Highly Efficient Synthesis of Terminal Alkenes from Ketones.

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Supporting Information

General information.....	S2
Synthesis of ketones.....	S3
Olefination procedures A to E.....	S7
Characterization of alkene products.....	S9

General: Unless otherwise noted, all non-aqueous reactions were performed under an oxygen-free atmosphere of argon with rigid exclusion of moisture from reagents and glassware. The solvents were dried using standard methods prior to use. TMSCHN₂ was prepared according to the literature.^{1,2} RhCl(PPh₃)₃ is commercially available, but was prepared from RhCl₃•3H₂O and 4 PPh₃ according to the literature.³ Methanol, ethanol, 2-propanol, benzyl alcohol, 2-butanol and 2-methyl-1-propanol was distilled over calcium hydride. The α -acetoxy- and α -benzoxyketones were prepared from the corresponding bromoketones by nucleophilic substitution with acetic or benzoic acid.⁴ Benzyloxyketones were prepared in 2 steps from the corresponding diol by monoprotection of the primary alcohol,⁵ followed by the oxydation of the secondary alcohol. Other alkoxyketones were prepared by protection of the corresponding hydroxyketones using standard procedures.⁶ Most alkyl and aromatic ketones are commercially available and were purified using standard methods prior to use. Analytical thin layer chromatography (TLC) was performed using EM Reagent 0.25 mm silica gel 60-F plates. Visualization of the developed chromatogram was performed by UV absorbance, aqueous cerium molybdate, ethanolic phosphomolybdic acid, or aqueous potassium permanganate. Flash chromatography was performed using EM Silica Gel 60 (230-400 mesh) with the indicated solvent system. Optical rotations were measured on a Perkin-Elmer 341 digital polarimeter at 589 nm. Data are reported as follows: $[\alpha]_D^{temp}$, concentration (c g/100mL), and solvent. ¹H NMR spectra were recorded in deuteriochloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (400, 400, 300 and 300 MHz respectively). Chemical shifts are reported in ppm on the δ scale from an internal standard of residual chloroform (7.27 ppm). Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet and br = broad), coupling constant in Hz, integration. ¹³C NMR spectra were recorded in deuteriochloroform, unless otherwise noted, on a Bruker AV-400, a Bruker ARX-400, a Bruker AMX-300 or a Bruker AV-300 spectrometers (100, 100, 75 and 75 MHz respectively) with complete proton decoupling. Chemical shifts are reported in ppm from the central peak of deuteriochloroform (76.9 ppm) on the δ scale. Mass spectra were obtained on a KRATOS MS-50 TC TA (FAB) or a Micromass Autospec-TOF (MAB) high resolution magnetic sector mass spectrometer by the Centre régional de spectrométrie de masse de l'Université de Montréal. The elementary analyses were performed by the Laboratoire d'analyse élémentaire de l'Université de Montréal or by the Canadian Microanalytical Service Ltd. High performance liquid chromatography (HPLC) analyses were performed on a Hewlett Packard 1100 Series quaternary gradient pump with diode-array detector interfaced with HP Chemstation software. Values for enantiomeric excess were determined using a chiral column. Data are reported as follows: column type, flow, solvent used, and retention time (t_r). Analytical gas chromatography (GLC) was carried out on a Hewlett Packard 6890 series gas chromatograph equipped with a split mode capillary injector and a flame ionization detector. Unless otherwise noted, injector and detector temperatures were 250 °C and the carrier gas was hydrogen. Data are reported as follows: column type, oven temperature, and retention time (t_r).

¹ Lebel, H.; Paquet, V. *J. Am. Chem. Soc.* **2004**, *126*, 320-328.

² As the quality of Aldrich's solution change from batch to batch, it is highly recommended to check the purity of commercial solution's (¹H NMR or GC-MS spectra) prior to use. For instance, we have experienced a batch that contain up to 50% of TMSCH₂Cl.

³ Osborn J. A.; Wilkinson, G. *Inorg. Synth.* **1990**, *28*, 77-79.

⁴ Hradil, P.; Hlavac, J.; Lemr, K. *J. Heterocycl. Chem.* **1999**, *36*, 141-144.

⁵ Leigh, D. A.; Martin, R. P.; Smart, J. P.; Truscetto, A. M. *Chem. Commun.* **1994**, 1373-1374.

⁶ Greene, T. W.; Wuts, P. G. M. *Protective Groups in Organic Synthesis* 3rd edition, John Wiley & Sons, Inc., New York, 1999, 779 p.

Synthesis of ketones.

(S)-4-Benzyloxy-1-phenyl-3-pentanone. To a solution of (*S*)-2-benzyloxy-*N*-methoxy-*N*-methylpropionamide⁷ (222 mg, 1.00 mmol) in THF (4 mL) at 0 °C, was added a solution of 4-phenethylmagnesium bromide in ether (1.2 mL of 2.5 M, 2.99 mmol). The resulting reaction mixture was stirred 1 h at 0 °C and then saturated NH₄Cl (10 mL) was added dropwise. The mixture was extracted with Et₂O (3 x 10 mL). The combined organic layers were washed with NaHCO₃ (10 mL), brine (10 mL), then were dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (10% EtOAc/hexanes). The title compound (161 mg, 60%) was obtained as a colorless oil. *R*_f 0.26 (10% EtOAc/hexanes). [α]_D = +32.0 (*c*, 0.76, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.38-7.24 (m, 6H), 7.22-7.18 (m, 4H), 4.50 (d, *J* = 12 Hz, 1H), 4.45 (d, *J* = 12 Hz, 1H), 3.92 (q, *J* = 7 Hz, 1H), 2.91 (s, 4H), 1.30 (d, *J* = 7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 212.3, 141.6, 138.0, 128.89, 128.87, 128.83, 128.3, 128.2, 126.5, 81.1, 72.2, 39.4, 29.7, 17.6; HMRS (MAB) calcd for C₁₈H₂₁O₂ [M+1]⁺: 269.154155. Found: 269.153484. The enantiomeric excess was determined to be 98% (86:1) by chiral HPLC analysis (Chiracel OJ, 1 mL/min, 1% 2-propanol/hexane, *t*_r 43.5 (minor), 51.6 (major)).

(S)-4-(*tert*-Butyldimethylsilyloxy)-1-phenyl-3-pentanone. To a solution of (*S*)-2-(*tert*-Butyldimethylsilyloxy)-*N*-methoxy-*N*-methylpropionamide⁸ (2.88 g, 11.8 mmol) in THF (100 mL) at 0 °C, was added a solution of 4-phenethylmagnesium bromide in ether (15 mL of 1.0 M, 14.5 mmol). The resulting reaction mixture was stirred 1 h at 0 °C and then saturated NH₄Cl (30 mL) was added dropwise. The mixture was extracted with Et₂O (3 x 50 mL). The combined organic layers were washed with NaHCO₃ (40 mL), brine (40 mL), then were dried over MgSO₄. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (2% EtOAc/hexanes). The title compound (2.74 g, 70%) was obtained as a colorless oil. *R*_f 0.61 (10% EtOAc/hexanes). ¹H NMR (300 MHz, CDCl₃) δ 7.31-7.27 (m, 2H), 7.21-7.17 (m, 3H), 4.15 (q, *J* = 7 Hz, 1H), 2.91 (s, 4H), 1.25 (d, *J* = 7 Hz, 3H), 0.91 (s, 9H), 0.07 (s, 6H); ¹³C NMR (75 MHz, CDCl₃) δ 213.6, 141.8, 128.8, 128.7, 126.4, 75.4, 38.8, 29.7, 26.1, 21.2, 18.5, -4.33, -4.62; HMRS (MAB) calcd for C₁₃H₁₉O₂Si₁ [M-C₄H₉]⁺: 235.115433. Found: 235.114884. The enantiomeric excess was determined to be 97% (59:1) by chiral GC analysis (20% Permethylated B-Cyclodextrin, 130 °C isotherm, *t*_r 17.8 (minor), 30.9 (major) of the corresponding alcohol product after treatment of the ketone with HF•MeCN.

(S)-2-(*tert*-Butyldimethylsilyloxy)hexanal. To a solution of (*S*)-1,2-hexanediol⁹ (2.00 g, 16.9 mmol) in DMF (90 mL) and THF (30 mL), was added imidazole (2.65 g, 39.0 mmol), followed by *tert*-butyldimethylsilyl chloride (5.60 g, 37.2 mmol). The resulting reaction mixture was stirred for 12 h. The reaction mixture was diluted with Et₂O (200 mL) and was washed with saturated NH₄Cl (75 mL), saturated NaHCO₃ (75 mL), brine (75 mL), then dried over MgSO₄. The solvent was

⁷ Tomooka, K.; Kikuchi, M.; Igawa, K.; Suzuki, M.; Keong, P. H.; Nakai, T. *Angew. Chem., Int. Edit.* **2000**, *39*, 4502-4505.

⁸ Sakai, A.; Aoyama, T.; Shioiri, T. *Tetrahedron Lett.* **2000**, *41*, 6859-6863.

⁹ Schaus, S. E.; Brandes, B. D.; Larrow, J. F.; Tokunaga, M.; Hansen, K. B.; Gould, A. E.; Furrow, M. E.; Jacobsen, E. N. *J. Am. Chem. Soc.* **2002**, *124*, 1307-1315.

removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (5% EtOAc/hexanes). The desired (*S*)-1,2-bis-(*tert*-butyldimethylsilyloxy)hexane (5.83 g, 99%) was obtained as a colorless oil.

To a solution of (*S*)-1,2-bis-(*tert*-butyldimethylsilyloxy)hexane (4.76 g, 13.7 mmol) in THF (140 mL), was added acetic acid (4 mL), followed by tetrabutylammonium fluoride (15 mL of 1.00 M solution in THF, 15 mmol). The resulting reaction mixture was stirred for 14 h, and then saturated NH_4Cl (75 mL) was added dropwise. The mixture was extracted with EtOAc (3 x 100 mL) and the combined organic layers were dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (5% EtOAc/hexane). (*S*)-2-(*tert*-butyldimethylsilyloxy)hexanol (1.93 g, 62%) was obtained as a colorless oil.

To a solution (*S*)-2-(*tert*-butyldimethylsilyloxy)hexanol (0.99 g, 4.26 mmol) in dichloromethane (40 mL) was added the Dess-Martin periodane¹⁰ (3.63 g, 8.55 mmol). The resulting reaction mixture was stirred for 12 h and then poured in a mixture of 10% $\text{Na}_2\text{S}_2\text{O}_4$ (20 mL) and saturated NaHCO_3 (20 mL). The resulting biphasic mixture was stirred until both layers became colorless. The two layers were separated and the aqueous layer was extracted with EtOAc (3 x 75 mL). The combined organic layers were washed with NaHCO_3 (50 mL) and brine (50 mL) then dried over MgSO_4 . The solvent was removed under reduced pressure and the desired aldehyde (0.92 g, 94%) was obtained as a colorless oil. $[\alpha]_D = -23.4$ (c, 1.23, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 9.59 (d, $J = 2$ Hz, 1H), 3.96 (dt, $J = 6, 2$ Hz, 1H), 1.66-1.58 (m, 2H), 1.41-1.31 (m, 4H), 1.00-0.88 (m, 3H), 0.92 (s, 9H), 0.08 (s, 3H), 0.07 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 204.3, 77.5, 32.2, 26.6, 25.6, 22.4, 18.1, 13.7, -4.8, -5.1; Anal. Calcd for $\text{C}_{12}\text{H}_{26}\text{O}_2\text{Si} \cdot 1/2\text{H}_2\text{O}$: C, 60.20; H, 11.37. Found: C, 60.25; H, 11.30.

(*S*)-4-(*tert*-Butyldimethylsilyloxy)-1-phenyl-3-octanone. To a solution of (*S*)-2-(*tert*-butyldimethylsilyloxy)hexanal (655 mg, 2.84 mmol) in THF (20 mL) was added dropwise at -78°C a solution of phenylethylmagnesium bromide (11.8 mL of 0.60 M solution in ether, 7.08 mmol). The resulting reaction mixture was stirred, while warmed up to 0°C over a 5 hours period. A mixture of 10% aqueous hydrochloric acid (10 mL) and saturated NH_4Cl (10 mL) was added dropwise at 0°C . The mixture was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with 10% aqueous hydrochloric acid (20 mL), NaHCO_3 (20 mL) and brine (20 mL), then dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (5% EtOAc/hexane). (*S*)-4-(*tert*-butyl-dimethylsilyloxy)-1-phenyl-3-octanol (559 mg, 58%) was obtained as a colorless oil.

To a solution of (*S*)-4-(*tert*-butyldimethylsilyloxy)-1-phenyl-3-octanol (382 mg, 1.13 mmol) in dichloromethane (12 mL) was added the Dess-Martin periodate¹⁰ (1.99 g, 4.69 mmol). The resulting reaction mixture was stirred for 12 h, then 10% $\text{Na}_2\text{S}_2\text{O}_4$ (10 mL), saturated NaHCO_3 (10 mL) and EtOAc (20 mL) were successively added. The resulting biphasic mixture was stirred until both layers became colorless. The two layers were separated and the aqueous layer was extracted with EtOAc (3 x 20 mL). The combined organic layers were washed with NaHCO_3 (2 x 20 mL) and brine (20 mL) then dried over MgSO_4 . The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (1% Et_3N , 10% EtOAc/hexanes). The desired ketone (563 mg, 95%) was obtained as a colorless oil. R_f 0.67, (5% EtOAc/hexanes). $[\alpha]_D = -12.6$ (c, 0.83, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.30-7.25 (m, 2H), 7.22-7.16 (m, 3H), 4.01 (dd, $J = 7, 5$ Hz, 1H), 2.88 (s, 4H), 1.61-1.48 (m, 2H), 1.32-1.22 (m, 4H), 0.91 (s, 9H), 0.86 (t, $J = 7$ Hz, 3H), 0.04 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 212.9, 141.2, 128.3 (2C), 125.9, 78.7, 38.7, 34.4, 29.1, 26.7, 25.6, 22.4, 18.0, 13.7, -5.07, -5.11; Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2\text{Si}$:

¹⁰ Boeckman, R. K.; Shao, P.; Mullins, J. J. *Organic Synthesis*, **1999**, 77, 141-149.

C, 71.80; H, 10.24. Found: C, 71.03; H, 10.42. The enantiomeric excess was determined to be >99% (>200:1) by chiral GC analysis (20% Permethylated B-Cyclodextrin, 180 °C isotherm, t_r 8.94 (minor), 9.61 (major)) of the corresponding alcohol product after treatment of the ketone with HF•MeCN.

(S)-4-Benzyloxy-1-phenyl-3-octanone. To a solution of 5% HF•CH₃CN (3 mL) was added (S)-4-(*tert*-butyldimethylsilyloxy)-1-phenyl-3-octanone (93 mg, 0.28 mmol). The resulting reaction mixture was stirred for 3 h, then was diluted with EtOAc (10 mL) and saturated NaHCO₃ (5 mL). The mixture was extracted with EtOAc (2 x 10 mL). The combined organic layers were washed with brine (15 mL) and dried over MgSO₄. (S)-4-hydroxy-1-phenyl-3-octanone (49 mg, 80%) was obtained as a colorless oil after flash chromatography (20% EtOAc/hexanes).

To a solution of (S)-4-hydroxy-1-phenyl-3-octanone (49 mg, 0.22 mmol) in DCM (6 mL) and cyclohexane (1.5 mL) was added successively benzyl 2,2,2-trichloroacetimidate (110 mg, 0.44 mmol) and triflic acid (5 mg, 0.02 mmol) at 0 °C. The cooling bath is removed and after 12 hours at room temperature, the reaction mixture was filtered. The organic layer is washed with saturated NaHCO₃ (5 mL) and brine (5 mL) and dried over MgSO₄. The solvent was removed under reduced pressure. The desired ketone (46 mg, 66%) was obtained as a colorless oil after flash chromatography (10% EtOAc/hexanes) R_f 0.33 (10% EtOAc/hexanes). $[\alpha]_D$ -6.6 (*c*, 1.03, CHCl₃); ¹H NMR (400 MHz, CDCl₃) δ 7.38-7.27 (m, 7H), 7.22-7.19 (m, 3H), 4.49 (d, *J* = 12 Hz, 1H), 4.36 (d, *J* = 12 Hz, 1H), 3.77 (dd, *J* = 8, 5. Hz, 1H), 2.94-2.85 (m, 4H), 1.67-1.53 (m, 2H), 1.38-1.22 (m, 4H), 0.87 (t, *J* = 7 Hz, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 212.7, 141.6, 138.0, 128.9, 128.8, 128.3, 126.5, 85.5, 72.8, 39.7, 32.1, 29.7, 27.7, 22.9, 14.3; HMRS (MAB) calcd for C₂₁H₂₆O₂ [M+1]⁺: 311.201105. Found: 311.202047. The enantiomeric excess was determined to be >99% (>200:1) by chiral HPLC analysis (Chiracel OJ, 1mL/min, 2% 2-propanol/hexane, t_r 13.0 (minor), 14.5 (major)).

(S)-1-(*tert*-Butyldimethylsilyloxy)-1,4-diphenyl-2-butanone. The title compound was prepared from crude (S)-(*tert*-butyldimethylsilyloxy)-2-phenylacetaldehyde¹¹ (375 mg, 1.50 mmol) according to the procedure described for the synthesis of (S)-4-(*tert*-butyldimethylsilyloxy)-1-phenyl-3-octanone. The desired alcohol (251 mg, 47%) was obtained as a mixture of diastereoisomers. Further oxidation of the alcohol (234 mg, 0.655 mmol) furnished the desired ketone (212 mg, 92%) as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.29 (5% EtOAc/hexanes). $[\alpha]_D$ = +34.8 (*c*, 0.98, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.41-7.30 (m, 2H), 7.35-7.20 (m, 6H), 7.16-7.06 (m, 2H), 5.09 (s, 1H), 2.97-2.92 (m, 1H), 2.80-2.72 (m, 3H), 0.93 (s, 9H), 0.06 (s, 3H), -0.02 (s, 3H); ¹³C NMR (75 MHz, CDCl₃) δ 210.1, 141.6, 139.0, 128.9, 128.8, 128.6, 128.4, 126.4, 126.3, 81.6, 37.9, 29.8, 26.2, 18.6, -4.52, -4.71; Anal. Calcd for C₂₂H₃₀O₂Si: C, 74.53; H, 8.53. Found: C, 74.45; H, 9.02. The enantiomeric excess was determined to be 94% (33:1) by chiral HPLC analysis (Chiracel OD, 1mL/min, 2% 2-propanol/hexane, t_r 33.3 (major), 41.7 (minor)) of the corresponding alcohol product after treatment of the ketone with HF•MeCN.

¹¹ Joly, G. D.; Jacobsen, E. N. *Org. Lett.* **2002**, *4*, 1795-1798.

(S)-1-Benzyloxy-1,4-diphenyl-2-butanone. The title compound was prepared from (S)-benzyloxyphenylacetaldehyde¹² (323 mg, 1.43 mmol) according to the procedure described for the synthesis of (S)-4-(*tert*-Butyldimethylsilanyloxy)-1-phenyl-3-octanone. The desired alcohol (245 mg, 51%) was obtained as a mixture of diastereoisomers. Further oxidation of the alcohol (78.0 mg, 0.235 mmol) furnished the desired ketone (77 mg, 99%) as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.37 (5% EtOAc/hexanes). $[\alpha]_D^{25} = +14.8$ (c, 0.61, CHCl₃); ¹H NMR (300 MHz, CDCl₃) δ 7.61-7.07 (m, 15H), 4.83 (s, 1H), 4.58 (d, $J = 12$ Hz, 1H), 4.43 (d, $J = 12$ Hz, 1H), 2.98-2.73 (m, 4H); ¹³C NMR (75 MHz, CDCl₃) δ 207.6, 140.8, 137.1, 135.8, 128.7, 128.41, 128.34, 128.24, 128.17, 127.8, 127.7, 127.0, 125.9, 86.4, 70.9, 39.0, 29.2; HMRS (MAB) calcd for C₂₃H₂₃O₂ [M+1]⁺: 331.169805. Found: 331.168710. The enantiomeric excess was determined to be 95% (39:1) by chiral HPLC analysis (Chiracel OD, 1mL/min, 2% 2-propanol/hexane, t_r 33.3 (major), 41.7 (minor)) of the corresponding alcohol product after treatment of the ketone with H₂, Pd/C in EtOAc.

¹² Chan, T. H.; Li, C. J. *Can. J. Chem.* **1992**, 70, 2726-2729.

General procedure for the methylenation of ketones.

Method A. THF

To a solution of chlorotris(triphenylphosphine)rhodium (0.023 g, 0.025 mmol) and triphenylphosphine (0.29 g, 1.10 mmol) in THF (10 mL) at 25 °C, was added 2-propanol (0.77 mL, 10.0 mmol) followed by the ketone (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.40 mL, 1.60 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 25 °C. When the reaction is completed by GC or TLC analysis, the solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel with a pre-absorption on silica or by distillation.

Method B. 1,4-Dioxane

To a solution of chlorotris(triphenylphosphine)rhodium (0.023 g, 0.025 mmol) and triphenylphosphine (0.29 g, 1.10 mmol) in 1,4-dioxane (10 mL) at 60 °C, was added 2-propanol (1.15 mL, 15.0 mmol) followed by the ketone (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.40 mL, 2.40 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 60 °C. When the reaction is completed by GC or TLC analysis, the solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel with a pre-absorption on silica or by distillation.

Method C : THF / Oxone work-up.

To a solution of chlorotris(triphenylphosphine)rhodium (0.023 g, 0.025 mmol) and triphenylphosphine (0.29 g, 1.10 mmol) in THF (10 mL) at 25 °C, was added 2-propanol (0.77 mL, 10.0 mmol) followed by the ketone (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.40 mL, 1.60 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 60 °C. When the reaction is completed by GC or TLC analysis, addition of Oxone (0.615 mg, 1.00 mmol) was done and NaHCO_3 was added to maintain the pH neutral in the case of acid sensitive products.¹³ The resulting mixture was stirred for 2 hours at 60 °C. The mixture was then diluted with dichloromethane (30 mL), washed with saturated NaHCO_3 (15 mL) and brine (15 mL). The organic layer was dried over MgSO_4 and the solvent was removed under reduced pressure. The crude alkene was purified by flash chromatography on silica gel or by distillation.

Method D : 1,4-Dioxane / Oxone work-up.

To a solution of chlorotris(triphenylphosphine)rhodium (0.023 g, 0.025 mmol) and triphenylphosphine (0.29 g, 1.10 mmol) in 1,4-dioxane (10 mL) at 60 °C, was added 2-propanol (1.15 mL, 15.0 mmol) followed by the ketone (1.00 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.40 mL, 2.40 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 60 °C. When the reaction is completed by GC or TLC analysis, addition of Oxone¹⁴ (0.615 mg, 1.00 mmol) was done and NaHCO_3 was added to maintain the pH neutral in the case of acid sensitive products. The resulting mixture was stirred for

¹³ Oxone (potassium peroxymonosulphate) is known as a stable and easily handled reagent, but should be always treated as potentially explosive, as all peroxides. However, no problems were encountered with this reagent in the present study.

2 hours at 60 °C. The mixture was then diluted with dichloromethane (30 mL), washed with saturated NaHCO₃ (15 mL) and brine (15 mL). The organic layer was dried over MgSO₄ and the solvent was removed under reduced pressure. The crude alkene was purified by flash chromatography on silica gel or by distillation.

Wittig procedure for the methylenation of ketones.

Method E : Methyltriphenylphosphonium bromide and NaHMDS in THF.

To a solution of methyltriphenylphosphonium bromide (393 mg, 1.10 mmol) in THF (10 mL), was added sodium hexamethyldisilazide (202 mg, 1.10 mmol). The resulting yellow mixture was stirred for 1 hour at room temperature. The ketone (1.00 mmol) was then added and the solution was stirred at 25 °C until the reaction is completed by GC analysis or by TLC. The solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel or by distillation.

Method F : Methyltriphenylphosphonium bromide and NaHMDS in 1,4-dioxane.

To a solution of methyltriphenylphosphonium bromide (393 mg, 1.10 mmol) in 1,4-dioxane (10 mL), was added sodium hexamethyldisilazide (202 mg, 1.10 mmol). The resulting yellow mixture was stirred for 1 hour at 60 °C. The ketone (1.00 mmol) was then added and the solution was stirred at 60 °C until the reaction is completed by GC analysis or by TLC. The solvent was removed under reduced pressure and the crude alkene was purified by flash chromatography on silica gel or by distillation.

Characterization of Alkene Products

5-(1-Acetoxymethylvinyl)benzo[1,3]dioxole (1). The title compound was prepared from 1-benzo[1,3]dioxol-5-yl-2-acetoxyethanone (64 mg, 0.29 mmol) according to the general procedure **A**. The desired alkene **1** (38 mg, 61%) was obtained as a colorless oil after flash chromatography (4% EtOAc/hexanes). R_f 0.22 (10% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 6.94 (s, 1H), 6.91 (d, $J = 9$ Hz, 1H), 6.79 (d, $J = 9$ Hz, 1H), 5.97 (s, 2H), 5.45 (s, 1H), 5.29 (s, 1H), 4.91 (s, 2H), 2.09 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 170.6, 147.7, 147.4, 141.8, 132.1, 119.5, 114.3, 108.0, 106.4, 101.0, 65.8, 20.9. Anal. Calcd for $\text{C}_{12}\text{H}_{12}\text{O}_4$: C, 65.45; H, 5.49. Found: C, 64.90; H, 5.68.

5-(1-Benzoxymethylvinyl)benzo[1,3]dioxole (2). The title compound was prepared from 1-benzo[1,3]dioxol-5-yl-2-benzyloxyethanone (71 mg, 0.25 mmol) according to the general procedure **A**. The desired alkene **2** (58 mg, 82%) was obtained as a white solid after flash chromatography (1% EtOAc/hexanes). R_f 0.38 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 8.04 (d, $J = 7$ Hz, 2H), 7.58-7.53 (m, 1H), 7.43 (t, $J = 7$ Hz, 2H), 7.02 (s, 1H), 6.99 (d, $J = 8$ Hz, 1H), 6.81 (d, $J = 8$ Hz, 1H), 5.97 (s, 2H), 5.51 (s, 1H), 5.40 (s, 1H), 5.18 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 148.3, 147.9, 142.4, 133.5, 132.7, 130.4, 130.1, 128.9, 120.1, 114.8, 108.6, 107.0, 101.6, 66.7. Anal. Calcd for $\text{C}_{17}\text{H}_{14}\text{O}_4$: C, 72.33; H, 5.00. Found: C, 72.40; H, 4.98.

1-(1-Benzoxymethylvinyl)-4-methoxybenzene (3). The title compound was prepared from 2-benzyloxy-1-(4-methoxyphenyl)ethanone (150 mg, 0.56 mmol) according to the general procedure **A**. The desired alkene **3** (122 mg, 82%) was obtained after flash chromatography (1% EtOAc/hexanes), as a colorless oil, which solidify upon standing. R_f 0.57 (20% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 8.08-8.05 (m, 2H), 7.58-7.53 (m, 1H), 7.49-7.41 (m, 4H), 6.93-6.90 (m, 2H), 5.56 (s, 1H), 5.40 (s, 1H), 5.24 (s, 2H), 3.82 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.7, 159.4, 142.2, 133.5, 130.9, 130.5, 130.1, 128.8, 127.6, 114.3, 114.0, 66.7, 55.7; Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10; H, 6.01. Found: C, 76.01; H, 6.29.

1-(1-Benzoxymethylvinyl)-4-bromobenzene (4). The title compound was prepared from 2-benzyloxy-1-(4-bromophenyl)ethanone (150 mg, 0.47 mmol) according to the general procedure **A**. The desired alkene **4** (110 mg, 74%) was obtained after flash chromatography (100% hexanes, then 2% EtOAc/hexanes), as a colorless oil, which solidify upon standing. R_f 0.43 (10% EtOAc/hexanes); mp 49 °C; ^1H NMR (400 MHz, CDCl_3) δ 8.04-8.01 (m, 2H), 7.58-7.36 (m, 7H), 5.62 (s, 1H), 5.50 (s, 1H), 5.21 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.0, 141.4, 136.8, 133.0, 131.5, 129.7, 129.5, 128.3, 127.5, 122.0, 115.9, 65.8; Anal. Calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$: C, 76.10; H, 6.01. Found: C, 76.01; H, 6.29.

(2-Benzoxymethyl)-4-phenylbutene (5). The title compound was prepared from 1-benzoxymethyl-4-phenyl-2-butanone (200 mg, 0.75 mmol) according to the general procedure A. The desired alkene **5** (148 mg, 74%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.50 (20% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 8.13-8.09 (m, 2H), 7.60-7.57 (m, 1H), 7.50-7.45 (m, 2H), 7.34-7.20 (m, 5H), 5.21 (s, 1H), 5.08 (s, 1H), 4.84 (s, 2H), 2.88 (t, J = 8 Hz, 2H), 2.50 (t, J = 8 Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 166.2, 143.2, 141.5, 132.9, 130.0, 129.5, 128.3, 128.29, 128.25, 125.9, 113.0, 67.2, 35.0, 34.0. Anal. Calcd for $\text{C}_{18}\text{H}_{18}\text{O}_2$: C, 81.28; H, 7.01. Found: C, 81.17; H, 6.81.

(2-Benzoxymethyl)-4-benzyloxyhexene (6). The title compound was prepared from 1-benzoxymethyl-4-benzyloxy-2-hexanone (70 mg, 0.21 mmol) according to the general procedure C. The desired alkene **6** (58 mg, 84%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.29 (5% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 8.10-8.06 (m, 2H), 7.60-7.55 (m, 1H), 7.48-7.42 (m, 2H), 7.38-7.25 (m, 5H), 5.15 (s, 1H), 5.01 (s, 1H), 4.79 (s, 2H), 4.51 (s, 2H), 3.50 (t, J = 6 Hz, 2H), 2.18 (t, J = 7 Hz, 2H), 1.69-1.58 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 166.7, 144.2, 139.0, 133.4, 130.7, 130.1, 128.81, 128.78, 128.0, 127.9, 112.9, 73.3, 70.5, 67.7, 33.5, 29.8, 24.6; Anal. Calcd for $\text{C}_{21}\text{H}_{24}\text{O}_3$: C, 77.75; H, 7.46. Found: C, 77.42; H, 7.70.

2-Phenethyl-2-propenol (7). To a solution of chlorotris(triphenylphosphine)rhodium (0.028 g, 0.031 mmol) and triphenylphosphine (323 mg, 1.28 mmol) in THF (12 mL) at 25 °C, was added 2-propanol (1.00 mL, 12.2 mmol) followed by 1-hydroxy-4-phenyl-2-butanone (200 mg, 1.22 mmol). To the resulting red mixture, was then added a solution of trimethylsilyldiazomethane (0.70 mL, 1.95 mmol). Gas evolution was observed and the resulting dark orange mixture was stirred at 25 °C. When the reaction is completed by GC or TLC analysis, a 1.0 M solution of TBAF in THF (1.50 mL, 1.50 mmol) was then added and the reaction was stirred for an additional 30 minutes. The reaction mixture was then diluted with dichloromethane (30 mL) and saturated NH_4Cl (30 mL). The aqueous layer was extracted with dichloromethane (4 x 10 mL). The combined organic layers were washed with brine (30 mL), then dried over magnesium sulfate. The solvent was then removed under reduced pressure and the crude alkene was purified by flash chromatography (20% EtOAc/hexanes) on silica gel with a pre-absorption on silica. The desired alkene **7** (119 mg, 60%) was obtained as a colorless oil. R_f 0.31 (20% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.26 (m, 2H), 7.22-7.19 (m, 3H), 5.08 (s, 1H), 5.93 (s, 1H), 4.10 (s, 2H), 2.80 (t, J = 8 Hz, 2H), 2.39 (t, J = 8 Hz, 2H), 1.45 (s (br), 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.3, 141.7, 128.2, 128.18, 125.8, 109.7, 65.9, 34.5, 34.1.

(2-Methoxymethoxymethyl)-4-phenylbutene (8). The title compound was prepared from 1-methoxymethoxy-4-phenyl-2-butanone (164 mg, 0.79 mmol) according to the general procedure A. The desired alkene **8** (120 mg, 74%) was obtained as a colorless oil after flash chromatography (7% EtOAc/hexanes). R_f 0.34 (10% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.27 (m, 2H), 7.21-7.16 (m, 3H), 5.09 (s, 1H), 4.97 (s, 1H), 4.65 (s, 2H), 4.03 (s, 2H), 3.39 (s, 3H), 2.80 (t, J =

8 Hz, 2H), 2.40 (t, $J = 8$ Hz, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.6, 142.3, 128.7, 126.3, 112.5, 96.1, 70.6, 55.8, 35.4, 34.5. HMRS (MAB) calcd for $\text{C}_{13}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$: 206.130680. Found: 206.131086.

(2-Benzyloxymethyl)-4-phenylbutene (9). The title compound was prepared from 1-benzyloxy-4-phenyl-2-butanone (371 mg, 1.46 mmol) according to the general procedure A. The desired alkene **9** (310 mg, 84%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.29 (5% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.49-7.46 (m, 4H) 7.39-7.27 (m, 3H), 7.22-7.19 (m, 3H), 5.09 (s, 1H), 4.99 (s, 1H), 4.51 (s, 2H), 4.00 (s, 2H), 2.80 (t, $J = 8$ Hz, 2H), 2.42 (t, $J = 8$ Hz, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.0, 142.4, 138.7, 128.84, 128.83, 128.78, 128.2, 128.0, 126.3, 112.7, 73.7, 72.4, 35.3, 34.6. Anal. Calcd for $\text{C}_{18}\text{H}_{20}\text{O}$: C, 85.67; H, 7.99. Found: C, 85.52; H, 8.44.

(2-Benzyloxymethyl)-4-phenylbutene (9). The title compound was prepared from 1-benzyloxy-4-phenyl-2-butanone (140 mg, 0.55 mmol) according to the general procedure E. The desired alkene **9** (86 mg, 62%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

4-Phenyl-2-(tetrahydropyran-2-yloxymethyl)butene (10). The title compound was prepared from 4-phenyl-1-(tetrahydropyran-2-yloxy)-2-butanone (156 mg, 0.64 mmol) according to the general procedure A. The desired alkene **10** (129 mg, 83%) was obtained as a colorless oil after flash chromatography (4% EtOAc/hexanes). R_f 0.13 (2% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.26 (m, 2H) 7.22-7.17 (m, 3H), 5.09 (s, 1H), 4.95 (s, 1H), 4.64 (t, $J = 3$ Hz, 1H), 4.23 (d, $J = 13$ Hz, 1H), 3.80 (d, $J = 13$ Hz, 1H), 3.90-3.85 (m, 1H), 3.57-3.49 (m, 1H), 2.88-2.78 (m, 2H), 2.40 (t, $J = 8$ Hz, 2H), 1.89-1.51 (m, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.9, 142.4, 128.77, 128.73, 126.2, 112.0, 98.2, 70.3, 62.5, 35.5, 34.6, 31.0, 25.9, 19.8. Anal. Calcd for $\text{C}_{16}\text{H}_{22}\text{O}_2$: C, 78.01; H, 9.00. Found: C, 77.91; H, 9.41.

4-Phenyl-2-(triethylsilyloxymethyl)butene (11). The title compound was prepared from 4-phenyl-1-(triethylsilyloxy)-2-butanone (153 mg, 0.55 mmol) according to the general procedure A. The desired alkene **11** (113 mg, 74%) was obtained as a colorless oil after flash chromatography (0.5% EtOAc/toluene). R_f 0.88 (0.5% EtOAc/toluene); ^1H NMR (300 MHz, CDCl_3) δ 7.34-7.26 (m, 3H), 7.22-7.17 (m, 5H), 5.09 (s, 1H), 4.89 (s, 1H), 4.10 (s, 2H), 2.81-2.76 (m, 2H), 2.34 (t, $J = 8$ Hz, 2H), 0.98 (t, $J = 8$ Hz, 9H), 0.63 (q, $J = 8$ Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.4, 142.5, 128.73, 128.72, 126.2, 109.6, 66.1, 34.9, 34.8, 7.23, 4.84.

4-Phenyl-2-(tert-butyldimethylsilyloxymethyl)butene (12). The title compound was prepared from 4-phenyl-1-(tert-butyldimethylsilyloxy)-2-butanone (200 mg, 0.72 mmol) according to the general procedure A. The desired alkene **12** (186 mg, 94%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.78 (10% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.32-7.26 (m, 3H), 7.22-7.17 (m, 2H), 5.07 (s, 1H), 4.88 (s, 1H), 4.10 (s, 2H), 2.80-2.75

(m, 2H), 2.33 (t, $J = 8$ Hz, 2H), 0.92 (s, 9H), 0.08 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.0, 142.0, 128.2(2C), 125.7, 109.9, 65.9, 34.4, 34.3, 25.8, 18.3, 7.23, -5.49.

4-Phenyl-2-(triisopropylsilyloxy)butene (13). The title compound was prepared from 4-phenyl-1-(triisopropylsilyloxy)-2-butanone (196 mg, 0.61 mmol) according to the general procedure A. The desired alkene **13** (189 mg, 97%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.83 (5% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.31-7.19 (m, 5H), 5.13 (s, 1H), 4.88 (s, 1H), 4.17 (s, 2H), 2.82-2.76 (m, 2H), 2.34 (t, $J = 8$ Hz, 2H), 1.16-1.04 (m, 3H), 1.08 (s, 18H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.1, 142.0, 128.2(2C), 125.7, 108.5, 66.0, 34.4, 34.3, 17.9, 11.9.

4-Phenyl-1-(triisopropylsilyloxy)butene (13). The title compound was prepared from 4-phenyl-1-(triisopropylsilyloxy)-2-butanone (97 mg, 0.30 mmol) according to the general procedure E. The desired alkene **13** (84 mg, 87%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes).

6-Benzyloxy-2-(benzyloxymethyl)hexene (14). The title compound was prepared from 1,6-bisbenzyloxyhexan-2-one (50 mg, 0.16 mmol) according to the general procedure C (reaction time: 2 h). The desired alkene **14** (42 mg, 84%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes); R_f 0.28 (5% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.26 (m, 10H), 5.07 (s, 1H), 4.95 (s, 1H), 4.52 (s, 2H), 4.50 (s, 2H), 3.98 (s, 2H), 3.50 (t, $J = 6$ Hz, 2H), 2.13 (t, $J = 7$ Hz, 2H), 1.68-1.55 (m, 4H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.3, 139.1, 138.9, 128.8 (2C), 128.1, 128.0, 127.94, 127.9, 112.2, 73.5, 73.3, 72.3, 70.6, 33.3, 29.9, 24.6; HMRS (MAB) calcd for $\text{C}_{21}\text{H}_{26}\text{O}_2$ $[M]^+$: 310.193280. Found: 310.191756.

6-Benzyloxy-2-(benzyloxymethyl)hexene (14). The title compound was prepared from 1,6-bisbenzyloxyhexan-2-one (50 mg, 0.16 mmol) according to the general procedure E (reaction time: 2 h). The desired alkene **14** (41 mg, 82%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

6-Benzyloxy-2-(tetrahydropyranyl-2-oxymethyl)hexene (15). The title compound was prepared from 6-benzyloxy-1-(tetrahydropyranyl-2-yloxy)hexan-2-one (50 mg, 0.16 mmol) according to the general procedure A (reaction time: 2 h). The desired alkene **15** (34 mg, 68%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.30 (8% EtOAc/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.25 (m, 5H), 5.05 (s, 1H), 4.90 (s, 1H), 4.62 (t, $J = 3$ Hz, 1H), 4.51 (s, 2H), 4.17 (d, $J = 13$ Hz, 1H), 3.90 (d, $J = 13$ Hz, 1H), 3.90-3.83 (m, 1H), 3.55-3.53 (m, 1H), 3.49 (t, $J = 6$ Hz, 2H), 2.09 (t, $J = 8$ Hz, 2H), 1.88-1.50 (m, 10H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.3, 139.0, 128.8, 128.0, 127.9, 111.6, 98.1, 73.3, 70.6, 70.1, 62.5, 33.5, 31.0, 29.9, 25.9, 24.6, 19.8; Anal. Calcd for $\text{C}_{19}\text{H}_{28}\text{O}_3$: C, 74.96; H, 9.27. Found: C, 74.46; H, 9.71.

6-Benzyloxy-2-(tetrahydropyranyl-2-oxymethyl)hexene (15). The title compound was prepared from 6-benzyloxy-1-(tetrahydropyranyl-2-yloxy)hexan-2-one (77 mg, 0.25 mmol) according to the

general procedure **E** (reaction time: 2 h). The desired alkene **15** (55 mg, 72%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

6-Benzyloxy-2-(triethylsilanyloxymethyl)hexene (16). The title compound was prepared from 6-benzyloxy-1-triethylsilanyloxyhexan-2-one (172 mg, 0.51 mmol) according to the general procedure **A**. The desired alkene **16** (142 mg, 83%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.25 (2% EtOAc/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.35-7.26 (m, 5H), 5.05 (s, 1H), 4.82 (s, 1H), 4.51 (s, 2H), 4.07 (s, 2H), 3.49 (t, J = 6 Hz, 2H), 2.04 (t, J = 8 Hz, 2H), 1.64-1.62 (m, 2H), 1.57-1.53 (m, 2H), 0.97 (t, J = 8 Hz, 9H), 0.62 (q, J = 8 Hz, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.8, 139.1, 128.8, 128.0, 127.9, 109.0, 73.3, 70.6, 65.9, 32.9, 29.9, 24.8, 7.20, 4.85.

6-Benzyloxy-2-(triethylsilanyloxymethyl)hexene (16). The title compound was prepared from 6-benzyloxy-1-triethylsilanyloxyhexan-2-one (50 mg, 0.15 mmol) according to the general procedure **E** (reaction time: 2 h). The desired alkene **16** (38 mg, 75%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

6-Benzyloxy-2-(tert-butyldimethylsilanyloxymethyl)hexene (17). The title compound was prepared from 6-benzyloxy-1-*tert*-butyldimethylsilanyloxyhexan-2-one (316 mg, 0.94 mmol) according to the general procedure **A**. The desired alkene **17** (238 mg, 77%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.24 (1% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.35-7.25 (m, 5H), 5.03 (s, 1H), 4.81 (s, 1H), 4.51 (s, 2H), 4.07 (s, 2H), 3.48 (t, J = 6 Hz, 2H), 2.03 (t, J = 8 Hz, 2H), 1.67-1.51 (m, 4H), 0.92 (s, 9H), 0.07 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.8, 139.0, 128.8, 128.0, 127.9, 108.9, 73.3, 70.6, 66.2, 32.9, 30.0, 26.3, 24.8, 18.8, -4.95; Anal. Calcd for $\text{C}_{20}\text{H}_{34}\text{O}_2\text{Si}$: C, 71.80; H, 10.24. Found: C, 71.64; H, 10.76.

6-Benzyloxy-2-(tert-butyldimethylsilanyloxymethyl)hexene (17). The title compound was prepared from 6-benzyloxy-1-*tert*-butyldimethylsilanyloxyhexan-2-one (85 mg, 0.25 mmol) according to the general procedure **E** (reaction time: 2 h). The desired alkene **17** (58 mg, 69%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

6-Benzyloxy-2-(triisopropylsilanyloxymethyl)hexene (18). The title compound was prepared from 6-benzyloxy-1-triisopropylsilanyloxyhexan-2-one (190 mg, 0.50 mmol) according to the general procedure **A**. The desired alkene **18** (189 mg, 73%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.10 (1% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.36-7.26 (m, 5H), 5.11 (s, 1H), 4.83 (s, 1H), 4.51 (s, 2H), 4.15 (s, 2H), 3.49 (t, J = 6 Hz, 2H), 2.04 (t, J = 8 Hz, 2H), 1.66-1.55 (m, 4H), 1.16-1.04 (m, 3H), 1.09 (s, 18H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.3, 138.5, 128.2, 127.5, 127.3, 108.0, 72.7, 70.1, 65.8, 32.4, 29.4, 24.3, 17.9, 11.9; Anal. Calcd for $\text{C}_{23}\text{H}_{40}\text{O}_2\text{Si}$: C, 73.34; H, 10.70. Found: C, 73.24; H, 11.41.

6-Benzyloxy-2-(triisopropylsilanyloxymethyl)hexene (18). The title compound was prepared from 6-benzyloxy-1-triisopropylsilanyloxyhexan-2-one (76 mg, 0.20 mmol) according to the

general procedure E (reaction time: 2 h). The desired alkene **18** (55 mg, 73%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

5-(1-Benzyloxymethylvinyl)benzo[1,3]dioxole (19). The title compound was prepared from 1-benzo[1,3]dioxol-5-yl-2-benzyloxyethanone (102 mg, 0.38 mmol) according to the general procedure C. The desired alkene **19** (75 mg, 74%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.20 (5% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.34–7.29 (m, 5H), 7.00 (s, 1H), 6.98 (d, J = 8 Hz, 1H), 6.78 (d, J = 8 Hz, 1H), 5.96 (s, 2H), 5.45 (s, 1H), 5.29 (s, 1H), 4.57 (s, 2H), 4.36 (s, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.1, 147.7, 144.0, 138.5, 133.4, 128.8, 128.2, 128.0, 120.2, 114.1, 108.5, 107.1, 101.4, 72.6, 72.2; HMRS (MAB) calcd for $\text{C}_{17}\text{H}_{16}\text{O}_3$ $[\text{M}]^+$: 268.109945. Found: 268.110376.

5-[1-(Tetrahydropyran-2-yloxymethyl)vinyl]benzo[1,3]dioxole (20). The title compound was prepared from 1-benzo[1,3]dioxol-5-yl-2-(tetrahydropyran-2-yloxy)ethanone (50 mg, 0.16 mmol) according to the general procedure C. The desired alkene **20** (42 mg, 83%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.30 (5% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.00 (s, 1H), 6.97 (d, J = 8 Hz, 1H), 6.78 (d, J = 8 Hz, 1H), 5.96 (s, 2H), 5.43 (s, 1H), 5.31 (s, 1H), 4.72 (t, J = 4 Hz, 1H), 4.59 (d, J = 13 Hz, 1H), 4.30 (d, J = 13 Hz, 1H), 3.92–3.83 (m, 1H), 3.55–3.51 (m, 1H), 1.87–1.51 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.6, 147.0, 143.5, 133.1, 119.5, 113.0, 107.9, 106.5, 100.9, 97.6, 68.6, 62.1, 30.4, 25.3, 19.2; HMRS (MAB) calcd for $\text{C}_{15}\text{H}_{18}\text{O}_4$ $[\text{M}]^+$: 262.120509. Found: 262.121393.

5-[1-(tert-Butyldimethylsilyloxymethyl)vinyl]benzo[1,3]dioxole (21). The title compound was prepared from 1-benzo[1,3]dioxol-5-yl-2-(tert-butyldimethylsilyloxy)ethanone (125 mg, 0.43 mmol) according to the general procedure C. The desired alkene **21** (109 mg, 87%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.48 (5% EtOAc/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 6.93 (s, 1H), 6.88 (d, J = 8 Hz, 1H), 6.77 (d, J = 8 Hz, 1H), 5.96 (s, 2H), 5.34–5.31 (m, 2H), 4.46 (s, 2H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 147.5, 146.9, 146.3, 133.2, 119.3, 110.4, 107.9, 106.6, 100.8, 64.7, 25.8, 18.2, -5.47; HMRS (MAB) calcd for $\text{C}_{16}\text{H}_{24}\text{O}_3$ $[\text{M}]^+$: 292.149473. Found: 292.148355.

5-[1-(tert-Butyldimethylsilyloxymethyl)vinyl]benzo[1,3]dioxole (21). The title compound was prepared from 1-benzo[1,3]dioxol-5-yl-2-(tert-butyldimethylsilyloxy)ethanone (109 mg, 0.37 mmol) according to the general procedure E. The desired alkene **21** (93 mg, 86%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

1-Methoxy-4-(1-benzyloxymethylvinyl)benzene (22). The title compound was prepared from 2-benzyloxy-1-(4-methoxyphenyl)ethanone (76 mg, 0.30 mmol) according to the general procedure

A. The desired alkene **22** (48 mg, 64%) was obtained as a white solid after flash chromatography (5% EtOAc/hexanes). R_f 0.57 (20% EtOAc/hexanes). mp 95 °C; ^1H NMR (400 MHz, CDCl_3) δ 7.46 (d, J = 7 Hz, 2H), 7.36-7.32 (m, 5H), 6.90 (d, J = 7 Hz, 2H), 5.50 (s, 1H), 5.30 (s, 1H), 4.57 (s, 2H), 4.41 (s, 2H), 3.83 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.2, 143.3, 138.1, 131.1, 128.2, 127.7, 127.4, 127.2, 113.6, 112.9, 72.1, 71.7, 55.2; HMRS (MAB) calcd for $\text{C}_{17}\text{H}_{18}\text{O}_2$ $[\text{M}]^+$: 254.130680. Found: 254.131112.

1-Methoxy-4-(1-benzyloxymethylvinyl)benzene (22). The title compound was prepared from 2-benzyloxy-1-(4-methoxyphenyl)ethanone (110 mg, 0.43 mmol) according to the general procedure **E**. The desired alkene **22** (64 mg, 59%) was obtained as a white solid after flash chromatography (5% EtOAc/hexanes).

1-Methoxy-4-(1-triethylsilyloxymethylvinyl)benzene (23). The title compound was prepared from 1-(4-methoxyphenyl)-2-(triethylsilyloxy)ethanone (138 mg, 0.49 mmol) according to the general procedure **A**. The desired alkene **23** (109 mg, 79%) was obtained as a colorless oil after flash chromatography (1% Ether/pentane). R_f 0.45 (5% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.37 (d, J = 8 Hz, 2H), 6.88 (d, J = 8 Hz, 2H), 5.36 (s, 1H), 5.34 (s, 1H), 4.51 (s, 2H), 3.82 (s, 3H), 0.99 (t, J = 8 Hz, 9H), 0.66 (q, J = 8 Hz, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.1, 146.1, 131.5, 127.0, 113.5, 109.9, 64.4, 55.1, 6.67, 4.37; HMRS (MAB) calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Si}$ $[\text{M}]^+$: 278.170209. Found: 278.170080.

1-Methoxy-4-(1-triethylsilyloxymethylvinyl)benzene (23). The title compound was prepared from 1-(4-methoxyphenyl)-2-(triethylsilyloxy)ethanone (124 mg, 0.44 mmol) according to the general procedure **E**. The desired alkene **23** (75 mg, 61%) was obtained as a colorless oil after flash chromatography (1% Ether/pentane).

1-Methoxy-4-(1-tert-butyldimethylsilyloxymethylvinyl)benzene (24). The title compound was prepared from 1-(4-methoxyphenyl)-2-(tert-butyldimethylsilyloxy)ethanone (144 mg, 0.51 mmol) according to the general procedure **C**. The desired alkene **24** (120 mg, 84%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.47 (5% EtOAc/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.36 (d, J = 9 Hz, 2H), 6.88 (d, J = 9 Hz, 2H), 5.36 (s, 1H), 5.32 (s, 1H), 4.51 (s, 2H), 3.82 (s, 3H), 0.94 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 159.6, 146.7, 132.0, 127.5, 114.0, 110.3, 65.2, 55.7, 26.3, 18.8, -4.90; HMRS (MAB) calcd for $\text{C}_{16}\text{H}_{26}\text{O}_2\text{Si}$ $[\text{M}]^+$: 278.170209. Found: 278.169631.

1-Methoxy-4-(1-tert-butyldimethylsilyloxymethylvinyl)benzene (24). The title compound was prepared from 1-(4-methoxyphenyl)-2-(tert-butyldimethylsilyloxy)ethanone (104 mg, 0.37 mmol) according to the general procedure **E**. The desired alkene **24** (89 mg, 86%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

1-Bromo-4-(1-benzyloxymethylvinyl)benzene (25). The title compound was prepared from 2-benzyloxy-1-(4-bromophenyl)ethanone (87 mg, 0.29 mmol) according to the general procedure **A**.

The desired alkene **25** (64 mg, 74%) was obtained as a colorless oil after flash chromatography (3% EtOAc/hexanes). R_f 0.48 (10% EtOAc/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.48 (d, J = 9 Hz, 2H), 7.38-7.32 (m, 7H), 5.58 (s, 1H), 5.41 (s, 1H), 4.57 (s, 2H), 4.40 (s, 2H); ^{13}C NMR (100 MHz, CDCl_3) δ 143.6, 138.4, 138.0, 131.9, 128.8, 128.3, 128.2, 128.1, 122.2, 115.8, 72.4, 72.3; HMRS (MAB) calcd for $\text{C}_{16}\text{H}_{15}\text{OBr}$ $[\text{M}]^+$: 302.030626. Found: 302.029336.

1-Bromo-4-(1-benzyloxymethylvinyl)benzene (25). The title compound was prepared from 2-benzyloxy-1-(4-bromophenyl)ethanone (58 mg, 0.19 mmol) according to the general procedure E. The desired alkene **25** (38 mg, 67%) was obtained as a colorless oil after flash chromatography (3% EtOAc/hexanes).

1-Bromo-4-(1-*tert*-butyldimethylsilyloxymethylvinyl)benzene (26). The title compound was prepared from 2-*tert*-butyldimethylsilyloxy-1-(4-bromophenyl)ethanone (96 mg, 0.29 mmol) according to the general procedure A. The desired alkene **26** (73 mg, 77%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.46 (5% EtOAc/hexanes). ^1H NMR (400 MHz, CDCl_3) δ 7.45 (d, J = 7 Hz, 2H), 7.29 (d, J = 7 Hz, 7H), 5.43 (s, 1H), 5.41 (s, 1H), 4.49 (s, 2H), 0.93 (s, 9H), 0.11 (s, 6H); ^{13}C NMR (100 MHz, CDCl_3) δ 146.4, 138.4, 131.8, 128.1, 122.0, 112.6, 65.0, 26.3, 18.8, -4.91; HMRS (MAB) calcd for $\text{C}_{16}\text{H}_{15}\text{OBr}$ $[\text{M}]^+$: 326.070155. Found: 326.071375.

1-Bromo-4-(1-*tert*-butyldimethylsilyloxymethylvinyl)benzene (26). The title compound was prepared from 2-*tert*-butyldimethylsilyloxy-1-(4-bromophenyl)ethanone (91 mg, 0.28 mmol) according to the general procedure E. The desired alkene **26** (73 mg, 82%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes).

(3-Methyl-3-butenyl)benzene (27). The title compound was prepared from 4-phenyl-2-butanone (150 mg, 1.00 mmol) according to the general procedure B. The desired alkene (130 mg, 88%) was obtained as a colorless oil after flash chromatography (1% ether/pentane). R_f 0.58 (1% ether/pentane); ^1H NMR (400 MHz, CDCl_3) δ 7.32-7.26 (m, 2H), 7.22-7.18 (m, 3H), 4.76 (s, 1H), 4.73 (s, 1H), 2.77 (t, J = 8 Hz, 2H), 2.33 (t, J = 9 Hz, 2H), 1.79 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 145.3, 142.1, 128.2, 128.1, 125.1, 110.0, 39.5, 34.1, 22.5; HMRS (MAB) calcd for $\text{C}_{11}\text{H}_{14}$ $[\text{M}-\text{H}]^+$: 146.109551. Found: 146.109390.

3-Methyl-3-butenyl)benzene (27). The title compound was prepared from 4-phenyl-2-butanone (122 mg, 0.83 mmol) according to the general procedure F. The desired alkene (98 mg, 81%) was obtained as a colorless oil after flash chromatography (1% ether/pentane).

(3-Ethyl-3-butenyl)benzene (28). The title compound was prepared from 1-phenyl-3-pentanone (245 mg, 1.51 mmol) according to the general procedure B. The desired alkene **28** (211 mg, 87%) was obtained as a colorless oil after flash chromatography (1% ether/pentane). R_f 0.59 (1% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.31-7.26 (m, 3H), 7.22-7.16 (m, 2H), 4.76 (s, 2H), 2.76 (t, J = 8 Hz, 2H), 2.34 (t, J = 8 Hz, 2H), 2.08 (q, J = 7 Hz, 2H), 1.06 (t, J = 7 Hz, 3H); ^{13}C

NMR (100 MHz, CDCl_3) δ 150.8, 142.2, 128.2, 128.1, 125.5, 107.8, 37.9, 34.3, 28.8, 12.2; HMRS (MAB) calcd for $\text{C}_{12}\text{H}_{16}$ $[\text{M}]^+$: 160.125201. Found: 160.125385.

(3-Ethyl-3-butenyl)benzene (28). The title compound was prepared from 1-phenyl-3-pentanone (81 mg, 0.50 mmol) according to the general procedure **F** (reaction time: 2 h). The desired alkene **28** (57 mg, 71%) was obtained as a colorless oil after flash chromatography (1% ether/pentane).

6-Benzyloxy-2-methylhexene (29).¹⁴ The title compound was prepared from 6-benzyloxy-2-hexanone¹⁵ (52 mg, 0.25 mmol) according to the general procedure **D** (reaction time: 2 h). The desired alkene **29** (40 mg, 78%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.39 (1% EtOAc/hexanes). ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.30 (m, 5H), 4.73 (s, 1H), 4.70 (s, 1H), 4.54 (s, 2H), 3.51 (t, J = 6 Hz, 2H), 2.05 (t, J = 7 Hz, 2H), 1.74 (s, 3H), 1.68-1.52 (m, 4H); ^{13}C NMR (75 MHz, CDCl_3) δ 145.7, 138.6, 128.2, 127.5, 127.4, 109.8, 72.8, 70.2, 37.5, 29.3, 24.1, 22.2; HMRS (MAB) calcd for $\text{C}_{14}\text{H}_{20}\text{O}$ $[\text{M}]^+$: 204.151415. Found: 204.151045.

6-Benzyloxy-2-methylhexene (29).¹⁴ The title compound was prepared from 6-benzyloxy-2-hexanone¹⁵ (52 mg, 0.25 mmol) according to the general procedure **F** (reaction time: 2 h). The desired alkene **29** (30 mg, 59%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes).

3-Phenethylcyclohexylmethylene (30). The title compound was prepared from 3-phenethylcyclohexanone¹⁶ (60 mg, 0.30 mmol) according to the general procedure **B** (reaction time: 1.5 h). The desired alkene **30** (55 mg, 93%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.40 (2% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.33-7.27 (m, 2H), 7.23-7.19 (m, 3H), 4.65 (s, 2H), 2.67 (t, J = 8 Hz, 2H), 2.40 (dd, J = 13, 4 Hz, 1H), 2.30-2.26 (m, 1H), 2.01 (dt, J = 13, 4 Hz, 1H), 1.87-1.75 (m, 3H), 1.63-1.58 (m, 2H), 1.50-1.32 (m, 2H), 1.20-1.16 (m, 1H); ^{13}C NMR (75 MHz, CDCl_3) δ 149.1, 142.8, 128.2, 128.17, 125.5, 106.9, 41.5, 38.6, 38.5, 35.0, 33.2, 32.3, 26.8; HMRS (MAB) calcd for $\text{C}_{15}\text{H}_{20}$ $[\text{M}]^+$: 200.156501. Found: 200.156994.

3-Phenethylcyclohexylmethylene (30). The title compound was prepared from 3-phenethylcyclohexanone¹⁶ (100 mg, 0.50 mmol) according to the general procedure **F** (reaction time: 1 h). The desired alkene **30** (62 mg, 63%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

2-Methyl-4-phenyl-1,3-butadiene (31).¹⁷ The title compound was prepared from benzylideneacetone (73 mg, 0.50 mmol) according to the general procedure **B** (reaction time: 1 h).

¹⁴ Lipshutz, B. H.; Crow, R.; Dimock, S. H.; Ellsworth, E. L.; Smith, R. A. J.; Behling, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 4063-4064.

¹⁵ Nishizawa, M.; Skwarczynski, M.; Imagawa, H.; Sugihara, T. *Chem. Lett.* **2002**, 12-13.

¹⁶ Totleben, M. J.; Curran, D. P.; Wipf, D. *J. Org. Chem.* **1992**, *57*, 1740-1744.

¹⁷ Meek, J. S.; Merrow, R. T.; Ramey, D. E.; Cristol, S. J. *J. Am. Chem. Soc.* **1951**, *22*, 5563-5565.

The desired alkene **31** (72 mg, 97%) was obtained as a colorless oil after flash chromatography (1% ether/pentane). R_f 0.60 (1% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.46-7.24 (m, 5H), 6.90 (d, J = 16 Hz, 1H), 6.55 (d, J = 16 Hz, 1H), 5.14 (s, 1H), 5.13 (s, 1H), 1.99 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 141.9, 137.2, 131.5, 128.54, 128.47, 127.3, 126.3, 117.2, 18.5.

2-Methyl-4-phenyl-1,3-butadiene (31).¹⁷ The title compound was prepared from benzylideneacetone (73 mg, 0.50 mmol) according to the general procedure **F** (reaction time: 1 h). The desired alkene **31** (57 mg, 79%) was obtained as a colorless oil after flash chromatography (1% ether/pentane).

5-Isopropenylbenzo[1,3]dioxole (32). The title compound was prepared from 1-benzo[1,3]dioxol-5-ylethanone (100 mg, 0.61 mmol) according to the general procedure **B**. The desired alkene **32** (86 mg, 87%) was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.27 (1% EtOAc/hexanes); ^1H NMR (400 MHz, CDCl_3) δ 7.02-6.96 (m, 2H), 6.81-6.79 (m, 1H), 5.98 (s, 2H), 5.28 (s, 1H), 5.02 (s, 1H), 2.13 (s, 3H); ^{13}C NMR (100 MHz, CDCl_3) δ 148.0, 147.4, 143.1, 136.0, 119.5, 111.7, 108.3, 106.4, 101.4, 22.5; IR (neat) 3077, 2966, 2892, 1602, 1502, 1489, 1296, 1228, 1038, 932, 885, 811, 629 cm^{-1} . HMRS (MAB) calcd for $\text{C}_{10}\text{H}_{10}\text{O}_2$ $[\text{M}-\text{H}]^+$: 162.068080. Found: 162.068231.

2-Benzyloxycyclohexylmethylen (33).¹⁸ The title compound was prepared from 2-benzyloxycyclohexanone¹⁹ (50 mg, 0.25 mmol) according to the general procedure **D** using PPh_3 (128 mg, 0.50 mmol) (reaction time: 4 h). The desired alkene **33** (41 mg, 82%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.32 (2% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 7.45-7.25 (m, 5H), 4.92 (s, 1H), 4.90 (s, 1H), 4.61 (d, J = 12 Hz, 1H), 4.40 (d, J = 12 Hz, 1H), 3.88-3.85 (m, 1H), 2.43-2.34 (m, 1H), 2.15-2.07 (m, 1H), 1.93-1.30 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.3, 139.0, 128.2, 127.4, 127.2, 108.7, 78.9, 69.6, 33.9, 32.2, 27.9, 22.1.

2-Benzyloxycyclohexylmethylen (33).¹⁸ The title compound was prepared from 2-benzyloxycyclohexanone¹⁹ (100 mg, 0.50 mmol) according to the general procedure **F** using 2 equiv of $\text{Ph}_3\text{PCH}_3\text{Br}$ and NaHMDS (reaction time: 4 h). The desired alkene **33** (76 mg, 77%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

2-Tetrahydropyran-2-yloxycyclohexylmethylen (34). The title compound was prepared from 2-tetrahydropyran-2-yloxycyclohexanone (30 mg, 0.15 mmol) according to the general procedure **D** using PPh_3 (80 mg, 0.30 mmol) (reaction time: 4 h). The desired alkene **34** (22 mg, 72%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.32 (2% EtOAc/hexanes); Major diastereoisomer ^1H NMR (300 MHz, CDCl_3) δ 5.03 (s, 1H), 4.82-4.75 (m, 2H), 3.93-3.90 (m, 2H), 3.51-3.46 (m, 1H), 2.43-2.34 (m, 1H), 1.93-1.40 (m, 13H); ^{13}C NMR (75

¹⁸ Ren, L.; Crudden, C. M. *J. Org. Chem.* **2002**, 67, 1746-1750.

¹⁹ Bisel, P.; Lauktien, G.; Weckert, E.; Frahm, A. W. *Tetrahedron Asymm.* **1998**, 9, 4027-4034.

MHz, CDCl₃) δ 149.4, 106.0, 95.1, 74.8, 62.0, 33.8, 32.8, 30.8, 27.6, 25.4, 23.5, 19.3; HMRS (MAB) calcd for C₁₂H₂₀O₂ [M]⁺: 196.146330. Found: 196.146706.

2-Tetrahydropyran-2-yloxycyclohexylmethylene (34). The title compound was prepared from 2-tetrahydropyran-2-yloxycyclohexanone (30 mg, 0.15 mmol) according to the general procedure **F** using 2 equiv of Ph₃PCH₃Br and NaHMDS (reaction time: 4 h). The desired alkene **34** (17 mg, 59%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

2-Triethylsilyloxycyclohexenylmethylene (35). The title compound was prepared from 2-triethylsilyloxycyclohexanone (30 mg, 0.13 mmol) according to the general procedure **D** using PPh₃ (68 mg, 0.26 mmol) (reaction time: 4 h). The desired alkene **35** (19 mg, 64%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). *R_f* 0.42 (2% EtOAc/hexanes); ¹H NMR (400 MHz, CDCl₃) δ 4.92 (s, 1H), 4.69 (s, 1H), 4.04 (s, 1H), 2.43-2.38 (m, 1H), 2.00-1.80 (m, 3H), 1.64-1.26 (m, 4H), 0.99-0.95 (m, 9H), 0.64-0.58 (m, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 105.0, 72.8, 37.6, 33.6, 27.7, 24.0, 6.8, 4.9; HMRS (MAB) calcd for C₁₃H₂₆OSi [M]⁺: 226.175294. Found: 226.176057.

2-Triethylsilyloxycyclohexenylmethylene (35). The title compound was prepared from 2-triethylsilyloxycyclohexanone (20 mg, 0.10 mmol) according to the general procedure **F** using 2 equiv of Ph₃PCH₃Br and NaHMDS (reaction time: 4 h). The desired alkene **35** (12 mg, 60%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

2-tert-Butyldimethylsilyloxycyclohexylmethylene (36).¹⁸ The title compound was prepared from 2-tert-butyldimethylsilyloxycyclohexanone¹⁹ (50 mg, 0.22 mmol) according to the general procedure **D** using PPh₃ (144 mg, 0.55 mmol), 2-propanol (0.34 mL, 4.40 mmol) and trimethylsilyldiazomethane (0.17 mL, 0.66 mmol) (reaction time: 4 h). The desired alkene **36** (36 mg, 71%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). *R_f* 0.23 (2% EtOAc/hexanes); ¹H NMR (300 MHz, CDCl₃) δ 4.90 (s, 1H), 4.69 (s, 1H), 4.04-4.01 (m, 1H), 2.43-2.37 (m, 1H), 1.97-1.26 (m, 7H), 0.92 (s, 9H), 0.06 (s, 6H); ¹³C NMR (100 MHz, CDCl₃) δ 151.4, 105.1, 73.1, 37.4, 33.5, 27.7, 25.7, 23.8, 18.2, -5.0.

2-tert-Butyldimethylsilyloxycyclohexylmethylene (36).¹⁸ The title compound was prepared from 2-triethylsilyloxycyclohexanone¹⁹ (50 mg, 0.23 mmol) according to the general procedure **F** using 2.5 equiv of Ph₃PCH₃Br and NaHMDS (reaction time: 4 h). The desired alkene **36** (26 mg, 52%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

2-Triisopropylsilyloxycyclohexylmethylene (37).¹⁸ The title compound was prepared from 2-triisopropylsilyloxycyclohexanone²⁰ (50 mg, 0.19 mmol) according to the general procedure **D** using PPh₃ (97 mg, 0.38 mmol) (reaction time: 4 h). The desired alkene **37** (45 mg, 90%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). *R_f* 0.30 (2%

²⁰ Overman, L. E.; Pennington, L. D. *Can. J. Chem.* **2000**, 78, 732-738.

EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 4.93 (s, 1H), 4.70 (s, 1H), 4.18-4.15 (m, 1H), 2.45-2.39 (m, 1H), 1.98-1.82 (m, 2H), 1.59-0.89 (m, 26H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.7, 105.4, 73.2, 37.6, 33.3, 28.0, 23.4, 18.0, 12.3.

2-Triisopropylsilyloxycyclohexylmethylene (37).¹⁸ The title compound was prepared from 2-triisopropylsilyloxycyclohexanone²⁰ (50 mg, 0.19 mmol) according to the general procedure **F** using LiHMDS (64 mg, 0.38 mmol) and 2.0 equiv of $\text{Ph}_3\text{PCH}_3\text{Br}$ (reaction time: 4 h). The desired alkene **37** (17 mg, 34%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

2-Benzoxycyclohexylmethylene (38).²¹ The title compound was prepared from 2-benzoxycyclohexanone²² (50 mg, 0.23 mmol) according to the general procedure **D** using PPh_3 (121 mg, 0.40 mmol) (reaction time: 4 h). The desired alkene **38** (40 mg, 80%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.26 (2% EtOAc/hexanes); ^1H NMR (300 MHz, CDCl_3) δ 8.10 (d, $J = 7$ Hz, 2H), 7.59-7.54 (m, 1H), 7.49-7.43 (m, 2H), 5.52-5.47 (m, 1H), 4.94 (s, 1H), 4.83 (s, 1H), 2.50-2.42 (m, 1H), 2.23-2.14 (m, 1H), 2.05-1.53 (m, 6H); ^{13}C NMR (75 MHz, CDCl_3) δ 165.4, 146.4, 132.7, 130.6, 129.5, 128.2, 107.6, 74.7, 33.3, 33.2, 27.4, 23.1.

2-Benzoxycyclohexylmethylene (38).²¹ The title compound was prepared from 2-benzoxycyclohexanone²² (50 mg, 0.23 mmol) according to the general procedure **F** using 2.0 equiv of $\text{Ph}_3\text{PCH}_3\text{Br}$ and NaHMDS (reaction time: 4 h). The desired alkene **38** (34 mg, 68%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes).

(S)-2-Benzyloxy-3-phenethyl-1-butene (39). The title compound was prepared from (S)-4-benzyloxy-1-phenyl-3-pentanone (48 mg, 0.18 mmol) according to the general procedure **D** (reaction time: 8 h). The desired alkene **39** (38 mg, 81%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.35 (5% EtOAc/hexanes). $[\alpha]_D -40.9$ (c, 0.97, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.16 (m, 10H), 5.10 (s, 1H), 5.02 (s, 1H), 4.50 (d, $J = 12$ Hz, 1H), 4.30 (d, $J = 12$ Hz, 1H), 3.96 (q, $J = 7$ Hz, 1H), 2.83 (t, $J = 8$ Hz, 2H), 2.48-2.32 (m, 2H), 1.32 (d, $J = 7$ Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 150.0, 142.6, 139.2, 128.8, 128.7 (2C), 128.1, 127.8, 126.3, 111.8, 79.1, 70.4, 34.7, 32.3, 21.0; HMRS (MAB) calcd for $\text{C}_{19}\text{H}_{22}\text{O}$ $[\text{M}]^+$: 266.167066. Found: 266.166678. The enantiomeric excess was determined to be 97% (76:1) by chiral GC analysis (20% Permethylated B-Cyclodextrin, 120 °C isotherm, t_r 38.4 (minor), 38.9 (major), 39.6 (minor), 40.6 (major) of the corresponding reduced alcohol product after treatment of the alkene **39** with hydrogen in the presence of Pd/C.

(S)-2-(tert-Butyldimethylsilyloxy)-3-phenethyl-1-butene (40). The title compound was prepared from (S)-4-(tert-butyldimethylsilyloxy)-1-phenyl-3-pentanone (95 mg, 0.32 mmol) according to the general procedure **D** (reaction time: 8 h). The desired alkene **40** (166 mg, 90%)

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²² Augustine, R. L. *J. Am. Chem. Soc.* **1963**, 581-582.

was obtained as a colorless oil after flash chromatography (1% EtOAc/hexanes). R_f 0.51 (5% EtOAc/hexanes). $[\alpha]_D -7.4$ (c , 0.83, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.40-7.18 (m, 5H), 5.06 (s, 1H), 4.82 (s, 1H), 4.27 (q, J = 6 Hz, 1H), 2.79 (t, J = 8 Hz, 2H), 2.47-2.24 (m, 2H), 1.25 (d, J = 6 Hz, 3H), 0.91 (m, 9H), 0.07 (s, 3H), 0.05 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 152.6, 142.5, 128.2 (2C), 125.6, 108.1, 71.9, 34.5, 32.6, 25.7, 23.5, 18.1, -4.93, -5.07; Anal. Calcd for $\text{C}_{18}\text{H}_{30}\text{OSi}$: C, 74.42; H, 10.41. Found: C, 74.34; H, 11.27. The enantiomeric excess was determined to be 95% (37:1) by chiral HPLC analysis (Chiracel OD, 1mL/min, 2% 2-propanol/hexane, t_r 17.6 (major), 21.4 (minor)) of the corresponding alcohol product after treatment of the alkene **40** with TBAF (1 M in THF) and acetic acid.

(S)-4-Benzyloxy-2-phenethyl-1-heptene (41). The title compound was prepared from (S)-4-benzyloxy-1-phenyl-3-octanone (96 mg, 0.31 mmol) according to the general procedure **D** using PPh_3 (203 mg, 0.77 mmol), 2-propanol (0.47 mL, 6.18 mmol) and trimethylsilyldiazomethane (170 μL , 0.99 mmol) (reaction time: 8 h). The desired alkene **41** (80 mg, 84%) was obtained as a colorless oil after flash chromatography (5% EtOAc/hexanes). R_f 0.49 (10% EtOAc/hexanes). $[\alpha]_D -32.7$ (c , 1.12, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.38-7.18 (m, 10H), 5.08 (s, 2H), 4.41 (d, J = 12 Hz, 1H), 4.25 (d, J = 12 Hz, 1H), 3.75 (t, J = 7 Hz, 1H), 2.84 (t, J = 8 Hz, 2H), 2.47-2.26 (m, 2H), 1.74-1.18 (m, 6H), 0.89 (t, J = 7 Hz, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.2, 142.1, 138.8, 128.3, 128.2, 128.1, 127.6, 127.2, 125.7, 112.2, 83.5, 69.9, 34.0, 33.8, 31.5, 28.0, 22.5, 13.9; Anal. Calcd for $\text{C}_{22}\text{H}_{28}\text{O} \cdot \text{H}_2\text{O}$: C, 80.94; H, 9.26. Found: C, 80.76; H, 9.13. The enantiomeric excess was determined to be 99% (>200:1) by chiral GC analysis (20% Permethylated B-Cyclodextrin, 180 $^\circ\text{C}$ isotherm, t_r 48.1 (minor), 50.1 (major)).

(S)-4-(tert-Butyldimethylsilyloxy)-2-phenethyl-1-heptene (42). The title compound was prepared from (S)-4-(tert-butyldimethylsilyloxy)-1-phenyl-3-octanone (103 mg, 0.31 mmol) according to the general procedure **D** using PPh_3 (201 mg, 0.77 mmol), 2-propanol (0.47 mL, 6.12 mmol) and trimethylsilyldiazomethane (192 μL , 0.98 mmol) (reaction time: 8 h). The desired alkene **42** (87 mg, 86%) was obtained as a colorless oil after flash chromatography (1% ether/hexanes). R_f 0.8 (10% EtOAc/hexanes). $[\alpha]_D -21.1$ (c , 1.22, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.15 (m, 5H), 5.00 (s, 1H), 4.87 (s, 1H), 4.07 (t, J = 6 Hz, 1H), 2.79 (t, J = 8 Hz, 2H), 2.44-2.36 (m, 1H), 2.29-2.21 (m, 1H), 1.56-1.43 (m, 2H), 1.35-1.15 (m, 4H), 0.91 (s, 9H), 0.89 (t, J = 8 Hz, 3H), 0.05 (s, 3H), 0.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.4, 128.2, 125.6, 124.3, 115.0, 109.3, 105.7, 36.1, 34.3, 32.0, 27.6, 25.7, 22.5, 18.1, 14.0, -4.74, -5.15; Anal. Calcd for $\text{C}_{21}\text{H}_{36}\text{O}$: C, 75.84; H, 10.91. Found: C, 75.11; H, 11.09. The enantiomeric excess was determined to be 99% (>200:1) by chiral GC analysis (20% Permethylated B-Cyclodextrin, 180 $^\circ\text{C}$ isotherm, t_r 48.1 (minor), 50.1 (major) of the corresponding benzylether product after treatment of the alkene **40** with TBAF, followed by reaction of the resulting alcohol with benzyl bromide and sodium hydride.

(S)-4-Phenyl-2-(1-benzyloxy-1-phenylmethyl)-1-butene (43). The title compound was prepared from (S)-1-benzyloxy-1,4-diphenyl-2-butanone (135 mg, 0.41 mmol) according to the general

procedure **D** (reaction time: 8 h). The desired alkene **43** (116 mg, 87%) was obtained as a colorless oil after flash chromatography (2% EtOAc/hexanes). R_f 0.47 (10% EtOAc/hexanes). $[\alpha]_D +9.1$ (c , 0.95, CHCl_3); ^1H NMR (300 MHz, CDCl_3) δ 7.41-7.10 (m, 15H), 5.27 (s, 1H), 5.11 (s, 1H), 4.86 (s, 1H), 4.54 (d, $J = 12$ Hz, 1H), 4.49 (d, $J = 12$ Hz, 1H), 2.75-2.62 (m, 2H), 2.38-2.14 (m, 2H); ^{13}C NMR (75 MHz, CDCl_3) δ 148.4, 141.9, 140.3, 138.4, 128.2 (3C), 128.1 (2C), 127.4, 127.3, 126.9, 125.6, 112.3, 84.0, 70.1, 34.1, 32.7; Anal. Calcd for $\text{C}_{24}\text{H}_{24}\text{O}$: C, 87.76; H, 7.37. Found: C, 87.54; H, 7.63. The enantiomeric excess was determined to be 95% (38:1) by chiral GC analysis (20% Permethylated B-Cyclodextrin, 150 °C isotherm, t_r 20.9 (minor), 21.5 (minor), 30.9 (major), 31.2 (major) of the corresponding reduced alcohol product after treatment of the alkene **43** with hydrogen in the presence of Pd/C.

(S)-4-Phenyl-2-(1-tert-butyldimethylsilyloxy-1-phenylmethyl)-1-butene (44). The title compound was prepared from (*S*)-1-(*tert*-butyldimethylsilyloxy)-1,4-diphenyl-2-butanone (144 mg, 0.40 mmol) according to the general procedure **D** using PPh_3 (159 mg, 0.61 mmol), 2-propanol (0.46 mL, 6.00 mmol) and trimethylsilyldiazomethane (185 μL , 0.93 mmol) (reaction time: 14 h). The desired alkene **44** (115 mg, 81%) was obtained as a colorless oil after flash chromatography (1% ether/hexanes). R_f 0.73 (5% EtOAc/hexanes). $[\alpha]_D +9.7$ (c , 0.91, CHCl_3); ^1H NMR (400 MHz, CDCl_3) δ 7.36-7.22 (m, 8H), 7.21-7.17 (m, 1H), 7.15-7.07 (m, 1H), 5.26 (s, 1H), 5.17 (s, 1H), 4.94 (s, 1H), 2.73-2.59 (m, 2H) 2.32-2.21 (m, 1H), 2.14-2.03 (m, 1H), 0.93 (s, 9H), 0.08 (s, 3H), -0.02 (s, 3H); ^{13}C NMR (75 MHz, CDCl_3) δ 151.2, 143.1, 142.1, 128.2, 128.1, 127.8, 126.8, 126.1, 125.6, 110.0, 78.4, 34.3, 31.9, 25.7, 18.2, -4.97, -5.11; HMRS (MAB) calcd for $\text{C}_{23}\text{H}_{32}\text{OSi}$: 352.222244. Found: 352.220725. The enantiomeric excess was determined to be 94% (36:1) by chiral HPLC analysis (Chiracel OD, 1mL/min, 2% 2-propanol/hexane, t_r 28.8 (minor), 30.4 (major)) of the corresponding alcohol product after treatment of the alkene **44** with TBAF (1 M in THF).