Supporting Information for

HFIP solvent enables alcohols to act as alkylating agents in stereoselective heterocyclization

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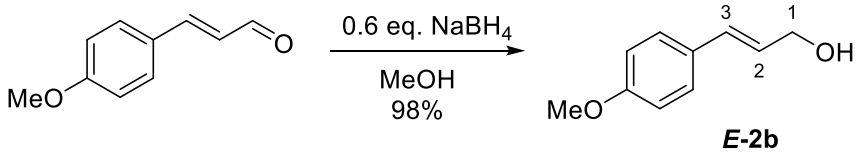
1. General experimental details

^{1}H NMR and ^{13}C NMR spectra were recorded on a 400 MHz or 500MHz spectrometer in $CDCl_3$ and referenced to residual solvent peaks. Chemical shifts were quoted in ppm (parts per million) to the nearest 0.01 ppm with signal splitting recorded as singlet (s), doublet (d), triplet (t), quartet (q), quintet (quint) septet (sept), multiplet (m) and broad singlet (br s). Coupling constants, *J*, were measured in Hz to the nearest 0.1 Hz. ^{1}H and ^{13}C NMR spectra were recorded at room temperature. All diastereomeric ratio values (d.r.) were based on the crude NMR. The numbering system drawn on the structures and used to assign the NMR peaks is not the same system that was used to generate the chemical name. Infrared spectra were recorded as thin films of neat samples on a Bruker Tensor 27 FT-IR spectrometer equipped with Attenuated Total Reflectance sampling accessories. High resolution mass spectra were given to four decimal places and were recorded on a Bruker MicroTof (resolution = 10000 FWHM) under conditions of electrospray ionization (ESI), electronic ionization (EI) or chemical ionization (CI). Melting points (m.p.) were obtained from recrystallized samples using a Lecia VMTG heated-stage microscope and were uncorrected. The solvent systems used for recrystallization were quoted in parentheses. Flash column chromatography (FCC) was performed using silica gel (60 Å, 0.033-0.070 mm, BDH) or using basic alumina (pH 9.5, 58 Å, 150 mesh, Sigma-Aldrich). TLC analyses were performed on Merck Kiesegel 60 F_{254} 0.25 mm precoated silica plates or Macherey-Nagel Alugram Alox N/UV_{254} 0.20 mm precoated alumina plates. Reagents obtained from Sigma-Aldrich, Alfa, Fluorochem and TCI suppliers were used directly as supplied All anhydrous reactions were carried out in flame dried glassware and under an inert atmosphere of argon provided by a balloon. All reactions were stirred with magnetic followers. THF, toluene and CH_2Cl_2 were dried by purification through two activated alumina purification columns. Brine refers to a saturated aqueous solution of NaCl.

2. Synthesis of allyl alcohols.

2.1. (2*E*)-3-(4-Methoxyphenyl)prop-2-en-1-ol (*E*-2b)



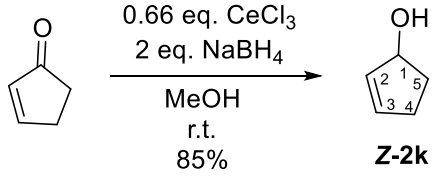
***E*-2b**

To a stirring solution of 4-methoxycinnamaldehyde (4.800 g, 29.62 mmol) in MeOH (56 mL) under Ar, $NaBH_4$ (0.840 g, 17.8 mmol) is slowly added at 0 °C. After 30 min. the ice bath is removed. The reaction was allowed to stir for 12 hours at r.t. The reaction is quenched with saturated NH_4Cl solution and the aqueous layer was extracted three times with Et_2O. The combined organic layers were washed with brine, dried over anhydrous $MgSO_4$ and the solvent was removed

in vacuo. Recrystalization afforded alcohol ***E*-2b** as a white solid (4.850 g, 98%). Spectroscopic properties matched those previously reported.[1]

Data for ***E*-2b**: **R_f** 0.5 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.32 (2H, d, *J* = 8.7 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 6.56 (1H, d, *J* = 15.9 Hz, 3-H), 6.24 (1H, dt, *J* = 15.8, 6.0 Hz, 2-H), 4.29 (2H, dd, *J* = 5.9, 1.2 Hz, 1-H_2), 3.81 (3H, s, OMe), 1.53 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.5 (C Ar), 131.1 (C-3), 129.6 (C Ar), 127.8 (2 x CH Ar), 126.4 (C-2), 114.2 (2 x CH Ar), 64.07 (C-1), 55.43 (OMe). **HRMS** (Cl): calculated for $C_{10}H_{13}O_2$ $[M+H]^+$ requires *m/z* 165.0916, found *m/z* 165.0919.

2.2. (±)-(*Z*)-Cyclopent-2-en-1-ol (*Z*-2k)

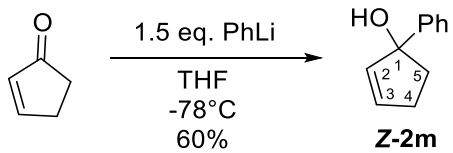


***Z*-2k**

Cerium trichloride (2.000 g, 8.197 mmol) was dissolved in 20 mL of methanol. Then cyclopent-2-enone (1.00 g, 12.3 mmol) was added. After 5 min. of vigorous stirring, sodium borohydride (934 mg, 24.6 mmol) was carefully added portionwise and the resulting heterogeneous mixture was stirred for 15 min. at r. t. Water was added dropwise until a clear solution is seen and then the mixture was extracted twice with Et_2O. The organic layers were collected, dried over $MgSO_4$ and the solvents were removed under vacuum. FCC (20% Et_2O) afforded ***Z*-2k** as a colorless oil (0.580 g, 85% yield). Spectroscopic properties matched those previously reported.[2]

Data for ***Z*-2k**: **R_f** 0.45 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.93-5.99 (1H, m, 3-H), 5.78-5.84 (1H, m, 2-H), 4.82-4.88 (1H, m, 1-H), 2.49 (1H, ddt, *J* = 16.6, 10.9, 5.4 Hz, 4-H_A), 2.17-2.31 (2H, m, 4-H_B and 5-H_A), 1.95 (1H, br s, OH), 1.61-1.76 (1H, m, 5-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 135.2 (C-3), 133.4 (C-2), 77.6 (C-1), 33.3 (C-5), 31.1 (C-4). **HRMS** (El): calculated for C_5H_7O $[M-H]^+$ requires *m/z* 83.0491, found *m/z* 83.049.

2.3. (±)-(*Z*)-1-Phenylcyclopent-2-en-1-ol (*Z*-2m)



***Z*-2m**

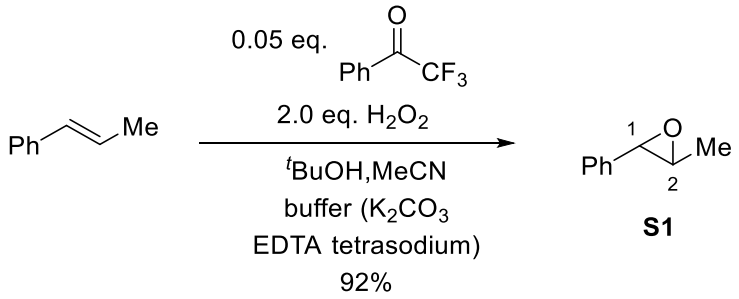
To a solution of Cyclopent-2-enone (0.51 mL, 6.1 mmol) in THF (40 mL) at -78 °C was added 1.88M PhLi (4.9 mL, 9.1 mmol). After the mixture was stirred at -78 °C for 1 hour, H_2O was added and allowed to warm to r.t. The mixture was extracted with Et_2O and the organic extract was washed with brine, dried over $MgSO_4$ and the solvents were removed under vacuum. The residue

was purified (FCC: gradient elution: 5% → 7% Et_2O - pentane) to yield ***Z*-2m** as a white solid (0.584 g, 60%). Spectroscopic properties matched those previously reported.[3]

Data for ***Z*-2m**: **R_f** 0.5 (60% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.43-7.47 (2H, m, Ar), 7.32-7.38 (2H, m, Ar), 7.23-7.28 (1H, m, Ar), 6.12 (1H, dt, *J* = 5.6, 2.4 Hz, 3-H), 5.88 (1H, dt, *J* = 5.5, 2.2 Hz, 2-H), 2.60-2.70 (1H, m, 4-H_A), 2.43-2.52 (1H, m, 4-H_B), 2.24-2.29 (1H, m, 5-H_2),1.98 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 147.0 (C Ar), 136.6 (C-2), 134.9 (C-3), 128.2 (2 x CH Ar), 126.8 (CH Ar), 124.9 (2 x CH Ar), 87.0 (C-1), 42.0 (C-5), 31.5 (C-4).

3. Synthesis of homoallyl alcohols.

3.1. (±)-2-Methyl-3-phenyloxirane (S1)

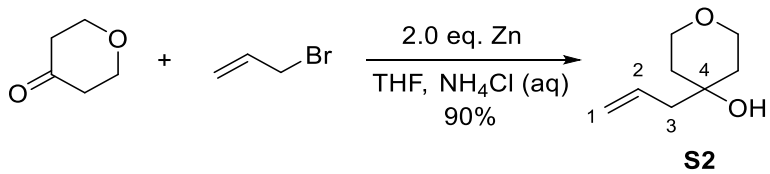


S1

Trans-β-Methylstyrene (2.000 g, 16.95 mmol) was placed in a round-bottom flask followed by 2,2,2-trifluoro-1-phenylethanone (147 mg, 0.846 mmol). *tert*-Butyl alcohol (25 mL), aqueous buffer solution (25 mL, 0.6 M K_2CO_3, 4 × 10^{-5} M EDTA tetrasodium salt), acetonitrile (1.9 mL), and 30% aqueous H_2O_2 (3.9 mL, 34 mmol) were added consecutively. The reaction mixture was allowed to stir for 1 h at room temperature. Then the reaction was quenched by addition of sodium thiosulfate solution, and the mixture was extracted twice with Et_2O. The organic layers were collected, dried over $MgSO_4$ and the solvents were removed under vacuum. FCC (2% Et_2O) afforded **S1** as a colorless oil (2.090 g, 92% yield). Spectroscopic properties matched those previously reported.[4]

Data for **S1**: **R_f** 0.45 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.22-7.39 (5H, m, Ar), 3.58 (1H, d, *J* = 2.1 Hz, 1-H), 3.05 (1H, qd, *J* = 5.1, 2.1 Hz, 2-H), 1.46 (3H, d, *J* = 5.1 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 137.9 (C Ar), 128.6 (2 x C-H Ar), 128.2 (C-H Ar), 125.7 (2 x C-H Ar), 59.2 (C-1), 59.2 (C-2), 18.1 (Me). **HRMS** (Cl): calculated for $C_9H_{10}O$ $[M]^+$ requires *m/z* 134.0726, found *m/z* 134.072.

3.2. 4-Allyltetrahydro-2*H*-pyran-4-ol (S2)

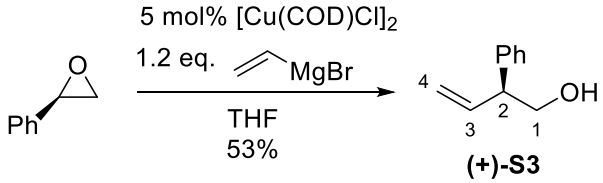


S2

Zinc dust (3.900 g, 61.03 mmol) was slowly added under vigorous stirring to a mixture of tetrahydro-4*H*-pyran-4-one (3.000 g, 30.00 mmol) and allyl bromide (9.000 g, 75.00 mmol) in 10 mL THF, and 30 mL of a saturated aqueous solution of ammonium chloride in such a way that the temperature did not exceed 40°C. The mixture was then stirred for 10 hours at room temperature, 100 ml of 10% aqueous sulfuric acid was added and the mixture was filtered. The organic phase was separated, and the aqueous phase was saturated with sodium chloride and extracted with diethyl ether. The extracts were combined with the organic phase and dried over anhydrous sodium sulfate, and the solvent was distilled off under reduced pressure. The residue was purified (FCC: gradient elution: 15% → 25% Et_2O - pentane) to yield **S2** as a colorless oil (3.830 g, 90%). Spectroscopic properties matched those previously reported.[5]

Data for **S2**: **R_f** 0.30 (60% EtOAc - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.86 (1H, ddt, *J* = 17.6, 10.2, 7.5 Hz, 2-H), 5.10-5.22 (2H, m, 1-H_2), 3.68-3.78 (4H, m, 2 x CH_2 tetrahydropyranyl), 2.23 (1H, d, *J* = 7.5 Hz, 3-H_2), 1.69 (2H, ddd, *J* = 13.8, 10.4, 5.8 Hz, CH_2 tetrahydropyranyl), 1.60 (1H, br s, OH), 1.42-1.51 (2H, m, CH_2 tetrahydropyranyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 132.6 (C-2), 119.8 (C-1), 68.4 (C-4), 63.9 (2 x CH_2 tetrahydropyranyl), 47.6 (C-3), 37.7 (2 x CH_2 tetrahydropyranyl).

3.3. (+)-(*S*)-2-Phenylbut-3-en-1-ol [(+)-S3]

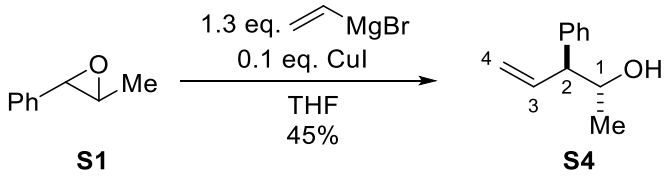


(+)-S3

To a solution of (*R*)-phenyloxirane (1.000 g, 8.326 mmol, 1.0 equiv.) and $[Cu(COD)Cl]_2$ (0.172 g, 0.415 mmol) in THF (12 mL) at –78°C was added vinylmagnesium bromide (10.0 mL, 10.0 mmol, 1.0 M solution in THF). The reaction was allowed to warm to r.t. over 8 h, then it was quenched by the addition of saturated NH_4Cl solution and extracted with EtOAc. The combined organics were dried over $MgSO_4$ and concentrated. The crude residue was purified (FCC: gradient elution: 15% → 20% Et_2O - pentane) to yield **(+)-S3** as a colorless oil (0.650 g, 53%). Spectroscopic properties matched those previously reported.[6] Racemic **S3** (55% yield) was made via the same procedure without using $[Cu(COD)Cl]_2$.

Data for **(+)-S3**: **R_f** 0.40 (40% Et_2O - pentane). $[\alpha]_D^{25}$ = +62.1 (0.01 g/mL, $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.20-7.37 (2H, m, Ar), 7.20-7.27 (3H, m, Ar), 6.00 (1H, ddd, *J* = 17.6, 10.4, 7.7 Hz, 3-H), 5.15-5.23 (2H, m, 4-H_2), 3.81 (2H, t, *J* = 6.0 Hz, 1-H_2), 3.52 (1H, q, *J* = 7.3 Hz, 2-H), 1.57 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 140.7 (C Ar), 138.3 (C-3), 128.9 (2 x C-H Ar), 128.1 (2 x C-H Ar), 127.1 (C-H Ar), 117.2 (C-4), 66.2 (C-1), 52.6 (C-2). **HRMS** (Cl): calculated for $C_{10}H_{12}O$ $[M]^+$ requires *m/z* 148.0883, found *m/z* 148.0882.

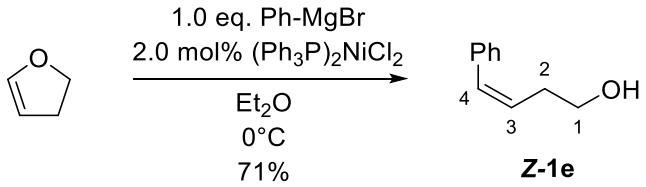
3.4. (±)- (2*R*,3*S*)-3-Phenylpent-4-en-2-ol (S4)



A 50 mL round bottom flask was flame dried and charged with a solution of copper (I) iodide (85.0 mg, 0.448 mmol) in diethyl ether (3.2 mL) and cooled to -78°C. The vinyl magnisium bromide solution (1M, 5.8 mL, 5.8 mmol) was added slowly. The resulting solution was stirred for 30 min. and then epoxide **S1** (0.600 g, 4.48 mmol) was added slowly. The solution was stirred overnight and allowed to warm to room temperature. The solution was cooled to 0°C and NH_4Cl (sat. aq.) was added. The aqueous layer was extracted three times with diethyl ether, dried over anhydrous $MgSO_4$, filtered, and concentrated. The crude residue was purified (FCC: gradient elution: 10% → 15% Et_2O - pentane) to yield **S4** as a yellow oil (0.325 g, 45%). Spectroscopic properties matched those previously reported.[7]

Data for **S4**: **R_f** 0.40 (40% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.32-7.37 (2H, m, Ar), 7.24-7.28 (3H, m, Ar), 6.04 (1H, ddd, *J* = 17.5, 9.8, 8.7 Hz, 3-H), 5.09-5.18 (2H, m, 4-H_2), 4.00-4.10 (1H, m, 1-H), 3.25 (1H, t, *J* = 8.2 Hz, 2-H), 1.51 (1H, br s, OH), 1.25 (3H, d, *J* = 6.2 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 141.0 (C Ar), 138.5 (C-3), 129.0 (2 x C-H Ar), 128.5 (2 x C-H Ar), 127.1 (C-H Ar), 117.0 (C-4), 70.6 (C-1), 59.1 (C-2), 20.8 (Me).

3.5. (3*Z*)-4-Phenylbut-3-en-1-ol (*Z*-1e)



To $(PPh_3)_3NiCl_2$ dry powder (0.094 g, 0.14 mmol), 2,3-dihydrofuran (0.54 mL, 7.1 mmol) in dry Et_2O (8.0 mL) was transferred dropwise *via* a cannula. The resulting suspension was cooled to 0 °C and PhMgBr (2.8 M, 2.56 mL, 7.14 mmol) was slowly added dropwise. After stirring for 1 h at 0 °C, the mixture was stirred at room temperature for 6 h, and then poured into sat. NH_4Cl solution (40 mL). The crude product was extracted with Et_2O (3 x 20 mL), then the organic layer was dried over Na_2SO_4, filtered and concentrated to dryness giving a crude residue. Purification using silica gel flash chromatography (cyclohexane/EtOAc, 80:20) afforded the alcohol ***Z*-1e** as a colorless oil (0.750 g, 71%). Spectroscopic properties matched those previously reported.[8]

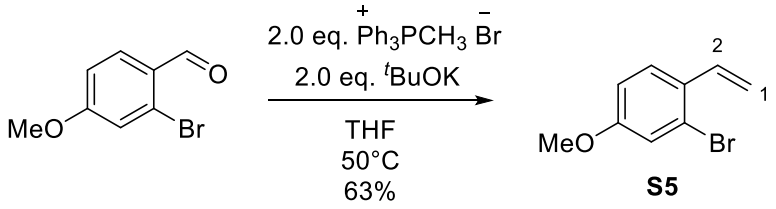
Data for ***Z*-1e**: **R_f**: 0.5 (100% EtOAc). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28-7.38 (4H, m,

Ar), 7.21-7.27 (1H, m, Ar), 6.59 (1H, d, *J* = 11.7 Hz, 4-H), 5.70 (1H, dt, *J* = 11.7, 7.4 Hz, 3-H), 3.75 (2H, t, *J* = 6.5 Hz, 1-H_2), 2.62 (2H, qd, *J* = 6.6, 1.8 Hz, 2-H_2), 1.54 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 137.3 (C Ar), 131.7 (C-4), 128.8 (2 x CH Ar), 128.4 (C-3), 128.3 (2 x CH Ar), 126.9 (CH Ar), 62.6 (C-1), 32.1 (C-2). **HRMS** (EI): calculated for $C_{10}H_{12}O$ $[M]^+$ requires *m/z* 148.0883, found *m/z* 148.0888.

4. General procedure for the synthesis of styrenes

A solution of triphenylphosphonium halide (1.2 eq. or 2.0 eq. or 2.3 eq.) in dry solvent (THF or Et_2O) was placed in a flame-dried round-bottomed flask. The solution was cooled to 0 °C, and the base (1.2 eq. of ^{t}BuOK or 2.0 eq. of ^{t}BuOK or 2.3 eq. of ^{t}BuOK or 4.5 eq. of NaH) was added in one portion. After stirring at 0 °C for 30 min, the aldehyde (1.0 equiv.) was added. The reaction mixture was gradually warmed to room temperature. After 12 h, the reaction was quenched by slow addition of saturated NH_4Cl. The phases were separated, and the aqueous phase was extracted twice with Et_2O. The combined organic layers were washed with brine, dried over Na_2SO_4. The solvent was evaporated under reduced pressure to give the corresponding styrene, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

4.1. 2-Bromo-4-methoxy-1-vinylbenzene (S5)

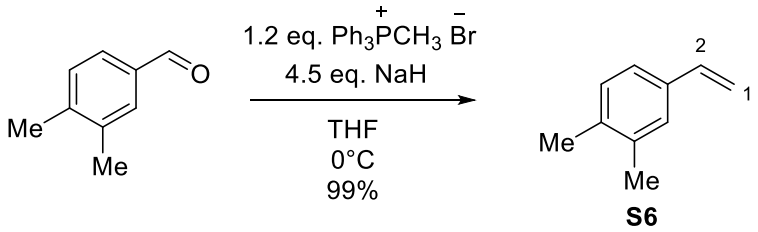


S5

Methyltriphenylphosphonium bromide (3.800 g, 10.64 mmol), ^{t}BuOK (1.200 g, 10.71 mmol), solution of 2-bromo-4-methoxybenzaldehyde (1.150 g, 5.333 mmol in 2.3 mL THF) and THF (4.6 mL) were subjected to the general procedure except the reaction was heated to 50°C after the KO^{t}Bu was added and before adding the aldehyde (FCC: pentane) to yield **S5** as a colorless oil (0.720 g, 63%). Spectroscopic properties matched those previously reported.[9]

Data for **S5**: **R_f** 0.50 (5% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.48 (1H, d, *J* = 8.7 Hz, Ar), 7.09 (1H, d, *J* = 2.4 Hz, Ar), 6.99 (1H, dd, *J* = 17.4, 10.9 Hz, 2-H), 6.85 (1H, dd, *J* = 8.7, 2.5 Hz, Ar), 5.59 (1H, d, *J* = 17.4 Hz, 1-H_A), 5.25 (1H, d, *J* = 10.9 Hz, 1-H_B), 3.80 (3H, s, OMe). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.7 (C Ar), 135.2 (C-2), 130.2 (C Ar), 127.3 (CH Ar), 124.1 (C Ar), 117.6 (CH Ar), 114.7 (C-1), 114.2 (CH Ar), 55.7 (OMe). **HRMS** (ESI): calculated for $C_9H_{10}BrO$ $[M+H]^+$ requires *m/z* 212.9910, found *m/z* 212.9909.

4.2. 2,4-Dimethyl-1-vinylbenzene (S6)

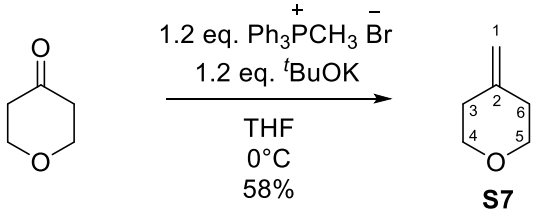


S6

Methyltriphenylphosphonium bromide (6.400 g, 17.92 mmol), NaH (1.613 g, 67.20 mmol), 3,4-dimethoxybenzaldehyde (2.000 g, 14.91 mmol) and THF (74.5 mL) were subjected to the general procedure (FCC: pentane) to yield **S6** as a colorless oil (2.000 g, 99%). Spectroscopic properties matched those previously reported.[10]

Data for **S6**: **R_f** 0.50 (pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.23 (1H, s, Ar), 7.19 (1H, d, *J* = 7.8 Hz, Ar), 7.12 (1H, d, *J* = 7.7 Hz, Ar), 6.70 (1H, dd, *J* = 17.6, 10.9 Hz, 2-H), 5.73 (1H, d, *J* = 17.6 Hz, 1-H_A), 5.20 (1H, d, *J* = 10.8 Hz, 1-H_B), 2.30 (3H, s, Me), 2.29 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 136.9 (C-2), 136.7 (C Ar), 136.4 (C Ar), 135.4 (C Ar), 129.9 (CH Ar), 127.6 (CH Ar), 123.8 (CH Ar), 112.7 (C-1), 19.9 (Me), 19.7 (Me). **HRMS** (ESI): calculated for $C_{10}H_{13}$ $[M+H]^+$ requires *m/z* 133.10118, found *m/z* 133.10120.

4.3. Methylenecyclohexane (S7)

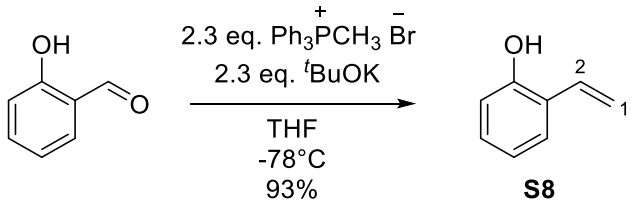


S7

Methyltriphenylphosphonium bromide (17.000 g, 47.592 mmol), ^{t}BuOK (5.370 g, 48.00 mmol), 4-oxotetrahydropyran (4.000 g, 40.00 mmol) and Et_2O (130 mL) were subjected to the general procedure (FCC: gradient elution: 3% → 5% Et_2O - pentane) to yield **S7** as a colorless oil (2.270 g, 58%). Spectroscopic properties matched those previously reported.[11]

Data for **S7**: **R_f** 0.40 (15% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 4.71 (2H, s, 1-H_2), 3.68 (4H, t, *J* = 5.5 Hz, 4-H_2 and 5-H_2), 2.25 (4H, t, *J* = 5.5 Hz, 3-H_2 and 6-H_2). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 144.7 (C-2), 108.4 (C-1), 69.5 (C-4 and C-5), 35.7 (C-3 and C-6). **HRMS** (EI): calculated for $C_6H_{10}O$ $[M]^+$ requires *m/z* 98.0726, found *m/z* 98.0729.

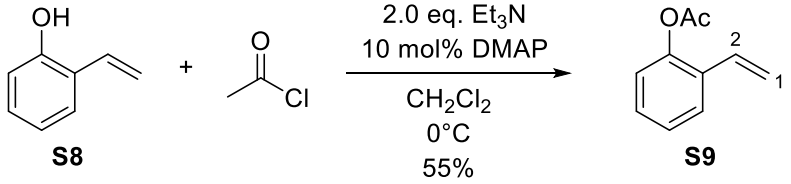
4.4. 2-Vinylphenol (S8)



Methyltriphenylphosphonium bromide (8.220 g, 23.01 mmol), ^{t}BuOK (2.580 g, 23.04 mmol), salicylaldehyde (1.220 g, 10.00 mmol) and THF (53 mL) were subjected to the general procedure except adding the salicylaldehyde at -78°C (FCC: gradient elution: 20% → 30% Et_2O - pentane) to yield **S8** as a colorless liquid (1.120 g, 93%). Spectroscopic properties matched those previously reported.[12]

Data for **S8**: **R_f** 0.5 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40 (1H, dd, *J* = 7.6, 1.7 Hz, Ar), 7.15 (1H, ddd, *J* = 8.1, 7.3, 1.6 Hz, Ar), 6.96 (1H, dd, *J* = 17.7, 11.2 Hz, 2-H), 6.90-6.95 (1H, m, Ar), 6.80 (1H, dd, *J* = 8.0, 1.2 Hz, Ar), 5.75 (1H, dd, *J* = 17.7, 1.4 Hz, 1-H_A), 5.37 (1H, dd, *J* = 11.2, 1.4 Hz, 1-H_B), 5.16 (1H, s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 152.9 (C Ar), 131.6 (C-2), 129.0 (C-H Ar), 127.5 (C-H Ar), 124.9 (C Ar), 121.0 (C-H Ar), 116.0 (C-H Ar and C-1). **HRMS** (Cl): calculated for C_8H_9O $[M+H]^+$ requires *m/z* 121.06479, found *m/z* 121.06465.

4.5. 2-Vinylphenyl acetate (S9)



2-Vinylphenol **S8** (0.480 g, 4.000 mmol) was dissolved in CH_2Cl_2 (40 mL) and the solution was cooled to 0 °C. Triethylamine (0.808 g, 8.000 mmol) and 4-dimethylaminopyridine (50.0 mg, 0.409 mmol) were added, followed by addition of acetyl chloride (0.468 g, 6.000 mmol). After 30 min, the reaction mixture was warmed up to r.t. and stirred for 2 h. The mixture was quenched with satd aq $NaHCO_3$ and the aqueous layer was separated and extracted with Et_2O. The combined extracts were washed with brine, dried over Na_2SO_4, filtered, and concentrated by rotary evaporation. FCC (5% Et_2O - pentane) afforded the acetate **S9** as a colorless oil (0.357 g, 55%). Spectroscopic properties matched those previously reported.[13]

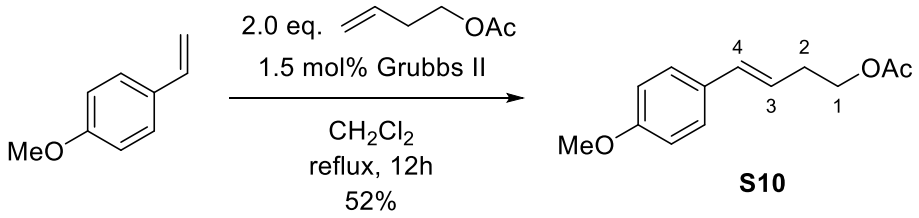
Data for **S9**: **R_f** 0.4 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.59 (1H, d, *J* = 7.7 Hz, Ar), 7.30 (1H, t, *J* = 7.6 Hz, Ar), 7.24 (1H, t, *J* = 7.5 Hz, Ar), 7.06 (1H, d, *J* = 8.0 Hz, Ar), 6.77 (1H, dd, *J* = 17.6, 11.1 Hz, 2-H), 5.78 (1H, dd, *J* = 17.7, 1.8 Hz, 1-H_A), 5.36 (1H, dd, *J* = 11.0, 1.8 Hz, 1-H_B), 2.35 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 169.4 (C=O), 148.1 (C Ar),

130.4 (C-2), 130.3 (C Ar), 128.8 (CH Ar), 126.6 (CH Ar), 126.3 (CH Ar), 122.7 (CH Ar), 116.5 (C-1), 21.0 (Ac Me). **HRMS** (El): calculated for $C_{10}H_{10}O_2$ $[M]^+$ requires *m/z* 162.0675, found *m/z* 162.0678.

5. General procedure for the Ru-catalyzed alkene metathesis reaction

To a flame-dried flask, charged with 1.5 mol% of Ru-catalyst, under Ar, at room temperature, was added 4.0 mL/mmol of dry CH_2Cl_2 (previously degassed, bubbling Ar during 30 min.). A solution of the mixture of alkenes in dry and degassed CH_2Cl_2 (1.0 mL/mmol) was added and the mixture was stirred under reflux. The reaction was monitored by TLC until completion, and the solvent was evaporated under reduced pressure to give the corresponding alkene, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

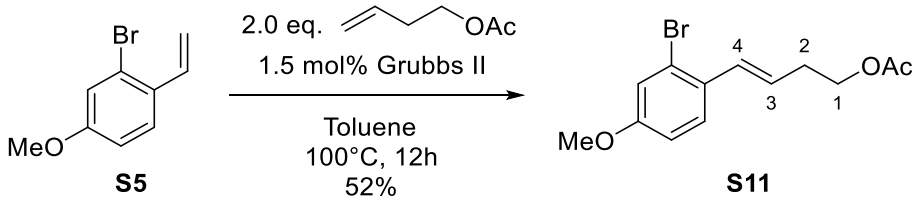
5.1. (3*E*)-4-(4-Methoxyphenyl)but-3-en-1-yl acetate (S10)



1-Methoxy-4-vinylbenzene (5.000 g, 37.28 mmol), but-3-en-1-yl acetate (8.510 g, 74.58 mmol) and Grubbs II (0.470 g, 0.554 mmol) were subjected to the general procedure (FCC: 5% Et_2O - pentane) to yield **S10** as a yellow oil (4.250 g, 52%). Spectroscopic properties matched those previously reported.[14]

Data for **S10**: $\mathbf{R_f}$ 0.30 (10% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$)** δ 7.28 (2H, d, *J* = 8.4 Hz, Ar), 6.84 (2H, m, *J* = 8.8 Hz, Ar), 6.41 (1H, d, *J* = 15.9 Hz, 4-H), 6.02 (1H, dt, *J* = 15.8 and 7.0 Hz, 3-H), 4.17 (1H, t, *J* = 6.8 Hz, 1-H_2), 3.79 (3H, s, OMe), 2.52 (1H, qd, *J* = 6.9 and 1.5 Hz, 2-H_2), 2.05 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$)** δ 171.1 (C=O), 159.0 (C Ar), 131.8 (C-4), 130.1 (C Ar), 127.2 (2 x CH Ar), 123.3 (C-3), 114.0 (2 x CH Ar), 63.9 (C-1), 55.3 (OMe), 32.4 (C-2), 21.0 (Ac Me). **HRMS** (ESI): calculated for $C_{13}H_{16}O_3Na$ $[M+Na]^+$ requires *m/z* 243.0991, found *m/z* 243.0994.

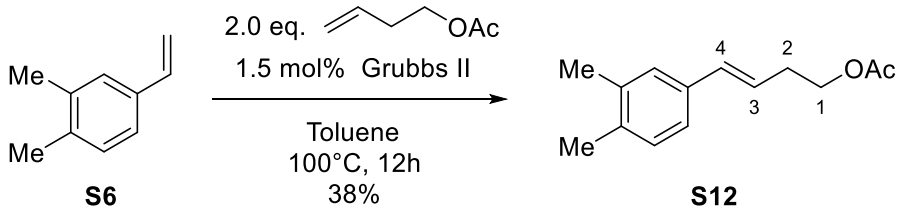
5.2. (3*E*)-4-(2-Bromo-4-methoxyphenyl)but-3-en-1-yl acetate (S11)



Styrene **S5** (0.648 g, 3.04 mmol), but-3-en-1-yl acetate (0.693 g, 6.08 mmol) and Grubbs II (39.0 mg, 0.0460 mmol) were subjected to the general procedure except conducting the reaction in toluene at 100°C (FCC: 5% Et_2O - pentane) to yield **S11** as a colorless oil (0.471 g, 52%).

Data for **S11**: **R_f** 0.3 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40 (1H, d, *J* = 8.7 Hz, Ar), 7.07 (1H, d, *J* = 2.7 Hz, Ar), 6.82 (1H, dd, *J* = 8.7, 2.7 Hz, Ar), 6.72 (1H, d, *J* = 15.8 Hz, 4-H), 5.99 (1H, dt, *J* = 15.7, 7.0 Hz, 3-H), 4.19 (2H, t, *J* = 6.6 Hz, 1-H_2), 3.79 (3H, s, OMe), 2.56 (2H, qd, *J* = 6.8, 1.4 Hz, 2-H_2), 2.06 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 171.2 (C=O), 159.2 (C Ar), 130.7 (C-4), 129.7 (C Ar), 127.4 (C-H Ar), 126.7 (C-3), 123.5 (C Ar), 117.5 (C-H Ar), 114.2 (C-H Ar), 63.6 (C-1), 55.6 (OMe), 32.4 (C-2), 21.0 (Ac Me). **HRMS** (Cl): calculated for $C_{13}H_{15}BrO_3Na$ $[M+Na]^+$ requires *m/z* 321.00968, found *m/z* 321.00946. **IR** (film) ν_{max} : 2980, 2360, 1734, 1600, 1232, 1026 cm^{-1}.

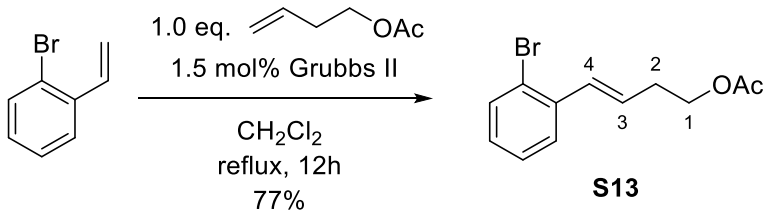
5.3. (3*E*)-4-(3,4-Dimethylphenyl)but-3-en-1-yl acetate (S12)



Styrene **S6** (0.513 g, 3.89 mmol), but-3-en-1-yl acetate (0.885 g, 7.77 mmol) and Grubbs II (49.0 mg, 0.0578 mmol) were subjected to the general procedure except conducting the reaction in toluene at 100°C (FCC: 10% Et_2O - pentane) to yield **S12** as a colorless oil (0.351 g, 38%).

Data for **S12**: **R_f** 0.3 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.15 (1H, s, Ar), 7.12-7.06 (2H, m, Ar), 6.43 (1H, d, *J* = 15.8 Hz, 4-H), 6.12 (1H, dt, *J* = 16.0, 7.0 Hz, 3-H), 4.19 (2H, t, *J* = 6.7 Hz, 1-H_2), 2.54 (2H, qd, *J* = 6.9, 1.4 Hz, 2-H_2), 2.26 (3H, s, Me), 2.25 (3H, s, Me), 2.07 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 171.2 (C=O), 136.7 (C Ar), 135.8 (C Ar), 135.0 (C Ar), 132.4 (C-4), 129.9 (C-H Ar), 127.4 (C-H Ar), 124.4 (C-3), 123.6 (C-H Ar), 63.9 (C-1), 32.5 (C-2), 21.1 (Ac Me), 19.9 (Me), 19.6 (Me). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) ν_{max} : 3656, 2980, 1736, 1232, 1033, 965 cm^{-1}.

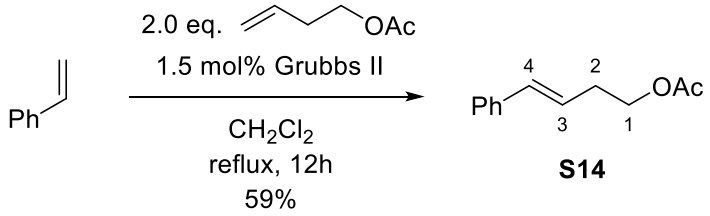
5.4. (3*E*)-4-(2-Bromophenyl)but-3-en-1-yl acetate (S13)



2-Bromostyrene (1.370 g, 7.527 mmol), but-3-en-1-yl acetate (0.855 g, 7.49 mmol) and Grubbs II (48.0 mg, 0.0566 mmol) were subjected to the general procedure (FCC: gradient elution: 4% → 5% Et_2O - pentane) to yield **S13** as a colorless oil (1.550 g, 77%).

Data for **S13**: **R_f** 0.40 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.48 (1H, dd, *J* = 7.8, 1.7 Hz, Ar), 7.22-7.28 (1H, m, Ar), 7.05-7.12 (1H, m, Ar), 6.80 (1H, d, *J* = 15.8 Hz, 4-H), 6.11 (1H, dt, *J* = 15.8, 7.0 Hz, 3-H), 4.22 (2H, t, *J* = 6.6 Hz, 1-H_2), 2.59 (2H, qd, *J* = 6.7, 1.5 Hz, 2-H_2), 2.07 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 171.2 (C=O), 137.3 (C Ar), 133.0 (CH Ar), 131.5 (C-4), 128.9 (C-3), 128.7 (CH Ar), 127.6 (CH Ar), 127.1 (CH Ar), 123.4 (C Ar), 63.6 (C-1), 32.6 (C-2), 21.1 (Ac Me). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) ν_{max} : 2963, 1735, 1472, 1233, 1041, 753 cm^{-1}.

5.5. (3*E*)-4-Phenylbut-3-en-1-yl acetate (S14)

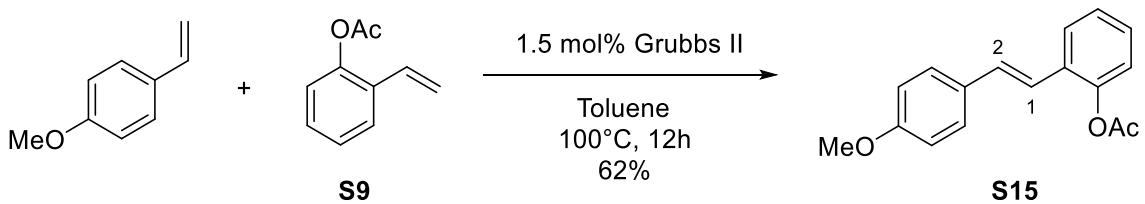


S14

Styrene (0.456 g, 4.38 mmol), but-3-en-1-yl acetate (1.000 g, 8.764 mmol) and Grubbs II (56.0 mg, 0.0660 mmol) were subjected to the general procedure (FCC: gradient elution: 5% → 8% Et_2O - pentane) to yield **S14** as a white solid (0.494 g, 59%). Spectroscopic properties matched those previously reported.[15]

Data for **S14**: **R_f** 0.50 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28-7.38 (4H, m, Ar), 7.19-7.25 (1H, m, Ar), 6.48 (1H, d, *J* = 15.9 Hz, 4-H), 6.18 (1H, dt, *J* = 15.9, 7.0 Hz, 3-H), 4.20 (2H, t, *J* = 6.7 Hz, 1-H_2), 2.55 (2H, qd, *J* = 6.8, 1.5 Hz, 2-H_2), 2.06 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 171.1 (C=O), 137.3 (C Ar), 132.4 (C-4), 128.6 (2 x CH Ar), 127.3 (CH Ar), 126.1 (2 x CH Ar), 125.6 (C-3), 63.8 (C-1), 32.4 (C-2), 21.0 (Ac Me). **HRMS** (ESI): calculated for $C_{12}H_{14}O_2Na$ $[M+Na]^+$ requires *m/z* 213.0886, found *m/z* 213.0888.

5.6. (1*E*)-2-(4-Methoxystyryl)phenyl acetate (S15)



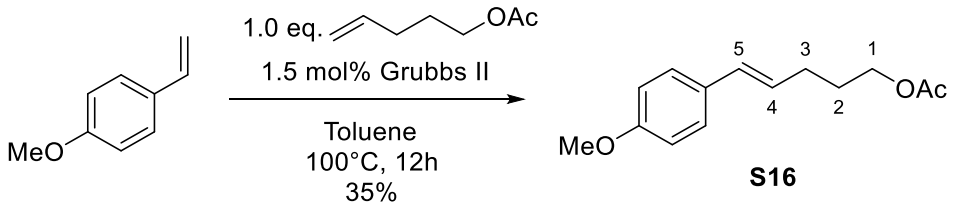
S9 **S15**

1-Methoxy-4-vinylbenzene (0.590 g, 4.40 mmol), acetate **S9** (0.357 g, 2.20 mmol) and Grubbs II (28.0 mg, 0.0330 mmol) were subjected to the general procedure except conducting the

reaction in toluene at 100°C (FCC: gradient elution: 10% → 12% Et_2O - pentane) to yield **S15** as a white solid (0.365 g, 62%). Spectroscopic properties matched those previously reported.[16]

Data for **S15**: **R_f** 0.40 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.64-7.69 (1H, m, Ar), 7.43 (2H ,d, *J* = 8.4 Hz, Ar), 7.21-7.29 (2H, m, Ar), 7.03-7.10 (2H, m, Ar and 2-H), 6.98 (1H, d, *J* = 16.3 Hz, 1-H), 6.90 (2H, d, *J* = 8.7 Hz, Ar), 3.84 (3H, s, OMe), 2.37 (3H, s, Ac Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 169.5 (C=O), 159.7 (C Ar), 148.1 (C Ar), 130.7 (C-2), 130.4 (C Ar), 130.1 (C Ar), 128.1 (CH Ar), 128.0 (2 x CH Ar), 126.5 (CH Ar), 126.4 (CH Ar), 122.8 (CH Ar), 119.8 (C-1), 114.3 (2 x CH Ar), 55.5 (OMe), 21.1 (Ac Me). **HRMS** (ESI): calculated for $C_{17}H_{16}O_3Na$ $[M+Na]^+$ requires *m/z* 291.09917, found *m/z* 291.09909.

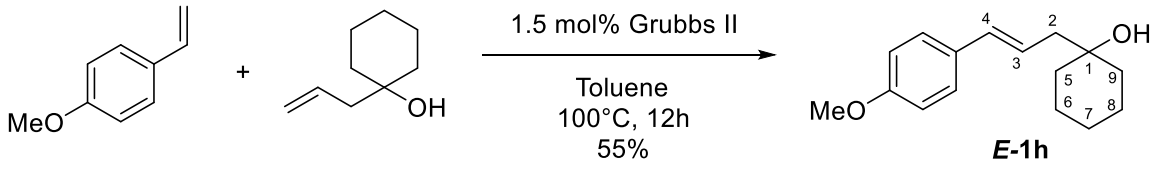
5.7. (4*E*)-5-(4-Methoxyphenyl)pent-4-en-1-yl acetate (S16)



1-Methoxy-4-vinylbenzene (0.499 g, 3.72 mmol), pent-4-en-1-yl acetate (0.952 mg, 7.44 mmol) and Grubbs II (47.0 mg, 0.0554 mmol) were subjected to the general procedure except conducting the reaction in toluene at 100°C (FCC: gradient elution: 8% → 10% Et_2O - pentane) to yield **S16** as a colorless oil (0.302 g, 35%). Spectroscopic properties matched those previously reported.[17]

Data for **S16**: **R_f** 0.40 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.27 (2H, d, *J* = 8.6 Hz, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.35 (1H, d, *J* = 15.9 Hz, 5-H), 6.05 (1H, dt, *J* = 15.8, 6.9 Hz, 4-H), 4.11 (2H, t, *J* = 6.6 Hz, 1-H_2), 3.79 (3H, s, OMe), 2.26 (2H, qd, *J* = 7.0, 1.5 Hz, 3-H_2), 2.05 (3H, s, Ac Me), 1.80 (2H, tt, *J* = 7.6, 6.4 Hz, 2-H_2). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 171.6 (C=O), 159.2 (C Ar), 130.8 (C Ar), 130.4 (C-5), 127.54 (C-4), 127.48 (2 x CH Ar), 114.3 (2 x CH Ar), 64.4 (C-1), 55.7 (OMe), 29.8 (C-3), 29.7 (C-2), 21.5 (Ac Me). **HRMS** (Cl): calculated for $C_{14}H_{19}O_3$ $[M+H]^+$ requires *m/z* 235.13287, found *m/z* 235.13284.

5.8. (3*E*)-1-[3-(4-Methoxyphenyl)allyl]cyclohexan-1-ol (*E*-1h)

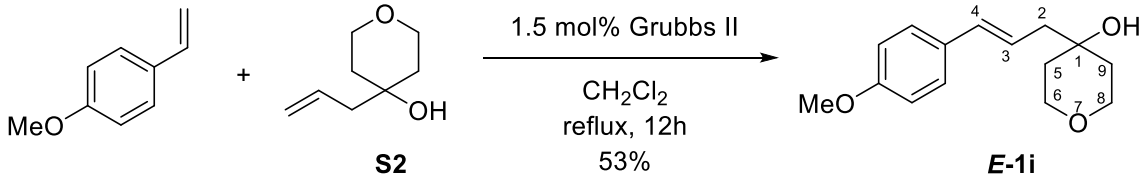


1-Methoxy-4-vinylbenzene (1.900 g, 14.17 mmol), 1-allylcyclohexanol (1.000 g, 7.138 mmol) and Grubbs II (90.0 mg, 0.106 mmol) were subjected to the general procedure except

conducting the reaction in toluene at 100°C (FCC: gradient elution: 12% → 20% Et_2O - pentane) to yield ***E*-1h** as a yellow oil (0.964 g, 55%).

Data for ***E*-1h**: **R_f** 0.3 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30 (2H, d, *J* = 8.7 Hz, Ar), 6.84 (2H, d, *J* = 8.7 Hz, Ar), 6.40 (1H, d, *J* = 15.8 Hz, 4-H), 6.15 (1H, dt, *J* = 15.5, 7.6 Hz, 3-H), 3.80 (3H, s, OMe), 2.34 (2H, dd, *J* = 7.6, 1.2 Hz, 2-H_2), 1.42-1.67 (9H, m, 5-H_2, 6-H_2, 8-H_2, 9-H_2 and 7-H_A), 1.22-1.36 (1H, m, 7-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.5 (C Ar), 133.2 (C-4), 130.3 (C Ar), 127.4 (2 x CH Ar), 123.1 (C-3), 114.0 (2 x CH Ar), 71.7 (C-1), 55.4 (OMe), 46.0 (C-2), 37.6 (2 x CH_2 cyclohexenyl), 25.9 (CH_2 cyclohexenyl), 22.3 (2 x CH_2 cyclohexenyl). **HRMS** (Cl): calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ requires *m/z* 269.15120, found *m/z* 269.15106. **IR** (film) ν_{max} : 3426, 2928, 1608, 1509, 1244, 967 cm^{-1}

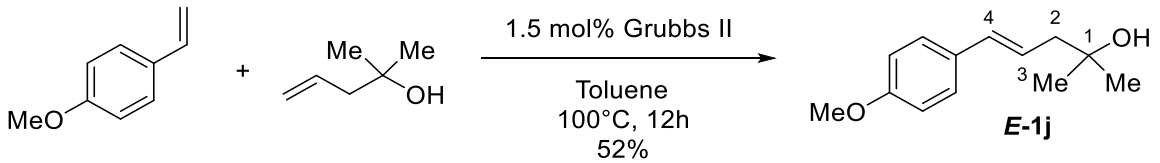
5.9. (3*E*)-1-[3-(4-Methoxyphenyl)allyl]tetrahydro-2*H*-pyran-1-ol (*E*-1i)



1-Methoxy-4-vinylbenzene (0.734 g, 5.48 mmol), alcohol **S2** (0.389 g, 2.73 mmol) and Grubbs II (35.0 mg, 0.0413 mmol) were subjected to the general procedure (FCC: gradient elution: 15% → 50% Et_2O - pentane) to yield ***E*-1i** as a yellow oil (0.365 g, 53%).

Data for ***E*-1i**: **R_f** 0.30 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.44 (1H, d, *J* = 15.8 Hz, 4-H), 6.12 (1H, dt, *J* = 15.5, 7.6 Hz, 3-H), 3.80 (3H, s, OMe), 3.74-3.80 (4H, m, 6-H_2 and 8-H_2), 2.37 (2H, dd, *J* = 7.7, 1.3 Hz, 2-H_2), 1.70-1.81 and 1.50-1.56 (4H, m, 5-H_2 and 9-H_2). .**^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.3 (C Ar), 134.3 (C-4), 130.0 (C Ar), 127.5 (2 x CH Ar), 131.6 (C-3), 114.1 (2 x CH Ar), 69.0 (C-1), 64.0 (C-6 and C-8), 55.5 (OMe), 46.8 (C-2), 37.8 (C-5 and C-9). **HRMS** (El): calculated for $C_{15}H_{20}O_3$ $[M]^+$ requires *m/z* 248.1407, found *m/z* 248.1408. **IR** (film) ν_{max} : 3408, 2950, 1606, 1509, 1244, 1096 cm^{-1}.

5.10. (3*E*)-4-(4-Methoxyphenyl)-1,1-dimethylbut-3-en-1-ol (*E*-1j)

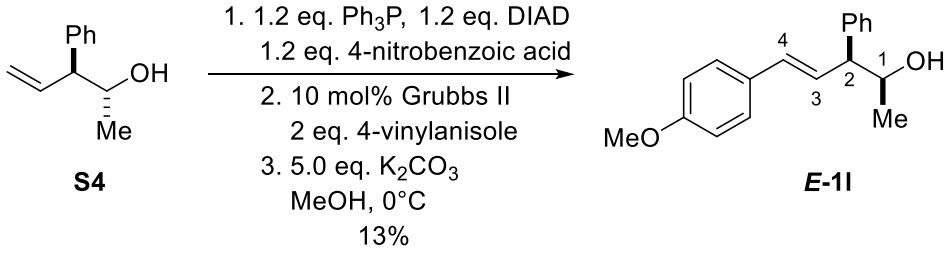


1-Methoxy-4-vinylbenzene (0.937 g, 6.99 mmol), 2-methylpent-4-en-2-ol (0.350 g, 3.50 mmol) and Grubbs II (45.0 mg, 0.0531 mmol) were subjected to the general procedure except

conducting the reaction in toluene at 100°C (FCC: gradient elution: 20% → 50% Et_2O - pentane) to yield ***E*-1j** as a yellow oil (0.376 g, 52%).

Data for ***E*-1j**: **R_f** 0.40 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31 (2H, d, *J* = 8.3 Hz, Ar), 6.85 (2H, d, *J* = 8.3 Hz, Ar), 6.41 (1H, d, *J* = 15.8 Hz, 4-H), 6.41 (1H, dt, *J* = 15.8, 7.6 Hz, 3-H), 3.81 (3H, s, OMe), 2.36 (2H, d, *J* = 7.6 Hz, 2-H_2), 1.63 (1H, br s, OH), 1.27 (6H, s, 2 x Me).**^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.1 (C Ar), 133.3 (C-4), 130.3 (C Ar), 127.4 (2 x CH Ar), 123.5 (C-3), 114.1 (2 x CH Ar), 71.0 (C-1), 55.5 (OMe), 47.5 (C-2), 29.4 (2 x Me) . **HRMS** (ESI): calculated for $C_{13}H_{18}O_2$ $[M]^+$ requires *m/z* 206.1301, found *m/z* 206.1306. **IR** (film) ν_{max} : 3385, 2970, 1576, 1244, 1174, 1033 cm^{-1}.

5.11. (±)-(2*S*,3*S*,3*E*)-5-(4-Methoxyphenyl)-3-phenylpent-4-en-2-ol (*E*-1l)

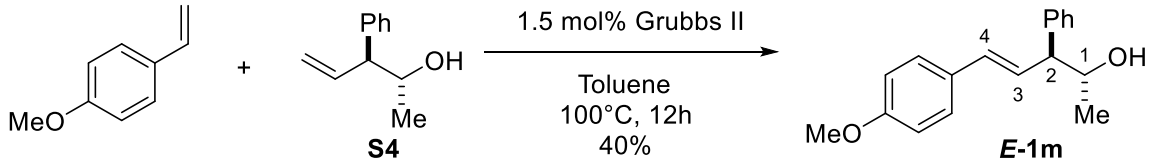


To a mixture of alcohol **S4** (0.060 g, 0.37 mmol), PPh_3 (0.116 g, 0.443 mmol) and para-nitrobenzoic acid (0.072 g, 0.44 mmol) in THF (1 mL) at –20°C was added dropwise DIAD (0.09 mL, 0.44 mmol) over a period of 30 min. The mixture was then stirred for 1 h while allowing to warm to 0 °C and then diluted with Et_2O and washed with an aqueous solution of $NaHCO_3$. The aqueous layer was extracted with Et_2O, and the combined organic layers were washed with brine, dried over $MgSO_4$, filtered, and concentrated. The crude was flushed through a layer of slica gel with 10% Et_2O in pentane, then the filtrate was concentrated and added to flame-dried flask, charged with 4-vinylanisole (0.013 g, 0.097 mmol), Grubbs II (4.1 mg, 0.0048 mmol) and degassed toluene (0.24 mL). The solution was heat at 100 °C for 24 hours. Then the solvent was evaporated and the crude was added to a flask charged with K_2CO_3 (23.0 mg, 0.162 mmol) and MeOH (1 mL) at 0 °C. The solution was sitrred for 2 hours, then concentrated in reduced pressure to give the crude residue which was purified (FCC: gradient elution: 13% → 20% Et_2O - pentane) to yield ***E*-1l** as a yellow oil (12.9 mg, 13%).

Data for ***E*-1l**: **R_f** 0.50 (70% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.28-7.35 (4H, m, Ar), 7.20-7.27 (3H, m, Ar), 6.83 (2H, d, *J* = 8.7 Hz, Ar), 6.50 (1H, d, *J* = 15.8 Hz, 4-H), 6.32 (1H, dd, *J* = 15.8, 9.2 Hz, 3-H), 4.04 (1H, quint, *J* = 6.7 Hz, 1-H), 3.79 (3H, s, OMe), 3.29 (1H, t, *J* = 8.4 Hz, 2-H), 1.92 (1H, br s, OH), 1.10 (3H, d, *J* = 6.1 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.3 (C Ar), 132.1 (C Ar), 132.7 (C-4), 129.8 (C Ar), 128.9 (2 x C-H Ar), 128.1 (2 x C-H Ar), 127.63 (2 x C-H Ar), 127.57 (C-3), 126.9 (C-H Ar), 114.1 (2 x C-H Ar), 70.8 (C-1), 58.5 (C-2),

55.5 (OMe), 20.9 (Me). **HRMS** (EI): calculated for $C_{18}H_{20}O_2$ $[M]^+$ requires *m/z* 268.1458, found *m/z* 268.1466. **IR** (film) ν_{max}: 3657, 2980, 1387, 1249, 1151, 1026 cm^{-1}.

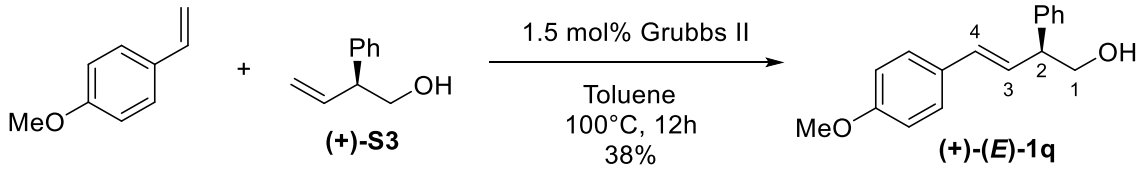
5.12. (±)-(2*R*,3*S*,3*E*)-5-(4-Methoxyphenyl)-3-phenylpent-4-en-2-ol (*E*-1m)



1-Methoxy-4-vinylbenzene (0.358 g, 2.67 mmol), alcohol **S4** (0.217 g, 1.34 mmol) and Grubbs II (17.0 mg, 0.0200 mmol) were subjected to the general procedure except conducting the reaction in toluene at 100°C (FCC: gradient elution: 13% → 20% Et_2O - pentane) to yield ***E*-1m** as a yellow oil (0.149 g, 40%).

Data for ***E*-1m**: **R_f** 0.40 (60% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.23-7.40 (7H, m, Ar), 6.83 (2H, d, *J* = 8.8 Hz, Ar), 6.43 (1H, d, *J* = 15.8 Hz, 4-H), 6.26 (1H, dd, *J* = 15.8, 8.8 Hz, 3-H), 4.08-4.18 (1H, m, 1-H), 3.80 (3H, s, OMe), 3.38 (1H, t, *J* = 8.3 Hz, 2-H), 1.54 (1H, br s, OH), 1.29 (3H, d, *J* = 6.2 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 141.4 (C Ar), 131.5 (C-4), 130.1 (C Ar), 129.0 (2 x C-H Ar), 128.6 (2 x C-H Ar), 127.9 (C-3), 127.5 (2 x C-H Ar), 127.1 (C-H Ar), 114.1 (2 x C-H Ar), 71.0 (C-1), 58.4 (C-2), 55.4 (OMe), 21.0 (Me). **HRMS (EI):** calculated for $C_{18}H_{20}O_2$ [M]+ requires *m/z* 268.1458, found *m/z* 268.1466. **IR** (film) ν_{max}: 3657, 2980, 1387, 1249, 1151, 1026 cm^{-1}.

5.13. (+)-(2*S*,3*E*)-4-(4-Methoxyphenyl)-2-phenylbut-3-en-1-ol [(+)-(*E*)-1q]



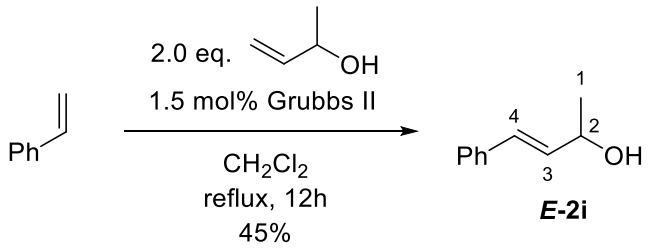
1-Methoxy-4-vinylbenzene (0.708 g, 5.28 mmol), alcohol **(+)-S3** (0.391 g, 2.64 mmol) and Grubbs II (33.6 mg, 0.0396 mmol) were subjected to the general procedure except conducting the reaction in toluene at 100°C (FCC: gradient elution: 15% → 20% Et_2O - pentane) to yield **(+)-(*E*)-1q** as a yellow solid (0.256 g, 38%). Spectroscopic properties matched those previously reported.[18]

Data for **(+)-(*E*)-1q**: **R_f** 0.40 (60% Et_2O - pentane). $[\alpha]_D^{25}$ = +61.2 (0.01 g/mL, $CHCl_3$) .**^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.23-7.40 (7H, m, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.48 (1H, d, *J* = 15.8 Hz, 4-H), 6.23 (1H, dd, *J* = 15.9, 8.0 Hz, 3-H), 3.87-3.93 (2H, m, 1-H_2), 3.80 (3H, s, OMe), 3.68 (1H, q, *J* = 7.2 Hz, 2-H), 1.53 (1H, s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.3 (C Ar), 141.2 (C Ar), 131.8 (C-4), 129.9 (C Ar), 129.0 (2 x CH Ar), 128.1 (2 x CH Ar), 127.6 (2 x CH Ar),

127.5 (C-3), 127.1 (CH Ar), 114.1 (2 x CH Ar), 66.6 (C-1), 55.4 (OMe), 52.0 (C-2). **HRMS** (CI): calculated for $C_{17}H_{18}O_2$ $[M]^+$ requires *m/z* 254.1301, found *m/z* 254.1295.

Racemic **(*E*)-1q** (38% yield) was made via the same procedure using racemic alcohol **S3**.

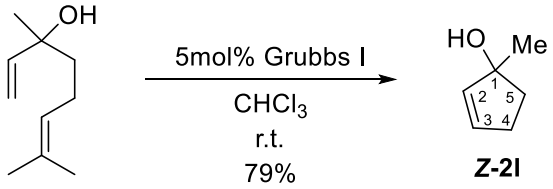
5.14. (±)- (3*E*)-4-Phenylbut-3-en-2-ol (*E*-2i)



Styrene (1.000 g, 9.606 mmol), but-3-en-2-ol (1.380 g, 19.14 mmol) and Grubbs II (122.0 mg, 0.1438 mmol) were subjected to the general procedure (FCC: 30% Et_2O - pentane) to yield ***E*-2i** as a yellow oil (0.712 g, 50%). Spectroscopic properties matched those previously reported.[19]

Data for ***E*-2i**: **R_f** 0.30 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.36-7.41 (2H, m, Ar), 7.29-7.35 (2H, m, Ar), 7.21-7.27 (1H, m, Ar), 6.57 (1H, d, *J* = 15.8 Hz, 4-H), 6.27 (1H, dd, *J* = 15.9, 6.4 Hz, 3-H), 4.44-4.55 (1H, m, 2-H), 1.66 (1H, br s, OH), 1.38 (3H, d, *J* = 6.4 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 136.8 (C Ar), 133.7 (C-3), 129.5 (C-4), 128.7 (2 x C-H Ar), 127.8 (C-H Ar), 126.6 (2 x C-H Ar), 69.1 (C-2), 23.5 (Me).

5.15. (±)-1-Methylcyclopent-2-en-1-ol (*Z*-2l)



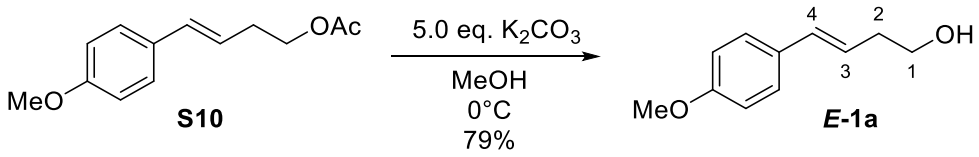
Linalool (0.500 g, 3.23 mmol) and Grubbs I (0.133 g, 0.161 mmol) were subjected to the general procedure except conducting the reaction at r.t. in $CHCl_3$ (FCC: gradient elution: 20% → 50% Et_2O - pentane) to yield ***Z*-2l** as a yellow oil (0.250 g, 79%). Spectroscopic properties matched those previously reported.[20]

Data for ***Z*-2l**: **R_f** 0.40 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.81 (1H, dt, *J* = 5.4, 2.3 Hz, 3-H), 5.69 (1H, dt, *J* = 5.4, 2.3 Hz, 2-H), 2.48 (1H, m, 4-H_A), 2.30 (1H, m, 4-H_B), 1.96 (1H, ddd, *J* = 13.4, 8.1, 4.8 Hz, 5-H_A), 1.89 (1H, ddd, *J* = 13.4, 8.1, 4.8 Hz, 5-H_B), 1.37 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 138.0 (C-2), 132.8 (C-3), 83.6 (C-1), 39.8 (C-5), 31.2 (C-4), 27.6 (Me).

6. General procedure for acetate deprotection

To a solution of acetate in MeOH (10.0 mL/mmol), 5.0 equiv of K_2CO_3 were added in one portion at 0°C. The reaction was monitored by TLC until completion. The mixture was filtered and the solvent was evaporated under reduced pressure to give the corresponding alcohol, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

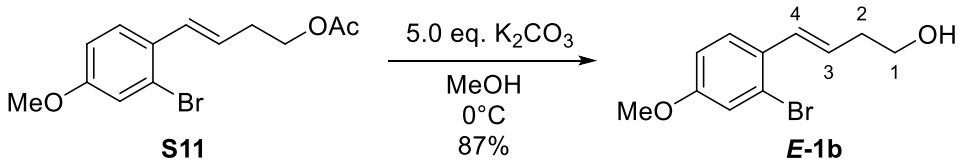
6.1. (3*E*)-4-(4-Methoxyphenyl)but-3-en-1-ol (*E*-1a)



Acetate **S10** (3.510 g, 15.95 mmol) and K_2CO_3 (6.580 g, 47.68 mmol) were subjected to the general procedure (FCC: gradient elution: 50% → 100% Et_2O - pentane) to yield ***E*-1a** as a white solid (2.230 g, 79%). Spectroscopic properties matched those previously reported.[21]

Data for ***E*-1a**: **R_f** 0.33 (75 % Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.30 (2H, d, *J* = 8.9 Hz, Ar), 6.84 (2H, d, *J* = 8.8 Hz, Ar), 6.45 (1H, d, *J* = 15.9 Hz, 4-H), 6.05 (1H, dt, *J* = 15.8, 7.2 Hz, 3-H), 3.80 (3H, s, OMe), 3.75 (2H, t, *J* = 7.5 Hz, 1-H_2), 2.43-2.50 (2H, m, 2-H_2), 1.47 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.0 (C Ar), 132.3 (C-4), 130.1 (C Ar), 127.2 (2 x CH Ar), 124.0 (C-3), 114.0 (2 x CH Ar), 62.1 (C-1), 55.3 (OMe), 36.4 (C-2). **HRMS** (Cl): calculated for $C_{11}H_{15}O_2$ $[M+H]^+$ requires *m/z* 179.1072, found *m/z* 179.1067.

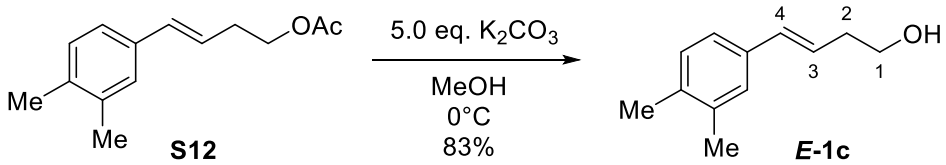
6.2. (3*E*)-4-(2-Bromo-4-methoxyphenyl)but-3-en-1-ol (*E*-1b)



Acetate **S11** (0.396 g, 1.32 mmol) and K_2CO_3 (0.913 g, 6.62 mmol) were subjected to the general procedure (FCC: gradient elution: 30% → 100% Et_2O - pentane) to yield ***E*-1b** as a yellow oil (0.296 g, 87%).

Data for ***E*-1b**: **R_f** 0.30 (80 % Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.42 (1H, d, *J* = 8.7 Hz, Ar), 7.07 (1H, d, *J* = 2.6 Hz, Ar), 6.82 (1H, dd, *J* = 8.7, 2.6 Hz, Ar), 6.75 (1H, d, *J* = 15.8 Hz, 4-H), 6.03 (1H, dt, *J* = 16.0, 7.1 Hz, 3-H), 3.78 (3H, s, OMe), 3.76 (2H, t, *J* = 6.7 Hz, 1-H_2), 2.51 (2H, dq, *J* = 6.3, 1.3 Hz, 2-H_2), 1.59 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ**159.3 (C Ar), 131.1 (C-4), 129.8 (C Ar), 127.6 (C-3), 127.5 (CH Ar), 123.6 (C Ar), 117.6 (CH Ar), 114.3 (CH Ar), 62.1 (C-1), 55.7 (OMe), 36.5 (C-2). **HRMS** (Cl): calculated for $C_{11}H_{14}O_2Br$ $[M+H]^+$ requires *m/z* 257.01717, found *m/z* 257.01703. **IR** (film) ν_{max} : 3341, 2980, 1599, 1487, 1281, 1025 cm^{-1}.

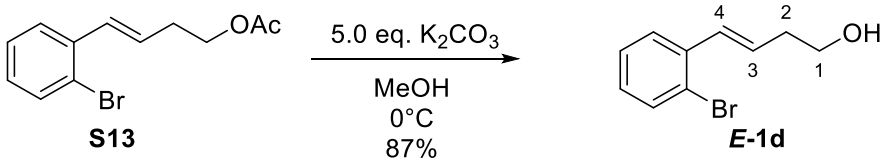
6.3. (3*E*)-4-(3,4-Dimethylphenyl)but-3-en-1-ol (*E*-1c)



Acetate **S12** (0.351 g, 1.50 mmol) and K_2CO_3 (1.039 g, 7.529 mmol) were subjected to the general procedure (FCC: gradient elution: 40% → 50% Et_2O - pentane) to yield ***E*-1c** as a yellow oil (0.251 g, 83%).

Data for ***E*-1c**: **R_f** 0.45 (80 % Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.15 (1H, d, *J* = 1.7 Hz, Ar), 7.03-7.12 (2H, m, Ar), 6.45 (1H, d, *J* = 15.9 Hz, 4-H), 6.14 (1H, dt, *J* = 15.8, 7.2 Hz, 3-H), 3.74 (2H, t, *J* = 6.3 Hz, 1-H_2), 2.47 (2H, qd, *J* = 6.3, 1.4 Hz, 2-H_2), 2.25 (3H, s, Me), 2.24 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 136.7 (C Ar), 135.9 (C Ar), 135.0 (C Ar), 132.9 (C-4), 129.9 (CH Ar), 127.5 (CH Ar), 126.1 (C-3), 123.7 (CH Ar), 62.2 (C-1), 36.6 (C-2), 19.9 (Me), 19.6 (Me). **HRMS** (EI): calculated for $C_{12}H_{16}O$ $[M]^+$ requires *m/z* 176.1196, found *m/z* 176.1194. **IR** (film) ν_{max} : 3335, 2980, 1382, 1154, 1045, 965 cm^{-1}.

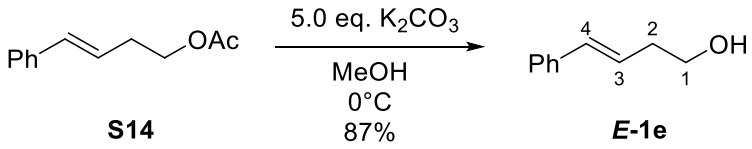
6.4. (3*E*)-4-(2-Bromophenyl)but-3-en-1-ol (*E*-1d)



Acetate **S13** (1.550 g, 5.784 mmol) and K_2CO_3 (4.000 g, 28.99 mmol) were subjected to the general procedure (FCC: gradient elution: 20% → 30% Et_2O - pentane) to yield ***E*-1d** as a colorless oil (1.138 g, 87%). Spectroscopic properties matched those previously reported.[22]

Data for ***E*-1d**: **R_f** 0.4 (80% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.53 (1H, dd, *J* = 8.0, 1.3 Hz, Ar), 7.50 (1H, dd, *J* = 7.8, 1.7 Hz, Ar), 7.22-7.28 (1H, m, Ar), 7.05-7.10 (1H, m, Ar), 6.83 (1H, d, *J* = 15.8 Hz, 4-H), 6.16 (1H, dt, *J* = 15.8, 7.1 Hz, 3-H), 3.79 (1H, t, *J* = 6.3 Hz, 1-H_2), 2.53 (1H, dtd, *J* = 7.7, 6.3, 1.5 Hz, 2-H_2), 1.57 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 137.3 (C Ar), 133.0 (CH Ar), 131.7 (C-4), 129.8 (C-3), 128.7 (CH Ar), 127.6 (CH Ar), 127.1 (CH Ar), 123.4 (C Ar), 62.1 (C-1), 36.6 (C-2). **HRMS** (CI): calculated for $C_{10}H_{10}OBr$ $[M-H]^+$ requires *m/z* 224.99113, found *m/z* 224.99095.

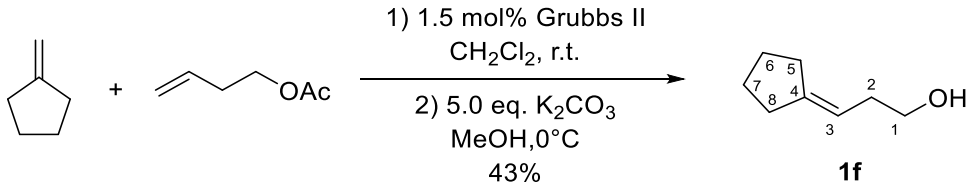
6.5. (3*E*)-4-Phenylbut-3-en-1-ol (*E*-1e)



Acetate **S14** (0.541 g, 2.85 mmol) and K_2CO_3 (1.970 g, 14.28 mmol) were subjected to the general procedure (FCC: gradient elution: 40% → 60% Et_2O - pentane) to yield ***E*-1e** as a colorless oil (0.369 g, 87%). Spectroscopic properties matched those previously reported.[23]

Data for ***E*-1e**: **R_f** 0.4 (75% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28-7.39 (4H, m, Ar), 7.19-7.25 (1H, m, Ar), 6.51 (1H, d, *J* = 15.8 Hz, 4-H), 6.21 (1H, dt, *J* = 15.9, 7.1 Hz, 3-H), 3.73-3.81 (2H, m, 1-H_2), 2.47-2.53 (2H, m, 2-H_2), 1.47 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 137.2 (C Ar), 132.9 (C-4), 128.6 (2 x CH Ar), 127.3 (CH Ar), 126.3 (C-3), 126.1 (2 x CH Ar), 62.0 (C-1), 36.4 (C-2). **HRMS** (CI): calculated for $C_{10}H_{17}ON$ $[M+NH_4]^+$ requires *m/z* 166.1232, found *m/z* 166.1227.

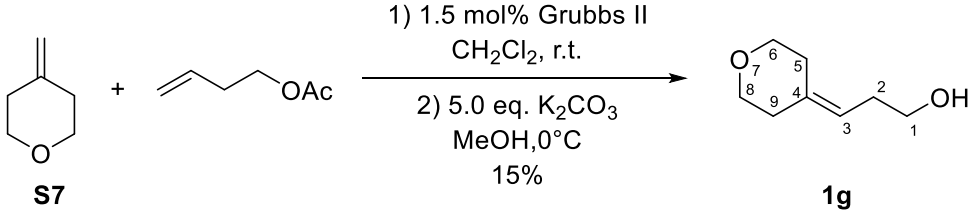
6.6. 3-Cyclopentylidenepropan-1-ol (1f)



To a solution of but-3-en-1-yl acetate (0.246 g, 2.19 mmol) in methylenecyclopentane (0.898 g, 11.0 mmol) at r.t. was added Grubbs II (26.0 mg, 0.0307 mmol). The mixture was stirred for 72 hours and concentrated in vacuo. To the crude was then added K_2CO_3 (1.600 g, 11.59 mmol) in MeOH (12 mL) at 0°C. The reaction was monitored by TLC until completion. The mixture was filtered and the solvent was evaporated under reduced pressure, that was purified (FCC: gradient elution: 20% → 30% Et_2O - pentane) to afford **1f** as a colorless oil (0.120 g, 43%).

Data for **1f**: **R_f** 0.4 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.20-5.27 (1H, m, 3-H), 3.63 (1H, t, *J* = 6.3 Hz, 1-H_2), 2.17-2.31 (6H, m, 2-H_2, 5-H_2 and 8-H_2), 1.56-1.72 (4H, m, 6-H_2 and 7-H_2), 1.49 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 147.3 (C-4), 115.5 (C-3), 62.6 (C-1), 33.9 and 33.3 (C-5 and C-8), 29.0 (C-2), 26.52 and 26.45 (C-6 and C-7). **HRMS** (ESI): calculated for $C_8H_{15}O$ $[M+H]^+$ requires *m/z* 127.11174, found *m/z* 127.11185. **IR** (film) ν_{max} : 3332, 2980, 2887, 1432, 1251, 1047 cm^{-1}.

6.7. 3-(Tetrahydro-4*H*-pyran-4-ylidene)propan-1-ol (1g)

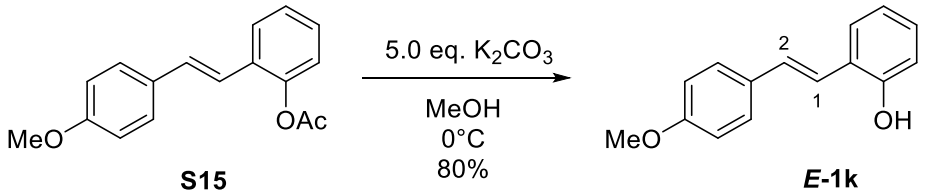


To a solution of but-3-en-1-yl acetate (0.182 g, 1.53 mmol), alkene **S7** (0.300 g, 3.06 mmol) in CH_2Cl_2 (8 mL) at r.t. was added Grubbs II (20.0 mg, 0.0236 mmol). The mixture was stirred for

72 hours and concentrated in vacuo. To the crude was then added K_2CO_3 (1.060 g, 7.681 mmol) in MeOH (7.7 mL) at 0°C. The reaction was monitored by TLC until completion. The mixture was filtered and the solvent was evaporated under reduced pressure, that was purified by chromatography on silica gel (FCC: gradient elution: 50% → 100% Et_2O - pentane) to afford **1g** as a colorless oil (0.033 g, 15%). Spectroscopic properties matched those previously reported.[24]

Data for **1g**: **R_f** 0.30 (Et_2O). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 5.20 (1H, t, *J* = 7.5 Hz, 3-H), 3.59-3.73 (6H, m, 1-H_2, 6-H_2 and 8-H_2), 2.19-2.35 (6H, m, 2-H_2, 5-H_2 and 9-H_2), 1.62 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 137.7 (C-4), 119.9 (C-3), 69.8 and 69.0 (C-6 and C-8), 62.6 (C-1), 37.1 and 30.6 (C-5 and C-9), 30.0 (C-2). **HRMS**: stable ion was not found in ESI, EI and CI.

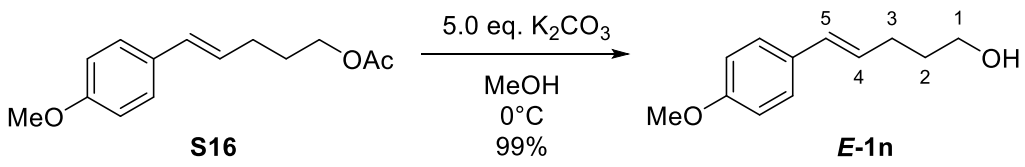
6.8. (1*E*)-2-(4-Methoxystyryl)phenol (*E*-1k)



Acetate **S15** (0.345 g, 1.29 mmol) and K_2CO_3 (0.888 g, 6.44 mmol) were subjected to the general procedure (FCC: gradient elution: 20% → 50% Et_2O - pentane) to yield ***E*-1k** as a white solid (0.230 g, 80%). Spectroscopic properties matched those previously reported.[25]

Data for ***E*-1k**: **R_f** 0.4 (50 % Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.42-7.52 (3H, m, Ar), 7.21 (1H, d, *J* = 16.4 Hz, 2-H), 7.11 (1H, t, *J* = 7.5 Hz, Ar), 7.05 (1H, d, *J* = 16.4 Hz, 1-H), 6.93 (1H, t, *J* = 7.8 Hz, Ar), 6.89 (2H, d, *J* = 8.5 Hz, Ar), 6.79 (1H, d, *J* = 8.0 Hz, Ar), 5.12 (1H, s, OH), 3.82 (3H, s, OMe). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.4 (C Ar), 153.0 (C Ar), 130.5 (C Ar), 129.9 (C-1), 128.4 (CH Ar), 127.9 (2 x CH Ar), 127.1 (CH Ar), 125.1 (C Ar), 121.2 (CH Ar), 121.0 (C-2), 116.0 (CH Ar), 114.2 (2 x CH Ar), 55.5 (OMe). **HRMS** (CI): calculated for $C_{15}H_{15}O_2$ $[M+H]^+$ requires *m/z* 227.10666, found *m/z* 227.10658.

6.9. (4*E*)-5-(4-Methoxyphenyl)pent-4-en-1-ol (*E*-1n)



Acetate **S16** (0.304 g, 1.30 mmol) and K_2CO_3 (0.896 g, 6.50 mmol) were subjected to the general procedure (FCC: gradient elution: 40% → 100% Et_2O - pentane) to yield ***E*-1n** as a white solid (0.249 g, 99%). Spectroscopic properties matched those previously reported.[26]

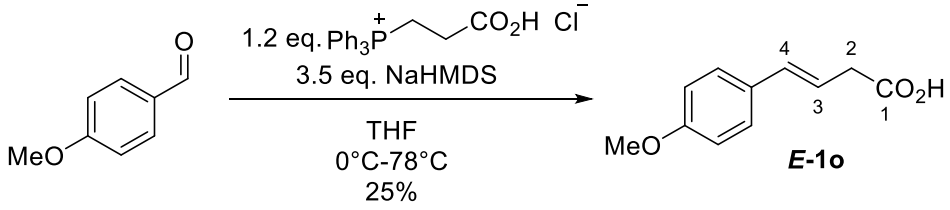
Data for ***E*-1n**: **R_f** 0.30 (60% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28 (2H, d, *J* = 8.7 Hz, Ar), 6.84 (2H, d, *J* = 8.7 Hz, Ar), 6.36 (1H, d, *J* = 15.8 Hz, 5-H), 6.09 (1H, dt, *J* = 15.7,

6.9 Hz, 4-H), 3.80 (3H, s, OMe), 3.70 (2H, t, *J* = 6.5 Hz, 1-H_2), 2.29 (2H, qd, J = 7.3, 1.5 Hz, 3-H_2), 1.74 (2H, tt, *J* = 7.7, 6.4 Hz, 2-H_2), 1.44 (1H, br s, OH). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.8 (C Ar), 130.6 (C Ar), 129.8 (C-5), 128.0 (C-4), 127.2 (2 x CH Ar), 114.0 (2 x CH Ar), 62.6 (C-1), 55.4 (OMe), 32.5 (C-2), 29.4 (C-3). **HRMS** (Cl): calculated for $C_{12}H_{17}O_2$ $[M+H]^+$ requires *m/z* 193.12231, found *m/z* 193.12245.

7. General procedure for the synthesis of *E*-styrenes with a carboxylic acid moiety.

To a solution of triphenylphosphonium salt (1.2 eq.) in THF (2 mL) was added dropwise a 1 M solution of NaHMDS (3.5 eq.) at 0 °C. The solution was then stirred for 30 min. After cooling to -78 °C**,** aldehyde (1.0 eq.) was added dropwise. The reaction was allowed to warm up to r.t. overnight. Add water and Et_2O and pour the mixture into a separatory funnel. Separate the aqueous layer and acidify with 1 M HCl until pH=1. Extract the aqueous layer with Et_2O twice. The organic layer was dried with $MgSO_4$. Then the solvent was evaporated under reduced pressure to give the acid. FCC afforded the corresponding carboxylic acid.

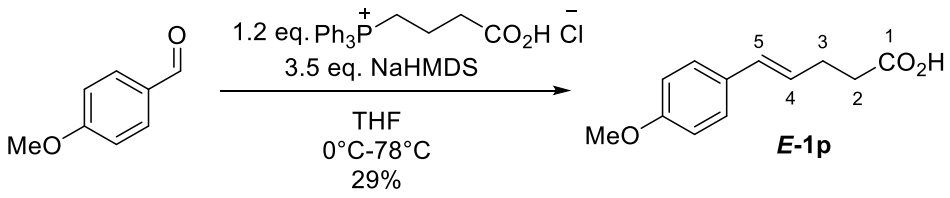
7.1. (3*E*)-4-(4-Methoxyphenyl)but-3-enoic acid (*E*-1o)



(2-Carboxyethyl)(triphenyl)phosphonium chloride (1.500 g, 4.054 mmol), NaHMDS (1M, 11.5 mL, 11.5 mmol) and 4-methoxybenzaldehyde (0.460 g, 3.37 mmol) were subjected to the general procedure (FCC: 100% EtOAc) to yield ***E*-1o** as a yellow solid (0.161 g, 25%). Spectroscopic properties matched those previously reported.[27]

Data for ***E*-1o**: **R_f**: 0.5 (100% EtOAc). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 10.07 (1H, br s, CO_2H), 7.31 (2H, d, *J* = 8.7 Hz, Ar), 6.85 (2H, d, *J* = 8.7 Hz, Ar), 6.46 (1H, d, *J* = 15.9 Hz, 4-H), 6.14 (1H, dt, *J* = 15.8, 7.1 Hz, 3-H), 3.81 (3H, s, OMe), 3.28 (2H, dd, *J* = 7.1, 1.5 Hz, 2-H_2). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 178.3 (C=O), 159.35 (C Ar), 133.5 (C-4), 129.6 (C Ar), 127.6 (2 x CH Ar), 118.7 (C-3), 114.1 (2 x CH Ar), 55.4 (OMe), 38.2 (C-2). **HRMS** (Cl): calculated for $C_{11}H_{12}O_3$ $[M]^+$ requires *m/z* 192.0786, found *m/z* 192.0788.

7.2. (4*E*)-5-(4-Methoxyphenyl)pent-4-enoic acid (*E*-1p)

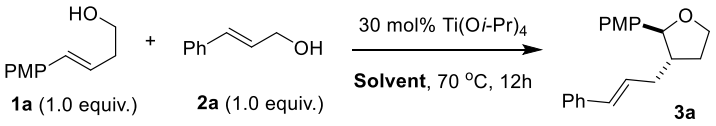


(2-Carboxypropyl)(triphenyl)phosphonium chloride (1.560 g, 4.063 mmol), NaHMDS (1M, 11.5 mL, 11.5 mmol) and 4-methoxybenzaldehyde (0.460 g, 3.37 mmol) were subjected to the general procedure (FCC: 100% EtOAc) to yield ***E*-1p** as a white solid (0.187 g, 29%). Spectroscopic properties matched those previously reported.[13]

Data for ***E*-1p**: **R_f**: 0.5 (100% EtOAc). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.28 (2H, d, *J* = 8.6 Hz, Ar), 6.84 (2H, d, *J* = 8.6 Hz, Ar), 6.39 (1H, d, *J* = 15.9 Hz, 5-H), 5.99-6.12 (1H, m, 4-H), 3.80 (3H, s, OMe), 2.50- 2.55 (4 H, m, 2-H_2 and 3-H_2). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 179.0 (C=O), 159.0 (C Ar), 130.7 (C-5), 130.2 (C Ar), 127.3 (2 x CH Ar), 125.9 (C-4), 114.1 (2 x CH Ar), 55.4 (OMe), 34.0 (C-3), 28.1 (C-2). **HRMS** (Cl): calculated for $C_{12}H_{14}O_3$ $[M]^+$ requires *m/z* 206.0943, found *m/z* 206.0947.

8. Screening of reaction conditions for the cyclisation of 1a to 3a.

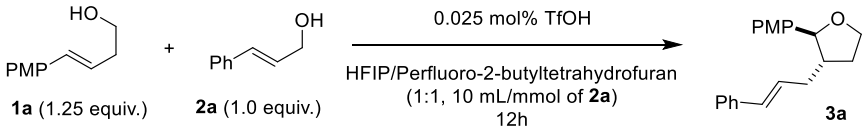
a) Solvent Screening: A range of different solvent and solvent ratios were examined for the model reaction.



Entry	Solvent (10 mL/mmol of **1a**)	Yield 3**a**
1	HFIP	52%
2	TFE	Trace
3	Nonafluoro-tert-butyl alcohol	20%
4	Perfluoro-2-butyltetrahydrofuran	0%
5	$CHCl_3$	0%
6	DCM	0%
7	Toluene	0%
8	Et_2O	0%
9	EtOAc	0%
10	MeCN	0%
11	THF	0%
12	IPA	0%
13	MeOH	0%
14	^{t}BuOH	0%
15	DMF	0%
16	DCM:HFIP 1:1	40%
17	DCM:HFIP 3:1	30%
18	DCM:HFIP 1:3	50%

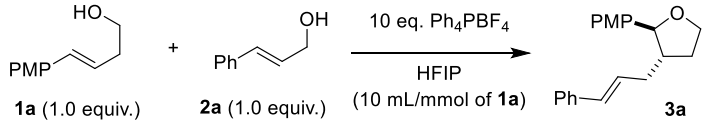
Screening of different solvents

b) Initiator Screening A range of different initiators were examined for the model reaction.



Entry	Temperature	Yield 3a
1	r.t.	0%
2	70 °C	0%

See ref. 28



Entry	Loading	Temperature	Time	Yield 3a
1[a]	10.0 eq.	0°C	5 min.	0%
2[b]	10.0 eq	0°C	12 h	35%
3[a]	10.0 eq	r.t.	5 min.	17%
4[b]	10.0 eq	r.t.	12 h	41%
5[a]	10.0 eq	40 °C	5 min.	22%
6[b]*	10.0 eq	40 °C	12 h	45%
7[c]*	0.3 eq.	70 °C	12 h	47%
8[c]*	1.0 eq.	70 °C	12 h	48%

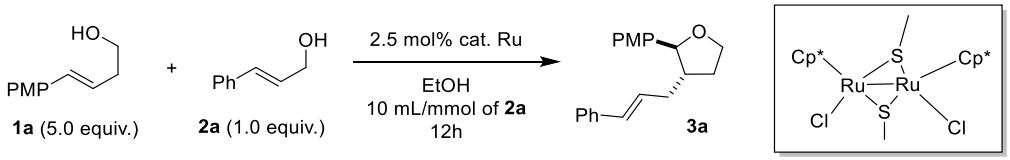
* Complete consumption of both **1a** and **2**[a]

[a] addition of alcohols into the solution of Ph_4BF_4 via syringe pump over 5 min.

[b] addition of alcohols into the solution of Ph_4BF_4 via syringe pump over 5 min. and then the reaction was stirred for 12 hours

[c] alcohols and Ph_4BF_4 were added simultaneously in one portion, and then the reaction was stirred for 12 hours

See ref. 29



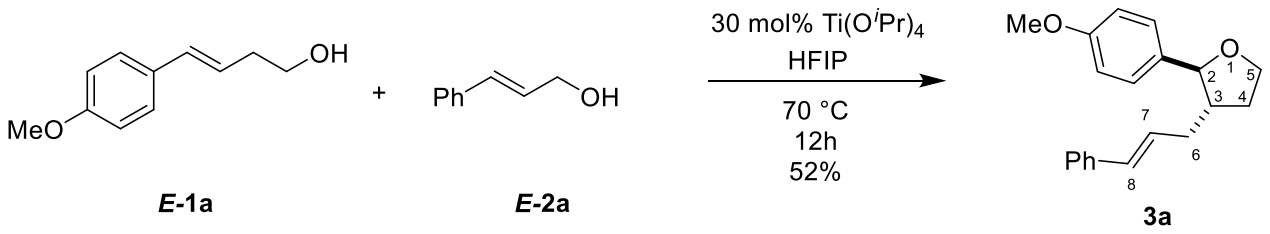
Entry	Temperature	Yield 3a
1	0°C	0%
2	r.t.	0%
3	70 °C	0%

See ref. 30

8.1. General procedure for the cyclization using alcohols as alkylating agents

To a microwave vial charged with a stirring bar, 1.0 eq. of alcohol **A**, 1.0 eq. of alcohol **B** and HFIP (10 mL/mmol of **A**) was added under argon. After fully dissolving the substrate, 30 mol% $Ti(O^iPr)_4$ was added. The reaction was stirred for 12 hours at 70°C. Then the solvent was removed under vacuum. The residue was purified by silica gel column chromatography to give the corresponding heterocycle.

8.2. (±)-(2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)tetrahydrofuran (3a)

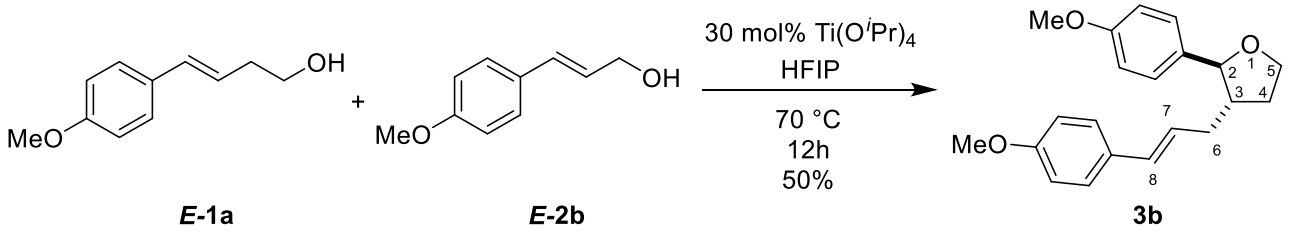


***E*-1a** ***E*-2a** **3a**

Alcohol ***E*-1a** (45.6 mg, 0.256 mmol), cinnamyl alcohol ***E*-2a** (31.8 mg, 0.256 mmol) and Ti(O^{i}Pr)$_4$ (21.8 mg, 0.0767 mmol) were subjected to the general procedure (FCC: gradient elution: 12% → 20% Et_2O - pentane) to yield **3a** as a colorless oil (39.0 mg, 52%).

Data for **3a**: **R_f** 0.50 (50% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.26-7.31 (6H, m, Ar), 7.18-7.23 (1H, m, Ar), 6.89 (2H, d, *J* = 8.7 Hz, Ar), 6.41 (1H, d, *J* = 15.7 Hz, 8-H), 6.14 (1H, dt, *J* = 15.8, 7.0 Hz, 7-H), 4.43 (1H, d, *J* = 7.2 Hz, 2-H), 4.12 (1H, q, *J* = 7.2 Hz, 5-H_A), 4.02 (1H, td, *J* = 8.3, 4.6 Hz, 5-H_B), 3.81 (3H, s, OMe), 2.40-2.48 (1H, m, 6-H_A), 2.22-2.29 (2H, m, 6-H_B and 4-H_A), 2.22-2.15 (1H, m, 3-H), 1.82 (1H, dq, *J* = 11.3, 7.7 Hz, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 137.6 (C Ar), 134.3 (C Ar), 131.5 (C-8), 128.6 (2 x C-H Ar), 128.6 (C-7), 127.8 (2 x C-H Ar), 127.2 (C-H Ar), 126.1 (2 x C-H Ar), 113.9 (2 x C-H Ar), 86.0 (C-2), 68.0 (C-5), 55.4 (OMe), 48.0 (C-3), 35.6 (C-6), 32.5 (C-4). **HRMS** (ESI): calculated for $C_{20}H_{23}O_2$ $[M+H]^+$ requires *m/z* 295.16926, found *m/z* 295.16925. **IR** (film) ν_{max}: 2930, 1512, 1244, 1031, 827, 692 cm^{-1}

8.3. (±)-(2*S*,3*S*)-2-(4-Methoxyphenyl)-3-[(2'E)-3'-(4-methoxyphenyl)allyl]tetrahydrofuran (3b)



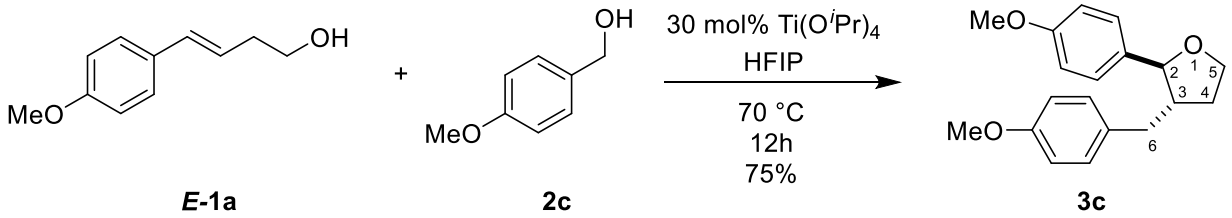
***E*-1a** ***E*-2b** **3b**

Alcohols ***E*-1a** (20.0 mg, 0.112 mmol) and ***E*-2b** (16.6 mg, 0.112 mmol) and Ti(O^{i}Pr)$_4$ (9.5 mg, 0.034 mmol) were subjected to the general procedure (FCC: gradient elution: 10% → 20% Et_2O - pentane) to yield **3b** as a colorless oil (18.1 mg, 50%).

Data for **3b**: **R_f** 0.50 (50% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$)** δ 7.27 (2H, d, *J* = 8.6 Hz, Ar), 7.22 (2H, d, *J* = 8.8 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 6.82 (2H, d, *J* = 8.8 Hz, Ar), 6.34 (1H, d, *J* = 15.8 Hz, 8-H), 5.97 (1H, dt, *J* = 15.8, 7.0 Hz, 7-H), 4.41 (1H, d, *J* = 7.2 Hz, 2-H), 4.10 (1H, q, *J* = 7.2 Hz, 5-H_A), 4.00 (1H, td, *J* = 8.3, 4.7 Hz, 5-H_B), 3.90 (6H, s, 2 x OMe), 2.37-2.44 (1H, m, 6-H_A), 2.13-2.26 (3H, m, 3-H, 4-H_A and 6-H_B), 1.75-1.84 (1H, m, 4-H_B). **^{13}C NMR**

(125 MHz, $CDCl_3$) δ 159.1 (C Ar), 158.8 (C Ar), 134.3 (C Ar), 130.7 (C-8), 130.3 (C Ar), 127.6 (2 x CH Ar), 127.1 (2 x CH Ar), 126.2 (C-7), 113.9 (2 x CH Ar), 113.8 (2 x CH Ar), 85.8 (C-2), 67.8 (C-5), 55.3 (2 x OMe), 48.0 (C-3), 35.5 (C-6), 32.4 (C-4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H_A, between 2-H and 7-H. **HRMS** (EI): calculated for $C_{21}H_{24}O_3$ $[M]^+$ requires *m/z* 324.1725, found *m/z* 324.1720. **IR** (film) ν_{max}: 2980, 1608, 1511, 1247, 1173, 1033 cm^{-1}.

8.4. (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)tetrahydrofuran (3c)

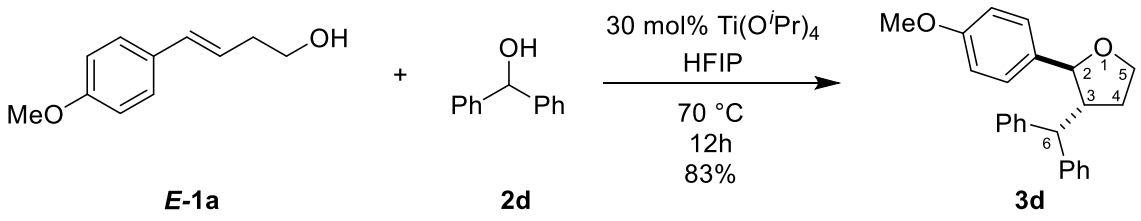


***E*-1a** **2c** **3c**

Alcohol ***E*-1a** (42.5 mg, 0.239 mmol), 4-methoxybenzyl alcohol **2c** (33.0 mg, 0.239 mmol) and Ti(O^{i}Pr)$_4$ (20.3 mg, 0.0715 mmol) were subjected to the general procedure (FCC: gradient elution: 10% → 14% Et_2O - pentane) to yield **3c** as a yellow oil (53.4 mg, 75%).

Data for **3c**: **R_f** 0.50 (60% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.24 (2H, d, *J* = 8.9 Hz, Ar), 7.05 (2H, d, *J* = 8.6 Hz, Ar), 6.88 (2H, d, *J* = 8.8 Hz, Ar), 6.81 (2H, d, *J* = 8.6 Hz, Ar), 4.45 (1H, d, *J* = 7.6 Hz, 2-H), 4.06 (1H, q, *J* = 8.4 Hz, 5-H_A), 4.01 (1H, td, *J* = 8.6, 4.9 Hz, 5-H_B), 3.81 (3H, s, OMe), 3.78 (3H, s, OMe), 2.80 (1H, dd, *J* = 13.6, 5.1 Hz, 6-H_A), 2.51 (1H, dd, *J* = 13.6, 9.7 Hz, 6-H_B), 2.25-2.36 (1H, m, 3-H), 2.00-2.10 (1H, m, 4-H_A), 1.71-1.82 (1H, m, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.1 (C Ar), 158.0 (C Ar), 134.4 (C Ar), 132.6 (C Ar), 129.8 (2 x CH Ar), 127.6 (2 x CH Ar), 113.9 (2 x CH Ar), 113.8 (2 x CH Ar), 85.8 (C-2), 67.9 (C-5), 55.4 (OMe), 55.3 (OMe), 50.0 (C-3), 37.3 (C-6), 32.4 (C-4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H_A, between 2-H and 6-H_B. **HRMS** (ESI): calculated for $C_{19}H_{22}O_3Na$ $[M+Na]^+$ requires *m/z* 321.14612, found *m/z* 321.14609. **IR** (film) ν_{max}: 2916, 1611, 1510, 1241, 1030, 828 cm^{-1}.

8.5. (±)-(2*S*,3*R*)-3-Benzhydryl-2-(4-methoxyphenyl)tetrahydrofuran (3d)

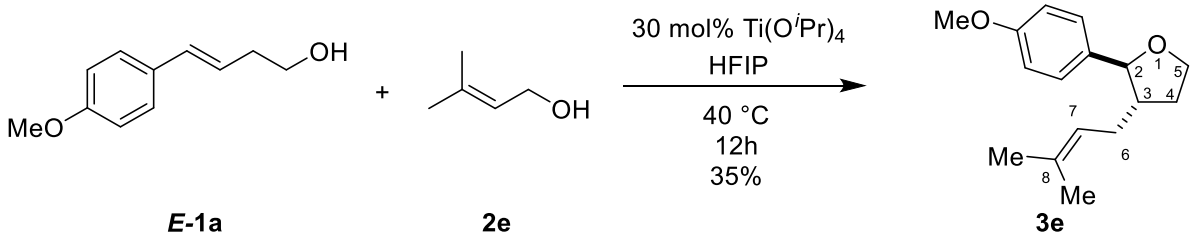


***E*-1a** **2d** **3d**

Alcohol ***E*-1a** (19.8 mg, 0.111 mmol), diphenylmethanol **2d** (20.5 mg, 0.111 mmol) and Ti(O^{i}Pr)$_4$ (9.5 mg, 0.033 mmol) were subjected to the general procedure (FCC: gradient elution: 10% → 20% Et_2O - pentane) to yield **3d** as a yellow foam (31.2 mg, 83%).

Data for **3d**: **R_f** 0.50 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.16-7.25 (4H, m, Ar), 7.06-7.15 (5H, m, Ar), 7.01-7.06 (1H, m, Ar), 6.79 (2H, d, *J* = 8.4 Hz, Ar), 6.63 (2H, d, *J* = 8.3 Hz, Ar), 4.55 (1H, d, *J* = 4.3 Hz, 2-H), 4.06 (1H, td, *J* = 8.3, 4.5 Hz, 5-H_A), 3.91 (1H, q, *J* = 7.9 Hz, 5-H_B), 3.84 (1H, d, *J* = 11.5 Hz, 6-H), 3.68 (3H, s, OMe), 3.03 (1H, ddt, *J* = 12.1, 8.4, 4.4 Hz, 3-H), 2.00-2.12 (1H, m, 4-H_A), 1.65 (1H, ddt, *J* = 11.8, 7.9, 4.5 Hz, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 144.1 (C Ar), 143.6 (C Ar), 135.7 (C Ar), 128.7 (2 x C-H Ar), 128.6 (2 x C-H Ar), 128.5 (2 x C-H Ar), 128.2 (2 x C-H Ar), 127.2 (2 x C-H Ar), 126.6 (CH Ar), 126.5 (CH Ar), 125.6 (C Ar), 113.6 (2 x C-H Ar), 84.7 (C-2), 67.8 (C-5), 55.7 (C-6), 55.4 (OMe), 51.6 (C-3), 31.2 (C-4). **HRMS** (Cl): calculated for $C_{24}H_{24}O_2Na$ $[M+Na]^+$ requires *m/z* 367.16685, found *m/z* 367.16638. **IR** (film) ν_{max}: 3656, 2980, 1492, 1239, 954, 750 cm^{-1}.

8.6. (±)-(2*S*,3*S*)-2-(4-Methoxyphenyl)-3-(3-methylbut-2-en-1-yl)tetrahydrofuran (3e)

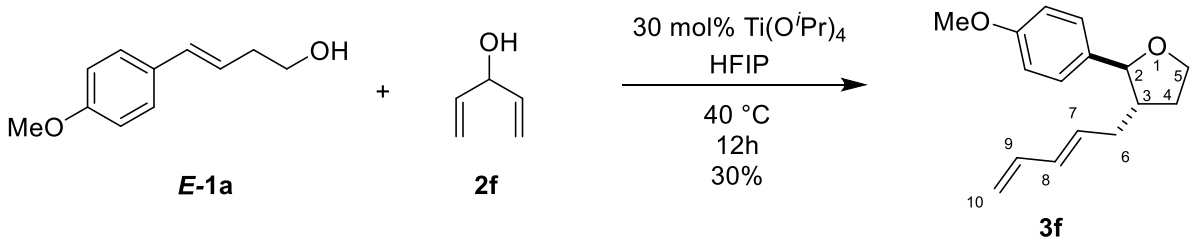


***E*-1a** 2e 3e

Alcohol ***E*-1a** (21.1 mg, 0.119 mmol), 3-methyl-2-buten-1-ol **2e** (0.03 mL, 0.3 mmol) and Ti(O^{i}Pr)$_4$ (10.1 mg, 0.0356 mmol) were subjected to the general procedure except using 2.0 eq. of 3-methyl-2-buten-1-ol and conducting the reaction at 40°C (FCC: gradient elution: 5% → 10% Et_2O - pentane) to yield **3e** as a colorless oil (10.3 mg, 35%).

Data for **3e**: **R_f** 0.40 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 (2H, d, *J* = 8.6 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 5.08 (1H, t, *J* = 7.1 Hz, 7-H), 4.37 (1H, d, *J* = 7.3 Hz, 2-H), 4.07 (1H, q, *J* = 8.3 Hz, 5-H_A), 3.98 (1H, td, *J* = 8.3, 5.0 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.11-2.23 (2H, m, 4-H_A and 6-H_A), 1.98-2.10 (2H, m, 3-H and 6- H_B), 1.69-1.76 (1H, m, 4-H_B), 1.67 (3H, s, Me), 1.58 (3H, s, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 134.7 (C Ar), 132.9 (C-8), 127.6 (2 x C-H Ar), 122.4 (C-7), 113.8 (2 x C-H Ar), 85.8 (C-2), 68.0 (C-5), 55.4 (OMe), 48.4 (C-3), 32.5 (C-4), 30.4 (C-6), 25.9 (Me), 18.0 (Me). **HRMS** (ESI): calculated for $C_{16}H_{23}O_2$ $[M+H]^+$ requires *m/z* 247.16926, found *m/z* 247.16937. **IR** (film) ν_{max}: 2980, 2360, 2341, 1513, 1380, 1246 cm^{-1}.

8.7. (±)-(2*S*,3*S*)-2-(4-Methoxyphenyl)-3-[(2'*E*,4'*E*)-penta-2,4-dien-1-yl]tetrahydrofuran (3f)

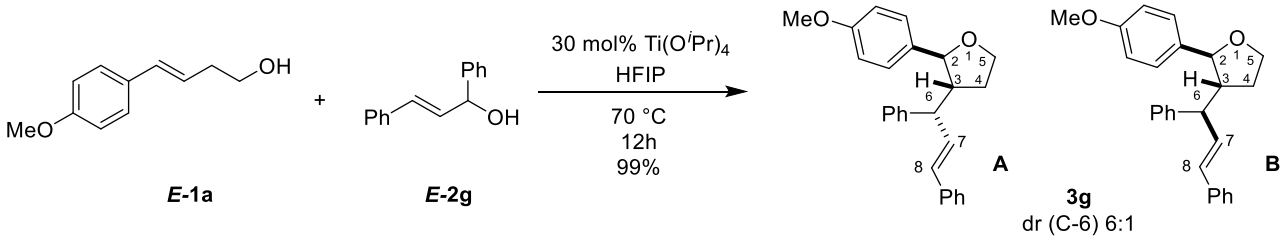


***E*-1a** **2f** **3f**

Alcohol ***E*-1a** (40.0 mg, 0.225 mmol), 1,4-pentadien-3-ol **2f** (0.05 mL, 0.6 mmol) and Ti(O^{i}Pr)$_4$ (19.1 mg, 0.0673 mmol) were subjected to the general procedure except using 2.0 eq. of 1,4-pentadien-3-ol and conducting the reaction at 40°C (FCC: gradient elution: 7% → 10% Et_2O - pentane) to yield **3f** as a colorless oil (16.5 mg, 30%).

Data for **3f**: **R_f** 0.40 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.24 (2H, d, *J* = 8.5 Hz, Ar), 6.88 (2H, d, *J* = 8.5 Hz, Ar), 6.27 (1H, dt, *J* = 16.9, 10.2 Hz, 9-H), 6.06 (1H, dd, *J* = 15.2, 10.4 Hz, 8-H), 5.62 (1H, dt, *J* = 14.3, 6.8 Hz, 7-H), 5.10 (1H, d, *J* = 17.0 Hz, 10-H_A), 4.98 (1H, d, *J* = 10.1 Hz, 10-H_B), 4.36 (1H, d, *J* = 6.7 Hz, 2-H), 4.08 (1H, q, *J* = 8.6 Hz, 5-H_A), 3.98 (1H, td, *J* = 8.2, 4.9 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.26-2.35 (1H, m, 6-H_A), 2.14-2.24 (1H, m, 4-H_A), 2.05-2.14 (2H, m, 3-H and 6-H_B), 1.68-1.79 (1H, m, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.2 (C Ar), 137.1 (C-9), 134.3 (C Ar), 132.7 (C-7), 132.6 (C-8), 127.7 (2 x CH Ar), 115.6 (C-10), 113.9 (2 x CH Ar), 85.9 (C-2), 67.9 (C-5), 55.4 (OMe), 47.8 (C-3), 35.1 (C-6), 32.4 (C-4). **HRMS** (CI): calculated for $C_{16}H_{21}O_2Na$ $[M+H]^+$ requires *m/z* 245.15361, found *m/z* 245.15364. **IR** (film) ν_{max}: 2980, 2360, 1513, 1381, 1246, 1072 cm^{-1}.

8.8. (±)-(2*S*, 3*R*)-3-[(1'*S*,2'*E*)-1,3-Diphenylallyl]-2-(4-methoxyphenyl)tetrahydrofuran and (±)- (2*S*, 3*S*)-3-[(1'*R*,2'*E*)-1,3-Diphenylallyl]-2-(4-methoxyphenyl)tetrahydrofuran (3g)



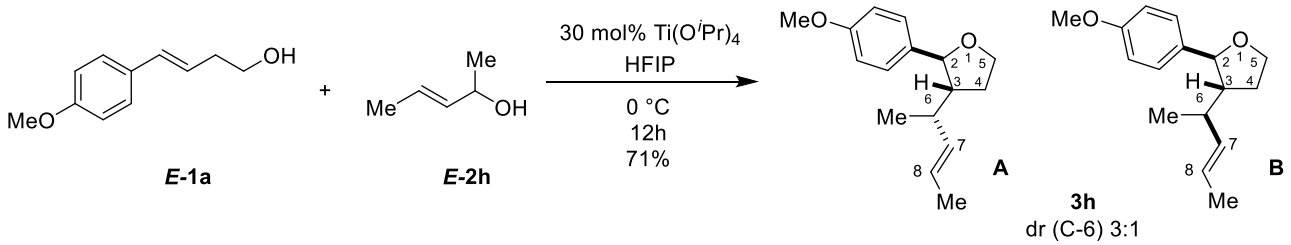
***E*-1a** ***E*-2g** **3g** dr (C-6) 6:1

Alcohol ***E*-1a** (42.4 mg, 0.238 mmol), *trans*-1,3-diphenyl-2-propen-1-ol ***E*-2g** (20.0 mg, 0.238 mmol) and Ti(O^{i}Pr)$_4$ (20.0 mg, 0.0704 mmol) were subjected to the general procedure (FCC: 15% Et_2O - pentane) to yield an inseparable 6:1 mixture of diastereomers **3g** as a colorless oil (87.1 mg, 99%).

Data for **major diastereomer A of 3g (from the mixture)**: **R_f** 0.40 (40% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.31-7.36 (2H, m, Ar), 7.15-7.29 (10H, m, Ar), 6.84 (2H, d, *J* = 8.7 Hz, Ar), 6.45 (1H, d, *J* = 15.7 Hz, 8-H), 6.12 (1H, dd, *J* = 15.7, 9.2 Hz, 7-H), 4.78 (1H, d, *J* = 6.0 Hz, 2-H), 4.11 (1H, td, *J* = 7.9, 5.8 Hz, 5-H_A), 3.96 (1H, dt, *J* = 8.4, 7.1 Hz, 5-H_B), 3.80 (3H, s, OMe), 3.49 (1H, t, *J* = 9.6 Hz, 6-H), 2.73 (1H, ddt, *J* = 10.3, 8.0, 6.1 Hz, 3-H), 1.96-2.08 (1H, m, 4-H_A), 1.72 (1H, ddt, *J* = 12.3, 7.6, 6.0 Hz, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.0 (C Ar), 143.4 (C Ar), 137.2 (C Ar), 135.20 (C Ar), 133.0 (C-7), 130.4 (C-8), 128.8 (2 x C-H Ar), 128.5 (2 x C-H Ar), 128.3 (2 x C-H Ar), 128.0 (2 x C-H Ar), 127.3 (C-H Ar), 126.7 (C-H Ar), 126.4 (2 x C-H Ar), 113.9 (2 x C-H Ar), 84.9 (C-2), 67.92 (C-5), 55.39 (OMe), 53.7 (C-6), 52.5 (C-3), 31.5 (C-4). **HRMS** (Cl): calculated for $C_{26}H_{25}O_2$ $[M-H]^+$ requires *m/z* 369.18491, found *m/z* 369.18475. **IR** (film) ν_{max}: 2979, 1511, 1451, 1244, 1030, 694 cm^{-1}.

Partial data for **minor diastereomer B of 3g (from the mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.36-7.39 (2H, m, Ar), 7.15-7.29 (8H, m, Ar), 6.95 (2H, d, *J* = 8.7 Hz, Ar), 6.77 (2H, d, *J* = 8.7 Hz, Ar), 6.49 (1H, d, *J* = 15.8 Hz, 8-H), 6.42 (1H, dd, *J* = 15.7, 8.7 Hz, 7-H), 4.60 (1H, d, *J* = 5.7 Hz, 2-H), 4.17 (1H, td, *J* = 8.0, 5.5 Hz, 5-H_A), 4.03 (1H, dt, *J* = 8.6, 7.3 Hz, 5-H_B), 3.79 (3H, s, OMe), 3.49 (1H, t, *J* = 9.6 Hz, 6-H), 2.66-2.69 (1H, m, 3-H), 2.15-2.19 (1H, m, 4-H_A), 2.06-2.12 (1H, m, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 143.0 (C Ar), 137.3 (C Ar), 135.15 (C Ar), 131.6 (C-7), 131.3 (C-8), 128.7 (2 x C-H Ar), 128.6 (2 x C-H Ar), 128.3 (2 x C-H Ar), 128.2 (2 x C-H Ar), 127.5 (C-H Ar), 127.3 (C-H Ar), 126.3 (2 x C-H Ar), 113.7 (2 x C-H Ar), 84.1 (C-2), 67.87 (C-5), 55.36 (OMe), 53.9 (C-6), 52.0 (C-3), 30.2 (C-4).

8.9. (±)-(2*S*, 3*S*)-2-(4-Methoxyphenyl)-3-[(1'*S*,2'*E*)-pent-3-en-2-yl]tetrahydrofuran and (±)-(2*S*, 3*R*)-2-(4-methoxyphenyl)-3-[(1'*R*,2'*E*)-pent-3-en-2-yl]tetrahydrofuran (3h)



***E*-1a** ***E*-2h** **3h** dr (C-6) 3:1

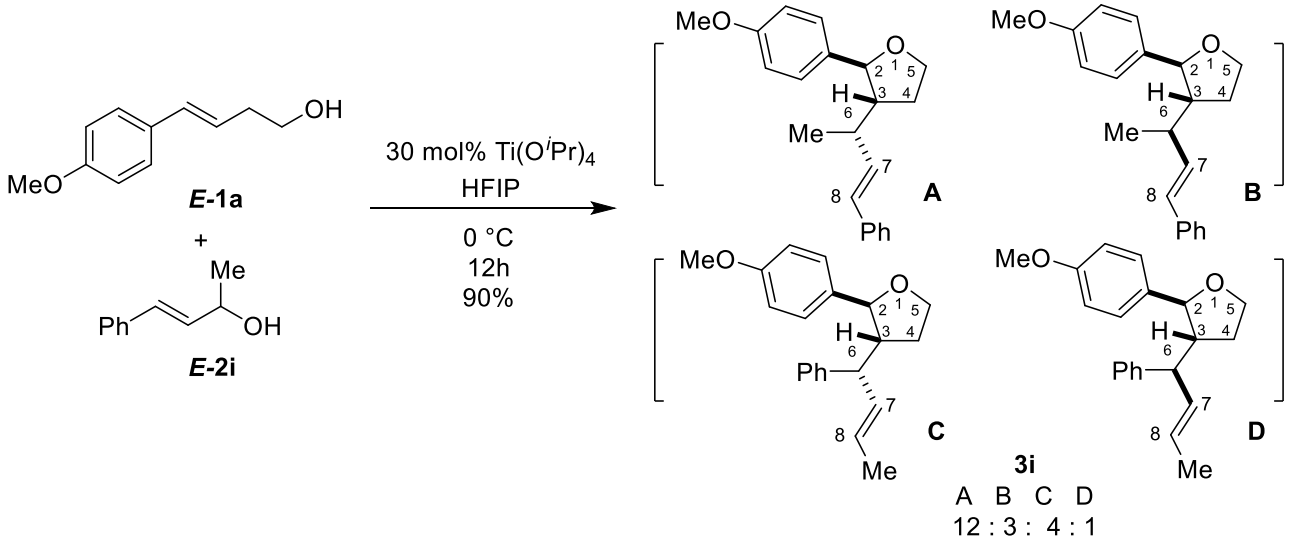
Alcohols ***E*-1a** (59.3 mg, 0.334 mmol) *trans*-3-penten-2-ol ***E*-2h** (57.4 mg, 0.668 mmol) and Ti(O^{i}Pr)$_4$ (28.0 mg, 0.100 mmol) were subjected to the general procedure except using 2 eq. of ***E*-2h** and conducting the reaction at 0°C (FCC: gradient elution: 4% → 10% Et_2O - pentane) to yield an inseparable 3:1 mixture of diastereomer **3h** as a colorless oil (58.3 mg, 71%).

Data for **major diastereomer A of 3h (from the mixture): R_f** 0.40 (25% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.20 (2H, d, *J* = 8.6 Hz, Ar), 6.85 (2H, d, *J* = 8.8 Hz, Ar), 5.33-5.43 (1H, m, 7-H), 5.12 (1H, dqd, *J* = 15.2, 8.4, 1.6 Hz, 8-H), 4.54 (1H, d, *J* = 6.7 Hz, 2-H), 4.05 (1H, q, *J* = 8.2 Hz, 5-H_A), 3.91 (1H, td, *J* = 8.0, 5.4 Hz, 5-H_B), 3.79 (3H, s, OMe), 2.14-2.23 (1H, m, 6-H),

2.07-2.14 (1H, m, 4-H_A), 1.99-2.07 (1H, m, 3-H), 1.75-1.85 (1H, m, 4-H_B), 1.57 (3H, dd, *J* = 4.7, 1.5 Hz, Me), 0.99 (3H, d, *J* = 6.7 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.9 (C Ar), 136.2 (C-8), 133.8 (C Ar), 128.2 (2 x CH Ar), 124.2 (C-7), 113.7 (2 x CH Ar), 84.3 (C-2), 68.1 (C-5), 55.4 (OMe), 53.0 (C-3), 39.8 (C-6), 30.7 (C-4), 19.0 (Me), 17.9 (Me). **HRMS** (Cl): calculated for $C_{16}H_{23}O_2$ $[M+H]^+$ requires *m/z* 247.16926, found *m/z* 247.16933. **IR** (film) ν_{max}: 3657, 2980, 2888, 1512, 1381, 1245 cm^{-1}.

Partial data for **minor diastereomer B of 3h (from the mixture): ^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.25 (2H, d, *J* = 8.7 Hz, Ar), 6.87 (2H, d, *J* = 8.8 Hz, Ar), 5.41-5.52 (1H, m, 7-H), 5.31-5.40 (1H, m, 8-H), 4.49 (1H, d, *J* = 7.3 Hz, 2-H), 4.03 (1H, q, J= 7.1 Hz, 5-H_A), 3.90 (1H, td, *J* = 8.2, 4.8 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.14-2.23 (1H, m, 6-H), 2.07-2.14 (1H, m, 4-H_A), 1.99-2.07 (1H, m, 3-H), 1.75-1.85 (1H, m, 4-H_B), 1.69 (3H, dd, *J* = 6.2, 1.5 Hz, Me), 0.95 (3H, d, *J* = 6.9 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 158.9 (C Ar), 135.2 (C Ar), 133.8 (C-8), 127.9 (2 x CH Ar), 125.7 (C-7), 133.9 (2 x CH Ar), 84.0 (C-2), 68.0 (C-5), 55.4 (OMe),53.2 (C-3), 37.7 (C-6), 29.2 (C-4), 20.5 (Me), 18.2 (Me).

8.10. (±)-(2*S*, 3*S*)-2-(4-Methoxyphenyl)-3-[(1'*S*, 2'*E*)-4-phenylbut-3-en-2-yl]tetrahydrofuran, (±)-(2*S*, 3*R*)-2-(4-methoxyphenyl)-3-[(1'*R*, 2'*E*)-4-phenylbut-3-en-2-yl]tetrahydrofuran, (2*S*,3*R*)-2-(4-methoxyphenyl)-3-[(1'*S*, 2'*E*)-1-phenylbut-2-en-1-yl]tetrahydrofuran and (2*S*,3*R*)-2-(4-methoxyphenyl)-3-[(1'*R*, 2'*E*)-1-phenylbut-2-en-1-yl]tetrahydrofuran (3i)



Alcohols ***E*-1a** (33.9 mg, 0.190 mmol), ***E*-2i** (28.2 mg, 0.190 mmol) and $Ti(O^iPr)_4$ (16.2 mg, 0.0570 mmol) were subjected to the general procedure except conducting the reaction at 0°C (FCC: 10% Et_2O - pentane) to yield **3i** as 4:1 dr mixture of **diastereomer A, B, C** and **D** (52.8 mg, 90%), which was partially separable into 2 clean fractions: first fraction of mixture of 13:1 **diasteromer A** and **B** (25.0 mg, 47%) as a colorless oil, and second fraction of mixture of 2:1 **diastereomer C** and

D as a colorless oil (10.0 mg, 19%).

Data for **diastereomer A of 3i: R_f** 0.45 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.23-7.28 (2H, m, Ar), 7.15-7.22 (5H, m, Ar), 6.79 (2H, d, *J* = 8.7 Hz, Ar), 6.34 (1H, d, *J* = 15.8 Hz, 8-H), 5.84 (1H, dd, *J* = 15.8, 8.6 Hz, 7-H), 4.57 (1H, d, *J* = 6.8 Hz, 2-H), 4.05-4.12 (1H, m, 5-H_A), 3.95 (1H, td, *J* = 8.2, 5.0 Hz, 5-H_B), 3.76 (3H, s, OMe), 2.36-2.45 (1H, m, 6-H), 2.17-2.25 (2H, m, 3-H and 4-H_A), 1.83-1.92 (1H, m, 4-H_B), 1.13 (3H, d, *J* = 6.8 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.0 (C Ar), 137.58 (C Ar), 135.3 (C-8), 135.1 (C Ar), 129.0 (C-7), 128.5 (2 x CH Ar), 128.4 (CH Ar), 127.1 (2 x CH Ar), 126.2 (2 x CH Ar), 113.8 (2 x CH Ar), 84.6 (C-2), 68.1 (C-5), 55.40 (OMe), 53.3 (C-3), 40.6 (C-6), 31.1 (C-4), 19.2 (Me). **NOESY- 2D (400 MHz, $CDCl_3$)**: between 2-H and 6-H, between 2-H and Me, between 2-H and 7-H, between 2-H and 8-H. **HRMS** (Cl): calculated for $C_{21}H_{25}O_2$ $[M+H]^+$ requires *m/z* 309.18491, found *m/z* 309.18491. **IR** (film) ν_{max}: 2980, 2885, 2360, 1512, 1243, 964 cm^{-1}.

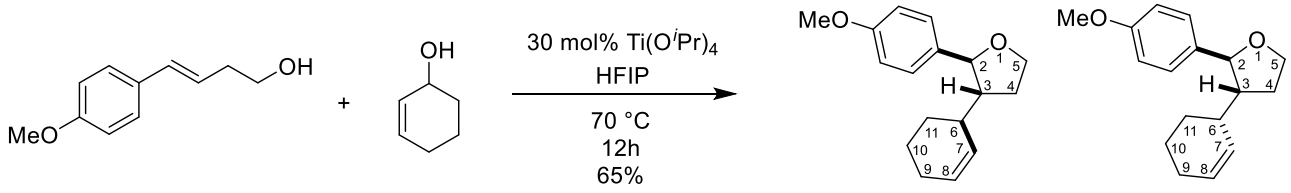
Partial data **diastereomer B of 3i**: **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.14-7.38 (7H, m, Ar), 6.89 (2H, d, *J* = 8.6 Hz, Ar), 6.41 (1H, d, *J* = 15.8 Hz, 8-H), 6.16 (1H, dd, *J* = 15.8, 8.6 Hz, 7-H), 4.56 (1H, d, *J* = 7.4 Hz, 2-H), 4.05-4.12 (1H, m, 5-H_A), 3.95 (1H, td, *J* = 8.2, 5.0 Hz, 5-H_B), 3.81 (3H, s, OMe), 2.36-2.45 (1H, m, 6-H), 2.17-2.25 (2H, m, 3-H and 4-H_A), 1.83-1.92 (1H, m, 4-H_B), 1.08 (3H, d, *J* = 6.8 Hz, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 137.64 (C Ar), 134.9 (C Ar), 133.2 (C-8), 130.4 (C-7), 129.0 (2 x CH Ar), 128.7 (2 x CH Ar), 128.0 (2 x CH Ar), 127.3 (CH Ar), 114.0 (2 x CH Ar), 84.1 (C-2), 68.0 (C-5), 55.43 (OMe), 53.2 (C-3), 38.4 (C-6), 29.8 (C-4), 20.2 (Me).

Data for **diastereomer C of 3i: R_f** 0.50 (40% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.13-7.32 (7H, m, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 5.52 (1H, dq, *J* = 15.2, 6.5 Hz, 8-H), 5.40 (1H, ddd, *J* = 15.1, 9.1, 1.5 Hz, 7-H), 4.72 (1H, d, *J* = 5.5 Hz, 2-H), 4.04 (1H, td, *J* = 8.2, 5.6 Hz, 5-H_A), 3.89 (1H, dt, *J* = 8.5, 7.2 Hz, 5-H_B), 3.81 (3H, s, OMe), 3.24-3.21 (1H, m, 6-H), 2.55 (1H, ddt, *J* = 10.7, 8.0, 5.6 Hz, 3-H), 1.91 (1H, dq, *J* = 12.7, 7.6 Hz, 4-H_A), 1.57-1.65 (1H, m, 4-H_B), 1.58 (3H, dd, *J* = 6.3, 1.6 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.9 (C Ar), 144.1 (C Ar), 135.7 (C Ar), 134.3 (C-7), 128.7 (2 x CH Ar), 128.1 (3 x CH Ar), 127.0 (CH Ar), 125.42 (C-8), 126.1 (CH Ar), 113.7 (2 x CH Ar), 84.7 (C-2), 67.90 (C-5), 55.44 (OMe), 53.4 (C-6), 52.3 (C-3), 31.1 (C-4), 18.0 (Me). **HRMS** (Cl): calculated for $C_{21}H_{25}O_2$ $[M+H]^+$ requires *m/z* 309.18491, found *m/z* 309.18512. **IR** (film) ν_{max} : 2980, 2360, 1728, 1513, 1245, 1062 cm^{-1}.

Partial data **diastereomer D of 3i**: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.18-7.21 (3H, m, Ar), 7.08-7.11 (2H, m, Ar), 6.90 (2H, d, *J* = 9.1 Hz, Ar), 6.72 (2H, d, *J* = 8.7 Hz, Ar), 5.65 (1H, ddd, *J* = 15.1, 8.9, 1.6 Hz, 7-H), 5.52 (1H, dq, *J* = 15.2, 6.5 Hz, 8-H), 4.49 (1H, d, *J* = 5.9 Hz, 2-H), 4.10 (1H, td, *J* = 8.0, 5.7 Hz, 5-H_A), 3.96 (1H, dt, *J* = 8.5, 7.2 Hz, 5-H_B), 3.76 (3H, s, OMe), 3.24-3.27 (1H, m, 6-H), 2.45-2.51 (1H, m, 3-H), 2.09 (1H, dq, *J* = 12.5, 7.5 Hz, 4-H_A), 2.00 (1H, ddt, *J* =

12.0, 7.5, 5.8 Hz, 4-H_B), 1.69 (3H, dd, *J* = 6.3, 1.5 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.7 (C Ar), 143.9 (C Ar), 135.4 (C Ar), 132.5 (C-7), 128.6 (2 x CH Ar), 127.9 (3 x CH Ar), 127.3 (2 x CH Ar), 125.39 (C-8), 113.6 (2 x CH Ar), 84.0 (C-2), 67.91 (C-5), 55.37 (OMe), 52.7 (C-3), 51.6 (C-6), 30.0 (C-4), 18.2 (Me).

8.11. (±)-(2*S*,3*R*)-3-[(1'*R*)-Cyclohex-2-en-1-yl]-2-(4-methoxyphenyl)tetrahydrofuran and (±)-(2*S*,3*R*)-3-[(1'*S*)-cyclohex-2-en-1-yl]-2-(4-methoxyphenyl)tetrahydrofuran (3j)



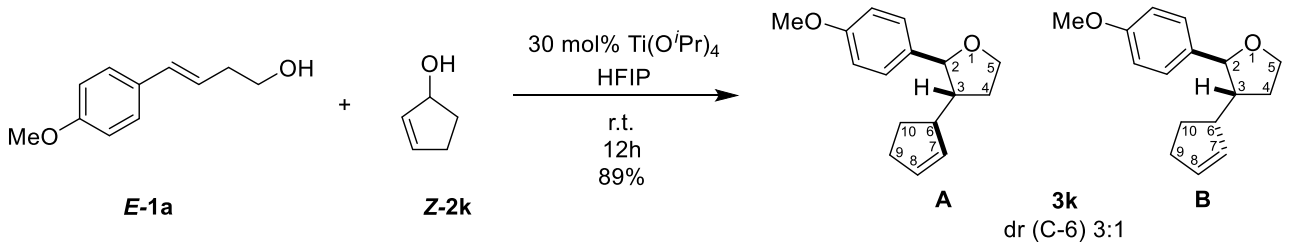
***E*-1a** ***Z*-2j** **A** **3j** dr (C-6) 2:1 **B**

Alcohol ***E*-1a** (53.8 mg, 0.302 mmol) and ***Z*-2j** (29.6 mg, 0.302 mmol) and Ti(O^{i}Pr)$_4$ (25.7 mg, 0.0905 mmol) were subjected to the general procedure (FCC: 6% Et_2O - pentane) to yield an inseparable 2:1 mixture of diastereomer **3j** as a colorless oil (50.6 mg, 65%).

Data for **major diastereomer A of 3j (from the mixture): R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.26 (2H, d, *J* = 8.3 Hz, Ar), 6.87 (2H, d, *J* = 8.8 Hz, Ar), 5.76-5.82 (1H, m, 8-H), 5.66-5.71 (1H, m, 7-H), 4.56 (1H, d, *J* = 7.5 Hz, 2-H), 3.99-4.10 (1H, m, 5-H_A), 3.89-3.96 (1H, m, 5-H_B), 3.80 (3H, s, OMe), 2.21-2.28 (1H, m, 6-H), 2.13-2.20 (1H, m, 3-H), 2.05-2.13 (1H, m, 4-H_A), 1.92-1.99 (2H, m, CH_2 cyclohexenyl), 1.83-1.90 (1H, m, 4-H_B), 1.61-1.70 (2H, m, 2 x CH cyclohexenyl), 1.40-1.54 (1H, m, CH cyclohexenyl), 1.13-1.27 (1H, m, CH cyclohexenyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.10 (C Ar), 135.2 (C Ar), 129.3 (C-8), 128.7 (C-7), 128.06 (2 x CH Ar), 113.86 (2 x CH Ar), 83.9 (C-2), 68.1 (C-5), 55.4 (OMe), 52.2 (C-3), 36.8 (C-6), 29.8 (C-4), 29.1 (CH_2 cyclohexenyl), 25.44 (CH_2 cyclohexenyl), 21.96 (CH_2 cyclohexenyl). **HRMS** (CI): calculated for $C_{17}H_{23}O_2$ $[M+H]^+$ requires *m/z* 259.16926, found *m/z* 259.16922. **IR** (film) ν_{max}: 3657, 2980, 2888, 1512, 1382, 1244 cm^{-1}.

Partial data for **minor diastereomer B of 3j (from the mixture)**: **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.27 (2H, d, *J* = 8.5 Hz, Ar), 6.87 (2H, d, *J* = 8.8 Hz, Ar), 5.62-5.65 (1H, m, 8-H), 5.41-5.47 (1H, m, 7-H), 4.60 (1H, d, *J* = 7.3 Hz, 2-H), 3.99-4.10 (1H, m, 5-H_A), 3.89-3.96 (1H, m, 5-H_B), 3.80 (3H, s, OMe), 2.21-2.28 (1H, m, 6-H), 2.05-2.13 (2H, m, 3-H and 4-H_A), 1.92-1.99 (2H, m, CH_2 cyclohexenyl), 1.77-1.91 (2H, m, 4-H_B and CH cyclohexenyl), 1.72-1.76 (1H, m, CH cyclohexenyl), 1.40-1.54 (1H, m, CH cyclohexenyl), 1.28-1.35 (1H, m, CH cyclohexenyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.13 (C Ar), 135.0 (C Ar), 130.4 (C-7), 128.1 (C-8), 128.05 (2 x CH Ar), 113.90 (2 x CH Ar), 83.7 (C-2), 67.9 (C-5), 55.4 (OMe), 52.0 (C-3), 37.2 (C-6), 30.2 (C-4), 26.8 (CH_2 cyclohexenyl), 25.35 (CH_2 cyclohexenyl), 22.01 (CH_2 cyclohexenyl).

8.12. (±)-(2*S*,3*R*)-3-[(1'*R*)-Cyclopent-2-en-1-yl]-2-(4-methoxyphenyl)tetrahydrofuran and (±)-(2*S*,3*R*)-3-[(1'*S*)-cyclopent-2-en-1-yl]-2-(4-methoxyphenyl)tetrahydrofuran (3k)

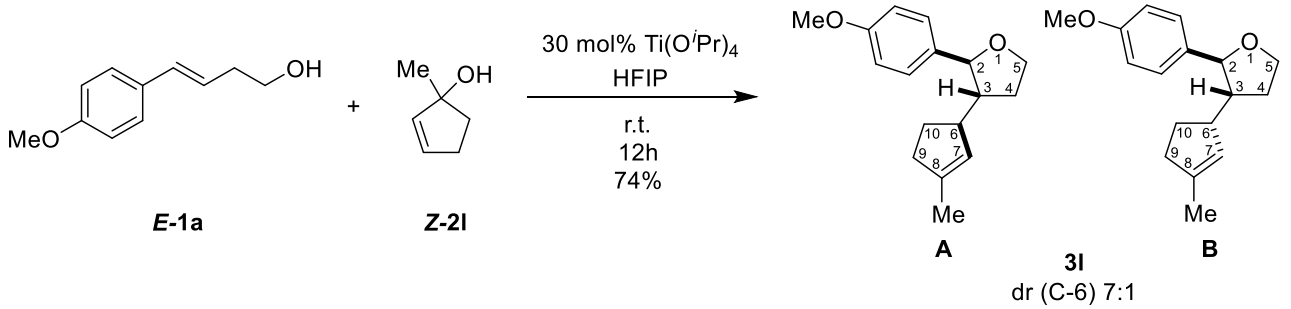


Alcohol ***E*-1a** (53.0 mg, 0.298 mmol) and ***Z*-2k** (50.0 mg, 0.596 mmol) and Ti(O^{i}Pr)$_4$ (25.4 mg, 0.0894 mmol) were subjected to the general procedure except using 2 eq. of the ***Z*-2k** and conducting the reaction at r.t. (FCC: 6% Et_2O - pentane) to yield an inseparable 3:1 mixture of diastereomer (3.5:1 dr shown in crude NMR) **3k** as a colorless oil (64.7 mg, 89%).

Data for **major diastereomer A of 3k (from the mixture): R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.26 (2H, d, *J* = 8.5 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 5.79-5.83 (1H, m, 7-H), 5.69-5.74 (1H, m, 8-H), 4.48 (1H, d, *J* = 6.3 Hz, 2-H), 4.06 (1H, q, *J* = 7.2 Hz, 5-H_A), 3.95 (1H, td, *J* = 8.4, 4.7 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.74-2.83 (1H, m, 6-H), 2.20-2.28 (2H, m, 9-H_2), 2.06-2.17 (2H, m, 3-H and 4-H_A), 1.87-1.97 (1H, m, 10-H_A), 1.75-1.86 (1H, m, 4-H_B), 1.25-1.36 (1H, m, 10-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 134.9 (C Ar), 132.5 (C-7), 132.4 (C-8), 128.1 (2 x CH Ar), 113.8 (2 x CH Ar), 85.2 (C-2), 68.0 (C-5), 55.4 (OMe), 52.6 (C-3), 47.3 (C-6), 32.3 (C-9), 30.4 (C-4), 29.0 (C-10). **HRMS** (EI): calculated for $C_{16}H_{20}O_2$ $[M]^+$ requires *m/z* 244.1458, found *m/z* 244.1466. **IR** (film) ν_{max}: 3677, 2988, 2898, 1510, 1342, 1244 cm^{-1}.

Partial data for **minor diastereomer B of 3k (from the mixture)**: **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.26 (2H, d, *J* = 8.5 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 5.67-5.69 (1H, m, 7-H), 5.45-5.50 (1H, m, 8-H), 4.50 (1H, d, *J* = 7.5 Hz, 2-H), 4.07 (1H, q, *J* = 7.1 Hz, 5-H_A), 3.95 (1H, td, *J* = 8.4, 4.7 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.74-2.83 (1H, m, 6-H), 2.28-2.34 (2H, m, 9-H_2), 2.06-2.17 (2H, m, 3-H and 4-H_A), 1.99-2.05 (1H, m, 10-H_A), 1.75-1.86 (1H, m, 4-H_B), 1.50-1.57 (1H, m, 10-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 134.8 (C Ar), 133.5 (C-7), 131.4 (C-8), 128.0 (2 x CH Ar), 113.9 (2 x CH Ar), 84.9 (C-2), 67.9 (C-5), 55.4 (OMe), 52.2 (C-3), 47.3 (C-6), 32.2 (C-9), 30.6 (C-4), 29.0 (C-10).

8.13. (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*S*)-3-methylcyclopent-2-en-1-yl]tetrahydrofuran and (±)-(2*S*,3*R*)-2-(4-methoxyphenyl)-3-[(1'*R*)-3-methylcyclopent-2-en-1-yl]tetrahydrofuran (3l)



***E*-1a** ***Z*-2l** **A** **3l** **B**

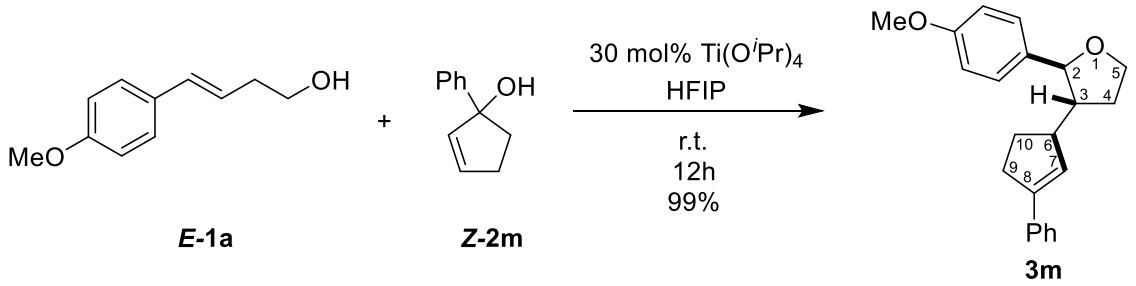
dr (C-6) 7:1

Alcohol ***E*-1a** (20.7 mg, 0.116 mmol) and ***Z*-2l** (22.9 mg, 0.232 mmol) and Ti(O^{i}Pr)$_4$ (9.9 mg, 0.035 mmol) were subjected to the general procedure except using 2.0 eq. of alcohol ***Z*-2l** and conducting reaction at r.t. (FCC: gradient elution: 6% → 12% Et_2O - pentane) to yield 2 clean fractions: first fraction of mixture of 10:1 **diasteromer A** and **B** (10.0 mg, 33%) as a colorless oil, and second fraction of mixture of 5.5:1 **diasteromer A** and **B** as a colorless oil (12.1 mg, 41%).

Data for **major diastereomer A of 3l (from the mixture): R_f** 0.40 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.25 (2H, d, *J* = 8.9 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 5.28-5.33 (1H, m, 7-H), 4.46 (1H, d, *J* = 7.3 Hz, 2-H), 4.06 (1H, q, *J* = 8.1 Hz, 5-H_A), 3.94 (1H, td, *J* = 8.3, 4.7 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.72-2.81 (1H, m, 6-H), 2.12-2.20 (2H, m, 9-H_2), 2.03-2.11 (2H, m, 3-H and 4-H_A), 1.94 (1H, ddt, *J* = 13.2, 8.3, 6.7 Hz, 10-H_A), 1.77-1.86 (1H, m, 4-H_B), 1.72 (3H, s, Me), 1.35 (1H, dtd, *J* = 12.8, 8.1, 6.4 Hz, 10-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 142.3 (C-8), 135.1 (C Ar), 128.03 (2 x C-H Ar), 126.2 (C-7), 113.8 (2 x C-H Ar), 85.2 (C-2), 68.0 (C-5), 55.4 (OMe), 53.0 (C-3), 47.5 (C-6), 36.6 (C-9), 30.4 (C-4), 29.9 (C-10), 16.9 (Me). **NOESY-2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H, between 2-H and 7-H, between 2-H and 10-H_B. **HRMS** (ESI): calculated for $C_{17}H_{22}O_2Na$ $[M+Na]^+$ requires *m/z* 281.15120, found *m/z* 281.15128. **IR** (film) ν_{max}: 2930, 1611, 1512, 1245, 1031, 828 cm^{-1}.

Partial data for **minor diastereomer B of 3l (from the mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.25 (2H, d, *J* = 8.9 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 5.08-5.11 (1H, m, 7-H), 4.49 (1H, d, *J* = 7.4 Hz, 2-H), 4.06 (1H, q, *J* = 8.1 Hz, 5-H_A), 3.94 (1H, td, *J* = 8.3, 4.7 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.72-2.81 (1H, m, 6-H), 2.12-2.20 (2H, m, 9-H_2), 2.03-2.11 (2H, m, 3-H and 4-H_A), 1.94 (1H, ddt, *J* = 13.2, 8.3, 6.7 Hz, 10-H_A), 1.77-1.86 (1H, m, 4-H_B), 1.72 (3H, s, Me), 1.35 (1H, dtd, *J* = 12.8, 8.1, 6.4 Hz, 10-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.1 (C Ar), 141.2 (C-8), 135.1 (C Ar), 127.95 (2 x C-H Ar), 127.3 (C-7), 113.9 (2 x C-H Ar), 84.8 (C-2), 67.9 (C-5), 55.4 (OMe), 52.5 (C-3), 47.6 (C-6), 36.5 (C-9), 30.6 (C-4), 28.3 (C-10), 16.8 (Me).

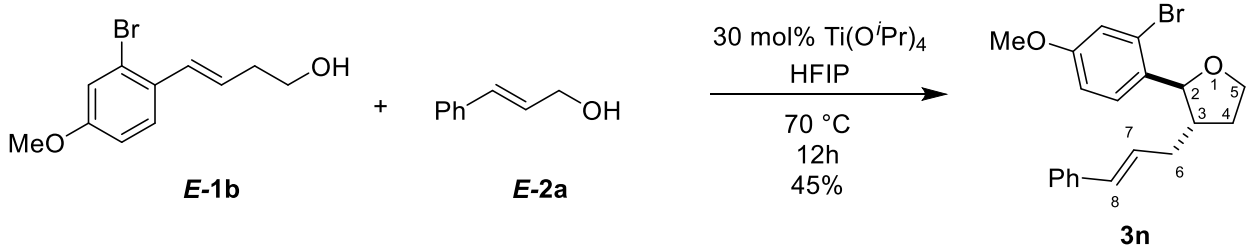
8.14. (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*S*)-3-phenylcyclopent-2-en-1-yl]tetrahydrofuran (3m)



Alcohol ***E*-1a** (38.0 mg, 0.212 mmol) and ***Z*-2m** (34.0 mg, 0.212 mmol) and Ti(O^{i}Pr)$_4$ (18.0 mg, 0.0633 mmol) were subjected to the general procedure except conducting reaction at r.t. (FCC: gradient elution: 7% → 15% Et_2O - pentane) to yield **3m** as a yellow oil (67.5 mg, 99%).

Data for **3m**: **R_f** 0.50 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.43 (2H, d, *J* = 8.6 Hz, Ar), 7.21-7.36 (5H, m, Ar), 6.88 (2H, d, *J* = 8.7 Hz, Ar), 6.15 (1H, q, *J* = 2.0 Hz, 7-H), 4.56 (1H, d, *J* = 7.2 Hz, 2-H), 4.13 (1H, q, *J* = 7.1 Hz, 5-H_A), 3.98 (1H, td, *J* = 8.4, 4.7 Hz, 5-H_B), 3.81 (3H, s, OMe), 2.96-3.04 (1H, m, 6-H), 2.61-2.71 (2H, m, 9-H_2), 2.19-2.27 (2H, m, 3-H and 4-H_A), 2.11 (1H, dtd, *J* = 13.1, 8.3, 5.0 Hz, 10-H_A), 1.90 (1H, ddd, *J* = 8.3, 7.3, 3.8 Hz, 4-H_B), 1.54 (1H, ddt, *J* = 12.9, 9.0, 7.1 Hz, 10-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.2 (C Ar), 143.8 (C-8), 136.5 (C Ar), 134.9 (C Ar), 128.4 (2 x C-H Ar), 128.1 (2 x C-H Ar), 127.5 (C-7), 127.4 (C-H Ar), 125.8 (2 x C-H Ar), 113.9 (2 x C-H Ar), 85.1 (C-2), 68.1 (C-5), 55.4 (OMe), 52.7 (C-3), 47.9 (C-6), 32.9 (C-9), 30.6 (C-4), 29.2 (C-10). **NOESY- 2D (400 MHz, $CDCl_3$)**: between 2-H and 6-H, between 2-H and 7-H, between 2-H and 10-H_B. **HRMS** (ESI): calculated for $C_{22}H_{24}O_2Na$ $[M+Na]^+$ requires *m/z* 343.16685, found *m/z* 343.16690. **IR** (film) ν_{max}: 2965, 1712, 1512, 1245, 1030, 827 cm^{-1}.

8.15. (±)-(2*S*,3*S*)-2-(2-Bromo-4-methoxyphenyl)-3-cinnamyltetrahydrofuran (3n)

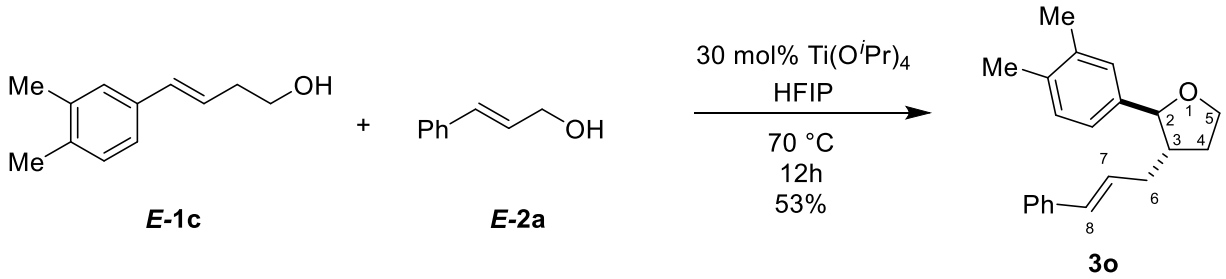


Alcohol ***E*-1b** (66.8 mg, 0.261 mmol), cinnamyl alcohol ***E*-2a** (35.0 mg, 0.261 mmol) and Ti(O^{i}Pr)$_4$ (22.0 mg, 0.0774 mmol) were subjected to the general procedure (FCC: gradient elution: 8%→12% Et_2O - pentane) to yield **3n** as a colorless oil (39.7 mg, 45%).

Data for **3n**: **R_f** 0.45 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.25-7.36 (5H, m, Ar), 7.17-7.22 (1H, m, Ar), 7.07 (1H, d, *J* = 2.6 Hz, Ar), 6.87 (1H, dd, *J* = 8.6, 2.6 Hz, Ar), 6.42 (1H, d, *J* = 15.8 Hz, 8-H), 6.18 (1H, dt, *J* = 15.8, 7.0 Hz, 7-H), 4.93 (1H, d, *J* = 5.6 Hz, 2-H), 4.19

(1H, td, *J* = 8.1, 5.6 Hz, 5-H_A), 4.01-4.08 (1H, m, 5-H_B), 3.78 (3H, s, OMe), 2.58 (1H, dddd, *J* = 13.0, 6.4, 4.6, 1.4 Hz, 6-H_A), 2.30-2.38 (1H, m, 6-H_B), 2.20-2.30 (1H, m, 3-H), 2.13 (1H, dq, *J* = 14.3, 7.3 Hz, 4-H_A), 1.77-1.88 (1H, m, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.3 (C Ar), 137.6 (C Ar), 134.0 (C Ar), 131.5 (C-8), 128.6 (3 x CH Ar), 128.5 (C-7), 127.2 (CH Ar), 126.1 (2 x CH Ar), 122.7 (C Ar), 117.7 (CH Ar), 114.0 (CH Ar), 84.4 (C-2), 68.2 (C-5), 55.7 (OMe), 47.8 (C-3), 35.9 (C-6), 31.0 (C-4). **HRMS** (CI): calculated for $C_{20}H_{22}BrO_2$ $[M+H]^+$ requires *m/z* 373.07977, found *m/z* 373.07950. **IR** (film) ν_{max} : 3658, 2980, 1602, 1491, 1283, 964 cm^{-1}.

8.16. (±)-(2*S*,3*S*)-3-Cinnamyl-2-(3,4-dimethylphenyl)tetrahydrofuran (3o)

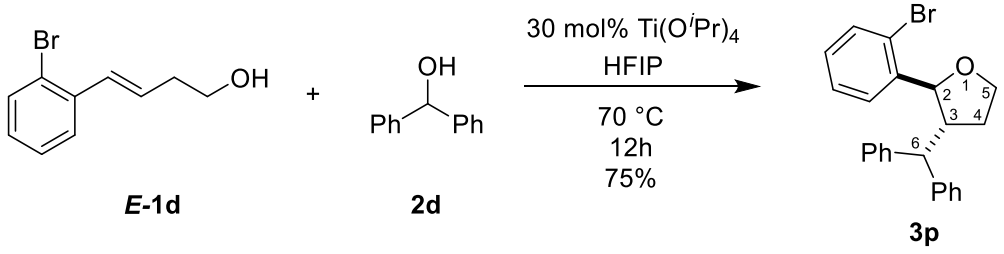


***E*-1c** + ***E*-2a** → **3o**

Alcohol ***E*-1c** (59.3 mg, 0.31 mmol), cinnamyl alcohol ***E*-2a** (41.6 mg, 0.310 mmol) and Ti(O^{i}Pr)$_4$ (26.4mg, 0.0930 mmol) were subjected to the general procedure (FCC: gradient elution: 6% → 20% Et_2O - pentane) to yield **3o** as a colorless oil (50.2 mg, 53%).

Data for **3o**: **R_f** 0.50 (25% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.27-7.31 (4H, m, Ar), 7.16-7.23 (1H, m, Ar), 7.05-7.13 (3H, m, Ar), 6.41 (1H, d, *J* = 15.8 Hz, 8-H), 6.14 (1H, dt, *J* = 15.8, 6.9 Hz, 7-H), 4.42 (1H, d, *J* = 6.3 Hz, 2-H), 4.12 (1H, dt, *J* = 8.4, 7.1 Hz, 5-H_A), 4.02 (1H, td, *J* = 8.3, 4.7 Hz, 5-H_B), 2.40-2.52 (1H, m, 6-H_A), 2.25 (6H, s, 2 x Me), 2.16-2.24 (3H, m, 3-H, 4-H_A and 6-H_B), 1.80 (1H, dddd, *J* = 13.4, 6.1, 3.9, 2.4 Hz, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 139.8 (C Ar), 137.6 (C Ar), 136.7 (C Ar), 135.9 (C Ar), 131.4 (C-8), 129.7 (CH Ar), 128.6 (2 x CH Ar and C-7), 127.7 (CH Ar), 127.2 (CH Ar), 126.1 (2 x CH Ar), 123.9 (CH Ar), 86.1 (C-2), 68.0 (C-5), 48.0 (C-3), 35.7 (C-6), 32.5 (C-4), 20.0 (Me), 19.6 (Me). **HRMS** (ESI): calculated for $C_{21}H_{25}O$ $[M+H]^+$ requires *m/z* 293.18999, found *m/z* 293.18997. **IR** (film) ν_{max} : 2971, 1497, 1449, 964, 743, 692 cm^{-1}

8.17. (±)-(2*S*,3*R*)-3-Benzhydryl-2-(2-bromophenyl)tetrahydrofuran (3p)

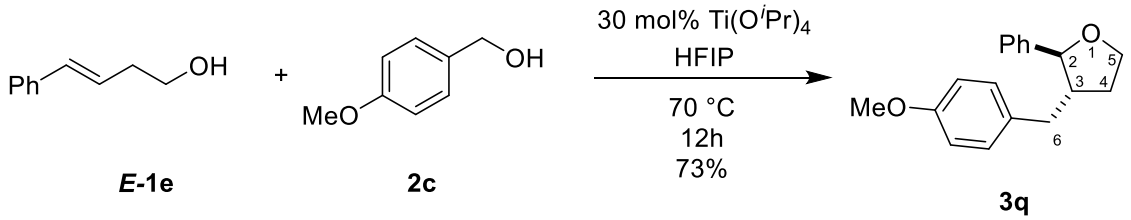


***E*-1d** + **2d** → **3p**

Alcohol ***E*-1d** (69.6 mg, 0.308 mmol), benzhydrol **2d** (56.7 mg, 0.308 mmol) and $Ti(O^iPr)_4$ (26.2 mg, 0.0923 mmol) were subjected to the general procedure (FCC: gradient elution: 5% → 7% Et_2O - pentane) to yield **3p** as a white foam (90.5 mg, 75%).

Data for **3p**: **R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.25-7.39 (4H, m, Ar), 7.17-7.24 (4H, m, Ar), 6.98-7.12 (6H, m, Ar), 5.08 (1H, d, *J* = 5.1 Hz, 2-H), 4.21 (1H, td, *J* = 8.3, 5.0 Hz, 5-H_A), 4.02 (1H, q, *J* = 8.0 Hz, 5-H_B), 4.00 (1H, d, *J* = 10.6 Hz, 6-H), 3.29 (1H, ddt, *J* = 10.6, 7.4, 5.1 Hz, 3-H), 2.11-2.23 (1H, m, 4-H_A), 1.79-1.89 (1H, m, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 144.0 (C Ar), 142.8 (C Ar), 141.6 (C Ar), 132.9 (CH Ar), 132.8 (CH Ar), 128.72 (3 x CH Ar), 128.69 (3 x CH Ar), 128.2 (3 x CH Ar), 127.2 (CH Ar), 126.5 (CH Ar), 126.4 (CH Ar), 122.8 (C Ar), 84.4 (C-2), 68.0 (C-5), 55.2 (C-6), 50.1 (C-3), 31.3 (C-4). **HRMS** (ESI): calculated for $C_{23}H_{21}OBrNa$ $[M+Na]^+$ requires *m/z* 415.06680, found *m/z* 415.06686. **IR** (film) ν_{max} : 3649, 2980, 2887, 1450, 1521, 1037 cm^{-1}.

8.18. (±)-(2*S*,3*S*)-3-(4-Methoxybenzyl)-2-phenyltetrahydrofuran (3q)

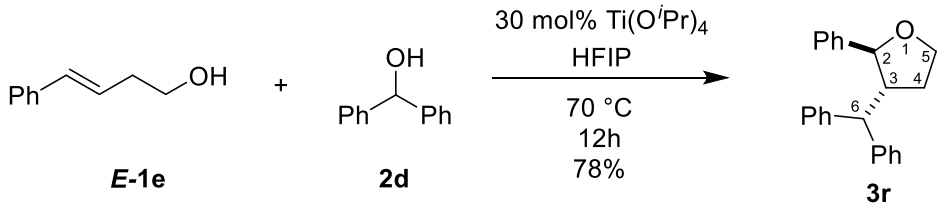


***E*-1e** **2c** **3q**

Alcohol ***E*-1e** (207.4 mg, 1.401 mmol), 4-methoxybenzylic alcohol **2c** (192.4 mg, 1.401 mmol) and $Ti(O^iPr)_4$ (119.3 mg, 0.4201 mmol) were subjected to the general procedure (FCC: gradient elution: 7% → 15% Et_2O - pentane) to yield **3q** as a colorless oil (274.0 mg, 73%).

Data for **3q**: **R_f** 0.50 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.24-7.37 (5H, m, Ar), 7.06 (2H, *J* = 8.6 Hz, Ar), 6.81 (2H, d, *J* = 8.6 Hz, Ar), 4.53 (1H, d, *J* = 7.2 Hz, 2-H), 4.09 (1H, q, *J* = 7.3 Hz, 5-H_A), 4.04 (1H, td, *J* = 8.2, 5.2 Hz, 5-H_B), 3.79 (3H, s, OMe), 2.84 (1H, dd, *J* = 13.6, 5.4 Hz, 6-H_A), 2.55 (1H, dd, *J* = 13.6, 9.5 Hz, 6-H_B), 2.34 (1H, dqd, *J* = 9.5, 7.5, 5.4 Hz, 3-H), 2.01-2.11 (1H, m, 4-H_A), 1.78 (1H, dq, *J* = 12.3, 7.8 Hz, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.1 (C Ar), 142.6 (C Ar), 132.6 (C Ar), 129.9 (2 x C-H Ar), 128.5 (2 x C-H Ar), 127.5 (C-H Ar), 126.2 (2 x C-H Ar), 113.9 (2 x C-H Ar), 85.6 (C-2), 68.1 (C-5), 55.4 (OMe), 50.2 (C-3), 37.5 (C-6), 32.4 (C-4). **HRMS** (ESI): calculated for $C_{18}H_{20}O_2Na$ $[M+Na]^+$ requires *m/z* 291.13555, found *m/z* 291.13568. **IR** (film) ν_{max}: 2980, 1510, 1243, 1177, 1034, 699 cm^{-1}.

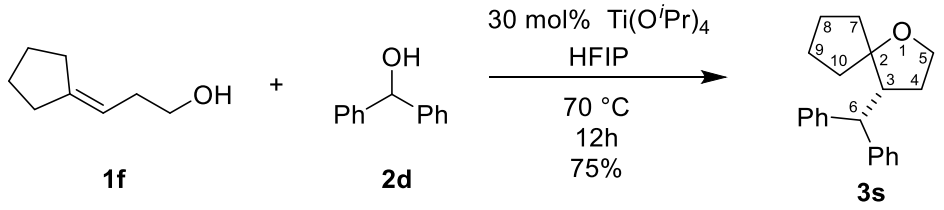
8.19. (±)-(2*S*,3*R*)-3-Benzhydryl-2-phenyltetrahydrofuran (3r)



Alcohol ***E*-1e** (57.3 mg, 0.387 mmol), benzhydrol **2d** (71.2 mg, 0.387 mmol) and $Ti(O^iPr)_4$ (33.0 mg, 0.116 mmol) were subjected to the general procedure (FCC: gradient elution: 7% → 10% Et_2O - pentane) to yield **3r** as a colorless oil (93.8 mg, 78%).

Data for **3r**: **R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.14-7.39 (13H, m, Ar), 7.01 (2H, d, *J* = 7.6 Hz, Ar), 4.76 (1H, d, *J* = 4.0 Hz, 2-H), 4.21 (1H, dt, *J* = 8.3, 4.2 Hz, 5-H_A), 4.07 (1H, q, *J* = 8.0 Hz, 5-H_B), 3.99 (1H, d, *J* = 11.6 Hz, 6-H), 3.19 (1H, ddt, *J* = 11.6, 7.9, 4.0 Hz, 3-H), 2.12-2.23 (1H, m, 4-H_A), 1.72-1.82 (1H, m, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 144.0 (C Ar), 143.7 (C Ar), 143.6 (C Ar), 128.7 (2 x C-H Ar), 128.6 (2 x C-H Ar), 128.4 (2 x C-H Ar), 128.09 (2 x C-H Ar), 128.07 (2 x C-H Ar), 126.9 (C-H Ar), 126.5 (C-H Ar), 126.4 (C-H Ar), 125.8 (2 x C-H Ar), 84.8 (C-2), 67.9 (C-5), 55.6 (C-6), 51.7 (C-3), 30.9 (C-4). **HRMS** (ESI): calculated for $C_{23}H_{22}ONa$ $[M+Na]^+$ requires *m/z* 337.15629, found *m/z* 337.15631. **IR** (film) ν_{max}: 2980, 2360, 1493, 1451, 1382, 1058 cm^{-1}.

8.20. (±)-(3*R*)-4-Benzhydryl-1-oxaspiro[4.4]nonane (3s)

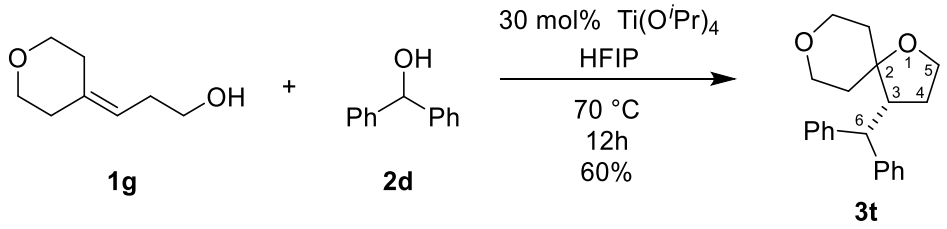


Alcohol **1f** (41.4 mg, 0.329 mmol), benzhydrol **2d** (60.4 mg, 0.329 mmol) and $Ti(O^iPr)_4$ (28.0 mg, 0.0986 mmol) were subjected to the general procedure (FCC: gradient elution: 5% → 7% Et_2O - pentane) to yield **3s** as a white foam (72.0 mg, 75%).

Data for **3s**: **R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.33-7.37 (4H, m, Ar), 7.22-7.28 (4H, m, Ar), 7.11-7.16 (2H, m, Ar), 3.79 (1H, d, *J* = 11.7 Hz, 6-H), 3.72 (1H, dt, *J* = 8.8, 4.4 Hz, 5-H_A), 3.69 (1H, q, *J* = 8.3 Hz, 5-H_B), 3.10 (1H, ddd, *J* = 11.7, 10.0, 7.6 Hz, 3-H), 1.93 (1H, dtd, *J* = 12.7, 7.5, 4.0 Hz, 4-H_A), 1.46-1.64 (6H, m, 4-H_B, 7-H_A, 8-H_A, 9-H_A and 10-H_2), 1.37-1.45 (1H, m, 9-H_B), 1.05-1.16 (2H, m, 7-H_B and 8-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 145.3 (C Ar), 143.8 (C Ar), 128.73 (2 x C-H Ar), 128.65 (2 x C-H Ar), 128.2 (2 x C-H Ar), 127.8 (2 x C-H Ar), 126.5 (C-H Ar), 126.3 (C-H Ar), 93.2 (C-2), 63.6 (C-5), 54.8 (C-6), 47.6 (C-3), 37.8 (C-7),

33.6 (C-4), 31.6 (C-10), 23.7 (C-9), 23.1 (C-8). **HRMS** (EI): calculated for $C_{21}H_{24}O$ $[M]^+$ requires *m/z* 292.1822, found *m/z* 292.1818. **IR** (film) ν_{max}: 2980, 2888, 1493, 1451, 1153, 947 cm^{-1}.

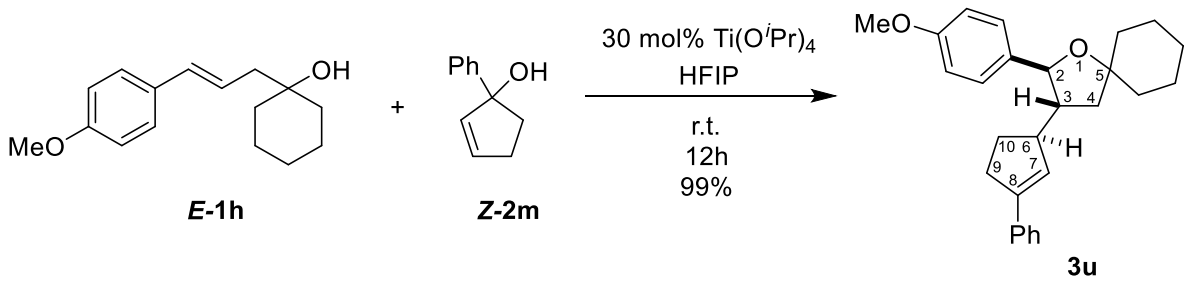
8.21. (±)-(3*R*)-4-Benzhydryl-1,8-dioxaspiro[4.5]decane (3t)



Alcohol **1g** (13.6 mg, 0.096 mmol), benzhydrol **2d** (17.7 mg, 0.096 mmol) and $Ti(O^iPr)_4$ (8.2 mg, 0.029 mmol) were subjected to the general procedure (FCC: gradient elution: 12% → 16% Et_2O - pentane) to yield **3t** as a yellow foam (17.7 mg, 60%).

Data for **3t**: $\mathbf{R_f}$ 0.40 (60% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31-7.39 (4H m, Ar), 7.22-7.32 (4H, m, Ar), 7.11-7.19 (2H, m, Ar), 3.61-3.82 (6H, m, 6-H, 5-H_2, CH_2 tetrahydropyranyl and CH tetrahydropyranyl), 3.55 (1H, ddd, *J* = 11.1, 4.6, 2.4 Hz, CH tetrahydropyranyl), 2.84 (1H, td, *J* = 11.4, 7.5 Hz, 3-H), 1.89 (1H, dtd, *J* = 12.8, 7.5, 3.2 Hz, 4-H_A), 1.59-1.75 (2H, m, 4-H_B and CH tetrahydropyranyl), 1.53 (1H, dd, *J* = 13.1, 2.2 Hz, CH tetrahydropyranyl), 1.14-1.23 (2H, m, CH_2 tetrahydropyranyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 145.1 (C Ar), 143.2 (C Ar), 128.9 (2 x C-H Ar), 128.8 (2 x C-H Ar), 128.1 (2 x C-H Ar), 127.7 (2 x C-H Ar), 126.4 (C-H Ar), 125.7 (C-H Ar), 80.2 (C-2), 65.0 (C-5), 64.0 (CH_2 tetrahydropyranyl), 63.9 (CH_2 tetrahydropyranyl), 53.5 (C-6), 51.8 (C-3), 37.8 (CH_2 tetrahydropyranyl), 32.7 (C-4), 31.2 (CH_2 tetrahydropyranyl). **HRMS** (ESI): calculated for $C_{21}H_{24}O_2Na$ $[M+Na]^+$ requires *m/z* 331.16685, found *m/z* 331.16690. **IR** (film) ν_{max}: 3657, 2980, 2888, 1382, 1251, 1151 cm^{-1}.

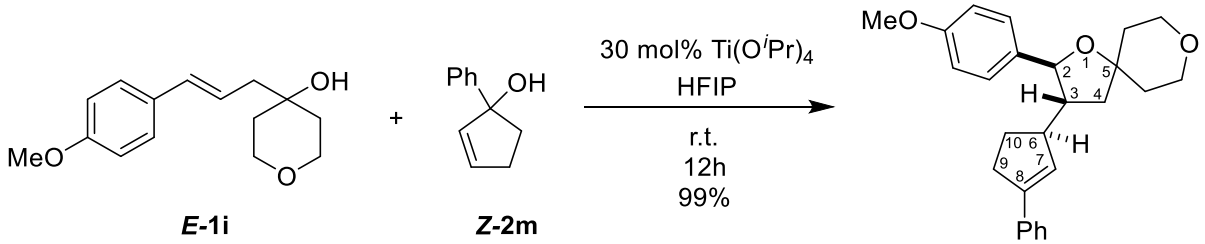
8.22. (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*S*)-3-phenylcyclopent-2-en-1-yl]-1-oxaspiro[4.5]decane (3u)



Alcohols ***E*-1h** (50.0 mg, 0.203 mmol) and ***Z*-2m** (32.5 mg, 0.203 mmol) and $Ti(O^iPr)_4$ (17.3 mg, 0.0609 mmol) were subjected to the general procedure except conducting the reaction at r.t. (FCC: gradient elution: 5% → 20% Et_2O - pentane) to yield **3u** as a yellow foam (78.3 mg, 99%).

Data for **3u**: **R_f** 0.40 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.40-7.46 (2H, m, Ar), 7.29-7.36 (4H, m, Ar), 7.21-7.28 (1H, m, Ar), 6.88 (2H, d, *J* = 8.7 Hz, Ar), 6.13 (1H, q, *J* = 2.0 Hz, 7-H), 4.60 (1H, d, *J* = 9.6 Hz, 2-H), 3.81 (3H, s, OMe), 2.83-2.94 (1H, m, 6-H), 2.53-2.66 (2H, m, 9-H_2), 2.18-2.27 (1H, m, 3-H), 2.14 (1H, dd, *J* = 11.9, 7.5 Hz, 4-H_A), 1.96 (1H, dtd, *J* = 13.2, 8.3, 4.9 Hz, 10-H_A), 1.59-1.82 (7H, m, 4-H_B and 3 x CH_2 cyclohexyl), 1.31-1.50 (5H, m, 10-H_B and 2 x CH_2 cyclohexyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.3 (C Ar), 143.6 (C-8), 136.5 (C Ar), 134.4 (C Ar), 128.6 (2 x C-H Ar), 128.4 (2 x C-H Ar), 127.5 (C-7), 127.3 (C-H Ar), 125.7 (2 x C-H Ar), 113.8 (2 x C-H Ar), 84.4 (C-2), 81.8 (C-5), 55.4 (OMe), 52.9 (C-3), 47.1 (C-6), 41.3 (C-4), 39.2 (CH_2 cyclohexyl), 38.9 (CH_2 cyclohexyl), 32.9 (C-9), 29.4 (C-10), 25.8 (CH_2 cyclohexyl), 24.2 (CH_2 cyclohexyl), 23.8 (CH_2 cyclohexyl). **HRMS** (ESI): calculated for $C_{27}H_{33}O_2$ $[M+H]^+$ requires *m/z* 389.24751, found *m/z* 389.24783. **IR** (film) ν_{max}: 3656, 2980, 2929, 1512, 1244, 1072 cm^{-1}.

8.23. (±)-(2*S*,3*R*)-2-(4-Methoxyphenyl)-3-[(1'*S*)-3-phenylcyclopent-2-en-1-yl]-1,8-dioxaspiro[4.5]decane (3v)



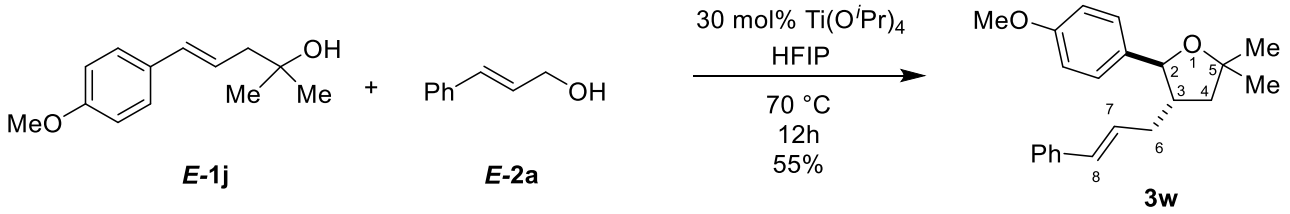
***E*-1i** ***Z*-2m** **3v**

Alcohols ***E*-1i** (60.0 mg, 0.242 mmol) and ***Z*-2m** (38.7 mg, 0.242 mmol) and Ti(O^{i}Pr)$_4$ (20.6 mg, 0.0725 mmol) were subjected to the general procedure except conducting the reaction at r.t. (FCC: gradient elution: 20% → 35% Et_2O - pentane) to yield **3v** as a yellow solid (94.0 mg, 99%).

Data for **3v**: **R_f** 0.30 (60% Et_2O - pentane). **M.p.**: 89 °C (10% EtOAc - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.43 (2H, d, *J* = 7.9 Hz, Ar), 7.23-7.36 (5H, m, Ar), 6.90 (2H, d, *J* = 7.9 Hz, Ar), 6.12 (1H, q, *J* = 2.0 Hz, 7-H), 4.62 (1H, d, *J* = 9.6 Hz, 2-H), 3.85-3.97 (2H, m, CH_2 tetrahydropyranyl), 3.68-3.75 (1H, m, CH tetrahydropyranyl), 3.59-3.68 (1H, m, CH tetrahydropyranyl), 2.86-2.95 (1H, m, 6-H), 2.55-2.68 (2H, m, 9-H_2), 2.22-2.31 (1H, m, 3-H), 2.15-2.21 (1H, m, 4-H_A), 1.99 (1H, dtd, *J* = 13.2, 8.2, 4.5 Hz, 10-H_A), 1.85-1.93 (1H, m, CH tetrahydropyranyl), 1.76-1.82 (3H, m, CH tetrahydropyranyl and CH_2 tetrahydropyranyl), 1.72 (1H, t, *J* = 11.6 Hz, 4-H_B), 1.38 (1H, dq, *J* = 15.2, 7.8 Hz, 10-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.4 (C Ar), 143.9 (C-8), 136.4 (C Ar), 133.8 (C Ar), 128.54 (2 x C-H Ar), 128.45 (2 x C-H Ar), 127.4 (C-H Ar), 127.1 (C-7), 125.8 (2 x C-H Ar), 113.9 (2 x C-H Ar), 84.6 (C-2), 78.5 (C-5), 65.6 (CH_2 tetrahydropyranyl), 65.5 (CH_2 tetrahydropyranyl), 55.4 (OMe), 52.6 (C-3), 46.9 (C-6), 41.9 (C-4), 39.4 (CH_2 tetrahydropyranyl), 39.0 (CH_2 tetrahydropyranyl), 32.9 (C-9), 29.4 (C-10). **HRMS**

(ESI): calculated for $C_{26}H_{30}O_3Na$ $[M+Na]^+$ requires *m/z* 413.20872, found *m/z* 413.21051. **IR** (film) ν_{max}: 3657, 2980, 1461, 1248, 1152, 1073 cm^{-1}.

8.24. (±)-(2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)-5,5-dimethyltetrahydrofuran (3w)

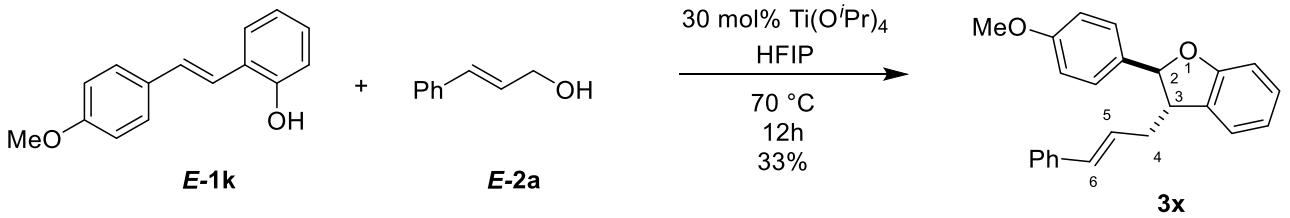


***E*-1j** ***E*-2a** **3w**

Alcohol ***E*-1j** (62.2 mg, 0.302 mmol), cinnamyl alcohol ***E*-2a** (40.5 mg, 0.302 mmol) and Ti(O^{i}Pr)$_4$ (25.7 mg, 0.0905 mmol) were subjected to the general procedure (FCC: gradient elution: 20% → 35% Et_2O - pentane) to yield **3w** as a colorless oil (51.8 mg, 55%).

Data for **3w**: **R_f** 0.50 (35% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.23-7.33 (6H, m, Ar), 7.15-7.22 (1H, m, Ar), 6.88 (2H, d, *J* = 8.7 Hz, Ar), 6.34 (1H, d, *J* = 15.8 Hz, 8-H), 6.05 (1H, dt, *J* = 15.8, 6.7 Hz, 7-H), 4.46 (1H, d, *J* = 9.4 Hz, 2-H), 3.79 (3H, s, OMe), 2.35 (1H, dddd, *J* = 13.5, 6.6, 4.2, 1.5 Hz, 6-H_A), 2.25 (1H, dddd, *J* = 9.2, 7.9, 3.9, 2.2 Hz, 3-H), 2.09-2.18 (2H, m, 4-H_A and 6-H_B), 1.61-1.71 (1H, m, 4-H_B), 1.39 (3H, s, Me), 1.38 (3H, s, Me). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.3 (C Ar), 137.6 (C Ar), 133.6 (C Ar), 131.1 (C-8), 128.6 (C-7), 128.6 (2 x CH Ar), 128.2 (CH Ar), 127.1 (2 x CH Ar), 126.1 (2 x CH Ar), 113.9 (2 x CH Ar), 85.8 (C-2), 80.0 (C-5), 55.4 (OMe), 48.7 (C-3), 46.1 (C-4), 34.8 (C-6), 29.9 (Me), 29.6 (Me). **HRMS** (ESI): calculated for $C_{22}H_{27}O_2$ $[M+H]^+$ requires *m/z* 323.20056, found *m/z* 323.20053. **IR** (film) ν_{max} : 2980, 2889, 1512, 1461, 1245, 1153 cm^{-1}.

8.25. (±)-(2*S*,3*S*)-3-Cinnamyl-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (3x)



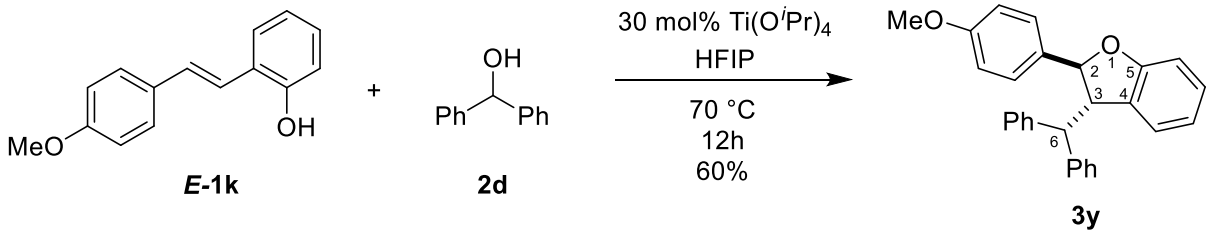
***E*-1k** ***E*-2a** **3x**

Alcohol ***E*-1k** (69.2 mg, 0.306 mmol), cinnamyl alcohol ***E*-2a** (41.0 mg, 0.306 mmol) and Ti(O^{i}Pr)$_4$ (26.0 mg, 0.0915 mmol) were subjected to the general procedure (FCC: 3% Et_2O - pentane) to yield **3x** as a colorless oil (30.8 mg, 33%).

Data for **3x**: **R_f** 0.30 (10% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.25-7.34 (6H, m, Ar), 7.16-7.24 (3H, m, Ar), 6.84-6.94 (4H, m, Ar), 6.50 (1H, d, *J* = 16.0 Hz, 6-H), 6.17 (1H, dt, *J* = 14.4, 7.2 Hz, 5-H), 5.35 (1H, d, *J* = 7.1 Hz, 2-H), 3.79 (3H, s, OMe), 3.58 (1H, q, *J* = 7.2 Hz, 3-H), 2.61-2.81 (2H, m, 4-H_2). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.62 (C Ar), 159.59 (C Ar), 137.3

(C Ar), 133.6 (C Ar), 132.7 (C-6), 127.0 (C Ar), 128.7 (3 x CH Ar), 127.7 (2 x CH Ar), 127.4 (CH Ar), 127.2 (C-5), 126.3 (2 x CH Ar), 124.5 (CH Ar), 120.8 (CH Ar), 114.1 (2 x CH Ar), 109.7 (CH Ar), 89.4 (C-2), 55.4 (OMe), 50.5 (C-3), 38.1 (C-4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 4-H_2, between 2-H and 5-H, between 2-H and 6-H. **HRMS** (ESI): calculated for $C_{24}H_{23}O_2$ $[M+H]^+$ requires *m/z* 343.16926, found *m/z* 343.16937. **IR** (film) ν_{max} : 3658, 2980, 1513, 1247, 956, 826 cm^{-1}.

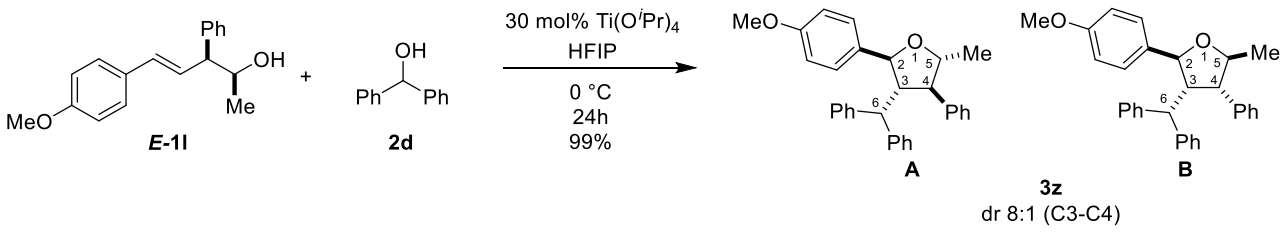
8.26. (±)-(2*S*,3*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-2,3-dihydrobenzofuran (3y)



Alcohol ***E*-1k** (20.2 mg, 0.0891 mmol), benzhydrol **2d** (16.4 mg, 0.0891 mmol) and $Ti(O^iPr)_4$ (7.6 mg, 0.027 mmol) were subjected to the general procedure (FCC: gradient elution: 4% → 10% Et_2O - pentane) to yield **3y** as a white foam (20.7 mg, 60%).

Data for **3y**: $\mathbf{R_f}$ 0.40 (15% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.19 -7.32 (10H, m, Ar), 7.13 (1H, t, *J* = 7.7 Hz, Ar), 6.83-6.89 (3H, m, Ar), 6.75 (2H, d, *J* = 8.7 Hz, Ar), 6.59 (1H, t, *J* = 7.6 Hz, Ar), 6.14 (1H, d, *J* = 7.6 Hz, Ar), 5.30 (1H, d, *J* = 4.1 Hz, 2-H), 4.26 (1H, dd, *J* = 11.5, 4.1 Hz, 3-H), 4.09 (1H, d, *J* = 11.5 Hz, 6-H), 3.77 (3H, s, OMe). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 160.0 (C-4), 159.4 (C-5), 142.7 (C Ar), 142.6 (C Ar), 134.5 (C Ar), 128.82 (5 x C-H Ar), 128.78 (2 x C-H Ar), 128.7 (C Ar), 128.5 (2 x C-H Ar), 127.2 (2 x C-H Ar), 126.96 (C-H Ar), 126.95 (C-H Ar), 126.3 (C-H Ar), 120.0 (C-H Ar), 113.9 (2 x C-H Ar), 109.4 (C-H Ar), 88.2 (C-2), 58.1 (C-6), 55.4 (OMe), 55.0 (C-3). **HRMS** (ESI): calculated for $C_{28}H_{24}O_2Na$ $[M+Na]^+$ requires *m/z* 415.16685, found *m/z* 415.16687. **IR** (film) ν_{max}: 2980, 2887, 2360, 1457, 1302, 1022 cm^{-1}.

8.27. (±)-(2*S*,3*S*,4*R*,5*R*)-3-Benzhydryl-2-(4-methoxyphenyl)-5-methyl-4-phenyltetrahydrofuran and (±)-(2*S*,3*S*,4*S*,5*S*)-3-benzhydryl-2-(4-methoxyphenyl)-5-methyl-4-phenyltetrahydrofuran (3z)



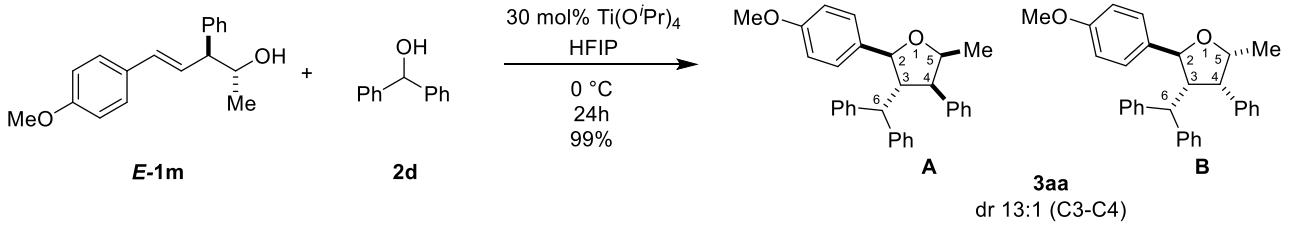
Alcohol ***E*-1l** (5.0 mg, 0.019 mmol), benzhydrol **2d** (3.5 mg, 0.019 mmol) and $Ti(O^iPr)_4$ (1.7 mg, 0.0057 mmol) were subjected to the general procedure except conducting the reaction at

0°C for 24 hours (FCC: gradient elution: 5% → 10% Et_2O - pentane) to yield inseparable 8:1 mixture of diastereomers **3z** as a colorless oil (8.0 mg, 99%).

Data for **major diastereomer A of 3z (from the mixture): R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.23 (2H, d, *J* = 8.1 Hz, Ar), 7.15 (2H, t, *J* = 7.5 Hz, Ar), 6.95-7.11 (11H, m, Ar), 6.76 (2H, d, *J* = 8.7 Hz, Ar), 6.65-6.68 (2H, m, Ar), 4.95 (1H, d, *J* = 4.6 Hz, 2-H), 4.26 (1H, dq, *J* = 8.7, 5.9 Hz, 5-H), 4.06 (1H, d, *J* = 11.1 Hz, 6-H), 3.79 (3H, s, OMe), 3.47 (1H, ddd, *J* = 11.4, 7.1, 4.7 Hz, 3-H), 2.64 (1H, dd, *J* = 8.8, 7.1 Hz, 4-H), 1.24 (3H, d, *J* = 6.0 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.6 (C Ar), 143.6 (C Ar), 142.5 (C Ar), 142.1 (C Ar), 135.7 (C Ar), 128.7 (2 x C-H Ar), 128.63 (2 x C-H Ar), 128.46 (2 x C-H Ar), 128.3 (2 x C-H Ar), 128.13 (2 x C-H Ar), 128.10 (2 x C-H Ar), 127.4 (2 x C-H Ar), 126.6 (C-H Ar), 126.3 (C-H Ar), 126.04 (C-H Ar), 113.8 (2 x C-H Ar), 84.6 (C-2), 83.4 (C-5), 61.3 (C-4), 60.9 (C-3), 59.5 (C-6), 55.4 (OMe), 19.5 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and Me, between 2-H and 6-H, between 2-H and 4-H, between 3-H and 5-H. **HRMS** (ESI): calculated for $C_{31}H_{30}O_2Na$ $[M+Na]^+$ requires *m/z* 457.21380, found *m/z* 457.21353. **IR** (film) ν_{max}: 2980, 2888, 1382, 1248, 1152, 954 cm^{-1}.

Partial data for **minor diastereomer B of 3z (from the mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.23 (2H, d, *J* = 8.1 Hz, Ar), 6.95-7.17 (13H, m, Ar), 6.80 (2H, d, *J* = 8.4 Hz, Ar), 6.53 (2H, d, *J* = 8.7 Hz, Ar), 4.77 (1H, d, *J* = 9.3 Hz, 2-H), 4.39-4.44 (1H, m, 5-H), 3.72 (3H, s, OMe), 3.62-3.68 (1H, m, 3-H), 3.49 (1H, d, *J* = 12.4 Hz, 6-H), 3.26 (1H, dd, *J* = 8.3, 4.1 Hz, 4-H), 1.49 (3H, d, *J* = 6.2 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.6 (C Ar), 143.7 (C Ar), 142.1 (C Ar), 140.6 (C Ar), 129.1 (C Ar), 128.57 (2 x C-H Ar), 128.53 (2 x C-H Ar), 128.4 (2 x C-H Ar), 128.0 (2 x C-H Ar), 127.9 (2 x C-H Ar), 127.8 (2 x C-H Ar), 127.4 (2 x C-H Ar), 126.5 (C-H Ar), 126.1 (C-H Ar), 125.95 (C-H Ar), 113.4 (2 x C-H Ar), 85.9 (C-2), 81.3 (C-5), 56.2 (C-4), 55.4 (OMe), 53.3 (C-3), 52.3 (C-6), 22.7 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 5-H, between 2-H and 6-H.

8.28. (±)-(2*S*,3*S*,4*R*,5*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-5-methyl-4-phenyltetrahydrofuran and (±)-(2*S*,3*S*,4*S*,5*R*)-3-benzhydryl-2-(4-methoxyphenyl)-5-methyl-4-phenyltetrahydrofuran (3aa)



***E*-1m** **2d** **A** **B**

3aa
dr 13:1 (C3-C4)

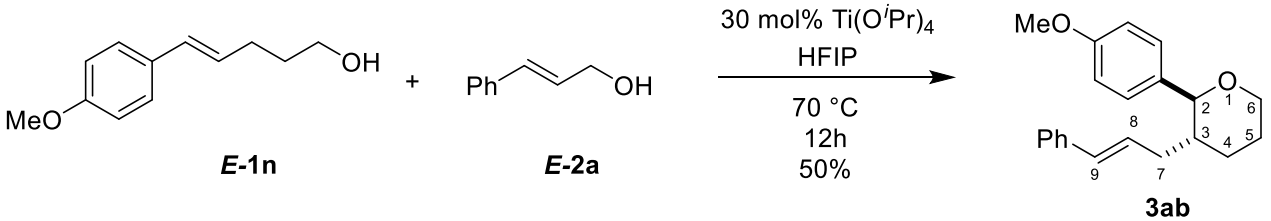
Alcohol ***E*-1m** (23.9 mg, 0.0864 mmol), benzhydrol **2d** (15.9 mg, 0.0864 mmol) and Ti(O^{i}Pr)$_4$ (7.3 mg, 0.026 mmol) were subjected to the general procedure except conducting the

reaction at 0°C for 24 hours (FCC: gradient elution: 5% → 6% Et_2O - pentane) to yield inseparable 13:1 mixture of diastereomers **3aa** as a colorless oil (37.7 mg, 99%).

Data for **major diastereomer A of 3aa (from the mixture): R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.17-7.27 (3H, m, Ar), 7.07-7.15 (5H, m, Ar), 6.96-7.06 (7H, m, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 6.64 (2H, d, *J* = 8.8 Hz, Ar), 4.58 (1H, d, *J* = 7.5 Hz, 2-H), 4.32 (1H, quint, *J* = 6.3 Hz, 5-H), 4.09 (1H, d, *J* = 11.4 Hz, 6-H), 3.75 (3H, s, OMe), 3.35 (1H, ddd, *J* = 11.2, 7.5, 3.5 Hz, 3-H), 3.01 (1H, dd, *J* = 6.4, 3.4 Hz, 4-H), 0.98 (3H, d, *J* = 6.3 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 143.6 (C Ar), 143.3 (C Ar), 142.7 (C Ar), 133.1 (C Ar), 129.2 (2 x C-H Ar), 128.59 (2 x C-H Ar), 128.57 (2 x C-H Ar), 128.51 (2 x C-H Ar), 128.41 (2 x C-H Ar), 128.37 (2 x C-H Ar), 128.07 (2 x C-H Ar), 126.5 (C-H Ar), 126.4 (C-H Ar), 126.1 (C-H Ar), 113.46 (2 x C-H Ar), 86.6 (C-2), 77.8 (C-5), 60.9 (C-3), 58.3 (C-6), 56.5 (C-4), 55.38 (OMe), 16.7 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 4-H, between 2-H and 5-H, between 2-H and 6-H, between 4-H and 6-H. **HRMS** (ESI): calculated for $C_{31}H_{30}O_2Na$ $[M+Na]^+$ requires *m/z* 457.21380, found *m/z* 457.21353. **IR** (film) ν_{max}: 2980, 2888, 1382, 1248, 1152, 954 cm^{-1}.

Partial data for **minor diastereomer B of 3aa (from the mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.31-7.42 (3H, m, Ar), 7.07-7.15 (5H, m, Ar), 6.96-7.06 (7H, m, Ar), 6.77 (2H, d, *J* = 8.6 Hz, Ar), 6.56 (2H, d, *J* = 8.6 Hz, Ar), 4.85-4.89 (1H, m, 5-H), 4.84 (1H, d, *J* = 7.5 Hz, 2-H), 3.80-3.87 (1H, m, 3-H), 3.73 (3H, s, OMe), 3.52 (1H, d, *J* = 11.9 Hz, 6-H), 3.31-3.34 (1H, m, 4-H), 1.02 (3H, d, *J* = 6.3 Hz, Me). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.4 (C Ar), 143.5 (C Ar), 137.2 (C Ar), 136.6 (C Ar), 128.63 (C Ar), 128.59 (2 x C-H Ar), 128.46 (2 x C-H Ar), 128.23 (2 x C-H Ar), 128.22 (2 x C-H Ar), 128.12 (2 x C-H Ar), 127.92 (2 x C-H Ar), 127.85 (2 x C-H Ar), 126.7 (C-H Ar), 126.6 (C-H Ar), 126.3 (C-H Ar), 113.48 (2 x C-H Ar), 84.8 (C-2), 78.9 (C-5), 57.3 (C-3), 55.41 (OMe), 54.8 (C-4), 53.1 (C-6), 16.9 (Me). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H, between 3-H and 5-H.

8.29. (±)-(2*S*,3*R*)-3-Cinnamyl-2-(4-methoxyphenyl)tetrahydro-2H-pyran (3ab)

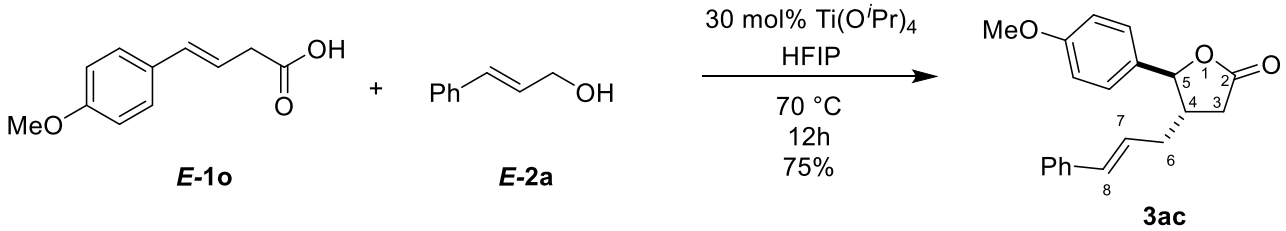


***E*-1n** ***E*-2a** **3ab**

Alcohol ***E*-1n** (50.5 mg, 0.263 mmol), cinnamyl alcohol ***E*-2a** (35.2 mg, 0.263 mmol) and $Ti(O^iPr)_4$ (22.4 mg, 0.0789 mmol) were subjected to the general procedure (FCC: gradient elution: 7% → 12% Et_2O - pentane) to yield **3ab** as a colorless oil (40.0 mg, 50%).

Data for **3ab**: **R_f** 0.50 (30% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.24-7.33 (6H, m, Ar), 7.15-7.23 (1H, m, Ar), 6.90 (2H, d, *J* = 8.7 Hz, Ar), 6.22 (1H, d, *J* = 15.7 Hz, 9-H), 6.00 (1H, dt, *J* = 14.9, 7.2 Hz, 8-H), 4.09 (1H, dt, *J* = 11.6, 4.1 Hz, 6-H_A), 3.94 (1H, d, *J* = 9.1 Hz, 2-H), 3.81 (3H, s, OMe), 3.54 (1H, td, *J* = 11.5, 2.6 Hz, 6-H_B), 2.04-2.12 (1H, m, 4-H_A), 1.96-2.04 (1H, m, 7-H_A), 1.72-1.87 (3H, m, 3-H, 5-H_A and 7-H_B), 1.62-1.70 (1H, m, 5-H_B), 1.34 (1H, qd, *J* = 13.0, 4.1 Hz, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.4 (C Ar), 137.7 (C Ar), 133.6 (C Ar), 131.5 (C-9), 128.8 (2 x C-H Ar), 128.6 (2 x C-H Ar), 128.2 (C-8), 127.0 (C-H Ar), 126.0 (2 x C-H Ar), 113.9 (2 x C-H Ar), 85.6 (C-2), 69.0 (C-6), 55.4 (OMe), 42.2 (C-3), 36.0 (C-7), 30.0 (C-4), 26.7 (C-5). **HRMS** (ESI): calculated for $C_{21}H_{25}O_2$ $[M+H]^+$ requires *m/z* 309.18491, found *m/z* 309.18488. **IR** (film) ν_{max}: 3658, 2980, 2933, 1512, 1241, 1075 cm^{-1}.

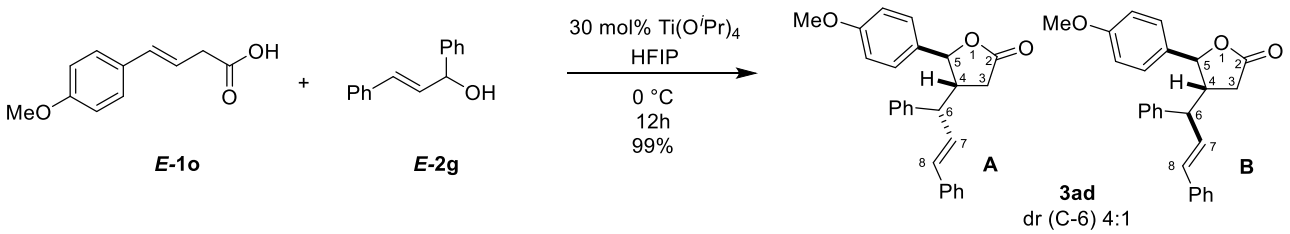
8.30. (±)-(4*S*,5*S*)-4-Cinnamyl-5-(4-methoxyphenyl)dihydrofuran-2(3H)-one (3ac)



Carboxylic acid ***E*-1o** (45.6 mg, 0.238 mmol), cinnamyl alcohol ***E*-2a** (31.8 mg, 0.238 mmol) and Ti(O^{i}Pr)$_4$ (20.0 mg, 0.0704 mmol) were subjected to the general procedure (FCC: gradient elution: 15% → 45% Et_2O - pentane) to yield **3ac** as a colorless oil (55.0 mg, 75%).

Data for **3ac**: **R_f** 0.50 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.19-7.34 (7H, m, Ar), 6.92 (2H, d, *J* = 8.7 Hz, Ar), 6.45 (1H, d, *J* = 15.9 Hz, 8-H), 6.04 (1H, dt, *J* = 15.8, 7.1 Hz, 7-H), 5.08 (1H, d, *J* = 7.6 Hz, 5-H), 3.82 (3H, s, OMe), 2.81 (1H, dd, *J* = 17.2, 7.9 Hz, 3-H_A), 2.54-2.68 (1H, m, 4-H), 2.46-2.54 (1H, m, 6-H_A), 2.42 (1H, dd, *J* = 17.2, 7.9 Hz, 3-H_B), 2.31-2.39 (1H, m, 6-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 176.0 (C=O), 160.0 (C Ar), 136.9 (C Ar), 133.0 (C-8), 130.1 (C Ar), 128.7 (2 x C-H Ar), 127.7 (2 x C-H Ar), 127.6 (C-H Ar), 126.2 (2 x C-H Ar), 125.9 (C-7), 114.2 (2 x C-H Ar), 86.1 (C-5), 55.4 (OMe), 44.5 (C-4), 35.4 (C-6), 35.0 (C-3). **HRMS** (Cl): calculated for $C_{20}H_{21}O_3$ $[M+H]^+$ requires *m/z* 309.14852, found *m/z* 309.14856. **IR** (film) ν_{max} : 2980, 1774, 1514, 1248, 1144, 1029 cm^{-1}.

8.31. (±)-(4*R*,5*S*)-4-[(1'*R*,2'*E*)-1,3-diphenylallyl]-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one and (±)-(4*R*,5*S*)-4-[(1'*S*,2'*E*)-1,3-diphenylallyl]-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)- one (3ad)



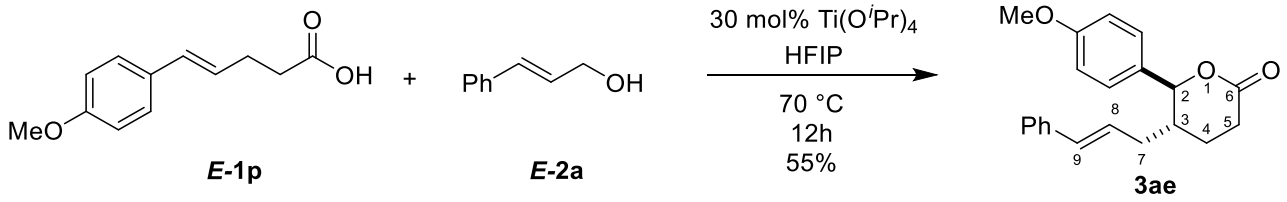
***E*-1o** ***E*-2g**

Carboxylic acid ***E*-1o** (200.0 mg, 1.031 mmol), *trans*-1,3-diphenyl-2-propen-1-ol ***E*-2g** (219.0 mg, 1.031 mmol) and Ti(O^{i}Pr)$_4$ (88.6 mg, 0.312 mmol) were subjected to the general procedure except conducting the reaction at at 0°C (FCC: gradient elution: 15% → 30% Et_2O - pentane) to yield separable 4:1 mixture of diastereomers **3ad** as a colorless oil (399.0 mg, 99%).

Data for **major diastereomer A of 3ad: R_f** 0.40 (70% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.32-7.37 (2H, m, Ar), 7.17-7.30 (10H, m, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 6.51 (1H, d, *J* = 15.7 Hz, 8-H), 6.10 (1H, dd, *J* = 15.7, 9.2 Hz, 7-H), 5.37 (1H, d, *J* = 5.7 Hz, 5-H), 3.79 (3H, s, OMe), 3.54 (1H, t, *J* = 9.5 Hz, 6-H), 2.96-3.06 (1H, m, 4-H), 2.64 (1H, dd, *J* = 18.0, 8.7 Hz, 3-H_A), 2.35 (1H, dd, *J* = 18.0, 7.1 Hz, 3-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 176.0 (C=O), 159.8 (C Ar), 141.3 (C Ar), 136.6 (C Ar), 132.0 (C-8), 131.1 (C Ar), 130.6 (C-7), 129.2 (2 x C-H Ar), 128.6 (2 x C-H Ar), 128.0 (2 x C-H Ar), 127.79 (2 x C-H Ar), 127.75 (C-H Ar), 127.3 (C-H Ar), 126.4 (2 x C-H Ar), 114.3 (2 x C-H Ar), 84.9 (C-5), 55.4 (OMe), 52.6 (C-6), 48.6 (C-4), 33.6 (C-3). **HRMS** (ESI): calculated for $C_{26}H_{24}O_3Na$ $[M+ Na]^+$ requires *m/z* 407.16177, found *m/z* 407.16190. **IR** (film) ν_{max} : 2982, 1764, 1524, 1278, 1124, 1019 cm^{-1}.

Data for **minor diastereomer B of 3ad: R_f** 0.50 (70% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.28-7.35 (6H, m, Ar), 7.17-7.26 (4H, m, Ar), 6.91 (2H, d, *J* = 8.7 Hz, Ar), 6.79 (2H, d, *J* = 8.8 Hz, Ar), 6.50 (1H, d, *J* = 15.7 Hz, 8-H), 6.27 (1H, dd, *J* = 15.7, 9.0 Hz, 7-H), 5.17 (1H, d, *J* = 4.8 Hz, 5-H), 3.78 (3H, s, OMe), 3.49 (1H, t, *J* = 9.2 Hz, 6-H), 2.90-2.97 (1H, m, 4-H), 2.81 (1H, dd, *J* = 17.9, 8.6 Hz, 3-H_A), 2.66 (1H, dd, *J* = 17.9, 5.9 Hz, 3-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 176.4 (C=O), 159.6 (C Ar), 141.3 (C Ar), 136.6 (C Ar), 132.7 (C-8), 131.2 (C Ar), 129.5 (C-7), 129.2 (2 x C-H Ar), 128.8 (2 x C-H Ar), 128.1 (2 x C-H Ar), 128.0 (C-H Ar), 127.4 (C-H Ar), 126.9 (2 x C-H Ar), 126.5 (2 x C-H Ar), 114.2 (2 x C-H Ar), 84.2 (C-5), 55.5 (OMe), 52.6 (C-6), 48.6 (C-4), 32.7 (C-3).

8.32. (±)-(5*R*,6*S*)-5-Cinnamyl-6-(4-methoxyphenyl)tetrahydro-2H-pyran-2-one (3ae)

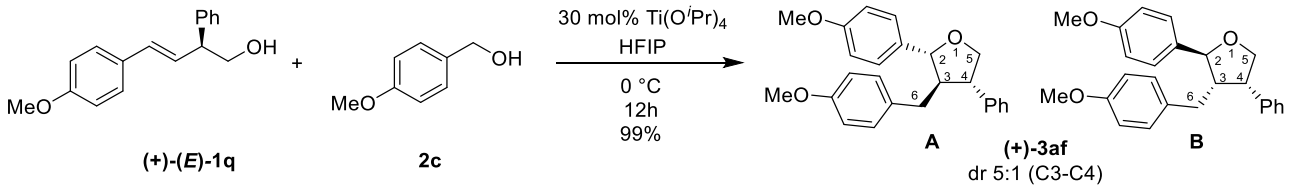


***E*-1p** ***E*-2a** **3ae**

Carboxylic acid ***E*-1p** (45.9 mg, 0.224 mmol), cinnamyl alcohol ***E*-2a** (30.0 mg, 0.224 mmol) and Ti(O^{i}Pr)$_4$ (19.0 mg, 0.0669 mmol) were subjected to the general procedure (FCC: gradient elution: 18% → 25% Et_2O - pentane) to yield **3ae** as a colorless oil (38.9 mg, 55%).

Data for **3ae**: **R_f** 0.50 (50% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.24-7.31 (6H, m, Ar), 7.17-7.26 (1H, m, Ar), 6.92 (2H, d, *J* = 8.7 Hz, Ar), 6.32 (1H, d, *J* = 15.8 Hz, 9-H), 6.00 (1H, ddd, *J* = 15.6, 8.2, 6.3 Hz, 8-H), 4.97 (1H, d, *J* = 9.4 Hz, 2-H), 3.81 (3H, s, OMe), 2.75 (1H, ddd, *J* = 17.9, 7.1, 4.6 Hz, 5-H_A), 2.61 (1H, ddd, *J* = 17.8, 9.5, 6.8 Hz, 5-H_B), 2.15-2.23 (1H, m, 7-H_A), 2.04-2.14 (2H, m, 3-H and 4-H_A), 1.91-2.04 (1H, m, 7-H_B), 1.74 (1H, dddd, *J* = 15.0, 11.3, 6.8, 4.7 Hz, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 171.1 (C-6), 159.7 (C Ar), 136.8 (C Ar), 132.6 (C-9), 130.1 (C Ar), 128.4 (2 x C-H Ar), 128.3 (2 x C-H Ar), 127.2 (C-H Ar), 125.9 (C-8), 125.8 (2 x C-H Ar), 113.8 (2 x C-H Ar), 86.1 (C-2), 55.1 (OMe), 39.4 (C-3), 34.7 (C-7), 29.3 (C-5), 24.3 (C-4). **HRMS** (Cl): calculated for $C_{21}H_{22}O_3$ $[M+H]^+$ requires *m/z* 323.16417, found *m/z* 323.16418. **IR** (film) ν_{max} : 2980, 1727, 1514, 1246, 1072, 966 cm^{-1}.

8.33. (+)-(2*R*,3*R*,4*S*)-3-(4-Methoxybenzyl)-2-(4-methoxyphenyl)-4-phenyltetrahydrofuran and (+)-(2*S*,3*S*,4*S*)-3-(4-methoxybenzyl)-2-(4-methoxyphenyl)-4-phenyltetrahydrofuran [(+)-3af]



(+)-(*E*)-1q **2c** **A** **(+)-3af** dr 5:1 (C3-C4) **B**

Alcohol **(+)-(*E*)-1q** (30.0 mg, 0.118 mmol), 4-methoxybenzylic alcohol **2c** (15.7 mg, 0.118 mmol) and Ti(O^{i}Pr)$_4$ (9.7 mg, 0.034 mmol) were subjected to the general procedure except conducting the reaction at at 0°C (FCC: gradient elution: 10% → 15% Et_2O - pentane) to yield inseparable 5:1 mixture of diastereomers **(+)-3af** as a colorless oil (43.8 mg, 99%, 99% ee).

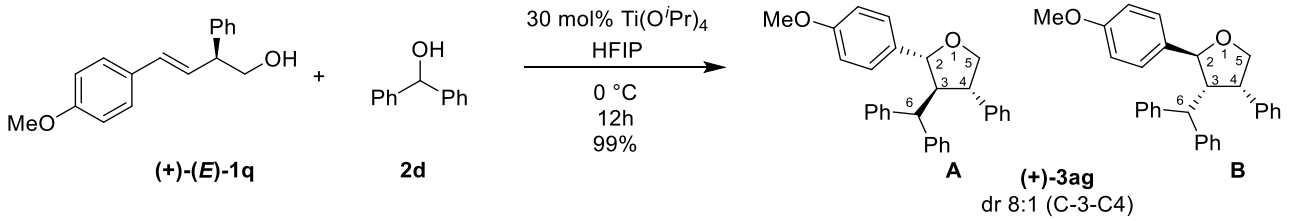
Data for **major diastereomer A of (+)-3af (from the mixture)**: **R_f** 0.50 (50% Et_2O - pentane). $[\alpha]_D^{25}$ = +39.6 (*c* = 6.75, $CHCl_3$). **^{1}H (500 MHz, $CDCl_3$) δ** 7.23-7.31 (4H, m, Ar), 7.14-7.22 (4H, m, Ar), 6.82-6.90 (3H, m, Ar), 6.68 (2H, d, *J* = 8.7 Hz, Ar), 4.61 (1H, d, *J* = 8.8 Hz, 2-H), 4.24 (1H, t, *J* = 8.4 Hz, 5-H_A), 4.06 (1H, t, *J* = 8.1 Hz, 5-H_B), 3.81 (3H, s, OMe), 3.75 (3H, s, OMe), 3.24 (1H, q, *J* = 8.2 Hz, 4-H), 2.66-2.79 (2H, m, 6-H_2), 2.59 (1H, m, 3-H). **^{13}C NMR (125 MHz,**

$CDCl_3$) δ 159.3 (C Ar), 158.0 (C Ar), 142.1 (C Ar), 133.6 (C Ar), 130.9 (C Ar), 130.5 (2 x C-H Ar), 128.7 (2 x C-H Ar), 128.1 (2 x C-H Ar), 127.7 (2 x C-H Ar), 126.5 (C-H Ar), 113.93 (2 x C-H Ar), 113.6 (2 x C-H Ar), 86.2 (C-2), 75.3 (C-5), 57.0 (C-3), 55.40 (OMe), 55.38 (OMe), 51.3 (C-4), 35.7 (C-6). **HRMS** (ESI): calculated for $C_{25}H_{26}O_3Na$ $[M+Na]^+$ requires *m/z* 397.17742, found *m/z* 397.17747. **IR** (film) ν_{max}: 2980, 2889, 1510, 1381, 1243, 1031 cm^{-1}.

Partial data for **minor diastereomer B of (+)-3af (from the mixture)**: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.32-7.37 (2H, m, Ar), 7.14-7.22 (4H, m, Ar), 6.82-6.90 (5H, m, Ar), 6.76 (2H, d, *J* = 8.7 Hz, Ar), 4.77 (1H, d, *J* = 7.7 Hz, 2-H), 5.50-5.56 (1H, m, 5-H_A), 4.30 (1H, dd, *J* = 8.6, 4.3 Hz, 5-H_B), 3.81 (3H, s, OMe), 3.78 (3H, s, OMe), 3.56 (1H, q, *J* = 6.1 Hz, 4-H), 2.66-2.79 (1H, m, 3-H), 2.43 (1H, dd, *J* = 14.6, 6.4 Hz, 6-H_A), 2.19 (1H, dd, *J* = 14.4, 8.8 Hz, 6-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.0 (C Ar), 157.9 (C Ar), 140.3 (C Ar), 134.8 (C Ar), 132.1 (C Ar), 129.9 (2 x C-H Ar), 129.0 (2 x C-H Ar), 128.4 (2 x C-H Ar), 127.5 (2 x C-H Ar), 126.6 (C-H Ar), 113.87 (2 x C-H Ar), 113.7 (2 x C-H Ar), 84.4 (C-2), 74.0 (C-5), 55.38 (OMe), 55.34 (OMe), 54.2 (C-3), 47.7 (C-4), 32.4 (C-6).

Racemic **(±)-3af** (99%, 5:1 dr) was made with the same procedure with racemic alcohol **(±)-(*E*)-1q**.

8.34. (+)-(2*R*,3*R*,4*S*)-3-Benzhydryl-2-(4-methoxyphenyl)-4-phenyltetrahydrofuran and (+)-(2*S*,3*S*,4*S*)-3-benzhydryl-2-(4-methoxyphenyl)-4-phenyltetrahydrofuran [(+)-3ag]



Alcohol **(+)-(*E*)-1q** (22.7 mg, 0.0894 mmol), benzhydrol **2d** (16.4 mg, 0.0894 mmol) and $Ti(O^iPr)_4$ (7.6 mg, 0.027 mmol) were subjected to the general procedure except conducting the reaction at at 0°C (FCC: gradient elution: 10% → 20% Et_2O - pentane) to yield inseparable 8:1 mixture of diastereomers **(+)-3ag** as a white foam (37.4 mg, 99%, 99% ee).

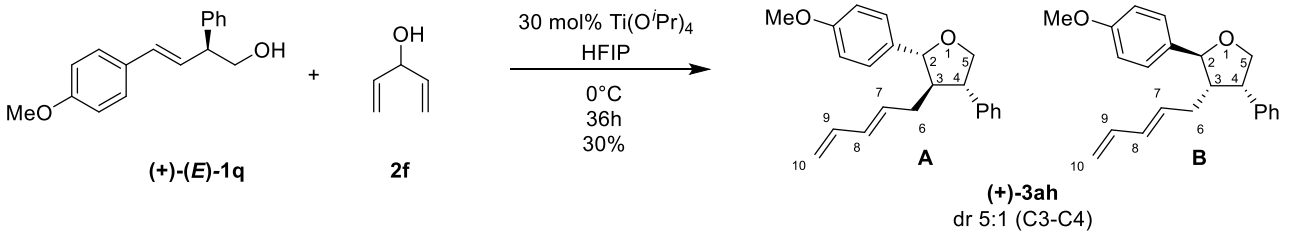
Data for **major diastereomer A of (+)-3ag (from the mixture): R_f** 0.30 (25% Et_2O - pentane). $[\alpha]_D^{25}$ = +2.5 (*c* = 10.0, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.00-7.23 (12H, m, Ar), 6.81-6.88 (5H, m, Ar), 6.67 (2H, d, *J* = 7.8 Hz, Ar), 4.64 (1H, d, *J* = 6.3 Hz, 2-H), 4.25 (1H, dd, *J* = 9.3, 7.3 Hz, 5-H_A), 4.17 (1H, dd, *J* = 9.3, 4.2 Hz, 5-H_B), 4.03 (1H, d, *J* = 11.3 Hz, 6-H), 3.76 (3H, s, OMe), 3.26 (1H, ddd, *J* = 11.1, 6.3, 4.5 Hz, 3-H), 3.19 (1H, dt, *J* = 7.2, 4.4 Hz, 4-H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.8 (C Ar), 145.3 (C Ar), 143.3 (C Ar), 142.8 (C Ar), 134.0 (C Ar), 128.7 (2 x C-H Ar), 128.5 (3 x C-H Ar), 128.44 (2 x C-H Ar), 128.40 (2 x C-H Ar), 128.3 (2 x C-H Ar), 128.1 (C-H Ar), 127.6 (2 x C-H Ar), 126.62 (C-H Ar), 126.56 (C-H Ar), 126.1 (C-H Ar),113.6 (2 x

C-H Ar), 87.4 (C-2), 75.1 (C-5), 60.8 (C-3), 58.7 (C-6), 55.4 (OMe), 52.1 (C-4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H, between 2-H and 4-H, between 4-H and 6-H. **HRMS** (ESI): calculated for $C_{30}H_{28}O_2Na$ $[M+Na]^+$ requires *m/z* 443.19815, found *m/z* 443.19785. **IR** (film) ν_{max}: 3649, 2980, 1513, 1453, 1302, 1248cm^{-1}.

Partial data for **minor diastereomer B of (+)-3ag (from the mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.00-7.23 (11H, m, Ar), 6.89-6.94 (2H, m, Ar), 6.78-6.81 (2H, m, Ar), 6.74 (2H, d, *J* = 8.7 Hz, Ar), 6.54 (2H, d, *J* = 8.7 Hz, Ar), 4.77 (1H, d, *J* = 9.0 Hz, 2-H), 4.60 (1H, dd, *J* = 8.7, 5.4 Hz, 5-H_A), 4.19-4.23 (1H, m, 5-H_B), 3.73 (3H, s, OMe), 3.64-3.71 (1H, m, 3-H), 3.56-3.62 (1H, m, 4-H), 3.39 (1H, d, *J* = 11.8 Hz, 6-H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 158.4 (C Ar), 143.6 (C Ar), 142.7 (C Ar), 141.1 (C Ar), 135.6 (C Ar), 129.1 (C-H Ar), 128.5 (3 x C-H Ar), 128.44 (2 x C-H Ar), 128.40 (2 x C-H Ar), 128.2 (2 x C-H Ar), 128.00 (2 x C-H Ar), 127.98 (2 x C-H Ar), 126.7 (C-H Ar), 126.3 (C-H Ar), 126.2 (C-H Ar), 113.4 (2 x C-H Ar), 84.6 (C-2), 75.2 (C-5), 55.5 (C-3), 55.4 (OMe), 52.8 (C-6), 49.7 (C-4). **NOESY- 2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H.

Racemic **(±)-3ag** (99%, 8:1 dr) was made with the same procedure with racemic alcohol **(±)-(*E*)-1q**.

8.35. (+)-(2*R*,3*R*,4*S*)-2-(4-Methoxyphenyl)-3-[(2'*E*)-penta-2,4-dien-1-yl]-4-phenyltetrahydrofuran and (+)-(2*S*,3*S*,4*S*)-2-(4-methoxyphenyl)-3-[(2'*E*)-penta-2,4-dien-1-yl]-4-phenyltetrahydrofuran [(+)-3ah]



Alcohol **(+)-(*E*)-1q** (30.0 mg, 0.118 mmol), bis-allyl alcohol **2f** (15.7 mg, 0.118 mmol) and $Ti(O^iPr)_4$ (9.7 mg, 0.034 mmol) were subjected to the general procedure except conducting the reaction at at 0°C for 36 hours (FCC: gradient elution: 7% → 9% Et_2O - pentane) to yield inseparable 5:1 mixture of diastereomers **(+)-3ah** as a colorless oil (11.3 mg, 30%, 99% ee).

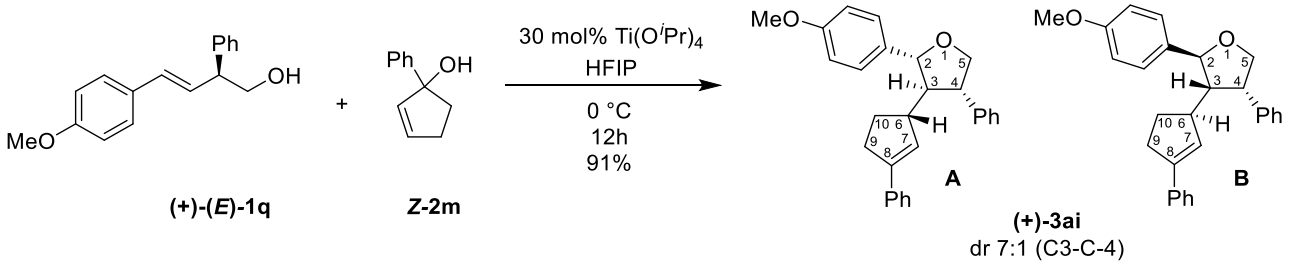
Data for **major diastereomer A of (+)-3ah (from the mixture)**: **R_f** 0.50 (25% Et_2O - pentane). $[\alpha]_D^{25}$ = +20.0 (*c* = 1.35, $CHCl_3$). **^{1}H (500 MHz, $CDCl_3$) δ** 7.19-7.37 (7H, m, Ar), 6.90 (2H, d, *J* = 8.7 Hz, Ar), 6.12 (1H, dt, *J* = 16.9, 10.2 Hz, 9-H), 5.97 (1H, dd, *J* = 15.1, 10.4 Hz, 8-H), 5.38-5.48 (1H, m, 7-H), 5.05 (1H, dd, *J* = 16.8, 1.7 Hz, 10-H_A), 4.94 (1H, dd, *J* = 10.0, 1.8 Hz, 10-H_B), 4.58 (1H, d, *J* = 8.9 Hz, 2-H), 4.28 (1H, t, *J* = 8.5 Hz, 5-H_A), 4.09 (1H, dd, *J* = 8.7, 7.8 Hz, 5-H_B), 3.82 (3H, s, OMe), 3.26 (1H, q, *J* = 8.3 Hz, 4-H), 2.27-2.34 (1H, m, 3-H), 2.20-2.27 (2H, m, 6-H_2). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.4 (C Ar), 142.0 (C Ar), 136.9 (C-9), 133.5 (C Ar), 133.3

(C-8), 131.5 (C-7), 128.8 (2 x C-H Ar), 128.1 (2 x C-H Ar), 127.9 (2 x C-H Ar), 126.8 (C-H Ar), 115.6 (C-10), 114.00 (2 x C-H Ar), 86.4 (C-2), 75.3 (C-5), 56.2 (C-3), 55.5 (OMe), 51.6 (C-4), 33.1 (C-6). **HRMS**: stable ion was not found in ESI, EI and CI. **IR** (film) ν_{max}: 2980, 2888, 1461, 1382, 1252, 1152 cm^{-1}.

Partial data for **minor diastereomer B of (+)-3ah (from the mixture)**: **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.19-7.37 (7H, m, Ar), 6.90 (2H, d, *J* = 8.7 Hz, Ar), 6.21 (1H, dt, *J* = 17.0, 10.3 Hz, 9-H), 5.84 (1H, dd, *J* = 15.3, 10.4 Hz, 8-H), 5.38-5.48 (1H, m, 7-H), 5.03 (1H, dd, *J* = 16.8, 1.7 Hz, 10-H_A), 4.94 (1H, dd, *J* = 10.0, 1.8 Hz, 10-H_B), 4.66 (1H, d, *J* = 8.5 Hz, 2-H), 4.51 (1H, dd, *J* = 8.7, 6.2 Hz, 5-H_A), 4.26 (1H, dd, *J* = 8.6, 3.7 Hz, 5-H_B), 3.81 (3H, s, OMe), 3.61 (1H, ddd, *J* = 10.3, 6.8, 3.4 Hz, 4-H), 2.42 (1H, qd, *J* = 8.6, 6.2 Hz, 3-H), 1.85-1.96 (1H, m, 6-H_A), 1.66-1.77 (1H, m, 6-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.3 (C Ar), 140.4 (C Ar), 137.1 (C-9), 134.5 (C Ar), 132.7 (C-7), 132.6 (C-8), 128.9 (2 x C-H Ar), 128.5 (2 x C-H Ar), 127.8 (2 x C-H Ar), 126.8 (C-H Ar), 115.4 (C-10), 113.95 (2 x C-H Ar), 84.5 (C-2), 74.3 (C-5), 55.5 (OMe), 52.6 (C-3), 48.3 (C-4), 30.6 (C-6).

Racemic **(±)-3ah** (30%, 5:1 dr) was made with the same procedure with racemic alcohol **(±)-(*E*)-1q**.

8.36. (+)-(2*R*,3*R*,4*S*)-2-(4-Methoxyphenyl)-4-phenyl-3-[(1'*S*)-3-phenylcyclopent-2-en-1-yl]tetrahydrofuran and (+)-(2*S*,3*S*,4*S*)-2-(4-methoxyphenyl)-4-phenyl-3-[(1'R)-3-phenylcyclopent-2-en-1-yl]tetrahydrofuran [(+)-3ai]



Alcohol **(+)-(*E*)-1q** (30.0 mg, 0.114 mmol) and **(*E*)-2m** (18.2 mg, 0.114 mmol) and $Ti(O^iPr)_4$ (9.7 mg, 0.034 mmol) were subjected to the general procedure except conducting the reaction at at 0°C (FCC: gradient elution: 10% → 15% Et_2O - pentane) to yield inseparable 7:1 mixture of diastereomers **(+)-3ai** as a yellow oil (41.7 mg, 91%, 99% ee).

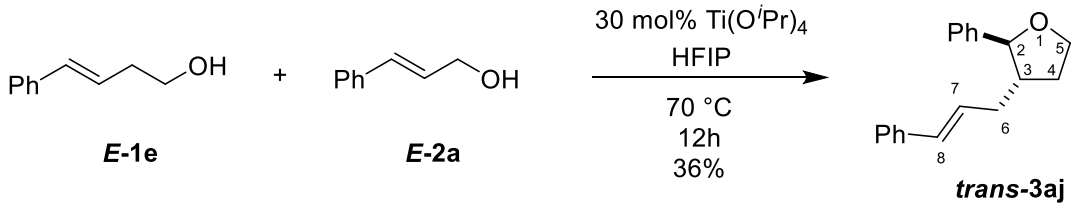
Data for **major diastereomer A of (+)-3ai (from the mixture)**: **R_f** 0.40 (30% Et_2O - pentane). $[\alpha]_D^{25}$ = +57.2 (*c* = 10.0, $CHCl_3$). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.19-7.44 (12H, m, Ar), 6.89 (2H, d, *J* = 8.7 Hz, Ar), 5.95 (1H, q, *J* = 2.0 Hz, 7-H), 4.73 (1H, d, *J* = 8.9 Hz, 2-H), 4.27 (1H, t, *J* = 8.5 Hz, 5-H_A), 4.10 (dd, J = 8.8, 7.3 Hz, 5-H_B), 3.82 (3H, s, OMe), 3.37 (1H, td, *J* = 8.4, 7.3 Hz, 4-H), 3.11 (1H, dtd, *J* = 11.7, 6.5, 6.0, 2.2 Hz, 6-H), 2.51-2.65 (3H, m, 3-H and 9-H_2), 1.97-2.08 (1H, m, 10-H_A), 1.48-1.56 (1H, m, 10-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.4 (C Ar),

143.5 (C-8), 143.4 (C Ar), 136.4 (C Ar), 134.4 (C Ar),128.9 (2 x C-H Ar), 128.5 (2 x C-H Ar), 128.39 (2 x C-H Ar), 127.8 (2 x C-H Ar), 127.6 (C-H Ar), 127.3 (C-7), 126.7 (C-H Ar), 125.8 (2 x C-H Ar),114.0 (2 x C-H Ar), 85.6 (C-2), 76.0 (C-5), 60.1 (C-3), 55.4 (OMe), 50.3 (C-4), 47.1 (C-6), 32.8 (C-9), 27.7 (C-10). **HRMS** (ESI): calculated for $C_{28}H_{28}O_2Na$ $[M+Na]^+$ requires *m/z* 419.19815, found *m/z* 419.19800. **IR** (film) ν_{max}: 2980, 1611, 1512, 1381, 1247, 1172 cm^{-1}.

Partial data for **minor diastereomer B of (+)-3ai (from the mixture)**: **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.19-7.44 (12H, m, Ar), 6.89 (2H, d, *J* = 8.7 Hz, Ar), 5.93 (1H, q, *J* = 2.1 Hz, 7-H), 4.90 (1H, d, *J* = 7.8 Hz, 2-H), 4.50 (1H, dd, J = 8.6, 6.0 Hz, 5-H_A), 4.22 (1H, dd, *J* = 8.6, 3.3 Hz, 5-H_B), 3.82 (3H, s, OMe), 3.73 (1H, td, *J* = 6.1, 3.2 Hz, 4-H), 2.51-2.65 (2H, m, 3-H and 6-H), 2.39-2.49 (2H, m, 9-H_2), 1.97-2.08 (1H, m, 10-H_A), 1.48-1.56 (1H, m, 10-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.3 (C Ar), 142.9 (C-8), 141.4 (C Ar), 136.5 (C Ar), 135.6 (C Ar),129.01 (2 x C-H Ar), 128.95 (2 x C-H Ar), 128.7 (C-7), 128.6 (2 x C-H Ar), 128.35 (2 x C-H Ar), 127.2 (C-H Ar), 126.8 (C-H Ar), 125.7 (2 x C-H Ar), 113.9 (2 x C-H Ar), 84.2 (C-2), 74.6 (C-5), 57.1 (C-3), 55.4 (OMe), 49.7 (C-4), 45.8 (C-6), 33.0 (C-9), 29.2 (C-10).

Racemic **(±)-3ai** (91%, 7:1 dr) was made with the same procedure with racemic alcohol **(±)-(*E*)-1q**.

8.37. (±)-(2*S*,3*S*)-3-Cinnamyl-2-phenyltetrahydrofuran (*trans*-3aj)

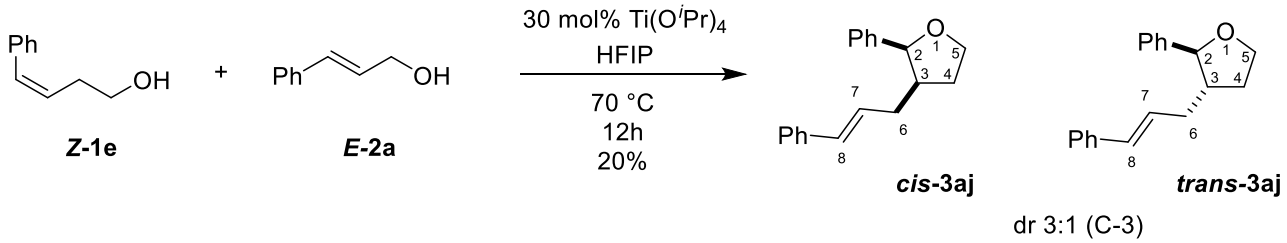


***E*-1e** ***E*-2a** ***trans*-3aj**

Alcohol ***E*-1e** (64.3 mg, 0.434 mmol), cinnamyl alcohol ***E*-2a** (58.0 mg, 0.434 mmol) and Ti(O^{i}Pr)$_4$ (37.0 mg, 0.130 mmol) were subjected to the general procedure (FCC: gradient elution: 6% → 12% Et_2O - pentane) to yield ***trans*-3aj** as a colorless oil (40.9 mg, 36%).

Data for ***trans*-3aj**: **R_f** 0.40 (20% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.35 (4H, d, *J* = 4.3 Hz, Ar), 7.28-7.31 (5H, m, Ar), 7.17-7.24 (1H, m, Ar), 6.42 (1H, d, *J* = 15.8 Hz, 8-H), 6.14 (1H, dt, *J* = 15.8, 6.9 Hz, 7-H), 4.49 (1H, d, *J* = 6.8 Hz, 2-H), 4.14 (1H, dt, *J* = 8.4, 7.1 Hz, 5-H_A), 4.04 (1H, td, *J* = 8.3, 4.7 Hz, 5-H_B), 2.47 (1H, dddd, *J* = 11.1, 6.6, 4.3, 1.4 Hz, 6-H_A), 2.17-2.32 (3H, m, 3-H, 4-H_A and 6-H_B), 1.78-1.87 (1H, m, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 142.5 (C Ar), 137.5 (C Ar), 131.6 (C-8), 128.6 (2 x CH Ar), 128.5 (2 x CH Ar), 128.4 (C-7), 127.6 (CH Ar), 127.2 (CH Ar), 126.4 (2 x CH Ar), 126.1 (2 x CH Ar), 86.1 (C-2), 68.2 (C-5), 48.2 (C-3), 35.7 (C-6), 32.5 (C-4). **NOESY- 2D (400 MHz, $CDCl_3$)**: between 2-H and 6-H_A, between 2-H and 6-H_B. **HRMS** (ESI): calculated for $C_{19}H_{21}O$ $[M+H]^+$ requires *m/z* 265.15869, found *m/z* 265.15872. **IR** (film) ν_{max} : 3657, 2980, 1451, 1251, 1153, 964 cm^{-1}.

8.38. (±)-(2*S*,3*R*)-3-Cinnamyl-2-phenyltetrahydrofuran and (±)-(2*S*,3*S*)-3-Cinnamyl-2-phenyltetrahydrofuran (*cis*-3aj and *trans*-3aj)



Alcohol ***Z*-1e** (53.5 mg, 0.361 mmol), cinnamyl alcohol ***E*-2a** (48.4 mg, 0.361 mmol) and $Ti(O^iPr)_4$ (30.1 mg, 0.106 mmol) were subjected to the general procedure (FCC: gradient elution: 6% → 12% Et_2O - pentane) to yield ***cis*-3aj**: ***trans*-3aj** as 3:1 dr mixture (19.7 mg, 20%), which was partially separable into 2 fractions: first fraction of ***cis*-3aj** (7.4 mg, 8%) as a colorless oil, and second fraction of 1.5:1 of diastereomers ***cis*-3aj** : ***trans*-3aj** as a colorless oil (12.3 mg, 12%).

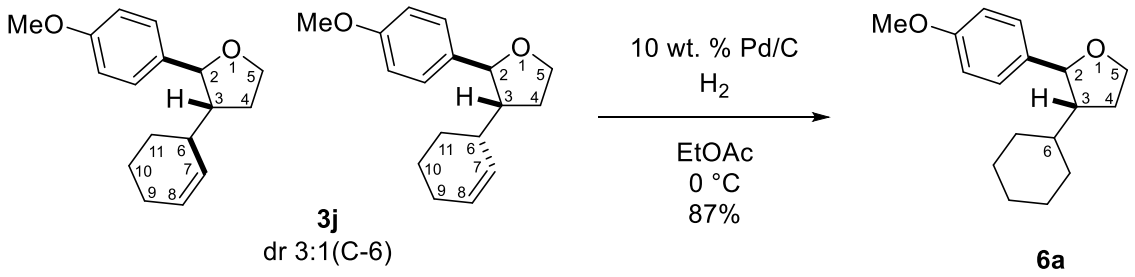
Data for ***cis*-3aj**: **R_f 0.40 (20% Et_2O - pentane). ^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.23-7.38 (8H, m, Ar), 7.17-7.23 (2H, m, Ar), 6.25 (1H, d, *J* = 15.8 Hz, 8-H), 6.01 (1H, ddd, *J* = 15.8, 7.9, 6.3 Hz, 7-H), 5.06 (1H, d, *J* = 6.7 Hz, 2-H), 4.22 (1H, td, *J* = 8.1, 5.1 Hz, 5-H_A), 3.95 (1H, q, *J* = 7.7 Hz, 5-H_B), 2.56 (1H, dqd, *J* = 11.2, 6.6, 4.7 Hz, 3-H), 2.17-2.22 (1H, m, 4-H_A), 1.85-1.97 (2H, m, 4-H_B and 6-H_A), 1.54-1.74 (1H, m, 6-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 140.6 (C Ar), 137.7 (C Ar), 131.2 (C-8), 129.2 (C-7), 128.6 (2 x CH Ar), 128.2 (2 x CH Ar), 127.2 (CH Ar), 127.1 (CH Ar), 126.6 (2 x CH Ar), 126.0 (2 x CH Ar), 83.4 (C-2), 67.6 (C-5), 43.5 (C-3), 33.7 (C-6), 31.1 (C-4). **NOESY- 2D (400 MHz, $CDCl_3$)**: between 2-H and 3-H. **HRMS** (ESI): calculated for $C_{19}H_{21}O$ $[M+H]^+$ requires *m/z* 265.15869, found *m/z* 265.15875. **IR** (film) ν_{max} : 3657, 2980, 2888, 1382, 1152, 954 cm^{-1}.

Data for ***trans*-3aj** matched those previously reported.

9. General proceure for the hydrogenation of an alkene.

Heterocycle **3** (1 eq.), EtOAc (2 mL) and 10 wt. % of Pd/C (10 wt. %) were added to a two-necked r.b.f. The flask was submerged in an ice bath, and then evacuated and backfilled with hydrogen five times. The reaction mixture was stirred vigorously under hydrogen atmosphere (balloon pressure) at 0°C for 2 hours. The reaction mixture was filtered through celite and flushed with EtOAc. The crude product was then concentrated in vacuo, and purified by flash column chromatography to afford the corresponding products.

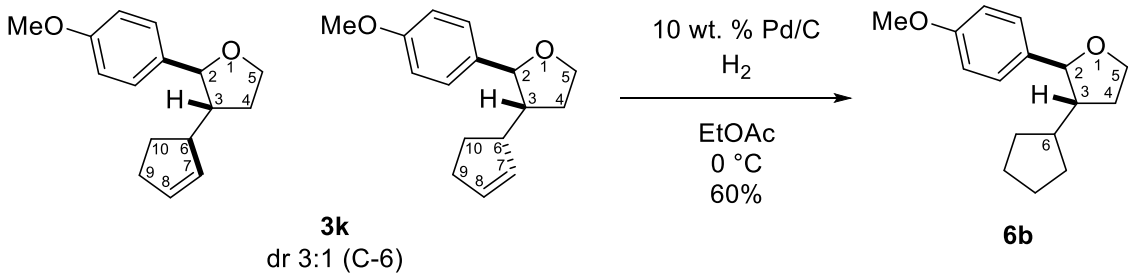
9.1. (±)-(2*S*,3*R*)-3-Cyclohexyl-2-(4-methoxyphenyl)tetrahydrofuran (6a)



Alkene **3j** (31.0 mg, 0.120 mmol), Pd/C (3.1 mg) and EtOAc (2 mL) were subjected to the general procedure (FCC: gradient elution: 7% → 15% Et_2O - pentane) to yield **6a** as a colorless oil (27.2 mg, 87%).

Data for **6a**: **R_f** 0.40 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.26 (2H, d, *J* = 8.6 Hz, Ar), 6.87 (2H, d, *J* = 8.7 Hz, Ar), 4.54 (1H, d, *J* = 7.7 Hz, 2-H), 4.02 (1H, q, *J* = 8.3 Hz, 5-H_A), 3.91 (1H, td, *J* = 8.1, 4.6 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.10 (1H, dddd, *J* = 11.4, 8.0, 6.8, 4.6 Hz, 4-H_A), 1.96-2.05 (1H, m, 3-H), 1.80-1.87 (1H, m, 4-H_B), 1.70-1.80 (2H, m, 2 x CH cyclohexyl), 1.53-1.65 (2H, m, 2 x CH cyclohexyl), 1.29-1.39 (1H, m, 6-H), 1.06-1.28 (4H, m, 2 x CH_2 cyclohexyl), 0.96-1.05 (1H, m, CH cyclohexyl), 0.79-0.91(1H, m, CH cyclohexyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.0 (C Ar), 135.5 (C Ar), 128.2 (2 x CH Ar), 113.8 (2 x CH Ar), 84.1 (C-2), 68.0 (C-5), 55.4 (OMe), 52.9 (C-3), 39.9 (C-6), 32.7 (CH_2 cyclohexyl), 30.5 (CH_2 cyclohexyl), 30.3 (C-4), 26.6 (CH_2 cyclohexyl), 26.53 (CH_2 cyclohexyl), 26.49 (CH_2 cyclohexyl). **HRMS** (ESI): calculated for $C_{17}H_{24}O_2Na$ $[M+Na]^+$ requires *m/z* 283.16685, found *m/z* 283.16675. **IR** (film) ν_{max} : 2980, 1764, 1612, 1514, 1247, 1161 cm^{-1}.

9.2. (±)-(2*S*,3*R*)-3-Cyclopentyl-2-(4-methoxyphenyl)tetrahydrofuran (6b)

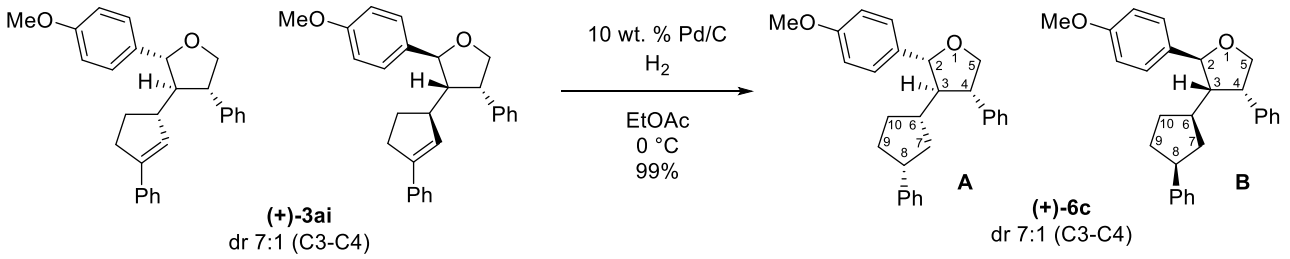


Alkene **3k** (30.0 mg, 0.122 mmol), Pd/C (3.0 mg) and EtOAc (2 mL) were subjected to the general procedure (FCC: gradient elution: 7% → 15% Et_2O - pentane) to yield **6b** as a colorless oil (18.1 mg, 60%).

Data for **6b**: **R_f** 0.40 (40% Et_2O - pentane). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.26 (2H, d, *J* = 8.7 Hz, Ar), 6.86 (2H, d, *J* = 8.7 Hz, Ar), 4.46 (1H, d, *J* = 7.4 Hz, 2-H), 4.06 (1H, q, *J* = 8.3 Hz, 5-H_A), 3.94 (1H, td, *J* = 8.2, 5.1 Hz, 5-H_B), 3.80 (3H, s, OMe), 2.11-2.20 (1H, m, 4-H_A), 2.06 (1H, quint, *J* = 7.7 Hz, 3-H), 1.75-1.84 (3H, m, 4-H_B, 6-H and CH cyclopentyl), 1.42-1.66 (5H, m, CH

cyclopentyl and 2 x CH_2 cyclopentyl), 1.16-1.28 (1H, m, CH cyclopentyl), 0.85-0.96 (1H, m, CH cyclopentyl). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 159.1 (C Ar), 135.2 (C Ar), 128.2 (2 x CH Ar), 113.8 (2 x CH Ar), 85.9 (C-2), 67.9 (C-5), 55.4 (OMe), 52.8 (C-3), 42.7 (C-6), 31.8 (CH_2 cyclopentyl), 31.6 (C-4), 31.0 (CH_2 cyclopentyl), 25.5 (CH_2 cyclopentyl), 25.0 (CH_2 cyclopentyl). **HRMS** (ESI): calculated for $C_{16}H_{22}O_2Na$ $[M+Na]^+$ requires *m/z* 269.15120, found *m/z* 269.15128. **IR** (film) ν_{max} : 2980, 1764, 1514, 1246, 1169, 1032 cm^{-1}.

9.3. (+)-(2*R*,3*R*,4*S*)-2-(4-Methoxyphenyl)-4-phenyl-3-[(1'*S*,3'*R*)-3-phenylcyclopentyl]tetrahydrofuran and (+)-(2*S*,3*S*,4*S*)-2-(4-methoxyphenyl)-4-phenyl-3-[(1'R,3'S)-3-phenylcyclopentyl]tetrahydrofuran [(+)-6c]



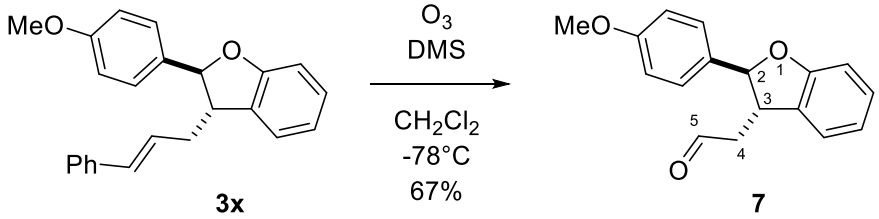
Alkene **(+)-3ai** (36.3 mg, 0.0917 mmol), Pd/C (3.6 mg) and EtOAc (2 mL) were subjected to the general procedure (FCC: gradient elution: 6% → 8% Et_2O - pentane) to yield an inseparable 7:1 mixture of diastereomer **(+)-6c** as a colorless oil (38.9 mg, 99%).

Data for **major diastereomer A of (+)-6c (from the mixture): R_f** 0.50 (25% Et_2O - pentane). $[\alpha]_D^{25}$ = +52.8 (*c* = 4.2, $CHCl_3$). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.40 (2H, d, *J* = 8.7 Hz, Ar), 7.19-7.38 (7H, m, Ar), 7.08-7.17 (3H, m, Ar), 6.92 (2H, d, *J* = 8.7 Hz, Ar), 4.64 (1H, d, *J* = 8.4 Hz, 2-H), 4.23 (1H, dd, *J* = 8.9, 8.0 Hz, 5-H_A), 4.08 (1H, dd, *J* = 8.9, 6.3 Hz, 5-H_B), 3.83 (3H, s, OMe), 3.34 (1H, td, *J* = 7.9, 6.3 Hz, 4-H), 2.96 (1H, dtd, *J* = 11.5, 9.0, 6.3 Hz, 8-H), 2.46 (1H, q, *J* = 8.0 Hz, 3-H), 2.15-2.26 (1H, m, 6-H), 2.10 (1H, dt, *J* = 12.3, 6.2 Hz, 7-H_A), 1.91-2.04 (1H, m, 9-H_A), 1.70 (1H, dddd, *J* = 14.2, 9.3, 8.1, 6.1 Hz, 10-H_A), 1.46-1.55 (1H, m, 9-H_B), 1.24 (1H, q, *J* = 11.9 Hz, 7-H_B), 1.13-1.21 (1H, m, 10-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.44 (C Ar), 146.0 (C Ar), 144.4 (C Ar), 134.2 (C Ar), 128.87 (2 x CH Ar), 128.85 (2 x CH Ar), 128.38 (2 x CH Ar), 127.7 (2 x CH Ar), 127.10 (2 x CH Ar), 126.6 (CH Ar), 126.0 (CH Ar), 114.0 (2 x CH Ar), 87.1 (C-2), 75.9 (C-5), 60.7 (C-3), 55.4 (OMe), 51.8 (C-4), 45.4 (C-8), 43.5 (C-8), 43.5 (C-6), 40.4 (C-7), 33.55 (C-9), 30.2 (C-10). **NOESY-2D (500 MHz, $CDCl_3$)**: between 2-H and 4-H, between 2-H and 6-H**,** between 2-H and 7-H_A, between 6-H and 8-H. **HRMS** (ESI): calculated for $C_{28}H_{30}O_2Na$ $[M+Na]^+$ requires *m/z* 421.21380, found *m/z* 421.21384. **IR** (film) ν_{max} : 2980, 2888, 1513, 1461, 1382, 1249 cm^{-1}.

Partial data for **minor diastereomer B (+)-6c (from the mixture): ^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.40 (2H, d, *J* = 8.7 Hz, Ar), 7.19-7.38 (7H, m, Ar), 7.08-7.17 (3H, m, Ar), 6.92 (2H, d, *J*

= 8.7 Hz, Ar), 4.86 (2H, d, *J* = 9.2 Hz, 2-H), 4.49 (1H, dd, *J* = 8.5, 5.8 Hz, 5-H_A), 4.13 (1H, dd, *J* = 8.6, 2.2 Hz, 5-H_B), 3.83 (3H, s, OMe), 3.53-3.60 (1H, m, 4-H), 2.70-2.80 (1H, m, 8-H), 2.55 (1H, td, *J* = 9.6, 6.9 Hz, 3-H), 2.06-2.16 (1H, m, 7-H_A), 1.91-2.04 (1H, m, 9-H_A), 1.75-1.81 (1H, m, 10-H_A), 1.62-1.66 (1H, m, 6-H), 1.40-1.46 (1H, m, 9-H_B), 1.20-1.29 (1H, m, 7-H_B), 1.11-1.19 (1H, m, 10-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 159.36 (C Ar), 146.5 (C Ar), 142.0 (C Ar), 135.7 (C Ar), 129.0 (2 x CH Ar), 128.5 (2 x CH Ar), 128.42 (2 x CH Ar), 127.8 (2 x CH Ar), 127.06 (2 x CH Ar), 126.7 (CH Ar), 125.89 (CH Ar), 113.9 (2 x CH Ar), 84.8 (C-2), 75.0 (C-5), 58.4 (C-3), 55.4 (OMe), 50.4 (C-4), 44.8 (C-8), 42.0 (C-7), 40.1 (C-6), 33.63 (C-10), 30.7 (C-9). **NOESY-2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H, between 6-H and 8-H**.**

10. (±)-2-[(2*S*,3*S*)-2-(4-Methoxyphenyl)-2,3-dihydrobenzofuran-3-yl]acetaldehyde (7)



Alkene **3x** (10.0 mg, 0.0292 mmol) and CH_2Cl_2 were added to a r.b.f. charged with a stirring bar under -78°C. The solution was bubbled with O_3 for 7-10 min until the blue color was observed, leave it for 2-3 min. Then bubbling O_2 for few min. and switch to N_2 bubbling for 3-4 min. until no blue color was seen. DMS was added under dry-ice bath, leave it for 10min. and let it warmed up to r.t. The crude product was then concentrated in vacuo, and then purified by flash column chromatography to afford **7** as a colorless oil (5.3 mg, 67%).

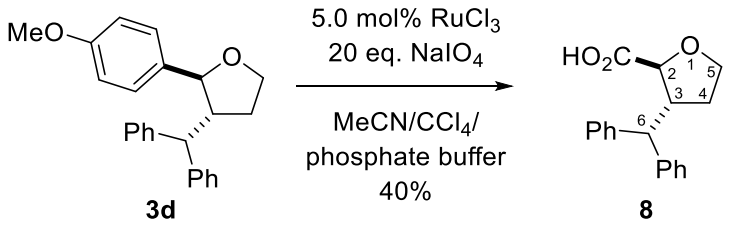
Data for **7**: **R_f** 0.30 (40% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 9.84 (1H, s, 5-H), 7.34 (2H, d, *J* = 8.6 Hz, Ar), 7.20 (1H, t, *J* = 7.7 Hz, Ar), 7.13 (1H, d, *J* = 8.6 Hz, Ar), 6.86-6.92 (4H, m, Ar), 5.25 (1H, d, *J* = 6.7 Hz, 2-H), 3.93 (1H, q, *J* = 6.7 Hz, 3-H), 3.80 (3H, s, OMe), 2.85-2.99 (2H, m, 4-H_2). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 200.4 (C-5), 159.9 (C Ar), 159.4 (C Ar), 132.5 (C Ar), 129.1 (C-H Ar), 129.0 (C Ar), 127.7 (2 x C-H Ar), 124.6 (C-H Ar), 121.2 (C-H Ar), 114.2 (2 x C-H Ar), 109.9 (C-H Ar), 89.6 (C-2), 55.5 (OMe), 49.0 (C-3), 44.9 (C-4). **HRMS** (ESI): calculated for $C_{17}H_{17}O_3$ $[M+H]^+$ requires *m/z* 269.11722, found *m/z* 269.11731. **IR** (film) ν_{max}: 3649, 2980, 2360, 1382, 1251, 1152 cm^{-1}.

11. General procedure for the Ru-catalyzed oxidation of aromatic rings to carboxylic acids

To a cold (0°C) solution of cyclobutane in 10.0 mL/mmol of a 2:2:3 mixture of CCl_4:MeCN:pH 7 buffer (Na_2HPO_4), $NaIO_4$ (20.0 equiv) was added in one portion. The mixture was stirred at that temperature for 15 min and $RuCl_3$ (5 mol%) was added in one portion. The

mixture was warmed up to room temperature. The reaction was monitored by TLC until completion, diluted with Et_2O and H_2O and extracted with Et_2O (3 x 3 mL/mmol). The water layer was acidified until pH 1 using concentrated HCl, and extracted with Et_2O (3 x 3 mL/mmol). The combined organic layers were dried using Na_2SO_4, filtered and the solvent was evaporated under reduced pressure to give the corresponding carboxylic acid, that was purified by chromatography on silica gel using the appropriate mixture of eluents.

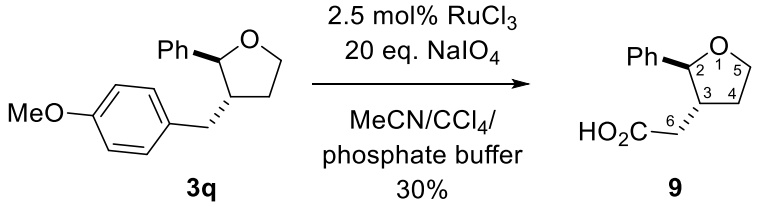
11.1. (±)-(2*S*,3*R*)-3-Benzhydryltetrahydrofuran-2-carboxylic acid (8)



Tetrahydrofurane **3d** (49.0 mg, 0.142 mmol), $RuCl_3$ (1.5 mg, 0.0071 mmol), $NaIO_4$ (0.588 g, 2.84 mmol) and CCl_4:MeCN: Na_2HPO_4 buffer (3 mL) were subjected to the general procedure (FCC: 5% DCM - MeOH) to yield **8** (16.0 mg, 40%) as a colorless oil.

Data for **8**: **R_f** 0.20 (10% DCM - MeOH). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.38 (2H, d, *J* = 7.6 Hz, Ar), 7.24-7.33 (6H, m, Ar), 7.16-7.21 (2H, m, Ar), 4.28 (1H, d, *J* = 2.4 Hz, 2-H), 4.03-4.14 (2H, m, 5-H_2), 3.87 (1H, d, *J* = 11.9 Hz, 6-H), 3.51 (1H, ddt, *J* = 12.0, 7.7, 2.5 Hz, 3-H), 1.96-2.06 (1H, m, 4-H_A), 1.69-1.76 (1H, m, 4-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 175.5 (C=O), 143.2 (C Ar), 142.9 (C Ar), 129.0 (2 x C-H Ar), 128.9 (2 x C-H Ar), 128.4 (2 x C-H Ar), 128.2 (2 x C-H Ar), 127.0 (C-H Ar), 126.9 (C-H Ar), 80.6 (C-2), 68.8 (C-5), 54.4 (C-6), 47.5 (C-3), 29.5 (C-4). **NOESY-2D (500 MHz, $CDCl_3$)**: between 2-H and 6-H. **HRMS** (ESl): calculated for $C_{18}H_{18}O_3Na$ $[M+Na]^+$ requires *m/z* 305.11482, found *m/z* 305.11484. **IR** (film) ν_{max}: 3658, 2980, 2888, 1461, 1461, 1252 cm^{-1}.

11.2. (±)-2-[(2*S*,3*R*)-2-Phenyltetrahydrofuran-3-yl]acetic acid (9)



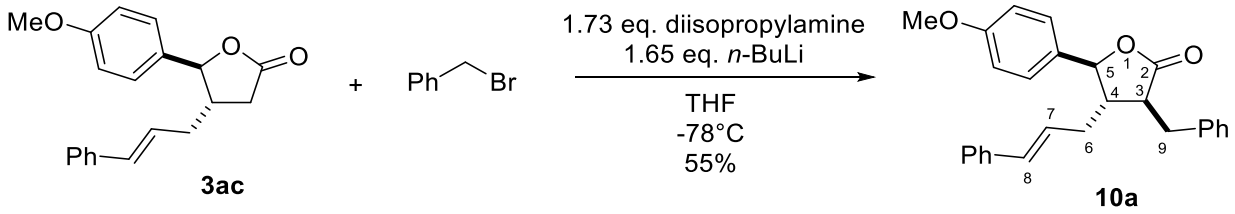
Tetrahydrofurane **3q** (80.0 mg, 0.299 mmol), $RuCl_3$ (1.6 mg, 0.0075 mmol), $NaIO_4$ (1.270 g, 5.937 mmol) and CCl_4:MeCN: Na_2HPO_4 buffer (3 mL) were subjected to the general procedure except using 2.5mol% of $RuCl_3$ (FCC: 5% DCM - MeOH) to yield **9** (18.8 mg, 30%) as a colorless oil.

Data for **9**: **R_f** 0.20 (5% DCM - MeOH). **^{1}H NMR (400 MHz, $CDCl_3$) δ** 7.31-7.35 (4H, m, Ar), 7.25-7.30 (1H, m, Ar), 4.45 (1H, d, *J* = 7.3 Hz, 2-H), 4.16 (1H, dt, *J* = 8.4, 7.3 Hz, 5-H_A), 4.04 (1H ,td, *J* = 8.4, 5.1 Hz, 5-H_B), 2.56 (1H, dd, *J* = 15.0, 4.5 Hz, 6-H_A), 2.42-2.51 (1H, m, 3-H), 2.31-2.41 (2H, m, 4-H_A and 6-H_B), 1.79 (1H, dq, *J* = 12.3, 7.8 Hz, 4-H_B). **^{13}C NMR (100 MHz, $CDCl_3$) δ** 177.7 (C=O), 141.3 (C Ar), 128.6 (2 x C-H Ar), 128.0 (C-H Ar), 126.4 (2 x C-H Ar), 85.7 (C-2), 68.0 (C-5), 44.2 (C-3), 36.2 (C-6), 32.3 (C-4). **HRMS** (ESI): calculated for $C_{12}H_{13}O_3$ $[M-H]^+$ requires *m/z* 205.08702, found *m/z* 205.08693. **IR** (film) ν_{max}: 3658, 2980, 2888, 1461, 1461, 1252 cm^{-1}.

12. General procedure for the acylation and alkylation of a lactone.

To a solution of diisopropylamine (1.15 eq.) in dry THF (1.92 mL/mmol) at −78 °C was added *n*-butyllithium (2.5 M in hexanes, 1.10 eq.) dropwise. The solution was stirred at 0 °C for 30 min and then cooled to −78 °C at which time lactone (1eq.) in THF (0.22 mL/mmol) was added over 10 min. The mixture was stirred at −78 °C for 0.5 hours and electrophile (1.0-1.5 eq.) was added quickly. The mixture was allowed to warm to room temperature, stirred for 3 hours, and quenched with saturated aqueous NH_4Cl. The mixture was extracted with Et_2O (50 mL × 3), and the organic phase was washed with brine, dried over Na_2SO_4 and concentrated. The residue was purified by column chromatography on silica gel to give the corresponding product.

12.1. (±)-(3*S*,4*S*,5*S*)-3-Benzyl-4-cinnamyl-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one (10a)

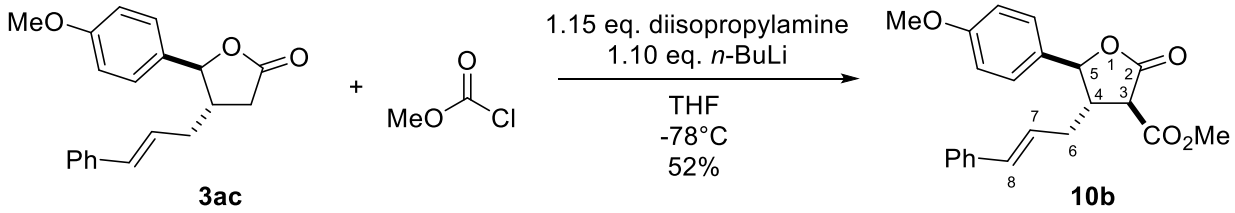


Lactone **3ac** (50.0 mg, 0.162 mmol), benzyl bromide (41.5 mg, 0.243 mmol), diisopropylamine (28.3 mg, 0.280 mmol) and *n*-BuLi (2.5M, 0.11 mL) were subjected to the general procedure (FCC: gradient elution: 15% → 25% Et_2O - pentane) to yield **10a** as a colorless oil (35.4 mg, 55%).

Data for **10a**: **R_f** 0.50 (60% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.16-7.34 (10H, m, Ar), 7.03 (2H, d, *J* = 8.7 Hz, Ar), 6.81 (2H, d, *J* = 8.7 Hz, Ar), 6.21 (1H, d, *J* = 15.7 Hz, 8-H), 5.84 (1H, dt, *J* = 15.4, 7.4 Hz, 7-H), 4.95 (1H, d, *J* = 9.0 Hz, 5-H), 3.77 (3H, s, OMe), 3.17 (1H, dd, *J* = 14.0, 5.2 Hz, 9-H_A), 3.07 (1H, dd, *J* = 14.0, 6.6 Hz, 9-H_B), 2.86 (1H, ddd, *J* = 10.5, 6.5, 5.2 Hz, 3-H), 2.34 (1H, ddt, *J* = 10.6, 8.8, 5.9 Hz, 4-H), 2.20-2.27 (2H, m, 6-H_2). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 177.7 (C=O), 160.1 (C Ar), 138.0 (C Ar), 136.7 (C Ar), 133.5 (C-8), 130.2 (C Ar), 129.7 (2 x C-H Ar), 128.9 (2 x C-H Ar), 128.7 (2 x C-H Ar), 128.3 (2 x C-H Ar), 127.7 (C-H Ar), 127.0 (C-H Ar), 126.2 (2 x C-H Ar), 125.3 (C-7), 114.2 (2 x C-H Ar), 83.9 (C-5), 55.5 (OMe), 48.3 (C-4),

47.0 (C-3), 35.3 (C-9), 33.9 (C-6). **NOESY-2D (500 MHz, $CDCl_3$)**: between 5-H and 6-H_2, between 5-H and 7-H, between 5-H and 8-H, between 5-H and 3-H, between 3-H and 6-H_2. **HRMS** (ESl): calculated for $C_{27}H_{26}O_3Na$ $[M+Na]^+$ requires *m/z* 421.17742, found *m/z* 421.17722. **IR** (film) ν_{max}: 2980, 1764, 1514, 1248, 1160, 1030 cm^{-1}.

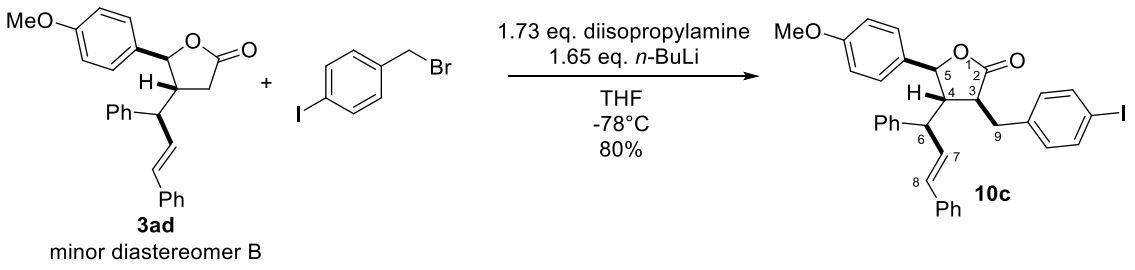
12.2. (±)-Methyl-(3*R*,4*S*,5*S*)-4-cinnamyl-5-(4-methoxyphenyl)-2-oxotetrahydrofuran-3-carboxylate (10b)



Lactone **3ac** (40.0 mg, 0.130 mmol), methyl chloroformate (18.3 mg, 0.195 mmol), diisopropylamine (15.2 mg, 0.149 mmol) and *n*-BuLi (2.5M, 0.057 mL) were subjected to the general procedure (FCC: gradient elution: 25% → 35% Et_2O - pentane) to yield **10b** as a colorless oil (24.7 mg, 52%).

Data for **10b**: **R_f** 0.50 (70% Et_2O - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.34 (2H, d, *J* = 8.7 Hz, Ar), 7.19-7.30 (5H, m, Ar), 6.94 (2H, d, *J* = 8.7 Hz, Ar), 6.43 (1H, d, *J* = 15.6 Hz, 8-H), 5.95 (1H, ddd, *J* = 15.8, 8.4, 6.5 Hz, 7-H), 5.03 (1H, d, *J* = 9.8 Hz, 5-H), 3.83 (3H, s, OMe), 3.66 (3H, s, OMe), 3.54 (1H, d, *J* = 11.7 Hz, 3-H), 3.14 (1H, dddd, *J* = 11.7, 9.8, 8.5, 5.0 Hz, 4-H), 2.47-2.56 (1H, m, 6-H_A), 2.29-2.38 (1H, m, 6-H_B). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 170.8 (C=O), 168.2 (C=O), 160.5 (C Ar), 136.7 (C Ar), 133.6 (C-8), 128.73 (2 x C-H Ar), 128.69 (2 x C-H Ar), 128.6 (C Ar), 127.8 (C-H Ar), 126.3 (2 x C-H Ar), 125.0 (C-7), 114.4 (2 x C-H Ar), 85.0 (C-5), 55.5 (OMe), 53.3 (C-3), 53.1 (OMe), 48.9 (C-4), 33.8 (C-6). **NOESY-2D (500 MHz, $CDCl_3$)**: between 5-H and 6-H_A, between 5-H and 6-H_B, between 5-H and 7-H, between 5-H and 3-H, between 3-H and 6-H_A, between 3-H and 6-H_B. **HRMS** (ESl): calculated for $C_{22}H_{22}O_5Na$ $[M+Na]^+$ requires *m/z* 389.13594, found *m/z* 389.13577. **IR** (film) ν_{max}: 2980, 1777, 1736, 1515, 1250, 1147 cm^{-1}.

12.3. (±)-(3*S*,4*S*,5*S*)-4-[(2'*E*)-1,3-Diphenylallyl]-3-(4-iodobenzyl)-5-(4-methoxyphenyl)dihydrofuran-2(3*H*)-one (10c)



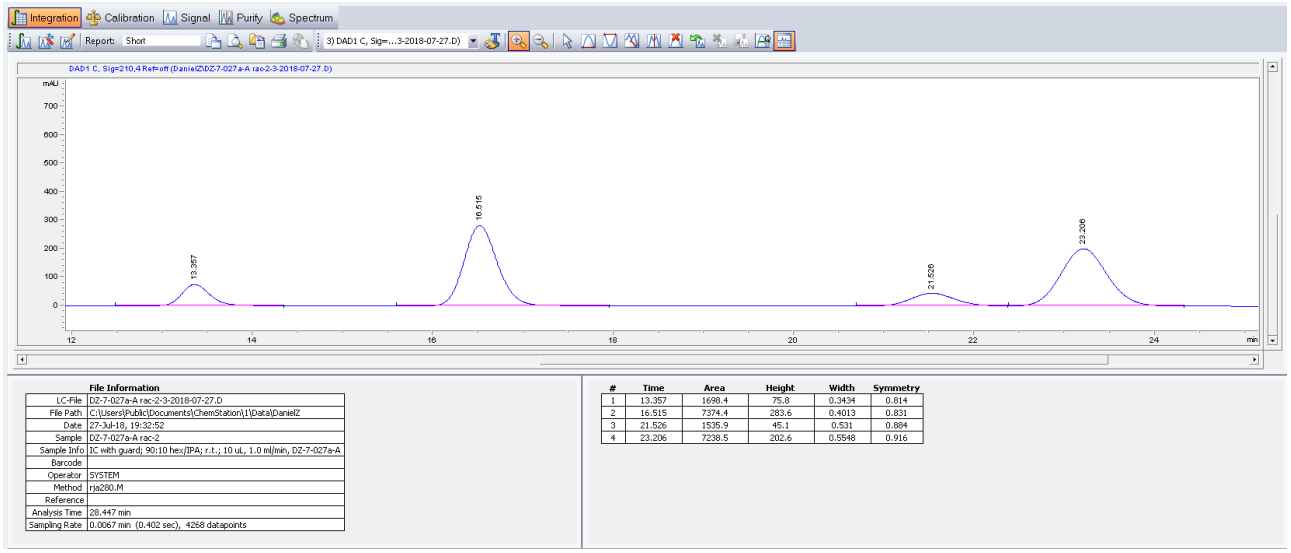
Lactone **3ad-minor diastereomer B** (100.0 mg, 0.2603 mmol), benzyl bromide (77.3 mg, 0.260 mmol), diisopropylamine (45.5 mg, 0.450 mmol) and *n*-BuLi (2.5M, 0.17 mL) were subjected to the general procedure except using 1.73 eq. of diisopropylamine, 1.63 eq. of *n*-BuLi (FCC: gradient elution: 15% → 25% Et_2O - pentane) to yield **10c** as a white solid (124.8 mg, 80%).

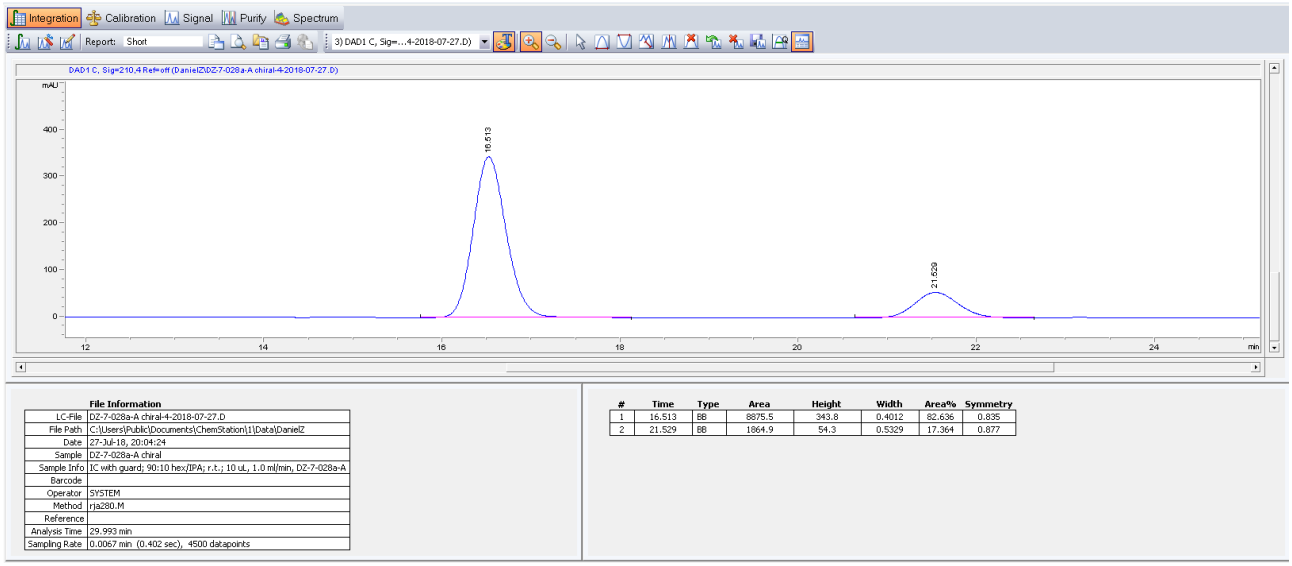
Data for **10c**: **R_f** 0.40 (50% Et_2O - pentane). **M.p.**: 78°C (10% EtOAc - pentane). **^{1}H NMR (500 MHz, $CDCl_3$) δ** 7.52 (2H, d, *J* = 8.2 Hz, Ar), 7.16-7.36 (8H, m, Ar), 7.06-7.10 (2H, m, Ar), 6.72 (2H, d, *J* = 8.2 Hz, Ar), 6.70 (2H, d, *J* = 8.7 Hz, Ar), 6.50 (2H, d, *J* = 8.6 Hz, Ar), 6.43 (1H, d, *J* = 15.6 Hz, 8-H), 5.84 (1H, dd, *J* = 15.6, 9.7 Hz, 7-H), 5.08 (1H, d, *J* = 4.9 Hz, 5-H), 3.78 (3H, s, OMe), 3.43 (1H, t, *J* = 9.7 Hz, 6-H), 2.98 (1H, dt, *J* = 7.8, 5.3 Hz, 3-H), 2.90 (1H, dd, *J* = 13.6, 5.0 Hz, 9-H_A), 2.81 (1H, dd, *J* = 13.6, 7.9 Hz, 9-H_B), 2.59-2.66 (1H, m, 4-H). **^{13}C NMR (125 MHz, $CDCl_3$) δ** 178.2 (C=O), 159.4 (C Ar), 141.1 (C Ar), 138.0 (2 x C-H Ar), 137.4 (C Ar), 136.4 (C Ar), 132.7 (C-8), 132.1 (C Ar), 131.9 (2 x C-H Ar), 129.3 (C-7), 129.2 (2 x C-H Ar), 128.8 (2 x C-H Ar), 128.2 (2 x C-H Ar), 128.0 (C-H Ar), 127.5 (C-H Ar), 126.7 (2 x C-H Ar), 126.5 (2 x C-H Ar), 114.0 (2 x C-H Ar), 92.4 (C Ar), 82.8 (C-5), 55.4 (OMe), 53.8 (C-6), 51.3 (C-4), 46.6 (C-3), 36.3 (C-9). **NOESY-2D (500 MHz, $CDCl_3$)**: between 5-H and 3-H, between 5-H and 6-H, between 5-H and 7-H, between 3-H and 6-H. **HRMS** (ESl): calculated for $C_{33}H_{29}IO_3Na$ $[M+Na]^+$ requires *m/z* 623.10536, found *m/z* 623.10535. **IR** (film) ν_{max}: 2980, 2360, 1764, 1461, 1382, 1251 cm^{-1}.

13. HPLC chromatograms.

Chiral high performance liquid chromatography (HPLC) was performed on Agilent 1200 series instruments using 4.6 mm * 250 mmL Chiralpak IC columns.

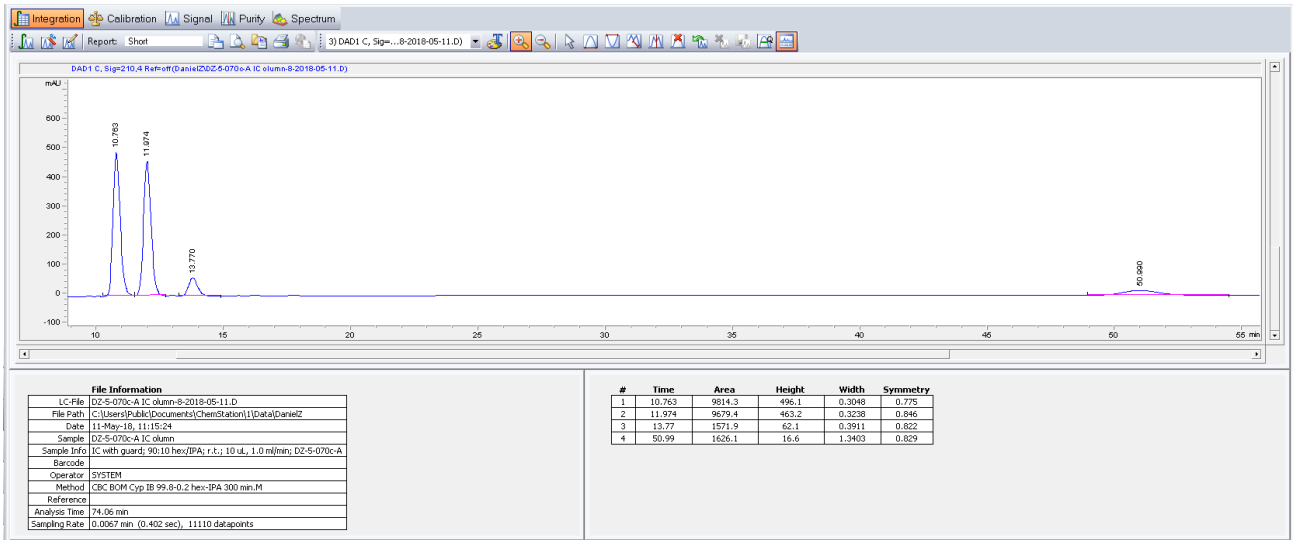
i) HPLC traces of **(±)-3af** and (+)-**3af**

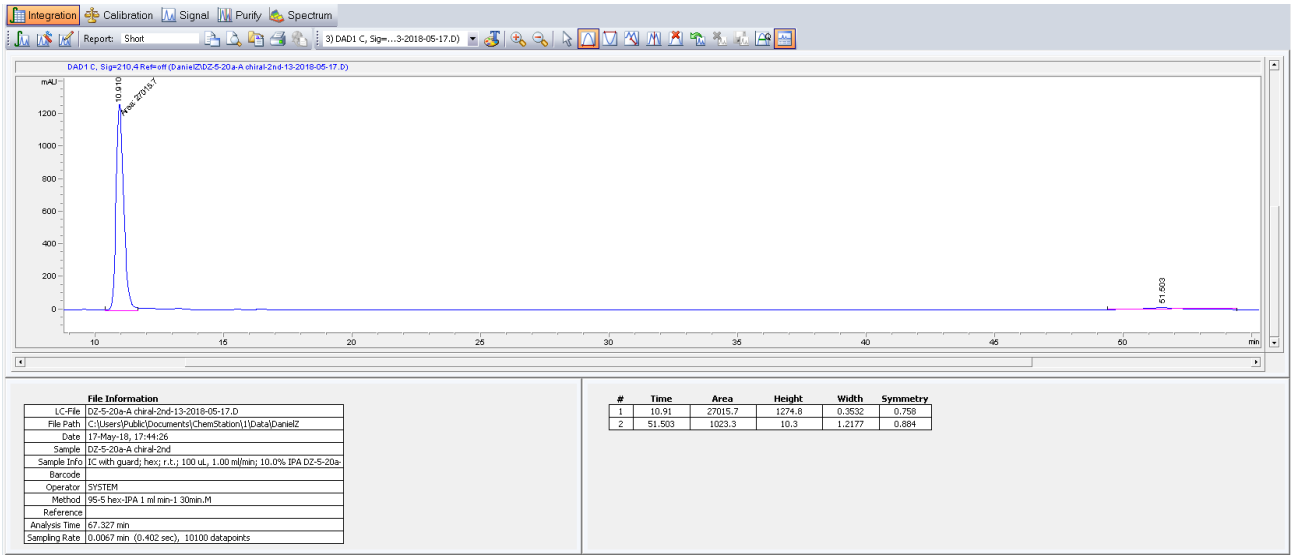




Compound **(+)-3af** was determined to be > 99% ee by chiral HPLC (Chiralpak IC); 90:10 Hexane–*i*-PrOH at 1.0 mL/min; 210 nm.

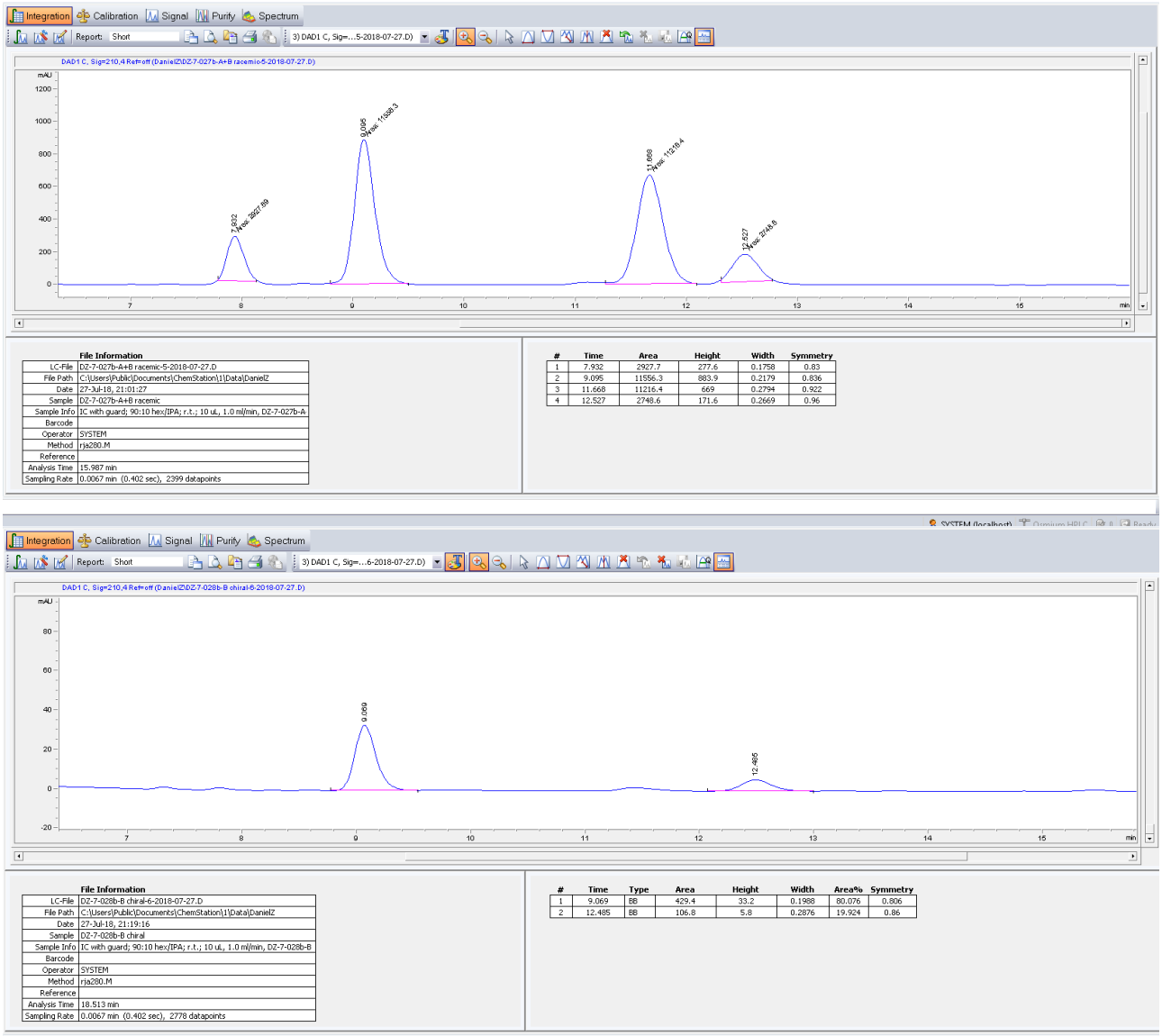
ii) HPLC traces of **(±)-3ag** and **(+)-3ag**





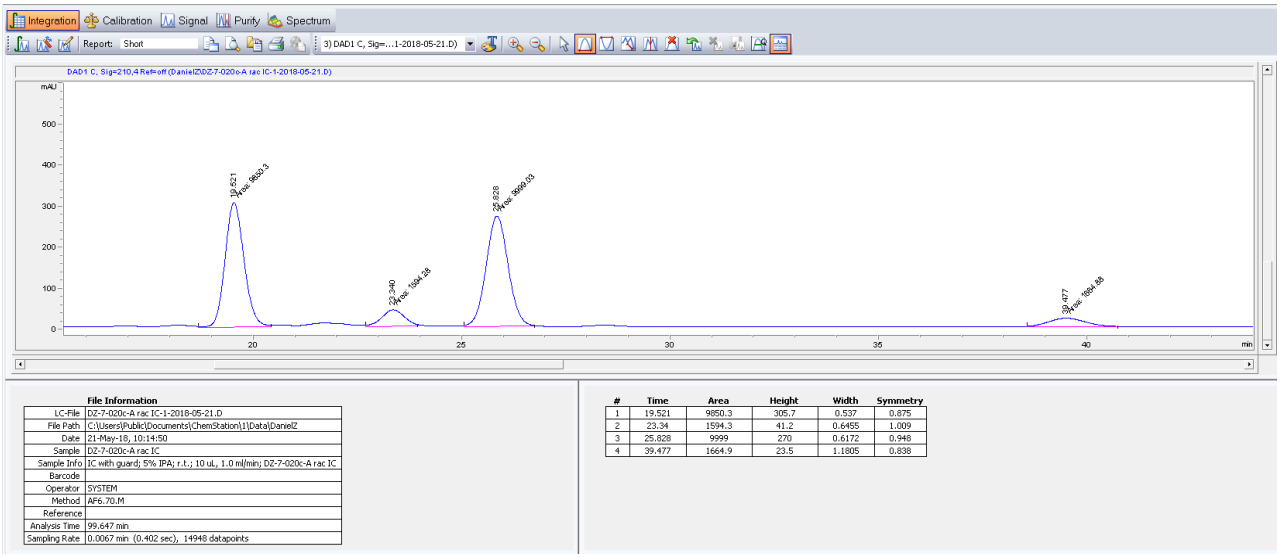
Compound **(+)-3ag** was determined to be > 99% ee by chiral HPLC (Chiralpak IC); 90:10 Hexane–*i*-PrOH at 1.0 mL/min; 210 nm.

iii) HPLC traces of **(±)-3ah** and **(+)-3ah**



Compound **(+)-3ah** was determined to be > 99% ee by chiral HPLC (Chiralpak IC); 90:10 Hexane–*i*-PrOH at 1.0 mL/min; 210 nm.

iv) HPLC traces of **(±)-3ai** and **(+)-3ai**



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Sample Info	IC with guard; 5% IPA; r.t.; 10 uL, 1.0 ml/min; DZ-7-020c-A rac IC
Barcode	
Operator	SYSTEM
Method	AF6.70.M
Reference	
Analysis Time	99.647 min
Sampling Rate	0.0067 min (0.402 sec), 14948 datapoints

#	Time	Area	Height	Width	Symmetry
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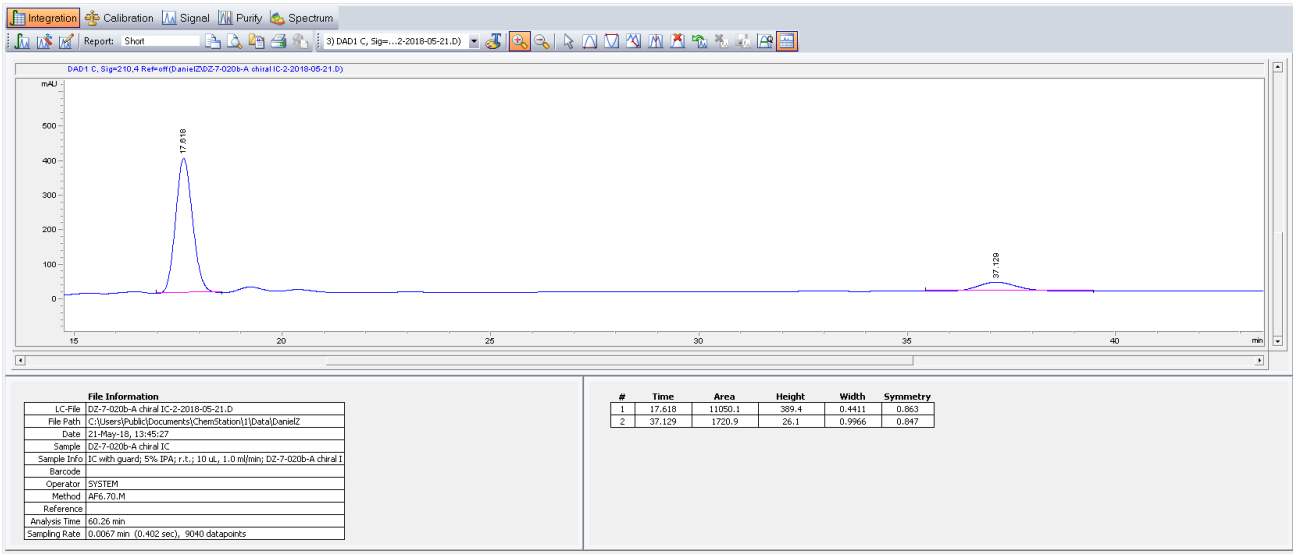
2	23.34	1594.3	41.2	0.6455	1.009
3	25.828	9999	270	0.6172	0.948
4	39.477	1664.9	23.5	1.1805	0.838



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Barcode	
Operator	SYSTEM
Method	AF6.70.M
Reference	
Analysis Time	60.26 min
Sampling Rate	0.0067 min (0.402 sec), 9040 datapoints

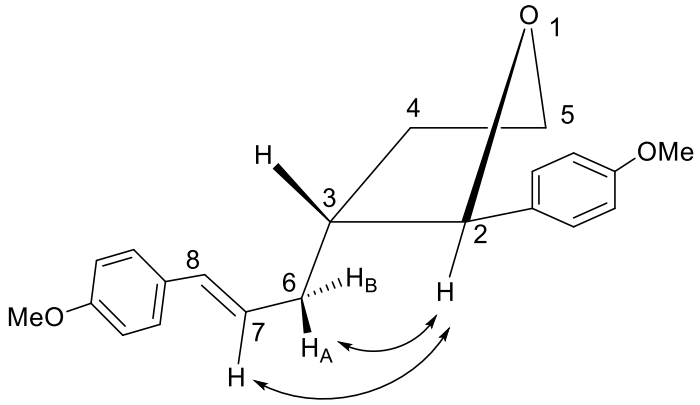
#	Time	Area	Height	Width	Symmetry
1	17.618	11050.1	389.4	0.4411	0.863
2	37.129	1720.9	26.1	0.9966	0.847

Compound **(+)-3ai** was determined to be > 99% ee by chiral HPLC (Chiralpak IC); 90:10 Hexane–*i*-PrOH at 1.0 mL/min; 210 nm.

14. NMR study of compounds 3b, 3aa and (+)-6c

The ^{1}H NMR spectrum of **3b** presents 2-H as a doublet (J = 7.2 Hz) that has COSY crosspeaks with 3-H, while 6-H_A is a multiplet that has COSY cross-peaks with 3-H, 6-H_B and 7-H. Unfortunately 6-H_B is overlapped with 3-H and 4-H_A appears as a multiplet.

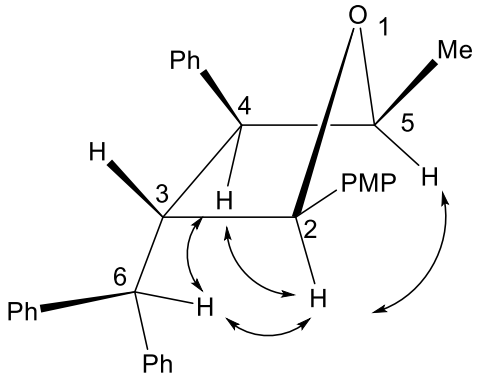
Additional support for the structure was found upon inspection of the NOESY 2D spectra of **3b**, that showed interactions between 2-H and 6-H_A and between 2-H and 7-H, among others, confirming the *trans* relative stereochemistry.



3b

The ^{1}H NMR spectrum of **3aa** presents 2-H as a doublet (J = 7.5 Hz) that has COSY crosspeaks with 3-H, while 4-H is a doublet of doublet (J = 6.4, 3.4 Hz) that has COSY cross-peaks with 3-H and 5-H. Moreover, 5-H is a quintet (J = 6.3 Hz) that has COSY cross-peaks with 4-H and Me. Finally, 6-H is a doublet (J = 11.4 Hz) that has COSY cross-peaks with 3-H.

Additional support for the structure was found upon inspection of the NOESY 2D spectra of **3aa**, that showed interactions between 2-H and 4-H, between 2-H and 5-H, between 2-H and 6-H, between 4-H and 6-H, among others, confirming the *trans-trans-cis* relative stereochemistry.

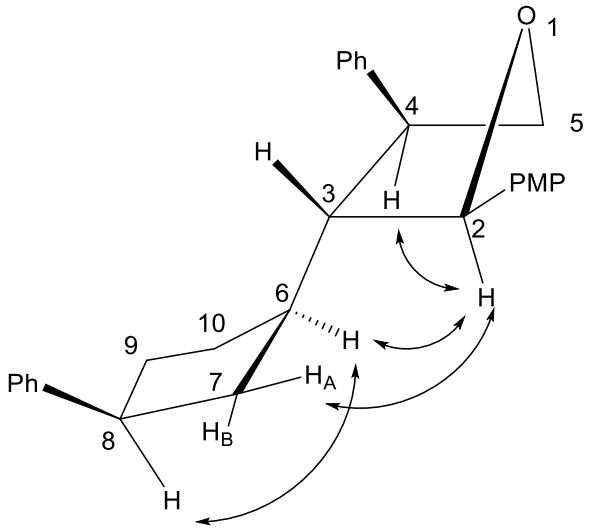


3aa

The ^{1}H NMR spectrum of **(+)-6c** presents 2-H as a doublet (J = 8.7 Hz) that has COSY crosspeaks with 3-H, while 4-H is a triplet of doublet (J = 7.9, 6.3 Hz) that has COSY crosspeaks

with 3-H and 5-H_2. Moreover, 6-H is a multiplet that has COSY crosspeaks with 3-H, 7-H_A, 7-H_B and 10-H_2. Finally, 8-H is a doublet of triplet of doublet (J = 11.5, 9.0, 6.3 Hz) that has COSY crosspeaks with 7-H_A, 7-H_B and 9-H_2.

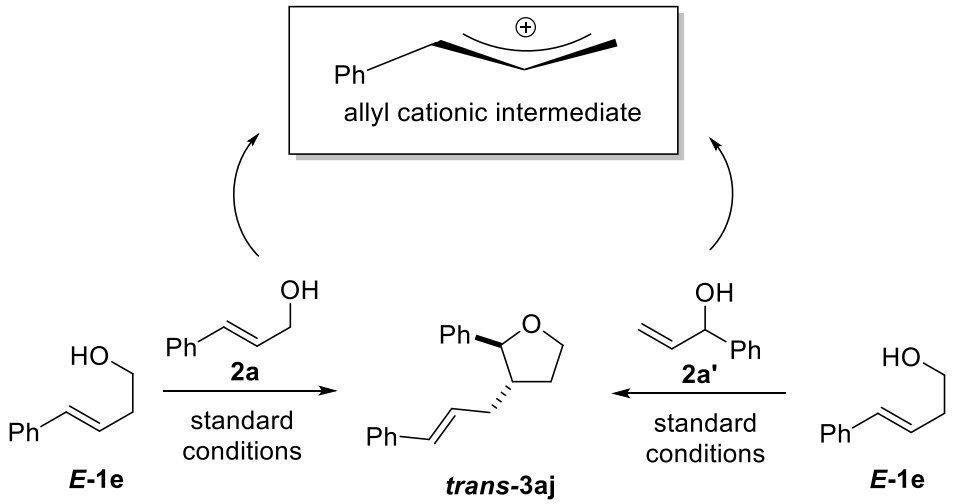
Additional support for the structure was found upon inspection of the NOESY 2D spectra of **(+)-6c**, that showed interactions between 2-H and 4-H, between 2-H and 6-H**,** between 2-H and 7-H_A, between 6-H and 8-H, among others, confirming the relative stereochemistry below.



(+)-6c

15. Mechanistic study

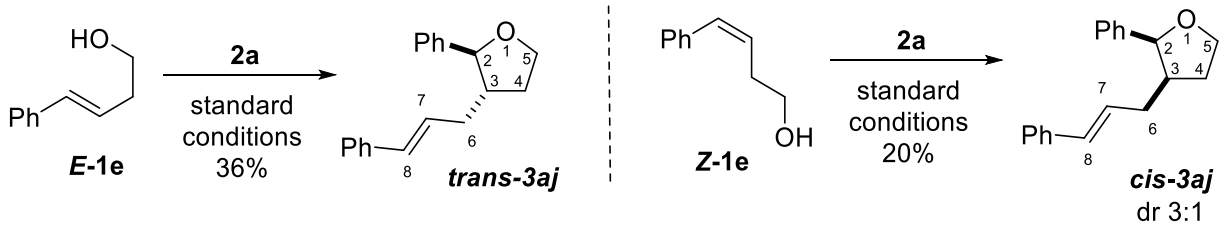
a) Evidence for an allyl cation intermediate



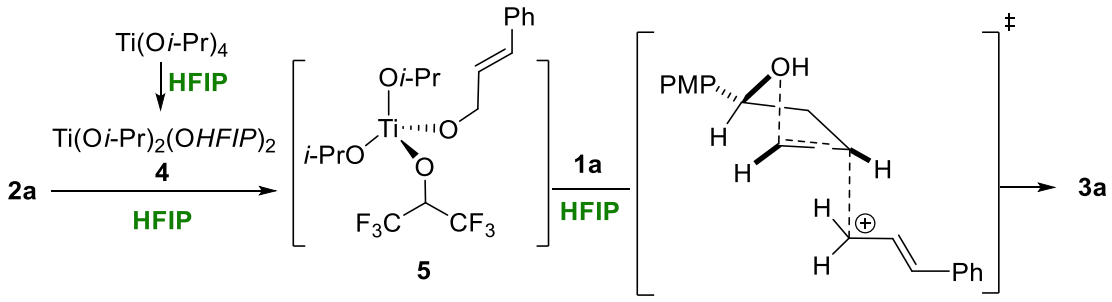
For those examples that involve allyl alcohols as alkylating agents, using two different regioisomeric allyl alcohols, **2a** and **2a´**, the same product ***trans*-3a** was obtained in similar yields, under identical conditions. These results support the formation of a common allyl cationic intermediate.

b) Evidence for concerted mechanism

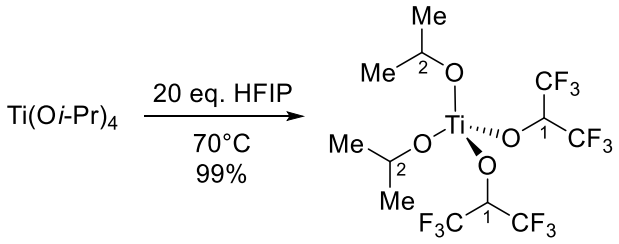
The possible influence of double bond geometry in homoallyl alcohol **1** was investigated. While the *E* isomer gives the *trans* diastereoisomer as a sole product, the *Z* isomer leads to a major *cis* product (stereochemistry was determined by NOESY-2D). These results point towards an asynchronous concerted mechanism.



c) Proposed mechanism



i) Isolation of stable titanium complex Ti(O*i*-Pr)$_2$(OHFIP)$_2$

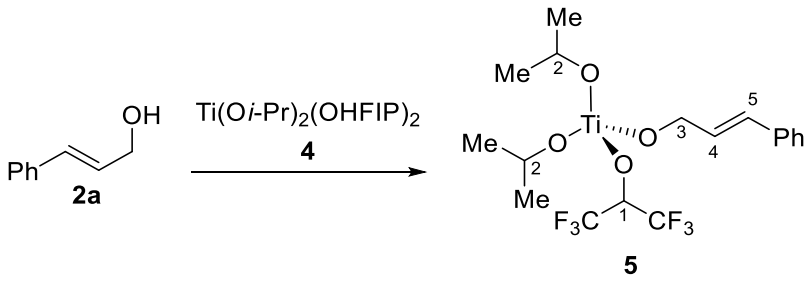


4

To a microwave vial charged with a stirring bar was added Ti(O*i*-Pr)$_4$ (100.0 mg, 0.3521 mmol) and HFIP (0.74 mL, 7.0 mmol), the solution was stirred under Ar at 70°C for 2 hours. Then the solvent was removed under reduced pressure to obtain a white foam.

Data for **4** Ti(O*i*-Pr)$_2$(OHFIP)$_2$: **^{1}H NMR (500 MHz, CDCl$_3$) δ** 4.82 (2H, m, 2 x 1-H), 4.64 (2H, m, 2 x 2-H), 1.29 (12H, d, *J* = 6.1 Hz, 4 x Me). **^{13}C NMR (125 MHz, CDCl$_3$) δ** 121.8 (q, *J* = 284.4 Hz, 4 x CF$_3$), 82.0 (2 x C-2), 78.9 (2 x C-1), 25.7 (4 x Me). **^{19}F NMR (471 MHz, CDCl$_3$) δ** -76.15 (12F, s, 4 x CF$_3$). **^{19}F (471 MHz, CDCl$_3$) - ^{1}H(500 MHz, CDCl$_3$) HOESY**: between CF$_3$ and Me (irradiate **^{19}F** @ -76.15 ppm). **HRMS** (EI): m/z (ESI+) 147.0 [100], 295.0 [81], 499.0 [1.2], 500.0 [0.3], 501.0 [0.8], $C_{12}H_{16}F_{12}O_4Ti$ $[M]^+$ predicted *m/z* 500.0331, found *m/z* 500.0311, Delta = + 3.9 ppm.

ii) **Evidence of intermediate complex 5**

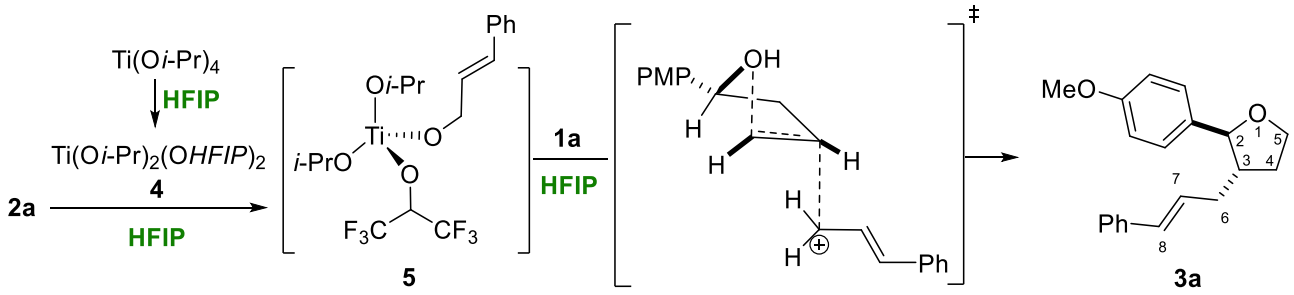


5

To a microwave vial charged with a stirring bar was added cinnamyl alcohol ***E*-2a** (23.5 mg, 0.175 mmol), Ti(O*i*-Pr)$_2$(OHFIP)$_2$ **4** (74.6 mg, 0.353 mmol) and CDCl$_3$ (2.0 mL). The solution was stirred under Ar for 10 min. and then the solution was transferred to an NMR tube for NMR experiments (the present of broad peaks in proton NMR made integration difficult).

Data for **5'**: **^{1}H NMR (500 MHz, CDCl$_3$) δ** 7.21-7.40 (5H, m, Ar), 6.60 (1H, d, *J* = 15.9 Hz, 5-H), 6.37 (1H, dt, *J* = 14.9, 5.8 Hz, 4-H), 4.38-4.66 (3H, m, 1-H and 3-H$_2$), 3.95-4.24 (2H, m, 2 x 2-H), 1.22 (12H, d, *J* = 6.2 Hz, 4 x Me). **^{19}F NMR (471 MHz, CDCl$_3$) δ** -75.65 (6F, s, 2 x CF$_3$). **NOESY- 2D (500 MHz, CDCl$_3$)**: between 3-H$_2$ and Me, between 2-H and Me.

iii) **Evidence of formation of product 3a from complex 5**



To a microwave vial charged with a stirring bar was added cinnamyl alcohol ***E*-2a** (23.5 mg, 0.175 mmol), Ti(O*i*-Pr)$_2$(OHFIP)$_2$ **4** (74.6 mg, 0.353 mmol) and $CDCl_3$ (2.0 mL). The solution was stirred under Ar for 10 min. and then alcohol **1a** (31.1 mg, 0.175 mmol) and HFIP (1.75 mL) were added. The reaction was heated overnigh at 70°C. Solvent was then removed by evaporator. Purification using silica gel flash chromatography (gradient elution: 12% → 20% Et_2O - pentane) afforded **3a** as a colorless oil (20.6 mg, 40%).

Data for **3a** matched those previously reported.

16. References

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