Rhodium-Catalyzed Asymmetric 1,6-Addition of Aryltitanates to Enynones Giving Axially Chiral Allenes

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Supporting Data

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under predried nitrogen or glovebox techniques under prepurified argon. NMR spectra were recorded on a JEOL JNM LA-500 spectrometer (500 MHz for ^1H , and 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR and chloroform-*d* (δ 77.00) for ^{13}C NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter. The high-resolution mass spectra (HRMS) were performed on Applied Biosystems Mariner 8295 API-TOF workstation (ESI-TOF) and JEOL JMS-HX110 spectrometer (FAB).

Materials. THF and Et_2O were distilled from benzophenone-ketyl under nitrogen prior to use. $[\text{RhCl}(\text{C}_2\text{H}_4)_2]_2$,¹ *N*-(2-pyridyl)triflimide,² phenyltitanium triisopropoxide ($\text{PhTi}(\text{OPr-}i)_3$),³ *p*-methoxyphenyltitanium triisopropoxide ($4\text{-MeOC}_6\text{H}_4\text{Ti}(\text{OPr-}i)_3$),³ *p*-fluorophenyltitanium triisopropoxide ($4\text{-FC}_6\text{H}_4\text{Ti}(\text{OPr-}i)_3$),⁴ and lithium isopropoxide⁴ were prepared according to the reported procedures. $\text{Ti}(\text{OPr-}i)_4$, chlorotrimethylsilane, and pivaloyl chloride were distilled before use. Phenyllithium in cyclohexane/ Et_2O , *n*-butyllithium in hexane, methyllithium in Et_2O , bromobenzene, 4-bromoanisole, and 1-bromo-4-fluorobenzene were purchased.

Preparation of Enynones 1a-1d. Enynones **1a-1d** were prepared from 3-(*p*-toluenesulfonyl)-2-cyclohexen-1-one according to the reported procedures.⁵ **3-(*p*-Toluenesulfonyl)-2-cyclohexen-1-one:** This compound was prepared according to the reported procedures,⁵ and used without further purification. ^1H NMR (CDCl_3) δ 1.95 (quintet,

$J = 6.5$ Hz, 2H), 2.29 (t, $J = 6.5$ Hz, 2H), 2.42 (s, 3H), 2.45 (td, $J = 6.3, 1.1$ Hz, 2H), 5.76 (t, $J = 1.1$ Hz, 1H), 7.34 (d, $J = 8.5$ Hz, 2H), 7.78 (d, $J = 8.5$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 20.74, 21.67, 28.55, 36.35, 116.74, 128.15, 130.07, 132.44, 146.12, 168.15, 198.57. HRMS (ESI-TOF) Calcd for $\text{C}_{13}\text{H}_{14}\text{O}_4\text{SNa}$: 289.0510 ($[\text{M}+\text{Na}]^+$). Found: 289.0506 ($[\text{M}+\text{Na}]^+$). **3-(1-Hexynyl)-2-cyclohexen-1-one (1a)**: purified by silica gel chromatography (Hexane/AcOEt = 7/1) and bulb-to-bulb distillation (87% yield); ^1H NMR (CDCl_3) δ 0.93 (t, $J = 7.4$ Hz, 3H), 1.39-1.48 (m, 2H), 1.52-1.59 (m, 2H), 2.01 (quintet, $J = 6.2$ Hz, 2H), 2.39 (t, $J = 7.1$ Hz, 2H), 2.40 (t, $J = 6.8$ Hz, 2H), 2.41 (td, $J = 6.2, 1.7$ Hz, 2H), 6.13 (t, $J = 1.7$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 13.45, 19.40, 21.87, 22.50, 30.27, 30.79, 37.20, 80.35, 102.27, 131.76, 144.51, 198.83. HRMS (ESI-TOF) Calcd for $\text{C}_{12}\text{H}_{17}\text{O}$: 177.1279 ($[\text{M}+\text{H}]^+$). Found: 177.1281 ($[\text{M}+\text{H}]^+$). **3-(Cyclohexylethynyl)-2-cyclohexen-1-one (1b)**: purified by silica gel chromatography (Hexane/AcOEt = 4/1) and bulb-to-bulb distillation (55% yield); ^1H NMR (CDCl_3) δ 1.29-1.39 (m, 3H), 1.44-1.57 (m, 3H), 1.67-1.75 (m, 2H), 1.79-1.87 (m, 2H), 2.01 (quintet, $J = 6.1$ Hz, 2H), 2.39 (t, $J = 6.1$ Hz, 2H), 2.42 (td, $J = 6.1, 1.6$ Hz, 2H), 2.58 (tt, $J = 9.0, 3.9$ Hz, 1H), 6.14 (t, $J = 1.6$ Hz, 1H). ^{13}C NMR (CDCl_3) δ 22.55, 24.69, 25.71, 29.94, 30.93, 32.16, 37.24, 80.40, 106.14, 131.75, 144.58, 198.84. HRMS (ESI-TOF) Calcd for $\text{C}_{14}\text{H}_{19}\text{O}$: 203.1435 ($[\text{M}+\text{H}]^+$). Found: 203.1425 ($[\text{M}+\text{H}]^+$). **3-(tert-Butylethynyl)-2-cyclohexen-1-one (1c)**: purified by silica gel chromatography (Hexane/AcOEt = 6/1) and bulb-to-bulb distillation (86% yield); This product was characterized by comparison of the spectroscopic data with those reported previously.⁶ **3-(4-Methoxyphenylethynyl)-2-cyclohexen-1-one (1d)**: purified by silica gel chromatography (Hexane/AcOEt = 4/1) and bulb-to-bulb distillation (52% yield); ^1H NMR (CDCl_3) δ 2.07 (quintet, $J = 6.5$ Hz, 2H), 2.44 (t, $J = 6.5$ Hz, 2H), 2.54 (td, $J = 6.5, 1.6$ Hz, 2H), 3.83 (s, 3H), 6.26 (t, $J = 1.6$ Hz, 1H), 6.88 (d, $J = 8.9$ Hz, 2H), 7.43 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 22.64, 30.60, 37.32, 55.34, 87.67, 100.35, 114.04, 114.19, 131.69, 133.64, 143.77, 160.61, 198.68. HRMS (ESI-TOF) Calcd for $\text{C}_{15}\text{H}_{15}\text{O}_2$: 227.1071 ($[\text{M}+\text{H}]^+$). Found: 227.1066 ($[\text{M}+\text{H}]^+$).

Preparation of Enynone 1e. 3-(*p*-Toluenesulfonyl)-2-cyclopenten-1-one was prepared from 1,3-cyclopentanedione (1.82 g, 18.6 mmol) in a manner similar to 3-(*p*-toluenesulfonyl)-2-cyclohexen-1-one.⁵ To a slurry of LiBr (2.42 g, 27.9 mmol, 1.5 eq), Pd(PPh₃)₄ (1.03 g, 0.891 mmol, 4.8 mol % Pd), and 3-(*p*-toluenesulfonyl)-2-cyclopenten-1-one in THF (30 mL) was added a solution of 1-hexynyltributyltin (9.39 g, 25.2 mmol) in THF (30 mL). The resulting mixture was heated to 80 °C for 48 h and cooled to room temperature. After concentrated in vacuo, the mixture was diluted with CH₂Cl₂ and washed with water. The aqueous layer was extracted twice with CH₂Cl₂, and the combined organic layers were washed with a 10% NH₃ solution, water, and saturated NaCl, before it was dried over MgSO₄ and filtered through a short pad of silica gel. After removal of the solvent, the crude mixture was purified by silica gel chromatography (Hexane/AcOEt = 3/1), followed by bulb-to-bulb distillation to give enynone **1e** as colorless oil (1.60 g, 53% yield).; **3-(*p*-Toluenesulfonyl)-2-cyclopenten-1-one**: ¹H NMR (CDCl₃) δ 2.42-2.46 (m, 2H), 2.48 (s, 3H), 2.65-2.70 (m, 2H), 5.92 (t, *J* = 1.5 Hz, 1H), 7.41 (d, *J* = 8.5 Hz, 2H), 7.86 (d, *J* = 8.5 Hz, 2H). ¹³C NMR (CDCl₃) δ 21.75, 28.63, 34.03, 115.02, 128.40, 130.25, 131.69, 146.69, 178.91, 204.71. HRMS (ESI-TOF) Calcd for C₁₂H₁₂O₄SNa: 275.0353 ([M+Na]⁺). Found: 275.0339 ([M+Na]⁺). **3-(1-Hexynyl)-2-cyclopenten-1-one (1e)**: ¹H NMR (CDCl₃) δ 0.94 (t, *J* = 7.4 Hz, 3H), 1.40-1.49 (m, 2H), 1.55-1.62 (m, 2H), 2.39-2.43 (m, 2H), 2.46 (t, *J* = 7.1 Hz, 2H), 2.68-2.72 (m, 2H), 6.19 (t, *J* = 1.8 Hz, 1H). ¹³C NMR (CDCl₃) δ 13.42, 19.58, 21.88, 30.14, 32.78, 34.66, 76.92, 107.56, 135.20, 158.32, 209.64. HRMS (ESI-TOF) Calcd for C₁₁H₁₅O: 163.1122 ([M+H]⁺). Found: 163.1127 ([M+H]⁺).

Rhodium-Catalyzed Asymmetric 1,6-Addition of Aryltitanates (ArTi(OPr-*i*)₄Li, (2)) to Enynones 1 in the Presence of Chlorotrimethylsilane. Aryltitanate ArTi(OPr-*i*)₄Li (**2**) was generated by either of the following three ways: (i) Ti(OPr-*i*)₄ (0.14 mL, 0.48 mmol) was added to a solution of phenyllithium (0.48 mL, 0.94 M in cyclohexane/Et₂O, 0.45 mmol) in THF (0.30 mL) at room temperature and the mixture was stirred at room temperature for 0.5 h. (ii) *n*-Butyllithium (0.29 mL, 1.56 M in hexane, 0.45

mmol) was added to a solution of aryl bromide ArBr (0.45 mmol) in Et₂O (1.0 mL) at -78 °C and the mixture was stirred at 0 °C for 1 h. Ti(OPr-*i*)₄ (0.14 mL, 0.48 mmol) was added to the ArLi solution at room temperature and the mixture was stirred at room temperature for 0.5 h.

(iii) THF (0.30 mL) was added to ArTi(OPr-*i*)₃ (0.45 mmol) and LiOPr-*i* (30 mg, 0.45 mmol) and the solution was stirred at room temperature for 0.5 h. To a solution of [RhCl(C₂H₄)₂]₂ (5.8 mg, 0.15 mmol, 10 mol % Rh), (*R*)-segphos (20 mg, 0.33 mmol, 1.1 eq to Rh), enynone **1** (0.30 mmol), and chlorotrimethylsilane (80 µL, 0.63 mmol) in THF (0.70 mL) was added a solution of ArTi(OPr-*i*)₄Li (**2**) (0.45 mmol) at 20 °C. After 0.5 h stirring at the same temperature, the mixture was concentrated under reduced pressure, treated with Et₂O (ca. 3 mL) and H₂O (ca. 50 µL), and filtered through a short Celite/MgSO₄ pad (eluent: Et₂O). The filtrate was concentrated in vacuo to give the crude allenylalkenyl silyl ether **3**. The yield of the silyl ether **3** was determined by ¹H NMR analysis of the crude product. The spectroscopic data of the silyl enol ethers are shown below:

3-(2-Phenylhexenyldiene)-1-(trimethylsilyloxy)cyclohexene (3am): ¹H NMR (CDCl₃) δ 0.22 (s, 9H), 0.92 (t, *J* = 7.5 Hz, 3H), 1.40 (sextet, *J* = 7.5 Hz, 2H), 1.49 (quintet, *J* = 7.4 Hz, 2H), 1.79-1.91 (m, 2H), 2.16 (t, *J* = 6.2 Hz, 2H), 2.32 (ddd, *J* = 14.2, 6.6, 5.3 Hz, 1H), 2.38 (ddd, *J* = 14.2, 8.8, 6.8 Hz, 1H), 2.42 (t, *J* = 7.5 Hz, 2H), 5.34 (s, 1H), 7.16 (tt, *J* = 7.4, 1.5 Hz, 1H), 7.29 (t, *J* = 7.4 Hz, 2H), 7.37 (d, *J* = 7.4 Hz, 2H). ¹³C NMR (CDCl₃) δ 0.37, 14.07, 22.40, 22.94, 27.17, 30.04, 30.08, 103.68, 104.20, 105.56, 126.09, 126.13, 128.18, 138.24, 152.76, 202.14.

3-(2-(4-Fluorophenyl)hexenyldiene)-1-(trimethylsilyloxy)cyclohexene (3an): ¹H NMR (CDCl₃) δ 0.22 (s, 9H), 0.91 (t, *J* = 7.3 Hz, 3H), 1.39 (sextet, *J* = 7.3 Hz, 2H), 1.47 (quintet, *J* = 7.4 Hz, 2H), 1.85 (quintet, *J* = 6.2 Hz, 2H), 2.16 (t, *J* = 6.2 Hz, 2H), 2.29-2.39 (m, 2H), 2.39 (t, *J* = 7.3 Hz, 2H), 5.33 (t, *J* = 1.1 Hz, 1H), 6.97 (t, *J* = 8.8 Hz, 2H), 7.31 (dd, *J* = 8.8, 5.4 Hz, 2H). ¹³C NMR (CDCl₃) δ 0.33, 14.01, 22.35, 22.92, 27.19, 29.97, 30.08, 30.29, 103.58, 104.46, 104.78, 114.93 (d, *J* = 21.6 Hz), 127.49 (d, *J* = 7.1 Hz), 134.20 (d, *J* = 3.1 Hz), 152.99, 161.52 (d, *J* = 244.1 Hz), 201.82 (d, *J* = 2.0 Hz).

3-(2-(4-Methoxyphenyl)hexenyldiene)-1-(trimethylsilyloxy)cyclohexene (3ao): ¹H NMR (CDCl₃) δ 0.22 (s, 9H), 0.91 (t, *J* =

7.2 Hz, 3H), 1.39 (sextet, $J = 7.2$ Hz, 2H), 1.48 (quintet, $J = 7.3$ Hz, 2H), 1.84 (quintet, $J = 6.0$ Hz, 2H), 2.15 (t, $J = 6.4$ Hz, 2H), 2.28-2.39 (m, 2H), 2.39 (t, $J = 7.2$ Hz, 2H), 3.80 (s, 3H), 5.33 (s, 1H), 6.84 (d, $J = 8.9$ Hz, 2H), 7.29 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 0.33, 14.05, 22.38, 22.94, 27.29, 30.02, 30.07, 30.24, 55.21, 103.99, 104.02, 105.01, 113.64, 127.10, 152.56, 158.17, 201.43. **3-(2-Cyclohexyl-2-phenylethenylidene)-1-(trimethylsilyloxy)cyclohexene (3bm):** ^1H NMR (CDCl_3) δ 0.22 (s, 9H), 1.08-1.18 (m, 2H), 1.18-1.23 (m, 1H), 1.36 (qt, $J = 12.7, 3.2$ Hz, 2H), 1.65-1.72 (m, 1H), 1.73-1.79 (m, 2H), 1.79-1.91 (m, 4H), 2.15 (td, $J = 6.3, 0.8$ Hz, 2H), 2.32 (ddd, $J = 14.5, 7.0, 5.2$ Hz, 1H), 2.37 (ddd, $J = 14.5, 7.2, 5.4$ Hz, 1H), 2.45 (tt, $J = 11.3, 3.2$ Hz, 1H), 5.34 (t, $J = 0.8$ Hz, 1H), 7.16 (tt, $J = 7.3, 1.1$ Hz, 1H), 7.29 (t, $J = 7.3$ Hz, 2H), 7.35 (d, $J = 7.3$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 0.39, 22.97, 26.43, 26.65, 27.36, 30.08, 33.13, 38.66, 104.06, 104.88, 112.09, 126.08, 126.56, 128.19, 137.90, 152.55, 201.89. **3-(2-Cyclohexyl-2-(4-methoxyphenyl)ethenylidene)-1-(trimethylsilyloxy)cyclohexene (3bo):** ^1H NMR (CDCl_3) δ 0.22 (s, 9H), 1.07-1.28 (m, 3H), 1.35 (qt, $J = 10.6, 3.1$ Hz, 2H), 1.63-1.80 (m, 3H), 1.80-1.93 (m, 4H), 2.15 (t, $J = 6.3$ Hz, 2H), 2.27-2.46 (m, 2H), 2.40 (tt, $J = 11.2, 3.2$ Hz, 1H), 3.79 (s, 3H), 5.33 (s, 1H), 6.84 (d, $J = 8.2$ Hz, 2H), 7.27 (d, $J = 8.2$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 0.42, 23.01, 26.47, 26.68, 27.51, 30.10, 33.13, 38.83, 55.30, 104.41, 104.76, 111.55, 113.72, 127.60, 129.40, 130.24, 152.40, 201.25. **3-(3,3-Dimethyl-2-phenylbutenylidene)-1-(trimethylsilyloxy)cyclohexene (3cm):** ^1H NMR (CDCl_3) δ 0.21 (s, 9H), 1.11 (s, 9H), 1.77 (quintet, $J = 6.3$ Hz, 2H), 2.03-2.14 (m, 2H), 2.23-2.34 (m, 2H), 5.32 (t, $J = 1.1$ Hz, 1H), 7.18-7.30 (m, 5H). ^{13}C NMR (CDCl_3) δ 0.39, 22.74, 27.63, 29.99, 30.19, 35.24, 101.54, 105.05, 115.85, 126.12, 127.58, 129.45, 138.89, 151.97, 199.73. **3-(2-(4-Methoxyphenyl)-2-phenylethenylidene)-1-(trimethylsilyloxy)cyclohexene (3dm):** ^1H NMR (CDCl_3) δ 0.23 (s, 9H), 1.86 (quintet, $J = 6.3$ Hz, 2H), 2.16 (td, $J = 6.3, 0.8$ Hz, 2H), 2.44 (t, $J = 6.3$ Hz, 2H), 3.81 (s, 3H), 5.43 (t, $J = 0.8$ Hz, 1H), 6.86 (d, $J = 8.8$ Hz, 2H), 7.24 (d, $J = 8.8$ Hz, 2H), 7.28-7.35 (m, 5H). ^{13}C NMR (CDCl_3) δ 0.15, 22.50, 27.00, 29.82, 54.98, 102.88, 103.81, 109.15, 113.41, 126.45, 127.89, 128.21, 129.36, 129.99, 137.99, 153.32, 203.94. **3-(2-**

Phenylhexenylidene)-1-(trimethylsilyloxy)cyclopentene (3em): ^1H NMR (CDCl_3) δ 0.26 (s, 9H), 0.92 (t, $J = 7.5$ Hz, 3H), 1.40 (sextet, $J = 7.5$ Hz, 2H), 1.51 (quintet, $J = 7.5$ Hz, 2H), 2.43 (t, $J = 7.5$ Hz, 2H), 2.46-2.54 (m, 2H), 2.65-2.79 (m, 2H), 5.16 (t, $J = 1.5$ Hz, 1H), 7.16 (t, $J = 7.5$ Hz, 1H), 7.28 (t, $J = 7.5$ Hz, 2H), 7.40 (d, $J = 7.5$ Hz, 2H). ^{13}C NMR (CDCl_3) δ -0.01, 14.03, 22.45, 25.76, 30.16, 30.55, 32.93, 103.87, 108.24, 111.56, 126.07, 126.12, 128.10, 138.63, 159.47, 198.43.

General Procedure for Conversion of Silyl Enol Ether 3 into Pivalate 4. To a solution of the crude silyl enol ether **3** in THF (2.0 mL) was added methyllithium (0.49 mL, 0.92 M in Et_2O , 0.45 mmol) at -78°C , and the mixture was stirred at 0°C for 0.5 h. To the solution, pivaloyl chloride (74 μL , 0.60 mmol) was added at -78°C , and the reaction mixture was stirred at room temperature for 0.5 h. The solvent was removed in vacuo, and the residue was diluted with Et_2O . The solution was washed with saturated NaHCO_3 , before it was dried over MgSO_4 and concentrated under reduced pressure. The crude product was purified by silica gel chromatography. The enantiomeric excess of the pivalate ester **4** was determined by HPLC analysis with a chiral stationary phase column (Daicel Chiralcel OD-H, eluent: Hexane). The results are summarized in Table 1. The NMR spectra, optical rotations, and the data of combustion analysis and HRMS of the pivalate esters are shown below: **3-(2-Phenylhexenylidene)-1-(trimethylacetoxycyclohexene (4am):** purified by PTLC (Hexane/ $\text{AcOEt} = 20/1$) (85% yield); ^1H NMR (CDCl_3) δ 0.92 (t, $J = 7.4$ Hz, 3H), 1.25 (s, 9H), 1.40 (sextet, $J = 7.4$ Hz, 2H), 1.46-1.54 (m, 2H), 1.85- 1.97 (m, 2H), 2.30 (td, $J = 6.1, 1.3$ Hz, 2H), 2.37-2.49 (m, 2H), 2.42 (t, $J = 7.4$ Hz, 2H), 5.82 (t, $J = 1.3$ Hz, 1H), 7.17 (tt, $J = 7.4, 1.3$ Hz, 1H), 7.28 (t, $J = 7.4$ Hz, 2H), 7.35 (d, $J = 7.4$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 13.97, 22.43, 22.58, 26.85, 27.03, 27.08, 29.95, 30.03, 38.83, 102.53, 106.45, 112.96, 126.15, 126.48, 128.23, 137.32, 149.50, 176.83, 203.65. $[\alpha]^{20}_{\text{D}} +19.2$ (c 1.05, CHCl_3) for 92% ee. Anal. Calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2$: C, 81.61; H, 8.93. Found: C, 81.36; H, 9.00. **3-(2-(4-Fluorophenyl)hexenylidene)-1-(trimethylacetoxycyclohexene (4an):** purified by PTLC (Hexane/ $\text{AcOEt} = 15/1$) (85% yield); ^1H NMR (CDCl_3) δ 0.92 (t, $J = 7.2$ Hz, 3H), 1.25 (s, 9H), 1.39 (sextet, $J = 7.2$ Hz, 2H), 1.43-1.53 (m, 2H), 1.92 (quintet, $J = 6.3$ Hz, 2H), 2.31 (t, $J = 6.3$ Hz, 2H), 2.39 (t, $J = 7.2$ Hz,

2H), 2.36-2.48 (m, 2H), 5.81 (s, 1H), 6.97 (t, $J = 8.5$ Hz, 2H), 7.30 (dd, $J = 8.5, 5.4$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 13.95, 22.40, 22.55, 26.84, 27.01, 27.08, 29.94, 30.15, 38.84, 102.76, 105.61, 112.83, 115.04 (d, $J = 21.6$ Hz), 127.60 (d, $J = 8.3$ Hz), 133.27 (d, $J = 3.1$ Hz), 149.71, 161.66 (d, $J = 244.1$ Hz), 176.82, 203.33 (d, $J = 2.1$ Hz). $[\alpha]^{20}_{\text{D}} +13.1$ (c 0.99, CHCl_3) for 91% ee. Anal. Calcd for $\text{C}_{23}\text{H}_{29}\text{O}_2\text{F}$: C, 77.49; H, 8.20. Found: C, 77.27; H, 8.15.

3-(2-(4-Methoxyphenyl)hexenylidene)-1-(trimethylacetoxycyclohexene (4ao): purified by PTLC (Hexane/AcOEt = 7/1) (83% yield); ^1H NMR (CDCl_3) δ 0.92 (t, $J = 7.3$ Hz, 3H), 1.25 (s, 9H), 1.39 (sextet, $J = 7.3$ Hz, 2H), 1.43-1.54 (m, 2H), 1.91 (quintet, $J = 5.9$ Hz, 2H), 2.30 (t, $J = 5.9$ Hz, 2H), 2.39 (t, $J = 7.3$ Hz, 2H), 2.36-2.47 (m, 2H), 3.79 (s, 3H), 5.81 (s, 1H), 6.84 (d, $J = 8.8$ Hz, 2H), 7.28 (d, $J = 8.8$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 13.99, 22.45, 22.63, 26.99, 27.05, 27.10, 30.04, 30.15, 38.84, 55.27, 102.42, 105.93, 113.24, 113.72, 127.25, 129.63, 149.37, 158.40, 176.90, 203.14. $[\alpha]^{20}_{\text{D}} +20.5$ (c 1.07, CHCl_3) for 93% ee. HRMS (FAB) Calcd for $\text{C}_{24}\text{H}_{32}\text{O}_3$: 388.2350 ($[\text{M}]^+$). Found: 388.2345 ($[\text{M}]^+$).

3-(2-Cyclohexyl-2-phenylethenylidene)-1-(trimethylacetoxycyclohexene (4bm): purified by PTLC (Hexane/AcOEt = 15/1) (91% yield); ^1H NMR (CDCl_3) δ 1.08-1.24 (m, 3H), 1.25 (s, 9H), 1.28-1.41 (m, 2H), 1.66-1.73 (m, 1H), 1.73-1.80 (m, 2H), 1.84-1.94 (m, 4H), 2.30 (td, $J = 6.3, 1.3$ Hz, 2H), 2.37-2.49 (m, 3H), 5.81 (t, $J = 1.3$ Hz, 1H), 7.17 (tt, $J = 7.2, 1.4$ Hz, 1H), 7.28 (t, $J = 7.2$ Hz, 2H), 7.33 (d, $J = 7.2$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 22.62, 26.29, 26.58, 26.60, 27.03, 27.08, 32.97, 33.12, 38.57, 38.81, 103.24, 112.92, 113.10, 126.42, 126.62, 128.24, 137.04, 149.37, 176.77, 203.39. $[\alpha]^{20}_{\text{D}} +8.8$ (c 1.05, CHCl_3) for 70% ee. HRMS (FAB) Calcd for $\text{C}_{25}\text{H}_{32}\text{O}_2$: 364.2401 ($[\text{M}]^+$). Found: 364.2410 ($[\text{M}]^+$).

3-(2-Cyclohexyl-2-(4-methoxyphenyl)ethenylidene)-1-(trimethylacetoxycyclohexene (4bo): purified by PTLC (Hexane/AcOEt = 10/1) (80% yield); ^1H NMR (CDCl_3) δ 1.05-1.41 (m, 5H), 1.25 (s, 9H), 1.64-1.72 (m, 1H), 1.71-1.79 (m, 2H), 1.82-1.95 (m, 4H), 2.29 (td, $J = 6.2, 1.1$ Hz, 2H), 2.35-2.47 (m, 3H), 3.80 (s, 3H), 5.80 (t, $J = 1.1$ Hz, 1H), 6.83 (d, $J = 8.9$ Hz, 2H), 7.25 (d, $J = 8.9$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 22.65, 26.33, 26.62, 26.63, 27.05, 27.10, 27.17, 32.96, 33.13, 38.71, 38.84, 55.25, 103.14, 112.39, 113.37, 113.76, 127.67, 129.29, 149.23, 158.36, 176.85, 202.92. $[\alpha]^{20}_{\text{D}} +14.9$ (c 1.01, CHCl_3) for 80% ee. HRMS (FAB) Calcd for $\text{C}_{26}\text{H}_{35}\text{O}_3$:

395.2586 ($[M+H]^+$). Found: 395.2573 ($[M+H]^+$). **3-(3,3-Dimethyl-2-phenylbutenyldiene)-1-(trimethylacetoxy)cyclohexene (4cm)**: purified by PTLC (Hexane/AcOEt = 20/1) (44% yield); ^1H NMR (CDCl_3) δ 1.12 (s, 9H), 1.24 (s, 9H), 1.83 (quintet, $J = 6.3$ Hz, 2H), 2.16-2.28 (m, 2H), 2.30-2.41 (m, 2H), 5.79 (t, $J = 1.4$ Hz, 1H), 7.19-7.24 (m, 3H), 7.24-7.29 (m, 2H). ^{13}C NMR (CDCl_3) δ 22.41, 27.01, 27.07, 27.29, 30.07, 35.14, 38.84, 99.94, 113.67, 116.59, 126.40, 127.67, 129.38, 138.05, 148.85, 176.81, 201.18. $[\alpha]^{20}_{\text{D}} -8.8$ (c 1.00, CHCl_3) for 26% ee. HRMS (FAB) Calcd for $\text{C}_{23}\text{H}_{30}\text{O}_2$: 338.2246 ($[M]^+$). Found: 338.2243 ($[M]^+$). **3-(2-(4-Methoxyphenyl)-2-phenylethyldiene)-1-(trimethylacetoxy)cyclohexene (4dm)**: purified by PTLC (Hexane/AcOEt = 7/1) (56% yield); ^1H NMR (CDCl_3) δ 1.25 (s, 9H), 1.93 (quintet, $J = 6.2$ Hz, 2H), 2.31 (td, $J = 6.2, 1.3$ Hz, 2H), 2.52 (t, $J = 6.2$ Hz, 2H), 3.81 (s, 3H), 5.92 (t, $J = 1.3$ Hz, 1H), 6.86 (d, $J = 8.9$ Hz, 2H), 7.21-7.28 (m, 1H), 7.23 (d, $J = 8.9$ Hz, 2H), 7.28-7.34 (m, 4H). ^{13}C NMR (CDCl_3) δ 13.72, 22.17, 22.32, 26.59, 26.77, 26.83, 29.70, 29.77, 38.57, 102.28, 106.19, 112.70, 125.89, 126.22, 127.98, 137.07, 149.25, 176.58, 203.39. $[\alpha]^{20}_{\text{D}} -1.7$ (c 1.00, CHCl_3) for 75% ee. HRMS (FAB) Calcd for $\text{C}_{26}\text{H}_{28}\text{O}_3$: 388.2037 ($[M]^+$). Found: 388.2039 ($[M]^+$). **3-(2-Phenylhexenyldiene)-1-(trimethylacetoxy)cyclopentene (4em)**: purified by short silica gel column (Hexane) (80% yield, contaminated with ca. 20% of dienyl ketone); ^1H NMR (CDCl_3) δ 0.92 (t, $J = 7.5$ Hz, 3H), 1.27 (s, 9H), 1.34-1.44 (m, 2H), 1.47-1.55 (m, 2H), 2.44 (t, $J = 7.5$ Hz, 2H), 2.67-2.84 (m, 4H), 5.98 (t, $J = 1.7$ Hz, 1H), 7.17 (tt, $J = 7.4, 1.2$ Hz, 1H), 7.29 (t, $J = 7.4$ Hz, 2H), 7.38 (d, $J = 7.4$ Hz, 2H). ^{13}C NMR (CDCl_3) δ 13.97, 22.40, 25.49, 26.97, 30.04, 30.29, 30.66, 39.12, 108.88, 109.97, 113.57, 126.16, 126.36, 128.15, 137.83, 154.08, 175.59, 199.92. $[\alpha]^{20}_{\text{D}} -10.8$ (c 1.00, CHCl_3) for 70% ee. HRMS (FAB) Calcd for $\text{C}_{22}\text{H}_{28}\text{O}_2$: 324.2089 ($[M]^+$). Found: 324.2087 ($[M]^+$).

Conversion of Silyl Enol Ether 3am into Triflate 5am. In a similar manner to the procedure of conversion of silyl enol ether **3** into pivalate **4**, the lithium enolate was generated from **3am** by treatment with methyllithium. To the solution was added a solution of *N*-(2-pyridyl)triflimide (215 mg, 0.60 mmol) in THF (1.0 mL) at -78 °C and the mixture was stirred at room temperature for 12 h. The reaction was quenched with H_2O (ca. 0.5 mL). The

solvent was removed in vacuo, and the residue was diluted with Et₂O. The mixture was washed with H₂O, before it was dried over MgSO₄ and concentrated under reduced pressure. The crude product was purified by PTLC (Hexane/AcOEt = 20/1) to give triflate **5am** (94.2 mg, 82% yield). The enantiomeric excess of **5am** was determined by HPLC analysis with a chiral stationary phase column (Daicel Chiralcel OD-H, eluent: Hexane). **3-(2-Phenylhexenylidene)-1-(trifluoromethanesulfonyloxy)cyclohexene (5am)**: ¹H NMR (CDCl₃) δ 0.93 (t, *J* = 7.2 Hz, 3H), 1.40 (sextet, *J* = 7.2 Hz, 2H), 1.44-1.54 (m, 2H), 1.96 (quintet, *J* = 6.9 Hz, 2H), 2.36-2.47(m, 2H), 2.46 (t, *J* = 7.2 Hz, 2H), 2.48 (td, *J* = 6.2, 1.4 Hz, 2H), 6.15 (t, *J* = 1.4 Hz, 1H), 7.21 (tt, *J* = 6.7, 1.9 Hz, 1H), 7.27-7.37 (m, 4H). ¹³C NMR (CDCl₃) δ 13.92, 22.35, 22.49, 26.40, 27.83, 29.93, 101.11, 107.62, 117.75, 118.86 (q, *J* = 319.4 Hz), 126.31, 127.05, 128.44, 136.45, 148.48, 205.00. [α]²⁰_D +16.0 (*c* 1.00, CHCl₃) for 92% ee. HRMS (FAB) Calcd for C₁₉H₂₂O₃SF₃: 387.1242 ([M+H]⁺). Found: 387.1234 ([M+H]⁺).

References

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Date : Wed May 21 01:53:10 2003

FileName : No562-tBu-1H.nmdata
Comment : N.T: No562: tBu-1H for
SliceHistory :
EXMODE : non

POINT : 65536 points
SAMPD : 65536 points
FREQU : 8000.0 Hz
FILTR : 4000 Hz
DELAY : 50.0 usec
DEADT : 72.1 usec
INTVL : 125.0 usec
TIMES : 16 times
DUMMY : 0 times
PD : 0.0300 sec
ACQTM : 8192.0000 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 0.12 Hz
PW1 : 5.80 usec
OBNUC : 1H
OBFRQ : 499.10 MHz
OBSET : 128885.00 Hz
RGAIN : 16

SCANS : 16 times

SLVNT : CDCL3
SPINNING : 11 Hz
TEMP : 23.7 C

Date : Wed May 21 02:23:20 2003

FileName : No562-tBu-13C.nmdata
Comment : N.T: No562: tBu-13C for
SliceHistory :
EXMODE : bcm

POINT : 32768 points
SAMPD : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.2 usec
INTVL : 29.5 usec
TIMES : 512 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.0000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 5.00 usec
OBNUC : 13C
OBFRQ : 125.40 MHz
OBSET : 143041.00 Hz
RGAIN : 31
IRNUC : 1H
IRFRQ : 499.10 MHz
IRSET : 128250.00 Hz
IRPPW : 50.0 usec
IRRNS : 0

SCANS : 512 times

SLVNT : CDCL3
SPINNING : 10 Hz
TEMP : 24.7 C

Date : Wed May 21 03:02:21 2003

FileName : No563-tBu-1H.nmdata
Comment : N.T: No563: tBu-1H for
SliceHistory :
EXMODE : non

POINT : 65536 points
SAMPO : 65536 points
FREQU : 8000.0 Hz
FILTR : 4000 Hz
DELAY : 50.0 usec
DEADT : 72.1 usec
INTVL : 125.0 usec
TIMES : 16 times
DUMMY : 0 times
PD : 0.0300 sec
ACQTM : 8192.0000 msec
PREDL : 0.01000 msec
INIWT : 1000.0000 msec
RESOL : 0.12 Hz
PW1 : 5.80 usec
OBNUC : 1H
OBFRQ : 499.10 MHz
OBSET : 128885.00 Hz
RGAIN : 20

SCANS : 16 times

SLVNT : CDCL3
SPINNING : 11 Hz
TEMP : 24.2 C

Date : Wed May 21 02:59:01 2003

FileName : No563-tBu-13C.nmdata
Comment : N.T: No563: tBu-13C for
SliceHistory :
EXMODE : bcm

POINT : 32768 points
SAMPO : 32768 points
FREQU : 33898.3 Hz
FILTR : 16950 Hz
DELAY : 11.8 usec
DEADT : 15.2 usec
INTVL : 29.5 usec
TIMES : 512 times
DUMMY : 1 times
PD : 2.0333 sec
ACQTM : 966.6560 msec
PREDL : 10.0000 msec
INIWT : 10.0000 msec
RESOL : 1.03 Hz
PW1 : 5.00 usec
OBNUC : 13C
OBFRQ : 125.40 MHz
OBSET : 143041.00 Hz
RGAIN : 33
IRNUC : 1H
IRFRQ : 499.10 MHz
IRSET : 128250.00 Hz
IRRPW : 50.0 usec
IRRNS : 0

SCANS : 512 times

SLVNT : CDCL3
SPINNING : 12 Hz
TEMP : 24.7 C

```

Date : Mon Jul 21 20:35:46 2003

FileName      : .LoadingFID.nmdata
Comment       : N.T. No611: Cy_OME_tBu-
SliceHistory  :
EXMODE        : non

POINT         : 65536 points
SAMPO         : 65536 points
FREQU         : 8000.0 Hz
FILTR         : 4000 Hz
DELAY         : 50.0 usec
DEADT         : 72.1 usec
INTVL         : 125.0 usec
TIMES         : 16 times
DUMMY         : 0 times
PD            : 0.0300 sec
ACGTM         : 8192.0000 msec
PREDL         : 0.01000 msec
INIWT         : 1000.0000 msec
RESOL         : 0.12 Hz
PW1           : 5.80 usec
OBNUC         : 1H
OBFREQ        : 499.10 MHz
OBSET         : 128885.00 Hz
RGAIN         : 26

SCANS         : 16 times

SLVNT         : CDCL3
SPINNING      : 13 Hz
TEMP          : 28.3 C

```

```

Date : Mon Jul 21 21:29:54 2003

FileName      : .LoadingFID.nmdata
Comment       : N.T: No611: Cy_0Me_tBu_13
SliceHistory  :
EXMODE        : bcm

POINT         : 32768 points
SAMPO         : 32768 points
FREQU         : 33898.3 Hz
FILTR         : 16950 Hz
DELAY         : 11.8 usec
DEADT         : 15.2 usec
INTVL         : 29.5 usec
TIMES         : 512 times
DUMMY         : 1 times
PD            : 2.0333 sec
ACQTM         : 966.6560 msec
PREDL         : 10.00000 msec
INIWT         : 10.0000 msec
RESOL         : 1.03 Hz
PW1           : 5.00 usec
OBNUC         : 13C
OBFREQ        : 125.40 MHz
OBSET         : 143041.00 Hz
RGAIN         : 33
IRNUC         : 1H
IRFREQ        : 499.10 MHz
IRSET         : 128250.00 Hz
IRAPW         : 50.0 usec
IRPNS         : 0

SCANS         : 202 times

SLVNT         : CDCL3
SPINNING      : 14 Hz
TEMP          : 29.0 C

```

Date : Mon Jul 21 13:46:46 2003

FileName : .LoadingFID.nmdata
 Comment : N.T: No611: OMe_tBu_1H
 SliceHistory :
 EXMODE : non

POINT : 65536 points
 SAMPO : 65536 points
 FREQU : 8000.0 Hz
 FILTR : 4000 Hz
 DELAY : 50.0 usec
 DEADT : 72.1 usec
 INTVL : 125.0 usec
 TIMES : 16 times
 DUMMY : 0 times
 PD : 0.0300 sec
 ACQTM : 8192.0000 msec
 PREDL : 0.01000 msec
 INIWT : 1000.0000 msec
 RESOL : 0.12 Hz
 PW1 : 5.80 usec
 OBNUC : 1H
 OBFREQ : 499.10 MHz
 OBSET : 128885.00 Hz
 RGAIN : 25

SCANS : 16 times

SLVNT : CDCL3
 SPINNING : 15 Hz
 TEMP : 28.8 C

Date : Thu May 22 01:50:13 2003

FileName : No596-tBu-13C.nmdata
 Comment : N.T: No596: tBu-13C for
 SliceHistory :
 EXMODE : bcm

POINT : 32768 points
 SAMPO : 32768 points
 FREQU : 33898.3 Hz
 FILTR : 16950 Hz
 DELAY : 11.8 usec
 DEADT : 15.2 usec
 INTVL : 29.5 usec
 TIMES : 512 times
 DUMMY : 1 times
 PD : 2.0333 sec
 ACQTM : 966.6560 msec
 PREDL : 10.00000 msec
 INIWT : 10.0000 msec
 RESOL : 1.03 Hz
 PW1 : 5.00 usec
 OBNUC : 13C
 OBFREQ : 125.40 MHz
 OBSET : 143041.00 Hz
 RGAIN : 32
 IRNUC : 1H
 IRFREQ : 499.10 MHz
 IRSET : 128250.00 Hz
 IRRPW : 50.0 usec
 IRRNS : 0

SCANS : 512 times

SLVNT : CDCL3
 SPINNING : 14 Hz
 TEMP : 24.2 C