C17'-C16'	121.5(2)	C12'-C17'-C16'	119.1(2)	C19'-C18'-C17'	121.2(2)
C18'-C19'-C20'	119.4(2)	C18'-C19'-C24'	117.2(2)	C20'-C19'-C24'	123.4(2)
C11'-C20'-O6'	118.0(2)	C11'-C20'-C19'	121.5(2)	O6'-C20'-C19'	120.5(2)
O2'-C22'-O3'	123.1(2)	O2'-C22'-C2'	123.2(2)	O3'-C22'-C2'	113.7(2)
O4'-C24'-O5'	123.7(2)	O4'-C24'-C19'	123.3(2)	O5'-C24'-C19'	113.0(2)

C1'-O1'-C21'	113.8(2)	C22'-O3'-C23'	115.7(2)	C24'-O5'-C25'	116.0(2)
C20'-O6'-C26'	113.4(2)				

X-Ray structure determination of (R)-9n. Compound (R)-9n, C₃₄H₂₀N₂O₈, crystallizes in the monoclinic space group P2₁ (systematic absences 0k0: k = odd) with a = 12.411(3) Å, b = 7.973(2) Å, c = 13.496(3) Å, β = 95.956(5)°, V = 1328.2(6) Å³, Z = 2 and d_{calc} = 1.462 g/cm³. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at a temperature of 143 K. Indexing was performed from a series of four 0.5° oscillation images with exposures of 5 seconds per frame. A hemisphere of data was collected using 10 second exposures and a crystal-to-detector distance of 35 mm. A total of 440 images were collected: one sweep was performed using φ-scans from -90° to +90° in 0.5° steps at ω = 0° and χ = 0° with a detector swing angle of -10°; a second sweep was done using ω-scans from -20° to +20° in 0.5° steps at χ = -90° and φ = 0° with a detector swing angle of -10°. Oscillation images were processed using CrystalClear,³⁵ producing a listing of unaveraged F² and σ(F²) values which were then passed to the teXsan³⁴ program package for further processing and structure solution on a Silicon Graphics O2 computer. A total of 8126 reflections were measured over the ranges 5.94 ≤ 2θ ≤ 50.7°, -14 ≤ h ≤ 12, -9 ≤ k ≤ 7, -13 ≤ l ≤ 15 yielding 3994 unique reflections (R_{int} = 0.0257). The intensity data were corrected for Lorentz and polarization effects and for absorption using REQAB³⁶ (minimum and maximum transmission 0.733, 1.000).

The structure was solved by direct methods (SIR92³⁵). Refinement was by full-matrix least squares based on F² using SHELXL-93,³⁶ All reflections were used during refinement (F²'s that were experimentally negative were replaced by F² = 0). The weighting scheme used was w=1/[σ²(F_o²)+0.0509P²+0.1282P] where P = (F_o² + 2F_c²)/3. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to R₁ = 0.0367 and wR₁ = 0.0852 for 3607 reflections for which F > 4σ(F) and R₁ = 0.0426, wR₁ = 0.0881 and GOF = 1.031 for all 3994 unique, non-zero reflections and 399 variables.³⁷ The maximum Δ/σ in the final cycle of least squares was 0.001 and the two most prominent peaks in the final difference Fourier were +0.175 and -0.172 e/Å³.

Table S6 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S7. Anisotropic thermal parameters are in Table S8. Tables S9 and S10 list bond distances and bond angles. Figure S3 is an ORTEP³⁸ representation of the molecule with 30% probability thermal ellipsoids displayed.

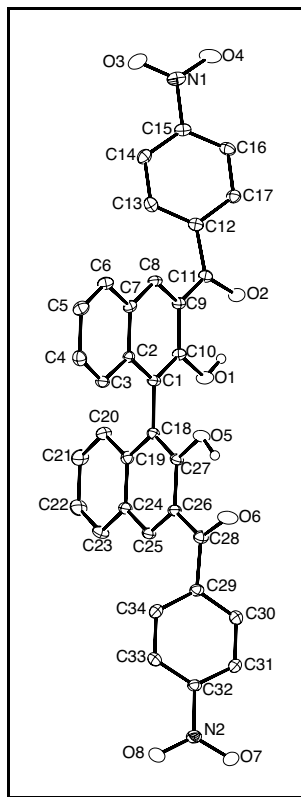


Figure S3. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table S6. Summary of structure determination of (*R*)-**9n**.

Formula:	$C_{34}H_{20}N_2O_8$
Formula weight:	584.52
Crystal class:	monoclinic
Space group:	$P2_1$ (#4)
Z	2
Cell constants:	
a	12.411(3) Å
b	7.973(2) Å
c	13.496(3) Å
β	95.956(5)°
V	1328.2(6) Å ³
μ	1.06 cm ⁻¹
crystal size, mm	0.40 x 0.30 x 0.05
D_{calc}	1.462 g/cm ³
F(000)	604
Radiation:	Mo-K α ($\lambda=0.71069$ Å)

2 θ range	5.94 – 50.7 °
hkl collected:	-14 ≤ h ≤ 12; -9 ≤ k ≤ 7; -13 ≤ l ≤ 15
No. reflections measured:	8126
No. unique reflections:	3994 ($R_{int}=0.0257$)
No. observed reflections	3607 ($F>4\sigma$)
No. reflections used in refinement	3994
No. parameters	399
R indices ($F>4\sigma$)	$R_1=0.0367$ $wR_2=0.0852$
R indices (all data)	$R_1=0.0426$ $wR_2=0.0881$
GOF:	1.031
Final Difference Peaks, e/Å ³	+0.175, -0.172

Table S7. Refined positional parameters for (R)-**9n**.

Atom	x	y	z	U_{eq} Å ²
C1	1.5042(2)	0.2045(3)	0.1754(2)	0.0218(5)
C2	1.5546(2)	0.2216(3)	0.0860(2)	0.0192(5)
C3	1.6677(2)	0.2441(3)	0.0860(2)	0.0244(5)
H3	1.7110(2)	0.2511(3)	0.1464(2)	0.032
C4	1.7144(2)	0.2558(3)	-0.0009(2)	0.0286(6)
H4	1.7891(2)	0.2690(3)	0.0012(2)	0.038
C5	1.6512(2)	0.2482(3)	-0.0940(2)	0.0304(6)
H5	1.6839(2)	0.2566(3)	-0.1528(2)	0.040
C6	1.5425(2)	0.2285(3)	-0.0971(2)	0.0274(5)
H6	1.5009(2)	0.2241(3)	-0.1584(2)	0.036
C7	1.4908(2)	0.2146(3)	-0.0084(2)	0.0212(5)
C8	1.3788(2)	0.1955(3)	-0.0106(2)	0.0230(5)
H8	1.3370(2)	0.1917(3)	-0.0719(2)	0.031
C9	1.3280(2)	0.1820(3)	0.0753(2)	0.0219(5)
C10	1.3941(2)	0.1806(3)	0.1698(2)	0.0222(5)
C11	1.2104(2)	0.1595(3)	0.0716(2)	0.0236(5)
C12	1.1355(2)	0.2071(3)	-0.0190(2)	0.0243(5)
C13	1.1546(2)	0.3422(3)	-0.0801(2)	0.0262(5)
H13	1.2167(2)	0.4068(3)	-0.0663(2)	0.035
C14	1.0810(2)	0.3811(3)	-0.1617(2)	0.0275(5)
H14	1.0935(2)	0.4707(3)	-0.2032(2)	0.037

C15	0.9892(2)	0.2842(3)	-0.1800(2)	0.0252(5)
C16	0.9669(2)	0.1518(3)	-0.1192(2)	0.0288(6)
H16	0.9037(2)	0.0894(3)	-0.1323(2)	0.038
C17	1.0407(2)	0.1146(3)	-0.0385(2)	0.0263(5)
H17	1.0269(2)	0.0264(3)	0.0034(2)	0.035
C18	1.5715(2)	0.2084(3)	0.2742(2)	0.0213(5)
C19	1.5688(2)	0.3496(3)	0.3391(2)	0.0231(5)
C20	1.4977(2)	0.4869(3)	0.3179(2)	0.0283(6)
H20	1.4517(2)	0.4876(3)	0.2590(2)	0.038
C21	1.4958(2)	0.6181(3)	0.3825(2)	0.0353(6)
H21	1.4488(2)	0.7071(3)	0.3665(2)	0.047
C22	1.5638(2)	0.6215(4)	0.4731(2)	0.0351(6)
H22	1.5611(2)	0.7115(4)	0.5166(2)	0.047
C23	1.6330(2)	0.4922(3)	0.4962(2)	0.0298(6)
H23	1.6777(2)	0.4941(3)	0.5560(2)	0.040
C24	1.6383(2)	0.3539(3)	0.4304(2)	0.0233(5)
C25	1.7083(2)	0.2187(3)	0.4544(2)	0.0237(5)
H25	1.7543(2)	0.2220(3)	0.5133(2)	0.032
C26	1.7105(2)	0.0810(3)	0.3928(2)	0.0222(5)
C27	1.6394(2)	0.0770(3)	0.3013(2)	0.0230(5)
C28	1.7800(2)	-0.0624(3)	0.4212(2)	0.0262(5)
C29	1.8600(2)	-0.0569(3)	0.5130(2)	0.0238(5)
C30	1.8451(2)	-0.1634(3)	0.5916(2)	0.0318(6)
H30	1.7823(2)	-0.2275(3)	0.5902(2)	0.042
C31	1.9228(2)	-0.1746(3)	0.6718(2)	0.0310(6)
H31	1.9129(2)	-0.2442(3)	0.7254(2)	0.041
C32	2.0151(2)	-0.0806(3)	0.6708(2)	0.0238(5)
C33	2.0325(2)	0.0281(3)	0.5946(2)	0.0286(6)
H33	2.0959(2)	0.0907(3)	0.5962(2)	0.038
C34	1.9524(2)	0.0406(3)	0.5160(2)	0.0298(6)
H34	1.9607(2)	0.1154(3)	0.4644(2)	0.040
N1	0.9118(2)	0.3217(3)	-0.26771(14)	0.0321(5)
N2	2.1000(2)	-0.0969(3)	0.75509(14)	0.0298(5)
O1	1.34816(12)	0.1562(3)	0.25597(11)	0.0332(4)
H1	1.2841(7)	0.132(4)	0.24294(11)	0.050
O2	1.16827(12)	0.1025(2)	0.14377(11)	0.0336(4)
O3	0.9362(2)	0.4309(3)	-0.32495(13)	0.0463(5)
O4	0.82754(14)	0.2412(3)	-0.27916(12)	0.0464(5)
O5	1.64077(13)	-0.0567(2)	0.23935(11)	0.0308(4)
H5a	1.683(2)	-0.128(2)	0.2649(9)	0.046
O6	1.7757(2)	-0.1933(2)	0.37239(12)	0.0426(5)

O7	2.08675(14)	-0.2038(3)	0.81891(13)	0.0426(5)
O8	2.17803(14)	-0.0029(3)	0.75913(13)	0.0414(5)
$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$				

Table S8. Refined thermal parameters (U's) for (R)-**9n**.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.0227(12)	0.0213(13)	0.0202(12)	-0.0025(9)	-0.0037(8)	0.0026(10)
C2	0.0227(11)	0.0145(12)	0.0197(11)	0.0003(9)	-0.0016(8)	0.0032(9)
C3	0.0243(12)	0.0252(14)	0.0223(12)	-0.0007(10)	-0.0043(8)	0.0004(10)
C4	0.0210(11)	0.029(2)	0.0358(13)	0.0005(11)	0.0043(9)	0.0001(11)
C5	0.0303(13)	0.037(2)	0.0246(13)	0.0031(11)	0.0064(9)	0.0041(12)
C6	0.0290(12)	0.033(2)	0.0200(12)	-0.0011(10)	0.0012(9)	0.0042(11)
C7	0.0230(11)	0.0208(13)	0.0198(11)	0.0006(10)	0.0019(8)	0.0054(10)
C8	0.0236(11)	0.0247(13)	0.0192(11)	-0.0006(9)	-0.0047(8)	0.0042(10)
C9	0.0232(11)	0.0232(13)	0.0189(12)	-0.0014(9)	0.0001(8)	0.0020(10)
C10	0.0221(11)	0.0267(14)	0.0178(12)	-0.0006(9)	0.0012(8)	0.0018(10)
C11	0.0234(12)	0.0259(14)	0.0213(12)	-0.0024(10)	0.0015(9)	0.0007(10)
C12	0.0215(11)	0.0297(14)	0.0218(12)	-0.0040(10)	0.0030(8)	0.0029(10)
C13	0.0212(11)	0.0239(13)	0.0335(13)	-0.0028(10)	0.0029(9)	0.0010(10)
C14	0.0319(13)	0.0228(14)	0.0281(13)	0.0022(10)	0.0046(10)	0.0063(11)
C15	0.0230(12)	0.0310(14)	0.0213(11)	-0.0038(10)	0.0006(8)	0.0097(10)
C16	0.0200(11)	0.040(2)	0.0263(12)	-0.0033(11)	0.0005(9)	-0.0029(11)
C17	0.0233(12)	0.034(2)	0.0222(12)	0.0019(11)	0.0033(9)	-0.0013(11)
C18	0.0182(11)	0.0248(13)	0.0203(11)	0.0011(9)	-0.0008(8)	-0.0023(10)
C19	0.0217(11)	0.0255(13)	0.0223(12)	0.0017(10)	0.0038(8)	-0.0005(10)
C20	0.0296(13)	0.031(2)	0.0234(13)	0.0012(10)	-0.0017(9)	0.0034(11)
C21	0.0393(14)	0.029(2)	0.0364(14)	-0.0024(12)	0.0000(10)	0.0114(13)
C22	0.0416(14)	0.029(2)	0.0343(14)	-0.0103(12)	0.0017(10)	0.0042(13)
C23	0.0308(13)	0.033(2)	0.0242(13)	-0.0096(10)	-0.0033(9)	-0.0008(11)
C24	0.0237(11)	0.0249(13)	0.0207(12)	-0.0013(10)	-0.0014(8)	-0.0006(10)
C25	0.0243(11)	0.0283(14)	0.0178(11)	-0.0021(10)	-0.0019(8)	-0.0032(10)
C26	0.0213(11)	0.0248(13)	0.0196(11)	0.0004(9)	-0.0025(8)	0.0006(10)
C27	0.0238(12)	0.0264(14)	0.0180(11)	-0.0034(10)	-0.0012(8)	-0.0032(10)
C28	0.0281(13)	0.0272(14)	0.0228(12)	-0.0036(11)	-0.0001(9)	0.0019(11)
C29	0.0218(12)	0.0232(13)	0.0251(12)	0.0003(10)	-0.0031(9)	0.0050(10)
C30	0.0271(13)	0.033(2)	0.0343(14)	0.0064(11)	-0.0024(10)	-0.0073(11)
C31	0.0315(14)	0.033(2)	0.0279(13)	0.0092(11)	-0.0016(9)	-0.0057(12)
C32	0.0246(12)	0.0224(13)	0.0231(12)	-0.0007(10)	-0.0043(9)	0.0038(10)
C33	0.0239(12)	0.030(2)	0.0313(13)	0.0010(11)	-0.0018(9)	-0.0046(11)
C34	0.0319(13)	0.030(2)	0.0274(13)	0.0075(11)	0.0004(9)	-0.0016(11)

N1	0.0326(12)	0.0392(14)	0.0242(11)	-0.0035(10)	0.0008(8)	0.0126(11)
N2	0.0298(11)	0.0265(12)	0.0308(11)	0.0012(9)	-0.0071(8)	0.0044(10)
O1	0.0251(8)	0.0535(13)	0.0207(8)	0.0032(8)	0.0019(6)	-0.0027(9)
O2	0.0263(8)	0.0505(12)	0.0240(9)	0.0057(8)	0.0022(6)	-0.0051(8)
O3	0.0577(13)	0.0445(13)	0.0347(11)	0.0103(10)	-0.0052(9)	0.0079(10)
O4	0.0270(10)	0.073(2)	0.0365(10)	-0.0025(10)	-0.0071(7)	0.0035(10)
O5	0.0358(10)	0.0258(10)	0.0278(9)	-0.0086(7)	-0.0109(7)	0.0072(8)
O6	0.0489(11)	0.0332(12)	0.0407(10)	-0.0112(9)	-0.0193(8)	0.0154(9)
O7	0.0439(11)	0.0397(12)	0.0403(10)	0.0140(9)	-0.0145(8)	-0.0044(9)
O8	0.0298(10)	0.0422(12)	0.0485(11)	0.0060(9)	-0.0140(8)	-0.0068(9)

The form of the anisotropic displacement parameter is:
 $\exp[-2p^2(a^*U_{11}h^2+b^*U_{22}k^2+c^*U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)]$.

Table S9. Bond distances (Å) in (*R*)-**9n**.

C1-C10	1.374(3)	C1-C2	1.423(3)	C1-C18	1.499(3)
C2-C3	1.415(3)	C2-C7	1.430(3)	C3-C4	1.365(3)
C4-C5	1.412(3)	C5-C6	1.355(3)	C6-C7	1.419(3)
C7-C8	1.397(3)	C8-C9	1.380(3)	C9-C10	1.442(3)
C9-C11	1.466(3)	C10-O1	1.361(2)	C11-O2	1.239(3)
C11-C12	1.506(3)	C12-C17	1.390(3)	C12-C13	1.392(3)
C13-C14	1.391(3)	C14-C15	1.378(3)	C15-C16	1.383(3)
C15-N1	1.476(3)	C16-C17	1.381(3)	C18-C27	1.370(3)
C18-C19	1.429(3)	C19-C20	1.416(3)	C19-C24	1.429(3)
C20-C21	1.363(3)	C21-C22	1.412(3)	C22-C23	1.358(4)
C23-C24	1.422(3)	C24-C25	1.400(3)	C25-C26	1.379(3)
C26-C27	1.442(3)	C26-C28	1.459(3)	C27-O5	1.356(3)
C28-O6	1.232(3)	C28-C29	1.505(3)	C29-C34	1.383(3)
C29-C30	1.386(3)	C30-C31	1.375(3)	C31-C32	1.371(3)
C32-C33	1.378(3)	C32-N2	1.474(3)	C33-C34	1.380(3)
N1-O4	1.223(3)	N1-O3	1.223(3)	N2-O8	1.221(3)
N2-O7	1.235(3)				

Table S10. Bond angles (deg) in (*R*)-**9n**.

C10-C1-C2	119.3(2)	C10-C1-C18	120.8(2)	C2-C1-C18	119.9(2)
C3-C2-C1	122.4(2)	C3-C2-C7	117.5(2)	C1-C2-C7	120.1(2)
C4-C3-C2	121.2(2)	C3-C4-C5	121.0(2)	C6-C5-C4	119.4(2)
C5-C6-C7	121.3(2)	C8-C7-C6	121.8(2)	C8-C7-C2	118.7(2)
C6-C7-C2	119.5(2)	C9-C8-C7	122.1(2)	C8-C9-C10	118.4(2)
C8-C9-C11	121.4(2)	C10-C9-C11	120.1(2)	O1-C10-C1	118.3(2)
O1-C10-C9	120.4(2)	C1-C10-C9	121.3(2)	O2-C11-C9	121.2(2)

O2-C11-C12	117.1(2)	C9-C11-C12	121.7(2)	C17-C12-C13	119.4(2)
C17-C12-C11	117.3(2)	C13-C12-C11	123.2(2)	C14-C13-C12	120.2(2)
C15-C14-C13	118.7(2)	C14-C15-C16	122.3(2)	C14-C15-N1	119.2(2)
C16-C15-N1	118.5(2)	C17-C16-C15	118.3(2)	C16-C17-C12	121.0(2)
C27-C18-C19	119.5(2)	C27-C18-C1	119.5(2)	C19-C18-C1	121.0(2)
C20-C19-C24	117.7(2)	C20-C19-C18	122.6(2)	C24-C19-C18	119.7(2)
C21-C20-C19	121.0(2)	C20-C21-C22	121.3(2)	C23-C22-C21	119.4(2)
C22-C23-C24	121.0(2)	C25-C24-C23	121.3(2)	C25-C24-C19	119.1(2)
C23-C24-C19	119.6(2)	C26-C25-C24	121.6(2)	C25-C26-C27	119.0(2)
C25-C26-C28	121.0(2)	C27-C26-C28	120.0(2)	O5-C27-C18	118.9(2)
O5-C27-C26	120.0(2)	C18-C27-C26	121.1(2)	O6-C28-C26	122.1(2)
O6-C28-C29	117.0(2)	C26-C28-C29	120.9(2)	C34-C29-C30	119.8(2)
C34-C29-C28	121.0(2)	C30-C29-C28	118.9(2)	C31-C30-C29	120.2(2)
C32-C31-C30	118.4(2)	C31-C32-C33	123.1(2)	C31-C32-N2	118.4(2)
C33-C32-N2	118.5(2)	C32-C33-C34	117.6(2)	C33-C34-C29	120.7(2)
O4-N1-O3	123.9(2)	O4-N1-C15	118.2(2)	O3-N1-C15	117.9(2)
O8-N2-O7	123.7(2)	O8-N2-C32	118.7(2)	O7-N2-C32	117.6(2)

X-Ray structure determination of (R)-9ff. Compound (R)-9ff, $C_{32}H_{22}S_2O_6$, crystallizes in the orthorhombic space group $P2_12_12_1$ (systematic absences $h00: h=\text{odd}$, $0k0: k=\text{odd}$, and $00l: l=\text{odd}$) with $a=5.4580(14)$ Å, $b=11.817(4)$ Å, $c=41.798(13)$ Å, $V=2695.9(14)$ Å³, $Z=4$ and $d_{\text{calc}}=1.396$ g/cm³. X-ray intensity data were collected on a Rigaku Mercury CCD area detector employing graphite-monochromated Mo-K α radiation ($\lambda=0.71069$ Å) at a temperature of 143 K. Indexing was performed from a series of four 0.5° oscillation images with exposures of 30 seconds per frame. A hemisphere of data was collected using 60 second exposures and a crystal-to-detector distance of 35 mm. A total of 440 images were collected: one sweep was performed using ϕ -scans from -90° to +90° in 0.5° steps at $\omega = 0^\circ$ and $\chi = 0^\circ$ with a detector swing angle of -10°; a second sweep was done using ω -scans from -20° to +20° in 0.5° steps at $\chi = -90^\circ$ and $\phi = 0^\circ$ with a detector swing angle of -10°. Oscillation images were processed using CrystalClear,³⁹ producing a listing of unaveraged F^2 and $\sigma(F^2)$ values which were then passed to the teXsan³⁴ program package for further processing and structure solution on a Silicon Graphics O2 computer. A total of 16558 reflections were measured over the ranges $5.2 \leq 2\theta \leq 50.68^\circ$, $-6 \leq h \leq 5$, $-14 \leq k \leq 12$, $-38 \leq l \leq 50$ yielding 4759 unique reflections ($R_{\text{int}} = 0.1135$). The intensity data were corrected for Lorentz and polarization effects and for absorption, using REQAB⁴⁰ (minimum and maximum transmission 0.557, 1.000).

The structure was solved by direct methods (SIR92³⁵). Refinement was by full-matrix least squares based on F^2 using SHELXL-93.³⁶ All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w=1/[\sigma^2(F_o^2) + 0.0863P^2 + 0.0000P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and

hydrogen atoms were refined using a “riding” model. Refinement converged to $R_1=0.0850$ and $wR_2=0.1704$ for 3371 reflections for which $F > 4\sigma(F)$ and $R_1=0.1324$, $wR_2=0.2427$ and $GOF = 1.073$ for all 4756 unique, non-zero reflections and 361 variables.³⁷ The maximum Δ/σ in the final cycle of least squares was 0.013 and the two most prominent peaks in the final difference Fourier were $+0.425$ and $-0.482 e/\text{\AA}^3$.

Table S11 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S12. Anisotropic thermal parameters are in Table S13. Tables S14 and S15 list bond distances and bond angles. Figure S4 is an ORTEP³⁸ representation of the molecule with 30% probability thermal ellipsoids displayed.

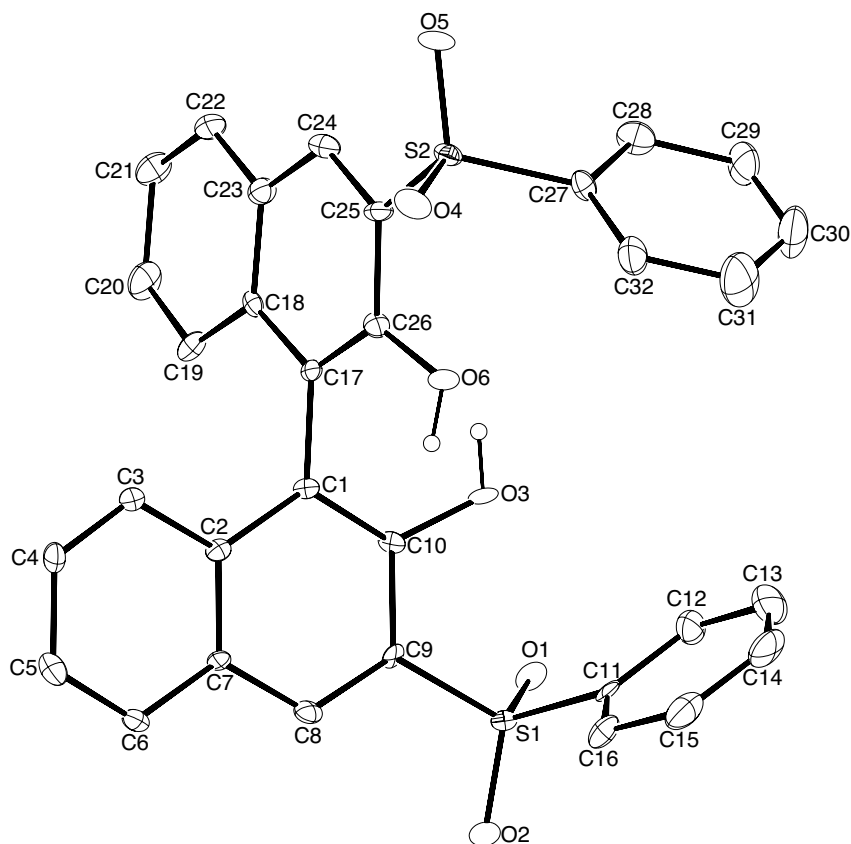


Figure S4. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table S11. Summary of structure determination of (*R*)-**9ff**.

Formula:	$C_{32}H_{22}S_2O_6$
Formula weight:	566.62
Crystal class:	orthorhombic
Space group:	$P2_12_12_1$ (#19)

Z	4
Cell constants:	
a	5.4580(14)Å
b	11.817(4)Å
c	41.798(13)Å
V	2695.9(14)Å ³
μ	2.43 cm ⁻¹
crystal size, mm	0.42 x 0.01 x 0.01
D _{calc}	1.396 g/cm ³
F(000)	1176
Radiation:	Mo-K α (λ =0.71069Å)
2 θ range	5.2 – 50.68 °
hkl collected:	-6 \leq h \leq 5; -14 \leq k \leq 12; -38 \leq l \leq 50
No. reflections measured:	16558
No. unique reflections:	4759 (R _{int} =0.1135)
No. observed reflections	3371 (F>4 σ)
No. reflections used in refinement	4756
No. parameters	361
R indices (F>4 σ)	R ₁ =0.0850 wR ₂ =0.1704
R indices (all data)	R ₁ =0.1324 wR ₂ =0.2427
GOF:	1.073
Final Difference Peaks, e/Å ³	+0.425, -0.482

Table S12. Refined positional parameters for (R)-**9ff**.

Atom	x	y	z	U _{eq} , Å ²
C1	0.6749(10)	0.5070(5)	0.3643(2)	0.0131(14)
C2	0.7916(11)	0.4198(6)	0.3452(2)	0.014(2)
C3	0.9843(12)	0.3520(6)	0.3583(2)	0.021(2)
H3	1.0291(12)	0.3604(6)	0.3796(2)	0.028
C4	1.1000(13)	0.2764(6)	0.3398(2)	0.025(2)
H4	1.2264(13)	0.2338(6)	0.3486(2)	0.033
C5	1.0369(14)	0.2592(7)	0.3075(2)	0.032(2)
H5	1.1192(14)	0.2056(7)	0.2953(2)	0.042
C6	0.8497(13)	0.3236(6)	0.2943(2)	0.026(2)

H6	0.8035(13)	0.3127(6)	0.2731(2)	0.035
C7	0.7305(11)	0.4052(5)	0.3131(2)	0.014(2)
C8	0.5523(12)	0.4777(6)	0.2992(2)	0.020(2)
H8	0.5081(12)	0.4674(6)	0.2780(2)	0.026
C9	0.4444(11)	0.5622(6)	0.3165(2)	0.015(2)
C10	0.5150(10)	0.5776(6)	0.3494(2)	0.013(2)
C11	0.3781(12)	0.7880(6)	0.2996(2)	0.020(2)
C12	0.280(2)	0.8721(6)	0.3189(2)	0.035(2)
H12	0.140(2)	0.8606(6)	0.3311(2)	0.046
C13	0.407(2)	0.9759(8)	0.3191(2)	0.052(3)
H13	0.355(2)	1.0336(8)	0.3326(2)	0.069
C14	0.605(2)	0.9935(8)	0.2998(2)	0.048(3)
H14	0.680(2)	1.0641(8)	0.2995(2)	0.064
C15	0.693(2)	0.9091(8)	0.2810(2)	0.042(2)
H15	0.830(2)	0.9214(8)	0.2682(2)	0.056
C16	0.5792(12)	0.8051(7)	0.2812(2)	0.025(2)
H16	0.6401(12)	0.7466(7)	0.2686(2)	0.033
C17	0.7401(11)	0.5292(6)	0.3984(2)	0.014(2)
C18	0.6524(11)	0.4590(6)	0.4238(2)	0.014(2)
C19	0.4912(12)	0.3687(6)	0.4180(2)	0.024(2)
H19	0.4544(12)	0.3487(6)	0.3970(2)	0.032
C20	0.3851(14)	0.3085(7)	0.4431(2)	0.035(2)
H20	0.2727(14)	0.2514(7)	0.4388(2)	0.046
C21	0.4481(14)	0.3342(7)	0.4752(2)	0.036(2)
H21	0.3792(14)	0.2938(7)	0.4920(2)	0.047
C22	0.613(2)	0.4199(7)	0.4810(2)	0.033(2)
H22	0.658(2)	0.4355(7)	0.5020(2)	0.044
C23	0.7152(12)	0.4846(6)	0.4561(2)	0.022(2)
C24	0.8748(11)	0.5762(6)	0.4628(2)	0.021(2)
H24	0.9197(11)	0.5921(6)	0.4838(2)	0.028
C25	0.9635(12)	0.6420(6)	0.4380(2)	0.019(2)
C26	0.8821(11)	0.6214(6)	0.4056(2)	0.018(2)
C27	1.0331(13)	0.8783(6)	0.4361(2)	0.021(2)
C28	0.8446(13)	0.9161(7)	0.4543(2)	0.033(2)
H28	0.7909(13)	0.8752(7)	0.4720(2)	0.044
C29	0.733(2)	1.0191(7)	0.4458(2)	0.042(2)
H29	0.603(2)	1.0465(7)	0.4580(2)	0.056
C30	0.808(2)	1.0778(8)	0.4206(3)	0.057(3)
H30	0.729(2)	1.1447(8)	0.4151(3)	0.075
C31	1.009(2)	1.0398(8)	0.4019(3)	0.064(3)
H31	1.065(2)	1.0822(8)	0.3846(3)	0.086

C32	1.122(2)	0.9379(7)	0.4099(2)	0.046(2)
H32	1.253(2)	0.9105(7)	0.3980(2)	0.061
S1	0.2310(3)	0.6537(2)	0.29893(4)	0.0188(4)
S2	1.1771(3)	0.7487(2)	0.44636(4)	0.0196(4)
O1	0.0126(8)	0.6601(4)	0.31804(11)	0.0222(12)
O2	0.1980(10)	0.6202(4)	0.26578(12)	0.0308(13)
O3	0.4098(9)	0.6688(4)	0.36332(11)	0.0279(13)
H3a	0.4584(9)	0.6745(4)	0.38181(11)	0.042
O4	1.3910(8)	0.7324(5)	0.42605(12)	0.0272(13)
O5	1.2185(8)	0.7491(4)	0.48054(11)	0.0272(11)
O6	0.9534(8)	0.7001(4)	0.38412(11)	0.0220(12)
H6a	0.9203(8)	0.6782(4)	0.36601(11)	0.033
$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$				

Table S13. Refined thermal parameters (U's) for (R)-**9ff**.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.008(3)	0.020(4)	0.011(4)	0.000(3)	0.000(3)	-0.001(3)
C2	0.011(3)	0.017(4)	0.015(4)	0.001(3)	-0.003(3)	-0.004(3)
C3	0.027(4)	0.020(4)	0.016(4)	-0.001(3)	-0.005(3)	0.004(3)
C4	0.030(4)	0.017(4)	0.029(5)	-0.002(4)	-0.006(3)	0.008(3)
C5	0.044(4)	0.020(4)	0.032(5)	-0.008(4)	-0.001(3)	0.000(4)
C6	0.037(4)	0.025(5)	0.016(4)	-0.007(4)	-0.005(3)	0.011(3)
C7	0.019(4)	0.015(4)	0.008(4)	0.003(3)	0.004(3)	-0.002(3)
C8	0.026(4)	0.018(4)	0.016(4)	-0.002(3)	-0.004(3)	-0.009(3)
C9	0.020(4)	0.013(4)	0.011(4)	0.008(3)	0.007(3)	0.000(3)
C10	0.006(3)	0.021(4)	0.012(4)	-0.003(3)	0.004(3)	0.000(3)
C11	0.027(4)	0.018(4)	0.014(4)	0.007(3)	-0.011(3)	0.003(3)
C12	0.054(5)	0.022(4)	0.028(5)	0.003(4)	0.007(4)	0.001(4)
C13	0.086(7)	0.026(5)	0.045(7)	-0.006(5)	-0.001(6)	-0.007(5)
C14	0.076(7)	0.027(5)	0.041(6)	0.020(5)	-0.015(5)	-0.016(5)
C15	0.048(5)	0.040(6)	0.038(6)	0.017(5)	-0.010(4)	-0.004(5)
C16	0.014(4)	0.032(5)	0.029(5)	0.012(4)	-0.002(3)	0.006(3)
C17	0.014(3)	0.017(4)	0.012(4)	0.000(3)	0.000(3)	0.008(3)
C18	0.009(3)	0.013(4)	0.021(4)	-0.004(3)	-0.002(3)	0.003(3)
C19	0.022(4)	0.027(5)	0.024(5)	0.008(4)	-0.004(3)	0.005(3)
C20	0.039(5)	0.027(5)	0.038(6)	0.011(4)	0.002(4)	-0.009(3)
C21	0.048(5)	0.034(5)	0.024(5)	0.013(4)	0.007(4)	-0.003(4)
C22	0.057(5)	0.027(5)	0.015(4)	0.004(4)	0.000(4)	0.002(4)
C23	0.024(4)	0.024(4)	0.019(4)	0.002(3)	0.001(3)	0.002(3)
C24	0.013(4)	0.032(5)	0.017(4)	-0.007(4)	-0.001(3)	0.005(3)

C25	0.019(4)	0.028(4)	0.010(4)	-0.002(3)	-0.001(3)	0.005(3)
C26	0.015(4)	0.019(4)	0.021(4)	-0.003(3)	-0.006(3)	0.000(3)
C27	0.023(4)	0.015(4)	0.026(5)	-0.003(3)	0.003(3)	-0.003(3)
C28	0.028(4)	0.041(5)	0.030(5)	-0.003(4)	0.006(4)	-0.002(4)
C29	0.038(5)	0.037(5)	0.050(6)	-0.002(5)	0.007(5)	0.020(4)
C30	0.069(7)	0.029(5)	0.071(8)	0.011(5)	0.006(6)	0.012(5)
C31	0.086(8)	0.037(6)	0.070(8)	0.014(6)	0.025(6)	-0.005(6)
C32	0.077(7)	0.023(5)	0.037(6)	0.002(5)	0.008(5)	0.006(5)
S1	0.0244(9)	0.0198(9)	0.0123(9)	-0.0004(8)	-0.0038(7)	0.0017(7)
S2	0.0209(9)	0.0220(9)	0.0159(9)	-0.0060(9)	-0.0033(7)	0.0002(8)
O1	0.013(2)	0.031(3)	0.022(3)	0.006(2)	-0.001(2)	0.004(2)
O2	0.045(3)	0.027(3)	0.020(3)	-0.001(2)	-0.013(2)	0.002(2)
O3	0.043(3)	0.032(3)	0.008(3)	-0.001(2)	-0.009(2)	0.014(2)
O4	0.019(3)	0.034(3)	0.028(3)	-0.009(3)	-0.001(2)	-0.008(2)
O5	0.034(3)	0.033(3)	0.015(3)	-0.007(3)	-0.009(2)	-0.009(3)
O6	0.033(3)	0.021(3)	0.011(3)	0.001(2)	-0.001(2)	-0.011(2)

The form of the anisotropic displacement parameter is:

$$\exp[-2p^2(a^*U_{11}h^2+b^*U_{22}k^2+c^*U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)].$$

Table S14. Bond distances (Å) in (*R*)-**9ff**.

C1-C10	1.359(9)	C1-C2	1.451(9)	C1-C17	1.491(9)
C2-C7	1.393(9)	C2-C3	1.431(9)	C3-C4	1.339(10)
C4-C5	1.409(10)	C5-C6	1.388(10)	C6-C7	1.404(9)
C7-C8	1.420(9)	C8-C9	1.366(10)	C9-C10	1.438(9)
C9-S1	1.751(7)	C10-O3	1.354(8)	C11-C16	1.357(10)
C11-C12	1.387(10)	C11-S1	1.779(7)	C12-C13	1.408(12)
C13-C14	1.363(13)	C14-C15	1.358(13)	C15-C16	1.377(11)
C17-C26	1.371(9)	C17-C18	1.429(9)	C18-C19	1.404(9)
C18-C23	1.429(10)	C19-C20	1.394(10)	C20-C21	1.418(11)
C21-C22	1.374(11)	C22-C23	1.407(10)	C23-C24	1.417(10)
C24-C25	1.382(10)	C25-C26	1.445(10)	C25-S2	1.753(7)
C26-O6	1.350(8)	C27-C28	1.357(10)	C27-C32	1.388(11)
C27-S2	1.773(7)	C28-C29	1.409(11)	C29-C30	1.327(13)
C30-C31	1.418(13)	C31-C32	1.393(13)	S1-O1	1.437(5)
S1-O2	1.452(5)	S2-O5	1.446(5)	S2-O4	1.456(5)

Table S15. Bond angles (deg) in (*R*)-**9ff**.

C10-C1-C2	117.6(6)	C10-C1-C17	119.0(6)	C2-C1-C17	123.1(5)
C7-C2-C3	118.3(6)	C7-C2-C1	120.9(6)	C3-C2-C1	120.6(6)
C4-C3-C2	120.0(7)	C3-C4-C5	122.3(7)	C6-C5-C4	118.8(7)
C5-C6-C7	119.6(7)	C2-C7-C6	120.9(6)	C2-C7-C8	118.8(6)
C6-C7-C8	120.2(6)	C9-C8-C7	121.4(7)	C8-C9-C10	118.8(6)
C8-C9-S1	121.1(6)	C10-C9-S1	120.1(5)	O3-C10-C1	124.3(6)
O3-C10-C9	113.4(6)	C1-C10-C9	122.3(6)	C16-C11-C12	122.4(7)
C16-C11-S1	119.3(6)	C12-C11-S1	118.4(6)	C11-C12-C13	116.0(8)
C14-C13-C12	121.2(9)	C13-C14-C15	120.8(9)	C14-C15-C16	119.4(9)
C11-C16-C15	120.1(8)	C26-C17-C18	119.2(6)	C26-C17-C1	119.0(6)
C18-C17-C1	121.8(6)	C19-C18-C23	118.4(6)	C19-C18-C17	121.5(6)
C23-C18-C17	120.0(6)	C20-C19-C18	121.2(7)	C19-C20-C21	120.2(7)
C22-C21-C20	118.9(7)	C21-C22-C23	122.0(7)	C22-C23-C24	121.0(7)
C22-C23-C18	119.3(7)	C24-C23-C18	119.7(6)	C25-C24-C23	119.9(7)
C24-C25-C26	120.0(6)	C24-C25-S2	119.2(5)	C26-C25-S2	120.8(5)
O6-C26-C17	124.4(6)	O6-C26-C25	114.8(6)	C17-C26-C25	120.9(6)
C28-C27-C32	122.7(8)	C28-C27-S2	118.9(6)	C32-C27-S2	118.4(6)
C27-C28-C29	118.0(8)	C30-C29-C28	121.3(8)	C29-C30-C31	120.8(9)
C32-C31-C30	118.8(9)	C27-C32-C31	118.4(9)	O1-S1-O2	116.2(3)
O1-S1-C9	110.5(3)	O2-S1-C9	108.3(3)	O1-S1-C11	108.6(3)
O2-S1-C11	108.4(3)	C9-S1-C11	104.1(3)	O5-S2-O4	116.8(3)
O5-S2-C25	107.6(3)	O4-S2-C25	108.8(3)	O5-S2-C27	107.8(3)
O4-S2-C27	109.2(3)	C25-S2-C27	106.1(3)		

X-Ray structure determination of 12. Compound **12**, $C_{24}H_{18}N_2O_5$, crystallizes in the triclinic space group $P\bar{1}$ with $a=7.771(3)$ Å, $b=16.799(5)$ Å, $c=7.511(3)$ Å, $\alpha=96.80(3)^\circ$, $\beta=92.78(4)^\circ$, $\gamma=88.03(3)^\circ$, $V=972.0(7)$ Å³, $Z=2$ and $d_{calc}=1.416$ g/cm³. The cell constants were determined from a least squares fit of the setting angles for 25 accurately centered reflections. X-ray intensity data were collected on a Rigaku AFC7 diffractometer employing graphite-monochromated Cu-K α radiation ($\lambda=1.54178$ Å) at a temperature of 295 K using the ω -2 θ scan technique. A total of 2837 reflections were measured over the ranges $5.3 \leq 2\theta \leq 120.1^\circ$, $0 \leq h \leq 8$, $-17 \leq k \leq 18$, $-8 \leq l \leq 8$ yielding 2618 unique reflections ($R_{int} = 0.0160$). The intensity data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods (SIR92³⁵). Refinement was by full-matrix least squares based on F^2 using SHELXL-93.³⁶ All reflections were used during refinement (F^2 's that were experimentally negative were replaced by $F^2 = 0$). The weighting scheme used was $w=1/[\sigma^2(F_o^2) + 0.0864P^2 + 0.2941P]$ where $P = (F_o^2 + 2F_c^2)/3$. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a "riding" model. Refinement converged to $R_1=0.0471$ and $wR_2=0.1385$ for 2351 reflections for which $F > 4\sigma(F)$ and $R_1=0.0514$, $wR_2=0.1438$ and $GOF = 1.095$ for

all 2618 unique, non-zero reflections and 281 variables.³⁷ The maximum Δ/σ in the final cycle of least squares was 0.000 and the two most prominent peaks in the final difference Fourier were +0.251 and -0.223 e/Å³.

Table S16 lists cell information, data collection parameters, and refinement data. Final positional and equivalent isotropic thermal parameters are given in Table S17. Anisotropic thermal parameters are in Table S18. Tables S19 and S20 list bond distances and bond angles. Figure S5 is an ORTEP³⁸ representation of the molecule with 30% probability thermal ellipsoids displayed.

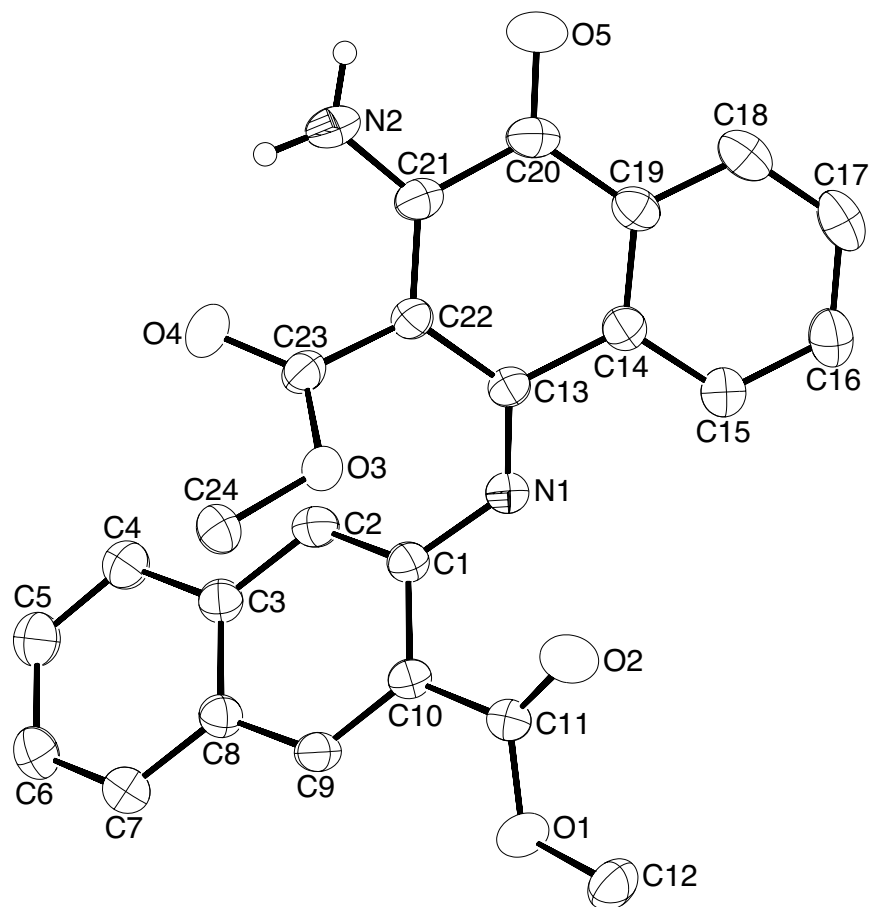


Figure S5. ORTEP drawing of the title compound with 30% probability thermal ellipsoids.

Table S16. Summary of structure determination of **12**.

Formula:	C ₂₄ H ₁₈ N ₂ O ₅
Formula weight:	414.40
Crystal class:	triclinic
Space group:	PT (#2)

Z	2
Cell constants:	
a	7.771(3)Å
b	16.799(5)Å
c	7.511(3)Å
α	96.80(3)°
β	92.78(4)°
γ	88.03(3)°
V	972.0(7)Å ³
μ	8.30 cm ⁻¹
crystal size, mm	0.35 x 0.18 x 0.08
D _{calc}	1.416 g/cm ³
F(000)	432
Radiation:	Cu-K α (λ =1.54178Å)
2 θ range	5.3 – 120.1 °
hkl collected:	0 ≤ h ≤ 8; -17 ≤ k ≤ 18; -8 ≤ l ≤ 8
No. reflections measured:	2837
No. unique reflections:	2618 (R _{int} =0.0160)
No. observed reflections	2351 (F>4 σ)
No. reflections used in refinement	2618
No. parameters	281
R indices (F>4 σ)	R ₁ =0.0471 wR ₂ =0.1385
R indices (all data)	R ₁ =0.0514 wR ₂ =0.1438
GOF:	1.095
Final Difference Peaks, e/Å ³	+0.251, -0.223

Table S17. Refined positional parameters for **12**.

Atom	x	y	z	U _{eq} Å ²
C1	0.2874(3)	0.25102(13)	0.7527(3)	0.0425(5)
C2	0.3424(3)	0.22489(14)	0.9129(3)	0.0474(6)
H2	0.4011(3)	0.25991(14)	0.9981(3)	0.063
C3	0.3127(3)	0.14676(14)	0.9523(3)	0.0456(6)
C4	0.3680(3)	0.1201(2)	1.1178(3)	0.0555(6)
H4	0.4281(3)	0.1544(2)	1.2035(3)	0.074

C5	0.3343(3)	0.0448(2)	1.1530(4)	0.0629(7)
H5	0.3705(3)	0.0283(2)	1.2630(4)	0.084
C6	0.2457(3)	-0.0082(2)	1.0256(4)	0.0629(7)
H6	0.2241(3)	-0.0597(2)	1.0510(4)	0.084
C7	0.1911(3)	0.0155(2)	0.8648(3)	0.0558(6)
H7	0.1325(3)	-0.0201(2)	0.7808(3)	0.074
C8	0.2221(3)	0.09328(13)	0.8234(3)	0.0453(6)
C9	0.1627(3)	0.12164(14)	0.6616(3)	0.0465(6)
H9	0.1009(3)	0.08753(14)	0.5771(3)	0.062
C10	0.1927(3)	0.19803(13)	0.6242(3)	0.0437(6)
C11	0.1307(3)	0.22446(14)	0.4496(3)	0.0481(6)
C12	-0.0712(3)	0.2034(2)	0.2060(3)	0.0637(7)
H12a	-0.1703(3)	0.1720(2)	0.1687(3)	0.096
H12b	0.0169(3)	0.1910(2)	0.1209(3)	0.096
H12c	-0.1030(3)	0.2594(2)	0.2121(3)	0.096
C13	0.4404(3)	0.37079(13)	0.7362(3)	0.0412(5)
C14	0.4137(3)	0.45795(13)	0.7213(3)	0.0445(6)
C15	0.2536(3)	0.4882(2)	0.6653(3)	0.0546(6)
H15	0.1617(3)	0.4540(2)	0.6401(3)	0.073
C16	0.2309(4)	0.5689(2)	0.6470(4)	0.0637(7)
H16	0.1234(4)	0.5889(2)	0.6108(4)	0.085
C17	0.3665(4)	0.6198(2)	0.6821(4)	0.0651(7)
H17	0.3506(4)	0.6737(2)	0.6665(4)	0.087
C18	0.5240(4)	0.5919(2)	0.7395(3)	0.0598(7)
H18	0.6149(4)	0.6267(2)	0.7637(3)	0.080
C19	0.5480(3)	0.51101(13)	0.7617(3)	0.0470(6)
C20	0.7158(3)	0.4822(2)	0.8297(3)	0.0536(6)
C21	0.7448(3)	0.3932(2)	0.8303(3)	0.0489(6)
C22	0.6174(3)	0.34093(13)	0.7696(3)	0.0422(5)
C23	0.6692(3)	0.25533(14)	0.7399(3)	0.0459(6)
C24	0.6337(3)	0.13191(14)	0.5622(3)	0.0574(7)
H24a	0.5779(3)	0.10964(14)	0.4515(3)	0.086
H24b	0.5911(3)	0.10740(14)	0.6598(3)	0.086
H24c	0.7558(3)	0.12193(14)	0.5570(3)	0.086
N1	0.3015(2)	0.33075(11)	0.7209(2)	0.0458(5)
N2	0.9048(3)	0.37331(14)	0.8843(3)	0.0682(6)
H2a	0.9360(3)	0.32363(14)	0.8829(3)	0.091
H2b	0.9768(3)	0.41016(14)	0.9205(3)	0.091
O1	-0.0071(2)	0.18514(10)	0.3806(2)	0.0598(5)
O2	0.1969(3)	0.27417(12)	0.3753(3)	0.0783(6)
O3	0.5982(2)	0.21709(8)	0.5895(2)	0.0462(4)

O4	0.7733(2)	0.22239(11)	0.8340(2)	0.0698(6)
O5	0.8325(3)	0.52676(12)	0.8792(3)	0.0806(6)
$U_{eq} = 1/3[U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*cc^*\cos\beta + 2U_{23}bb^*cc^*\cos\alpha]$				

Table S18. Refined thermal parameters (U's) for **12**.

Atom	U ₁₁	U ₂₂	U ₃₃	U ₂₃	U ₁₃	U ₁₂
C1	0.0362(11)	0.0407(14)	0.0505(12)	0.0052(10)	0.0003(9)	-0.0023(9)
C2	0.0466(12)	0.047(2)	0.0473(12)	0.0019(10)	-0.0038(9)	-0.0071(10)
C3	0.0426(11)	0.0461(14)	0.0487(12)	0.0073(10)	0.0023(9)	-0.0023(10)
C4	0.0599(14)	0.055(2)	0.0515(13)	0.0092(11)	-0.0051(10)	-0.0027(11)
C5	0.070(2)	0.063(2)	0.0580(14)	0.0199(13)	-0.0056(12)	-0.0013(13)
C6	0.068(2)	0.052(2)	0.071(2)	0.0219(13)	-0.0007(13)	-0.0041(12)
C7	0.0562(14)	0.049(2)	0.0621(14)	0.0076(12)	-0.0017(11)	-0.0053(11)
C8	0.0415(11)	0.0432(14)	0.0517(12)	0.0072(10)	0.0027(9)	-0.0030(9)
C9	0.0420(11)	0.046(2)	0.0504(12)	0.0018(10)	-0.0030(9)	-0.0080(10)
C10	0.0363(11)	0.0440(14)	0.0507(12)	0.0063(10)	-0.0017(9)	-0.0044(9)
C11	0.0497(12)	0.0427(14)	0.0515(12)	0.0051(11)	-0.0052(10)	-0.0060(10)
C12	0.061(2)	0.074(2)	0.0546(14)	0.0091(13)	-0.0148(11)	0.0007(13)
C13	0.0431(11)	0.0423(14)	0.0374(10)	0.0034(9)	-0.0046(8)	-0.0033(10)
C14	0.0511(12)	0.0440(14)	0.0381(11)	0.0034(10)	0.0013(9)	-0.0019(10)
C15	0.0546(13)	0.050(2)	0.0595(14)	0.0086(11)	-0.0007(11)	0.0018(11)
C16	0.073(2)	0.052(2)	0.067(2)	0.0104(13)	0.0037(13)	0.0128(14)
C17	0.092(2)	0.040(2)	0.064(2)	0.0064(12)	0.0180(14)	0.0067(14)
C18	0.077(2)	0.045(2)	0.0574(14)	-0.0008(12)	0.0140(12)	-0.0098(13)
C19	0.0575(13)	0.043(2)	0.0400(11)	0.0001(10)	0.0048(9)	-0.0071(11)
C20	0.0546(14)	0.057(2)	0.0484(12)	0.0009(11)	-0.0030(10)	-0.0168(12)
C21	0.0438(12)	0.058(2)	0.0447(12)	0.0060(10)	-0.0039(9)	-0.0087(10)
C22	0.0445(12)	0.0429(14)	0.0392(11)	0.0062(9)	-0.0051(9)	-0.0042(10)
C23	0.0403(11)	0.053(2)	0.0445(12)	0.0090(10)	-0.0054(9)	-0.0025(10)
C24	0.062(2)	0.042(2)	0.066(2)	0.0026(11)	-0.0034(11)	0.0041(11)
N1	0.0440(10)	0.0418(12)	0.0508(10)	0.0043(8)	-0.0047(8)	-0.0032(8)
N2	0.0445(11)	0.072(2)	0.086(2)	0.0056(12)	-0.0167(10)	-0.0117(10)
O1	0.0552(10)	0.0720(12)	0.0532(9)	0.0143(8)	-0.0146(7)	-0.0145(8)
O2	0.0973(14)	0.0762(14)	0.0658(11)	0.0265(10)	-0.0208(10)	-0.0355(11)
O3	0.0491(8)	0.0430(10)	0.0455(8)	0.0059(7)	-0.0063(6)	0.0018(7)
O4	0.0718(12)	0.0635(12)	0.0706(11)	0.0098(9)	-0.0299(9)	0.0095(9)
O5	0.0719(12)	0.0697(13)	0.099(2)	0.0076(11)	-0.0227(11)	-0.0305(11)

The form of the anisotropic displacement parameter is:

$$\exp[-2p^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2b^*c^*U_{23}kl+2a^*c^*U_{13}hl+2a^*b^*U_{12}hk)].$$

Table S19. Bond distances (Å) in **12**.

C1-C2	1.373(3)	C1-N1	1.397(3)	C1-C10	1.427(3)
C2-C3	1.408(3)	C3-C4	1.413(3)	C3-C8	1.418(3)
C4-C5	1.359(4)	C5-C6	1.399(4)	C6-C7	1.361(3)
C7-C8	1.409(3)	C8-C9	1.409(3)	C9-C10	1.376(3)
C10-C11	1.487(3)	C11-O2	1.200(3)	C11-O1	1.329(3)
C12-O1	1.443(3)	C13-N1	1.285(3)	C13-C22	1.468(3)
C13-C14	1.488(3)	C14-C15	1.392(3)	C14-C19	1.395(3)
C15-C16	1.384(4)	C16-C17	1.375(4)	C17-C18	1.364(4)
C18-C19	1.394(3)	C19-C20	1.465(3)	C20-O5	1.213(3)
C20-C21	1.504(4)	C21-N2	1.333(3)	C21-C22	1.371(3)
C22-C23	1.474(3)	C23-O4	1.211(3)	C23-O3	1.336(3)
C24-O3	1.440(3)				

Table S20. Bond angles (deg) in **12**.

C2-C1-N1	122.0(2)	C2-C1-C10	118.9(2)	N1-C1-C10	118.6(2)
C1-C2-C3	122.1(2)	C2-C3-C4	122.1(2)	C2-C3-C8	119.2(2)
C4-C3-C8	118.7(2)	C5-C4-C3	120.6(2)	C4-C5-C6	120.8(2)
C7-C6-C5	120.1(2)	C6-C7-C8	121.0(2)	C9-C8-C7	123.1(2)
C9-C8-C3	118.0(2)	C7-C8-C3	118.8(2)	C10-C9-C8	122.3(2)
C9-C10-C1	119.4(2)	C9-C10-C11	120.2(2)	C1-C10-C11	120.3(2)
O2-C11-O1	122.8(2)	O2-C11-C10	125.1(2)	O1-C11-C10	112.1(2)
N1-C13-C22	127.8(2)	N1-C13-C14	114.5(2)	C22-C13-C14	117.7(2)
C15-C14-C19	118.5(2)	C15-C14-C13	120.5(2)	C19-C14-C13	121.0(2)
C16-C15-C14	120.2(2)	C17-C16-C15	120.3(2)	C18-C17-C16	120.6(2)
C17-C18-C19	119.7(2)	C18-C19-C14	120.6(2)	C18-C19-C20	119.3(2)
C14-C19-C20	120.1(2)	O5-C20-C19	122.6(2)	O5-C20-C21	119.3(2)
C19-C20-C21	118.0(2)	N2-C21-C22	126.1(2)	N2-C21-C20	113.0(2)
C22-C21-C20	120.8(2)	C21-C22-C13	120.4(2)	C21-C22-C23	116.4(2)
C13-C22-C23	123.2(2)	O4-C23-O3	121.8(2)	O4-C23-C22	124.7(2)
O3-C23-C22	113.3(2)	C13-N1-C1	126.1(2)	C11-O1-C12	116.2(2)
C23-O3-C24	115.3(2)				

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$$wR_2 = \{ \sum w (F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2 \}^{1/2}$$

$$GOF = \{ \sum w (F_o^2 - F_c^2)^2 / (n - p) \}^{1/2}$$

where n = the number of reflections and p = the number of parameters refined.

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