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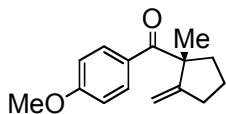
Supporting Information

General Information. Unless otherwise noted all commercial materials were used without purification. Pd(II)-catalyzed reactions were carried out in air with no precautions to exclude air or moisture. Diethyl ether and dichloromethane for these reactions were obtained from EMD and stored over 3 Å molecular sieves. All other reactions were carried out under a nitrogen atmosphere with dry solvents unless otherwise noted. Small-scale reactions (< 10 mL) were carried out in Fisher Scientific disposable scintillation vials. Catalyst **A** was synthesized as reported by Sodeoka.¹ TLC analysis of reaction mixtures was performed on Merck silica gel 60 F254 TLC plates. Flash chromatography was carried out on Merck 60 silica gel (32-63 µm). ¹H, ³¹P and ¹³C NMR spectra were recorded with Bruker AVB-400, AVQ-400, and AV-300 spectrometers and referenced to CHCl₃ (7.26 ppm). Analytical data were obtained via the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley. The enantiomeric excess of products (with the exceptions of **8** and **28**) was determined with a Shimidzu VP Series Chiral HPLC with detection at 210, 254 and 280 nm wavelengths. The enantiomeric excess of **8** was determined by using europium tris[3-(heptafluoropropylhydroxymethylene)-(-)-camphorate] as a chiral shift reagent. The enantiomeric excess of **28** was determined using a Hewlett Packard HP 6850 GC equipped with a Chiraldex G-TA (30.0 m x 0.25 mm) column.

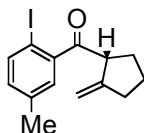
Substrates **1**, **3**, **5**, **9**, **11** and **17** were prepared by alkylation of the corresponding ketone or amide lithium enolate with 5-iodopentyne followed by conversion to the silyl-enol ether or silyl ketene aminal using TBSOTf and TEA and, where applicable, E and Z isomers were separated by flash chromatography (**1c**; 1:1 E:Z, **3**; <1:10 E:Z, **5**; 1:1 E:Z, **9**; 6:1 E:Z). Substrate **7** was prepared using the tosylate of the corresponding enyne (**7**; 1:3 E:Z). For **13** and **15**, alkylation of the amide lithium enolate with 5-(trimethylsilyl)pent-4-ynyl trifluoromethanesulfonate was followed by conversion to the silyl ketene aminal with LHMDs/TIPSCl and TMS removal with K₂CO₃/MeOH.

(R)-BinaphanePd(OH₂)₂(OTf)₂ (B). A suspension of (MeCN)₂PdCl₂ (31.1 mg, 0.120 mmol) and (R)-Binaphane (84.4 mg, 0.121 mmol) was heated to 80°C in acetonitrile (20 mL) for 1 h. The solvent was removed and the orange residue was passed through a plug of neutral alumina (8:1 dichloromethane/methanol eluent) to give an orange powder which was recrystallized from chloroform to give (R)-BinaphanePdCl₂ as pale yellow cubes (66 mg, 63%, ³¹P NMR (162 MHz, CDCl₃) δ 83.6). The product was dissolved in dichloromethane, AgOTf (2 equiv) was added and the mixture was stirred vigorously for 4 hours. The solution was passed through a celite plug, concentrated under vacuum to yield a pale yellow powder (65 mg, 79%, ³¹P NMR (162 MHz, CDCl₃) δ 91-89 br). Refrigeration of a dilute dichloromethane solution layered with ether gave X-ray quality crystals

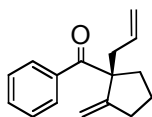
General Procedure for the Pd Catalyzed Cyclization. A solution of substrate (0.02 mmol), acetic acid (2 drops, 10 µL) and (R)-DTBMSegphosPd(OTf)₂ (10 mol%) or (R)-BinaphanePd(OH₂)₂(OTf)₂ (5 mol%) in diethyl ether (1 mL) was stirred until the reaction was complete as determined by TLC. The solvent was removed and the residue was purified on silica to give the products described below.



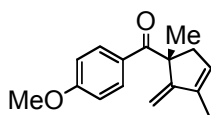
Ketone 2. HPLC Chiralcel WHELK-O column (99.5:0.5 hexanes:isopropanol, 1.0 mL/min) t_R: 19.6 min (major); 24.4 min (minor): 91% ee. ¹H NMR (300 MHz, CDCl₃) δ 7.81 (d, *J* = 8.1, 2H), 6.85 (d, *J* = 8.1, 2H), 5.00 (t, *J* = 2.2, 1H), 4.78 (t, *J* = 2.2, 1H), 3.83 (s, 3H), 2.70 (m, 2H), 2.36 (m, 1H), 1.88 (m, 2H), 1.68 (m, 1H), 1.34 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 203.2, 158.4, 131.9, 129.2, 113.3, 108.3, 58.8, 55.6, 40.3, 33.9, 26.7, 24.3. Anal. Calcd for C₁₅H₁₈O₂: C, 78.23; H, 7.88. Found: C, 77.89; H, 7.95.



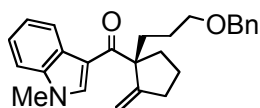
Ketone 4. HPLC Chiralcel WHELK-O column (99.5:0.5 hexanes:isopropanol, 1.0 mL/min) t_R: 14.3 min (major); 17.4 min (minor): 85% ee. ¹H NMR (300 MHz, CDCl₃) δ 7.75 (d, *J* = 8.1, 1H), 7.14 (s, 1H), 6.93 (d, *J* = 8.1, 1H), 5.03 (t, *J* = 2.2, 1H), 4.74 (t, *J* = 2.2, 1H), 4.15 (m, 1H), 2.50-2.15 (m, 3H) 2.35 (s, 3H), 2.05-1.80 (m, 2H), 1.68 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 205.2, 150.2, 145.1, 139.9, 137.9, 132.2, 129.3, 109.4, 77.2, 55.1, 33.8, 29.9, 25.1, 20.9. Anal. Calcd for C₁₄H₁₅IO: C, 51.55; H, 4.76. Found: C, 51.31; H, 4.76.



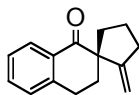
Ketone 6. HPLC Chiralcel WHELK-O column (99.5:0.5 hexanes:isopropanol, 1.0 mL/min) t_R ; 7.1 min (major); 8.4 min (minor): 88% ee. ^1H NMR (300 MHz, CDCl_3) δ 7.66 (d, $J = 8.1$, 2H), 7.44 (t, $J = 8.1$, 1H), 7.36 (d, $J = 8.1$, 2H), 5.80 (m, 1H), 5.13 (s, 1H), 5.07 (s, 1H), 5.02 (m, 1H), 4.90 (t, $J = 2.2$, 1H), 2.77 (m, 1H), 2.65 (m, 2H), 2.36 (m, 1H), 2.23 (m, 1H), 1.70 – 2.00 (m, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 204.7, 155.6, 138.1, 135.4, 131.0, 128.5, 127.8, 117.7, 109.1, 62.1, 43.0, 35.5, 33.7, 23.7. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}$: C, 84.91; H, 8.02. Found: C, 84.59; H, 8.32.



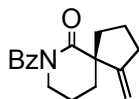
Ketone 8. Enantiomeric excess determined by chiral shift reagent (Europium) 73% ee. (d, $J = 8.1$, 2H). 6.81 (d, $J = 8.1$, 2H), 5.94 (s, 1H), 4.89 (s, 1H), 4.58 (s, 1H), 3.82 (s, 3H), 3.04 (d, $J = 16.5$, 1H), 2.35 (d, $J = 16.5$, 1H), 1.93 (s, 3H), 1.34 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 201.0, 162.7, 161.6, 139.7, 132.0, 131.0, 128.2, 113.2, 103.3, 56.5, 55.4, 45.3, 27.8, 12.9. Anal. Calcd for $\text{C}_{16}\text{H}_{18}\text{O}_2$: C, 79.31; H, 7.49. Found: C, 78.97; H, 7.67.



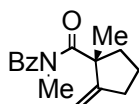
Indole 10. HPLC Chiralcel WHELK-O column (85:15 hexanes:isopropanol, 1.0 mL/min) t_R ; 20.3 min (major); 25.6 min (minor): 89% ee. ^1H NMR (300 MHz, CDCl_3) δ 8.50 (m, 1H), 7.94 (s, 1H), 7.31 (m, 8H), 5.18 (s, 1H), 5.10 (s, 1H), 4.48 (s, 2H), 3.81 (s, 3H), 3.55 (t, $J = 6.4$, 2H), 2.67 (m, 1H), 2.57 (m, 2H), 2.16 (m, 1H), 1.95-1.60 (m, 6H). ^{13}C NMR (126 MHz, CDCl_3) δ 197.9, 156.8, 138.7, 136.5, 135.0, 128.3, 127.6, 127.4, 123.3, 123.1, 122.4, 113.3, 109.3, 108.7, 72.7, 70.9, 62.6, 37.3, 34.7, 33.5, 33.4, 25.6, 22.3. Anal. Calcd for $\text{C}_{26}\text{H}_{29}\text{NO}_2$: C, 80.59; H, 7.54; N, 3.61. Found: C, 80.20; H, 7.30; N, 3.35.



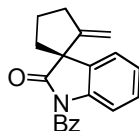
Ketone 12.² HPLC Chiralcel WHELK-O column (99.5:0.5 hexanes:isopropanol, 1.0 mL/min) t_R ; 12.2 min (minor); 15.0 min (major): 87% ee.



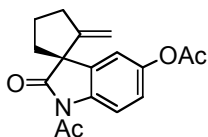
Lactam 14. HPLC Chiralcel WHELK-O column (95:5 hexanes:isopropanol, 1.0 mL/min) t_R ; 27.3 min (minor); 29.9 min (major): 98% ee. ^1H NMR (300 MHz, CDCl_3) δ 7.57 (d, $J = 7.2$, 2H), 7.48 (t, $J = 7.2$, 1H), 7.39 (t, $J = 7.2$, 2H), 5.20 (t, $J = 2.2$, 1H), 5.13 (t, $J = 2.2$, 1H), 3.90 (m, 2H), 2.51 (m, 3H), 2.22 (m, 1H), 2.02 (m, 2H), 1.80 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 177.5, 175.0, 156.5, 136.6, 131.3, 128.1, 127.3, 107.8, 55.3, 46.9, 39.9, 35.0, 34.3, 23.5, 20.0. Anal. Calcd for $\text{C}_{17}\text{H}_{19}\text{NO}_2$: C, 75.81; H, 7.11; N, 5.20. Found: C, 76.31; H, 6.96; N, 4.80.



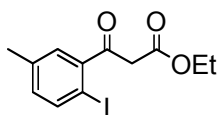
Amide 16. HPLC Chiralcel OJ column (95:5 hexanes:isopropanol, 1.0 mL/min) t_R ; 12.3 min (major); 16.5 min (minor): 80% ee. ^1H NMR (400 MHz, CDCl_3) δ 7.62 (d, $J = 7.5$, 2H), 7.52 (t, $J = 7.5$, 1H), 7.43 (t, $J = 7.5$, 2H), 4.86 (m, 2H), 3.15 (s, 3H), 2.68-2.38 (m, 3H), 1.91 (m, 1H), 1.77 (m, 2H), 1.40 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 182.1, 174.5, 157.1, 132.1, 128.7, 128.6, 107.4, 56.1, 39.5, 35.2, 33.5, 28.0, 23.7. HRMS (EI) for $[\text{C}_{16}\text{H}_{19}\text{NO}_2]^+$ calcd, 257.1416. found 257.1413.



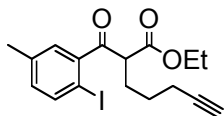
Oxindole 18a. HPLC Chiralcel WHELK-O column (95:5 hexanes:isopropanol, 1.0 mL/min) t_R ; 8.8 min (minor); 11.6 min (major): 91% ee. ^1H NMR (500 MHz, CDCl_3) δ 7.89 (d, $J = 7.5$, 1H), 7.69 (d, $J = 7.5$, 2H), 7.57 (t, $J = 7.5$, 1H), 7.45 (t, $J = 7.5$, 2H), 7.35 (t, $J = 7.5$, 1H), 7.23 (t, $J = 7.5$, 1H), 7.18 (d, $J = 7.5$, 1H), 5.10 (t, $J = 2.3$, 1H), 4.59 (t, $J = 2.3$, 1H), 2.69 (m, 2H), 2.38 (m, 1H), 2.18 (m, 2H), 1.96 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 178.8, 169.2, 155.1, 140.3, 134.4, 134.1, 132.8, 129.0, 128.2, 128.1, 125.3, 123.2, 114.7, 109.1, 58.7, 38.8, 33.5, 24.2. HRMS (EI) for $[\text{C}_{20}\text{H}_{17}\text{NO}_2]^+$ calcd 303.1260, found 303.1260.



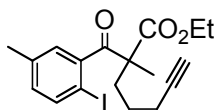
Oxindole 18b. HPLC Chiralcel OJ column (93:7 hexanes:ethanol, 1.0 mL/min) t_R : 15.0 min (major); 21.2 min (minor): 82% ee. ^1H NMR (500 MHz, CDCl_3) δ 8.26 (d, $J = 8.0$, 1H), 7.02 (dd, $J = 8.0$, 2.5, 1H), 6.89 (d, $J = 2.5$, 1H), 5.01 (t, $J = 2.3$, 1H), 4.47 (t, $J = 2.3$, 1H), 2.76 (m, 1H), 2.65 (s, 3H), 2.63 (m, 1H), 2.40 (m, 1H), 2.30 (s, 3H), 2.25 (m, 1H), 2.12 (m, 1H), 1.97 (m, 1H). ^{13}C NMR (126 MHz, CDCl_3) δ 180.1, 170.9, 169.4, 154.4, 148.1, 137.5, 134.9, 121.1, 117.2, 116.5, 110.1, 58.7, 39.5, 33.6, 27.0, 24.2, 21.1. HRMS (EI) for $[\text{C}_{17}\text{H}_{17}\text{NO}_4]^+$ calcd, 299.1158, found 299.1163.



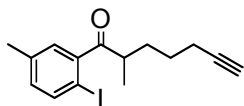
Ketoester 25. To a solution of 2-iodo-5-methylbenzoic acid (24.5 g, 93.5 mmol) in dichloromethane (250 mL) was added oxalyl chloride (9.0 mL, 103 mol) and 10 drops of DMF. The solution was stirred for 2 h and concentrated to afford the crude acid chloride. In a separate flask, ethyl acetate (12.0 mL, 122 mmol) was added to a solution of LDA (140 mmol) in diethyl ether (200 mL) at -78°C and stirred for 20 min. The acid chloride was then suspended in ether (50 mL) and added to the solution of the enolate. After 30 min at -78°C , the reaction mixture was poured into 1 M HCl and the aqueous layer further extracted with ether (2 x 200 mL). The organic layer was washed with brine (1 x 100 mL), dried with MgSO_4 , filtered and concentrated. Flash chromatography (hexanes:EtOAc, 30:1) afforded the ketoester **25** as an amber oil (18.4 g, 59%), which exists as a 1.35:1.0 mixture of ketone and enol isomers. ^1H NMR (300 MHz, CDCl_3) δ 12.35 (enol, s, 1H), 7.87 (keto, d, $J = 8.1$, 1H), 7.78 (enol, d, $J = 8.1$, 1H), 7.28 (keto, d, $J = 1.8$, 1H), 7.20 (enol, d, $J = 1.8$, 1H), 6.95 (keto, dd, $J = 8.1$, 1.8, 1H), 6.90 (enol, dd, $J = 8.1$, 1.8, 1H), 5.31 (enol, s, 1H), 4.25 (enol, q, $J = 7.2$, 2H), 4.18 (keto, q, $J = 7.2$, 2H), 3.95 (keto, s, 2H), 2.32 (keto, s, 3H), 2.29 (enol, s, 3H), 1.32 (enol, t, $J = 7.2$, 3H), 1.29 (keto, t, $J = 7.2$, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 196.4, 174.5, 172.8, 167.1, 142.7, 141.0, 140.3, 139.8, 138.5, 133.6, 132.5, 130.7, 129.9, 93.0, 87.6, 61.8, 60.8, 48.4, 31.9, 22.9, 21.2, 21.1, 14.6, 14.4. Anal. Calcd for $\text{C}_{12}\text{H}_{13}\text{IO}_3$: C, 43.39; H, 3.95. Found: C, 43.70; H, 4.05.



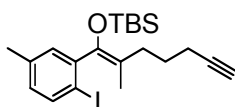
Ketoester 26. To a suspension of NaH (2.8 g, 70 mmol, 60% in mineral oil) in THF (500 mL) was added ketoester **25**. The suspension was stirred until evolution of hydrogen ceased and a clear solution was obtained (30 min). A solution of 5-iodo-1-pentyne (13.6 g, 70 mmol) in DMF (70 mL) was added and the reaction mixture heated to 80° C for 20 h. The reaction mixture was cooled to room temperature, poured into saturated aqueous NH₄Cl (500 mL) and the aqueous layer was further extracted with diethyl ether (3 x 300 mL). The organic layer was washed with brine (400 mL), dried with MgSO₄, filtered and concentrated. Flash chromatography (benzene) gave ketoester **26** as a pale yellow oil (14.0 g, 51%) which exists as a 1.5:1.0 mixture of ketone and enol isomers. ¹H NMR (300 MHz, CDCl₃) δ 12.74 (enol, s, 1H), 7.78 (keto, d, *J* = 8.1, 1H), 7.73 (enol, d, *J* = 8.1, 1H), 7.25 (keto, d, *J* = 1.8, 1H), 7.07 (enol, d, *J* = 1.8, 1H), 6.95 (keto, dd, *J* = 8.1, 1.8, 1H), 6.89 (enol, dd, *J* = 8.1, 1.8, 1H), 4.32 (enol, m, 2H), 4.22 (keto, t, *J* = 7.2, 1H), 4.14 (keto, m, 2H), 2.33 (keto, s, 3H), 2.31 (enol, s, 3H), 2.00-2.30 (m, 6H), 1.97 (keto, t, *J* = 2.7, 1H), 1.79 (enol, t, *J* = 2.7, 1H), 1.67 (m, 2H), 1.38 (enol, t, *J* = 7.2, 3H), 1.19 (keto, t, *J* = 7.2, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 198.9, 173.7, 172.3, 169.4, 143.2, 140.9, 140.2, 139.4, 138.5, 138.4, 133.4, 131.7, 130.1, 129.6, 128.6, 80.1, 84.4, 69.2, 68.4, 61.8, 61.2, 56.9, 28.8, 27.8, 26.5, 26.3, 21.2, 18.6, 14.5, 14.3. Anal. Calcd for C₁₇H₁₉IO₃: C, 51.27; H, 4.81. Found: C, 51.08; H, 4.91.



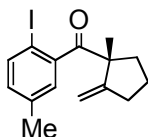
Ketoester 27. To a suspension of NaH (60% in mineral oil, 1.53 g, 38.3 mmol) in DMF (200 mL) at 0° C was added ketoester **26** (12.7 g, 31.9 mmol) followed by iodomethane (4.0 mL, 64 mmol). The suspension was stirred for 1 h at 0° C, poured into water (500 mL) and extracted with Et₂O (3 x 200 mL). The organic phase was washed with brine (300 mL), dried MgSO₄, filtered and concentrated. Flash chromatography (hexanes:EtOAc, 20:1) gave ketoester **27** as a colorless oil (10.5 g, 80%). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, *J* = 8.1, 1H), 6.99 (d, *J* = 1.8, 1H), 6.90 (dd, *J* = 8.1, 1.8, 1H), 4.11 (m, 2H), 2.28 (s, 3H), 2.20 (m, 3H), 2.02 (m, 1H), 1.95 (t, *J* = 2.7, 1H), 1.63 (m, 1H), 1.51 (s, 3H), 1.48 (m, 1H), 1.16 (t, *J* = 7.2, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 203.1, 172.5, 144.2, 140.2, 137.6, 132.0, 126.6, 88.1, 83.7, 68.8, 61.5, 59.3, 35.6, 23.7, 21.1, 20.2, 18.8, 13.9. Anal. Calcd for C₁₈H₂₁IO₃: C, 52.44; H, 5.13. Found: C, 53.32, H, 5.60.



Ketone 19. A solution of ketoester **27** (8.0 g, 19.4 mmol) in ethanol (600 mL) and 1M NaOH (150 mL) was stirred at room temperature for 48 h. The reaction mixture was then concentrated to 200 mL, neutralized with 1M HCl (200 mL) and extracted with Et₂O (3 x 200 mL). The organic phase was then washed with water (300 mL) and brine (300 mL), dried with MgSO₄, filtered and concentrated. Flash chromatography (hexanes:EtOAc, 15:1) gave ketone **19** as a colorless oil (2.8 g, 42%). ¹H NMR (400 MHz, CDCl₃) δ 7.72 (d, *J* = 8.1, 1H), 7.09 (d, *J* = 2.0, 1H), 6.90 (dd, *J* = 8.1, 2.0, 1H), 3.25 (m, 1H), 2.30 (s, 3H), 2.19 (m, 2H), 1.92 (t, *J* = 2.7, 1H), 1.87 (m, 1H), 1.56 (m, 3H), 1.28 (d, *J* = 6.8, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 208.3, 144.8, 140.2, 138.1, 132.4, 128.7, 87.6, 84.1, 68.7, 44.2, 31.6, 26.0, 21.0, 18.5, 16.1. Anal. Calcd for C₁₅H₁₇IO: C, 52.96; H, 5.04. Found: C, 53.33; H, 5.30.



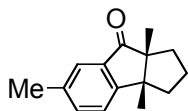
Z-Silyl enol ether 28. To a solution of ketone **19** (2.75 g, 8.1 mmol) in dichloromethane (60 mL) was added triethylamine (12 mL, 80 mmol) and TBSOTf (3.0 mL, 13.0 mmol). The solution was stirred at room temperature overnight, then poured into saturated aqueous NaHCO₃ (200 mL) and extracted with hexanes (2 x 200 mL). The organic phase was washed with brine (200 mL), dried with MgSO₄, filtered and concentrated. Flash chromatography (100% hexanes) gave Z-silyl enol ether **28** as a colorless oil (2.66 g, 72%) as well as the E-isomer (700 mg, 19%). ¹H NMR (500 MHz, C₆D₆) δ 7.57 (d, *J* = 8.0, 1H), 6.97 (d, *J* = 1.5, 1H), 6.35 (dd, *J* = 8.0, 1.5, 1H), 2.56 (m, 1H), 2.27 (m, 3H), 1.88 (s, 3H), 1.84 (t, *J* = 2.7, 1H), 1.80 (m, 2H), 1.44 (s, 3H), 1.00 (s, 9H), -0.08 (s, 3H), -0.10 (s, 3H). ¹³C NMR (126 MHz, C₆D₆) δ 145.8, 143.6, 139.0, 137.4, 131.6, 130.0, 115.0, 96.4, 84.4, 68.6, 30.1, 26.7, 25.7, 20.2, 18.6, 18.1, 17.0, -4.2, -4.3. Anal. Calcd for C₂₁H₃₁IOSi: C, 55.50; H, 6.88. Found: C, 55.92; H, 7.19.



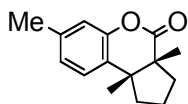
Ketone 20. To a solution of Z-silyl enol ether **28** (2.94 g, 6.47 mmol) in Et₂O (300 mL) was added AcOH (3.6 mL, 63 mmol) and R-DTBMSegphosPd(OTf)₂ (**A**) (1.05 g, 10 mol %). The clear yellow solution was stirred for 4 days, during which a yellow precipitate formed. The

solvent was removed and the residue dried under vacuum. The residue was extracted with hexanes (300 mL, and 2 x 100 mL) and concentrated. Flash chromatography (hexanes:EtOAc, 20:1) gave ketone **20** as a colorless oil (2.1 g, 96%). HPLC Chiralcel WHELK-O column (99.5:0.5 hexanes:isopropanol, 1.0 mL/min) t_R ; 9.9 min (major); 16.6 min (minor): 95% ee. $[\alpha]_D = -98.3^\circ$ (CHCl₃, c 0.29 g/100 mL). ¹H NMR (500 MHz, CDCl₃) δ 7.64 (d, $J = 8.1$, 1H), 6.98 (d, $J = 2.2$, 1H), 6.85 (dd, $J = 8.1, 2.2$, 1H), 5.14 (t, $J = 2.0$, 1H), 5.03 (t, $J = 2.0$, 1H), 2.50 (m, 1H), 2.34 (m, 1H), 2.26 (s, 3H), 2.19 (m, 1H), 1.83 (m, 1H), 1.68 (m, 2H), 1.42 (s, 3H). ¹³C NMR (126 MHz, CDCl₃) δ 209.6, 156.2, 146.6, 138.8, 137.6, 130.8, 127.6, 109.0, 87.5, 59.0, 38.3, 34.4, 25.6, 24.0, 21.1. Anal. Calcd for C₁₅H₁₇IO: C, 52.96; H, 5.04. Found: C, 53.42; H, 5.17.

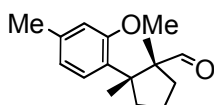
Catalyst recovery: The bright yellow residue was dissolved in dichloromethane (20 mL) and layered with Et₂O (5 mL) and hexanes (80 mL) and stored in the freezer for 1 week at which point large orange crystals had formed. The solvent was decanted and the crystals dried under vacuum to give (R)-DTBMSegphosPd(OTf)₂ (950 mg, 91%) which gave identical chemical yields and enantiomeric excess when reused in the reaction.



Ketone 29. To a solution of ketone **20** (2.0 g, 5.88 mmol) in DMF (30 mL) was added Pd(OAc)₂ (130 mg, 0.58 mmol), PPh₃ (325 mg, 1.24 mmol), triethylamine (2.7 mL, 19.5 mmol) and formic acid (0.64 mL, 16.7 mmol). The reaction mixture was heated to 80° C for 1 h, cooled to room temperature, poured into water (100 mL) and extracted with Et₂O (3 x 100 mL). The organic phase was washed with brine (100 mL), dried with MgSO₄, filtered and concentrated. Flash chromatography (hexanes:EtOAc, 20:1) gave ketone **29** as a colorless oil (1.21 g, 96%). $[\alpha]_D = -9.62^\circ$ (CHCl₃, c 0.21 g/100 mL). ¹H NMR (500 MHz, CDCl₃) δ 7.47 (m, 2H), 6.38 (d, $J = 8.0$, 1H), 2.39 (s, 3H), 2.11 (m, 1H), 1.97 (m, 1H), 1.72 (m, 1H), 1.50 (m, 2H), 1.33 (s, 3H), 1.17 (s, 3H), 0.92 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ 212.5, 159.6, 137.3, 136.7, 135.9, 123.6, 123.0, 58.8, 51.8, 42.1, 40.6, 23.6, 23.2, 21.0, 19.3. Anal. Calcd for C₁₅H₁₈O: C, 84.07; H, 8.47. Found: C, 83.77; H, 8.57.

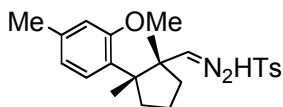


Lactone 21. To a solution of ketone **29** (1.02 g, 4.74 mmol) and urea-hydrogen peroxide (17.8 g, 190 mmol) in dichloromethane (70 mL) at -10°C was added trifluoroacetic anhydride (6.7 mL, 47 mmol). After stirring for 10 min, $\text{BF}_3 \cdot \text{Et}_2\text{O}$ (40 mL) was added. The reaction temperature was maintained at -10°C and the solution was stirred for 6 h. The solution was then warmed to 10°C and stirred for an additional 4 h. The solution was then poured into water (100 mL) and extracted with Et_2O (3 x 80 mL). The organic phase was then washed with brine (100 mL), dried with MgSO_4 , filtered and concentrated. Flash chromatography (benzene) gave lactone **21** as a colorless oil (530 mg, 48%). Starting ketone **29** was also recovered (150 mg, 11%). $[\alpha]_{\text{D}} = +25.0^{\circ}$ (CHCl_3 , c 0.11 g/100 mL). ^1H NMR (300 MHz, CDCl_3) δ 7.19 (d, $J = 7.8$, 1H), 6.93 (dd, $J = 7.8, 0.9$, 1H), 6.80 (d, $J = 0.9$, 1H), 2.33 (m, 1H), 2.31 (s, 3H), 2.08 (m, 1H), 1.55-1.89 (m, 4H), 1.21 (s, 3H), 1.23 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 174.0, 149.7, 138.5, 126.6, 126.1, 125.7, 117.3, 51.3, 47.8, 39.1, 36.0, 22.1, 21.2, 20.3, 18.3. Anal. Calcd for $\text{C}_{15}\text{H}_{18}\text{O}_2$: C, 78.23; H, 7.88. Found: C, 77.85; H, 8.11.

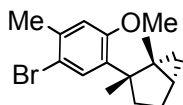


Aldehyde 22. LAH was added portionwise to a solution of lactone **21** (530 mg, 2.30 mmol) in THF (40 mL) until no further gas was evolved. The reaction mixture was quenched with 1M HCl (100 mL) and extracted with Et_2O (3 x 80 mL). The combined organics were then washed with water (100 mL), brine (100 mL), dried with MgSO_4 , filtered and concentrated. The crude diol was then dissolved in DMF (40 mL) and to this solution was added iodomethane (0.215 mL, 3.5 mmol) and K_2CO_3 (960 mg, 7.0 mmol). The reaction mixture was stirred for 90 min, diluted with 1M HCl (100 mL) and extracted with Et_2O (3 x 100 mL). The organic phase was then washed with brine (100 mL), dried with MgSO_4 and concentrated. The crude alcohol was dissolved in dichloromethane (100 mL), and to this solution was added solid NaHCO_3 (2.4 g, 28.6 mmol) and Des Martin periodinane (3.4 g, 8.0 mmol). The reaction mixture was stirred for 30 min at room temperature, then was poured into saturated aqueous NaHCO_3 (100 mL) and the aqueous phase was further extracted with Et_2O (2 x 100 mL). The organic phase was washed with saturated aqueous sodium sulfite (100 mL), brine (100 mL) dried with MgSO_4 , filtered and concentrated. Flash chromatography (hexanes:EtOAc, 20:1) gave aldehyde **22** as a white solid (460 mg, 81% over 3 steps). $[\alpha]_{\text{D}} = -59.9^{\circ}$ (CHCl_3 , c 0.10 g/100 mL). ^1H NMR (400 MHz, CDCl_3) δ 9.06 (s,

1H), 7.14 (d, $J = 8.0$, 1H), 6.72 (dd, $J = 8.0$, 1.0, 1H), 6.64 (d, $J = 1.0$, 1H), 3.72 (s, 3H), 2.40 (m, 1H), 2.32 (s, 3H), 1.97 (m, 2H), 1.84 (m, 2H), 1.49 (m, 1H), 1.32 (s, 3H), 1.29 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 205.2, 157.4, 137.8, 130.9, 127.5, 121.1, 112.1, 57.6, 54.4, 50.7, 41.2, 36.8, 24.3, 22.1, 21.2, 17.8. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: C, 78.01; H, 9.00. Found: C, 77.84; H, 9.07.

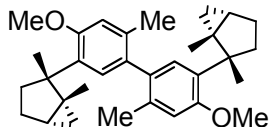


Tosyl hydrazone 30. To a solution of aldehyde **22** (453 mg, 1.84 mmol) in methanol (40 mL) was added p-tosyl hydrazide (445 mg, 2.44 mmol) and 10 drops of concentrated HCl. The solution was stirred for 2 h, poured into saturated aqueous NaHCO_3 (100 mL) and extracted with EtOAc (3 x 100 mL). The organic phase was washed with brine (100 mL) dried with MgSO_4 , filtered and concentrated. Flash chromatography (hexanes:EtOAc, 5:1) gave tosyl hydrazone **30** as a white foam (560 mg, 73%). $[\alpha]_D = -78.3^\circ$ (CHCl_3 , c 0.09 g/100mL). ^1H NMR (300 MHz, CDCl_3) δ 7.73 (d, $J = 8.1$, 2H), 7.30 (d, $J = 8.1$, 2H), 7.23 (s, 1H), 6.78 (d, $J = 8.0$, 1H), 6.66 (s, 1H), 6.57 (s, 1H), 6.45 (d, $J = 8.0$, 1H), 3.60 (s, 3H), 2.45 (s, 3H), 2.25 (s, 3H), 2.10 (m, 1H), 1.94 (m, 1H), 1.72 (m, 3H), 1.51 (m, 1H), 1.28 (s, 3H), 1.22 (s, 3H). ^{13}C NMR (126 MHz, CDCl_3) δ 160.1, 158.2, 144.1, 137.7, 135.8, 131.0, 129.6, 128.3, 128.2, 121.0, 112.9, 55.0, 51.6, 51.4, 39.6, 37.5, 22.9, 21.3, 21.0, 20.6. Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{N}_2\text{O}_3\text{S}$: C, 66.64; H, 7.29; N, 6.76. Found: C, 66.32; H, 7.48; N, 6.84.

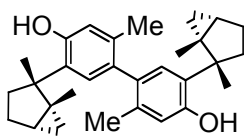


Bromide 23. To a suspension of NaH (120 mg, 3.0 mmol, 60% in mineral oil) in o-dichlorobenzene (30 mL) was added tosyl hydrazone **30** (148 mg, 0.357 mmol). The reaction mixture was heated to 160°C for 5 min, cooled, poured into water (100 mL) and extracted with hexanes (4 x 60 mL). The combined organics were washed with water (100 mL), brine (100 mL), dried with MgSO_4 , filtered and concentrated. The crude product consisted of small amounts of impurities inseparable by chromatography. To a solution of the crude product in chloroform (40 mL) at 0°C was added solid NaHCO_3 (84 mg, 1.0 mmol) and bromine (0.037 mL, 0.72 mmol). The solution was warmed to room temperature, stirred for 10 min and concentrated. Flash chromatography (100% hexanes) gave bromide **23** as a colorless oil (75 mg, 68% over 2 steps) which crystallized upon standing. ^1H NMR (300 MHz, CDCl_3) δ 7.69 (s, 1H), 6.74 (s, 1H), 3.77 (s, 3H), 2.37 (s, 3H), 2.18 (m, 1H), 1.93 (m, 1H), 1.62 (m, 1H), 1.37 (s, 3H), 1.31 (s, 3H), 1.19

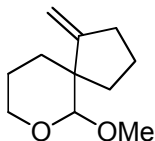
(m, 1H), 1.08 (m, 1H), 0.52 (m, 2H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.8, 136.9, 135.6, 131.7, 114.8, 114.0, 55.3, 48.3, 35.3, 29.6, 25.2, 23.9, 22.73, 22.70, 18.8, 16.1. (See attached CIF file for X-ray data.)



Dimethyl-(-)-laurebiphenyl 31. To a solution of bromide **23** (95 mg, 0.31 mmol) in diethyl ether (15 mL) at -78°C was added *tert*-butyl lithium (1.7 M in pentane, 0.50 mL) and the solution was stirred for 10 min. A suspension of CuCN (14 mg, 0.16 mmol) in diethyl ether (2 mL) was added. The solution was stirred for 10 min, followed by addition of a solution of duroquinone (80 mg, 0.49 mmol) in diethyl ether (2 mL). The solution was warmed to room temperature, stirred for 2 h, quenched with 1 M HCl (10 mL) and extracted with diethyl ether (3 x 10 mL), dried and concentrated. Flash chromatography (hexanes:EtOAc, 400:1) gave dimethyl-laurebiphenyl **31** as a colorless oil (36 mg, 51%) as well as des-bromo **23** (17 mg, 22%). $[\alpha]_{\text{D}} = -13.5^\circ$ (CHCl_3 , c 0.10 g/100 mL). ^1H NMR (300 MHz, CDCl_3) δ 7.41 (s, 1H), 7.36 (s, 1H), 6.77 (s, 2H), 3.84 (s, 6H), 2.25 (m, 2H), 2.13 (s, 3H), 2.08 (s, 3H), 1.94 (m, 2H), 1.62 (m, 2H), 1.44 (s, 3H), 1.43 (s, 3H), 1.26 (m, 2H), 1.25 (s, 6H), 1.01 (m, 2H), 0.49 (m, 4H). ^{13}C NMR (126 MHz, CDCl_3) δ 157.6, 134.8, 134.7, 134.2, 134.1, 133.5, 133.4, 130.6, 112.9, 55.2, 48.6, 35.9, 35.7, 35.0, 31.9, 30.0, 29.9, 25.7, 25.6, 24.0, 23.9, 23.4, 23.2, 20.4, 19.4, 19.3, 16.7, 16.6. HRMS (EI) for $[\text{C}_{32}\text{H}_{42}\text{O}_2]^+$ calcd 459.3218, found 459.3221.



(-)-Laurebiphenyl 24. To a suspension of sodium hydride (48 mg, 60% in mineral oil washed twice with hexanes) in DMF (10 mL) was added ethane thiol (0.12 mL, 1.6 mmol) and the solution was stirred until evolution of hydrogen ceased. A solution of **31** (36 mg, 0.079 mmol) in DMF (5 mL) was added. The solution was heated to 150°C for 5 days, quenched with 1 M HCl, extracted with diethyl ether (3 x 20 mL), washed with brine (1 x 30 mL) and dried over MgSO_4 . Flash chromatography (hexanes:EtOAc, 5:1) gave (-)-laurebiphenyl **24** as a white solid (24 mg, 70%). $[\alpha]_{\text{D}} = -14.5^\circ$ (CHCl_3 , c 0.10 g/100 mL). ^1H NMR and ^{13}C NMR match the literature data³ (See attached spectra). HRMS (EI) for $[\text{C}_{30}\text{H}_{38}\text{O}_2]^+$ calcd 430.2869, found 430.2872.

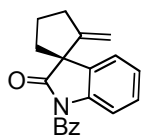


Acetal **28**.

A solution of vinyl ether **27** (18.0 mg, 0.12 mmol), acetic acid (80 μ L), methanol (20 μ L) and (R)-DTBMSegphosPd(OTf)₂ (1.1 mg, 1 mol%) in 2 mL diethyl ether was stirred for 2 h at room temperature. The reaction was neutralized with saturated aqueous sodium bicarbonate (5 mL) and extracted with diethyl ether. Flash chromatography (hexanes:EtOAc 50:1) gave acetal **28** as a volatile oil (9 mg, 46%). Chiraldex G-TA; 90 °C hold 0 min, then 5 °C/min to 150 °C; 2.0 mL/min He carrier gas), t_R 8.93 min (minor), 9.46 min (major), 66% ee. ¹H NMR (500 MHz, CDCl₃) δ 4.97 (s, 1H), 4.94 (s, 1H), 4.15 (s, 1H), 3.92 (m, 1H), 3.54 (m, 1H), 3.38 (s, 3H), 2.47 (m, 2H), 1.97 (m, 1H), 1.68 (m, 1H), 1.66-1.48 (m, 6H). ¹³C NMR (75.5 MHz, CDCl₃) δ 157.7, 107.5, 105.5, 64.5, 56.5, 49.0, 34.7, 33.7, 33.6, 23.2, 22.6.

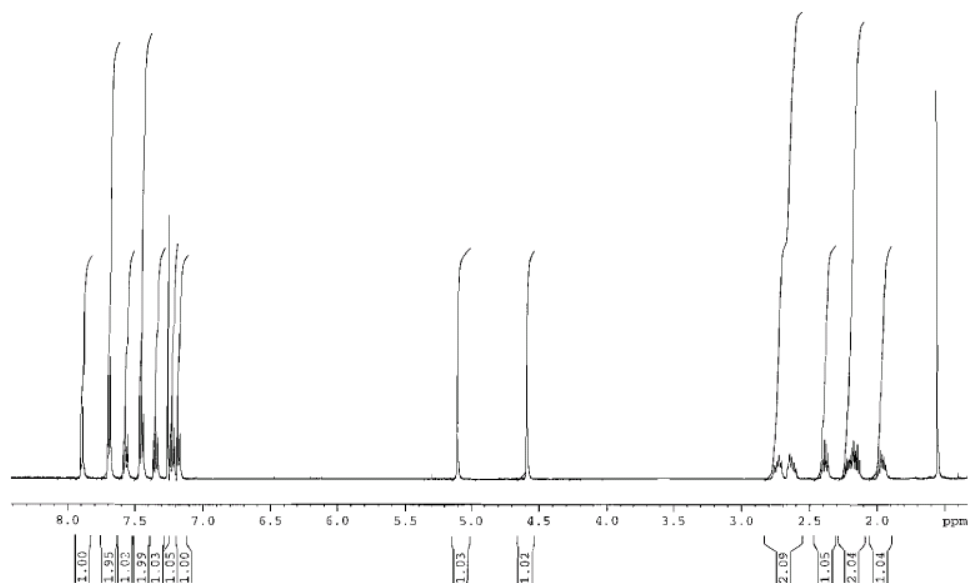
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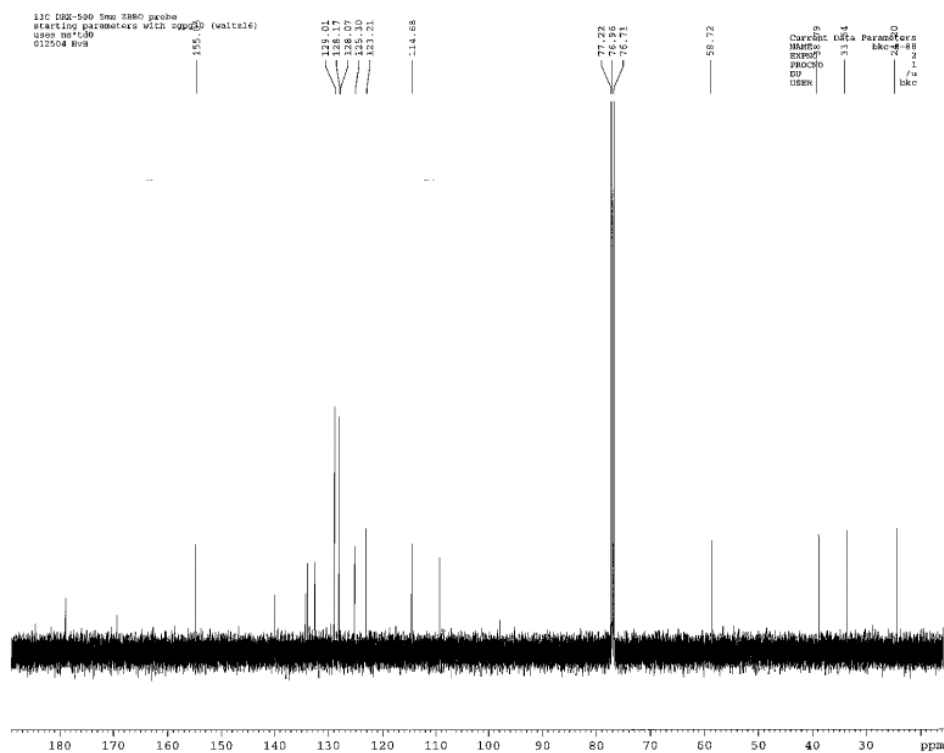


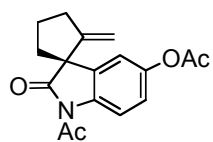
Oxindole 18a.

^1H NMR



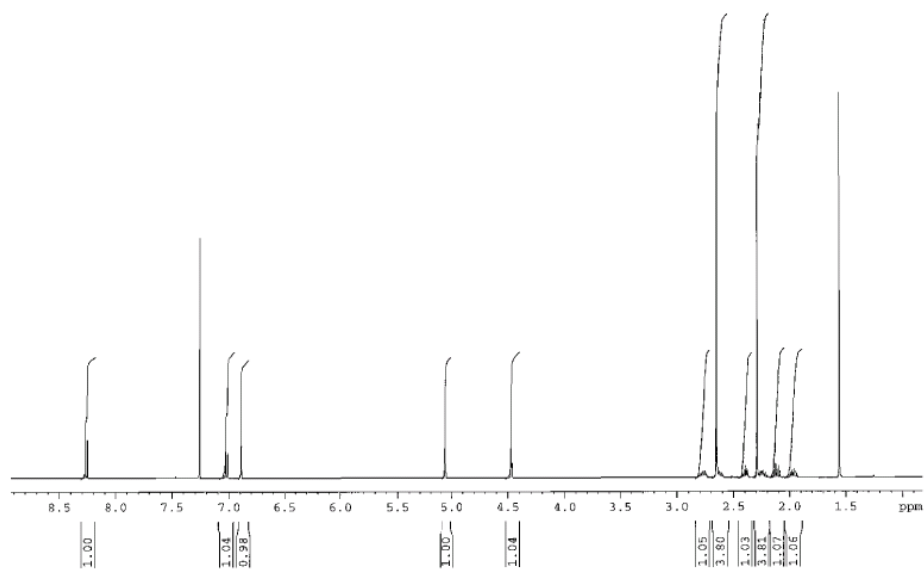
^{13}C NMR



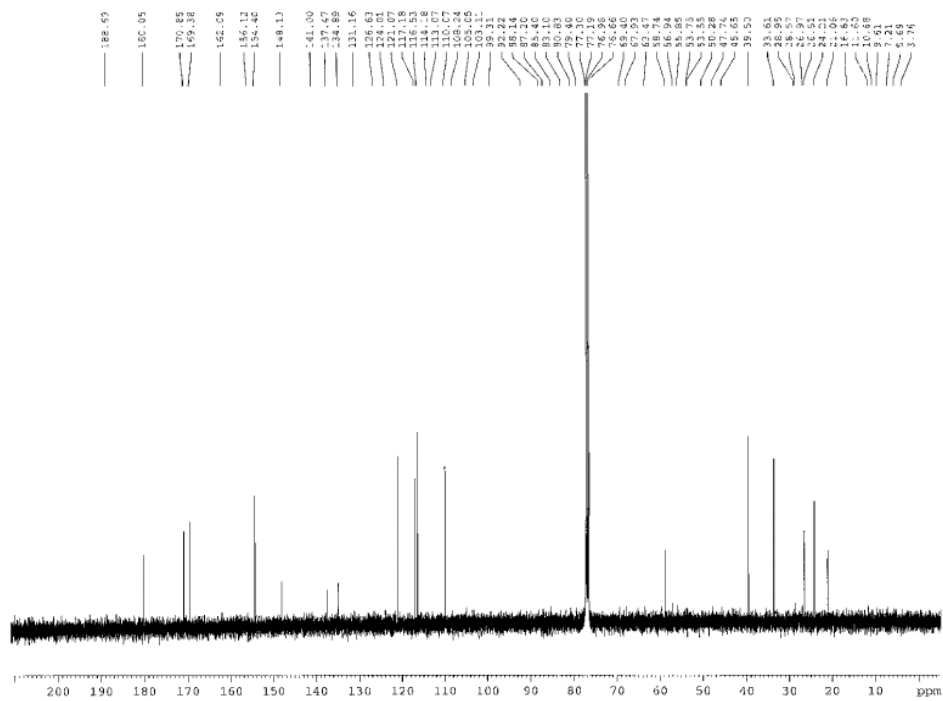


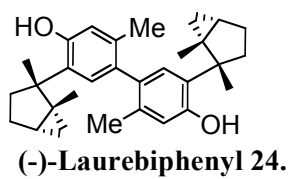
Oxindole 18b

^1H NMR

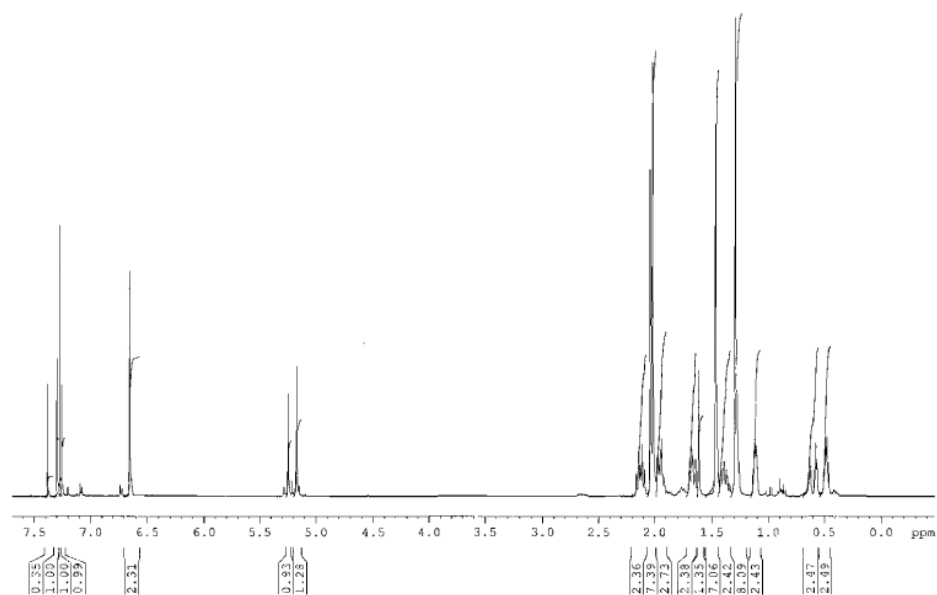


^{13}C NMR

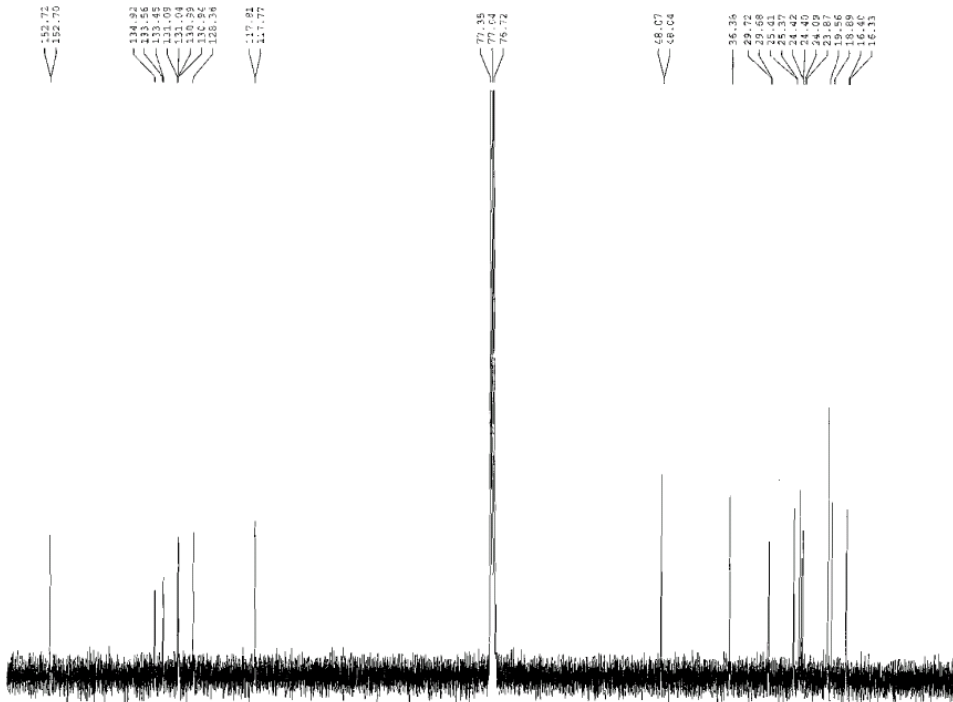


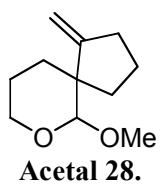


^1H NMR

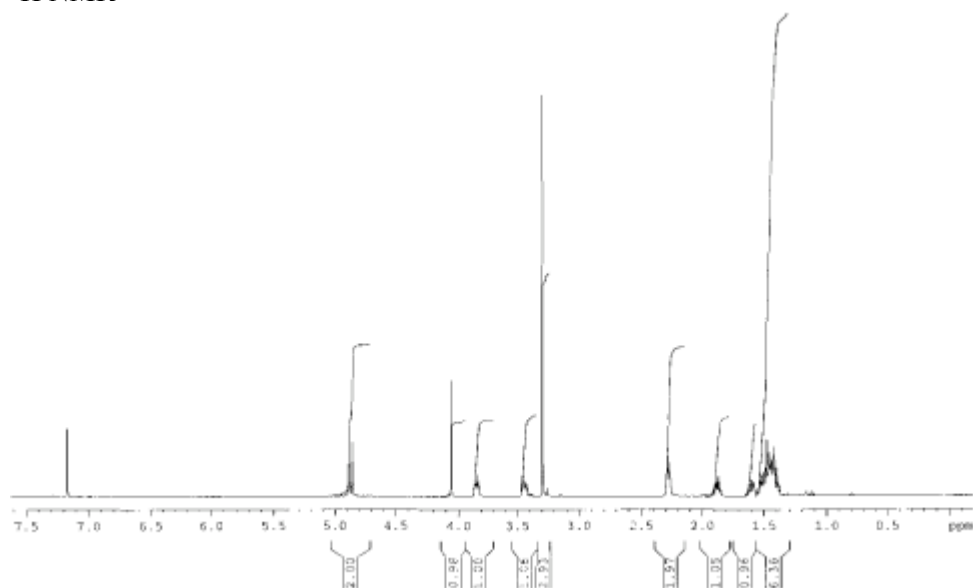


^{13}C NMR





^1H NMR



^{13}C NMR

