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

Matthew J. Campbell and F. Dean Toste*

Department of Chemistry, University of California, Berkeley, California 94720

fdtoste@berkeley.edu

Table of Contents

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 (N_2) 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). ^{1}H, ^{13}C, ^{19}F and ^{31}P NMR spectra were recorded with Bruker AVB-400, AVQ-400, and DRX-500 spectrometers and chemical shifts are reported in ppm, relative to $CHCl_3$ (7.26 ppm for ^{1}H, and 77.0 ppm for ^{13}C) or d_6-DMSO (2.50 ppm for ^{1}H, and 39.5 ppm for ^{13}C) unless otherwise noted. ^{1}H 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. $Ph_3PAuNTf_2$ was either prepared immediately before use by sonicating a 1:1 mixture of Ph_3PAuCl and $AgNTf_2$ 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 $Ph_3PAuNTf_2$.

An amber vial was charged with the imine (0.28 mmol), alkyne, and isocyanate in reagent grade chloroform (0.90 mL). A solution of $Ph_3PAuNTf_2$ 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. ^{1}H 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/$AgNTf_2$.

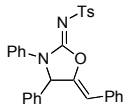
An amber vial was charged with the imine (0.14 mmol), alkyne (0.17 mmol), and isocyanate (0.17 mmol) in reagent grade solvent (0.10 mL, chloroform or toluene). In a separate amber vial was added (*S*,*S*)-**L4**AuCl (0.0058 g, 0.007 mmol), $AgNTf_2$ (0.0027 g, 0.007 mmol), and reagent grade solvent (0.20 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. ^{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 (C) for the asymmetric multicomponent reaction using 10 mol % (*R*,*R*)-L4AuCl/AgNTf$_2$.

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*)-**L4**AuCl (0.0051 g, 0.006 mmol), AgNTf$_2$ (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.

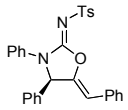
General Procedure (D) for the asymmetric multicomponent reaction using 10 mol % (*R*,*R*)-L4AuCl/AgNTf$_2$.

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*)-**L4**AuCl (0.0051 g, 0.006 mmol), AgNTf$_2$ (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.

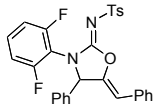


(*Z*)-*N*-((*Z*)-5-benzylidene-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9aA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylideneaniline (0.051 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and 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: 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) δ 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) δ 153.2, 146.9, 142.7, 139.7, 136.3, 134.6, 132.2, 129.5, 129.3, 129.2, 129.1, 128.8, 128.6, 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 $[C_{29}H_{24}O_3N_2S+Na]^+$: *m*/*z* 503.1400, found 503.1397.

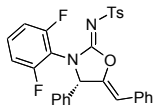


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9aA). The title compound was prepared according to General Procedure B using (*E*)-*N*-benzylideneaniline (0.026 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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.

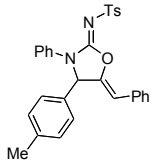


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(2,6-difluorophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9bA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylidene-2,6-difluoroaniline (0.061 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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) δ 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) δ 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**

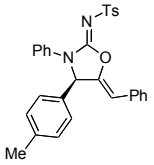
(376 MHz, $CDCl_3$, 298 K) δ 112.52 (t, *J* = 7.3 Hz, 1F), 116.53 (t, *J* = 7.8 Hz, 1F); **TLC** (30% EtOAc/hexanes) R_f 0.26; **HRMS** (ESI) calc for $[C_{29}H_{22}O_3N_2F_2S+H]^+$: *m*/*z* 517.1392, found 517.1391.



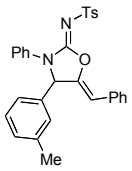
(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3-(2,6-difluorophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*S*)-9bA). The title compound was prepared according to General Procedure D using (*E*)-*N*-benzylidene-2,6-difluoroaniline (0.013 g, 0.061 mmol), phenylacetylene (0.0075 g, 0.073 mmol), *p*-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (*R*,*R*)-**L4**AuCl (0.0050 g, 0.006 mmol), and $AgNTf_2$ (0.0024 g, 0.006 mmol) in methylene chloride. After 6 days, ^{1}H 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) T_R (major) 14.2 min, T_R (minor) 15.4 min.



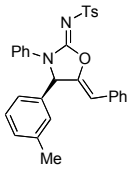
(*Z*)-*N*-((*Z*)-5-benzylidene-3-phenyl-4-(*p*-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9cA). The title compound was prepared according to General Procedure A using (*E*)-*N*-(4-methylbenzylidene)aniline (0.055 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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: >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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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) R_f 0.37; **HRMS** (ESI) calc for $[C_{30}H_{26}O_3N_2S+Na]^+$: *m*/*z* 517.1556, found 517.1552.



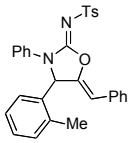
(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-phenyl-4-(*p*-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9cA). The title compound was prepared according to General Procedure B using (*E*)-*N*-(4-methylbenzylidene)aniline (0.028 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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: 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) T_R (major) 11.6 min, T_R (minor) 16.2 min.



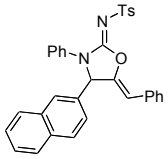
(*Z*)-*N*-((*Z*)-5-benzylidene-3-phenyl-4-(*m*-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9dA). The title compound was prepared according to General Procedure A using (*E*)-*N*-(3-methylbenzylidene)aniline (0.055 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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: >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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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) R_f 0.37; **HRMS** (ESI) calc for $[C_{30}H_{26}O_3N_2S+Na]^+$: *m*/*z* 517.1556, found 517.1554.



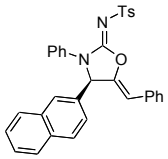
(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-phenyl-4-(*m*-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9dA). The title compound was prepared according to General Procedure B using (*E*)-*N*-(3-methylbenzylidene)aniline (0.028 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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 (0.052 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.



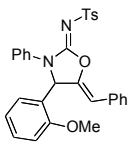
(*Z*)-*N*-((*Z*)-5-benzylidene-3-phenyl-4-(*o*-tolyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9eA). The title compound was prepared according to General Procedure A using (*E*)-*N*-(2-methylbenzylidene)aniline (0.055 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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 (0.109 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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{1}H NMR** (500 MHz, d_6-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); **^{13}C NMR** (125 MHz, d_6-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) R_f 0.35; **HRMS** (ESI) calc for $[C_{30}H_{26}O_3N_2S+H]^+$: *m*/*z* 495.1730, found 495.1733.



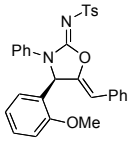
(*Z*)-*N*-((*Z*)-5-benzylidene-3-phenyl-4-(naphthalene-2-yl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9fA). The title compound was prepared according to General Procedure A using (*E*)-*N*-(naphthalen-2-ylmethylene)aniline (0.065 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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: 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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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), 7.42–7.18 (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); **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K) δ 153.3, 146.9, 142.7, 139.7, 134.5, 133.5, 132.9, 132.1, 129.8, 129.2, 129.1, 128.8, 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) R_f 0.32; **HRMS** (ESI) calc for $[C_{33}H_{26}O_3N_2S+Na]^+$: *m*/*z* 553.1556, found 553.1553.



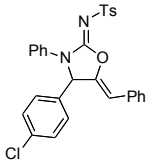
(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-phenyl-4-(naphthalene-2-yl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9fA). The title compound was prepared according to General Procedure B using (*E*)- *N*-(naphthalen-2-ylmethylene)aniline (0.033 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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: 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 $Ph_3PAuNTf_2$ (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, 126.5, 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 $[C_{30}H_{26}O_4N_2S+H]^+$: *m*/*z* 511.1686, found 511.1680.

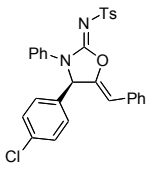


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-4-(2-methoxyphenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9gA). The title compound was prepared according to General Procedure B using (*E*)-*N*-(2-methoxybenzylidene)aniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**AuCl (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.

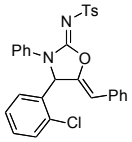


(*Z*)-*N*-((*Z*)-5-benzylidene-3-phenyl-4-(4-chlorophenyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide

(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 $Ph_3PAuNTf_2$ (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, 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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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) R_f 0.35; **HRMS** (ESI) calc for $[C_{29}H_{23}O_3N_2ClS+Na]^+$: *m*/*z* 537.1010, found 537.1009.

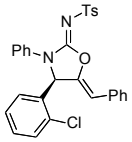


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-phenyl-4-(4-chlorophenyl)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9hA). The title compound was prepared according to General Procedure B using (*E*)-*N*-(4-chlorobenzylidene)aniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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: 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.

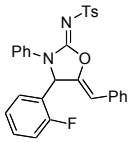


(*Z*)-*N*-((*Z*)-5-benzylidene-4-(2-chlorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9iA). The title compound was prepared according to General Procedure A using (*E*)-*N*-(2-chlorobenzylidene)aniline (0.123 g, 0.50 mmol), phenylacetylene (0.062 g, 66 μL, 0.60 mmol), *p*-toluenesulfonyl isocyanate (0.118 g, 91 μL, 0.60 mmol), and $Ph_3PAuNTf_2$ (0.018 g, 0.025 mmol) in

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* = 7.58 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 $[C_{29}H_{23}O_3N_2ClS+H]^+$: *m*/*z* 515.1191, found 515.1187.

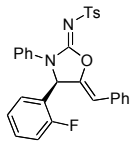


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-4-(2-chlorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9iA). The title compound was prepared according to General Procedure B using (*E*)-*N*-(2-chlorobenzylidene)aniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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: 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.

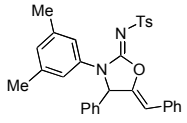


(*Z*)-*N*-((*Z*)-5-benzylidene-4-(2-fluorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9jA). The title compound was prepared according to General Procedure A using (*E*)-*N*-(2-fluorobenzylidene)aniline (0.056 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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 = 8.6 Hz), 129.2, 128.8, 128.6, 127.8, 127.1, 126.7, 125.0 (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, 128.0, 127.1, 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 $[C_{29}H_{23}O_3N_2FS+H]^+$: m/z 499.1486, found 499.1485.

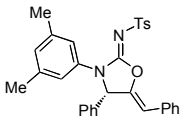


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-4-(2-fluorophenyl)-3-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9jA). The title compound was prepared according to General Procedure B using (*E*)-*N*-(2-fluorobenzylidene)aniline (0.028 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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 (0.038 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.

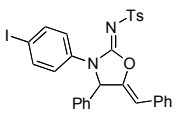


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(3,5-dimethylphenyl)-4-phenyloxazolidin-2-ylidene)-4-

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 $Ph_3PAuNTf_2$ (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: 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; **^{1}H NMR** (400 MHz, d_6-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); **^{13}C NMR** (100 MHz, d_6-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) R_f 0.43; **HRMS** (ESI) calc for $[C_{31}H_{28}O_3N_2S+Na]^+$: *m*/*z* 531.1713, found 531.1711.

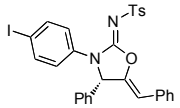


(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3-(3,5-dimethylphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*S*)-9kA). The title compound was prepared according to General Procedure D using (*E*)-*N*-benzylidene-3,5-dimethylaniline (0.013 g, 0.061 mmol), phenylacetylene (0.0075 g, 0.073 mmol), *p*-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (*R*,*R*)-**L4**AuCl (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 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.

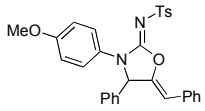


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-iodophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9lA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylidene-4-iodoaniline (0.086 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 35 °C, ^{1}H NMR analysis of the crude mixture gave the diastereomeric ratio: 16:1. The title compound (0.129 g, 0.21

mmol, 76% 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}) 1610, 1567, 1418, 288, 763, 693; **^{1}H NMR** (400 MHz, d_6-DMSO, 298 K) δ 7.86 (d, J = 8.3 Hz, 2H), 7.72 (d, J = 8.8 Hz, 2H), 7.54 (d, J = 7.5 Hz, 2H), 7.42–7.25 (m, 12H), 6.55 (d, J = 2.0 Hz, 1H), 5.60 (d, J = 2.0 Hz, 1H), 2.34 (s, 3H); **^{13}C NMR** (100 MHz, d_6-DMSO, 298 K) δ 152.9, 148.0, 142.7, 139.7, 137.8, 136.5, 134.2, 132.3, 129.5, 129.3, 129.2, 128.6, 128.4, 127.7, 127.6, 126.8, 126.1, 105.2, 92.9, 64.9, 21.0; **TLC** (30% EtOAc/hexanes) R_f 0.47; **HRMS** (ESI) calc for $[C_{29}H_{23}O_3N_2IS+Na]^+$: m/z 629.0358, found 629.0362.

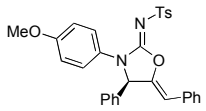


(*Z*)-*N*-((*S*,*Z*)-5-benzylidene-3-(4-iodophenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*S*)-9lA). The title compound was prepared according to General Procedure D using (*E*)-*N*-benzylidene-4-iodoaniline (0.019 g, 0.061 mmol), phenylacetylene (0.0075 g, 0.073 mmol), *p*-toluenesulfonyl isocyanate (0.0144 g, 0.073 mmol), (*R*,*R*)-**L4**AuCl (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 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) T_R (major) 19.0 min, T_R (minor) 15.9 min.

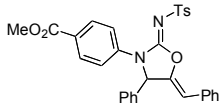


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9mA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylidene-4-methoxyaniline (0.059 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (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: 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; **^{1}H NMR** (400 MHz, d_6-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); **^{13}C NMR** (100 MHz, d_6-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,

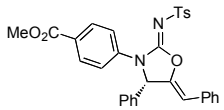
114.3, 105.1, 65.8, 55.3, 20.9; **TLC** (30% EtOAc/hexanes) R_f 0.25; **HRMS** (ESI) calc for $[C_{30}H_{26}O_4N_2S+Na]^+$: *m*/*z* 533.1506, found 533.1504.



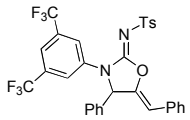
(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-(4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9mA). The title compound was prepared according to General Procedure B using (*E*)-*N*-benzylidene-4-methoxyaniline (0.030 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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 (0.049 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_R (major) 15.4 min, T_R (minor) 13.9 min.



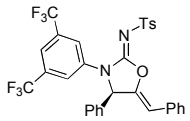
Methyl 4-((2*Z*,5*Z*)-5-benzylidene-4-phenyl-2-(tosylimino)oxazolidin-3-yl)benzoate (9nA). The title compound was prepared according to General Procedure A using (*E*)-methyl 4-(benzylideneamino)benzoate (0.067 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 35 °C, ^{1}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^{-1}) 1713, 1623, 1595, 1427, 1144, 1012, 815, 771; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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_f 0.27; **HRMS** (ESI) calc for $[C_{31}H_{26}O_5N_2S+Na]^+$: *m*/*z* 561.1455, found 561.1452.



Methyl 4-((*S*,*2Z*,5*Z*)-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*)-**L4**AuCl (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.

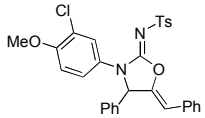


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(3,5-bis(trifluoromethyl)phenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9oA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylidene-3,5-bis(trifluoromethyl)aniline (0.089 g, 0.28 mmol), phenylacetylene (0.035 g, 36 μL, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 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) δ 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) δ 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) δ 62.38 (s, 6F); **TLC** (30% EtOAc/hexanes) R_f 0.68; **HRMS** (ESI) calc for $[C_{31}H_{22}O_3N_2F_6S+H]^+$: *m*/*z* 617.1328, found 617.1330.

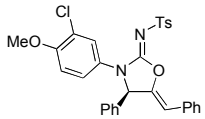


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-(3,5-bis(trifluoromethyl)phenyl)-4-phenyloxazolidin-2-ylidene)-4-

methylbenzenesulfonamide ((*R*)-9oA). The title compound was prepared according to General Procedure B using (*E*)-N-benzylidene-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*)-**L4**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: 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.

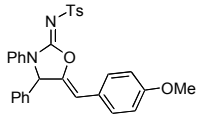


(*Z*)-*N*-((*Z*)-5-benzylidene-3-(3-chloro-4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9pA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylidene-3-chloro-4-methoxyaniline (0.123 g, 0.50 mmol), phenylacetylene (0.062 g, 66 μL, 0.60 mmol), *p*-toluenesulfonyl isocyanate (0.118 g, 91 μL, 0.60 mmol), and $Ph_3PAuNTf_2$ (0.018 g, 0.025 mmol) in chloroform (2.5 mL total volume). After 48 h at room temperature, ^{1}H 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; **^{1}H NMR** (400 MHz, d_6-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); **^{13}C NMR** (100 MHz, d_6-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 $[C_{30}H_{25}O_4N_2ClS+H]^+$: *m*/*z* 545.1289, found 545.1291.

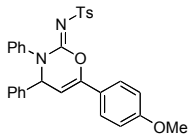


(*Z*)-*N*-((*R*,*Z*)-5-benzylidene-3-(3-chloro-4-methoxyphenyl)-4-phenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide ((*R*)-9pA). The title compound was prepared according to General Procedure B using (*E*)-*N*-benzylidene-3-chloro-4-methoxyaniline (0.034 g, 0.14 mmol), phenylacetylene (0.017 g, 18 μL, 0.17 mmol), *p*-toluenesulfonyl isocyanate (0.033 g, 25 μL, 0.17 mmol), (*S*,*S*)-**L4**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

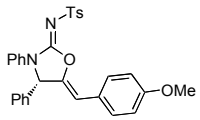
additional 36 h, ^{1}H NMR analysis of the crude mixture gave the diastereomeric ratio: 6:1. The title compound (0.053 g, 0.098 mmol, 70% yield, 77% ee) was isolated as a white solid after flash chromatography, eluting with a gradient from 30 to 40% ethyl acetate/hexanes. X-ray quality crystals were 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.



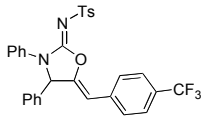
(*Z*)-*N*-((*Z*)-5-(4-methoxybenzylidene)-3,4-diphenyloxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9qA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylideneaniline (0.051 g, 0.28 mmol), 1-ethynyl-4-methoxybenzene (0.045 g, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at room temperature, ^{1}H 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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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) R_f 0.27; **HRMS** (ESI) calc for $[C_{30}H_{26}O_4N_2S+H]^+$: *m/z* 511.1686, found 511.1682.



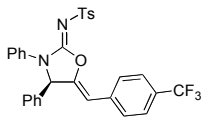
(*Z*)-*N*-(6-(4-methoxyphenyl)-3,4-diphenyl-3,4-dihydro-2*H*-1,3-oxazin-2-ylidene)-4-methylbenzenesulfonamide (9qB). The title compound was isolated from the above reaction as a yellow semi-solid after flash chromatography, eluting with a gradient from 30 to 40% ethyl acetate/hexanes. Analytical data for the title compound: **IR** (thin film, cm^{-1}) 2980, 1557, 1179, 1144, 1086, 692, 664; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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) R_f 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*)-**L4**AuCl (0.0050 g, 0.006 mmol), and $AgNTf_2$ (0.0024 g, 0.006 mmol) in toluene. After 5 days, ^{1}H 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.

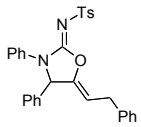


(*Z*)-*N*-((*Z*)-3,4-diphenyl-5-(4-(trifluoromethyl)benzylidene)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9rA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylideneaniline (0.051 g, 0.28 mmol), 1-ethynyl-4-(trifluoromethyl)benzene (0.058 g, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 50 °C, ^{1}H 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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 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; **^{19}F NMR** (374 MHz, $CDCl_3$) δ 61.76 (s, 3F); **TLC** (30% EtOAc/hexanes) R_f 0.33; **HRMS** (ESI) calc for $[C_{30}H_{23}O_3N_2F_3S+H]^+$: *m*/*z* 549.1454, found 549.1452.

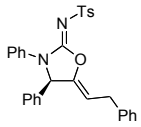


(*Z*)-*N*-((*R*,*Z*)-3,4-diphenyl-5-(4-(trifluoromethyl)benzylidene)oxazolidin-2-ylidene)-4-

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*)-**L4**AuCl (0.0058 g, 0.007 mmol), and $AgNTf_2$ (0.0027 g, 0.007 mmol) in toluene. After 6 days, ^{1}H 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) T_R (major) 9.4 min, T_R (minor) 44.5 min.

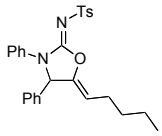


(*Z*)-*N*-((*Z*)-3,4-diphenyl-5-(2-phenylethylidene)oxazolidin-2-ylidene)-4-methylbenzenesulfonamide (9sA). The title compound was prepared according to General Procedure A using (*E*)-*N*-benzylideneaniline (0.051 g, 0.28 mmol), 3-phenyl-1-propyne (0.040 g, 0.34 mmol), *p*-toluenesulfonyl isocyanate (0.067 g, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 50 °C, ^{1}H 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; **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K) δ 153.2, 147.8, 142.6, 139.6, 138.9, 136.3, 134.5, 129.3, 129.1, 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) R_f 0.24; **HRMS** (ESI) calc for $[C_{30}H_{26}O_3N_2S+H]^+$: *m*/*z* 495.1737, found 495.1737.



(*Z*)-*N*-((*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*)-**L4**AuCl (0.0058 g, 0.007 mmol), and $AgNTf_2$ (0.0027 g, 0.007 mmol) in toluene. After 6 days, ^{1}H 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_R (major) 10.5 min, T_R (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, 52 μL, 0.34 mmol), and $Ph_3PAuNTf_2$ (0.0104 g, 0.014 mmol) in chloroform. After 48 h at 50 °C, ^{1}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^{-1}) 1615, 1584, 1318, 1112, 892, 686; **^{1}H NMR** (400 MHz, $CDCl_3$, 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–.084 (m, 3H); **^{13}C NMR** (100 MHz, $CDCl_3$, 298 K) δ 153.6, 147.3, 142.5, 139.7, 136.7, 134.7, 129.2, 129.1, 129.0, 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_f 0.31; **HRMS** (ESI) calc for $[C_{27}H_{28}O_3N_2S+H]^+$: *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 (1*S*,2*S*)-2-(diphenylphosphino)cyclohexanamine and anhydrous methylene chloride (0.1–0.2 M) under N_2 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.

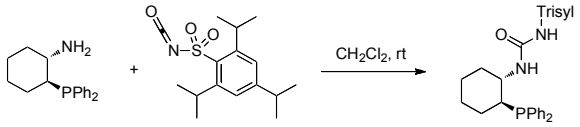
A scintillation vial was charged with *N*-substituted phosphine (1.0 equiv), $Me_2S{\cdot}AuCl$[2] (1.0 equiv), and methylene chloride (0.1 M phosphine) with no precautions to preclude air or moisture. The mixture was sonicated for 30 sec and allowed to stand at room temperature. After 30 min, the reaction was analyzed by ^{1}H and ^{31}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-*bis*(trifluoromethyl)phenyl isocyanate, ethyl isocyanate, diphosgene, benzoyl isocyanate, 1-adamantanecarbonyl chloride, 2,4,6-triisopropylbenzoyl chloride, phthalic anhydride (phthlate prepared in toluene at 130 ºC), and 3,5-*bis*(trifluoromethyl)phenyl isothiocyanate. *p*-Toluenesulfonyl chloride and 2,4,6-trimethylphenylsulfonyl chloride were also commercially available, but it was necessary to prepare the gold(I) chloride complex of (1*S*,2*S*)-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 *tert*-leucine-derived isocyanate was prepared by the procedure of Jacobsen.[3]

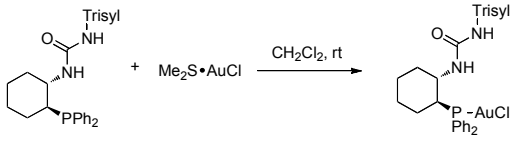
2,4,6-Trimethylbenzoyl isocyanate and 2,4,6-triisopropylbenzoyl isocyanate were synthesized by refluxing the corresponding primary amides with 3–6 equiv of oxalyl chloride in anhydrous dichloroethane (0.15 M amide) for 20 hours followed by concentration of the reaction mixture and use of the isocyanates without further purification.

2,5-Dimethylphenylsulfonyl isocyanate, 2,4,6-trimethylphenylsulfonyl isocyanate and 2,4,6-triisopropylphenylsulfonyl isocyanate were synthesized by refluxing the corresponding primary sulfonamides with *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}H NMR confirmed full conversion of the sulfonamide, the reaction was concentrated to dryness and the isocyanates were used directly without further purification.



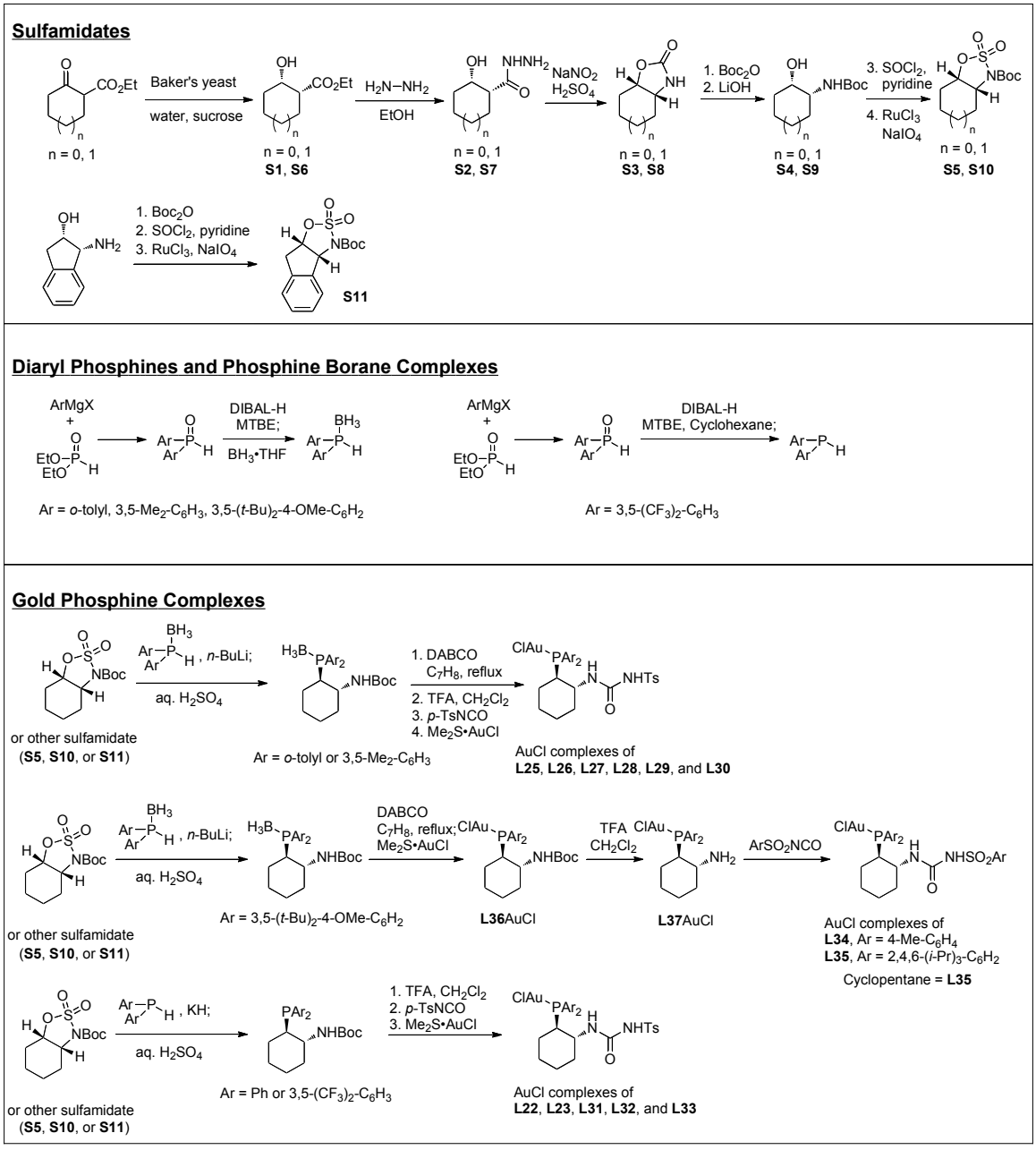
***N*-(((1*S*,2*S*)-2-(diphenylphosphino)cyclohexyl)carbamoyl)-2,4,6-triisopropylbenzenesulfonamide (L4).** A flame-dried scintillation vial equipped with a magnetic stir bar was charged with 2,4,6-triisopropylbenzenesulfonyl isocyanate (0.220 g, 0.71 mmol), (1*S*,2*S*)-2-(diphenylphosphino)cyclohexanamine (0.200 g, 0.71 mmol), and anhydrous methylene chloride (4.0 mL) under 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}H NMR** (400 MHz, $CDCl_3$, 298 K) δ 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}C NMR** (100 MHz, $CDCl_3$, 298 K) δ 153.5,

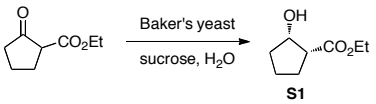
151.3, 150.4, 136.1 (d, *J* = 13.1 Hz), 135.7 (d, *J* = 16.9 Hz), 134.5 (d, *J* = 20.7 Hz), 132.9, 132.6 (d, *J* = 18.3 Hz), 128.9, 128.5 (d, *J* = 6.0 Hz), 128.2, 128.1 (d, *J* = 7.7 Hz), 123.9, 49.6 (d, *J* = 18.7 Hz), 39.3 (d, *J* = 18.0 Hz), 34.1, 31.3, 29.9. 25.4 (d, *J* = 3.7 Hz), 24.9, 24.8, 24.7, 24.0, 23.5, 23.4, 23.3; **^{31}P NMR** (163 MHz, $CDCl_3$, 298 K) δ –10.7; **HRMS** (ESI) calc for $[C_{34}H_{45}O_3N_2PS+H]^+$: *m*/*z* 593.2961, found 593.2951.



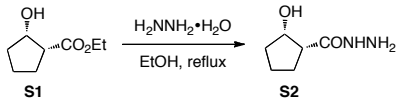
***N*-(((1*S*,2*S*)-2-(diphenylphosphino)cyclohexyl)carbamoyl)-2,4,6-triisopropylbenzenesulfonamide gold(I) chloride ((*S*,*S*)-L4AuCl).** A scintillation vial was charged with *N*-(((1*S*,2*S*)-2-(diphenylphosphino)cyclohexyl)carbamoyl)-2,4,6-triisopropylbenzenesulfonamide (**L4)** (0.450 g, 0.76 mmol), $Me_2S{\cdot}AuCl$[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) δ 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) δ 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) δ 40.0; **HRMS** (ESI) calc for $[C_{34}H_{45}O_3N_2AuClPS+Na]^+$: *m*/*z* 847.2135, found 847.2130.

Scheme S1. Preparation of gold(I) complexes from L22-L37



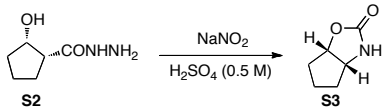


(1*R*,2*S*)-Ethyl 2-hydroxycyclopentanecarboxylate. The title compound was prepared by a modification of the procedure of Bertau.[4] Sucrose (625 g) was dissolved in deionized water (3.25 L) and heated to 30 ºC with overhead stirring. Baker's yeast (250 g) was then added and allowed to stir without heating 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.[5]



S1 S2

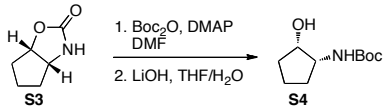
(1*R*,2*S*)-2-Hydroxycyclopentanecarbohydrazide. The title compound was prepared by a modification of the procedure of Bertau.[4] To a 100 mL round-bottomed flask equipped with a magnetic stir bar and a condenser was added (1*R*,2*S*)-ethyl 2-hydroxycyclopentanecarboxylate (31.0 g, 196 mmol), hydrazine hydrate (15.7 g, 15.3 mL, 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) δ 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) δ 172.7, 73.3, 47.7, 34.3, 25.9, 21.5.



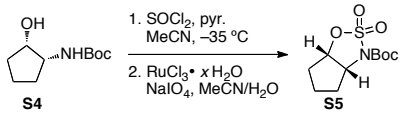
S2 S3

(3a*R*,6a*S*)-Perhydrocyclopenta[d]oxazol-2-one. The title compound was prepared by a modification of the procedure of Bertau.[4] To a 1.0 L Erlenmeyer flask equipped with a magnetic stir bar was added (1*R*,2*S*)-2-hydroxycyclopentanecarbohydrazide (22.7 g, 157 mmol) and 0.5 M aqueous H_2SO_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

mL). The residue was extracted with methylene chloride (2 x 60 mL), dried with Na_2SO_4, 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] **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K) δ 160.4, 82.1, 56.6, 34.2, 33.6, 21.7;

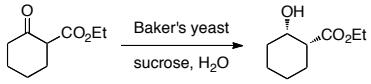


***tert*-Butyl ((1*R*,2*S*)-2-hydroxycyclopentyl)carbamate.** To a 250 mL round-bottomed flask equipped with a magnetic stir bar was added (3aR,6aS)-perhydrocyclopenta[d]oxazol-2-one (3.9 g, 30.7 mmol), 4-(dimethylamino)pyridine (1.88 g, 15.4 mmol), and anhydrous DMF (80 mL). To this solution was added Boc_2O (8.7 g, 40.0 mmol) and allowed to stir at room temperature for 1 h. The reaction was quenched with sat. aqueous NH_4Cl (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 $MgSO_4$, 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 $MgSO_4$, filtered, and evaporated. The residue was purified on a 1" silica plug, eluting first with 30% ethyl acetate/hexanes to yield the title compound (3.12 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] **^{1}H NMR** (400 MHz, $CDCl_3$, 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).



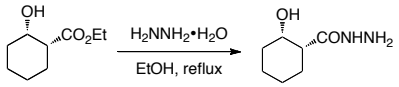
(3a*R*,6a*S*)-*tert*-Butyl tetrahydrocyclopenta[*d*][1,2,3]oxathiazole-3(3aH)-carboxylate 2,2-dioxide. To a flame-dried 250 mL round-bottomed flask equipped with a magnetic stir bar was added anhydrous acetonitrile (35 mL) and thionyl chloride (5.25 g, 3.20 mL, 44.1 mmol) under N_2. The solution was cooled to –45 ºC. Then a solution of *tert*-butyl ((1*R*,2*S*)-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

$MgSO_4$, 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 ºC. $NaIO_4$ (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 $MgSO_4$, 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.[9] **^{1}H NMR** (400 MHz, $CDCl_3$, 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); **^{13}C NMR** (125 MHz, $CDCl_3$, 298 K) δ 148.8, 84.9, 83.5, 61.0, 32.5, 32.0, 27.7, 22.4; **HRMS** (ESI) calc for $[C_{10}H_{17}O_5NS+Na]^+$: *m*/*z* 286.0720, found 286.0722.



S6

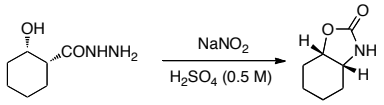
(1*R*,2*S*)-Ethyl 2-hydroxycyclohexanecarboxylate. The title compound was prepared by a modification of the procedure of Bertau.[4] Sucrose (390 g) was dissolved in deionized water (2.0 L) and heated to 30 ºC with overhead stirring. Baker's yeast (156 g) was then added and allowed to stir without heating 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 $MgSO_4$, filtered, and concentrated. The residue was distilled (91–95 ºC, 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.[10]



S6 **S7**

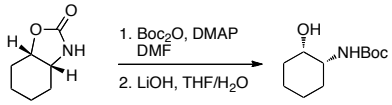
(1*R*,2*S*)-2-Hydroxycyclohexanecarbohydrazide. The title compound was prepared by a modification of the procedure of Bertau.[4] To a 100 mL round-bottomed flask equipped with a magnetic stir bar and a condenser was added (1*R*,2*S*)-ethyl 2-hydroxycyclohexanecarboxylate (8.0 g, 46.5 mmol), hydrazine 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 CH_2Cl_2 (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.[6] **^{1}H NMR** (400 MHz, d_6-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).



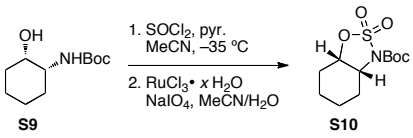
S7 **S8**

(3a*R*,7a*S*)-Hexahydrobenzo[*d*]oxazol-2(3*H*)-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 (1*R*,2*S*)-2-hydroxycyclohexanecarbohydrazide (5.55 g, 35.1 mmol) and 0.5 M aqueous H_2SO_4 (88 mL). After dissolution, the solution was cooled to 0 ºC. 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_2SO_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) δ 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).



S8 **S9**

***tert*-Butyl ((1*R*,2*S*)-2-hydroxycyclohexyl)carbamate.** To a 250 mL round-bottomed flask equipped with a magnetic stir bar was added (3a*R*,7a*S*)-hexahydrobenzo[*d*]oxazol-2(3*H*)-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_2O (5.96 g, 27.3 mmol) and allowed to stir at room temperature for 2 h. The reaction was quenched with sat. aqueous NH_4Cl (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 ºC. 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) δ 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).



(3a*R*,7a*S*)-*tert*-Butyl hexahydro-3*H*-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 N_2. The solution was cooled to –40 ºC. Then a solution of *tert*-butyl ((1*R*,2*S*)-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 ºC. Pyridine (6.56 mL, 81.3 mmol) was added slowly and stirred at –40 ºC 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 $MgSO_4$, 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 ºC. $NaIO_4$ (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 $MgSO_4$, filtered, and evaporated. The crude product was passed through a 1" 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.[9] **^{1}H NMR** (400 MHz, $CDCl_3$, 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 Guo[9] 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]

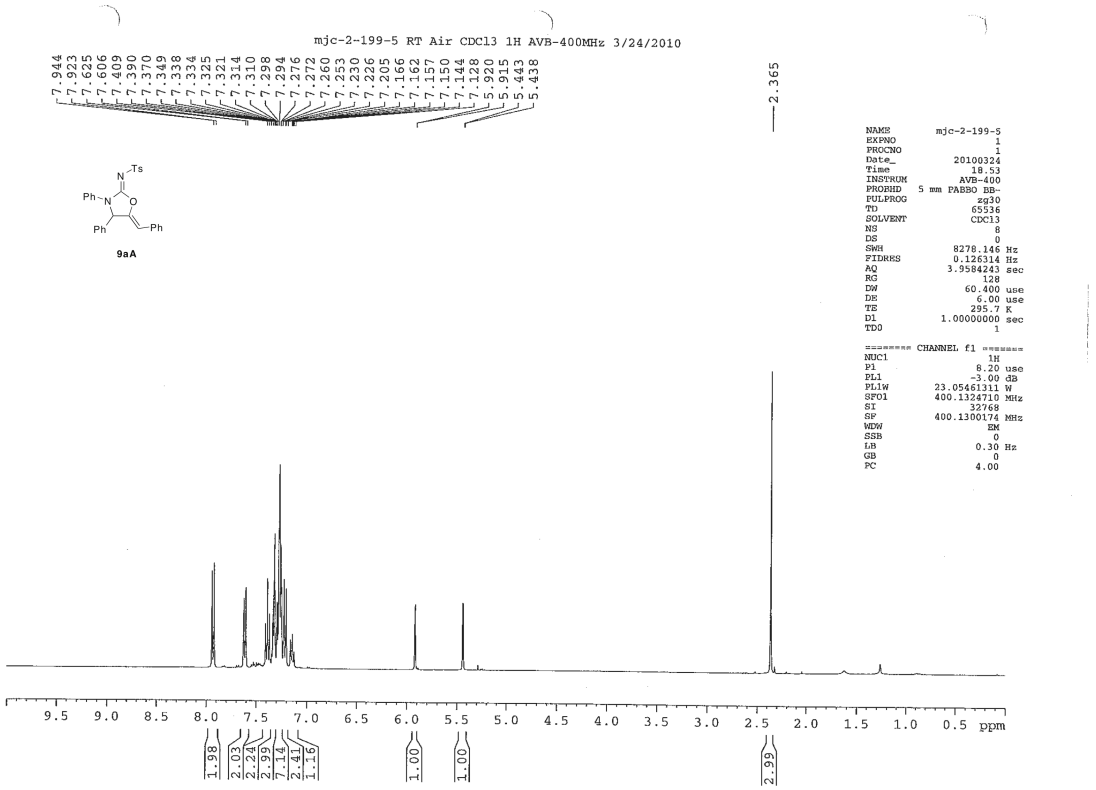
General procedure for screening catalysts: the asymmetric addition of phenylacetylene to (*E*)-*N*-benzylideneaniline. A stock solution of (*E*)-*N*-benzylideneaniline (0.0034 g, 0.019 mmol/100 µL methylene chloride) and phenylacetylene (0.0039 g, 0.038 mmol/100 µL methylene chloride was prepared. The 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 $AgNTf_2$ (0.0003 g, 0.008 mmol/100 µL methylene chloride). This mixture was sonicated for 30

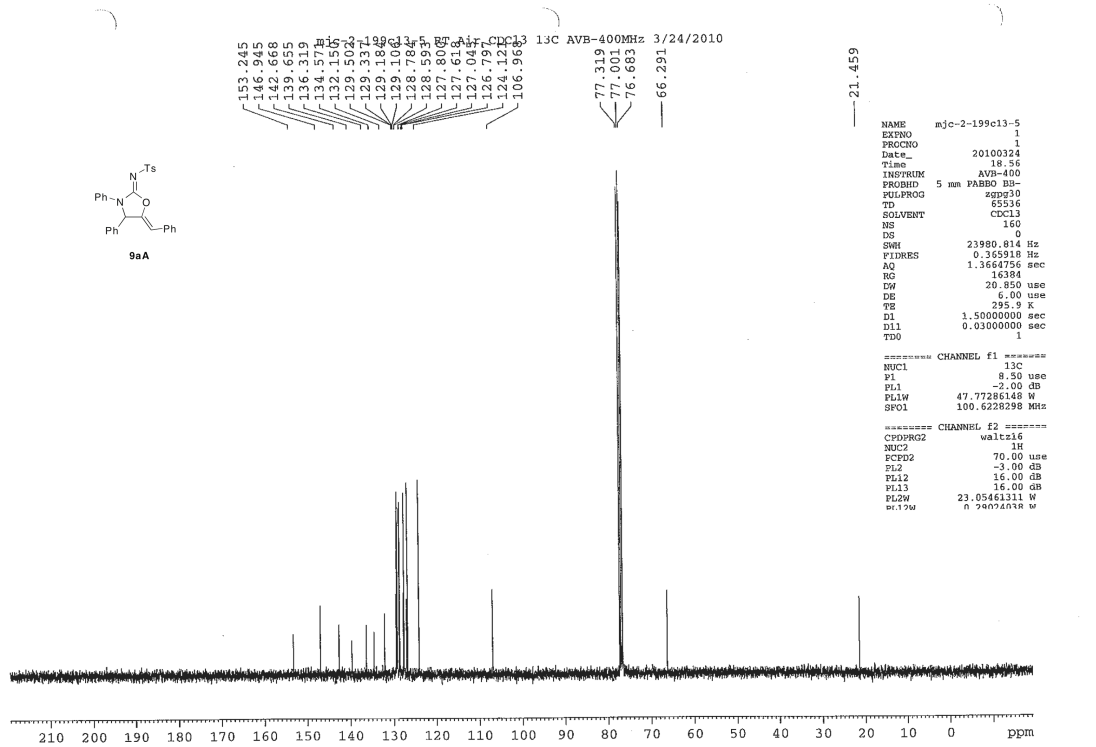
seconds and then filtered through glass microfiber to afford a colorless solution of the catalyst. The catalyst solution (100 μL) was added quickly to the first vial, which was then sealed with a PTFE-lined screw cap (imine molarity ~0.1 M). The reaction was left to stand at room temperature for 3 h. 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

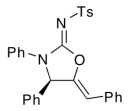
1. N. Mézailles, L. Ricard and F. Gagosz, *Org. Lett.*, 2005, **7**, 4133-4136.
2. N. Nishina and Y. Yamamoto, *Synlett*, 2007, **2007**, 1767,1770.
3. Y.-Q. Fang and E. N. Jacobsen, *J. Am. Chem. Soc.*, 2008, **130**, 5660-5661.
4. M. Bertau, M. Bürli, E. Hungerbühler and P. Wagner, *Tetrahedron: Asymmetry*, 2001, **12**, 2103-2107.
5. K. Kanai, H. Wakabayashi and T. Honda, *Org. Lett.*, 2000, **2**, 2549-2551.
6. F. Fulop, E. Semega, G. Dombi and G. Bernáth, *J. Het. Chem.*, 1990, **27**, 951-955.
7. J. R. Dehli and V. Gotor, *J. Org. Chem.*, 2002, **67**, 6816-6819.
8. A. Cerri, M. Torri, S. Armaroli, L. Banfi, G. Bianchi, G. Carzana, P. Ferrari, R. Micheletti, S. Sputore, and M. P. Zappavigna, WO2007118832, 2007.
9. R. Guo, S. Lu, X. Chen, C.-W. Tsang, W. Jia, C. Sui-Seng, D. Amoroso and K. Abdur-Rashid, *J. Org. Chem.*, 2009, **75**, 937-940.
10. O. Kanno and I. Kawamoto, *Tetrahedron*, 2000, **56**, 5639-5648.
11. T. Ohkuma, D. Ishii, H. Takeno and R. Noyori, *J. Am. Chem. Soc.*, 2000, **122**, 6510-6511.
12. C. A. Busacca, J. C. Lorenz, N. Grinberg, N. Haddad, M. Hrapchak, B. Latli, H. Lee, P. Sabila, A. Saha, M. Sarvestani, S. Shen, R. Varsolona, X. Wei and C. H. Senanayake, *Org. Lett.*, 2005, **7**, 4277-4280.
13. C. A. Busacca, J. C. Lorenz, P. Sabila, N. Haddad and C. H. Senanyake, *Org. Synth.*, 2007, **84**, 242.

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



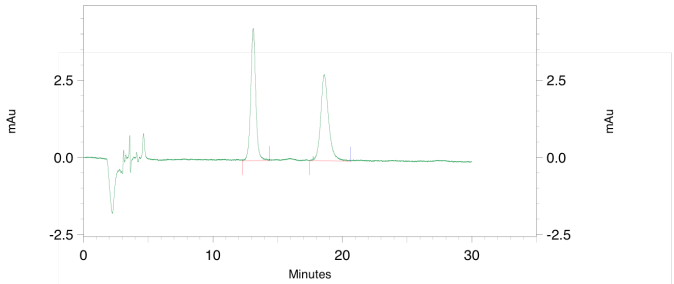


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9aA

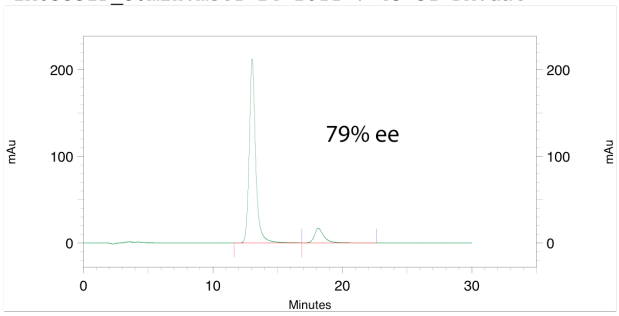
mjc-2-199-5
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-2-199-5
IA6535IP_30min.met3-25-2010 10-54-21 AM.dat



5: 288 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
13.120	115688	49.295	207
18.612	118997	50.705	262

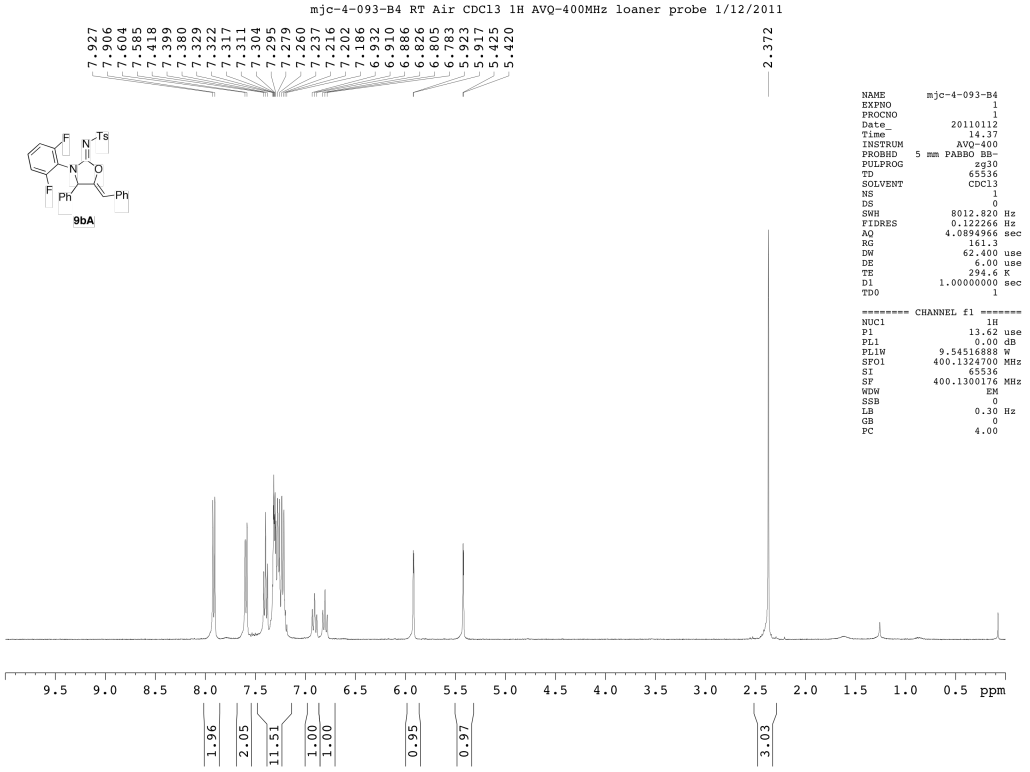
mjc-4-165-A
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-A
IA6535IP_30min.met1-24-2011 7-45-31 PM.dat

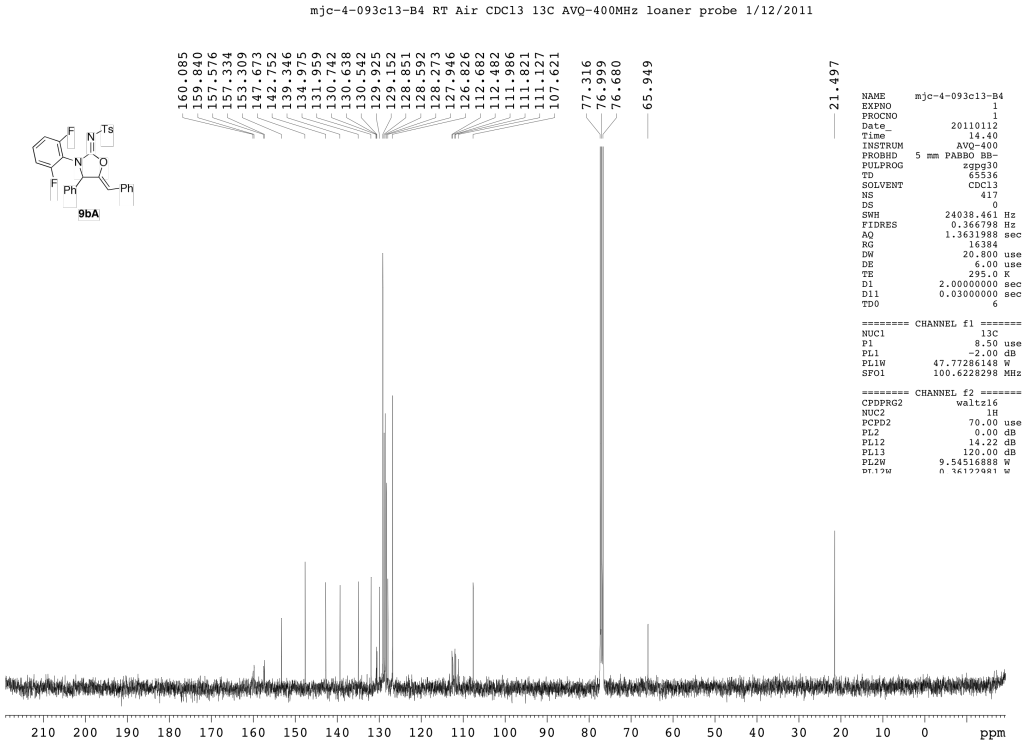


5: 288 nm, 4
nm Results

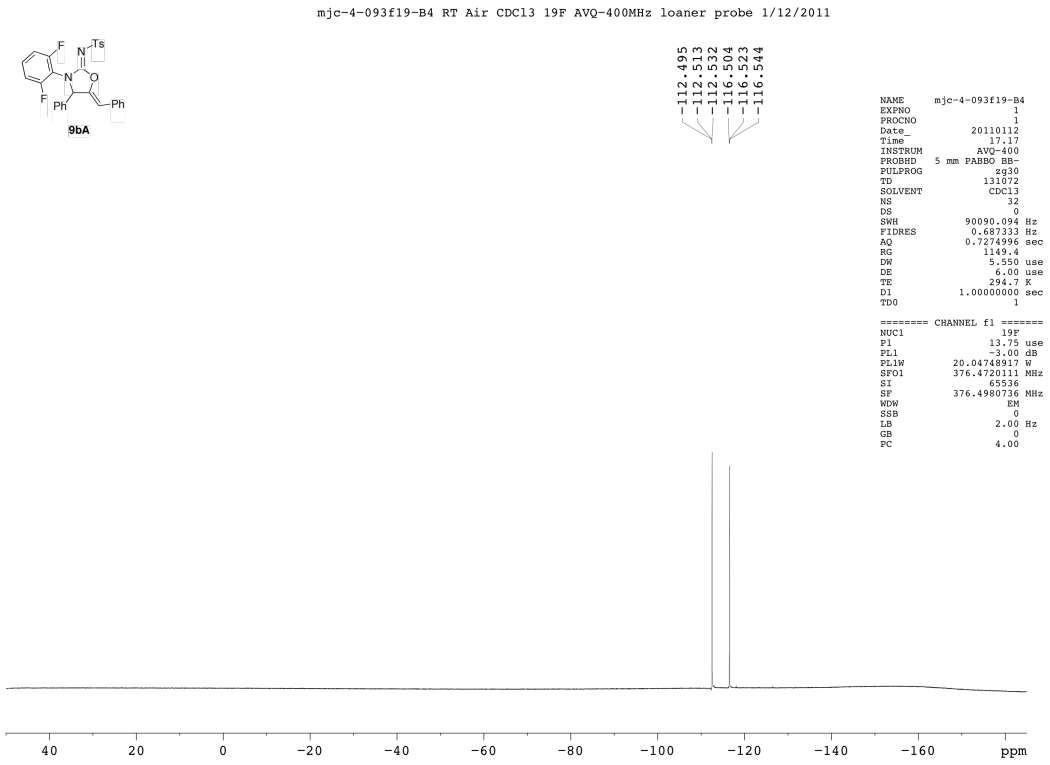
Retention Time	Area	Area Percent	Lambda Max
13.032	7318932	89.407	208
18.132	867152	10.593	207

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

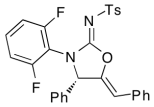




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

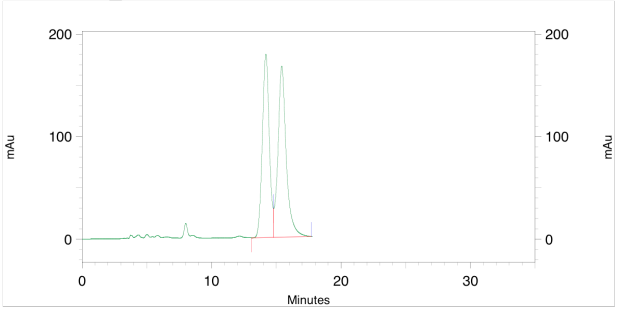


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*S*)-9bA

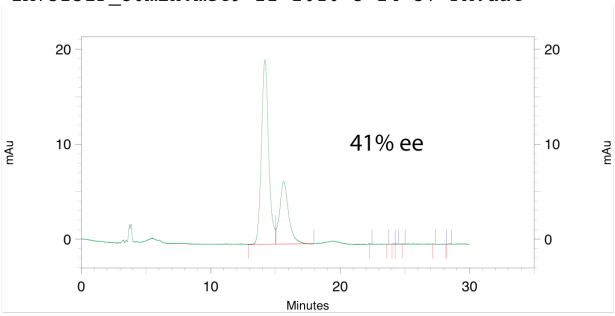
mjc-4-093-B
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-093-B
IA7525IP_30min.met9-22-2010 5-05-31 PM.dat



5: 288 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
14.200	6703587	47.415	207
15.424	7434597	52.585	207

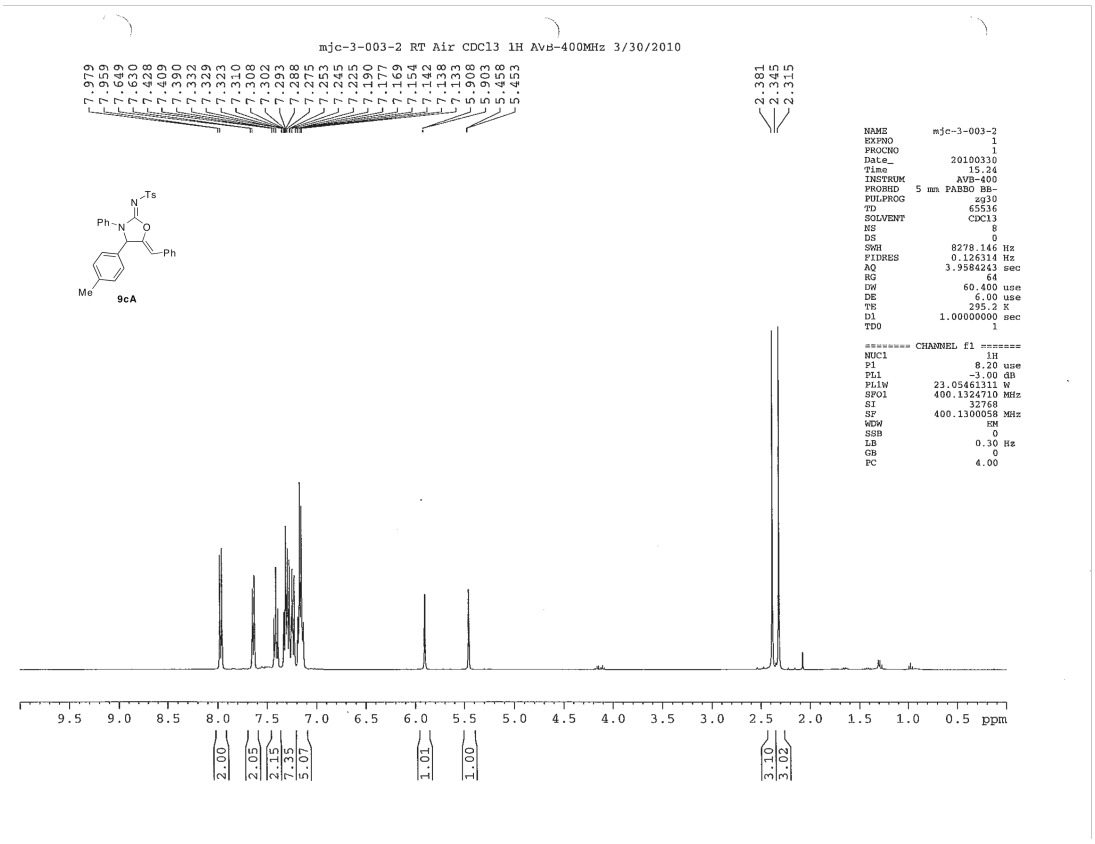
mjc-4-095-B
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-095-B
IA7525IP_30min.met9-22-2010 5-24-57 PM.dat

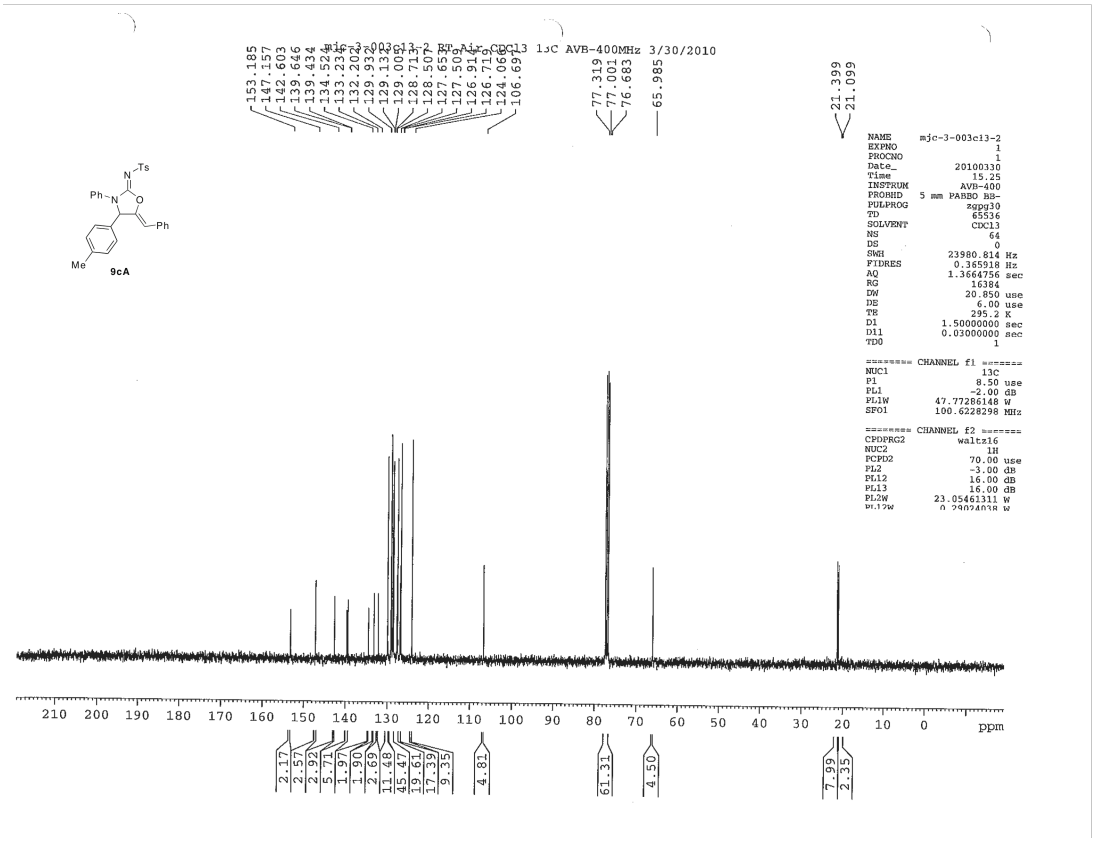


5: 288 nm, 4
nm Results

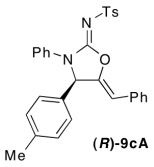
Retention Time	Area	Area Percent	Lambda Max
14.192	758739	70.320	207
15.636	318448	29.514	207

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



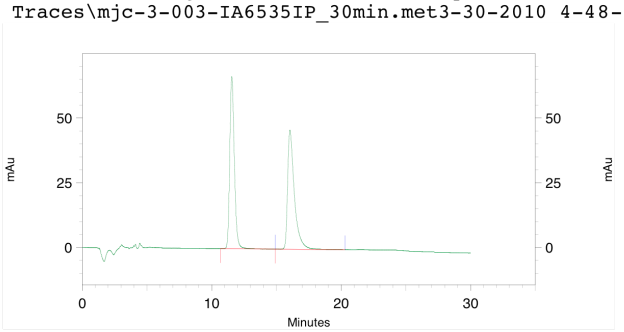


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9cA

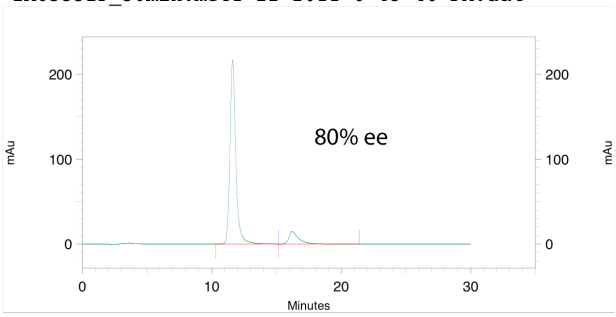
mjc-3-003
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-3-003-IA6535IP_30min.met3-30-2010 4-48-06 PM.dat



5: 287 nm, 4 nm Results

Retention Time	Area	Area Percent	Lambda Max
11.548	1652448	49.794	206
16.044	1666134	50.206	206

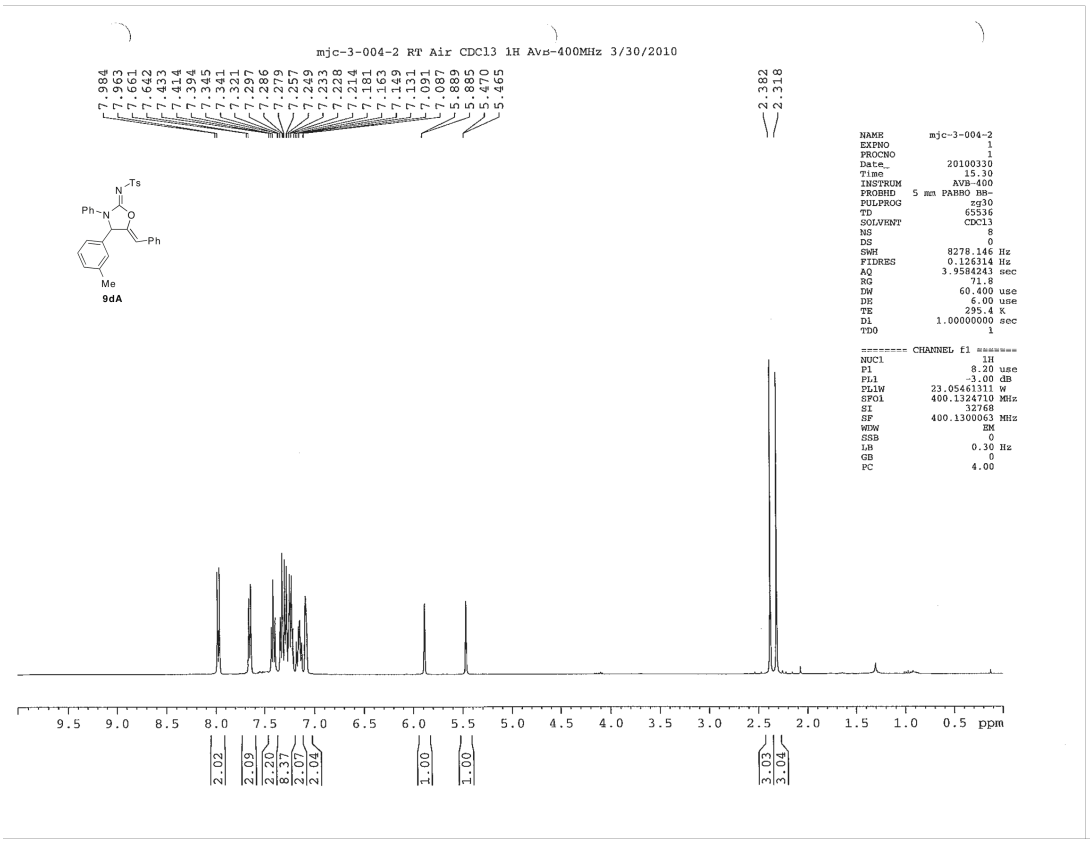
mjc-4-165-B
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-B IA6535IP_30min.met1-22-2011 6-43-46 PM.dat

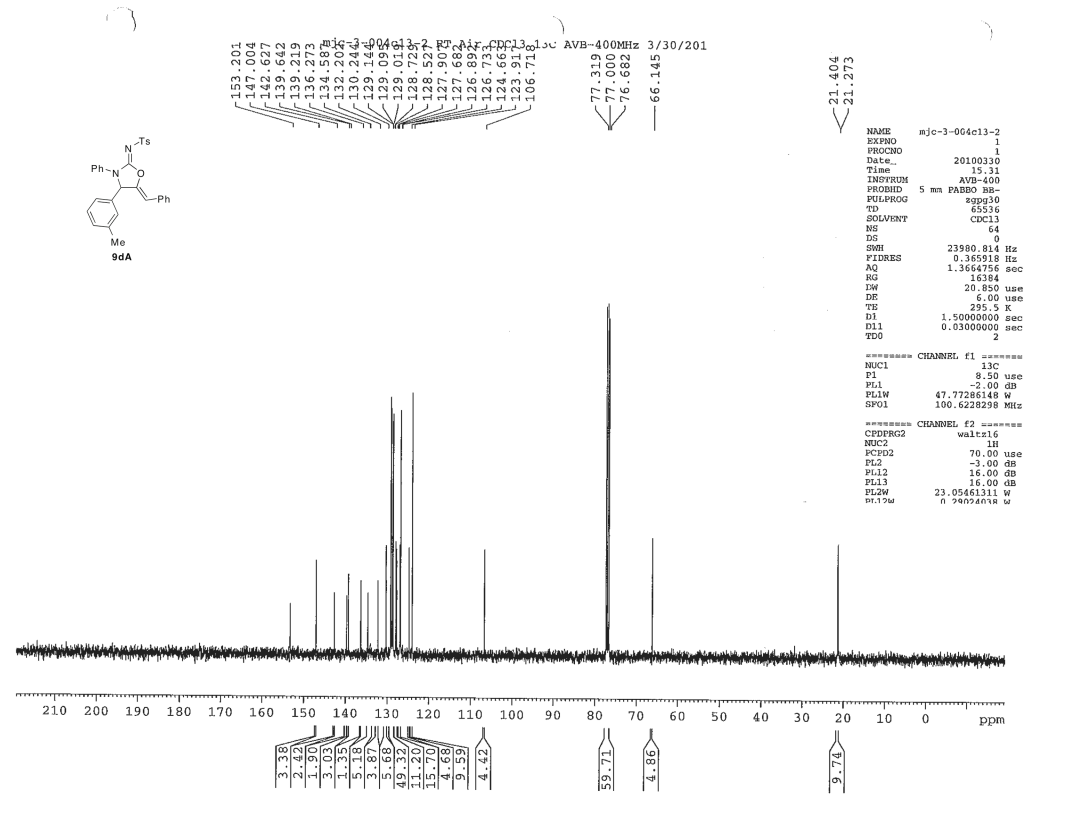


5: 288 nm, 4 nm Results

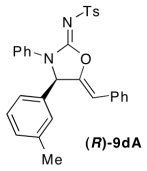
Retention Time	Area	Area Percent	Lambda Max
11.616	6842736	89.759	208
16.212	780679	10.241	207

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



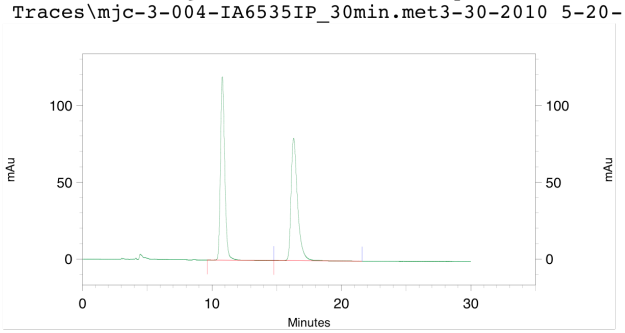


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9dA

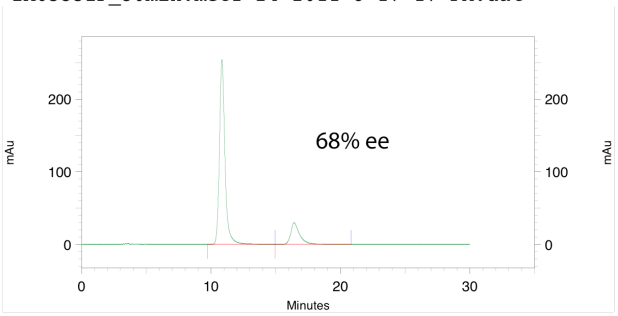
mjc-3-004
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-3-004-IA6535IP_30min.met3-30-2010 5-20-25 PM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
10.800	2725525	49.834	190
16.308	2743712	50.166	206

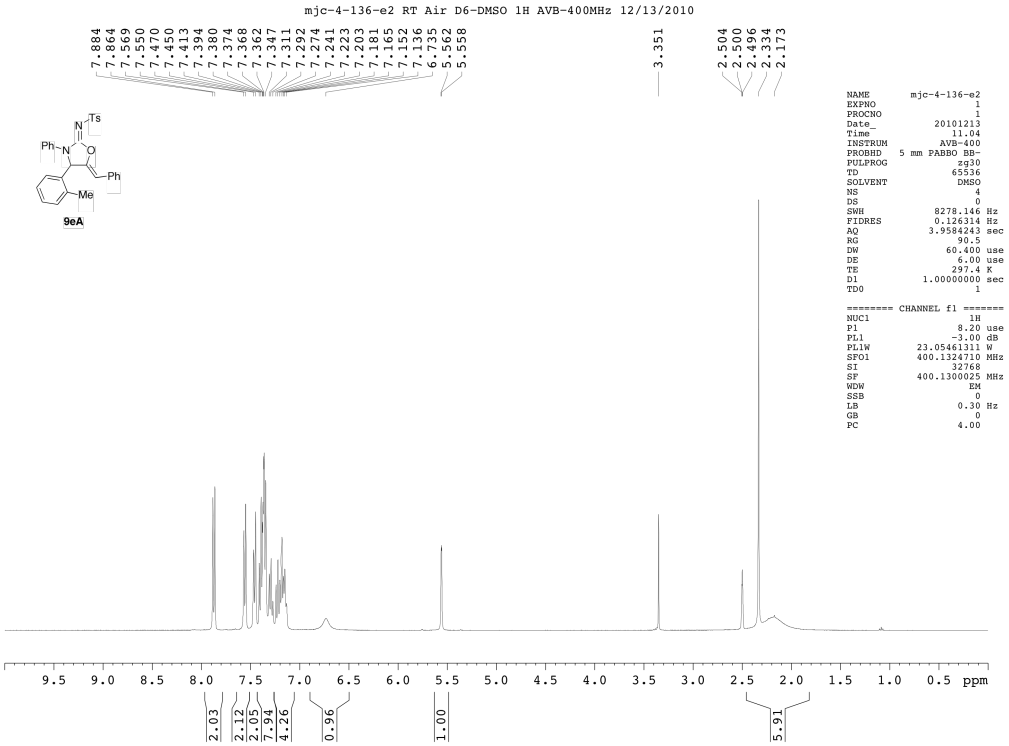
mjc-4-165-C
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-C IA6535IP_30min.met1-24-2011 8-17-17 PM.dat

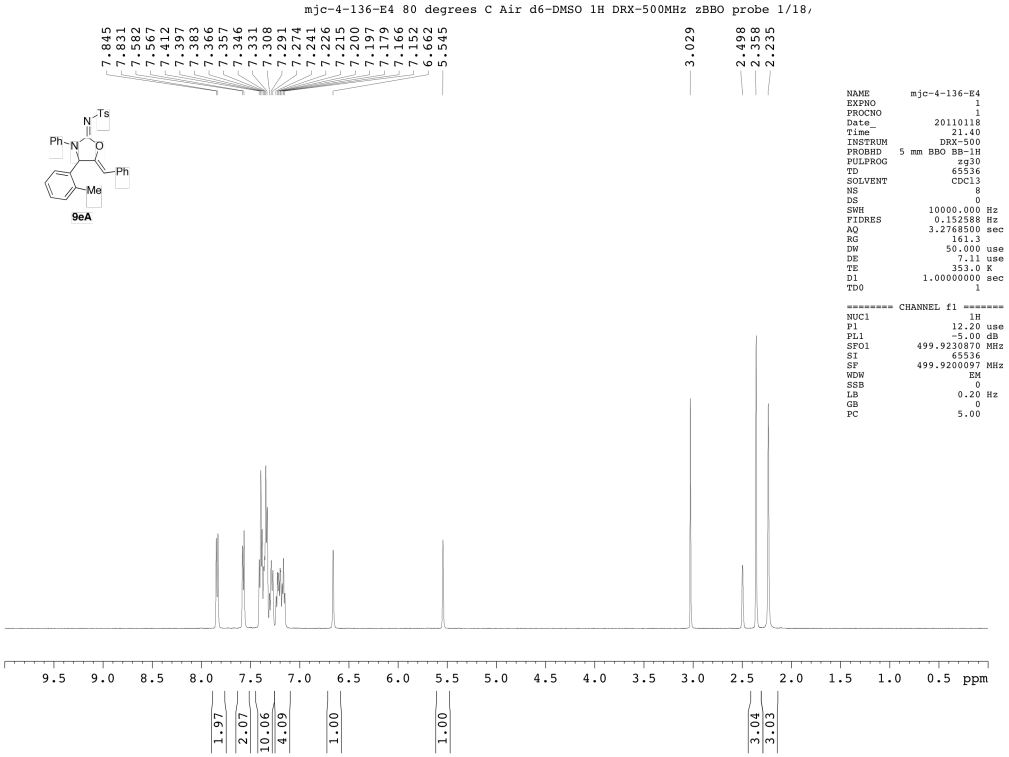


5: 288 nm, 4
nm Results

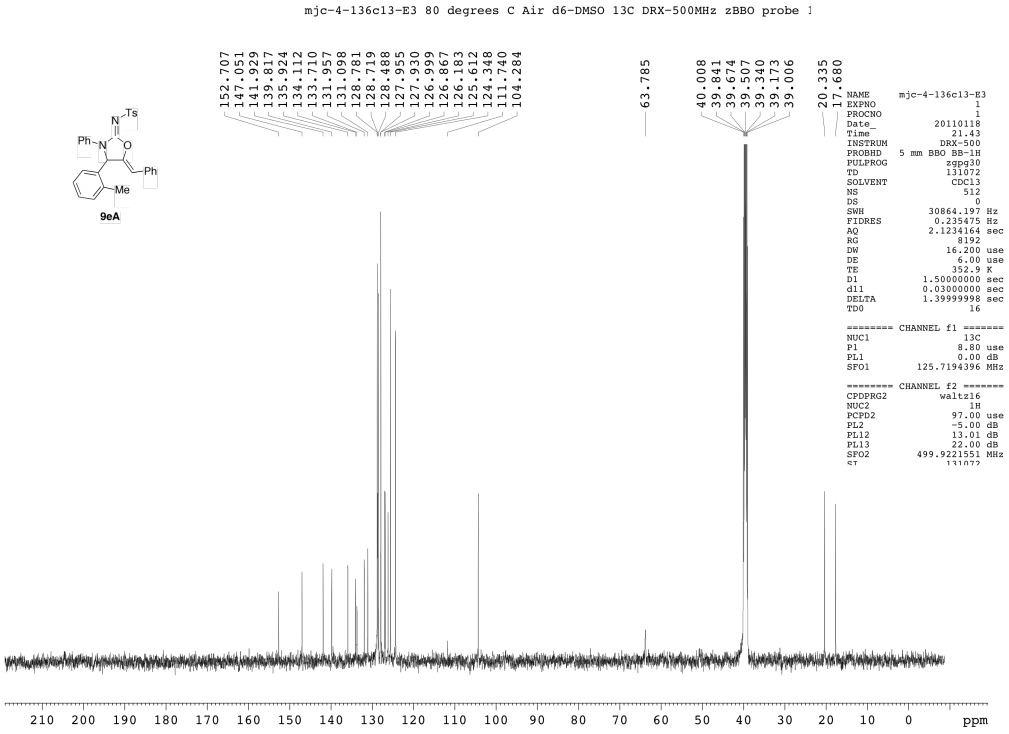
Retention Time	Area	Area Percent	Lambda Max
10.844	7550646	84.117	208
16.420	1425695	15.883	207

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

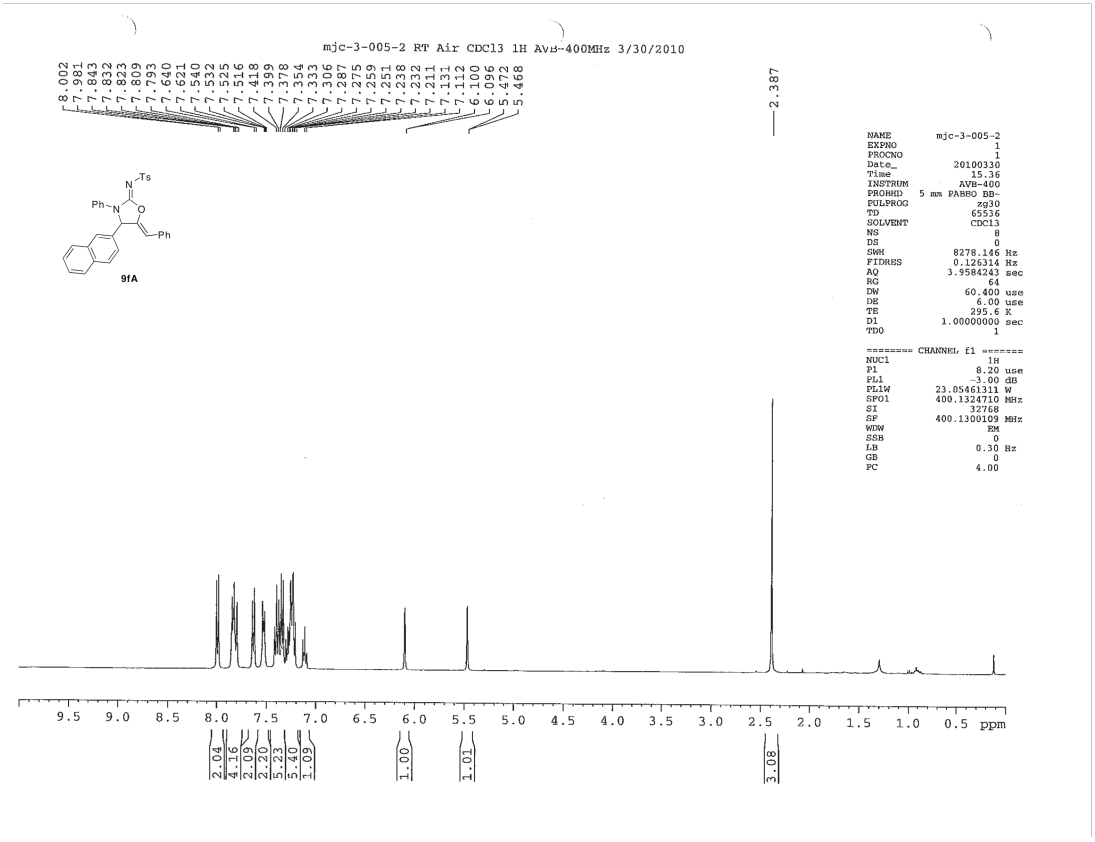


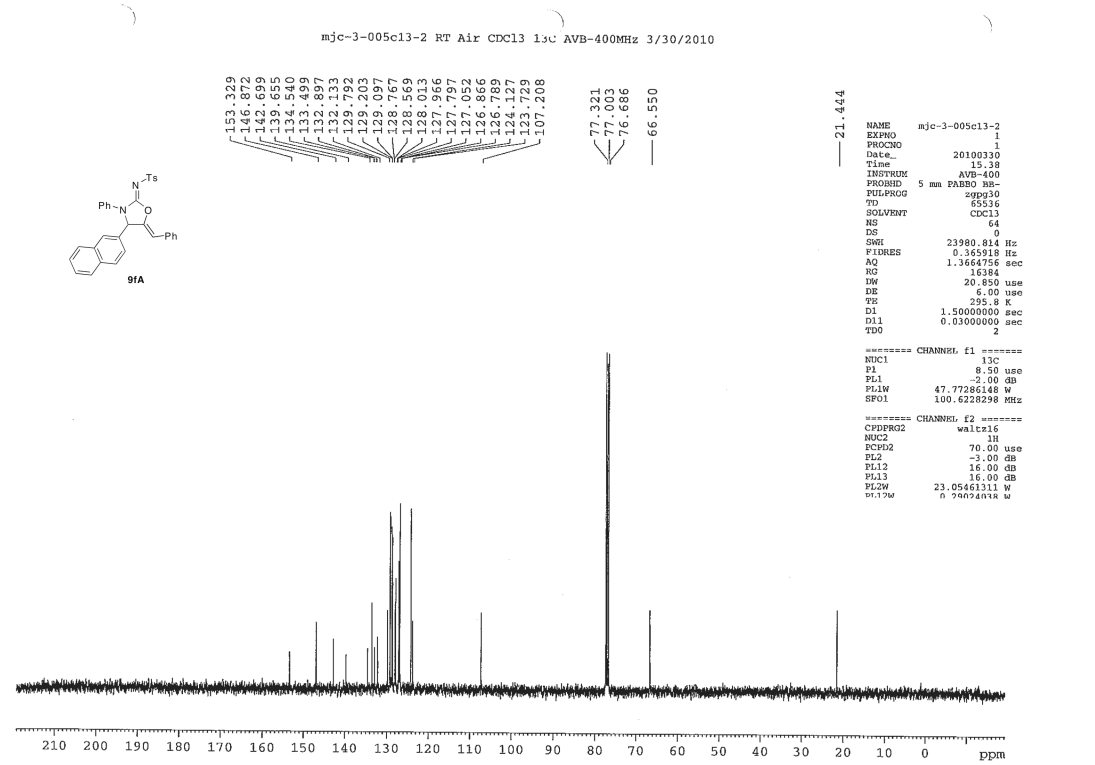


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

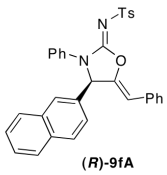


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



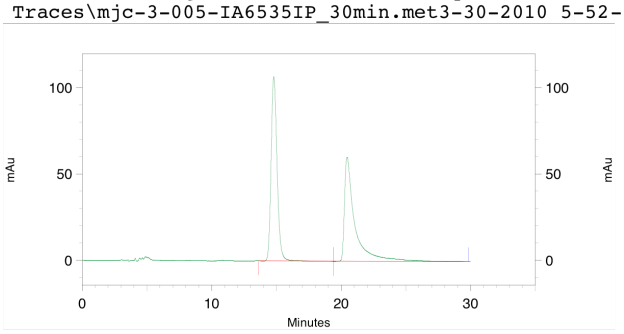


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9fA

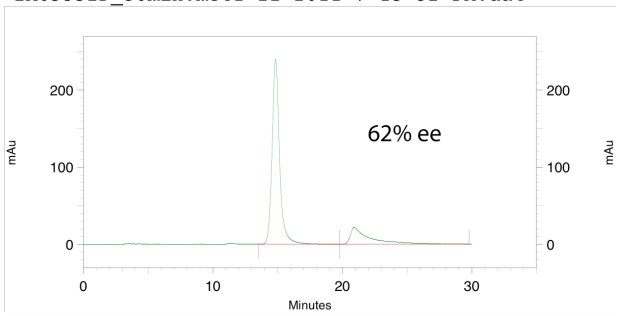
mjc-3-005
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-3-005-IA6535IP_30min.met3-30-2010 5-52-46 PM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
14.796	3364311	50.137	224
20.464	3345987	49.863	224

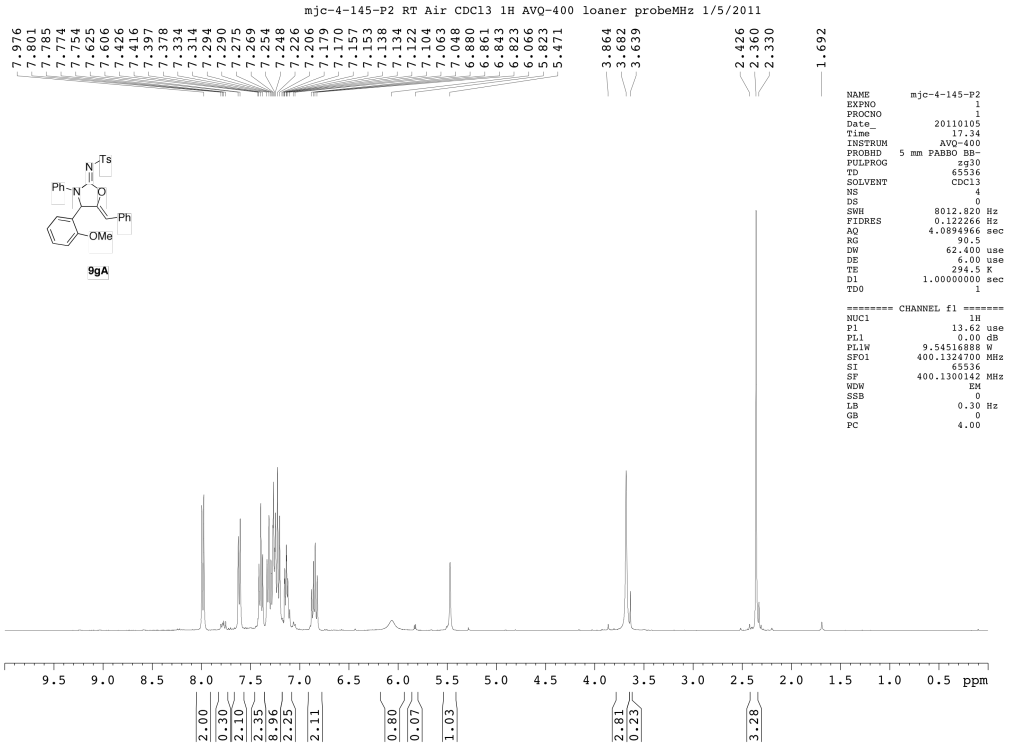
mjc-4-165-E
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-E IA6535IP_30min.met1-22-2011 7-15-32 PM.dat

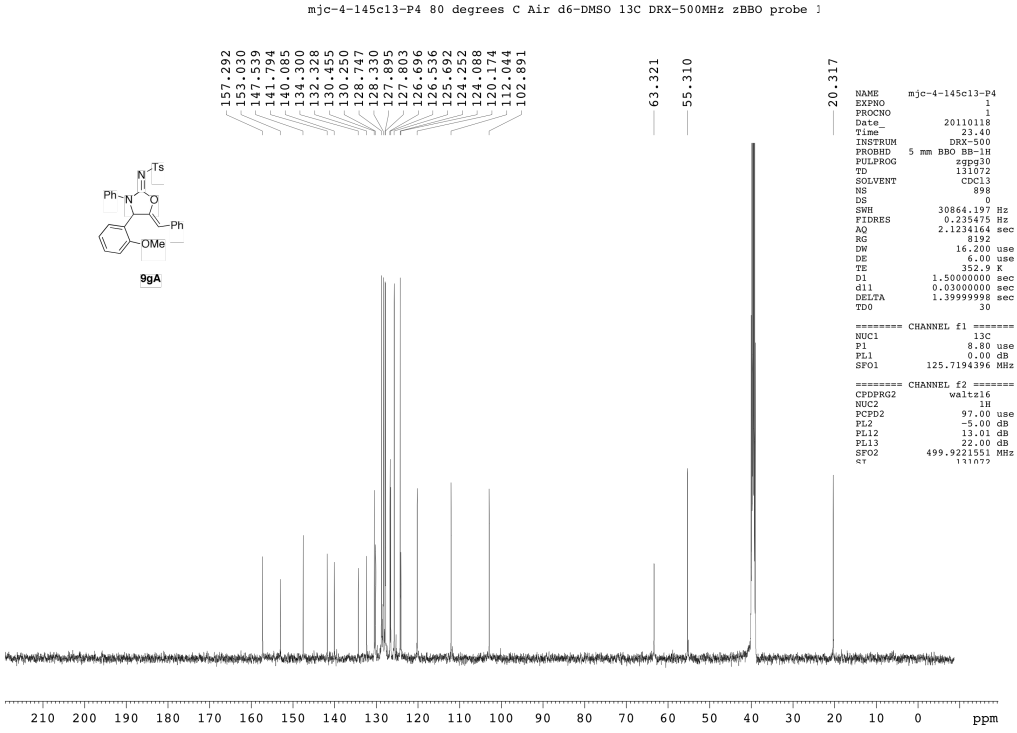


5: 288 nm, 4
nm Results

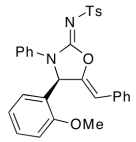
Retention Time	Area	Area Percent	Lambda Max
14.840	9610549	81.006	224
20.900	2253515	18.994	225

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



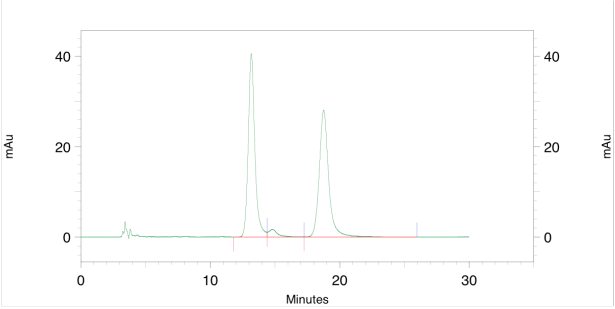


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9gA

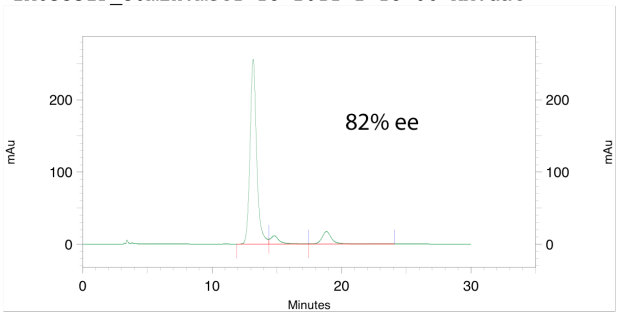
mjc-4-145-P
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-145-P
IA6535IP_30min.met1-18-2011 3-53-41 AM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
13.172	1454293	49.275	207
14.792	82619	2.799	207
18.760	1414487	47.926	207

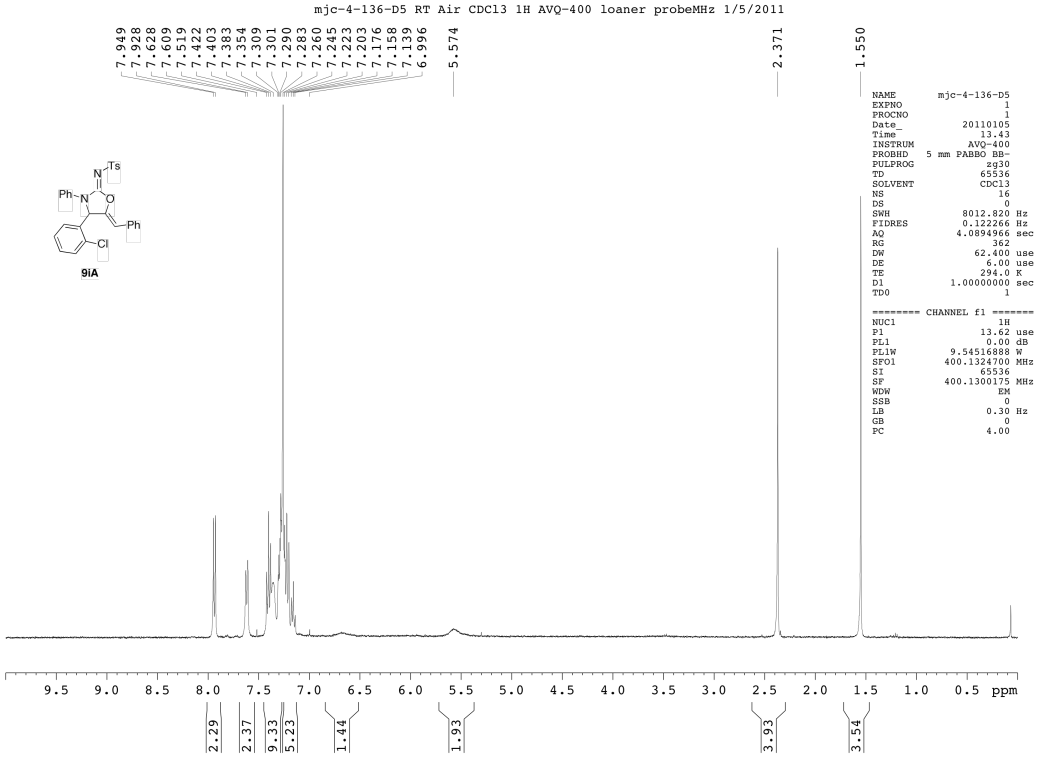
mjc-4-153-L
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-153-L
IA6535IP_30min.met1-18-2011 2-18-06 AM.dat

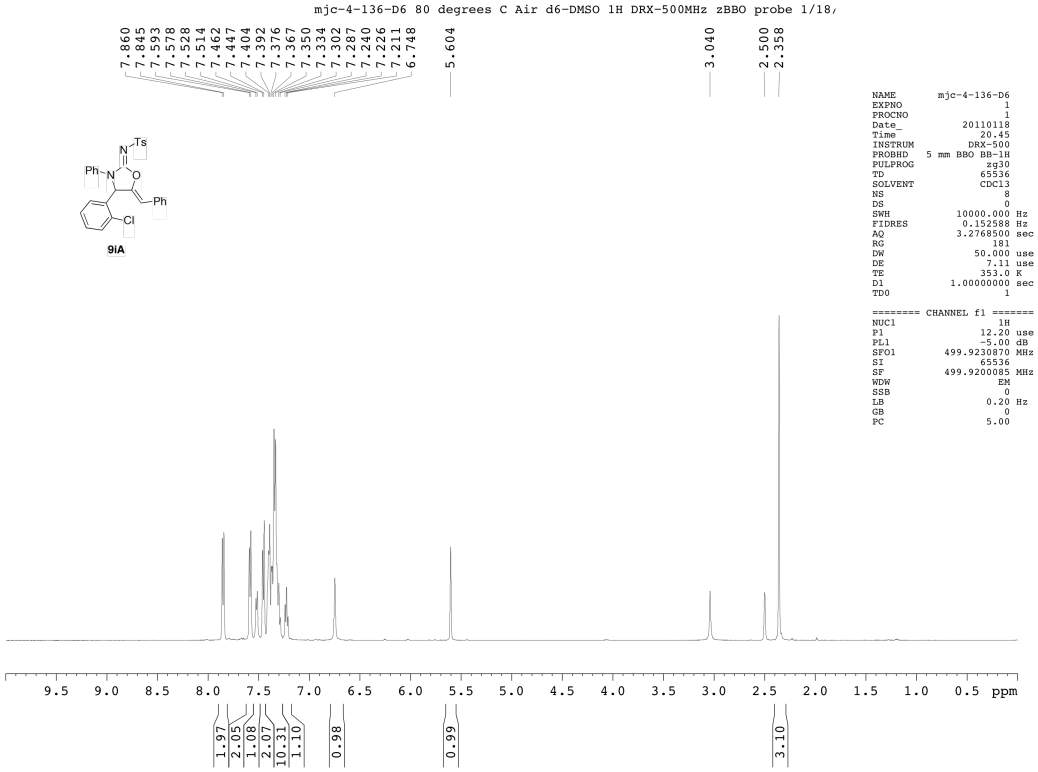


5: 287 nm, 4
nm Results

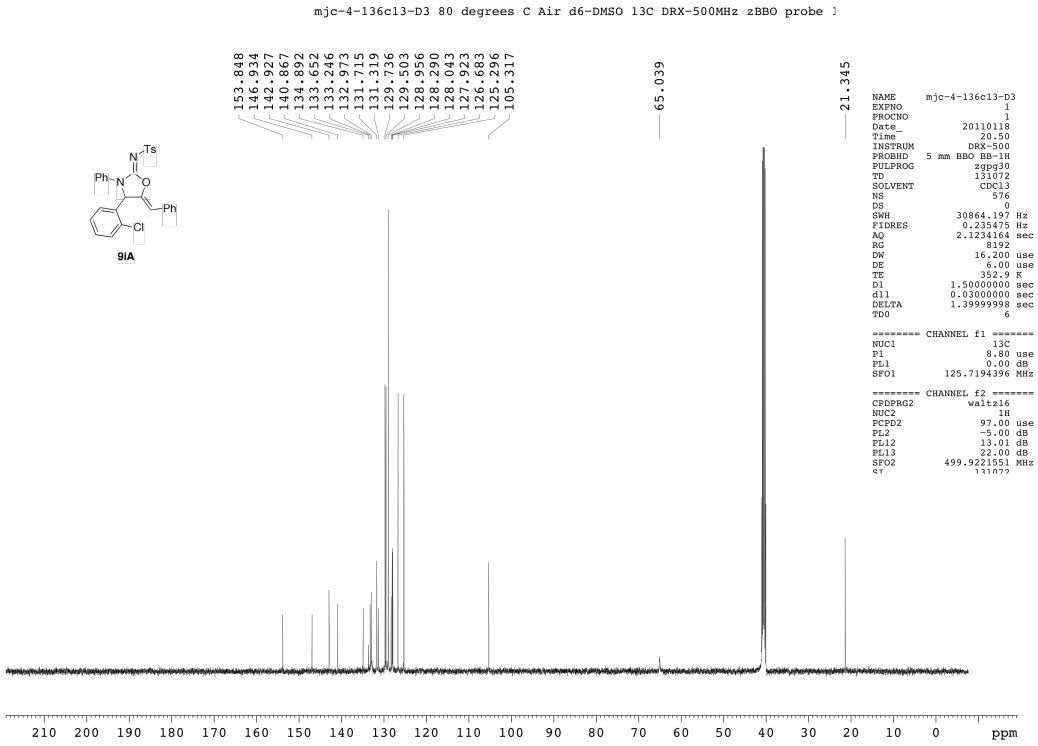
Retention Time	Area	Area Percent	Lambda Max
13.176	9111308	86.499	208
14.816	543191	5.157	207
18.840	878969	8.345	207

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

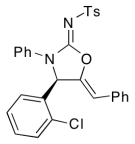




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

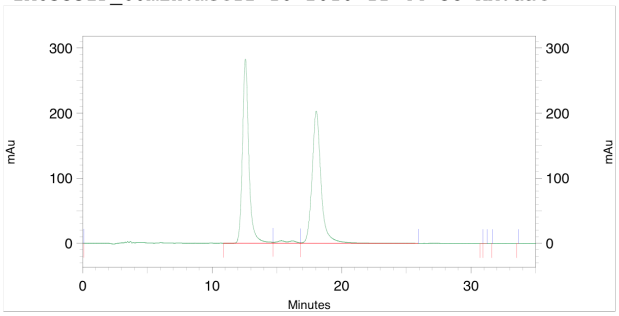


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9iA

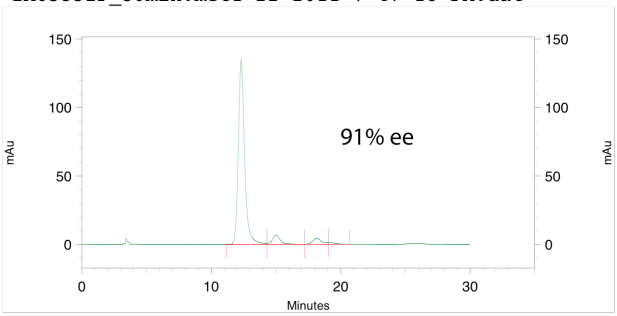
mjc-4-136-D
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-136-D
IA6535IP_60min.met12-16-2010 11-44-38 AM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.572	9674223	48.933	208
15.348	320507	1.621	207
18.044	9773924	49.437	208

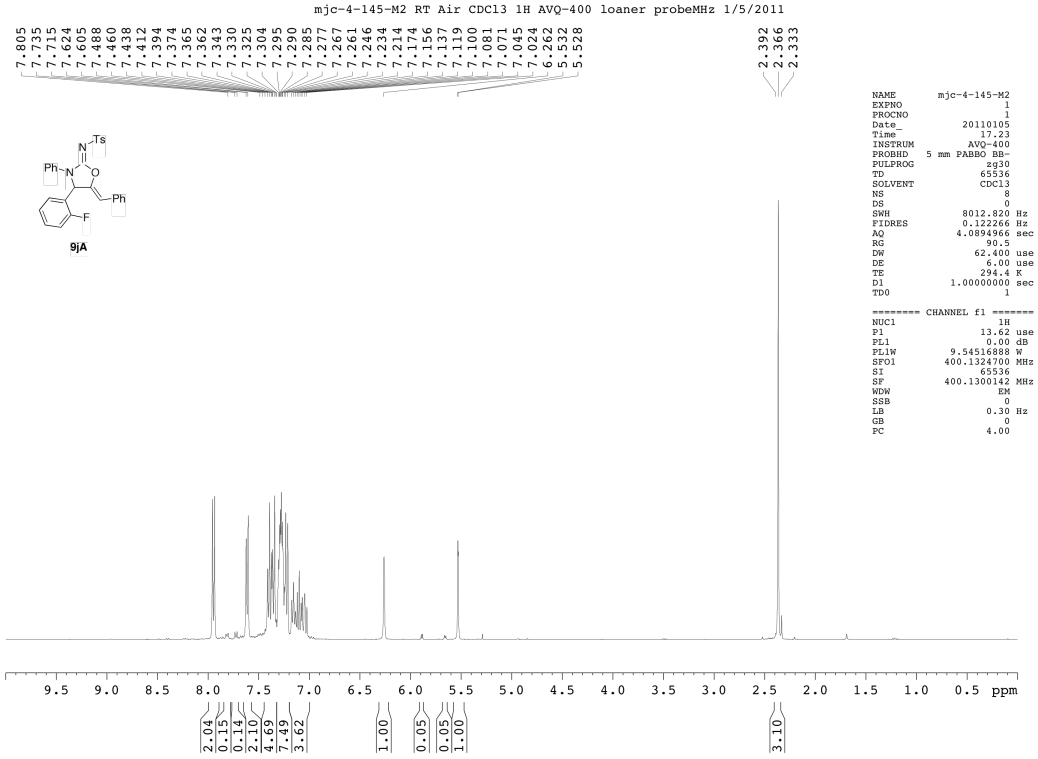
mjc-4-165-N
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-N
IA6535IP_30min.met1-22-2011 7-47-18 PM.dat

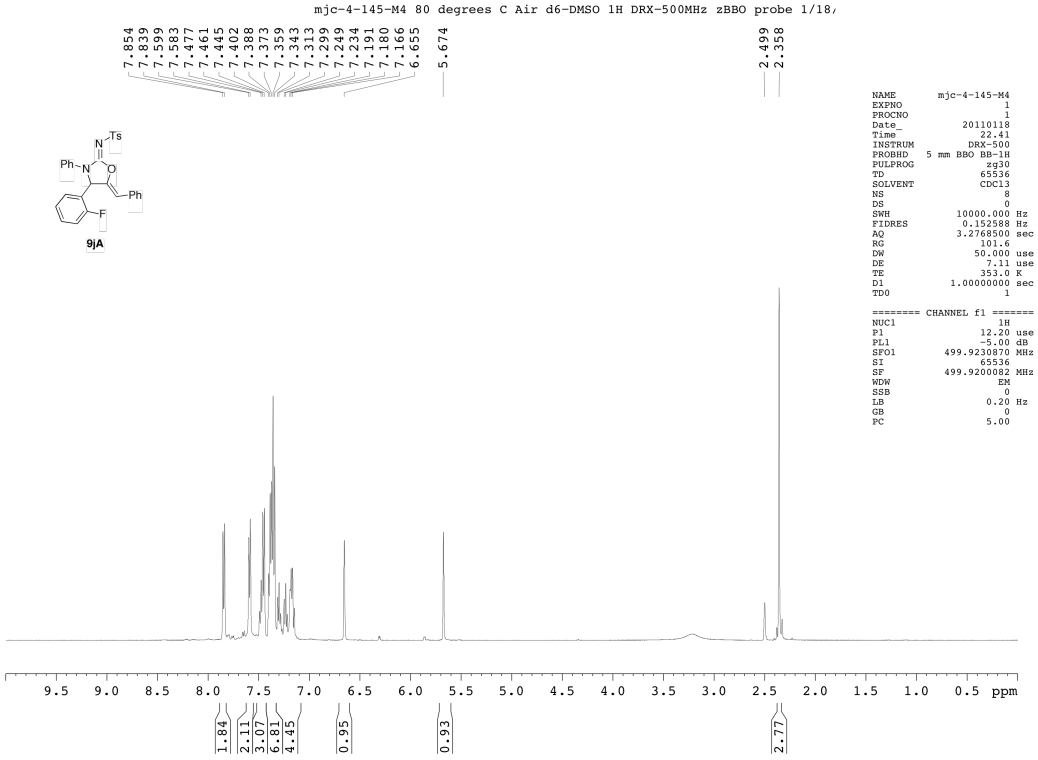


5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.316	4533602	88.885	208
15.028	296778	5.819	207
18.164	221088	4.335	207
19.148	49036	0.961	208

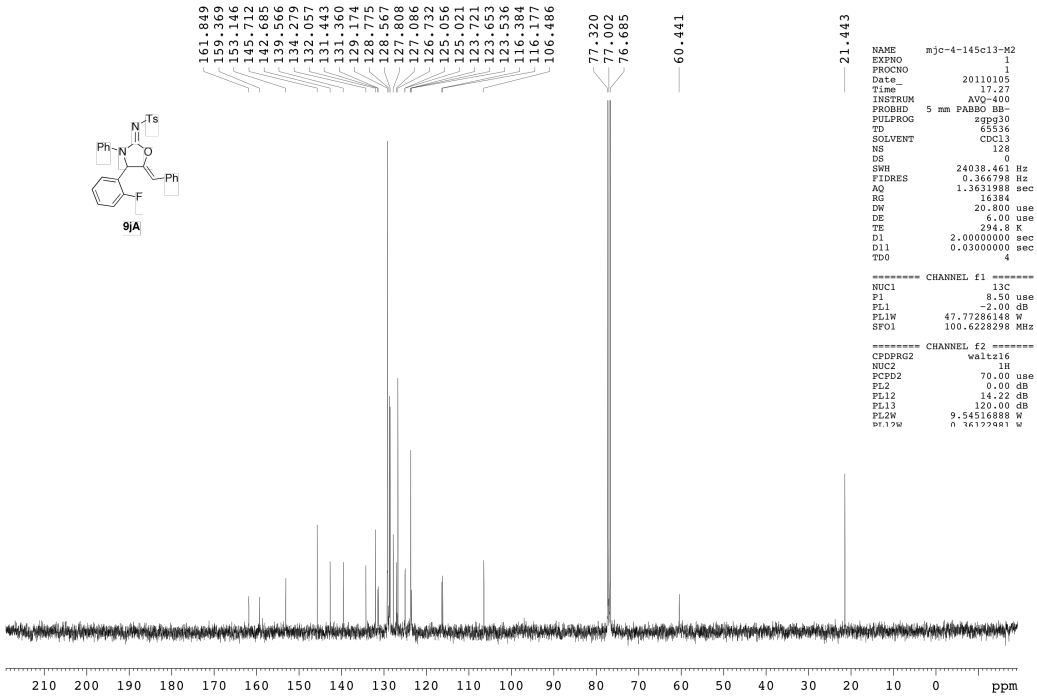
^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



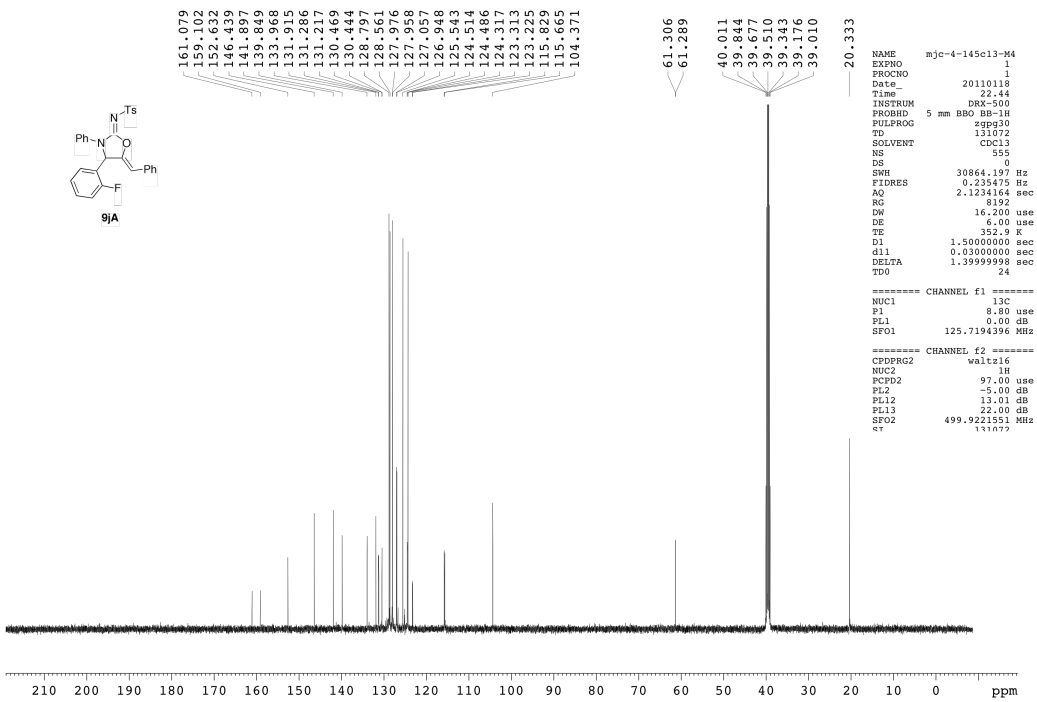


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

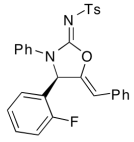
mjc-4-145c13-M2 RT Air CDCl3 13C AVQ-400 loaner probeMHz 1/5/2011



mjc-4-145c13-M4 80 degrees C Air d6-DMSO 13C DRX-500MHz zBBO probe 1

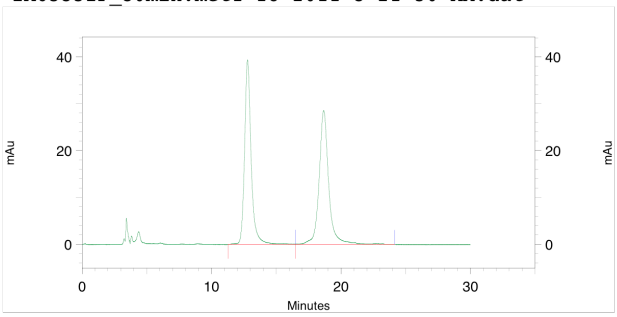


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9jA

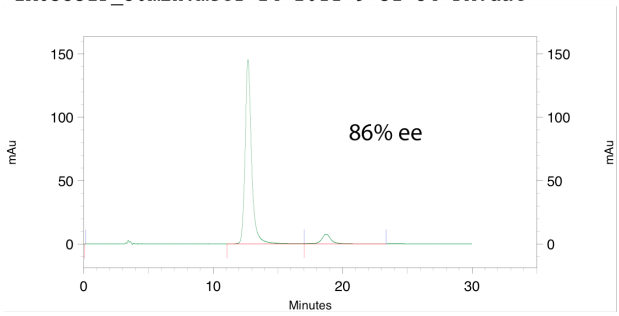
mjc-4-145-M
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-145-M IA6535IP_30min.met1-18-2011 3-21-50 AM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.780	1393922	48.631	207
18.668	1472384	51.369	207

mjc-4-165-K
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-K IA6535IP_30min.met1-24-2011 9-52-34 PM.dat

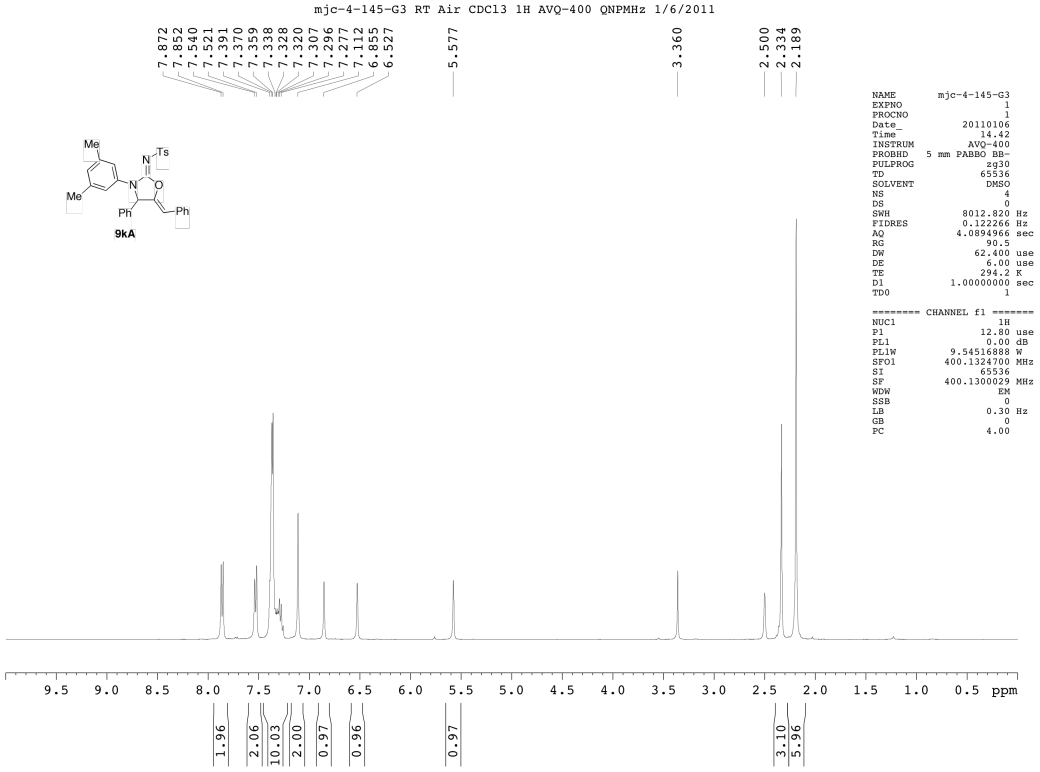


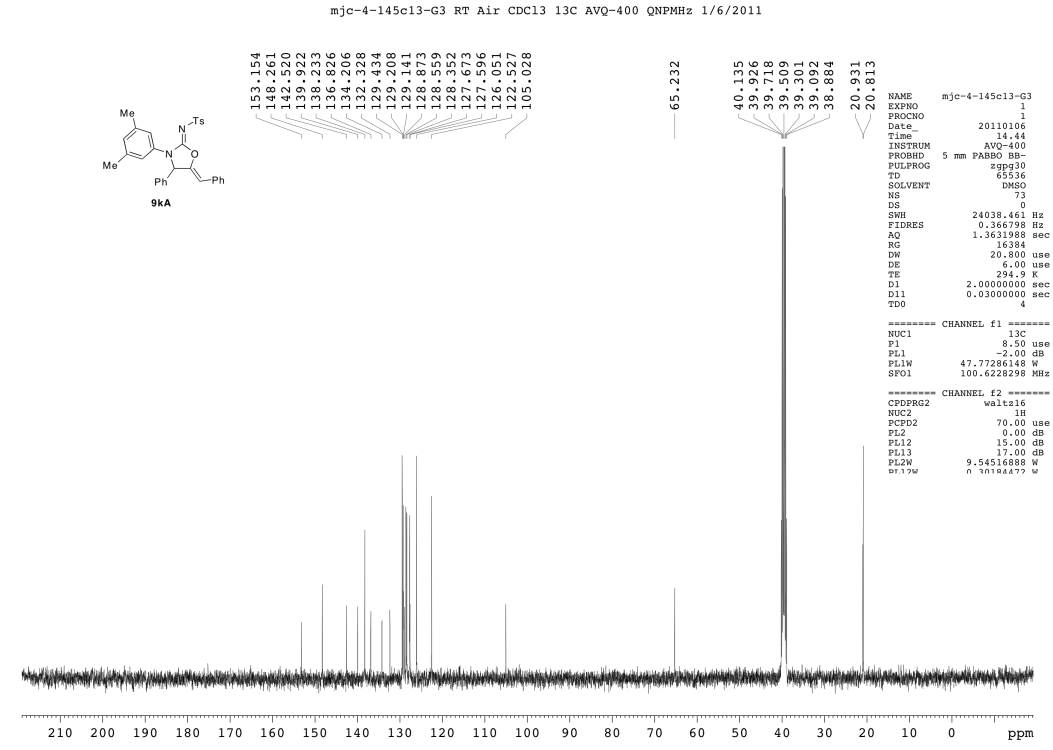
5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.692	5026312	92.886	208
18.732	384882	7.113	207

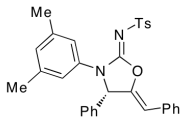
^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

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



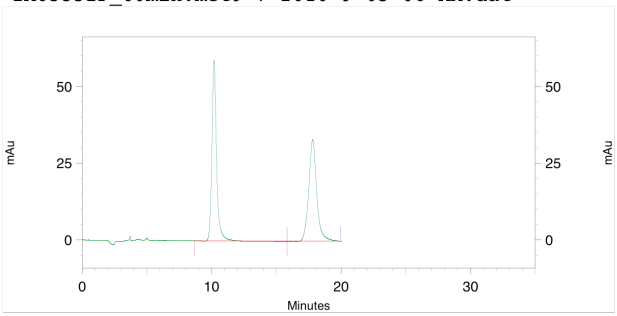


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*S*)-9kA

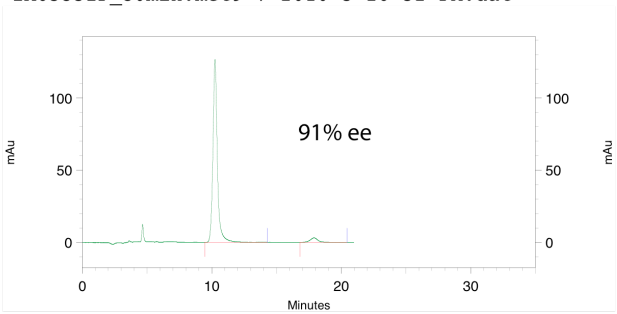
mjc-4-052-G
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-052-G
IA6535IP_60min.met9-7-2010 9-05-06 AM.dat



5: 288 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
10.192	1432592	50.416	208
17.808	1408938	49.584	208

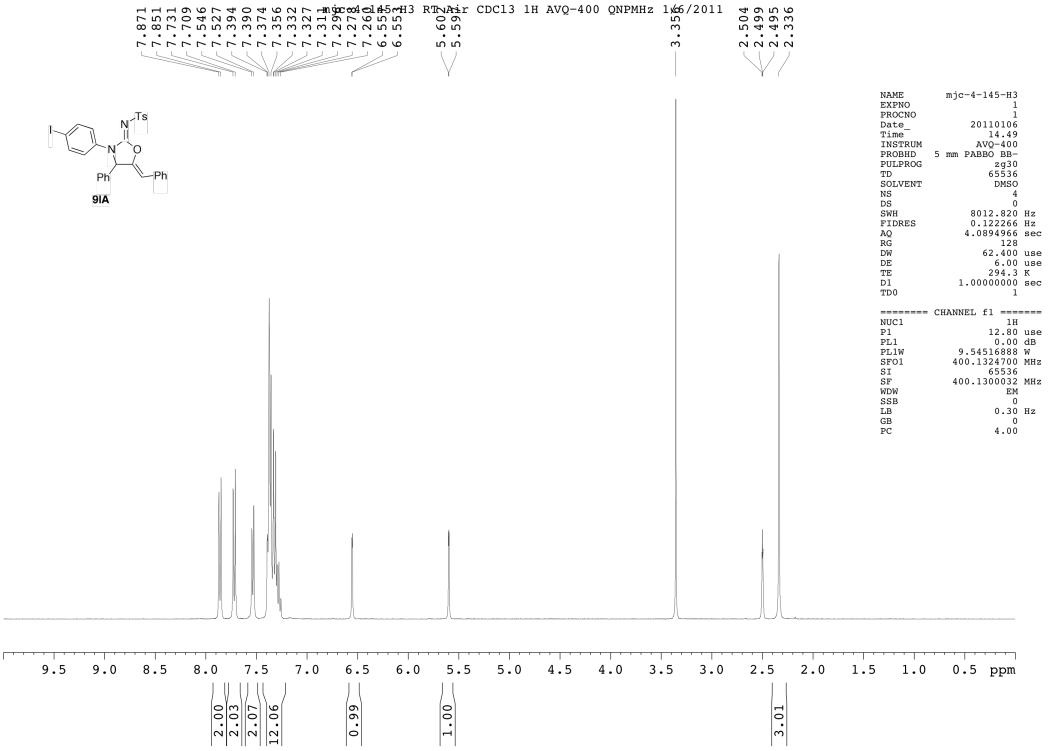
mjc-4-072-A
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-072-A
IA6535IP_30min.met9-7-2010 5-26-52 PM.dat

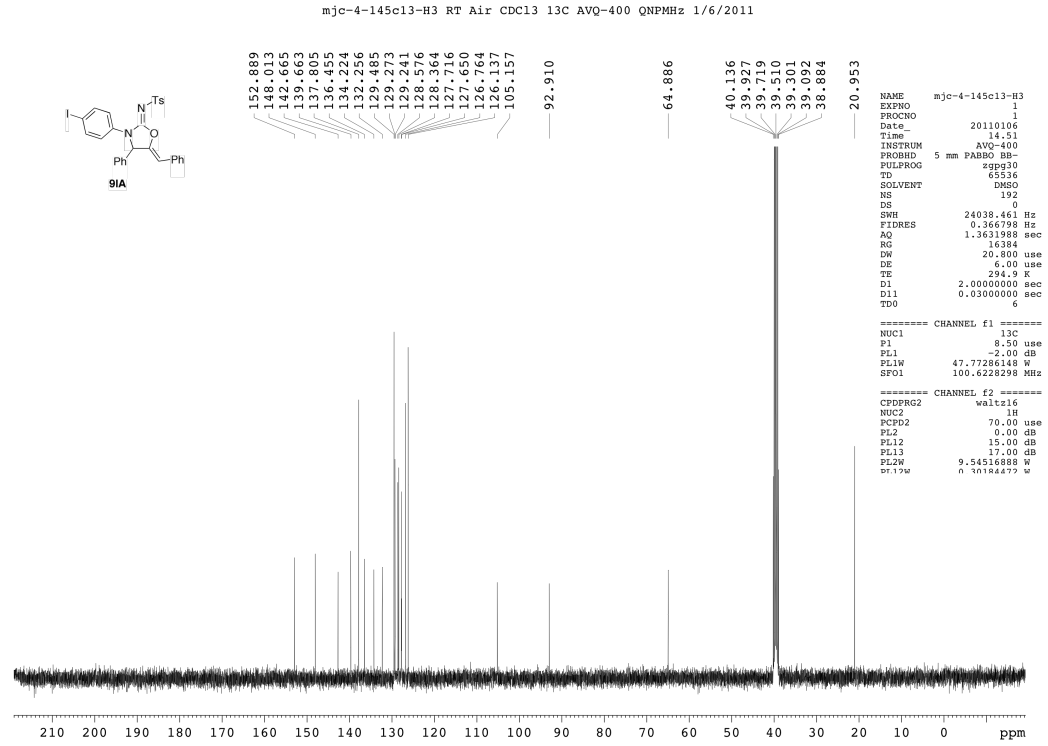


5: 288 nm, 4
nm Results

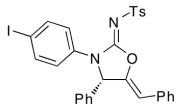
Retention Time	Area	Area Percent	Lambda Max
10.248	3034892	95.626	208
17.912	138831	4.374	208

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



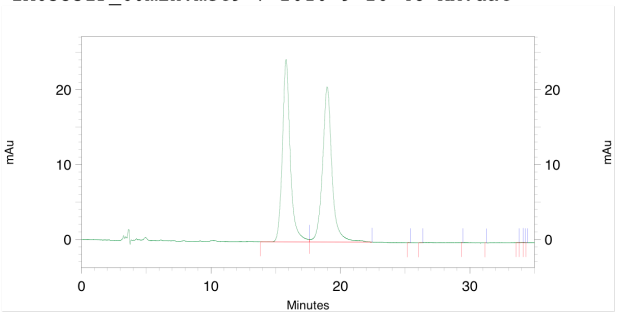


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*S*)-9IA

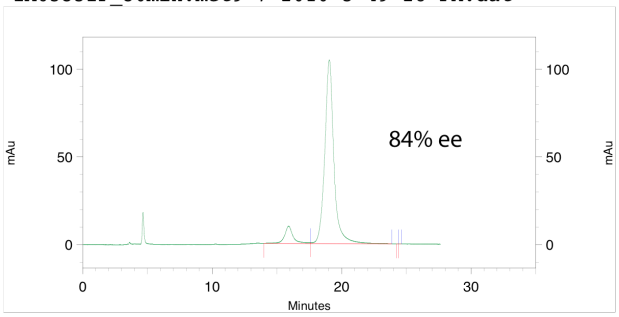
mjc-4-052-H
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-052-H
IA6535IP_60min.met9-7-2010 9-26-48 AM.dat



5: 288 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
15.808	1033181	49.394	208
18.976	1055905	50.481	208

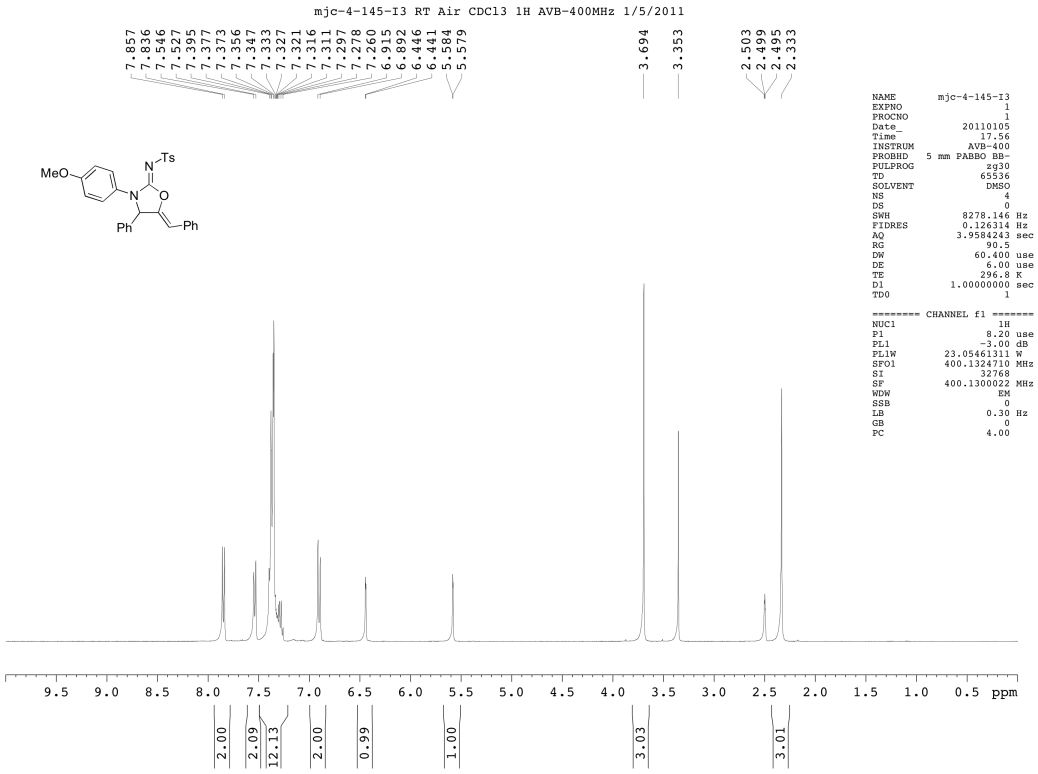
mjc-4-072-B
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-072-B
IA6535IP_30min.met9-7-2010 5-49-28 PM.dat

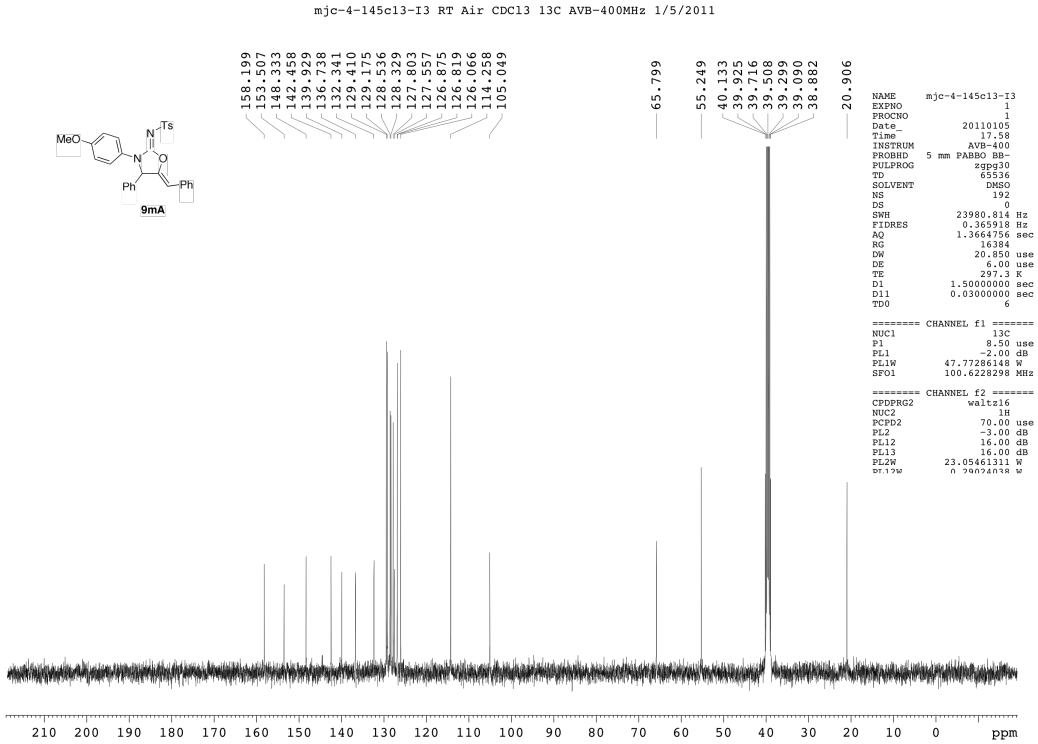


5: 288 nm, 4
nm Results

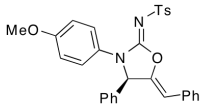
Retention Time	Area	Area Percent	Lambda Max
15.904	445291	8.022	208
19.044	5105122	91.972	208

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



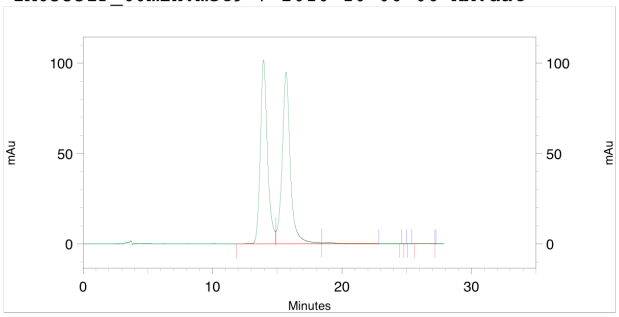


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9mA

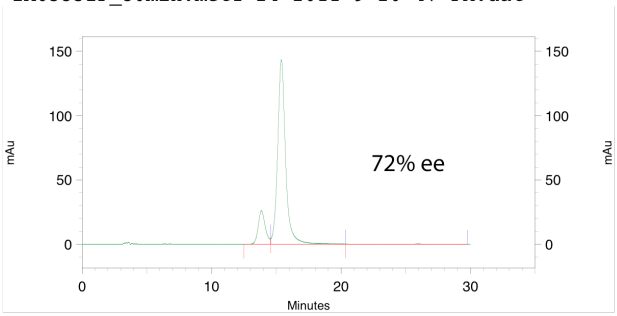
mjc-4-052-I
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-052-I
IA6535IP_60min.met9-7-2010 10-06-06 AM.dat



5: 288 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
13.940	3900587	48.043	208
15.684	4160274	51.241	208

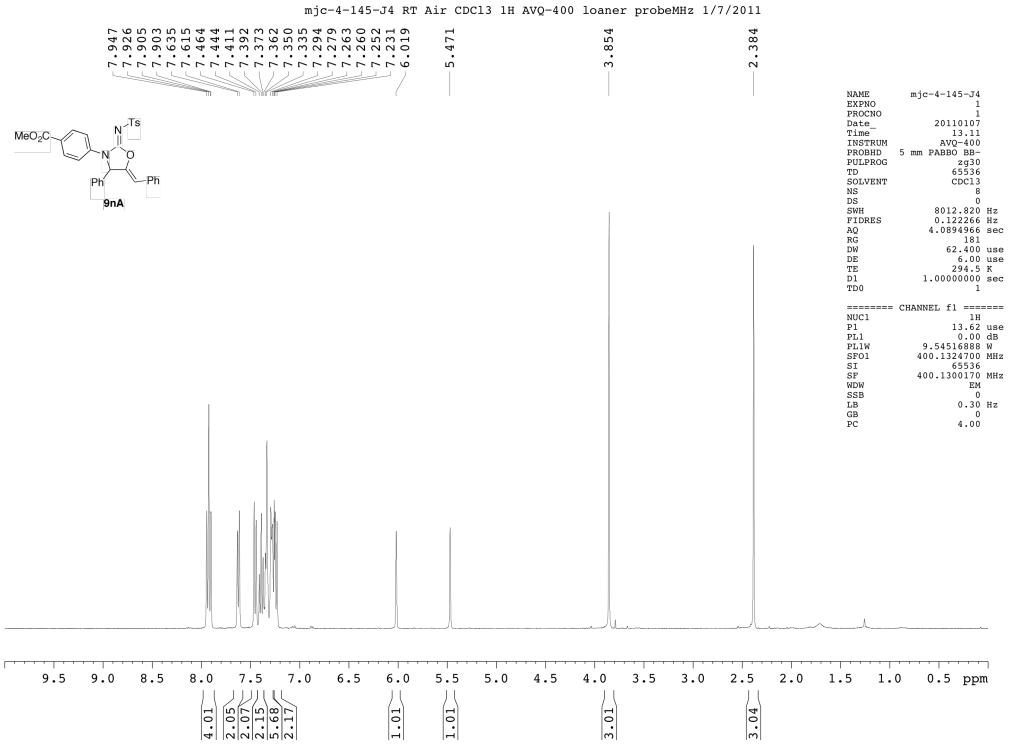
mjc-4-165-H
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-H
IA6535IP_30min.met1-24-2011 9-20-47 PM.dat

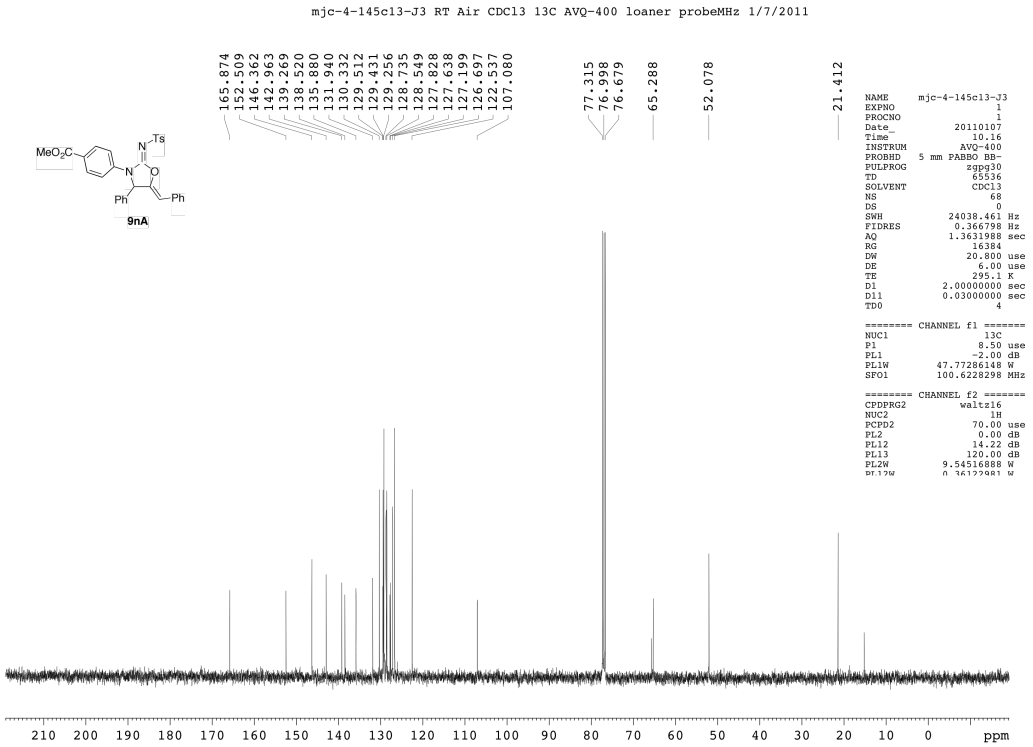


5: 288 nm, 4
nm Results

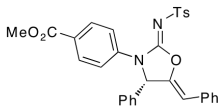
Retention Time	Area	Area Percent	Lambda Max
13.856	986000	13.854	207
15.392	6108121	85.823	208

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



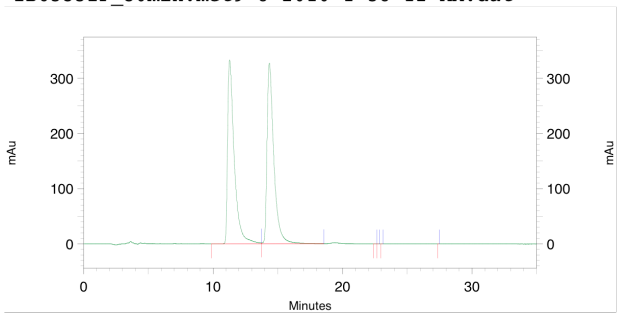


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*S*)-9nA

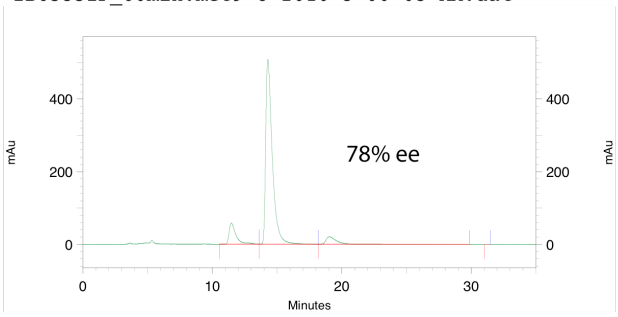
mjc-4-052-J
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-052-J
IB6535IP_30min.met9-8-2010 1-58-12 AM.dat



5: 288 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
11.280	11925625	49.908	208
14.352	11968427	50.087	208

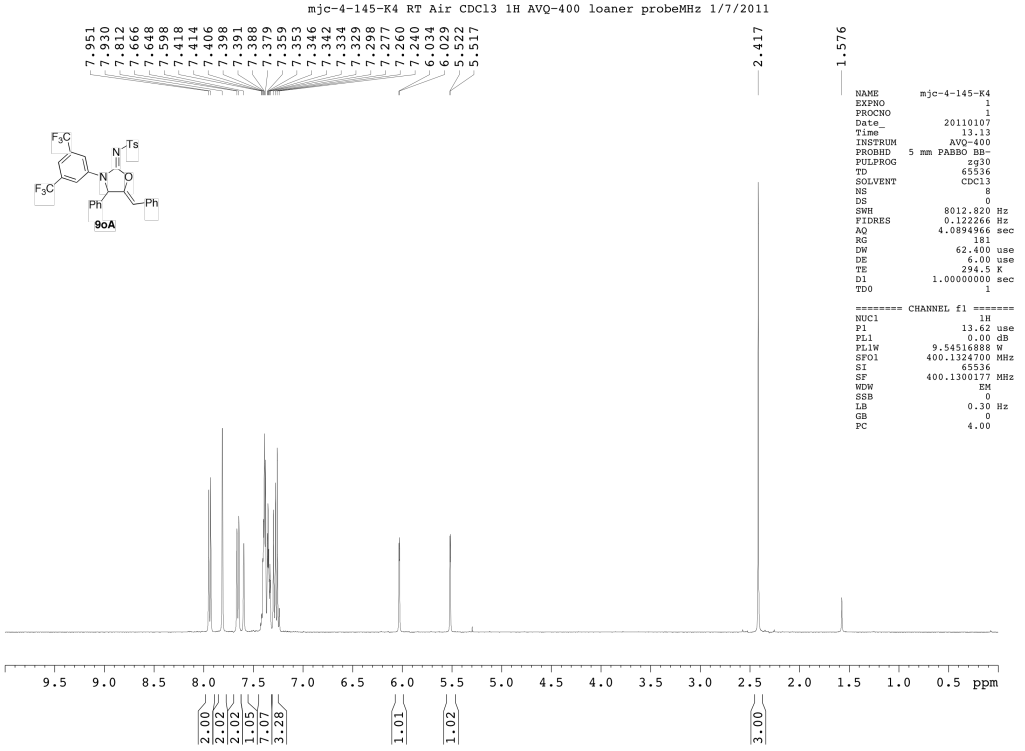
mjc-4-072-D
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-072-D
IB6535IP_60min.met9-8-2010 3-00-03 AM.dat

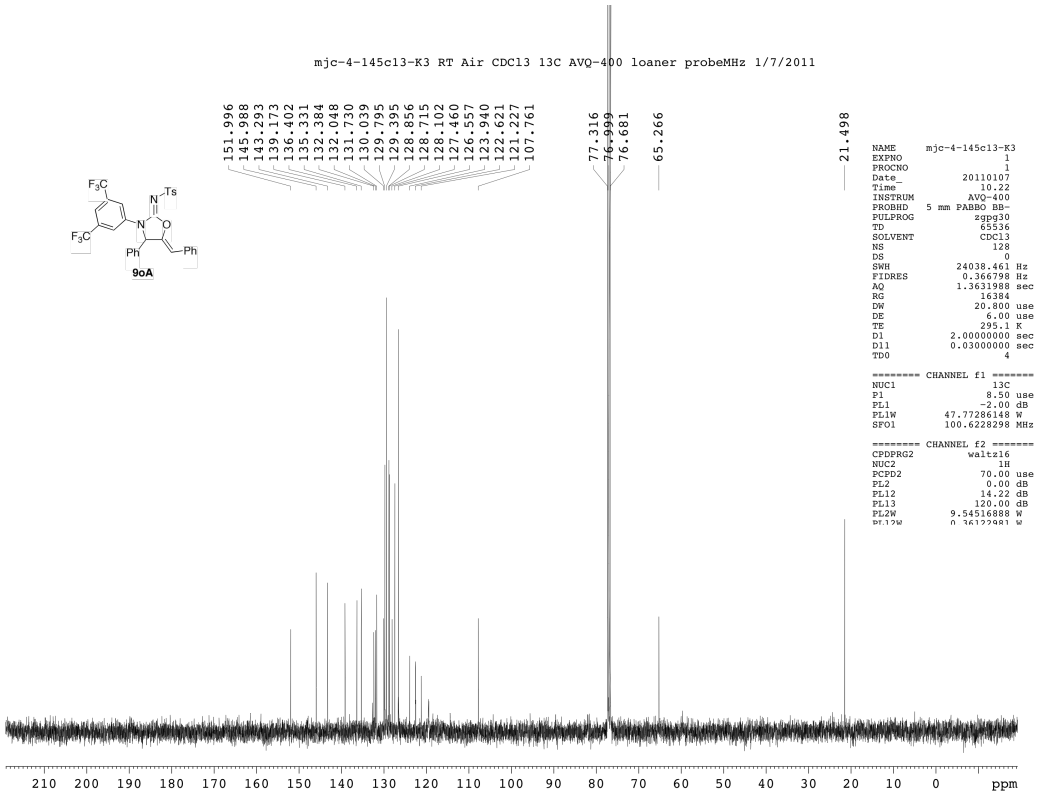


5: 288 nm, 4
nm Results

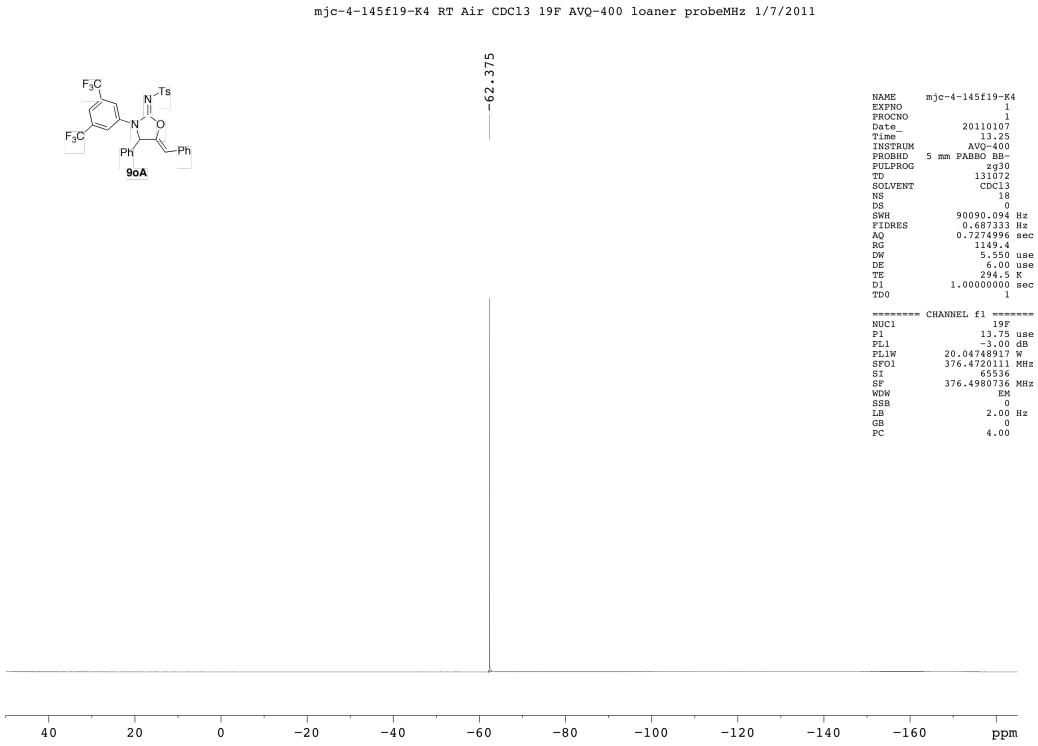
Retention Time	Area	Area Percent	Lambda Max
11.472	2225145	10.312	208
14.292	18159258	84.156	208
19.044	1191221	5.521	207

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

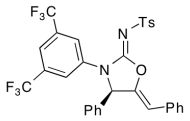




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

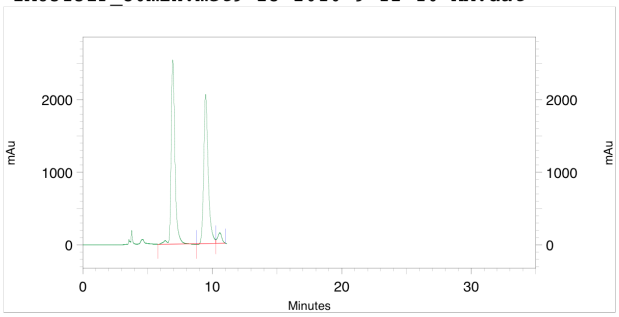


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9oA

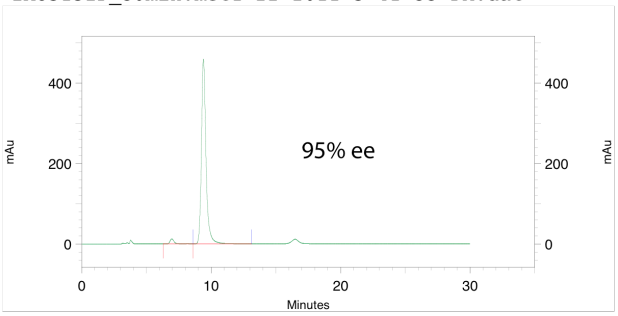
mjc-4-095-C
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-093-C
IA8515IP_30min.met9-23-2010 9-12-10 AM.dat



2: 239 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
6.948	51202459	49.521	219
9.484	48959176	47.351	214
10.588	3233856	3.128	209

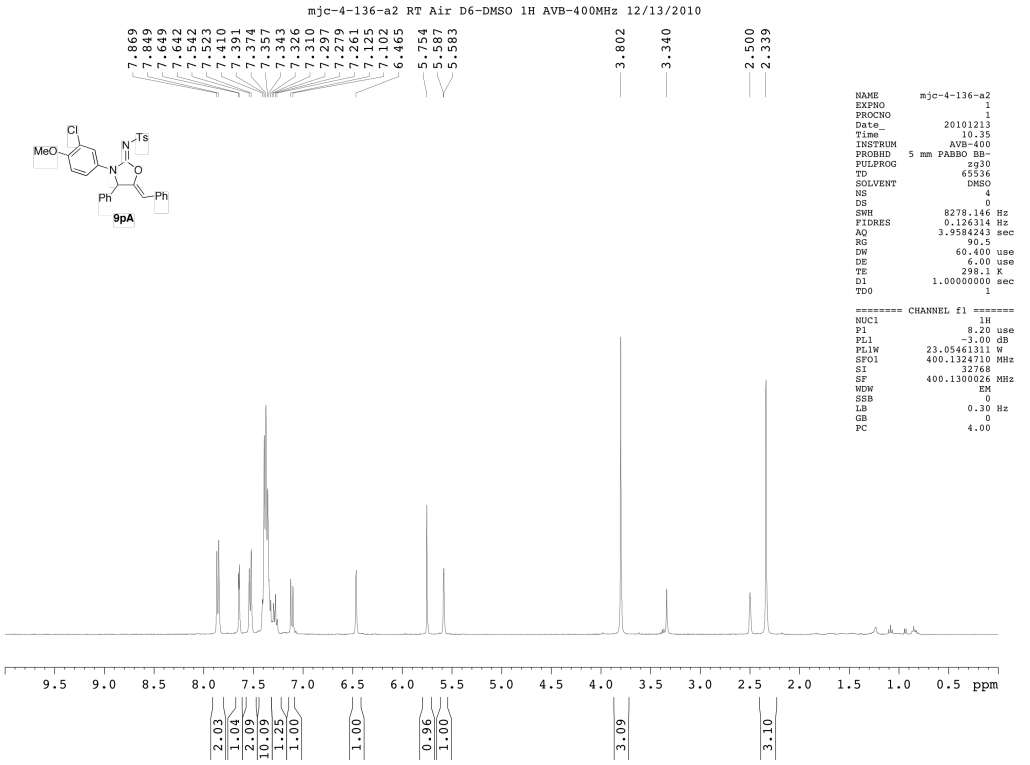
mjc-4-165-J
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-J
IA8515IP_30min.met1-22-2011 5-41-33 PM.dat

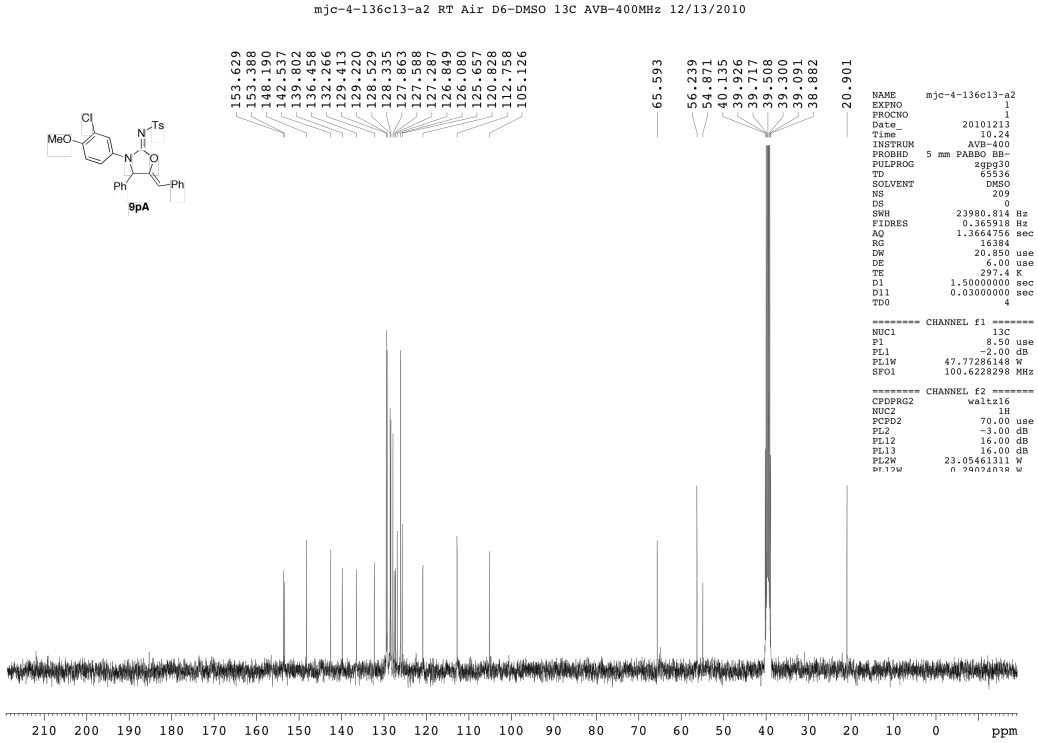


2: 239 nm, 4
nm Results

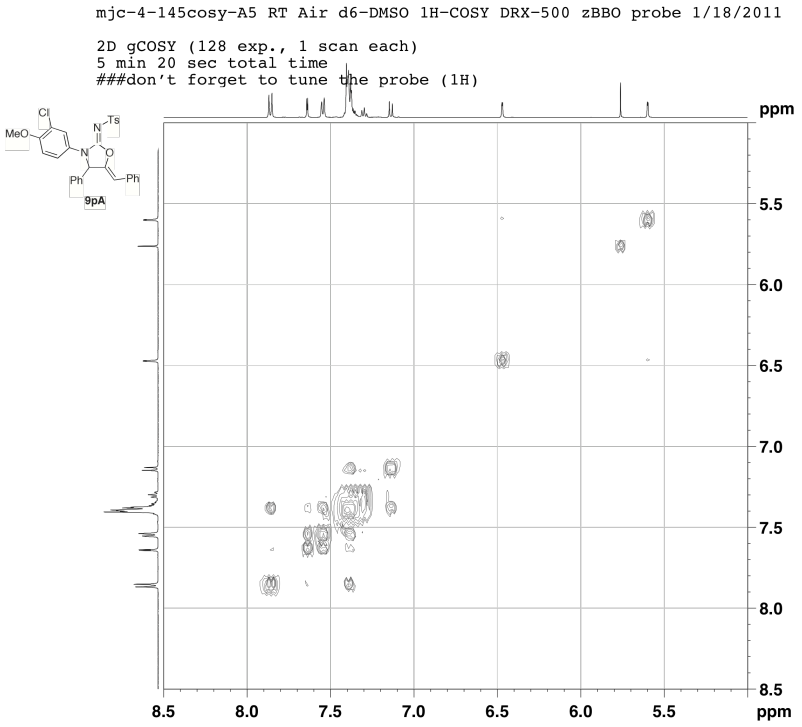
Retention Time	Area	Area Percent	Lambda Max
6.964	266690	2.326	207
9.404	11198257	97.674	208

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

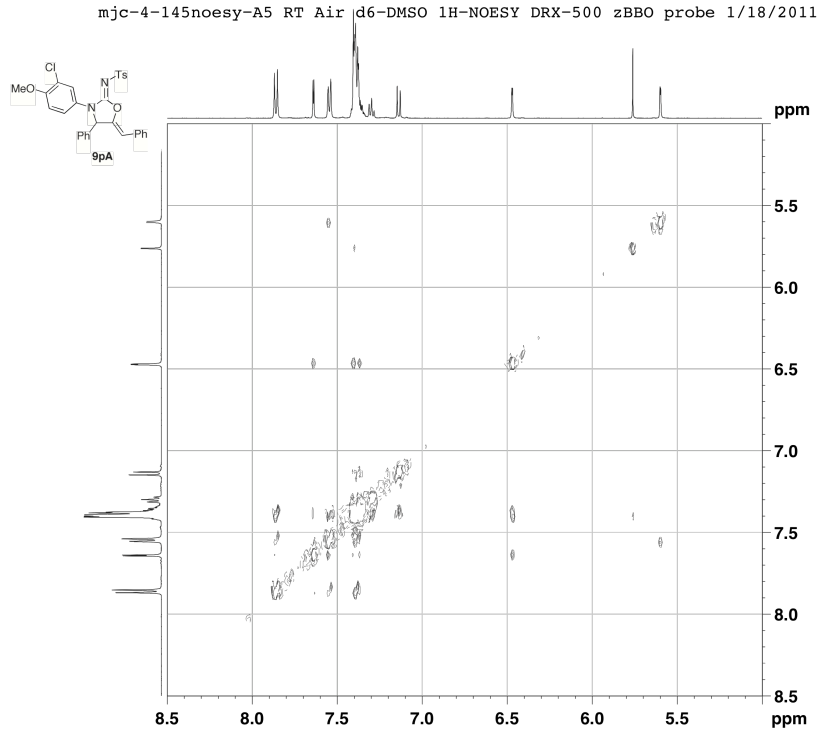




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

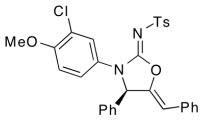



```
NAME        mjc-4-136cosy-A5
EXPNO                      1
PROCNO                     1
Date_               20110118
Time                   13.13
INSTRUM              DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG           cosygpqf
TD                     2048
SOLVENT               CDCl3
NS                         1
DS                        16
SWH                7002.801 Hz
FIDRES             3.419337 Hz
AQ                 0.1462772 sec
RG                     812.7
DW                    71.400 usec
DE                     6.00 usec
TE                    305.0 K
d0                 0.00000300 sec
D1                 2.00000000 sec
d13                0.00000400 sec
D16                0.00020000 sec
IN0                0.00014280 sec

======== CHANNEL f1 ========
NUC1                       1H
P0                      12.20 usec
P1                      12.20 usec
PL1                     -5.00 dB
SFO1            499.9230745 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPNAM2               SINE.100
GPZ1                    10.00 %
GPZ2                    10.00 %
P16                   1000.00 usec
ND0                        1
TD                       128
SFO1                499.9231 MHz
FIDRES              54.709385 Hz
SW                     14.008 ppm
FnMODE                     QF
SI                       1024
SF                499.9200000 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       5.00
SI                        512
MC2                        QF
SF                499.9200000 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
```



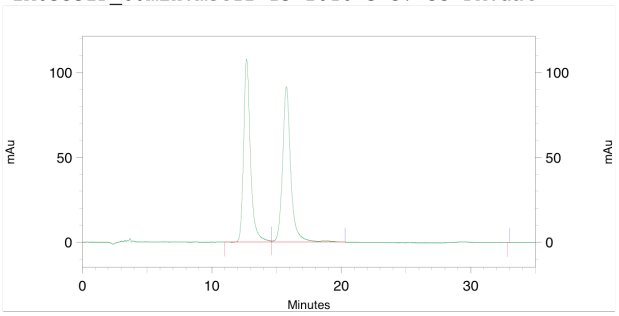

```
NAME        mjc-4-136noesy-A5
EXPNO                      1
PROCNO                     1
Date_               20110118
Time                   13.19
INSTRUM              DRX-500
PROBHD    5 mm BBO BB-1H
PULPROG          noesygpph
TD                     2048
SOLVENT               CDCl3
NS                         2
DS                         4
SWH                5000.000 Hz
FIDRES             2.441406 Hz
AQ                 0.2048500 sec
RG                       362
DW                   100.000 usec
DE                     7.11 usec
TE                    305.0 K
d0                 0.00000447 sec
D1                 1.00000000 sec
D8                 0.69999999 sec
D16                0.00020000 sec
IN0                0.00020000 sec
TAU                0.34880000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.20 usec
p2                      24.40 usec
PL1                     -5.00 dB
SFO1            499.9220497 MHz

====== GRADIENT CHANNEL =====
GPNAM1               SINE.100
GPNAM2               SINE.100
GPZ1                    40.00 %
GPZ2                   -40.00 %
P16                   1000.00 usec
ND0                        1
TD                       256
SFO1                499.922 MHz
FIDRES             19.531250 Hz
SW                     10.002 ppm
FnMODE                  TPPI
SI                       1024
SF                499.9200000 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       5.00
SI                        256
MC2                     TPPI
SF                499.9200000 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```

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



(*R*)-9pA

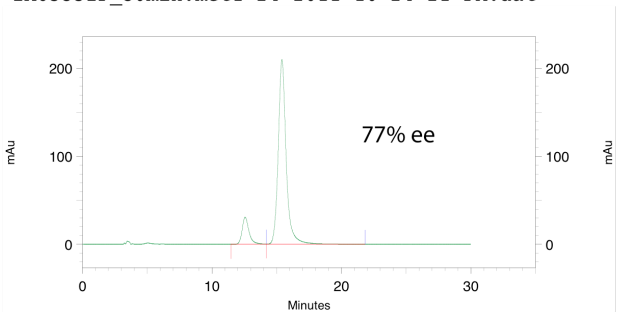
mjc-4-136-A
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-136-A
IA6535IP_60min.met12-15-2010 5-37-33 PM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
12.684	3968454	49.451	208
15.760	4055367	50.534	208

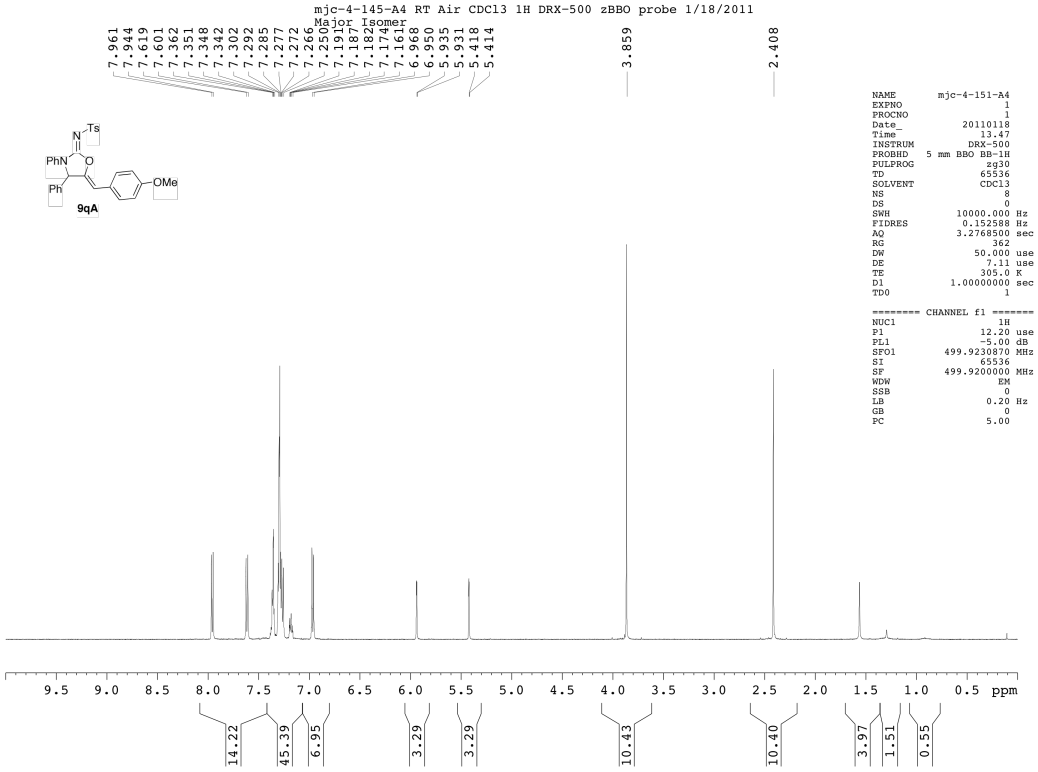
mjc-4-165-M
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-165-M
IA6535IP_30min.met1-24-2011 10-24-21 PM.dat

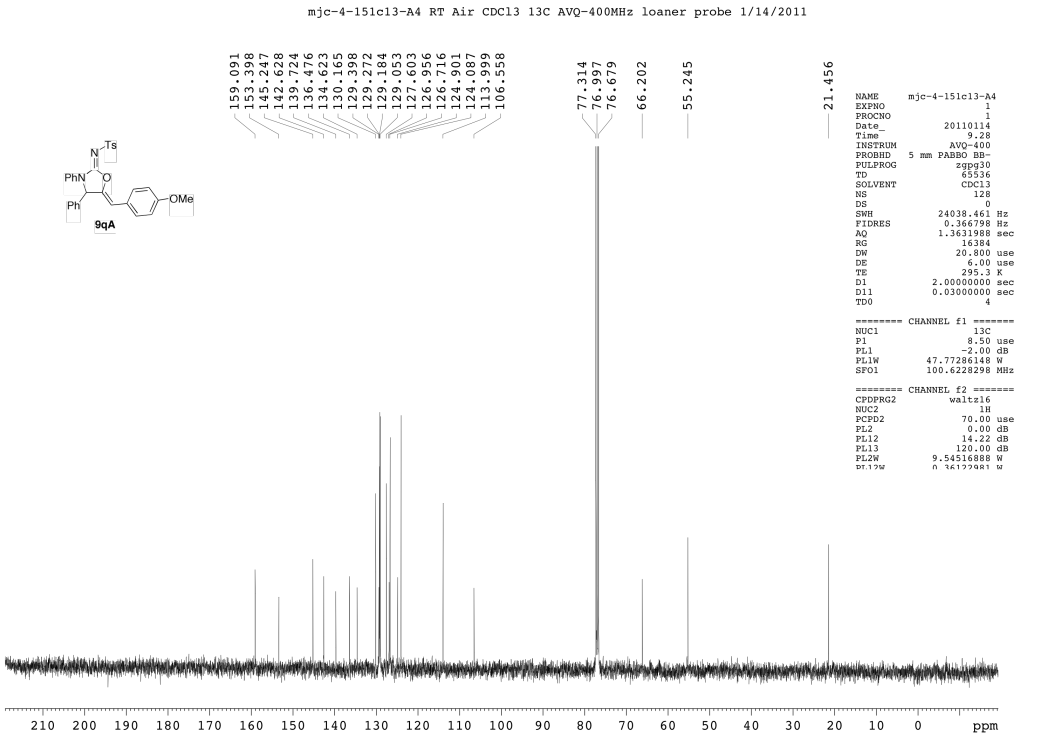


5: 287 nm, 4
nm Results

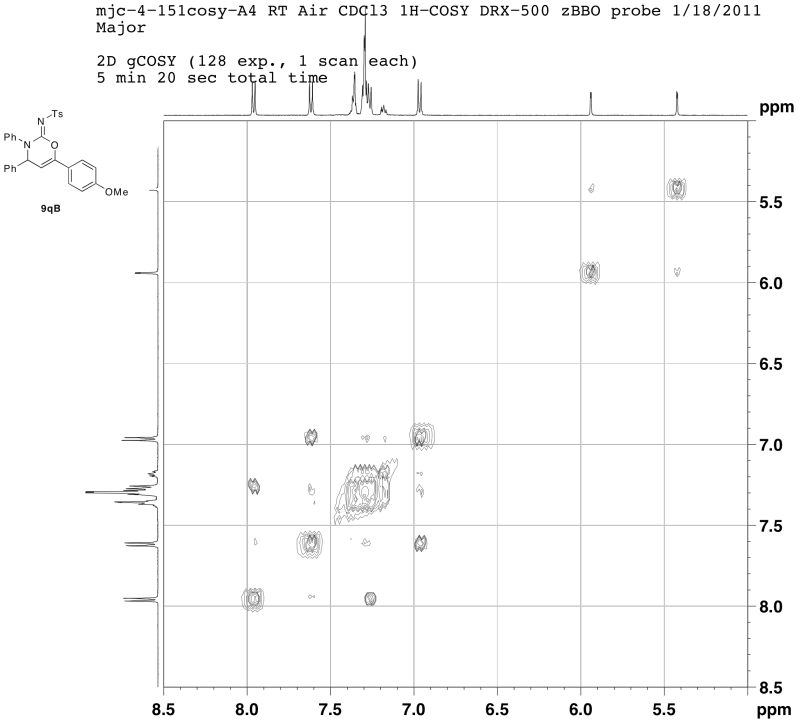
Retention Time	Area	Area Percent	Lambda Max
12.560	1146615	11.324	208
15.404	8979198	88.676	208

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

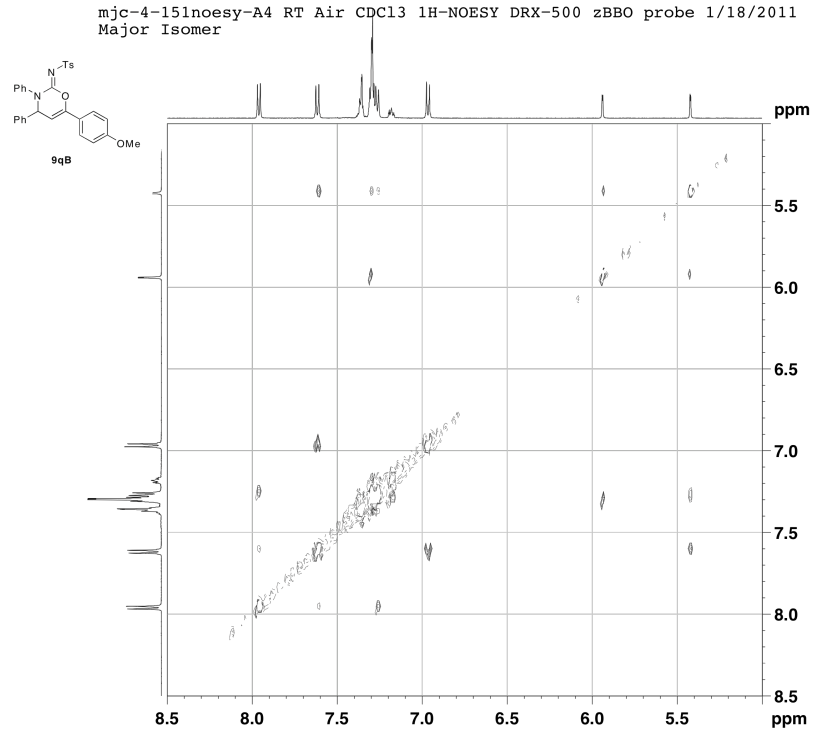




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

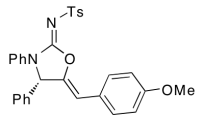



```
NAME        mjc-4-151cosy-A4
EXPNO                      1
PROCNO                     1
Date_               20110118
Time                   13.48
INSTRUM              DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            cosygpqf
TD                     2048
SOLVENT               CDCl3
NS                         1
DS                        16
SWH                7002.801 Hz
FIDRES             3.419337 Hz
AQ                 0.1462772 sec
RG                     812.7
DW                    71.400 usec
DE                     6.00 usec
TE                    305.0 K
d0                0.00000300 sec
D1                2.00000000 sec
d13               0.00000400 sec
D16               0.00020000 sec
IN0               0.00014280 sec

======== CHANNEL f1 ========
NUC1                       1H
P0                      12.20 usec
P1                      12.20 usec
PL1                     -5.00 dB
SFO1            499.9230745 MHz

====== GRADIENT CHANNEL =====
GPNAM1              SINE.100
GPNAM2              SINE.100
GPZ1                   10.00 %
GPZ2                   10.00 %
P16                  1000.00 usec
ND0                        1
TD                       128
SFO1                499.9231 MHz
FIDRES              54.709385 Hz
SW                     14.008 ppm
FnMODE                     QF
SI                       1024
SF                499.9200000 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
PC                       1.40
SI                        512
MC2                        QF
SF                499.9200000 MHz
WDW                      SINE
SSB                         0
LB                       0.00 Hz
GB                          0
```



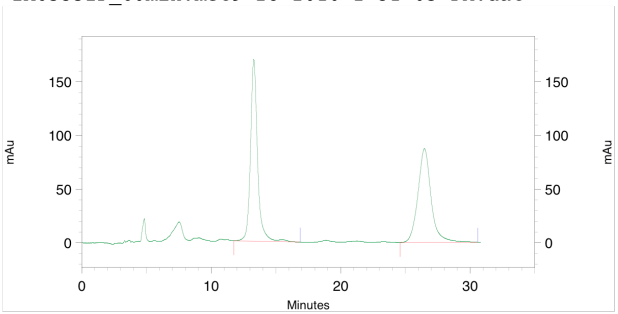

```
NAME        mjc-4-151noesy-A4
EXPNO                      1
PROCNO                     1
Date_               20110118
Time                   13.54
INSTRUM              DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG          noesygpph
TD                     2048
SOLVENT               CDCl3
NS                         2
DS                         4
SWH                5000.000 Hz
FIDRES             2.441406 Hz
AQ                 0.2048500 sec
RG                     456.1
DW                   100.000 usec
DE                     7.11 usec
TE                    305.0 K
d0                0.00000847 sec
D1                1.00000000 sec
D8                0.69999999 sec
D16               0.00020000 sec
IN0               0.00020000 sec
TAU               0.34880000 sec

======== CHANNEL f1 ========
NUC1                       1H
P1                      12.20 usec
p2                      24.40 usec
PL1                     -5.00 dB
SFO1            499.9220497 MHz

====== GRADIENT CHANNEL =====
GPNAM1              SINE.100
GPNAM2              SINE.100
GPZ1                   40.00 %
GPZ2                  -40.00 %
P16                  1000.00 usec
ND0                        1
TD                       256
SFO1                499.922 MHz
FIDRES             19.531250 Hz
SW                     10.002 ppm
FnMODE                 TPPI
SI                       1024
SF                499.9200000 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
PC                       5.00
SI                        256
MC2                    TPPI
SF                499.9200000 MHz
WDW                     QSINE
SSB                         2
LB                       0.00 Hz
GB                          0
```

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



(*S*)-9qA

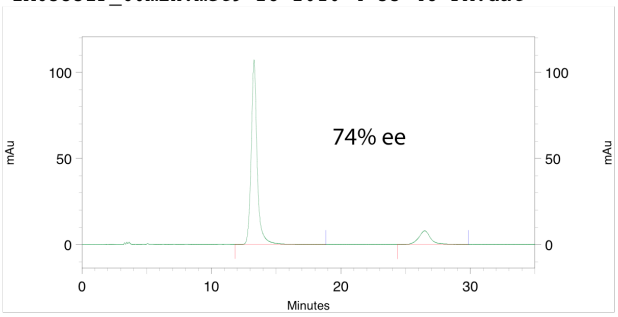
mjc-4-105-A-rac
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-105-A-rac
IA6535IP_60min.met9-28-2010 2-31-05 PM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
13.288	6472920	51.253	208
26.476	6156496	48.747	208

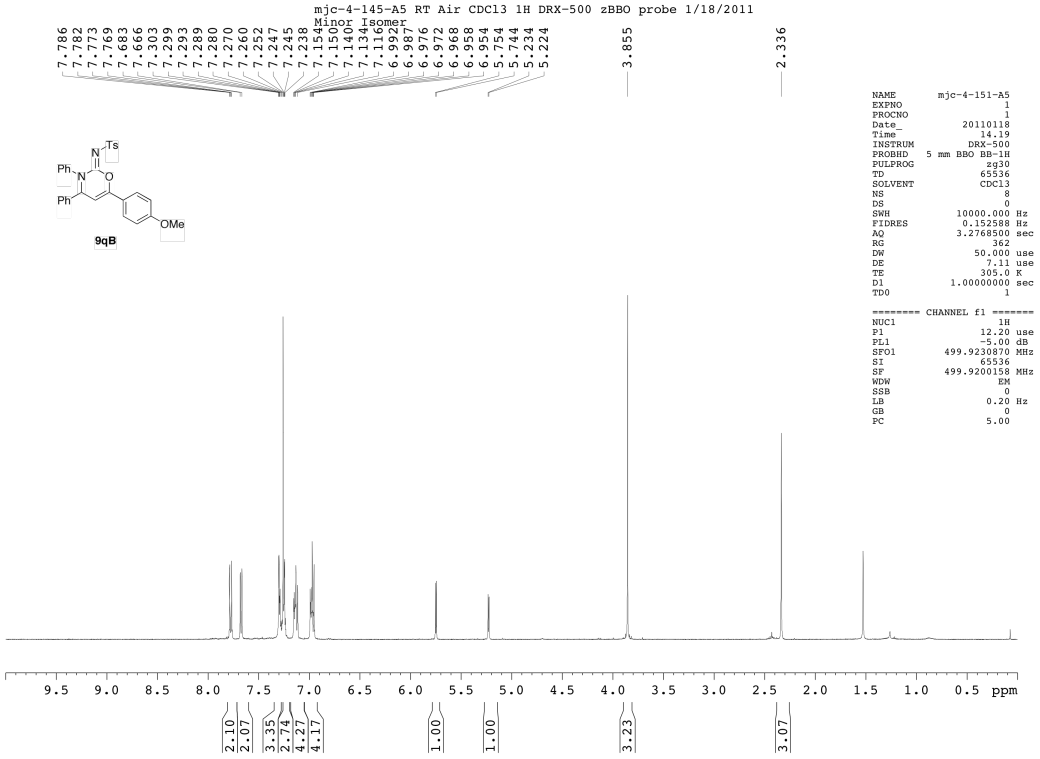
mjc-4-105-A
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-105-A
IA6535IP_60min.met9-28-2010 4-55-48 PM.dat

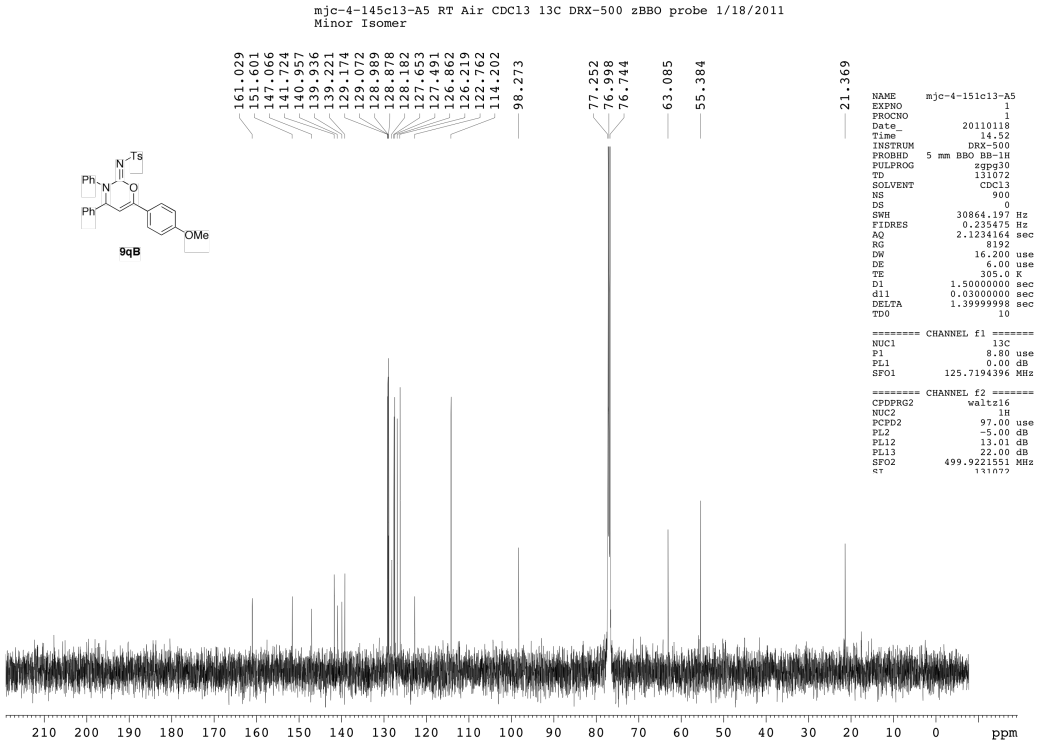


5: 287 nm, 4
nm Results

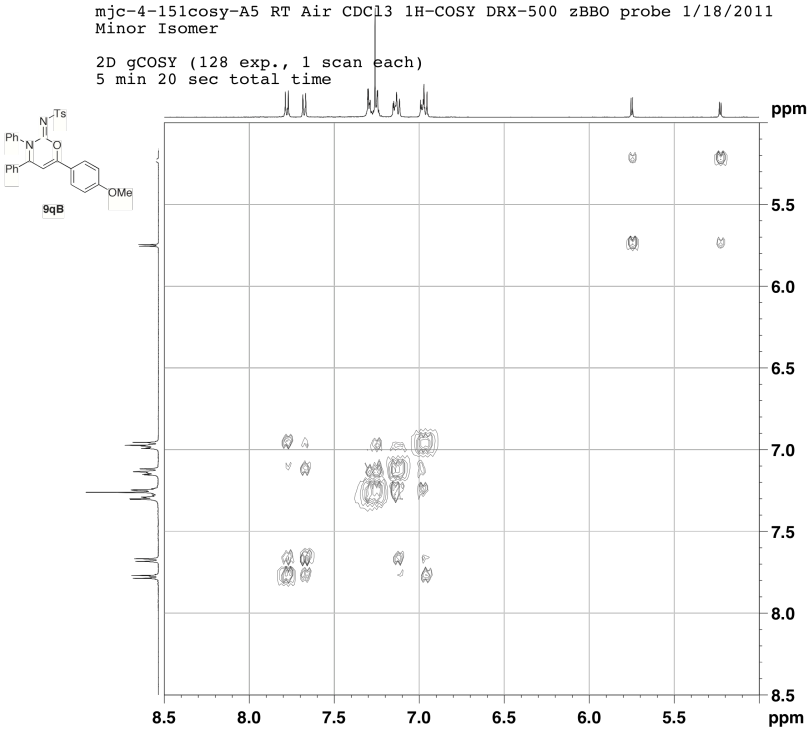
Retention Time	Area	Area Percent	Lambda Max
13.296	3424982	86.833	208
26.472	519369	13.167	208

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

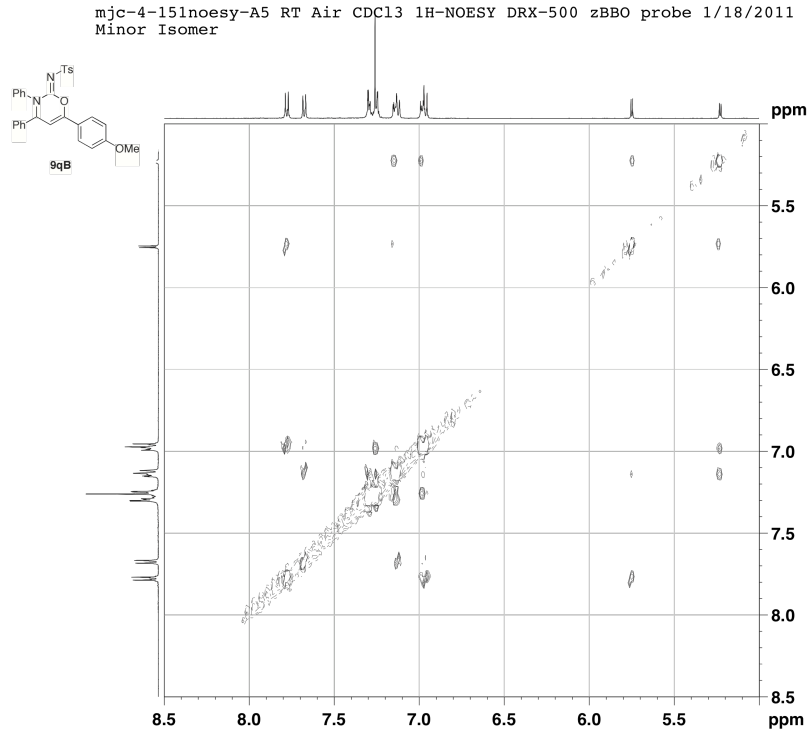




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

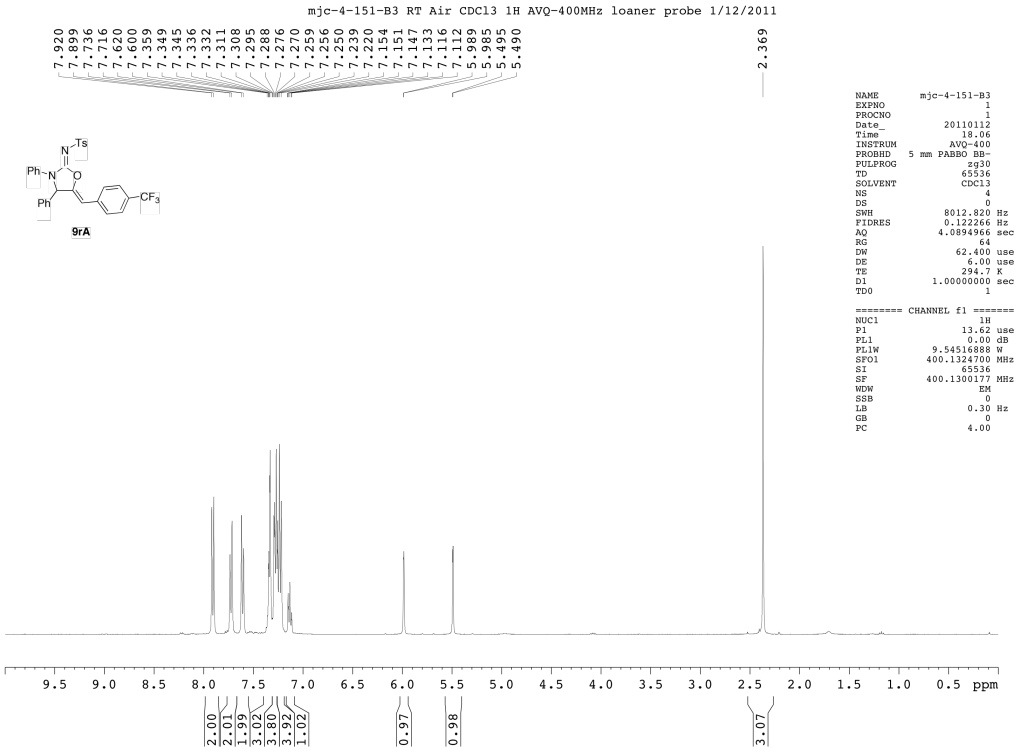


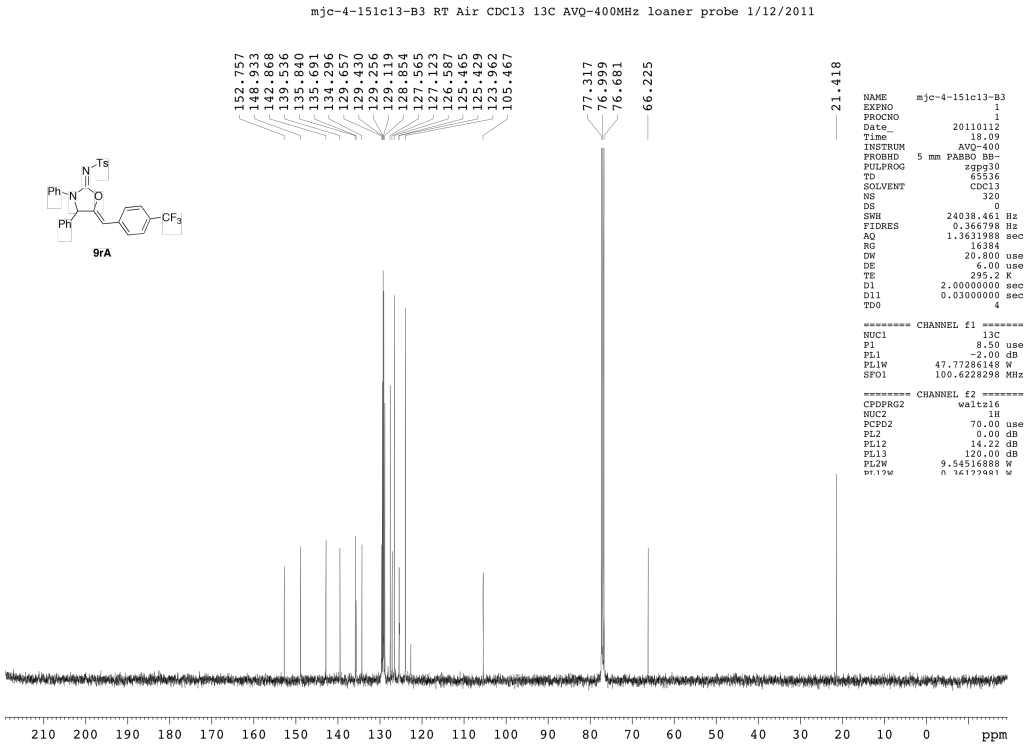

```
NAME          mjc-4-151cosy-A5
EXPNO                        1
PROCNO                       1
Date_                 20110118
Time_                    14.21
INSTRUM                DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG              cosygpqf
TD                       2048
SOLVENT                 CDCl3
NS                           1
DS                          16
SWH                  7002.801 Hz
FIDRES               3.419337 Hz
AQ                   0.1462772 sec
RG                       812.7
DW                      71.400 usec
DE                        6.00 usec
TE                       305.0 K
d0                 0.00000300 sec
D1                 2.00000000 sec
d13                0.00000400 sec
D16                0.00020000 sec
IN0                0.00014280 sec

======== CHANNEL f1 ========
NUC1                         1H
P0                       12.20 usec
P1                       12.20 usec
PL1                      -5.00 dB
SFO1                499.9230745 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPZ1                     10.00 %
GPZ2                     10.00 %
P16                    1000.00 usec
ND0                          1
TD                         128
SFO1                 499.9231 MHz
FIDRES              54.709385 Hz
SW                      14.008 ppm
FnMODE                       QF
SI                         1024
SF                499.9200155 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
PC                        1.40
SI                         512
MC2                          QF
SF                499.9200188 MHz
WDW                       SINE
SSB                          0
LB                        0.00 Hz
GB                           0
```



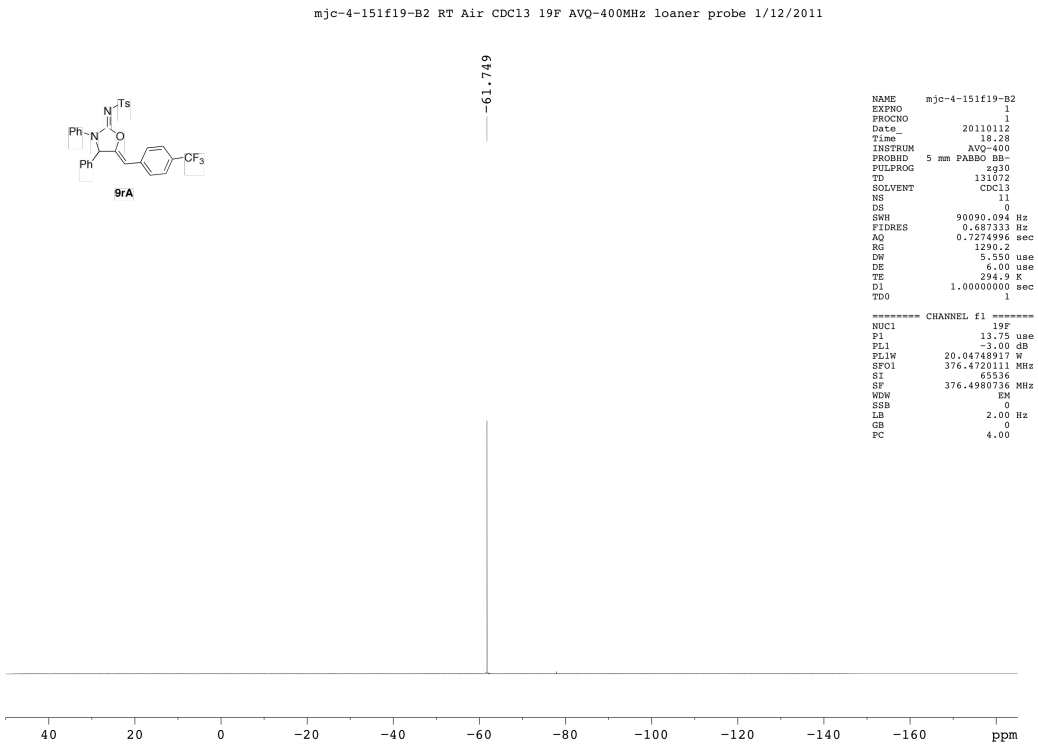

```
NAME          mjc-4-151noesy-A5
EXPNO                        1
PROCNO                       1
Date_                 20110118
Time_                    14.28
INSTRUM                DRX-500
PROBHD   5 mm BBO BB-1H
PULPROG            noesygpph
TD                       2048
SOLVENT                 CDCl3
NS                           2
DS                           4
SWH                  5000.000 Hz
FIDRES               2.441406 Hz
AQ                   0.2048500 sec
RG                       645.1
DW                     100.000 usec
DE                        7.11 usec
TE                       305.0 K
d0                 0.00008447 sec
D1                 1.00000000 sec
D8                 0.69999999 sec
D16                0.00020000 sec
IN0                0.00020000 sec
TAU                0.34880000 sec

======== CHANNEL f1 ========
NUC1                         1H
P1                       12.20 usec
p2                       24.40 usec
PL1                      -5.00 dB
SFO1                499.9220497 MHz

====== GRADIENT CHANNEL =====
GPNAM1                SINE.100
GPNAM2                SINE.100
GPZ1                     40.00 %
GPZ2                    -40.00 %
P16                    1000.00 usec
ND0                          1
TD                         256
SFO1                 499.922 MHz
FIDRES              19.531250 Hz
SW                      10.002 ppm
FnMODE                    TPPI
SI                         1024
SF                499.9200128 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
PC                        5.00
SI                         256
MC2                       TPPI
SF                499.9200150 MHz
WDW                      QSINE
SSB                          2
LB                        0.00 Hz
GB                           0
```

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

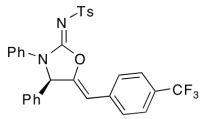




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

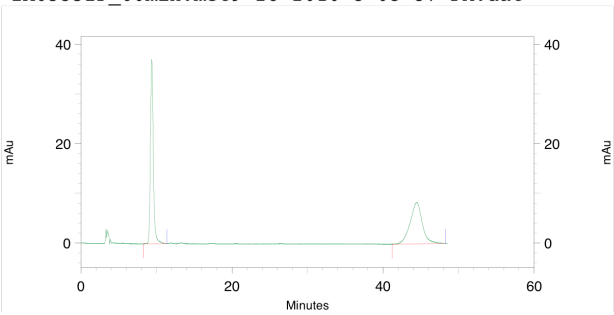


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9rA

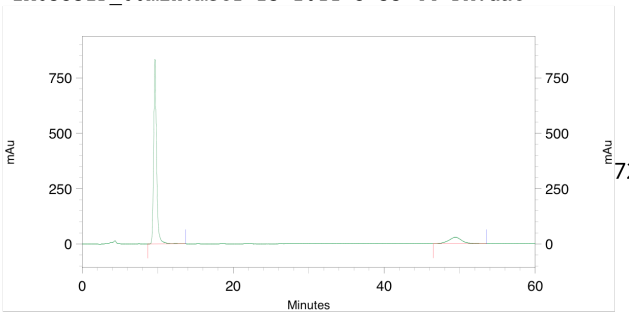
mjc-4-105-B-rac
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-105-B-rac
IA6535IP_60min.met9-28-2010 3-03-37 PM.dat



5: 287 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
9.368	983487	51.251	207
44.452	935462	48.749	208

mjc-4-160-C
C:\EZStart\Projects\Default\Data\Campbell\mjc-4-160-C
IA6535IP_60min.met1-25-2011 3-55-44 PM.dat

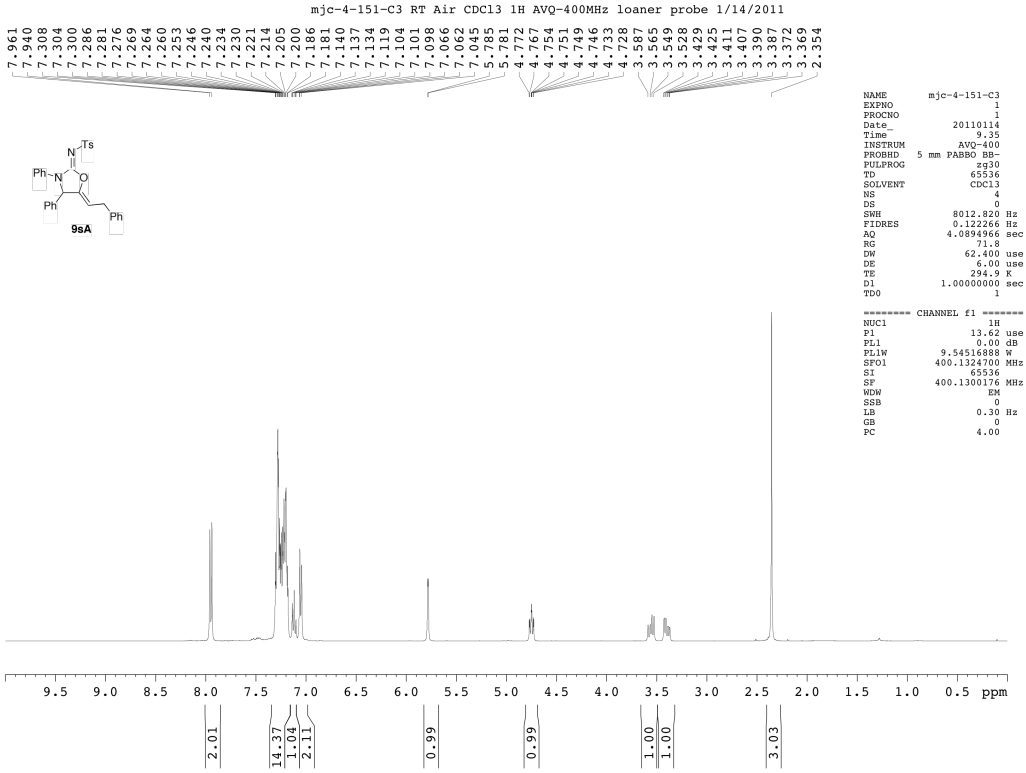


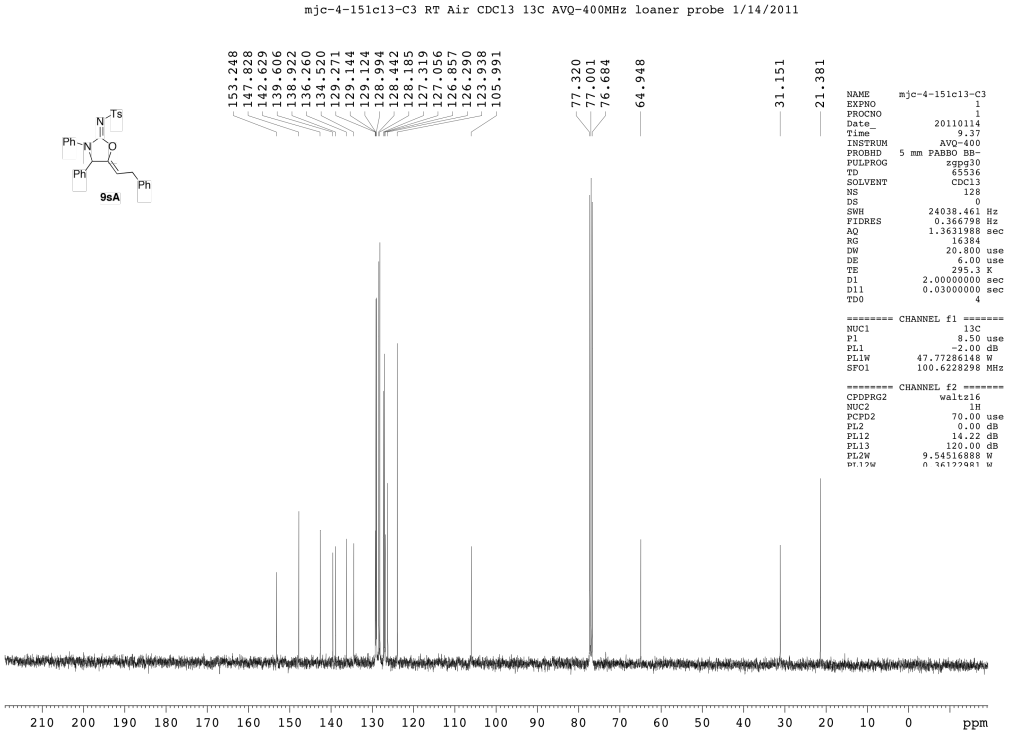
72% ee

5: 287 nm, 4
nm Results

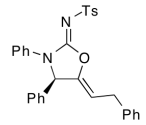
Retention Time	Area	Area Percent	Lambda Max
9.640	22204639	86.223	207
49.448	3548072	13.777	207

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



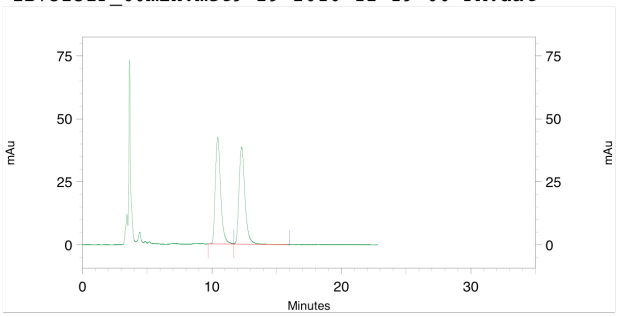


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



(*R*)-9sA

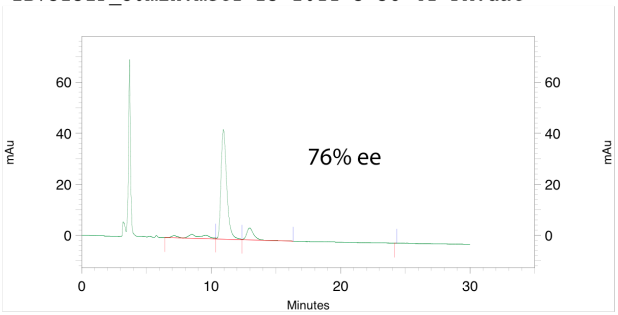
mjc-4-105-C-rac
C:\EZStart\Projects\Default\Data\Campbell\Published Traces\mjc-4-105-C-rac
IB7525IP_60min.met9-29-2010 12-19-00 PM.dat



2: 239 nm, 4
nm Results

Retention Time	Area	Area Percent	Lambda Max
10.452	1223322	49.884	208
12.300	1229016	50.116	208

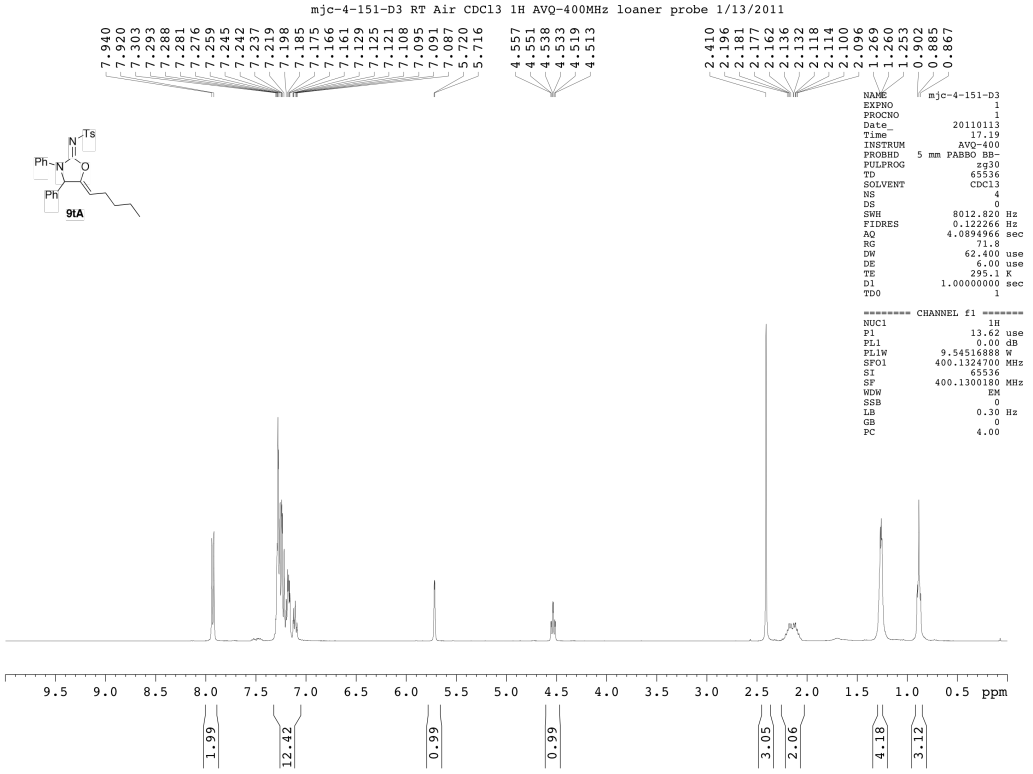
mjc-4-160-D
C:\EZStart\Projects\Default\Data\Campbell\mjc-4-160-D
IB7525IP_30min.met1-25-2011 5-58-41 PM.dat

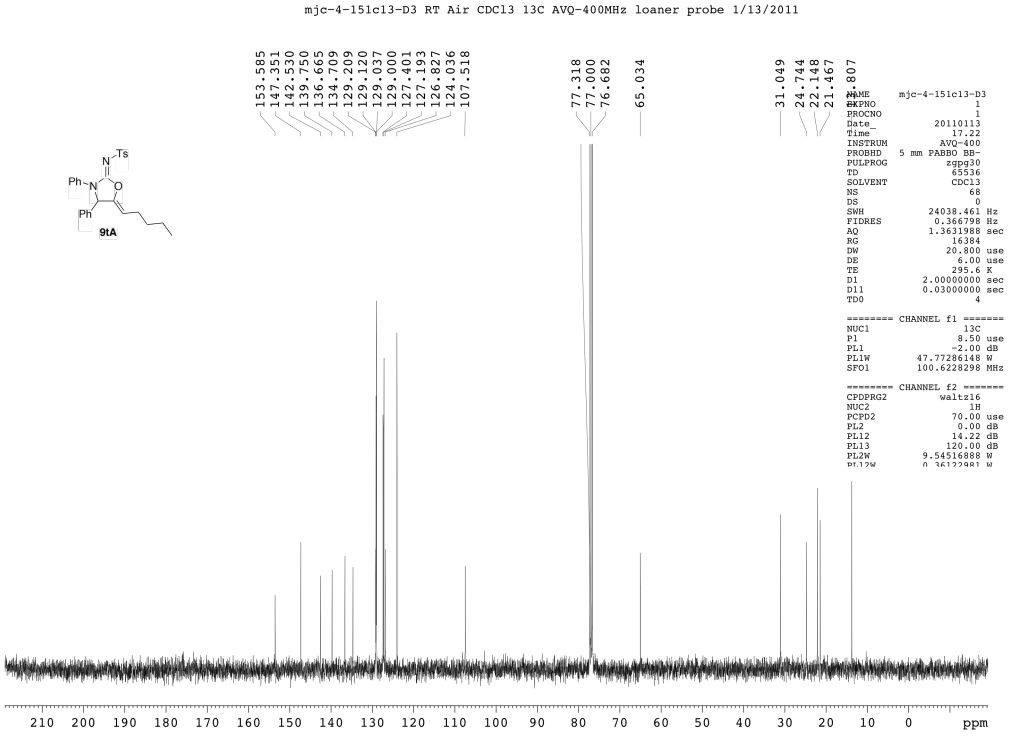


2: 239 nm, 4
nm Results

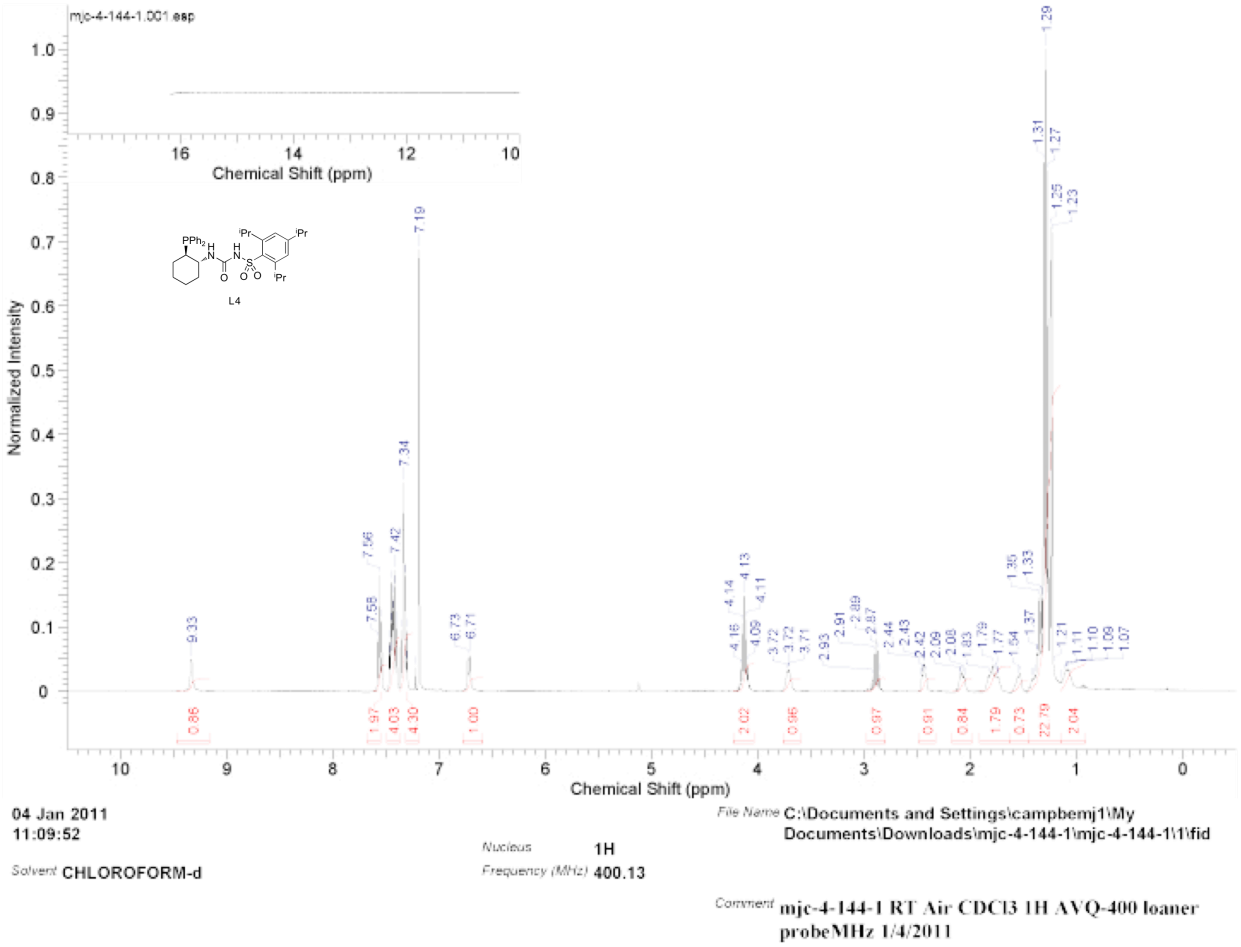
Retention Time	Area	Area Percent	Lambda Max
8.528	150646	9.173	223
10.944	1313897	80.009	207
12.972	177485	10.808	206

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

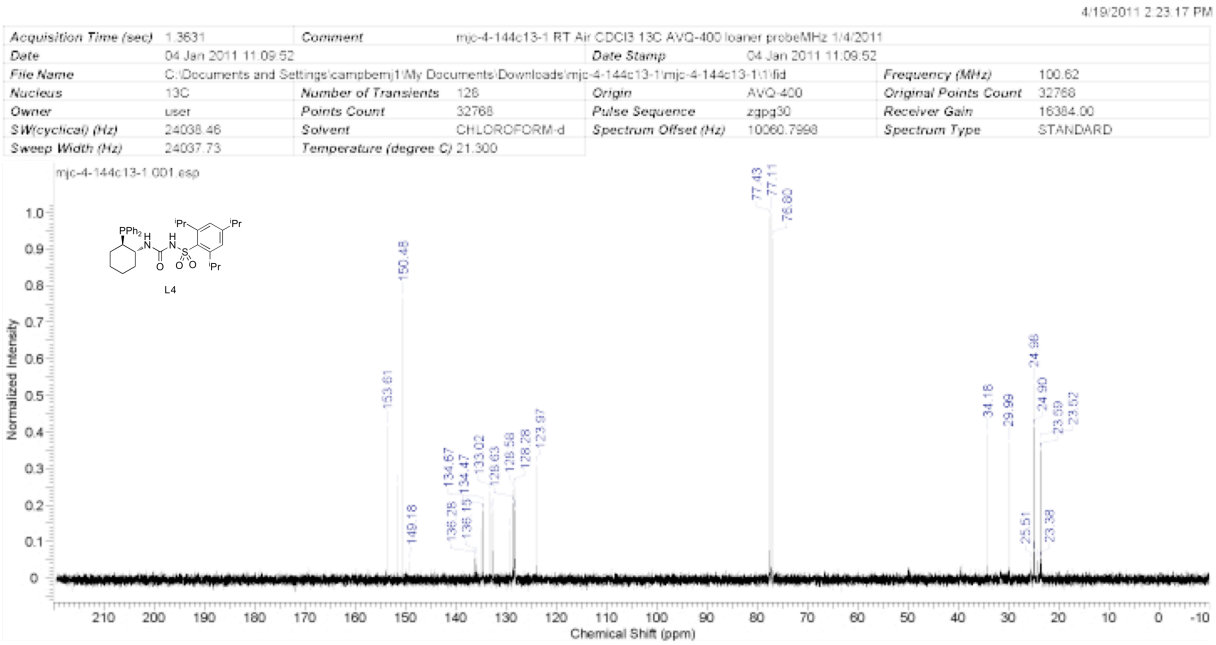




^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces

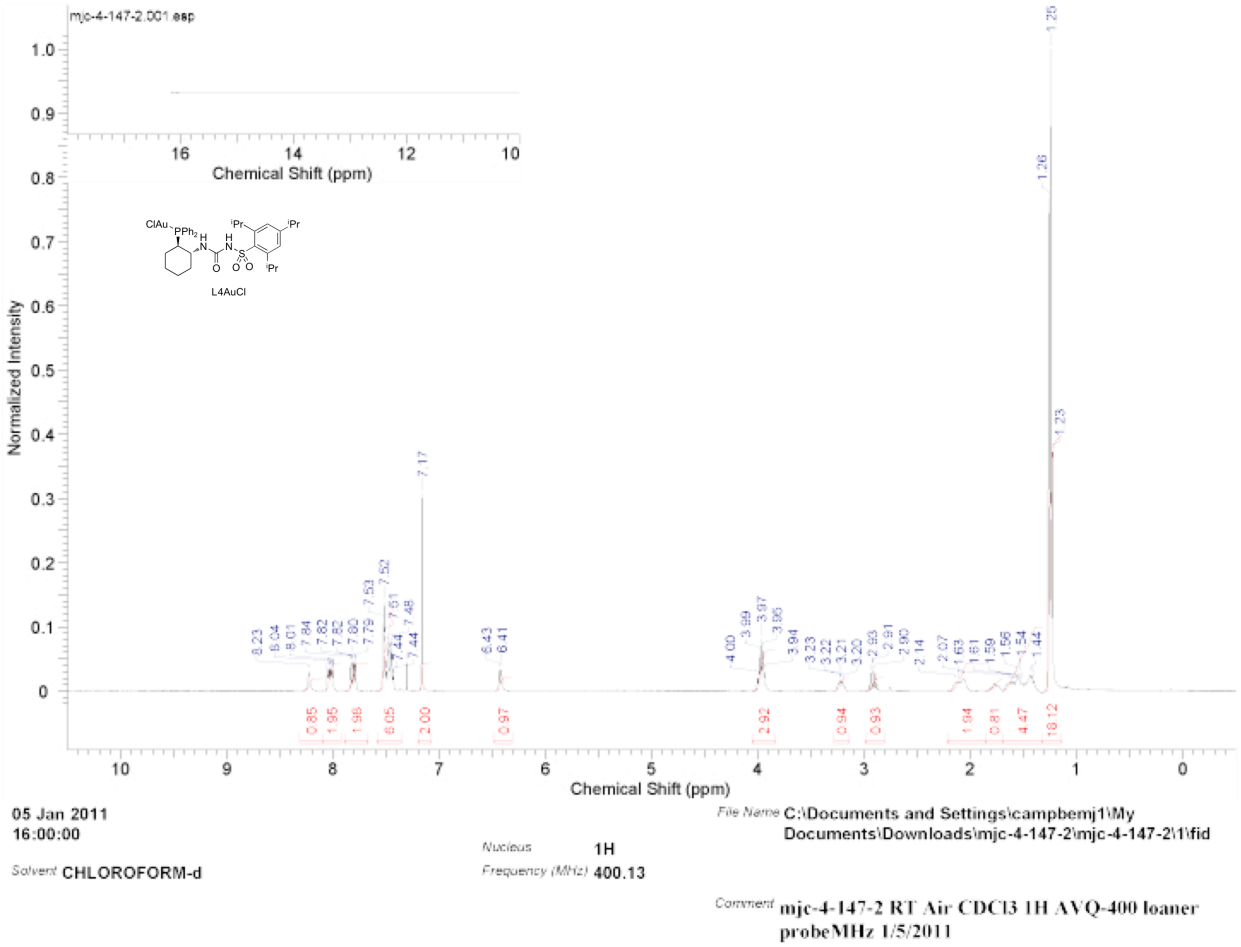


^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



C:\Documents and Settings\campbemj1\My Documents\Downloads\mjc-4-144c13-1\mjc-4-144c13-1\mjc-4-144c13-1.001.esp

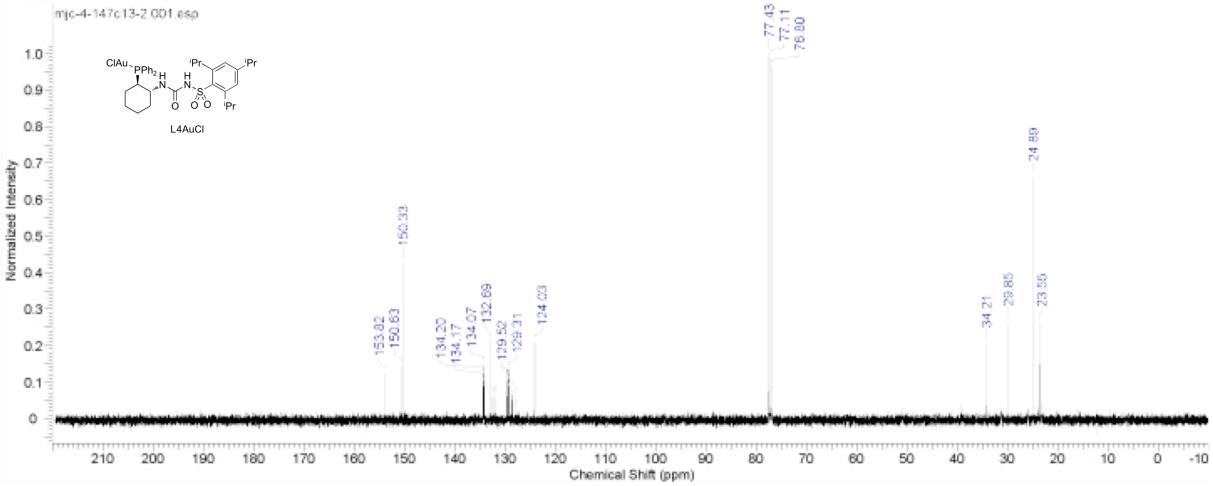
^{1}H NMR, ^{13}C NMR, ^{19}F NMR Spectra and HPLC Traces



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

4/19/2011 2:27:27 PM

Acquisition Time (sec)	1.3631	*Comment*	mjc-4-147c13-2 RT Air CDCl3 13C AVQ-400 loaner probeMHz 1/5/2011				
Date	05 Jan 2011 16:04:16			*Date Stamp*	05 Jan 2011 16:04:16		
File Name	C:\Documents and Settings\campbemj1\My Documents\Downloads\mjc-4-147c13-2\mjc-4-147c13-2\1\fid					*Frequency (MHz)*	100.62
Nucleus	13C	*Number of Transients*	126	*Origin*	AVQ-400	*Original Points Count*	32768
Owner	user	*Points Count*	32768	*Pulse Sequence*	zgpg30	*Receiver Gain*	16384.00
SW(cyclical) (Hz)	24038.46	*Solvent*	CHLOROFORM-d	*Spectrum Offset (Hz)*	10060.7998	*Spectrum Type*	STANDARD
Sweep Width (Hz)	24037.73	*Temperature (degree C)*	21.700				



C:\Documents and Settings\campbemj1\My Documents\Downloads\mjc-4-147c13-2\mjc-4-147c13-2\mjc-4-147c13-2 001.esp