Supporting Information

Enantioselective Synthesis of Cyclic Carbamimidates via a Three-Component Reaction of Imines, Terminal Alkynes, and p-Toluenesulfonylisocyanate using a Monophosphine Gold(I) Catalyst

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Experimental Section

Materials and Methods: General. Unless otherwise noted commercial materials were used without further purification. Reagent grade solvents were used in all gold(I)-catalyzed reactions without the exclusion of air or moisture. Gold(I)-catalyzed reactions were conducted in amber glass 1 dram vials fitted with a PTFE-lined threaded cap (Thermo Scientific catalog No. B7800-2A). All other reactions were conducted in flame-dried glassware under an inert (N₂) atmosphere with magnetic stirring and dried solvent, unless otherwise noted. Solvents were dried by passage through an activated alumina column under nitrogen. Thin-layer chromatography (TLC) analysis was performed using Merck silica gel 60 F254 TLC plates, and visualized by staining UV and/or cerium sulfate. Flash column chromatography was carried out on Merck 60 silica gel (32–63 µm). ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded with Bruker AVB-400, AVQ-400, and DRX-500 spectrometers and chemical shifts are reported in ppm, relative to CHCl₃ (7.26 ppm for ¹H, and 77.0 ppm for ¹³C) or d₆-DMSO (2.50 ppm for ¹H, and 39.5 ppm for ¹³C) unless otherwise noted. ¹H NMR data are reported as follows: chemical shift, multiplicity (s = singlet, br s = broad singlet, d = doublet, br d = broad doublet, t =
triplet, q = quartet, m = multiplet), coupling constants (Hz), and integration. Mass spectra were recorded at the University of California, Berkeley Microanalytical Facility with electrospray ionization (ESI) in positive mode. Infrared spectral data were recorded on a Thermo Scientific Nicolet iS10 spectrometer fitted with a Smart iTR device as neat solids or thin films. Yield refers to isolated yield of analytically pure material unless otherwise noted. Liquid benzaldehydes were purified by the following procedure. The neat aldehydes were washed sequentially with a 1 M sodium hydroxide solution and a saturated aqueous sodium bicarbonate solution, dried with magnesium sulfate, and distilled under reduced pressure. 4-Chlorobenzaldehyde was sublimed under reduced pressure. 3-Naphthaldehyde was used without prior purification. All other reagents were obtained from Acros or Sigma-Aldrich and used without further purification. Ph3PAuNTf2 was either prepared immediately before use by sonicating a 1:1 mixture of Ph3PAuCl and AgNTf2 in the desired solvent and filtering off the precipitated AgCl though a glass microfiber plug or was prepared and isolated as reported by Gagosz.1

**General Procedure (A) for the racemic multicomponent reaction using Ph3PAuNTf2.**

An amber vial was charged with the imine (0.28 mmol), alkyne, and isocyanate in reagent grade chloroform (0.90 mL). A solution of Ph3PAuNTf2 in chloroform (0.40 mL) was added quickly and the vial was sealed with a PTFE-lined screw cap (imine molarity ~0.2 M). The reaction was left to stand at the indicated temperature (room temperature, 35 °C or 50 °C) for the indicated time period. 1H NMR analysis of the crude reaction mixture provided the diastereomeric ratio. The reaction mixture was then either directly loaded on silica and purified via flash chromatography, eluting with the indicated solvent system, or evaporated and recrystallized.

**General Procedure (B) for the asymmetric multicomponent reaction using 5 mol % (S,S)-L4AuCl/AgNTf2.**

An amber vial was charged with the imine (0.14 mmol), alkyne (0.17 mmol), and isocyanate (0.17 mmol) in reagent grade solvent (0.10 mL, chloroform or toluene). In a separate amber vial was added (S,S)-L4AuCl (0.0058 g, 0.007 mmol), AgNTf2 (0.0027 g, 0.007 mmol), and reagent grade solvent (0.20 mL). This mixture was sonicated for 30 seconds and then filtered through glass microfiber to afford a colorless solution of the catalyst. (In practice, the catalyst was made on at least two times this scale to ensure 0.20 mL of the catalyst solution could be added to the reaction to overcome loss of material during the filtration step) The catalyst solution (0.20 mL) was added quickly to the first vial, which was then sealed with a PTFE-lined screw cap (imine molarity ~0.4 M). The reaction was left to stand at room temperature for the indicated time period. For reactions where water was added after the completion of the alkyne addition to facilitate the cyclization, water (1.2 µL, 0.07 mmol) was shaken with chloroform (0.20 mL). This solution was then added to the reaction mixture after the imine was completely consumed, as judged by TLC analysis. 1H NMR analysis of the crude reaction mixture provided the diastereomeric ratio. The reaction mixture was then directly loaded on silica and purified via flash chromatography, eluting with the indicated solvent system.
**General Procedure (C) for the asymmetric multicomponent reaction using 10 mol % \((R,R)\)-L4AuCl/AgNTf₂.**

An amber vial was charged with the imine (0.061 mmol), alkyne (0.12 mmol), and isocyanate (0.12 mmol) in reagent grade chloroform (0.40 mL). In a separate amber vial was added \((R,R)\)-L4AuCl (0.0051 g, 0.006 mmol), AgNTf₂ (0.0024 g, 0.006 mmol), and reagent grade chloroform (0.20 mL). This mixture was sonicated for 30 seconds and then filtered through glass microfiber to afford a colorless solution of the catalyst. (In practice, the catalyst was made on at least two times this scale to ensure 0.20 mL of the catalyst solution could be added to the reaction to overcome loss of material during the filtration step) The catalyst solution (0.20 mL) was added quickly to the first vial, which was then sealed with a PTFE-lined screw cap (imine molarity ~0.2 M). The reaction was left to stand at room temperature for the indicated time period. \(^1\)H NMR analysis of the crude reaction mixture provided the diastereomeric ratio. The reaction mixture was then directly loaded on silica and purified via flash chromatography, eluting with the indicated solvent system.

**General Procedure (D) for the asymmetric multicomponent reaction using 10 mol % \((R,R)\)-L4AuCl/AgNTf₂.**

An amber vial was charged with the imine (0.061 mmol), alkyne (0.073 mmol), and isocyanate (0.073 mmol) in reagent grade methylene chloride (0.15 mL). In a separate amber vial was added \((R,R)\)-L4AuCl (0.0051 g, 0.006 mmol), AgNTf₂ (0.0024 g, 0.006 mmol), and reagent grade methylene chloride (0.10 mL). This mixture was sonicated for 30 seconds and then filtered through glass microfiber to afford a colorless solution of the catalyst. (In practice, the catalyst was made on at least two times this scale to ensure 0.10 mL of the catalyst solution could be added to the reaction to overcome loss of material during the filtration step) The catalyst solution (0.10 mL) was added quickly to the first vial, which was then sealed with a PTFE-lined screw cap (imine molarity ~0.2 M). The reaction was left to stand at room temperature for the indicated time period. \(^1\)H NMR analysis of the crude reaction mixture provided the diastereomeric ratio. The reaction mixture was then directly loaded on silica and purified via flash chromatography, eluting with the indicated solvent system.

**(Z)-N-((Z)-5-benzylidene-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9aA).** The title compound was prepared according to General Procedure A using (E)-N-benzylideneaniline (0.051 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), \(p\)-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and \(\text{Ph}_3\text{PAuNTf}_2\) (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, \(^1\)H NMR analysis of the crude mixture gave the diastereomeric ratio: 17:1. The title compound (0.113 g, 0.24 mmol, 84% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl
acetate/hexanes. Analytical data for the title compound: IR (thin film, cm\(^{-1}\)) 1611, 1587, 1080, 773, 698, 681, 659; \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K) \(\delta\) 7.93 (d, \(J = 8.4\) Hz, 2H), 7.61 (d, \(J = 7.6\) Hz, 2H), 7.39 (t, \(J = 7.8\) Hz, 2H), 7.35–7.15 (m, 12H), 7.15–7.10 (m, 1H), 5.92 (d, \(J = 2.0\) Hz, 1H), 5.44 (d, \(J = 2.0\) Hz, 1H), 2.37 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 298 K) \(\delta\) 153.2, 147.7, 142.7, 139.7, 136.3, 134.6, 132.2, 129.5, 129.3, 129.2, 129.1, 128.8, 127.8, 127.6, 127.0, 126.8, 124.1, 107.0, 66.3, 21.5; TLC (30% EtOAc/hexanes) \(R_f\) 0.34; HRMS (ESI) calc for \([C_{29}H_{22}O_3N_2S+Na]^+\): \(m/z\) 503.1400, found 503.1397.

(Z)-N-((R,Z)-5-benzylidene-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9aA). The title compound was prepared according to General Procedure B using (E)-N-benzylideneaniline (0.026 g, 0.14 mmol), phenylacetylene (0.017 g, 18 \(\mu\)L, 0.17 mmol), \(p\)-toluenesulfonyl isocyanate (0.033 g, 25 \(\mu\)L, 0.17 mmol), (S,S)-L\(_4\)AuCl (0.0058 g, 0.007 mmol), and AgNTf\(_2\) (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, \(^1\)H NMR analysis of the crude mixture gave the diastereomeric ratio: 8:1. The title compound (0.051 g, 0.106 mmol, 76% yield, 79% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) \(T_R\) (major) 13.0 min, \(T_R\) (minor) 18.1 min.

(Z)-N-((Z)-5-benzylidene-3-(2,6-difluorophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9bA). The title compound was prepared according to General Procedure A using (E)-N-benzylidene-2,6-difluoroaniline (0.061 g, 0.28 mmol), phenylacetylene (0.035 g, 36 \(\mu\)L, 0.34 mmol), \(p\)-toluenesulfonyl isocyanate (0.067 g, 52 \(\mu\)L, 0.34 mmol), and Ph\(_3\)PAuNTf\(_2\) (0.0104 g, 0.014 mmol) in chloroform. After 6 days at room temperature, \(^1\)H NMR analysis of the crude mixture gave the diastereomeric ratio: 2.4:1. The title compound (0.080 g, 0.15 mmol, 55% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm\(^{-1}\)) 1627, 1609, 1591, 1241, 933, 885; \(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K) \(\delta\) 7.92 (d, \(J = 8.3\) Hz, 2H), 7.59 (d, \(J = 7.4\) Hz, 2H), 7.40 (t, \(J = 7.6\) Hz, 2H), 7.36–7.17 (m, 9H), 6.91 (t, \(J = 9.4\) Hz, 1H), 6.81 (t, \(J = 8.9\) Hz, 1H), 5.92 (d, \(J = 2.2\) Hz, 1H), 5.42 (d, \(J = 2.2\) Hz, 1H), 2.37 (s, 3H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\), 298 K) \(\delta\) 158.8 (dd, \(J = 260.0, 3.3\) Hz), 158.6 (dd, \(J = 260.0, 4.4\) Hz), 153.3, 147.7, 142.7, 139.3, 135.0, 132.0, 130.6 (t, \(J = 9.9\) Hz), 129.9, 129.2, 129.1, 128.8, 128.6, 128.3, 127.9, 126.8, 112.6 (dd, \(J = 20.4, 3.1\) Hz), 111.9 (dd, \(J = 19.6, 3.2\) Hz), 111.1 (t, \(J = 15.9\) Hz), 107.6, 66.0 (d, \(J = 4.0\) Hz), 21.5; \(^{19}\)F NMR
(376 MHz, CDCl₃, 298 K) δ 112.52 (t, J = 7.3 Hz, 1F), 116.53 (t, J = 7.8 Hz, 1F); TLC (30% EtOAc/hexanes) Rₓ 0.26; HRMS (ESI) calc for [C₂₉H₂₂O₃N₂F₂S+H⁺]: m/z 517.1392, found 517.1391.

(Z)-N-((S,Z)-5-benzylidene-3-(2,6-difluorophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((S)-9bA). The title compound was prepared according to General Procedure D using (E)-N-benzylidene-2,6-difluoroaniline (0.013 g, 0.061 mmol), phenylacetylene (0.01075 g, 0.073 mmol), p-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (R,R)-L₄AuCl (0.0050 g, 0.006 mmol), and AgNTf₂ (0.0024 g, 0.006 mmol) in methylene chloride. After 6 days, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 1.7:1. The title compound (0.015 g, 0.030 mmol, 48% yield, 41% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IB, hexane/IPA= 75:25, flow rate=1 ml/min) Tᵣ (major) 14.2 min, Tᵣ (minor) 15.4 min.

(Z)-N-((Z)-5-benzylidene-3-phenyl-4-(p-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9cA). The title compound was prepared according to General Procedure A using (E)-N-(4-methylbenzylidene)aniline (0.055 g, 0.28 mmol), phenylacetylene (0.035 g, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: >20:1. The title compound (0.111 g, 0.22 mmol, 80% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1615, 1584, 1085, 769, 692, 663; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.97 (d, J = 8.0 Hz, 2H), 7.64 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.6 Hz, 2H), 7.35–7.20 (m, 7H), 7.20–7.10 (m, 5H), 5.91 (d, J = 2.0 Hz, 1H), 5.46 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 153.2, 147.2, 142.6, 139.6, 139.4, 134.5, 133.2, 132.2, 129.9, 129.1, 129.0, 128.7, 128.5, 127.7, 127.5, 126.9, 126.7, 124.1, 106.7, 66.0, 21.4, 21.1; TLC (30% EtOAc/hexanes) Rₓ 0.37; HRMS (ESI) calc for [C₃₀H₂₆O₃N₂S+Na⁺]: m/z 517.1556, found 517.1552.
(Z)-N-((R,Z)-5-benzylidene-3-phenyl-4-(p-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9cA). The title compound was prepared according to General Procedure B using (E)-N-(4-methylbenzyldiene)aniline (0.028 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluene sulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf₂ (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 11:1. The title compound (0.053 g, 0.106 mmol, 76% yield, 80% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) Tᵣ (major) 11.6 min, Tᵣ (minor) 16.2 min.

(Z)-N-((Z)-5-benzylidene-3-phenyl-4-(m-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9dA). The title compound was prepared according to General Procedure A using (E)-N-(3-methylbenzyldiene)aniline (0.055 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluene sulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: >20:1. The title compound (0.115 g, 0.23 mmol, 83% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1616, 1583, 1157, 1086, 681, 666; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.93 (d, J = 8.4 Hz, 2H), 7.65 (d, J = 7.6 Hz, 2H), 7.41 (t, J = 7.8 Hz, 2H), 7.35–7.20 (m, 8H), 7.20–7.10 (m, 2H), 7.10–7.05 (m, 2H), 5.89 (d, J = 2.0 Hz, 1H), 5.47 (d, J = 2.0 Hz, 1H), 2.38 (s, 3H), 2.32 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 153.2, 147.0, 142.6, 139.6, 139.2, 136.3, 134.6, 132.2, 130.2, 129.1, 129.1, 129.0, 128.7, 128.5, 127.9, 127.7, 126.9, 126.7, 124.7, 123.9, 106.7, 66.1, 21.4, 21.3; TLC (30% EtOAc/hexanes) Rₓ 0.37; HRMS (ESI) calc for [C₃₀H₂₆O₃N₂S+Na]⁺: m/z 517.1556, found 517.1554.
(Z)-N-((R,Z)-5-benzylidene-3-phenyl-4-(m-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9dA). The title compound was prepared according to General Procedure B using (E)-N-(3-methylbenzylidene)aniline (0.028 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf₂ (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 8:1. The title compound (0.052 g, 0.105 mmol, 75% yield, 68% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T_R (major) 10.8 min, T_R (minor) 16.4 min.

(Z)-N-((Z)-5-benzylidene-3-phenyl-4-(o-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9eA). The title compound was prepared according to General Procedure A using (E)-N-(2-methylbenzylidene)aniline (0.055 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 17:1. The title compound (0.109 g, 0.22 mmol, 79% yield) was isolated as a white solid after flash chromatography, eluting with 0.5% methanol/methylene chloride. Analytical data for the title compound: IR (thin film, cm⁻¹) 1611, 1585, 1161, 1081, 692, 659; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.87 (d, J = 8.2 Hz, 2H), 7.56 (d, J = 7.6 Hz, 2H), 7.46 (d, J = 7.9 Hz, 2H), 7.42–7.24 (m, 8H), 7.24–7.12 (m, 4H), 6.74 (br s, 1H), 5.56 (d, J = 1.8 Hz, 1H), 2.33 (s, 3H), 2.18 (br s, 3H); ¹H NMR (500 MHz, d₆-DMSO, 353 K) δ 7.84 (d, J = 7.0 Hz, 2H), 7.57 (d, J = 7.5 Hz, 2H), 7.42–7.12 (m, 14H), 6.66 (s, 1H), 5.55 (s, 1H), 2.36 (s, 3H), 2.24 (br s, 3H); ¹³C NMR (125 MHz, d₆-DMSO, 353 K) δ 152.7, 147.1, 141.9, 139.8, 135.9, 134.1, 133.7, 132.0, 131.1, 128.8, 128.7, 128.5, 128.0, 127.9, 127.0, 126.9, 126.2, 125.6, 124.3, 111.7, 104.3, 63.8, 20.3, 17.7; TLC (30% EtOAc/hexanes) Rf 0.35; HRMS (ESI) calc for [C₃₀H₂₆O₃N₂S+H]⁺: m/z 495.1730, found 495.1733.
(Z)-N-(Z)-5-benzylidene-3-phenyl-4-(naphthalene-2-yl)oxazolidin-2-ylidene)-4-
methylbenzenesulfonamide (9fA). The title compound was prepared according to General Procedure A using (E)-N-(naphthalene-2-ylmethylene)aniline (0.065 g, 0.28 mmol), phenylacetylene (0.035 g, 0.36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 0.28 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 19:1. The title compound (0.116 g, 0.22 mmol, 78% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1625, 1586, 1414, 1158, 853, 779, 708, 661; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.99 (d, J = 7.6 Hz, 2H), 7.85–7.75 (m, 4H), 7.63 (d, J = 7.6 Hz, 2H), 7.55–7.48 (m, 2H), 7.52–7.42 (m, 10H), 7.15–7.10 (m, 1H), 6.10 (d, J = 1.6 Hz, 1H), 5.47 (d, J = 2.6 Hz, 1H), 2.39 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 153.3, 146.9, 142.7, 139.7, 134.5, 132.9, 132.1, 129.8, 129.2, 129.1, 128.6, 128.0, 128.0, 127.8, 127.1, 126.9, 126.8, 124.1, 123.7, 107.2, 66.6, 21.4 (3 signals missing); TLC (30% EtOAc/hexanes) Rf 0.32; HRMS (ESI) calc for [C₃₃H₂₆O₃N₂S+Na]⁺: m/z 553.1556, found 553.1553.

(Z)-N-((R,Z)-5-benzylidene-3-phenyl-4-(naphthalene-2-yl)oxazolidin-2-ylidene)-4-
methylbenzenesulfonamide ((R)-9fA). The title compound was prepared according to General Procedure B using (E)-N-(naphthalene-2-ylmethylene)aniline (0.033 g, 0.14 mmol), phenylacetylene (0.017 g, 0.18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 0.25 µL, 0.17 mmol), (S,S)-L₄AuCl (0.0058 g, 0.007 mmol), and AgNTf₂ (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 9:1. The title compound (0.050 g, 0.095 mmol, 68% yield, 62% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T_R (major) 12.0 min, T_R (minor) 17.0 min.
(Z)-N-((Z)-5-benzylidene-4-(2-methoxyphenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9gA). The title compound was prepared according to General Procedure A using (E)-N-benzylideneaniline (0.051 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph$_3$PAuNTf$_2$ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 13:1. The title compound (0.130 g of a 15:1 mixture of regioisomers, 0.122 g, 0.24 mmol, 85% yield) was isolated as a mixture of regioisomers as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm$^{-1}$) 1615, 1583, 1167, 1143, 1085, 893, 760, 681, 664; $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.99 (d, $J$ = 8.3 Hz, 2H), 7.62 (d, $J$ = 7.4 Hz, 2H), 7.40 (t, $J$ = 7.5 Hz, 2H), 7.35–7.16 (m, 8H), 7.16–7.08 (m, 2H), 6.90–6.80 (m, 2H), 6.07 (br s, 1H), 5.47 (s, 1H), 3.68 (br s, 3H), 2.36 (s, 3H); $^1$H NMR (500 MHz, d$_6$-DMSO, 353 K) δ 7.67 (d, $J$ = 8.0 Hz, 2H), 7.57 (d, $J$ = 7.5 Hz, 2H), 7.42–7.22 (m, 12H), 7.20 (t, $J$ = 7.5 Hz, 1H), 6.97 (d, $J$ = 8.0 Hz, 1H), 6.88 (t, $J$ = 7.5 Hz, 1H), 6.46 (d, $J$ = 2.0 Hz, 1H), 5.56 (d $J$ = 2.0 Hz, 1H), 3.62 (s, 3H), 2.37 (s, 3H); $^{13}$C NMR (125 MHz, d$_6$-DMSO, 353 K) δ 157.3, 153.0, 147.5, 141.8, 140.1, 134.3, 132.3, 130.5, 130.2, 128.7, 128.3, 127.9, 127.8, 126.7, 125.7, 124.3, 124.1, 120.2, 112.0, 102.9, 63.6, 55.3, 20.3; TLC (30% EtOAc/hexanes) $R_f$ 0.21; HRMS (ESI) calc for [C$_{30}$H$_{26}$O$_4$N$_2$S+]$^+$: m/z 511.1686, found 511.1680.

(Z)-N-((R,Z)-5-benzylidene-4-(2-methoxyphenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9gA). The title compound was prepared according to General Procedure B using (E)-N-(2-methoxybenzylidene)aniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf$_2$ (0.0027 g, 0.007 mmol) in chloroform. After 6 days, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 7:1. The title compound (0.043 g, 0.084 mmol, 60% yield, 82% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) $T_R$ (major) 13.2 min, $T_R$ (minor) 18.8 min.
(9hA). The title compound was prepared according to General Procedure A using (E)-N-(4-chlorobenzylidene)aniline (0.060 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 14:1. The title compound (0.117 g, 0.23 mmol, 81 % yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1622, 1584, 1086, 890, 703, 690; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.93 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.35 – 7.19 (m, 11H), 7.18 – 7.14 (m, 1H), 5.93 (d, J = 2.0 Hz, 1H), 5.43 (d, J = 2.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 153.0, 146.4, 142.8, 139.5, 135.4, 134.7, 134.2, 131.9, 129.5, 129.2, 129.1, 129.0, 128.7, 128.6, 127.9, 127.1, 126.7, 124.0, 107.1, 65.3, 21.4; TLC (30% EtOAc/hexanes) Rf 0.35; HRMS (ESI) calc for [C₂₉H₂₃O₃N₂ClS⁺Na⁺]: m/z 537.1010, found 537.1009.

(Z)-N-((R,Z)-5-benzylidene-3-phenyl-4-(4-chlorophenyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9hA). The title compound was prepared according to General Procedure B using (E)-N-(4-chlorobenzylidene)aniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L₄AuCl (0.0058 g, 0.007 mmol), and AgNTf₂ (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 6:1. The title compound (0.045 g, 0.087 mmol, 63 % yield, 79% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T_R (major) 12.0 min, T_R (minor) 17.0 min.

(Z)-N-((Z)-5-benzylidene-4-(2-chlorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9iA). The title compound was prepared according to General Procedure A using (E)-N-(2-chlorobenzylidene)aniline (0.123 g, 0.50 mmol), phenylacetylene (0.062 g, 66 µL, 0.60 mmol), p-toluenesulfonyl isocyanate (0.118 g, 91 µL, 0.60 mmol), and Ph₃PAuNTf₂ (0.018 g, 0.025 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 14:1. The title compound (0.117 g, 0.23 mmol, 81 % yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1622, 1584, 1086, 890, 703, 690; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.93 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.4 Hz, 2H), 7.39 (t, J = 7.4 Hz, 2H), 7.35 – 7.19 (m, 11H), 7.18 – 7.14 (m, 1H), 5.93 (d, J = 2.0 Hz, 1H), 5.43 (d, J = 2.0 Hz, 1H), 2.36 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 153.0, 146.4, 142.8, 139.5, 135.4, 134.7, 134.2, 131.9, 129.5, 129.2, 129.1, 129.0, 128.7, 128.6, 127.9, 127.1, 126.7, 124.0, 107.1, 65.3, 21.4; TLC (30% EtOAc/hexanes) Rf 0.35; HRMS (ESI) calc for [C₂₉H₂₃O₃N₂ClS⁺Na⁺]: m/z 537.1010, found 537.1009.
chloroform (2.5 mL total volume). After 72 hours at room temperature, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 17:1. The title compound (0.175 g, 0.34 mmol, 68% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes.

Analytical data for the title compound: IR (thin film, cm$^{-1}$) 1615, 1585, 1318, 1167, 1147, 892, 756, 703, 686; $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.93 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 7.7$ Hz, 1H), 7.41 (t, $J = 7.6$ Hz, 2H), 7.42–7.32 (m, 3H), 7.32–7.22 (m, 6H), 7.21 (d, $J = 8.3$ Hz, 2H), 7.18–7.13 (m, 1H), 6.66 (br s, 1H), 5.58 (br s, 1H), 2.37 (s, 3H); $^1$H NMR (500 MHz, d$_6$-DMSO, 353 K) δ 7.85 (d, $J = 7.5$ Hz, 2H), 7.58 (d, $J = 7.5$ Hz, 2H), 7.52 (d, $J = 7.0$ Hz, 1H), 7.45 (d, $J = 7.5$ Hz, 2H), 7.42–7.35 (m, 10H), 7.23 (t, $J = 7.3$ Hz, 1H), 6.75 (s, 1H), 5.60 (s, 1H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, d$_6$-DMSO, 353 K) δ 152.8, 145.9, 141.9, 139.9, 133.9, 132.6, 132.2, 132.0, 130.7, 130.3, 128.7, 128.5, 128.1, 127.9, 127.3, 127.0, 126.9, 125.7, 124.3, 104.3, 64.0, 20.3 (1 missing signal); TLC (30% EtOAc/hexanes) R$_f$ 0.25; HRMS (ESI) calc for [C$_{29}$H$_{23}$O$_3$N$_2$ClS+H]$^+$: m/z 515.1191, found 515.1187.

(Z)-N-((R,Z)-5-benzylidene-4-(2-chlorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9iA). The title compound was prepared according to General Procedure B using (E)-N-(2-chlorobenzylidene)aniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf$_2$ (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 7:1. The title compound (0.044 g, 0.086 mmol, 61% yield, 91% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) $T_R$ (major) 12.3 min, $T_R$ (minor) 18.2 min.

(Z)-N-((Z)-5-benzylidene-4-(2-fluorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9jA). The title compound was prepared according to General Procedure A using (E)-N-(2-fluorobenzylidene)aniline (0.056 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph$_3$PAuNTf$_2$ (0.0104 g, 0.014 mmol) in
chloroform. After 20 h at 35 °C, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 14:1. The title compound (0.117 g of a 20:1 mixture of regioisomers, 0.111 g, 0.22 mmol, 80% yield) was isolated as a mixture of regioisomers as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm$^{-1}$) 2981, 1615, 1584, 1168, 1144, 1086, 761, 664; $^1$H NMR (400 MHz, CDCl$_3$, 298 K) δ 7.95 (d, $J$ = 8.3 Hz, 2H), 7.61 (d, $J$ = 7.3 Hz, 2H), 7.40 (t, $J$ = 7.7 Hz, 2H), 7.35 (d, $J$ = 7.6 Hz, 2H), 7.34–7.24 (m, 5H), 7.22 (d, $J$ = 7.1 Hz, 2H), 7.16 (t, $J$ = 7.4 Hz, 1H), 7.10 (td, $J$ = 7.6, 0.9 Hz, 1H), 7.05 (dd, $J$ = 10.2, 8.4 Hz, 1H), 6.26 (d, $J$ = 1.8 Hz, 1H), 5.53 (d, $J$ = 1.8 Hz, 1H), 2.37 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) δ 160.6 (d, $J$ = 249.4 Hz), 153.1, 145.7, 142.7, 139.6, 134.3, 132.0, 131.4 (d, $J$ = 3.6 Hz), 123.7, 123.6 (d, $J$ = 11.8 Hz), 116.3 (d, $J$ = 20.8 Hz), 106.5, 60.4 (d, $J$ = 1.8 Hz), 21.4 (2 carbon signals missing); $^1$H NMR (500 MHz, $d_6$-DMSO, 353 K) δ 7.85 (d, $J$ = 7.5 Hz, 2H), 7.59 (d, $J$ = 8.0 Hz, 2H), 7.49–7.12 (m, 14H), 6.66 (s, 1H), 5.67 (s, 1H), 2.36 (s, 3H); $^{13}$C NMR (125 MHz, $d_6$-DMSO, 353 K) δ 160.1 (d, $J$ = 248.6 Hz), 152.6, 146.4, 141.9, 139.8, 134.0, 131.9, 131.3 (d, $J$ = 8.6 Hz), 130.5 (d, $J$ = 3.1 Hz), 128.8, 128.6, 128.0, 128.1, 126.1, 126.9, 125.5, 124.5 (d, $J$ = 3.5 Hz), 124.3, 123.3 (d, $J$ = 11.1 Hz), 115.7 (d, $J$ = 20.6 Hz), 104.4, 61.3 (d, $J$ = 2.2 Hz), 20.3; TLC (30% EtOAc/hexanes) $R_f$ 0.25; HRMS (ESI) calc for [C$_{29}$H$_{23}$O$_3$N$_2$FS+H]$^+$: m/z 499.1486, found 499.1485.

(Z)-N-((R,Z)-5-benzylidene-4-(2-fluorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonylamide ((R)-9jA). The title compound was prepared according to General Procedure B using (E)-N-(2-fluorobenzylidene)aniline (0.028 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf$_2$ (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 8:1. The title compound (0.038 g, 0.077 mmol, 55% yield, 86% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) $T_R$ (major) 12.7 min, $T_R$ (minor) 18.7 min.

(Z)-N-((Z)-5-benzylidene-3-(3,5-dimethylphenyl)-4-phenyloxazolidin-2-ylidene)-4-
methylbenzenesulfonamide (9kA). The title compound was prepared according to General Procedure A using (E)-N-benzylidene-3,5-dimethylaniline (0.059 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 19:1. The title compound (0.114 g, 0.22 mmol, 80% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 20 to 25% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1625, 1590, 1284, 1091, 867, 777; ¹H NMR (400 MHz, d₆-DMSO, 298 K) δ 7.86 (d, J = 8.1 Hz, 2H), 7.53 (d, J = 7.6 Hz, 2H), 7.45–7.25 (m, 10H), 7.11 (s, 2H), 6.86 (s, 1H), 6.23 (d, J = 1.0 Hz, 1H), 5.58 (d, J = 1.0 Hz, 1H), 2.33 (s, 3H), 2.19 (s, 6H); ¹³C NMR (100 MHz, d₆-DMSO, 298 K) δ 153.2, 148.3, 142.5, 139.9, 138.2, 136.8, 134.2, 132.3, 129.4, 129.2, 129.1, 128.9, 128.6, 128.4, 127.7, 127.6, 126.1, 122.5, 105.0, 65.2, 20.9, 20.8; TLC (30% EtOAc/hexanes) Rf 0.43; HRMS (ESI) calc for [C₃₁H₂₈O₃N₂S+Na]+: m/z 531.1713, found 531.1711.

(Z)-N-((S,Z)-5-benzylidene-3-(3,5-dimethylphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((S)-9kA). The title compound was prepared according to General Procedure D using (E)-N-benzylidene-3,5-dimethylaniline (0.013 g, 0.061 mmol), phenylacetylene (0.0075 g, 0.073 mmol), p-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (R,R)-L4AuCl (0.0050 g, 0.006 mmol), and AgNTf₂ (0.0024 g, 0.006 mmol) in methylene chloride. After 96 h, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio of 3:1 and showed 15% uncyclized urea was still present. The title compound (0.012 g, 0.023 mmol, 38% yield, 91% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 20 to 25% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T_R (major) 10.2 min, T_R (minor) 17.9 min.

(Z)-N-((Z)-5-benzylidene-3-(4-iodophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9lA). The title compound was prepared according to General Procedure A using (E)-N-benzylidene-4-iodoaniline (0.086 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 35 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 16:1. The title compound (0.129 g, 0.21
(Z)-N-((S,Z)-5-benzylidene-3-(4-iodophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((S)-91A). The title compound was prepared according to General Procedure D using (E)-N-benzylidene-4-iodoaniline (0.019 g, 0.061 mmol), phenylacetylene (0.0075 g, 0.073 mmol), p-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (R,R)-L4AuCl (0.0050 g, 0.006 mmol), and AgNTf2 (0.0024 g, 0.006 mmol) in methylene chloride. After 96 h, 1H NMR analysis of the crude mixture gave the diastereomeric ratio of 3:1 and showed 22% uncyclized urea was still present. The title compound (0.016 g, 0.026 mmol, 43% yield, 84% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 20 to 25% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) TR (major) 19.0 min, TR (minor) 15.9 min.

(Z)-N-((Z)-5-benzylidene-3-(4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9mA). The title compound was prepared according to General Procedure A using (E)-N-benzylidene-4-methoxycyanilne (0.059 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 0.52 µL, 0.34 mmol), and Ph3PAuNTf2 (0.0104 g, 0.014 mmol) in chloroform. After 20 h at 35 °C, 1H NMR analysis of the crude mixture gave the diastereomeric ratio: 18:1. The title compound (0.104 g, 0.20 mmol, 73% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30 to 35% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1608, 1585, 1512, 1301, 1115, 1084, 668; 1H NMR (400 MHz, d6-DMSO, 298 K) δ 7.85 (d, J = 8.3 Hz, 2H), 7.53 (d, J = 7.4 Hz, 2H), 7.45–7.25 (m, 12H), 6.90 (d, J = 9.0 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H), 5.58 (d, J = 2.0 Hz, 1H), 3.70 (s, 3H), 2.33 (s, 3H); 13C NMR (100 MHz, d6-DMSO, 298 K) δ 158.2, 153.5, 148.3, 142.5, 139.9, 136.7, 132.3, 129.4, 129.2, 129.2, 128.5, 128.3, 127.8, 127.6, 126.9, 126.8, 126.1,
114.3, 105.1, 65.8, 55.3, 20.9; **TLC** (30% EtOAc/hexanes) *R*<sub>f</sub> 0.25; **HRMS** (ESI) calc for [C<sub>30</sub>H<sub>26</sub>O<sub>4</sub>N<sub>2</sub>S+Na]<sup>+</sup>: m/z 533.1506, found 533.1504.

(Z)-<i>N</i>-(<i>R</i>,<i>Z</i>)-5-benzylidene-3-(4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((<i>R</i>)-9mA). The title compound was prepared according to General Procedure B using (<i>E</i>)-<i>N</i>-benzylidene-4-methoxyaniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), <i>p</i>-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (<i>S</i>,<i>S</i>)-<i>L4</i>AuCl (0.0058 g, 0.007 mmol), and AgNTf<sub>2</sub> (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, <sup>1</sup>H NMR analysis of the crude mixture gave the diastereomeric ratio: 8:1. The title compound (0.049 g, 0.097 mmol, 69% yield, 72% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30 to 35% ethyl acetate/hexanes. Analytical data for the title compound: **HPLC** (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) *T*<sub>R</sub> (major) 15.4 min, *T*<sub>R</sub> (minor) 13.9 min.

Methyl 4-((2<i>Z</i>,5<i>Z</i>)-5-benzylidene-4-phenyl-2-(tosylimino)oxazolidin-3-yl)benzoate (9nA). The title compound was prepared according to General Procedure A using (<i>E</i>)-methyl 4-(benzylideneamino)benzoate (0.067 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), <i>p</i>-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 35 °C, <sup>1</sup>H NMR analysis of the crude mixture gave the diastereomeric ratio: 18:1. Diethyl ether (3 mL) was layered onto the reaction mixture and left to stand overnight. The crude product was filtered and recrystallized from ethanol (12 mL) to afford the title compound (0.113 g, 0.21 mmol, 75% yield) as a white solid. Analytical data for the title compound: **IR** (thin film, cm<sup>-1</sup>) 1713, 1623, 1595, 1427, 1144, 1012, 815, 771; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.96–7.89 (m, 4H), 7.63 (d, *J* = 8.2 Hz, 2H), 7.45 (dd, *J* = 8.9, 1.2 Hz, 2H), 7.39 (t, *J* = 7.8 Hz, 2H), 7.35–7.22 (m, 6H), 7.24 (d, *J* = 8.1 Hz, 2H), 6.02 (s, 1H), 5.47 (s, 1H), 3.85 (s, 3H), 2.38 (s, 3H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, 298 K) δ 165.9, 152.5, 146.4, 143.0, 139.3, 138.5, 135.9, 131.9, 130.3, 129.5, 129.4, 129.3, 128.7, 128.5, 127.8, 127.6, 127.2, 126.7, 122.5, 107.1, 65.3, 52.1, 21.4; **TLC** (30% EtOAc/hexanes) *R*<sub>f</sub> 0.27; **HRMS** (ESI) calc for [C<sub>31</sub>H<sub>26</sub>O<sub>5</sub>N<sub>2</sub>S+Na]<sup>+</sup>: m/z 561.1455, found 561.1452.
Methyl 4-((S,2Z,5Z)-5-benzylidene-4-phenyl-2-(tosylimino)oxazolidin-3-yl)benzoate ((S)-9nA). The title compound was prepared according to General Procedure D using (E)-methyl 4-(benzylideneamino)benzoate (0.0155 g, 0.061 mmol), phenylacetylene (0.0075 g, 0.073 mmol), p-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (R,R)-L4AuCl (0.0050 g, 0.006 mmol), and AgNTf$_2$ (0.0024 g, 0.006 mmol) in methylene chloride. After 96 h, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio of 4:1 and showed 20% uncyclized urea was still present. The title compound (0.015 g, 0.027 mmol, 45% yield, 78% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 30 to 35% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IB, hexane/IPA= 65:35, flow rate=1 ml/min) $T_R$ (major) 14.3 min, $T_R$ (minor) 11.5 min.

(Z)-N-((Z)-5-benzylidene-3-(3,5-bis(trifluoromethyl)phenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9oA). The title compound was prepared according to General Procedure A using (E)-N-benzylidene-3,5-bis(trifluoromethyl)aniline (0.089 g, 0.28 mmol), phenylacetylene (0.035 g, 36 µL, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph$_3$PAuNTf$_2$ (0.010 g, 0.014 mmol) in chloroform. After 48 h at 35 °C, $^1$H NMR analysis of the crude mixture gave the diastereomeric ratio: 5:1. Diethyl ether (3 mL) was layered onto the reaction mixture and left to stand overnight. The crude product was filtered and recrystallized from ethanol (15 mL) to afford the title compound (0.112 g, 0.18 mmol, 65% yield) as a white solid. Analytical data for the title compound: IR (thin film, cm$^{-1}$) 1637, 1609, 1307, 907, 883, 801, 716; $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ 7.94 (d, $J = 8.3$ Hz, 2H), 7.81 (s, 2H), 7.66 (d, $J = 8.6$ Hz, 2H), 7.60 (s, 1H), 7.43–7.32 (m, 7H), 7.29 (d, $J = 8.4$ Hz, 2H), 7.27–7.23 (m, 1H), 6.03 (d, $J = 2.0$ Hz, 1H), 5.52 (d, $J = 2.0$ Hz, 1H), 2.42 (s, 3H); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ 152.0, 146.0, 143.3, 139.2, 136.4, 135.3, 132.2 (q, $J = 33.7$ Hz), 131.7, 130.0, 129.8, 129.4, 128.9, 128.7, 128.1, 127.5, 126.6, 122.6 (q, $J = 278.3$ Hz), 122.6 (q, $J = 3.4$ Hz), 119.5 (m), 107.8, 65.3, 21.5; $^{19}$F NMR (376 MHz, CDCl$_3$, 298 K) $\delta$ 62.38 (s, 6F); TLC (30% EtOAc/hexanes) $R_f$ 0.68; HRMS (ESI) calc for [C$_{31}$H$_{22}$O$_3$N$_2$F$_6$S+H]$^+$: m/z 617.1328, found 617.1330.

(Z)-N-((R,Z)-5-benzylidene-3-(3,5-bis(trifluoromethyl)phenyl)-4-phenyloxazolidin-2-ylidene)-4-
methylbenzenesulfonamide ((R)-9oA). The title compound was prepared according to General Procedure B using (E)-N-benzyldene-3,5-bis(trifluoromethyl)aniline (0.045 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf2 (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an additional 36 h, 1H NMR analysis of the crude mixture gave the diastereomeric ratio: 5:1. The title compound (0.042 g, 0.067 mmol, 48% yield, 95% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 10 to 15% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 85:15, flow rate=1 ml/min) T_R (major) 14.2 min, T_R (minor) 15.4 min.

(Z)-N-((Z)-5-benzyldiene-3-(3-chloro-4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9pA). The title compound was prepared according to General Procedure A using (E)-N-benzyldene-3-chloro-4-methoxyaniline (0.123 g, 0.50 mmol), phenylacetylene (0.062 g, 66 µL, 0.60 mmol), p-toluenesulfonyl isocyanate (0.118 g, 91 µL, 0.60 mmol), and Ph3PAuNTf2 (0.018 g, 0.025 mmol) in chloroform (2.5 mL total volume). After 48 h at room temperature, 1H NMR analysis of the crude mixture gave the diastereomeric ratio: 17:1. The title compound (0.205 g, 0.38 mmol, 75% yield) was isolated as large colorless rods after concentrating to dryness, redissolving in methylene chloride (1.0 mL), and layering with hexanes (4.0 mL). Analytical data for the title compound: IR (thin film, cm⁻¹) 1614, 1597, 1503, 1085, 909, 696; 1H NMR (400 MHz, d6-DMSO, 298 K) δ 7.86 (d, J = 8.2 Hz, 2H), 7.65 (d, J = 2.5 Hz, 1H), 7.53 (d, J = 7.6 Hz, 2H), 7.42–7.30 (m, 9H), 7.28 (t, J = 7.3 Hz, 1H), 7.11 (d, J = 9.0 Hz, 1H), 6.47 (d, J = 1.7 Hz, 1H), 5.75 (s, 1H), 5.59 (d, J = 1.7 Hz, 1H), 3.80 (s, 3H), 2.34 (s, 3H); 13C NMR (100 MHz, d6-DMSO, 298 K) δ 153.6, 153.4, 148.2, 142.5, 139.8, 136.5, 132.3, 129.4, 129.2, 128.5, 128.3, 127.9, 127.6, 127.3, 126.9, 126.1, 125.7, 120.8, 112.8, 105.1, 65.6, 56.3, 54.9, 20.9; TLC (30% EtOAc/hexanes) R_f 0.16; HRMS (ESI) calc for [C₃₀H₂₃O₃N₂ClSiH⁺]: m/z 545.1289, found 545.1291.

(Z)-N-((R,Z)-5-benzyldiene-3-(3-chloro-4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9pA). The title compound was prepared according to General Procedure B using (E)-N-benzyldene-3-chloro-4-methoxyaniline (0.034 g, 0.14 mmol), phenylacetylene (0.017 g, 18 µL, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf2 (0.0027 g, 0.007 mmol) in chloroform. After 4 h the wet chloroform solution was added. After an
additional 36 h. ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 6:1. The title compound (0.053 g, 0.098 mmol, 70% yield, 77% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 30 to 40% ethyl acetate/hexanes. X-ray quality crystals were obtained by dissolving 0.050 g in methylene chloride (1.0 mL) and layering on diethyl ether (1.0 mL) and hexanes (3.0 mL). Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T_R (major) 15.4 min, T_R (minor) 12.6 min.

(Z)-N-((Z)-5-(4-methoxybenzylidene)-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9qA). The title compound was prepared according to General Procedure A using (E)-N-benzylideneaniline (0.051 g, 0.28 mmol), 1-ethynyl-4-methoxybenzene (0.045 g, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol) and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at room temperature, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 2.4:1. The title compound (0.062 g, 0.12 mmol, 43% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 30 to 40% ethyl acetate/hexanes.

Analytical data for the title compound: IR (thin film, cm⁻¹) 1621, 1585, 1167, 1145, 1129, 757, 684; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.96 (d, J = 8.3 Hz, 2H), 7.62 (d, J = 8.8 Hz, 2H), 7.38–7.28 (m, 3H), 7.33–7.24 (m, 8H), 7.20–7.12 (m, 1H), 6.97 (d, J = 8.9 Hz, 2H), 5.93 (d, J = 2.0 Hz, 1H), 5.42 (d, J = 2.0 Hz, 1H), 3.87 (s, 3H), 2.41 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 159.1, 153.4, 145.2, 142.6, 139.7, 136.5, 134.6, 130.2, 129.4, 129.3, 129.2, 129.1, 127.6, 127.0, 126.7, 124.9, 124.1, 114.0, 106.6, 66.2, 55.2, 21.5; TLC (30% EtOAc/hexanes) Rₜ 0.27; HRMS (ESI) calc for [C₃₀H₂₆O₄N₂S+H]⁺ m/z 511.1686, found 511.1682.

(Z)-N-(6-(4-methoxyphenyl)-3,4-diphenyl-3,4-dihydro-2H-1,3-oxazin-2-ylidene)-4-methylbenzenesulfonamide (9qB). The title compound was isolated from the above reaction as a yellow semi-solid after flash chromatography, eluting with a gradient from 30 to 40% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 2980, 1557, 1179, 1144, 1086, 692, 664; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.78 (d, J = 9.0 Hz, 2H), 7.67 (d, J = 8.3 Hz, 2H), 7.32–7.22 (m, 6H), 7.18–7.10 (m, 4H), 7.00–6.94 (m, 4H), 5.75 (d, J = 4.8 Hz, 1H), 5.23 (d, J = 4.8 Hz, 1H), 3.86 (s, 3H), 2.34 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 161.0, 151.6, 147.1, 141.7, 141.0, 139.9, 139.2, 129.2, 129.1, 129.0, 128.9, 128.2, 127.6, 127.5, 126.9, 126.2, 122.8, 114.2, 98.3, 63.1, 55.4, 21.4; TLC (30% EtOAc/hexanes) Rₜ 0.13.
(Z)-N-((S,Z)-5-(4-methoxybenzylidene)-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((S)-9qA). The title compound was prepared according to General Procedure C using (E)-N-benzylideneaniline (0.011 g, 0.061 mmol), 1-ethynyl-4-methoxybenzene (0.016 g, 0.12 mmol), p-toluenesulfonyl isocyanate (0.024 g, 18 µL, 0.12 mmol), (R,R)-L4AuCl (0.0050 g, 0.006 mmol), and AgNTf2 (0.0024 g, 0.006 mmol) in toluene. After 5 days, 1H NMR analysis of the crude mixture gave the diastereomeric ratio of 1:1.8 and a yield of 25% of the title compound using nitrobenzene as an internal standard. The title compound (74% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T_R (major) 13.3 min, T_R (minor) 26.5 min.

(Z)-N-((Z)-3,4-diphenyl-5-(4-(trifluoromethyl)benzylidene)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9rA). The title compound was prepared according to General Procedure A using (E)-N-benzylideneaniline (0.051 g, 0.28 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (0.058 g, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph3PAuNTf2 (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 50 °C, 1H NMR analysis of the crude mixture gave the diastereomeric ratio: >20:1. The reaction mixture was concentrated to dryness and then recrystallized (scratching with a glass rod was necessary to initiate crystallization) from ethanol (2.0 mL) to afford the title compound (0.113 g, 0.21 mmol, 75% yield) as a white solid. Analytical data for the title compound: IR (thin film, cm⁻¹) 1629, 1321, 1159, 1088, 1067, 766; 1H NMR (400 MHz, CDCl3, 298 K) δ 7.91 (d, J = 8.3 Hz, 2H), 7.73 (d, J = 8.2 Hz, 2H), 7.61 (d, J = 8.3 Hz, 2H), 7.38–7.18 (m, 11H), 7.13 (tt, J = 7.1, 1.4 Hz, 1H), 5.99 (d, J = 1.8 Hz, 1H), 5.49 (d, J = 2.0 Hz, 1H), 2.37 (s, 3H); 13C NMR (100 MHz, CDCl3, 298 K) δ 152.7, 148.9, 142.9, 139.5, 135.8, 135.7, 134.3, 129.7, 129.4, 129.3, 129.2 (q, J = 32.4 Hz), 129.1, 128.8, 127.6, 127.1, 126.6, 125.4 (q, J = 3.7 Hz), 124.0 (q, J = 270.0 Hz), 124.0, 105.5, 66.2, 21.4; 19F NMR (374 MHz, CDCl3) δ -61.76 (s, 3F); TLC (30% EtOAc/hexanes) Rf 0.33; HRMS (ESI) calc for [C30H23O3F3N2S+H]⁺: m/z 549.1454, found 549.1452.

(Z)-N-((R,Z)-3,4-diphenyl-5-(4-(trifluoromethyl)benzylidene)oxazolidin-2-ylidene)-4-
**methylbenzenesulfonamide ((R)-9rA).** The title compound was prepared according to General Procedure B using (E)-N-benzylideneaniline (0.025 g, 0.14 mmol), 1-ethynyl-4-((trifluoromethyl)benzene (0.036 g, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf₂ (0.0027 g, 0.007 mmol) in toluene. After 6 days, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: >20:1. The title compound (0.065 g, 0.119 mmol, 85% yield, 72% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: HPLC (Chiral Technology Chiral Pak IA, hexane/IPA= 65:35, flow rate=1 ml/min) T₉ (major) 9.4 min, T₉ (minor) 44.5 min.

![Chemical structure](image)

**Z-((Z)-3,4-diphenyl-5-(2-phenylethylidene)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9sA).** The title compound was prepared according to General Procedure A using (E)-N-benzylideneaniline (0.051 g, 0.28 mmol), 3-phenyl-1-propyne (0.040 g, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 52 µL, 0.34 mmol), and Ph₃PAuNTf₂ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 50 °C, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 15:1. The title compound (0.100 g, 0.20 mmol, 72% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: IR (thin film, cm⁻¹) 1615, 1585, 1167, 1129, 891, 685; ¹H NMR (400 MHz, CDCl₃, 298 K) δ 7.95 (d, J = 8.3 Hz, 2H), 7.33–7.16 (m, 14H), 7.12 (tt, J = 7.7, 1.3 Hz, 1H), 7.17–7.05 (m, 2H), 5.78 (d, J = 1.8 Hz, 1H), 4.75 (ddd, J = 8.5, 7.3, 2.1 Hz, 1H), 3.56 (dd, J = 15.2, 3.8 Hz, 1H), 3.40 (ddd, J = 15.3, 7.2, 1.6 Hz, 1H), 2.35 (s, 3H); ¹³C NMR (100 MHz, CDCl₃, 298 K) δ 153.2, 147.8, 142.6, 139.6, 138.9, 136.3, 134.5, 129.3, 129.1, 129.0, 128.4, 128.2, 127.3, 127.0, 126.9, 126.3, 123.9, 106.0, 64.9, 31.2, 21.4; TLC (30% EtOAc/hexanes) R₉ 0.24; HRMS (ESI) calc for [C₃₉H₃₆O₃N₂S]+: m/z 495.1737, found 495.1737.

![Chemical structure](image)

**Z-((R,Z)-3,4-diphenyl-5-(2-phenylethylidene)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((R)-9sA).** The title compound was prepared according to General Procedure B using (E)-N-benzylideneaniline (0.025 g, 0.14 mmol), 3-phenyl-1-propyne (0.024 g, 0.17 mmol), p-toluenesulfonyl isocyanate (0.033 g, 25 µL, 0.17 mmol), (S,S)-L4AuCl (0.0058 g, 0.007 mmol), and AgNTf₂ (0.0027 g, 0.007 mmol) in toluene. After 6 days, ¹H NMR analysis of the crude mixture gave the diastereomeric ratio: 6:1. The title compound (0.046 g, 0.092 mmol, 66% yield, 76% ee) was isolated as a white solid after flash chromatography, eluting with a
gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: **HPLC** (Chiral Technology Chiral Pak IB, hexane/IPA= 72:25, flow rate=1 ml/min) T<sub>R</sub> (major) 10.5 min, T<sub>R</sub> (minor) 12.3 min.

(Z)-4-methyl-N-((Z)-5-pentylidene-3,4-diphenyloxazolidin-2-ylidene)benzenesulfonamide (9tA). The title compound was prepared according to General Procedure A using (E)-N-benzylideneaniline (0.051 g, 0.28 mmol), 1-hexyne (0.028 g, 0.34 mmol), p-toluenesulfonyl isocyanate (0.067 g, 0.67 µL, 0.34 mmol), and Ph<sub>3</sub>PAuNTf<sub>2</sub> (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 50 °C, <sup>1</sup>H NMR analysis of the crude mixture gave the diastereomeric ratio: 1.6:1. The title compound (0.060 g, 0.13 mmol, 47% yield) was isolated as a white solid after flash chromatography, eluting with a gradient from 25 to 30% ethyl acetate/hexanes. Analytical data for the title compound: **IR** (thin film, cm<sup>−1</sup>) 1615, 1584, 1318, 1112, 892, 686; **1H NMR** (400 MHz, CDCl<sub>3</sub>, 298 K) δ 7.93 (d, J = 8.3 Hz, 2H), 7.33–7.08 (m, 12H), 5.72 (d, J = 1.9 Hz, 1H), 4.53 (td, J = 7.6, 2.1 Hz, 1H), 2.41 (s, 3H), 2.25–2.05 (m, 2H), 1.31–1.20 (m, 4H), 0.92–0.84 (m, 3H); **13C NMR** (100 MHz, CDCl<sub>3</sub>, 298 K) δ 153.6, 147.3, 142.5, 139.7, 136.7, 134.7, 129.2, 129.1, 129.0, 127.4, 127.2, 126.8, 124.0, 107.5, 65.0, 31.1, 24.7, 22.2, 21.5, 13.8; **TLC** (30% EtOAc/hexanes) R<sub>f</sub> 0.31; **HRMS** (ESI) calc for [C<sub>27</sub>H<sub>28</sub>O<sub>3</sub>N<sub>2</sub>S+H]<sup>+</sup>: m/z 461.1893, found 461.1890.

**General methods for preparing N-substituted 2-(diphenylphosphino)cyclohexanamines and their corresponding gold(I) complexes.** A flame-dried scintillation vial equipped with a magnetic stir bar was charged with (1S,2S)-2-(diphenylphosphino)cyclohexanamine and anhydrous methylene chloride (0.1–0.2 M) under N<sub>2</sub> at room temperature. The requisite acylating agent (1.0–1.1 equiv) was then added. Triethylamine (1.1 equiv) was added prior to the acylating agent when chloroformates, acid chlorides, BOC anhydride, or diphosgene (for the preparation of the symmetrical bis-phosphine urea) was used. When the starting amine was fully consumed as judged by TLC analysis, the crude reaction mixture was loaded directly onto a silica column and eluted with the desired solvent mixture to afford the N-substituted phosphine. A scintillation vial was charged with N-substituted phosphine (1.0 equiv), Me<sub>2</sub>S·AuCl<sub>2</sub> (1.0 equiv), and methylene chloride (0.1 M phosphine) with no precautions to preclude air or moisture. The mixture was sonicated for 30 sec and allowed to stand at room temperature. After 30 min, the reaction was analyzed by <sup>1</sup>H and <sup>31</sup>P NMR. The mixture was filtered through glass microfiber and concentrated to ~0.5–1.0 mL. To this solution was layered diethyl ether (4 mL) and hexanes (8 mL) and allowed to stand in the dark for 24 hours. Alternatively, the phosphine gold(I) complex could be purified with flash chromatography, eluting with 1 or 2% methanol/methylene chloride.
The following acylating agents were commercially available: \( p \)-toluenesulfonyl isocyanate, phenyl isocyanate, 3,5-\textit{bis}(trifluoromethyl)phenyl isocyanate, ethyl isocyanate, diphosgene, benzoyl isocyanate, 1-adamantanecarbonyl chloride, 2,4,6-trisopropylbenzoyl chloride, phthalic anhydride (phthlate prepared in toluene at 130 °C), and 3,5-\textit{bis}(trifluoromethyl)phenyl isothiocyanate. \( p \)-Toluenesulfonyl chloride and 2,4,6-\textit{trimethylphenylsulfonyl chloride were also commercially available, but it was necessary to prepare the gold(I) chloride complex of (1S,2S)-2-(diphenylphosphino)cyclohexanamine prior to sulfonation. Without prior protection of the phosphine with gold(I), oxygen transfer from sulfur to phosphorus occurred during the sulfonation reaction to provide a mixture of diastereotopic sulfinyl urea phosphine oxides.

The \textit{tert}-leucine-derived isocyanate was prepared by the procedure of Jacobsen.\textsuperscript{3} 2,4,6-Trimethylbenzoyl isocyanate and 2,4,6-trisopropylbenzoyl isocyanate were synthesized by refluxing the corresponding primary amides with 3–6 equiv of oxalyl chloride in anhydrous dichloroethane (0.15 M amide) for 20 hours followed by concentration of the reaction mixture and use of the isocyanates without further purification.

2,5-Dimethylphenylsulfonyl isocyanate, 2,4,6-trimethylphenylsulfonyl isocyanate and 2,4,6-trisopropylphenylsulfonyl isocyanate were synthesized by refluxing the corresponding primary sulfonamides with \( \text{\textit{n}} \)-butyl isocyanate (0.3 equiv) in chlorobenzene (0.15 M sulfonamide). To this refluxing solution was added diphosgene (2.0 equiv) dropwise over 2.5 hours. After \( ^1 \text{H} \) NMR confirmed full conversion of the sulfonamide, the reaction was concentrated to dryness and the isocyanates were used directly without further purification.

\[
\begin{align*}
\text{NH}_2 \quad \text{O} \quad \text{O} \quad \text{N} \\
\text{CH}_2\text{Cl}_2, \text{rt} \\
\end{align*}
\]

\( N\text{-}((1S,2S)-2\text{-}(\text{diphenylphosphino})\text{cyclohexyl})\text{carbamoyl})\text{-}2,4,6\text{-}\text{triisopropylbenzenesulfonamide (L4).} \) A flame-dried scintillation vial equipped with a magnetic stir bar was charged with 2,4,6-triisopropylbenzenesulfonfyl isocyanate (0.220 g, 0.71 mmol), (1S,2S)-2-(diphenylphosphino)cyclohexanamine (0.200 g, 0.71 mmol), and anhydrous methylene chloride (4.0 mL) under \( \text{N}_2 \). After 3 h at room temperature, the crude reaction mixture was loaded directly onto a silica column and eluted with a gradient of 1 to 2% methanol/methylene chloride. The title compound (0.329 g, 0.55 mmol, 78% yield) was isolated as a white solid. Analytical data for the title compound: \( ^1 \text{H} \) NMR (400 MHz, CDCl\textsubscript{3}, 298 K) \( \delta \) 9.36 (br s, 1H), 7.59 (t, \( J = 7.0 \) Hz, 2H), 7.53–7.42 (m, 4H), 7.40–7.33 (m, 4H), 7.22 (s, 2H), 6.75 (br d, \( J = 8.1 \) Hz, 1H), 4.16 (sept, \( J = 6.7 \) Hz, 2H), 3.80–3.70 (m, 1H), 2.92 (sept, \( J = 6.9 \) Hz, 1H), 2.52–2.46 (m, 1H), 2.15–2.07 (m, 1H), 1.90–1.72 (m, 2H), 1.65–1.52 (m, 1H), 1.50–1.30 (m, 3H), 1.33 (d, \( J = 6.8 \) Hz, 6H), 1.31 (d, \( J = 6.8 \) Hz, 6H), 1.27 (d, \( J = 6.9 \) Hz, 3H), 1.27 (d, \( J = 6.9 \) Hz, 3H), 1.18–1.05 (m, 1H); \( ^{13} \text{C} \) NMR (100 MHz, CDCl\textsubscript{3}, 298 K) \( \delta \) 153.5,
151.3, 150.4, 136.1 (d, $J = 13.1$ Hz), 135.7 (d, $J = 16.9$ Hz), 134.5 (d, $J = 20.7$ Hz), 132.9, 132.6 (d, $J = 18.3$ Hz), 128.9, 128.5 (d, $J = 6.0$ Hz), 128.2, 128.1 (d, $J = 7.7$ Hz), 123.9, 49.6 (d, $J = 18.7$ Hz), 39.3 (d, $J = 18.0$ Hz), 34.1, 31.3, 29.9. 25.4 (d, $J = 3.7$ Hz), 24.9, 24.8, 24.7, 24.0, 23.5, 23.4, 23.3; $^{31}$P NMR (163 MHz, CDCl$_3$, 298 K) $\delta$ –10.7; HRMS (ESI) calc for [C$_{34}$H$_{45}$O$_3$N$_2$PS+H]$^+$: $m/z$ 593.2961, found 593.2951.

$N$-((1S,2S)-2-(diphenylphosphino)cyclohexyl)carbamoyl)-2,4,6-triisopropylbenzenesulfonamide gold(I) chloride (S,S-L4AuCl). A scintillation vial was charged with $N$-((1S,2S)-2-(diphenylphosphino)cyclohexyl)carbamoyl)-2,4,6-triisopropylbenzenesulfonamide (L4) (0.450 g, 0.76 mmol), Me$_2$S-AuCl$^2$ (0.224 g, 0.76 mmol), and methylene chloride (6.0 mL) with no precautions to preclude air or moisture. The mixture was sonicated for 30 sec and allowed to stand at room temperature. After 30 min, the reaction was judged complete by $^1$H and $^{31}$P NMR. The mixture was filtered through glass microfiber and concentrated to ~1.5 mL. To this solution was layered diethyl ether (4 mL) and hexanes (8 mL) and allowed to stand in the dark for 24 hours. The white precipitate was isolated by filtration and washed with 10% methylene chloride/hexanes (5 mL) to afford the title compound (0.505 g, 0.61 mmol, 81% yield) as a white solid. Analytical data for the title compound: $^1$H NMR (400 MHz, CDCl$_3$, 298 K) $\delta$ 8.18 (br s, 1H), 8.03–7.94 (m, 2H), 7.81–7.74 (m, 2H), 7.52–7.37 (m, 6H), 7.12 (s, 2H), 6.38 (br d, $J = 8.0$ Hz, 1H), 3.92 (sept, $J = 6.7$ Hz, 2H), 3.98–3.85 (m, 1H), 3.23–3.12 (m, 1H), 2.87 (sept, $J = 6.9$ Hz, 1H), 2.15–1.96 (m, 2H), 1.80–1.65 (m, 1H), 1.65–1.30 (m, 5H), 1.21 (d, $J = 7.0$ Hz, 12H), 1.19 (d, $J = 6.9$ Hz, 6H); $^{13}$C NMR (100 MHz, CDCl$_3$, 298 K) $\delta$ 153.7, 150.5, 150.3, 134.1 (d, $J = 13.7$ Hz), 134.0 (d, $J = 13.3$ Hz), 132.6, 132.1 (d, $J = 2.5$ Hz), 131.8 (d, $J = 2.6$ Hz), 129.4 (d, $J = 11.9$ Hz), 129.2 (d, $J = 11.6$ Hz), 128.7 (d, $J = 59.8$ Hz), 128.0 (d, $J = 58.6$ Hz), 127.7, 50.7 (d, $J = 3.4$ Hz), 38.8 (d, $J = 35.2$ Hz), 34.1, 31.0 (d, $J = 8.4$ Hz), 29.8, 25.7 (d, $J = 4.0$ Hz), 24.8, 23.6 (d, $J = 9.7$ Hz), 23.5, 23.4, 23.0; $^{31}$P NMR (163 MHz, CDCl$_3$, 298 K) $\delta$ 40.0; HRMS (ESI) calc for [C$_{34}$H$_{45}$O$_3$N$_2$AuClPS+Na]$^+$: $m/z$ 847.2135, found 847.2130.
Scheme S1. Preparation of gold(I) complexes from L22-L37

**Sulfamidates**

\[
\text{Baker's yeast} \quad \text{water, sucrose} \quad \text{S1, S6}
\]

**Diallyl Phosphines and Phosphine Borane Complexes**

\[
\begin{align*}
\text{ArMgX} + \text{PhBH}_2\text{THF} & \rightarrow \text{H}_2\text{BH}_2\text{Ar} \quad \text{Ar} = \alpha\text{-tolyl, 3,5-Me}_2\text{C}_6\text{H}_3, 3,5-(i\text{-Bu})_2\text{4-OMeC}_6\text{H}_3 \\
\text{ArMgX} + \text{PhBH}_2\text{THF} & \rightarrow \text{H}_2\text{BH}_2\text{Ar} \quad \text{Ar} = 3,5-(\text{CF}_3)_2\text{C}_6\text{H}_3
\end{align*}
\]

**Gold Phosphine Complexes**

\[
\text{or other sulfamidate (S5, S10, or S11)}
\]

\[
\begin{align*}
\text{H}_2\text{H}_2\text{B}_{\text{Ar}}\text{NHBOC} & \quad \text{aq. H}_2\text{SO}_4 \\
\text{Ar} = \alpha\text{-tolyl or 3,5-Me}_2\text{C}_6\text{H}_3 \\
\text{AuCl complexes of L25, L26, L27, L28, L29, and L30}
\end{align*}
\]

\[
\text{H}_2\text{H}_2\text{B}_{\text{Ar}}\text{NHBOC} + \text{DABCO} \rightarrow \text{L36AuCl} \\
\text{Ar} = 3,5-(i\text{-Bu})_2\text{4-OMeC}_6\text{H}_3 \\
\text{AuCl complexes of L34, Ar = 4-Me-C}_6\text{H}_4 \\
\text{L35, Ar = 2,4,6-(i\text{-Pr})_3\text{C}_6\text{H}_2} \\
\text{Cyclopentane} = \text{L35}
\]

\[
\text{H}_2\text{H}_2\text{B}_{\text{Ar}}\text{NHBOC} + \text{DABCO} \rightarrow \text{L37AuCl} \\
\text{Ar} = \text{Ph or 3,5-(CF}_3)_2\text{C}_6\text{H}_3 \\
\text{AuCl complexes of L22, L23, L31, L32, and L33}
\]

\[
\text{H}_2\text{H}_2\text{B}_{\text{Ar}}\text{NHBOC} + \text{DABCO} \rightarrow \text{L36AuCl} \\
\text{Ar} = \text{Ph or 3,5-(CF}_3)_2\text{C}_6\text{H}_3 \\
\text{AuCl complexes of L22, L23, L31, L32, and L33}
\]

\[
\text{H}_2\text{H}_2\text{B}_{\text{Ar}}\text{NHBOC} + \text{DABCO} \rightarrow \text{L37AuCl} \\
\text{Ar} = \text{Ph or 3,5-(CF}_3)_2\text{C}_6\text{H}_3 \\
\text{AuCl complexes of L22, L23, L31, L32, and L33}
\]

\[
\text{Baker's yeast} \quad \text{sucrose, H}_2\text{O} \quad \text{S1}
\]
(1R,2S)-Ethyl 2-hydroxycyclopentanecarboxylate. The title compound was prepared by a modification of the procedure of Bertau. Sucrose (625 g) was dissolved in deionized water (3.25 L) and heated to 30 ºC with overhead stirring. Baker’s yeast (250 g) was then added and allowed to stir without heating for 1 h. Ethyl 2-oxocyclopentanecarboxylate (39.0 g, 36.2 mL, 250 mmol) was added at once and stirred at room temperature. The reaction was judged complete after 18 hours (TLC analysis) at which time Celite (150 g) was added. The reaction mixture was filtered through a 7” Buchner funnel, washing the cake with water (200 mL). The combined water layers were saturated with NaCl and extracted with diethyl ether (5 x 500 mL). The combined organic layers were dried with MgSO\(_4\), filtered, and concentrated. The residue was distilled (75–80 ºC, 0.5 mbar) to give the title compound as a clear, colorless oil (32.1 g, 203 mmol, 81%). The analytical data was consistent with that reported in the literature.

(1R,2S)-2-Hydroxycyclopentanecarbohydrazide. The title compound was prepared by a modification of the procedure of Bertau. To a 100 mL round-bottomed flask equipped with a magnetic stir bar and a condenser was added (1R,2S)-ethyl 2-hydroxycyclopentanecarboxylate (31.0 g, 196 mmol), hydrazine hydrate (15.7 g, 314 mmol), and absolute ethanol (16 mL). The mixture was heated to reflux for 2.4 h. The solvent was removed. The residue was taken up in ethanol (250 mL) and diluted with 1,2-dichloroethane (400 mL) to initiate crystallization. The fine, long, colorless crystals were filtered to leave the title compound (20.2 g). The filtrate was concentrated and again crystallized to obtain a second crop (6.0 g) to give a total of 26.2 g (182 mmol, 93% yield). The analytical data was consistent with that reported in the literature.\(^6\) \(^1\)H NMR (400 MHz, \(d_6\)-DMSO, 298 K) \(\delta\) 8.97 (br s, 1H), 4.72 (d, \(J = 3.0\) Hz, 1H), 4.18 (br s, 3H), 2.38 (ddd, \(J = 9.9, 8.3, 4.6\) Hz, 1H), 1.95–1.80 (m, 1H), 1.80–1.43 (m, 5H); \(^{13}\)C NMR (125 MHz, \(d_6\)-DMSO, 298 K) \(\delta\) 172.7, 73.3, 47.7, 34.3, 25.9, 21.5.

(3aR,6aS)-Perhydrocyclopenta[d]oxazol-2-one. The title compound was prepared by a modification of the procedure of Bertau. To a 1.0 L Erlenmeyer flask equipped with a magnetic stir bar was added (1R,2S)-2-hydroxycyclopentanecarbohydrazide (22.7 g, 157 mmol) and 0.5 M aqueous H\(_2\)SO\(_4\) (360 mL). After dissolution, the solution was cooled to −2 ºC. A solution of NaNO\(_2\) (19.6 g, 283 mmol) in water (250 mL) was added dropwise over 1 h. After the addition the mixture was allowed to reach room temperature naturally over ~3 h. The reaction was then stirred at room temperature for 18 hours. The solution was saturated with NaCl and cooled in an ice bath to crystallize the product, which was filtered and washed with sat. aqueous NaCl (100
ethyl acetate (20 mL). The combined organic layers were washed with sat. aqueous NaCl (10 mL), dried with MgSO₄, filtered, and evaporated to leave the title compound (8.77 g, 69 mmol, 44% yield) as a white solid. The analytical data was consistent with that reported in the literature.⁷ ¹H NMR (400 MHz, CDCl₃, 298 K) δ 5.59 (br s, 1H), 5.06 (dd, J = 7.0, 5.8 Hz, 1H), 4.27 (t, J = 6.6 Hz, 1H), 2.15–2.05 (m, 1H), 1.90–1.50 (m, 5H); ¹³C NMR (125 MHz, CDCl₃, 298 K) δ 160.4, 82.1, 56.6, 34.2, 33.6, 21.7;

tert-Butyl ((1R,2S)-2-hydroxycyclopentyl)carbamate. To a 250 mL round-bottomed flask equipped with a magnetic stir bar was added (3aR,6aS)-perhydrocyclopenta[d]oxazol-2-one (3.9 g, 30.7 mmol), 4-(dimethylamino)pyridine (1.88 g, 15.4 mmol), and anhydrous DMF (80 mL). To this solution was added Boc₂O (8.7 g, 40.0 mmol) and allowed to stir at room temperature for 1 h. The reaction was quenched with sat. aqueous NH₄Cl (60 mL) and extracted with ethyl acetate (3 x 60 mL). The combined organic layers were washed with 5% aqueous NaCl (4 x 50 mL), sat. aqueous NaCl (40 mL), dried with MgSO₄, filtered and evaporated. The residue was dissolved in THF (100 mL) and cooled to 0 ºC. A solution of LiOH (7.4 g, 310 mmol) in water (75 mL) was added dropwise at 0 ºC and allowed to warm to room temperature naturally overnight. The solution was saturated with NaCl and extracted with ethyl acetate (3 x 150 mL). The combined organic layers were dried with MgSO₄, filtered, and evaporated. The residue was purified on a 1” silica plug, eluting first with 30% ethyl acetate/hexanes to yield the title compound (3.12 g, 15.5 mmol, 50% yield), then with ethyl acetate to provide (3aR,6aS)-perhydrocyclopenta[d]oxazol-2-one. The analytical data was consistent with that reported in the literature.⁸ ¹H NMR (400 MHz, CDCl₃, 298 K) δ 5.05 (br d, J = 7.6 Hz, 1H), 4.09 (br s, 1H), 3.75 (br s, 1H), 2.69 (br s, 1H), 2.00–1.70 (m, 3H), 1.67–1.45 (m, 3H), 1.41 (s, 9H).

(3aR,6aS)-tert-Butyl tetrahydrocyclopenta[d][1,2,3]oxathiazole-3(3aH)-carboxylate 2,2-dioxide. To a flame-dried 250 mL round-bottomed flask equipped with a magnetic stir bar was added anhydrous acetonitrile (35 mL) and thionyl chloride (5.25 g, 3.20 mL, 44.1 mmol) under N₂. The solution was cooled to –45 ºC. Then a solution of tert-butyl ((1R,2S)-2-hydroxycyclopentyl)carbamate (3.55 g, 17.6 mmol) in acetonitrile (20 mL) was added dropwise, maintaining the temperature at –45 ºC. Pyridine (7.10 mL, 88 mmol) was added slowly and stirred at –45 ºC for 2 h. Then the reaction was allowed to slowly warm to room temperature over 3 h. The solvents were removed and the residue was taken up in ethyl acetate (100 mL) and water (20 mL). The organic layer was washed with sat. aqueous NaCl (10 mL). The combined aqueous layers were back-extracted with ethyl acetate (20 mL). The combined organic layers were washed with sat. aqueous NaCl (10 mL), dried with
MgSO₄, filtered, and evaporated. The residue was dissolved in acetonitrile (30 mL) and water (30 mL). Ruthenium(III) chloride hydrate (0.009 g, 0.04 mmol) was added and the mixture was cooled to 0 °C. NaIO₄ (5.65 g, 26.4 mmol) was added and the reaction was allowed to warm to room temperature with stirring for 2 h. The mixture was extracted with diethyl ether (2 x 50 mL), washed with sat. aqueous NaCl (10 mL), dried with MgSO₄, filtered, and evaporated. The residue was taken up in methylene chloride (15 mL) and then diluted with hexanes (300 mL) to yield the title compound (2.60 g, 9.88 mmol, 56% yield) as an off-white precipitate. The analytical data was consistent with that reported in the literature.

1H NMR (400 MHz, CDCl₃, 298 K) δ 5.18–5.13 (m, 1H), 4.58–4.52 (m, 1H), 2.25–2.15 (m, 1H), 2.08–1.92 (m, 3H), 1.90–1.75 (m, 2H), 1.55 (s, 9H); 13C NMR (125 MHz, CDCl₃, 298 K) δ 148.8, 84.9, 83.5, 61.0, 32.5, 32.0, 27.7, 22.4; HRMS (ESI) calc for [C₁₀H₁₇O₅NS+Na]⁺: m/z 286.0720, found 286.0722.

(1R,2S)-Ethyl 2-hydroxycyclohexanecarboxylate. The title compound was prepared by a modification of the procedure of Bertau. Sucrose (390 g) was dissolved in deionized water (2.0 L) and heated to 30 °C with overhead stirring. Baker’s yeast (156 g) was then added and allowed to stir without heating for 1 h. Ethyl 2-oxocyclohexanecarboxylate (26.6 g, 25.0 mL, 156 mmol) was added at once and stirred at room temperature. The reaction was judged complete after 18 hours (TLC analysis) at which time Celite (200 g) was added. The reaction mixture was filtered through a 7” Buchner funnel, washing the cake with water (200 mL). The combined water layers were saturated with NaCl and extracted with diethyl ether (4 x 500 mL). The combined organic layers were dried with MgSO₄, filtered, and concentrated. The residue was distilled (91–95 °C, 0.5 mbar) to give the title compound as a clear, colorless oil (19.2 g, 111 mmol, 71%). The analytical data was consistent with that reported in the literature.

1H NMR (400 MHz, CDCl₃, 298 K) δ 8.93 (br s, 1H), 3.92–

(1R,2S)-2-Hydroxycyclohexanecarbohydrazide. The title compound was prepared by a modification of the procedure of Bertau. To a 100 mL round-bottomed flask equipped with a magnetic stir bar and a condenser was added (1R,2S)-ethyl 2-hydroxycyclohexanecarboxylate (8.0 g, 46.5 mmol), hydrazine hydrate (3.7 g, 3.6 mL, 74.4 mmol), and absolute ethanol (4 mL). The mixture was heated to reflux for 2.5 h. The solvent was removed. The residue was recrystallized from CH₂Cl₂ (20 mL), cooling to –30 °C. The fine, long, colorless crystals were filtered to leave the title compound (6.05 g, 38.2 mmol, 82% yield). The analytical data was consistent with that reported in the literature. 1H NMR (400 MHz, d₆-DMSO, 298 K) δ 8.93 (br s, 1H), 3.92–
3.87 (m, 1H), 3.82 (br s, 3H), 2.14 (ddd, $J = 11.5, 3.9, 2.7$ Hz, 1H), 1.76–1.48 (m, 4H), 1.42–1.22 (m, 3H), 1.22–1.10 (m, 1H).

(3aR,7aS)-Hexahydrobenzo[d]oxazol-2(3H)-one. The title compound was prepared by a modification of the procedure of Bertau.\(^4\) To a 150 mL Erlenmeyer flask equipped with a magnetic stir bar was added (1R,2S)-2-hydroxycyclohexanecarbohydrazide (5.55 g, 35.1 mmol) and 0.5 M aqueous H\(_2\)SO\(_4\) (88 mL). After dissolution, the solution was cooled to 0 °C. A solution of NaNO\(_2\) (4.4 g, 63.5 mmol) in water (66 mL) was added dropwise over 30 min. After the addition the mixture was allowed to reach room temperature naturally over ~3 h. The reaction was then stirred at room temperature for 21 hours. The solution was saturated with NaCl. The residue was extracted with methylene chloride (3 x 60 mL), dried with Na\(_2\)SO\(_4\), filtered, and evaporated to leave the title compound (2.97 g, 20.9 mmol, 60% yield) as a white solid. The analytical data was consistent with that reported in the literature.\(^7\)\(^,\)\(^1\)H NMR (300 MHz, CDCl\(_3\), 298 K) \(\delta\) 6.40 (br s, 1H), 4.55 (dt, $J = 6.5, 4.8$ Hz, 1H), 3.72 (q, $J = 6.6$ Hz, 1H), 2.00–1.88 (m, 1H), 1.85–1.65 (m, 2H), 1.65–1.32 (m, 4H), 1.32–1.15 (m, 1H).

\(\text{Boc}_2\text{O}\), \(\text{DMAP}\)

\(\text{LiOH}\), \(\text{THF}/\text{H}_2\text{O}\)

\(\text{NaOH}\)

\(\text{Boc}_2\text{O}\)

\(\text{DMF}\)

\(\text{LiOH}\), \(\text{THF}/\text{H}_2\text{O}\)

**tert-Butyl ((1R,2S)-2-hydroxycyclohexyl)carbamate.** To a 250 mL round-bottomed flask equipped with a magnetic stir bar was added (3aR,7aS)-hexahydrobenzo[d]oxazol-2(3H)-one (2.97 g, 20.9 mmol), 4-(dimethylamino)pyridine (1.28 g, 10.5 mmol), and anhydrous DMF (60 mL). To this solution was added Boc\(_2\)O (5.96 g, 27.3 mmol) and allowed to stir at room temperature for 2 h. The reaction was quenched with sat. aqueous NH\(_4\)Cl (40 mL) and extracted with ethyl acetate (3 x 50 mL). The combined organic layers were washed with 5% aqueous NaCl (4 x 25 mL), aqueous HCl (1M, 25 mL), sat. aqueous NaCl (25 mL), dried with MgSO\(_4\), filtered and evaporated. The residue was dissolved in THF (100 mL) and cooled to 0 °C. A solution of LiOH (4.68 g, 195 mmol) in water (39 mL) was added at once at room temperature and stirred for 2 h. The solution was extracted with ethyl acetate (3 x 100 mL). The combined organic layers were dried with MgSO\(_4\), filtered, and evaporated. The residue was purified on a 1” silica plug, eluting first with 30% ethyl acetate/hexanes to yield the title compound (3.55 g, 16.5 mmol, 79% yield). The analytical data was consistent with that reported in the literature.\(^11\)\(^,\)\(^1\)H NMR (400 MHz, CDCl\(_3\), 298 K) \(\delta\) 4.95 (br d, $J = 6.8$ Hz, 1H), 3.95–3.88 (m, 1H), 3.58 (br s, 1H), 2.35 (br s, 1H), 1.77–1.65 (m, 1H), 1.65–1.47 (m, 5H), 1.46–1.25 (m, 2H), 1.42 (s, 9H).
(3aR,7aS)-tert-Butyl hexahydro-3H-benzo[d][1,2,3]oxathiazole-3-carboxylate 2,2-dioxide. To a flame-dried 250 mL round-bottomed flask equipped with a magnetic stir bar was added anhydrous acetonitrile (45 mL) and thionyl chloride (4.84 g, 2.95 mL, 40.7 mmol) under N₂. The solution was cooled to −40 °C. Then a solution of tert-butyl ((1R,2S)-2-hydroxycyclohexyl)carbamate (3.50 g, 16.3 mmol) in acetonitrile (20 mL) and anhydrous methylene chloride (20 mL) was added dropwise, maintaining the temperature at −40 °C. Pyridine (6.56 mL, 81.3 mmol) was added slowly and stirred at −40 °C for 1 h. Then the reaction was allowed to slowly warm to room temperature over 3 h. The solvents were removed and the residue was taken up in ethyl acetate (60 mL) and water (40 mL). The organic layer was washed with sat. aqueous NaCl (3 x 10 mL), dried with MgSO₄, filtered, and evaporated. The residue was dissolved in acetonitrile (60 mL) and methylene chloride (12 mL). Ruthenium(III) chloride hydrate (0.030 g, 0.13 mmol) was added and the mixture was cooled to 0 °C. NaIO₄ (9.27 g, 43.4 mmol) in water (60 mL) was added and the reaction was allowed to warm to room temperature with stirring for 3 h. The mixture was extracted with diethyl ether (2 x 100 mL), washed with sat. aqueous NaCl (2 x 25 mL), dried with MgSO₄, filtered, and evaporated. The crude product was passed through a " silica plug, eluting with methylene chloride. The residue was taken up in methylene chloride (15 mL) and then diluted with hexanes (300 mL) to yield the title compound (2.75 g, 9.9 mmol, 61% yield) as white needles. The analytical data was consistent with that reported in the literature.¹⁹¹H NMR (400 MHz, CDCl₃, 298 K) δ 4.95 (q, J = 3.3 Hz, 1H), 4.14 (ddd, J = 10.6, 6.0, 4.3 Hz, 1H), 2.35–2.25 (m, 2H), 1.85–1.58 (m, 4H), 1.58–1.45 (m, 1H), 1.54 (s, 9H), 1.21 (tdt, J = 13.8, 12.5, 3.3 Hz, 1H).

Procedure for the preparation of gold(I) complexes with L22-L37

Procedures were used in direct analogy with the published procedures by Guo⁹ for phosphide sulfamidate ring-opening, borane phosphide deprotection, and Boc-deprotection in the sequence provided by scheme S1 (page S24).⁹ Formation of sulfonylureas and gold complexation was analogous to that reported for L4. Phosphines and phosphide borane complexes were prepared by the method of Buscacca.¹²,¹³

General procedure for screening catalysts: the asymmetric addition of phenylacetylene to (E)-N-benzylideneaniline. A stock solution of (E)-N-benzylideneaniline (0.0034 g, 0.019 mmol/100 µL methylene chloride) and phenylacetylene (0.0039 g, 0.038 mmol/100 µL methylene chloride was prepared. The stock solution (100 µL) was added to an amber vial. In a separate amber vial was prepared a stock solution of the desired gold(I) catalyst with the corresponding gold(I) chloride complex (0.011 mmol/100 µL methylene chloride) and AgNTf₂ (0.0003 g, 0.008 mmol/100 µL methylene chloride). This mixture was sonicated for 30
seconds and then filtered through glass microfiber to afford a colorless solution of the catalyst. The catalyst solution (100 µL) was added quickly to the first vial, which was then sealed with a PTFE-lined screw cap (imine molarity ~0.1 M). The reaction was left to stand at room temperature for 3 h. The reaction mixture was then directly loaded onto a Monster-pette packed with silica and purified via flash chromatography, eluting with 2.5% ethyl acetate/hexanes. Modification of these standard reaction parameters (solvent, silver salt, concentration, catalyst loading, additives) was made accordingly when desired. The enantiomeric excess of the purified propargyl amine was determined by HPLC analysis. **HPLC** (Chiral Technology Chiral Pak AD-H, hexane/IPA= 95:5, flow rate=1 ml/min) \( T_R \) (S enantiomer) 9.5 min, \( T_R \) (R enantiomer) 10.5 min.

**References**

$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces
$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces
$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces
**1H NMR, 13C NMR, 19F NMR Spectra and HPLC Traces**

![1H NMR, 13C NMR, 19F NMR Spectra and HPLC Traces](image)

**Table 1:**

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**Note:**

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- S 5
$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces
$\text{H NMR, } ^{13}\text{C NMR, } ^{19}\text{F NMR Spectra and HPLC Traces}$

![Diagram of a molecule](image)

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5: 287 nm, 4 nm Results

80% ee
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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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5: 287 nm, 4 nm Results

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces
**1H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces**

![Chemical Structure](image)

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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![Chemical Structure](image)

**$^1$H NMR Results**

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(S18)
$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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**1H NMR, 13C NMR, 19F NMR Spectra and HPLC Traces**

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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\(^1\)H NMR, \(^{13}\)C NMR, \(^{19}\)F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

![Chemical Structure Image]

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H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^{1}H$ NMR, $^{13}C$ NMR, $^{19}F$ NMR Spectra and HPLC Traces
H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$\text{H NMR, }^{13}\text{C NMR, }^{19}\text{F NMR Spectra and HPLC Traces}$

S 37
\textbf{\( ^1 \)H NMR, \( ^{13} \)C NMR, \( ^{19} \)F NMR Spectra and HPLC Traces}

\textbf{Electronic Supplementary Material (ESI) for Chemical Science}

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**$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces**

![NMR Spectra and HPLC Traces](image)

**S 39**
$^{1}$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces
$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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$^1$H NMR, $^{13}$C NMR, $^{19}$F NMR Spectra and HPLC Traces

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![HPLC Trace 1](Image1)

5 i 287 nm, 4
nm Results

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![HPLC Trace 2](Image2)

72% ee

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1H NMR, 13C NMR, 19F NMR Spectra and HPLC Traces

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Retention Time | Area    | Area Percent | Lambda Max |
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