Supporting Information for

Rhodium-Catalyzed Enantioselective Conjugate Addition of Organoboronic Acids to α,β -Unsaturated Sulfones**

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General procedures and spectroscopic data for the synthesis of the starting alkenes, enantioselective conjugate additions and Julia-Kocienski olefinations.

General. All anaerobic and moisture-sensitive manipulations were carried out with standard Schlenk techniques under argon. All reagents were obtained from commercial suppliers and were used without further purification. Dichloromethane, tetrahydrofuran (THF), 1,2-dimethoxyethane (DME) and 1,4-dioxane were dried and stored over microwave-activated 4Å molecular sieves. Reactions were monitored by thin-layer chromatography carried out on 0.25 mm Merck silica gel plates (Merck-60 230-400 mesh). Merck-60 230-400 mesh silica gel was used for flash column chromatography. NMR spectra were recorded on Bruker AC-200 or AC-300 instruments and calibrated using residual undeuterated solvent (CDCl₃) as internal reference. For fluoro containing compounds the observed list of peaks is given as the ¹³C NMR data. Melting points were determined in open-end capillary tubes on a GallemKamp apparatus. Optical rotations were measured on a Perkin-Elmer 241C polarimeter. High-Performance Liquid Chromatography (HPLC) was conducted on an Agilent 1100 instrument, using Daicel Chiralpak AD and Chiralcel OD columns. For simplicity reasons, in the compounds named in this

section the sulfone moiety has been always considered as substituent.

Diethyl (2-pyridylsulfonyl)methyl phosphonate.

2-Mercaptopyridine (1.33 g, 12 mmol,) was added to a suspension of K_2CO_3 (1.66 g, 12 mmol) in anhydrous THF (20 mL). After 5 min. of stirring, diethyl iodomethylphosphonate (1.72 mL, 10 mmol) was added to the suspension and the mixture was heated at 100 °C for 24 h. After that time, the mixture was cooled to room temperature, quenched with a saturated solution of NH_4Cl (ca 10 mL) and extracted with AcOEt (3x10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was removed in vacuo. The crude mixture was dissolved in AcOEt (17 mL) and water (1.5 mL) was added to the stirred solution, followed by sodium tungstate dihydrate (0.33 g, 1 mmol). Hydrogen peroxide (30% aqueous, 3.1 mL, 30 mmol) was added slowly at 0-15 °C. The reaction was stirred for 30 min, warmed to 25 °C, and monitored by TLC until completion (2 h). The mixture was cooled to 0 °C and excess H_2O_2 was decomposed by the controlled addition of saturated $NaHCO_3$ (5 mL). The layers were separated and the aqueous layer was washed with AcOEt (3x5 mL). The combined organic layers were dried over anhydrous Na_2SO_4 and the solvent was eliminated. The crude mixture was purified by column chromatography (AcOEt) to afford diethyl (2-pyridylsulfonyl)methyl phosphonate as a pale yellow oil (2.29 g, 7.8 mmol, 78% overall yield). 1H NMR (300 MHz): 8.72 (ddd, J = 0.8, 1.6 and 4.4 Hz, 1H), 8.09 (dt, J = 1.2 and 8.1 Hz, 1H), 7.96 (td, J = 2.0 and 7.7 Hz, 1H), 7.55 (ddd, J = 1.2, 4.8 and 7.7 Hz, 1H), 4.17-4.07 (m, 4H), 4.09 (d, J = 16.6 Hz, 2H), 1.26 (t, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz): 157.3, 149.9, 138.1, 127.5, 121.9, 63.4, 63.3, 49.6, 47.7, 16.1, 16.0.

Typical procedure for the synthesis of the α,β -unsaturated sulfones: Synthesis of (*E*)-1-((2-pyridyl)sulfonyl)-1-propene (1g**).**

To a stirred suspension of K_2CO_3 (208 mg, 1.5 mmol) in 5 mL of anhydrous CH_2Cl_2 under argon at room temperature, was added via syringe a solution of diethyl (2-pyridylsulfonyl)methyl phosphonate (293 mg, 1.0 mmol) in 1 mL of anhydrous CH_2Cl_2 (1 M). The suspension was allowed to stir for 5 min., then acetaldehyde (84 μ L, 1.5 mmol) was added and the mixture was stirred at room temperature for 24 h. The solution was then quenched with saturated NH_4Cl (5 mL), the mixture was diluted with CH_2Cl_2 (5 mL) and the aqueous layer extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , the solvent was removed in vacuo, and the crude mixture was purified by column chromatography (AcOEt:hexanes, 1:1) to give **1g** (155 mg, 0.85 mmol, 85% yield). 1H NMR (300 MHz): 8.71 (m, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.93 (dt, J = 1.3 and 7.5 Hz, 1H), 7.50 (bdd, J = 4.2 and 7.5 Hz, 1H), 7.10 (dq, J = 7.0 and 15.1 Hz, 1H), 6.56 (dq, J = 1.6 and 15.1 Hz, 1H), 1.97 (dd, J = 1.6 and 7.0 Hz, 3H). ^{13}C NMR (75 MHz): 158.4, 150.2, 145.5, 138.1, 129.0, 127.0, 121.7, 17.5.

(*E*)-1-((2-Pyridyl)sulfonyl)-1-heptene (1i**).**

1H NMR (300 MHz): 8.74-8.70 (m, 1H), 8.07 (d, J = 8.1 Hz, 1H), 7.93 (dt, J = 1.3 and 7.5 Hz, 1H), 7.50 (bdd, J = 4.2 and 7.5 Hz, 1H), 7.11 (dt, J = 6.9 and 15.4 Hz, 1H), 6.52 (dt, J = 1.6 and 15.4 Hz, 1H), 2.28 (dq, J = 1.6 and 6.9 Hz, 2H), 1.54-1.40 (m, 2H), 1.36-1.20 (m, 4H), 0.86 (m, 3H). ^{13}C NMR (75 MHz): 158.4, 150.2, 150.1, 138.1, 127.4, 127.0, 121.7, 31.6, 31.0, 27.0, 22.1, 13.7.

(*E*)-3-Methyl-((2-pyridyl)sulfonyl)-1-butene (1j**).**

1H NMR (300 MHz): 8.73-8.69 (m, 1H), 8.06 (d, J = 8.1 Hz, 1H), 7.93 (dt, J = 1.3 and 7.5 Hz, 1H), 7.50 (bdd, J = 4.2 and 7.5 Hz, 1H), 7.09 (dd, J = 6.1 and 15.4 Hz, 1H), 6.49 (dd, J = 1.6 and 15.4 Hz, 1H), 2.56 (m, 1H), 1.07 (d, J = 6.9 Hz, 6H). ^{13}C NMR (75 MHz): 158.5, 155.7, 150.3, 138.1, 127.0, 125.5, 121.8, 30.9, 20.7.

(E)-2-Naphthyl-1-((2-pyridyl)sulfonyl)ethene (1k).

¹H NMR (300 MHz): 8.71 (m, 1H), 8.07 (d, *J* = 8.1 Hz, 1H), 8.03-7.76 (m, 6H), 7.66-7.45 (m, 4H), 7.21 (d, *J* = 15.4 Hz, 1H). ¹³C NMR (75 MHz): 158.6, 150.4, 145.1, 138.2, 134.6, 133.0, 131.2, 129.8, 128.9, 128.7, 127.8, 127.8, 127.1, 126.9, 124.6, 123.5, 121.8.

Typical procedure for the rhodium-catalyzed enantioselective conjugate addition of organoboronic acids to α,β -unsaturated pyridyl sulfones: Synthesis of (S)-2-phenyl-1-((2-pyridyl)sulfonyl)propane (2g).

1 mL of anhydrous 1,4-dioxane and 0.1 mL of water were sequentially added to a mixture of [Rh(acac)(C₂H₄)₂] (3.9 mg, 0.015 mmol), (*S,S*)-chiraphos (6.4 mg, 0.015 mmol), phenyl boronic acid (303 mg, 2.5 mmol) and the α,β -unsaturated sulfone **1g** (91.5 mg, 0.500 mmol), previously placed under argon in a Schlenk tube. The pale yellow solution was stirred at 100 °C for 12 h, after which time the resulting orange mixture was cooled to rt, diluted with CH₂Cl₂ (ca. 3 mL) and filtered through a short pad of silica gel (eluent: CH₂Cl₂). After concentration of the filtrate, the residue was purified by flash chromatography (AcOEt:hexanes, 2:3) to give **2g** (128 mg, 0.49 mmol, 98% yield).

M.p.: 90-92 °C. ¹H NMR (300 MHz): 8.73-8.69 (m, 1H), 7.84-7.74 (m, 2H), 7.41 (ddd, *J* = 1.2, 4.2 and 7.5 Hz, 1H), 7.18-7.03 (m, 5H), 3.89 (dd, *J* = 6.5 and 14.2 Hz, 1H), 3.58-3.42 (m, 2H), 1.41 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (75 MHz): 157.5, 150.0, 143.3, 137.8, 128.5, 127.0, 126.7, 122.0, 58.7, 35.0, 22.1. [α]_D = +9.6 (*c* 0.5, CHCl₃). HPLC: 81% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.6 mLmin⁻¹, λ = 254 nm; *t*_R/min = 25.7 (*R*) and 29.1 (*S*)].

(S)-2-(4-Fluorophenyl)-1-((2-pyridyl)sulfonyl)propane (3).

M.p.: 96-98 °C. ¹H NMR (300 MHz): 8.62 (dt, *J* = 1.2 and 4.7 Hz, 1H), 7.83-7.76 (m, 2H), 7.46-7.42 (m, 1H), 7.07-7.00 (m, 2H), 6.85-6.77 (m, 2H), 3.98 (dd, *J* = 6.9 and 13.7 Hz, 1H), 3.56-3.41 (m, 2H), 1.39 (d, *J* = 6.9 Hz, 3H). ¹³C NMR (75 MHz): 163.1, 157.6, 150.0,

138.9, 137.9, 128.6, 128.5, 127.0, 122.0, 115.4, 115.1, 58.7, 34.4, 22.3. $[\alpha]_D = +10.4$ (c 0.51, CHCl_3). HPLC: 84% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.6 mLmin^{-1} , $\lambda = 254 \text{ nm}$; $t_R/\text{min} = 35.5$ (R) and 40.1 (S)].

(S)-2-(4-Methoxyphenyl)-1-((2-pyridyl)sulfonyl)propane (4).

^1H NMR (300 MHz): 8.63 (dt, $J = 1.2$ and 4.4 Hz , 1H), 7.83-7.74 (m, 2H), 7.44 (ddd, $J = 2.0$, 4.4 and 6.4 Hz , 1H), 7.00-6.95 (m, 2H), 6.63-6.68 (m, 2H), 3.85 (dd, $J = 6.9$ and 14.1 Hz , 1H), 3.72 (s, 3H), 3.55-3.35 (m, 2H), 1.38 (d, $J = 6.9 \text{ Hz}$, 3H). ^{13}C NMR (75 MHz): 158.2, 157.6, 149.9, 137.8, 135.4, 128.0, 126.8, 122.0, 113.8, 59.0, 55.2, 34.2, 22.2. $[\alpha]_D = -29.2$ (c 0.59, CHCl_3). HPLC: 77% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.6 mLmin^{-1} , $\lambda = 254 \text{ nm}$; $t_R/\text{min} = 43.4$ (R) and 51.2 (S)].

(S)-2-Phenyl-1-((2-pyridyl)sulfonyl)heptane (5).

M.p.: 85-87 °C. ^1H NMR (300 MHz): 8.56 (dt, $J = 1.2$ and 4.4 Hz , 1H), 7.71-7.64 (m, 2H), 7.34 (q, $J = 4.4 \text{ Hz}$, 1H), 7.09-6.94 (m, 5H), 3.94 (dd, $J = 6.9$ and 15.0 Hz , 1H), 3.55 (dd, $J = 5.3$ and 15.0 Hz , 1H), 3.26-3.20 (m, 1H), 1.85-1.71 (m, 1H), 1.68-1.52 (m, 1H), 1.27-0.96 (m, 6H), 0.84-0.73 (m, 3H). ^{13}C NMR (75 MHz): 157.4, 149.8, 141.3, 137.6, 128.2, 127.7, 126.7, 126.6, 122.0, 57.7, 40.6, 36.3, 31.3, 26.5, 22.3, 13.9. $[\alpha]_D = -29.4$ (c 0.51, CHCl_3). HPLC: 84% ee [Daicel Chiralcel OD column, hexane/isopropanol 90:10, 0.6 mLmin^{-1} , $\lambda = 254 \text{ nm}$; $t_R/\text{min} = 26.7$ (R) and 36.3 (S)].

(S)-2-(4-Fluorophenyl)-1-((2-pyridyl)sulfonyl)heptane (6).

M.p.: 65-67°C. ^1H NMR (300 MHz): 8.56 (dt, $J = 1.2$ and 4.9 Hz , 1H), 7.75-7.63 (m, 2H), 7.40-7.35 (m, 1H), 6.96-6.89 (m, 2H), 6.77-6.69 (m, 2H), 3.92 (dd, $J = 9.3$ and 15.0 Hz , 1H), 3.52 (dd, $J = 4.9$ and 15.0 Hz , 1H), 3.26-3.20 (m, 1H), 1.82-1.67 (m, 1H), 1.64-1.48 (m, 1H), 1.25-0.96 (m, 6H), 0.84-0.72 (m, 3H). ^{13}C NMR (75 MHz): 163.0, 159.7, 157.4, 149.8, 137.6, 137.0, 136.9, 129.3, 129.2, 126.7, 121.9, 115.1, 114.8, 57.7, 40.0, 36.4, 31.3, 26.4, 22.3, 13.8. $[\alpha]_D = -30.5$ (c 1, CHCl_3). HPLC: 87% ee [Daicel Chiralcel OD column,

hexane/isopropanol 90:10, 0.6 mLmin⁻¹, λ = 254 nm; t_R /min = 18.1 (R) and 28.1 (S)].

(S)-2-(4-Methoxyphenyl)-1-((2-pyridyl)sulfonyl)heptane (7).

¹H NMR (300 MHz): 8.58 (dt, J = 1.2 and 4.9 Hz, 1H), 7.73-7.65 (m, 2H), 7.39-7.33 (m, 1H), 6.91-6.86 (m, 2H), 6.61-6.56 (m, 2H), 3.92 (dd, J = 8.9 and 14.6 Hz, 1H), 3.72 (s, 3H), 3.53 (dd, J = 5.3 and 14.6 Hz, 1H), 3.24-3.18 (m, 1H), 1.82-1.67 (m, 1H), 1.64-1.48 (m, 1H), 1.25-0.96 (m, 6H), 0.84-0.72 (m, 3H). ¹³C NMR (75 MHz): 158.1, 157.6, 149.8, 137.5, 133.3, 128.7, 126.6, 122.1, 113.6, 58.1, 55.1, 39.9, 36.4, 31.4, 26.5, 22.3, 13.9. $[\alpha]_D$ = +30.5 (c 0.38, CHCl₃). HPLC: 81% ee [Daicel Chiralcel OD column, hexane/isopropanol 90:10, 0.5 mLmin⁻¹, λ = 254 nm; t_R /min = 32.1 (R) and 42.3 (S)].

(S)-3-Methyl-2-phenyl-1-((2-pyridyl)sulfonyl)butane (8).

M.p.: 87-89 °C. ¹H NMR (300 MHz): 8.53 (dt, J = 1.2 and 4.4 Hz, 1H), 7.62-7.50 (m, 2H), 7.32-7.27 (m, 1H), 7.00-6.85 (m, 5H), 4.08 (dd, J = 10.9 and 15.0 Hz, 1H), 3.65 (dd, J = 3.6 and 15.0 Hz, 1H), 3.05-2.98 (m, 1H), 1.92-1.87 (m, 1H), 0.96 (d, J = 6.9 Hz, 3H), 0.71 (d, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz): 157.2, 149.7, 139.5, 137.4, 128.6, 127.8, 126.5, 126.4, 122.1, 55.5, 47.4, 33.4, 20.5, 19.7. $[\alpha]_D$ = +22.2 (c 0.51, CHCl₃). HPLC: 78% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.6 mLmin⁻¹, λ = 254 nm; t_R /min = 33.6 (R) and 46.5 (S)].

(S)-2-(4-Fluorophenyl)-3-methyl-1-((2-pyridyl)sulfonyl)butane (9).

¹H NMR (300 MHz): 8.55 (ddd, J = 0.8, 1.6 and 4.9 Hz, 1H), 7.65 (dt, J = 1.6 and 7.7 Hz, 1H), 7.53 (dt, J = 1.2 and 8.1 Hz, 1H), 7.35 (ddd, J = 1.2, 4.9 and 7.7 Hz, 1H), 6.89-6.80 (m, 2H), 6.71-6.61 (m, 2H), 4.05 (dd, J = 11.3 and 15.0 Hz, 1H), 3.69 (dd, J = 3.6 and 15.0 Hz, 1H), 3.05-2.98 (m, 1H), 1.90-1.82 (m, 1H), 0.95 (d, J = 6.9 Hz, 3H), 0.69 (d, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz): 163.0, 159.7, 157.3, 149.8, 137.5, 135.3, 130.2, 130.1, 126.6, 122.1, 114.7, 114.5, 55.6, 46.7, 33.4, 20.6, 19.7. $[\alpha]_D$ = +29.3 (c 0.67, CHCl₃). HPLC: 85% ee [Daicel Chiralcel OD column,

hexane/isopropanol 90:10, 0.5 mLmin⁻¹, λ = 254 nm; t_R /min = 23.8 (R) and 41.3 (S)].

(S)-2-(4-Methoxyphenyl)-3-methyl-1-((2-pyridyl)sulfonyl)butane (10).

¹H NMR (300 MHz): 8.56 (ddd, J = 0.8, 1.6 and 4.9 Hz, 1H), 7.61 (dt, J = 1.6 and 7.7 Hz, 1H), 7.51 (d, J = 7.7 Hz, 1H), 7.31 (ddd, J = 1.2, 4.9 and 7.7 Hz, 1H), 6.81-6.76 (m, 2H), 6.53-6.48 (m, 2H), 4.06 (dd, J = 10.9 and 15.0 Hz, 1H), 3.70 (s, 3H), 3.63 (dd, J = 3.6 and 15.0 Hz, 1H), 3.00-2.94 (m, 1H), 1.90-1.82 (m, 1H), 0.95 (d, J = 6.9 Hz, 3H), 0.71 (d, J = 6.9 Hz, 3H). ¹³C NMR (75 MHz): 158.0, 157.4, 149.7, 137.4, 131.4, 129.7, 126.4, 122.2, 113.2, 55.9, 55.1, 46.6, 33.4, 20.6, 19.7. $[\alpha]_D$ = +31.6 (c 0.49, CHCl₃). HPLC: 76% ee [Daicel Chiralcel OD column, hexane/isopropanol 90:10, 0.6 mLmin⁻¹, λ = 254 nm; t_R /min = 33.4 (R) and 46.4 (S)].

(R)-2-(2-Naphthyl)-2-phenyl-1-((2-pyridyl)sulfonyl)ethane (11).

M.p.: 127-129 °C. ¹H NMR (300 MHz): 8.47 (ddd, J = 0.8, 1.6 and 5.0 Hz, 1H), 7.71-7.65 (m, 2H), 7.59-7.53 (m, 2H), 7.49 (dt, J = 1.2 and 8.1 Hz, 1H), 7.46-7.37 (m, 2H), 7.33 (dt, J = 1.6 and 8.1 Hz, 1H), 7.24-7.05 (m, 7H), 4.83 (t, J = 7.3 Hz, 1H), 4.45 (dd, J = 8.1 and 15.0 Hz, 1H), 4.26 (dd, J = 6.9 and 15.0 Hz, 1H). ¹³C NMR (75 MHz): 156.9, 149.7, 140.9, 138.1, 137.1, 133.0, 132.1, 128.6, 128.3, 127.7, 127.6, 127.3, 126.9, 126.5, 126.4, 126.1, 126.0, 125.9, 122.1, 56.7, 46.2. $[\alpha]_D$ = -23.6 (c 0.5, CHCl₃). HPLC: 87% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.6 mLmin⁻¹, λ = 254 nm; t_R /min = 63.3 (R) and 70.4 (S)].

(R)-2-(4-Fluorophenyl)-2-(2-naphthyl)-1-((2-pyridyl)sulfonyl)ethane (12).

M.p.: 123-125 °C. ¹H NMR (300 MHz): 8.49 (ddd, J = 0.8, 1.6 and 4.5 Hz, 1H), 7.74-7.65 (m, 2H), 7.63-7.50 (m, 3H), 7.48-7.37 (m, 3H), 7.22-7.11 (m, 4H), 6.89-6.79 (m, 2H), 4.83 (t, J = 7.3 Hz, 1H), 4.38 (dd, J = 7.7 and 15.0 Hz, 1H), 4.28 (dd, J = 7.3 and 15.0 Hz, 1H). ¹³C NMR (75 MHz): 163.2, 159.9, 157.0, 149.7, 138.1, 137.2, 136.7, 133.0, 132.2, 129.5, 129.4, 128.5, 127.7, 127.4, 126.5,

126.3, 126.2, 126.0, 125.8, 122.1, 115.5, 115.2, 56.7, 45.4. $[\alpha]_D = -35.9$ (c 0.51, CHCl_3). HPLC: 92% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.6 mLmin⁻¹, $\lambda = 254$ nm; $t_R/\text{min} = 63.7$ (*R*) and 81.8 (*S*)].

(*R*)-2-(4-Methoxyphenyl)-2-(2-naphtyl)-1-((2-pyridyl)sulfonyl)ethane (13).

¹H NMR (300 MHz): 8.43 (ddd, $J = 0.8, 1.6$ and 5.0 Hz, 1H), 7.71-7.64 (m, 2H), 7.59-7.53 (m, 2H), 7.54-7.45 (m, 1H), 7.46-7.32 (m, 3H), 7.21-7.08 (m, 4H), 6.71-6.66 (m, 2H), 4.78 (t, $J = 7.3$ Hz, 1H), 4.39 (dd, $J = 7.7$ and 14.5 Hz, 1H), 4.24 (dd, $J = 6.9$ and 14.5 Hz, 1H), 3.71 (s, 3H). ¹³C NMR (75 MHz): 158.4, 157.1, 149.7, 138.5, 137.1, 133.1, 132.2, 128.8, 128.3, 127.7, 127.4, 126.3, 126.2, 126.1, 126.0, 125.9, 122.2, 114.0, 56.9, 55.2, 45.4. $[\alpha]_D = -21.1$ (c 0.75, CHCl_3). HPLC: 85% ee [Daicel Chiralpak AD column, hexane/isopropanol 90:10, 0.7 mLmin⁻¹, $\lambda = 254$ nm; $t_R/\text{min} = 86.6$ (*R*) and 110.2 (*S*)].

Typical procedure for the Julia-Kocienski olefination: Synthesis of (*1E*, 3*R*)-1,3-diphenyl-1-butene,^[1] (*R*)-14.

To a stirred solution of the starting chiral non racemic 2-pyridyl sulfone **2g** (46 mg, 0.176 mmol) dissolved in anhydrous DME (4.6 mL, 0.033 M) under argon and cooled at -78 °C were added via syringe (530 μL , 0.264 mmol) of a solution of potassium hexamethyldisilazide (0.5 M in toluene). The yellow-orange solution was stirred for 3 min., then benzaldehyde (27 μL , 0.264 mmol) was added and the mixture was stirred at -78 °C for 2 h. The pale yellow solution was quenched with saturated NH_4Cl at the same temperature, the mixture was diluted with CH_2Cl_2 (5 mL) and the aqueous layer was extracted with CH_2Cl_2 (3x10 mL). The combined organic layers were dried over anhydrous Na_2SO_4 , the solvent was removed in vacuo and the resulting pale yellow oil which was purified by column chromatography (hexanes) to give (*R*)-**14** (34 mg, 0.163 mmol, 93% yield). ¹H NMR (300 MHz): 7.51-7.30 (m, 10H), 6.61-

6.49 (m, 2H), 3.83-3.74 (m, 1H), 1.62 (d, J = 7.0 Hz, 3H). ^{13}C NMR (75 MHz): 145.6, 137.6, 135.2, 128.6, 128.4, 127.3, 127.0, 126.2, 126.1, 42.5, 21.2. $[\alpha]_{\text{D}} = +32.0$ (c 0.4, CHCl_3). HPLC: 81% ee (this ee was identical to that of the starting sulfone (*S*)-**2g**). The absolute (*R*) configuration was determined by comparison of the optical rotation and chiral HPLC data with the literature values^[1] $[[\alpha]_{\text{D}}$ lit (*S*)-**14**= -39.3 (c 2.51, CHCl_3), 93% ee. Daicel Chiralcel OD column, hexane/isopropanol 99.5:0.5, 0.2 mLmin⁻¹, λ = 215 nm; t_{R} /min = 29.6 (*S*) and 31.8 (*R*)].

(*E*)-1-(4-Fluorophenyl)-3-phenyl-1-butene (15).

^1H NMR (300 MHz): 7.36-7.20 (m, 7H), 7.01-6.96 (m, 2H), 6.42-6.27 (m, 2H), 3.69-3.59 (m, 1H), 1.45 (d, J = 6.9 Hz, 3H). ^{13}C NMR (75 MHz): 163.7, 160.4, 145.5, 135.0, 133.7, 128.5, 127.6, 127.5, 127.4, 127.3, 126.3, 115.5, 115.2, 42.5, 21.2.

(*E,E*)-1,5-Diphenyl-1,3-hexadiene (16).

Mixture of (*E,E*) and (*E,Z*) isomers, ratio 87:13. (*E,E*) isomer: ^1H NMR (300 MHz): 7.47-7.29 (m, 10H), 6.78 (dd, J = 10.1 and 15.4 Hz), 6.49 (d, J = 15.4 Hz), 6.19 (dd, 10.1 and 15.0 Hz, 1H), 6.01 (dd, J = 6.9 and 15.0 Hz, 1H), 3.64-3.55 (m, 1H), 1.49-1.39 (d, J = 6.9 Hz, 3H). (*E,Z*) isomer (significant signals): ^1H NMR (300 MHz): 6.58 (d, J = 15.8 Hz, 1H), 6.17 (t, J = 10.5 Hz, 1H), 5.64 (t, J = 10.5 Hz, 1H), 4.08 (m, 1H).

(*E*)-5-Methyl-2-phenyl-3-hexene (17).

^1H NMR (300 MHz): 7.30-7.00 (m, 5H), 5.54 (ddd, J = 1.2, 6.5 and 15.4 Hz, 1H), 5.41 (ddd, J = 0.8, 6.5 and 15.4 Hz, 1H), 3.46-3.37 (m, 1H), 2.30-2.22 (m, 1H), 1.33 (d, J = 6.9 Hz, 3H), 0.98 (d, J = 6.5 Hz, 3H), 0.97 (d, J = 6.5 Hz, 3H). ^{13}C NMR (75 MHz): 146.7, 136.4, 131.9, 128.3, 127.2, 125.9, 42.1, 31.0, 29.7, 22.6, 21.6.

(*E*)-3-(4-Fluorophenyl)-1-phenyl-1-butene (18).

^1H NMR (300 MHz): 7.45-7.21 (m, 7H), 7.09-7.02 (m, 2H), 6.49-6.35 (m, 2H), 3.69 (dq, J = 6.9 and 14.2 Hz, 1H), (d, J = 6.9 Hz, 3H). ^{13}C

NMR (75 MHz): 163.0, 159.8, 141.2, 137.4, 135.0, 128.8, 128.7, 128.6, 128.5, 127.1, 126.1, 115.3, 115.0, 41.8, 21.3.

(E)-1,3-Diphenyl-1-octene (19).

¹H NMR (300 MHz): 7.44-7.20 (m, 10H), 6.49-6.35 (m, 2H), 3.46 (q, *J* = 7.3 Hz, 1H), 1.92-1.78 (m, 2H), 1.47-1.24 (m, 6H), 1.01-0.84 (m, 3H). ¹³C NMR (75 MHz): 144.7, 137.6, 134.5, 129.2, 128.4, 127.6, 127.0, 126.1, 49.2, 35.8, 31.8, 27.3, 22.5, 14.1.

References

[1] P. Knochel, L. Schwink, *Chem. Eur. J.* **1998**, 4, 950-968.