A New *cine*-Substitution of Alkenyl Sulfones with Aryltitanium Reagents Catalyzed by Rhodium: Mechanistic Studies and Catalytic Asymmetric Synthesis of Allylarenes

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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 , 76.5 MHz for ^2H , and 125 MHz for ^{13}C). Chemical shifts are reported in δ ppm referenced to an internal SiMe_4 standard for ^1H NMR, chloroform-*d* (δ 7.26) for ^2H NMR, and chloroform-*d* (δ 77.05) for ^{13}C NMR. Optical rotations were measured on a JASCO DIP-370 polarimeter.

Materials. THF was distilled from sodium benzophenone-ketyl under nitrogen prior to use. Hexane was distilled from Na/K alloy undn, s flask with a Teflon stopcock under nitrogen. Rhodium complex, $[\text{Rh}(\text{OH})((S)\text{-binap})]_2$ was prepared according to the reported procedure.¹ Alkenyl sulfones, (*E*)-1-phenylsulfonyl-1-octene (**1a**)^{2,3}, 2-phenylsulfonyl-1-octene (**1b**)⁴, (*E*)-1-phenylsulfonyl-2-phenylethene (**1c**)^{2,5} and 1-phenylsulfonyl-cyclohexene (**4**)⁶ were prepared according to the reported procedures. 4-Bromoanisole, 4-bromobenzotrifluoride, bis(cyclopentadiene)Supporting Information, 1-octyne, and benzenesulfonyl chloride were used as received. Chlorotriisopropoxytitanium⁷, bis(cyclopentadienyl)zirconium chloride hydride⁸, 1-deuterio-1-octyne⁹ were prepared according to the reported procedures.

Preparation of Aryltitanium Triisopropoxide (2).¹⁰ A typical procedure is given for the preparation of phenyltitanium triisopropoxide ($\text{PhTi}(\text{OPr-}i)_3$) (**2m**). To a solution of chlorotriisopropoxytitanium (24.5 g, 94.0 mmol) in THF (100 mL) was added dropwise phenyllithium (100 mL, 0.94 M in cyclohexane and diethyl ether, 94.0 mmol) over 5 min at -78°C under nitrogen. After completion of the addition, the cooling bath was removed and the mixture was stirred for 2 h. The solution was concentrated in vacuo and dry hexane was added to the residue. The suspension was passed through celite to remove lithium chloride under nitrogen. Concentration of the filtrate and recrystallization from dry hot hexane to give the phenyltitanium triisopropoxide (**2m**) as a slightly yellow solid (23.2 g, 76.8 mmol, 82% yield) which was stored in a glovebox.; **2m**; ^1H NMR (CDCl_3) δ 1.25 (d, J = 6.3 Hz, 18H), 4.70 (br septet, J = 6.3 Hz, 3H), 7.09-7.12 (m, 3H), 7.51-7.56 (br m, 2H). **4-Methoxyphenyltitanium Triisopropoxide (2n)**; ^1H NMR (CDCl_3) δ 1.29 (d, J = 6.1 Hz, 18H), 3.76 (s, 3H), 4.63 (br septet, J = 6.1 Hz, 3H), 6.66 (d, J = 8.0 Hz, 2H), 7.57 (d, J = 8.0 Hz, 2H).; A solution of 4-methoxyphenyllithium was prepared by the slow addition of *n*-butyllithium in hexane to 4-bromoanisole in THF. **4-Trifluoromethylphenyltitanium Triisopropoxide (2o)**; ^1H NMR (CDCl_3) δ 1.25 (d, J = 6.1 Hz, 18H), 4.67 (br septet, J = 6.1 Hz, 3H), 7.35 (d, J = 7.8 Hz, 2H), 7.62 (d, J = 7.8 Hz, 2H).; A solution of 4-trifluoromethylphenyllithium was prepared by the slow addition of *n*-butyllithium in hexane to 4-bromobenzotrifluoride in THF.

Preparation of (*E*)-2-Deuterio-1-phenylsulfonyl-1-octene (1a-2-*d*₁). To a solution of bis(cyclopentadienyl)zirconium dichloride (2.92 g, 10.0 mmol) in THF (19 mL) was added a solution of LiAlD_4 (84.0 mg, 2.00 mmol) in THF (3 mL) at r.t. under nitrogen. The resulting mixture was allowed to stirred for 90 min and 1-octyne (1.10 g, 10.0 mmol) was added. After 1 h, benzenesulfonyl chloride (2.65 g, 15.0 mmol) was added and the mixture was heated to 40°C for 3 h. The mixture was diluted with hexane and was filtered through a short silica gel column (Et_2O). Further purification by silica gel chromatography (Hexane/ EtOAc = 9/1) gave **1a-2-*d*₁** (1.53 g, 6.04 mmol, 76% yield).; ^2H NMR (CHCl_3) δ 7.00.

Preparation of (*E*)-1-Deuterio-1-phenylsulfonyl-1-octene (1a-1-*d*₁). To a solution of bis(cyclopentadienyl)zirconium chloride hydride (1.55 g, 6.00 mmol) in THF (12 mL) was added 1-deuterio-1-octyne (447 mg, 4.02 mmol) at r.t. under nitrogen. After 1 h,

benzenesulfonyl chloride (1.07 g, 6.03 mmol) was added and the mixture was heated to 40 °C for 3 h. The mixture was diluted with hexane and was filtered through a short silica gel column (Et₂O). Further purification by silica gel chromatography (Hexane/EtOAc = 9/1) gave **1a-1-d₁** (510 mg, 2.01 mmol, 50% yield).; ²H NMR (CHCl₃) δ 6.34.

Preparation of 2-Phenylsulfonyl-2-nonene (6). This was prepared from **1a** according to the reported procedures;¹¹ purified by PTLC (hexane) (74% yield); Anal. Calcd for C₁₅H₂₂O₂S: C, 67.63; H, 8.32. Found: C, 67.66; H, 8.19.; ¹H NMR (CDCl₃) δ 0.88 (t, *J* = 7.0 Hz, 3H), 1.25-1.33 (m, 6H), 1.48 (quint, *J* = 7.4 Hz, 2H), 1.82 (s, 3H), 2.18 (q, *J* = 7.5 Hz, 2H), 6.91 (tq, *J* = 7.6, 1.2 Hz, 1H), 7.52 (t, *J* = 7.5 Hz, 2H), 7.60 (t, *J* = 7.6 Hz, 1H), 7.85 (d, *J* = 7.4 Hz, 2H). ¹³C NMR (CDCl₃) δ 11.46, 13.99, 22.49, 28.19, 28.37, 28.85, 31.49, 127.96, 129.04, 133.04, 136.54, 139.38, 141.43.

General Procedure of Rhodium-Catalyzed *cis*-Substitution of Alkenyl Sulfones with Aryltitanium Reagents. [Rh(OH)((*S*)-binap)]₂ (4.5 mg, 3.0 μmol) and alkenyl sulfone (0.200 mmol) were placed under argon in a schlenk tube, and treated with a solution of ArTi(OPr-*i*)₃ (**2**) (0.400 mmol) in THF (0.5 mL) at r.t. The schlenk tube was immersed in a bath maintained at 40 °C for 12 h. The resulting mixture was cooled to r.t., treated with hexane (ca. 3 mL) and H₂O (ca. 50 μL), and filtered through a celite (eluent: hexane). After concentration of the filtrate, the residue was purified by PTLC on silica gel to give the corresponding product. **2-Phenyl-1-octene (3am):**¹² purified by PTLC (hexane) (87% yield); ¹H NMR (CDCl₃) δ 0.87 (t, *J* = 7.1 Hz, 3H), 1.21-1.35 (m, 6H), 1.44 (quint, *J* = 7.5 Hz, 2H), 2.49 (t, *J* = 7.7 Hz, 2H), 5.04 (d, *J* = 1.4 Hz, 1H), 5.25 (d, *J* = 1.4 Hz, 1H), 7.25 (t, *J* = 7.3 Hz, 1H), 7.31 (t, *J* = 7.3 Hz, 2H), 7.40 (d, *J* = 7.8 Hz, 2H). The geometry of the olefinic protons was assigned based on the following NOE data.

(*E*)-1-Deuterio-2-phenyl-1-octene ((*E*)-3am-d₁): purified by PTLC (hexane) (84% yield); ²H NMR (CHCl₃) δ 5.04. **(*Z*)-1-Deuterio-2-phenyl-1-octene ((*Z*)-3am-d₁):** purified by PTLC (hexane) (86% yield); ²H NMR (CHCl₃) δ 5.25. **(*E*)-1-Phenyl-1-octene (3bm):**¹³ purified by PTLC (hexane) (93% yield). **1,1-Diphenylethene (3cm):**¹⁴ purified by PTLC (hexane) (99% yield). **1-(4-Methoxyphenyl)-1-phenylethene (3cn):**¹⁵ purified by PTLC (hexane/AcOEt = 4/1) (99% yield). **1-(4-Trifluorophenyl)-1-phenylethene (3co):**¹⁶ purified by PTLC (hexane) (97% yield). **(+)-(R)-3-Phenylcyclohexene (5m):**¹⁷ purified by PTLC (hexane) (94% yield); [α]_D²⁰ +147.7 (*c* 1.00, benzene) for >99% ee. The enantiomeric purity was determined by GC analysis with chiral stationary phase column, CP-CHIRASIL-DEX-CB. The absolute configuration was determined to be *R* by comparison of its specific rotation with the reported value.¹⁸ **(+)-3-(4-Methoxyphenyl)cyclohexene (5n):**¹⁷ purified by PTLC (hexane/EtOAc = 10/1) (99% yield); [α]_D²⁰ +145.8 (*c* 1.00, benzene) for 99.9% ee. The enantiomeric purity was determined by HPLC analysis with chiral stationary phase column, Chiralcel OB-H (hexane). **(-)-3-(4-Methoxyphenyl)-1-nonene (7):** purified by PTLC (hexane/Et₂O = 20/1) (46% yield); Anal. Calcd for C₁₆H₂₄O: C, 82.70; H, 10.41. Found: C, 82.53; H, 10.19.; ¹H NMR (CDCl₃) δ 0.86 (t, *J* = 7.2 Hz, 3H), 1.16-1.30 (m, 8H), 1.60-1.71 (m, 2H), 3.18 (q, *J* = 7.5 Hz, 1H), 3.78 (s, 3H), 4.97-5.00 (m, 2H), 5.88-5.95 (m, 1H), 6.84 (d, *J* = 8.6 Hz, 2H), 7.09 (d, *J* = 8.6 Hz, 2H). ¹³C NMR (CDCl₃) δ 14.12, 22.68, 27.52, 29.30, 31.82, 35.52, 49.03, 55.25, 113.48, 113.79, 128.47, 136.79, 142.93, 157.88.; [α]_D²⁰ -27.0 (*c* 1.00, CHCl₃) for 99.2% ee. The enantiomeric purity was determined by HPLC analysis with chiral

stationary phase column, Chiralcel OJ (hexane). For the determination of the enantiomeric purity, racemic samples of **5m**, **5n**, and **7** were also prepared by use of racemic binap.

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