Supporting Information
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Supporting Information

A straightforward approach towards functionalized amino acids and pipecolinic acids via Ru-catalyzed allylic alkylation

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1) General remarks S2
2) Experimental data S2
3) Copies of nmr spectra S16
4) References S39
1) General remarks

All air- or moisture-sensitive reactions were carried out in dried glassware (>100 °C) under an atmosphere of nitrogen or argon. Dried solvents were distilled before use: THF was distilled from Na/benzophenone. The products were purified by flash chromatography on silica gel columns (Macherey-Nagel 60, 0.063-0.2 mm). Mixtures of ethyl acetate and petroleum ether were generally used as eluents. Analytical TLC was performed on precoated silica gel plates (Sigma-Aldrich). Visualization was accomplished with UV-light or KMnO4 solution. 1H and 13C NMR spectra were recorded with a Bruker AC-400 [400 MHz (1H) and 100 MHz (13C)] spectrometer in CDCl3. Chemical shifts are reported in ppm relative to TMS, and CHCl3 was used as the internal standard. Optical rotations were measured on a PerkinElmer Model 341 in a tempered (20 ± 0.1 °C) 1 dm cuvette. The light source was a Na-vapor lamp (λ = 589 nm). HRMS were recorded with a MAT 95Q from Finnigan. GC spectra were recorded either with a Shimadzu (GC-2010, autoinjector AOC-20i, FID-detector) or with a Varian (CP3380, auto-injection, FID-detector).

2) Experimental data

Monosubstituted cis-butene diol derivatives 1’a-f were prepared following previously reported procedures.[1][2][3][4][5]

(Z)-Diethyl-(4-hydroxybut-2-en-1-yl) phosphate (1’g)

To a solution of 0.21 mL (225 mg, 2.45 mmol) cis-butene diol (96%) in 2.5 mL abs. dichloromethane were added 0.40 mL (391 mg, 4.94 mmol) pyridine and 30.7 mg (0.249 mmol) 4-dimethylaminopyridine (99%) and the reaction mixture was cooled to 0°C. To this solution, 0.37 mL (444 mg, 2.50 mmol) diethyl chlorophosphate (97%) were added dropwise and the reaction was allowed to warm to room temperature overnight. For workup, water was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane and the combined organic layers were dried over Na2SO4. After purification by column chromatography (silica gel, PE:EA 50:50, 40:60) 440 mg (1.96 mmol, 80%) product 1’g were obtained.

Colourless liquid. 1H-NMR (400 MHz, CDCl3): δ = 1.33 (td, 3J6,5 = 7.1 Hz, 4J6,p = 0.8 Hz, 6 H, 6-H), 3.09 (bs, 1 H, OH), 4.09 (dq, 3J5,p = 7.2 Hz, 3J5,6 = 7.1 Hz, 4 H, 5-H), 4.20 (dd, 3J1,2 = 6.8 Hz, 4J1,3 = 0.8 Hz, 2 H, 1-H), 4.66 (m, 2 H, 4-H), 5.72 (m, 1 H, 3-H), 5.91 (m, 1 H, 2-H).

13C-NMR (100 MHz, CDCl3): δ = 16.1 (dq, 3J6,p = 7.3 Hz, C-6), 57.9 (t, C-1), 62.6 (dt, 2J4,p = 5.1 Hz, C-4), 63.8 (dt, 2J5,p = 5.8 Hz, C-5), 73.1 (m, 3J2,p = 4.3 Hz, C-3), 134.3 (d, C-2). HRMS (Cl) calcd for C8H18O5P [M+H]+: 255.0886, found: 255.0852.
(Z)-4-[(trimethylsilyl)oxy]but-2-en-1-yl benzoate (1a)

To a solution of 981 mg (5.10 mmol) 1’a and 2.16 mL (1.57 g, 15.4 mmol) triethylamine (99%) in 10 mL THF were added 1.00 mL (856 mg, 7.88 mmol) TMSCl at rt. The reaction was stirred overnight and filtrated through a pad of Celite®. The crude product was purified by column chromatography (silica gel, PE:EA 90:10) to give 1.15 g (4.35 mmol, 85%) product 1a.

Colourless oil. 1H-NMR (400 MHz, CDCl₃): δ = 0.15 (s, 9 H, 1-H), 4.32 (d, 3 J₂,₃ = 6.0 Hz, 2 H, 2-H), 4.90 (d, 3 J₅,₄ = 6.4 Hz, 2 H, 5-H), 5.73 (dtt, 3 J₄,₃ = 11.2 Hz, 3 J₄,₅ = 6.4 Hz, 4 J₄,₂ = 1.5 Hz, 1 H, 4-H), 5.81 (dtt, 3 J₃,₄ = 11.2 Hz, 3 J₃,₂ = 6.0 Hz, 4 J₃,₅ = 1.4 Hz, 1 H, 3-H), 7.43 (m, 2 H, 8-H), 7.56 (m, 1 H, 10-H), 8.04 (m, 2 H, 9-H). 13C-NMR (100 MHz, CDCl₃): δ = 0.5 (q, C-1), 58.7 (t, C-2), 60.7 (t, C-5) 124.5 (d, C-4), 128.3 (d, C-8), 129.6 (d, C-9), 130.1 (s, C-7), 132.9 (d, C-10), 133.9 (d, C-3), 166.4 (s, C-6).

Phosphates 1c-f were prepared following previously reported procedures.[6][7]

(Z)-4-[(triethylsilyl)oxy]but-2-en-1-yl diethylphosphate (1b)

A solution of 511 mg (2.53 mmol) 1’b, 0.51 mL (498 mg, 6.30 mmol) pyridine and 31 mg (0.25 mmol) 4-dimethylaminopyridine (99%) in 12.5 mL abs. dichloromethane was cooled to 0°C before 0.45 mL (540 mg, 3.13 mmol) diethyl chlorophosphate (97%) were added drop-wise. The reaction was allowed to warm to room temperature overnight and was hydrolyzed with water. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na₂SO₄ and the crude product was purified by column chromatography (silica gel, PE:EA 80:20, 50:50) to give 559 mg (1.65 mmol, 65%) of product 1b.

Slightly yellow liquid. 1H-NMR (400 MHz, CDCl₃): δ = 0.61 (q, 3 J₂,₁ = 8.0 Hz, 6 H, 2-H), 0.95 (t, 3 J₁,₂ = 8.0 Hz, 9 H, 1-H), 1.33 (td, 3 J₈,₇ = 7.2 Hz, 4 J₈,p = 0.8 Hz, 6 H, 8-H), 4.10 (qd, 3 J₇,₈ = 7.2 Hz, 3 J₇,p = 7.2 Hz, 4 H, 7-H), 4.25 (d, 3 J₃,₄ = 5.6 Hz, 2 H, 3-H), 4.63 (m, 2 H, 6-H), 5.62 (dtt, 3 J₅,₄ = 11.2 Hz, 3 J₅,₆ = 6.9 Hz, 4 J₅,₃ = 1.6 Hz, 1 H, 5-H), 5.73 (m, 1 H, 1-H). 13C-NMR (100 MHz, CDCl₃): δ = 4.4 (t, C-2), 6.7 (q, C-1), 16.1 (dq, 3 J₉,p = 6.5 Hz, C-8), 59.0 (t, C-3), 63.1 (dt, 2 J₆,p = 5.1 Hz, C-6), 63.7 (dt, 2 J₇,p = 5.9 Hz, C-7), 124.9 (dd, 3 J₅,p = 7.2 Hz, C-5), 133.6 (d, C-4). HRMS (CI) calced for C₁₄H₃₂O₅PSi [M+H]+: 339.1751, found: 339.1741.

Phosphates 1c-f were prepared following previously reported procedures.[6][7]

tert-Butyl (Z)-6-[{(triethylsilyl)oxy}-2-(2,2,2-trifluoroacetamido)hex-4-enoate (2b)

Preparation according to the general procedure for Ru-catalyzed allylic alkylation (0.500 mmol scale). The reaction was hydrolyzed with NH₄OAc/HOAc-buffer. Purification by column chromatography (silica gel, PE:EA 90:10, 50:50) gave 62 mg (0.151 mmol, >98% Z, S3
31%) of product 2b. Furthermore 55 mg (0.185 mmol, 38%) of the TES-deprotected product were isolated.

Colourless oil. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 0.62 (q, $^3$J$_{2,1}$ = 8.0 Hz, 6 H, 2-H), 0.96 (t, $^3$J$_{1,2}$ = 8.0 Hz, 9 H, 1-H), 1.48 (s, 9 H, 12-H), 2.69 (dd, $^3$J$_{6,5}$ = 7.2 Hz, $^3$J$_{6,7}$ = 6.6 Hz, 2 H, 6-H), 4.19 (m, 2 H, 3-H), 4.46 (td, $^3$J$_{7,6}$ = 6.6 Hz, $^2$J$_{2,NH}$ = 6.4 Hz, 1 H, 7-H), 5.36 (dtt, $^3$J$_{5,4}$ = 10.3 Hz, $^3$J$_{5,6}$ = 7.2 Hz, $^4$J$_{5,3}$ = 1.6 Hz, 1 H, 5-H), 5.74 (dtt, $^3$J$_{4,5}$ = 10.3 Hz, $^3$J$_{4,3}$ = 6.0 Hz, $^4$J$_{4,6}$ = 1.2 Hz, 1 H, 4-H), 7.28 (bs, 1 H, NH). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 4.2 (t, C-2), 6.6 (q, C-1), 27.9 (q, C-12), 29.4 (t, C-6), 52.5 (d, C-7), 59.0 (t, C-3), 83.2 (s, C-11), 115.7 (q, $^1$J$_{9,F}$ = 286 Hz, C-9), 123.7 (d, C-5), 133.6 (d, C-4), 156.8 (q, $^2$J$_{8,F}$ = 37.2 Hz, C-8), 169.2 (s, C-10).

Elementary analysis calcd for C$_{18}$H$_{32}$F$_3$NO$_4$Si: C 52.53, H 7.84, N 3.40, found: C 52.55, H 7.80, N 3.70. HRMS (CI) calcd for C$_{14}$H$_{25}$F$_3$NO$_4$Si [M-C$_4$H$_9$+2H$^+$]: 356.1494, found: 356.1525. GC (CP-Chirasil-Dex CB, 80°C, 10 min, 80°C 180°C (1°C/min) 40 min): t$_R$ = 99.18 min.

Compounds 2c-g were prepared via Ru-catalyzed allylic alkylations. The spectroscopical data were in accordance with previously reported data.[7][8]

5-[(Triethylsilyloxy]pent-3-yn-2-ol (3)

To a solution of 4.26 g (25.0 mmol) TES-protected propargylic alcohol in 100 mL abs. THF were added 19.5 mL (31.2 mmol) n-butyllithium (1.6 M in hexanes) dropwise at −78°C. The reaction mixture was stirred for 15 min at the indicated temperature before 3.5 mL (2.73 g, 62.0 mmol) acetaldehyde were added slowly. The reaction was stirred for one hour at −78°C and hydrolyzed with sat. NH$_4$Cl solution at this temperature. The solution was allowed to warm to room temperature and was diluted with EA. The layers were separated and the aqueous phase was extracted three times with EA. The combined organic layers were dried over Na$_2$SO$_4$ and the crude product was purified by column chromatography (silica gel, PE:EA 70:30). 5.22 g (24.4 mmol, 98%) of product 3 were obtained.

Colourless liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta$ = 0.64 (q, $^3$J$_{2,1}$ = 8.0 Hz, 6 H, 2-H), 0.97 (t, $^3$J$_{1,2}$ = 8.0 Hz, 9 H, 1-H), 1.44 (d, $^3$J$_{6,5}$ = 6.8 Hz, 3 H, 7-H), 1.94 (d, $^3$J$_{OH,6}$ = 4.4 Hz, 1 H, OH), 4.33 (d, $^3$J$_{3,6}$ = 2.0 Hz, 2 H, 3-H), 4.55 (m, 1 H, 6-H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta$ = 4.4 (t, C-2), 6.6 (q, C-1), 24.1 (q, C-7), 51.3 (t, C-3), 58.4 (d, C-6), 82.5 (s, C-4), 86.6 (s, C-5). Elementary analysis calcd for C$_{11}$H$_{23}$O$_2$Si: C 61.63, H 10.34, found: C 61.50, H 10.28. HRMS (CI) calcd for C$_{11}$H$_{23}$O$_2$Si [M+H$^+$]: 215.1463, found: 215.1468.
(Z)-5-[(Triethylsilyl)oxy]pent-3-en-2-ol (4)

102 mg (0.475 mmol) 3 were dissolved in 5 mL MeOH and 19.0 µL (20.7 mg, 0.159 mmol) quinoline (99%) and 10.4 mg Lindlar-catalyst (5 w% Pd on CaCO₃, poisoned with Pb) were added. The reaction mixture was hydrogenated for 5 min at 30 psi (2.07 bar) and filtrated through a pad of Celite®. After purification by column chromatography (silica gel, PE:EA 70:30) 88.1 mg (0.407 mmol, 86%) of product 4 were obtained.

Colourless oil. ¹H-NMR (400 MHz, CDCl₃): δ = 0.62 (q, ³J₂,₁ = 8.0 Hz, 6 H, 2-H), 0.96 (t, ³J₁,₂ = 8.0 Hz, 9 H, 1-H), 1.25 (d, ³J₇,₆ = 6.4 Hz, 3 H, 7-H), 2.27 (bs, 1 H, OH), 4.20 (ddd, ³J₃ₐ,₃₉ = 12.7 Hz, ³J₃₉,₅ = 5.2 Hz, ³J₅,₆ = 0.8 Hz, 1 H, 3-H₉), 4.30 (ddd, ³J₃₉,₃ₙ = 12.7 Hz, ³J₃ₙ,₄ = 4.4 Hz, ³J₅,₆ = 1.2 Hz, 1 H, 3-H₉), 4.61 (qd, ³J₆,₇ = 6.4 Hz, ³J₆,₅ = 6.4 Hz, 1H, 6-H), 5.57 (m, 2 H, 4-H, 5-H). ¹³C-NMR (100 MHz, CDCl₃): δ = 4.4 (t, C-2), 6.7 (q, C-1), 23.3 (q, C-7), 59.1 (t, C-3), 63.9 (d, C-6), 129.8 (d, C-4, C-5), 135.6 (d, C-4, C-5). HRMS (CI) calcd for C₁₁H₂₅O₂Si [M+H]+: 217.1618, found: 217.1636.


10.9 g (44.4 mmol) 4, 20.7 mL (19.3 g, 222 mmol) vinyl acetate (99%) and 481 mg Novozyme® 435 were mixed and shaked for 30 hours at rt. The enzyme was removed by filtration and the filtrate was concentrated in vacuo. Purification by column chromatography (silica gel, PE:EA 90:10, 80:20) gave 4.35 g (19.1 mmol, 43%, >99% ee) alcohol (S)-4 and 5.42 g (21.0 mmol, 47%, 99% ee) acetate (R)-5a.

Colourless liquid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.62 (q, ³J₂,₁ = 8.0 Hz, 6 H, 2-H), 0.96 (t, ³J₁,₂ = 8.0 Hz, 9 H, 1-H), 1.25 (d, ³J₇,₆ = 6.0 Hz, 3 H, 7-H), 2.28 (bs, 1 H, OH), 4.20 (m, 1 H, 3-H₉), 4.30 (m, 1 H, 3-H₉), 4.61 (qd, ³J₆,₇ = 6.4 Hz, ³J₆,₅ = 6.4 Hz, 1H, 6-H), 5.57 (m, 2 H, 4-H, 5-H). ¹³C-NMR (100 MHz, CDCl₃): δ = 4.4 (t, C-2), 6.7 (q, C-1), 23.3 (q, C-7), 59.1 (t, C-3), 63.9 (d, C-6), 129.8 (d, C-4, C-5), 135.6 (d, C-4, C-5). HRMS (CI) calcd for C₁₁H₂₅O₂Si [M+H]+: 217.1618, found: 217.1642. GC of alcohol (S)-4 after conversion to acetate (S)-5a (CP-Chirasil-Dex CB, 125°C, 30 min): tᵦ[(S)-5a] = 17.42 min. Optical rotation: [α]₂⁰ = −3.2° (c = 1.00, CHCl₃, >99% ee).

Colourless liquid. ¹H-NMR (400 MHz, CDCl₃): δ = 0.61 (q, ³J₂,₁ = 8.0 Hz, 6 H, 2-H), 0.95 (t, ³J₁,₂ = 8.0 Hz, 9 H, 1-H), 1.28 (d, ³J₇,₆ = 6.0 Hz, 3 H, 7-H), 2.01 (s, 3 H, 9-H), 4.30 (dd, ³J₃₉,₃ₙ = 5.2 Hz, ³J₃ₙ,₄ = 4.4 Hz, ³J₅,₆ = 1.2 Hz, 1 H, 3-H₉), 4.61 (qd, ³J₆,₇ = 6.4 Hz, ³J₆,₅ = 6.4 Hz, 1H, 6-H), 5.57 (m, 2 H, 4-H, 5-H). ¹³C-NMR (100 MHz, CDCl₃): δ = 4.4 (t, C-2), 6.7 (q, C-1), 23.3 (q, C-7), 59.1 (t, C-3), 63.9 (d, C-6), 129.8 (d, C-4, C-5), 135.6 (d, C-4, C-5). HRMS (CI) calcd for C₁₁H₂₅O₂Si [M+H]+: 217.1618, found: 217.1642. GC of alcohol (S)-4 after conversion to acetate (S)-5a (CP-Chirasil-Dex CB, 125°C, 30 min): tᵦ[(S)-5a] = 17.42 min. Optical rotation: [α]₂⁰ = −3.2° (c = 1.00, CHCl₃, >99% ee).
6.0 Hz, $^3J_{3,5}=1.8$ Hz, 2 H, 3-H), 5.40 (ddt, $^3J_{5,4}=11.2$ Hz, $^3J_{5,6}=8.8$ Hz, $^4J_{5,3}=1.8$ Hz, 1 H, 5-H), 5.60 (m, 2 H, 4-H, 6-H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 4.4$ (t, C-2), 6.7 (q, C-1), 20.7 (q, C-7), 21.3 (q, C-9), 59.1 (t, C-3), 67.0 (d, C-6), 129.6 (d, C-5), 132.2 (d, C-4), 170.2 (s, C-8). HRMS (CI) calcd for C$_{13}$H$_{27}$O$_3$Si [M+H]$^+$: 259.1724, found: 259.1695. GC (CP-Chirasil-Dex CB, 125°C, 30 min): $t_R((R)-5a) = 18.02$ min. Optical rotation: $[\alpha]_{20}^D = -3.6^\circ$ (c = 1.00, CHCl$_3$, 99% ee).

$(S,Z)$-5-[(Triethylsilyl)oxy]pent-3-en-2-yl acetate [(S)-5a]

To a solution of 547 mg (2.53 mmol) (S)-4 in 12.5 mL abs. dichloromethane were added 0.51 mL (500 mg, 6.32 mmol) pyridine and 30.7 mg (0.249 mmol) 4-dimethylaminopyridine (99%). The reaction mixture was cooled to 0°C and 287 $\mu$L (310 mg, 3.04 mmol) acetic anhydride were added. The reaction was allowed to warm to room temperature overnight. The reaction was hydrolyzed with water and 378 $\mu$L (382 mg, 6.25 mmol) ethanolamine. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The crude product was purified by column chromatography (silica gel, PE:EA 90:10, 80:20). 587 mg (2.27 mmol, 90%) product (S)-5a were obtained.

![Diagram](image1)

Colourless liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 0.61$ (q, $^3J_{2,1}=8.0$ Hz, 6 H, 2-H), 0.96 (t, $^3J_{1,2}=8.0$ Hz, 9 H, 1-H), 1.28 (d, $^3J_{7,6}=6.0$ Hz, 3 H, 7-H), 2.01 (s, 3 H, 9-H), 4.30 (dd, $^3J_{3,4}=6.0$ Hz, $^3J_{3,5}=1.6$ Hz, 2 H, 3-H), 5.40 (ddt, $^3J_{5,4}=10.8$ Hz, $^3J_{5,6}=8.8$ Hz, $^4J_{5,3}=1.6$ Hz, 1 H, 5-H), 5.61 (m, 2 H, 4-H, 6-H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 4.4$ (t, C-2), 6.7 (q, C-1), 20.8 (q, C-7), 21.3 (q, C-9), 59.1 (t, C-3), 67.0 (d, C-6), 129.7 (d, C-5), 132.2 (d, C-4), 170.2 (s, C-8). HRMS (CI) calcd for C$_{13}$H$_{27}$O$_3$Si [M+H]$^+$: 259.1724, found: 259.1725. Optical rotation: $[\alpha]_{20}^D = +15.4^\circ$ (c = 1.00, CHCl$_3$, >99% ee).

$(S,Z)$-5-[(Triethylsilyl)oxy]pent-3-en-2-yl benzoate [(S)-5b]

496 mg (2.29 mmol) (S)-4 were dissolved in 9.0 mL abs. dichloromethane and 0.46 mL (453 mg, 5.73 mmol) pyridine and 28.0 mg (0.227 mmol) 4-dimethylaminopyridine (99%) were added. The reaction mixture was cooled to 0°C before a solution of 691 mg (2.75 mmol) benzoic anhydride (90%) in 2.5 mL abs. dichloromethane was added dropwise. The reaction was allowed to warm to room temperature overnight and was hydrolyzed with water and 342 $\mu$L (346 mg, 5.66 mmol) ethanolamine. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were washed with brine and dried over Na$_2$SO$_4$. The crude product was purified by column chromatography (silica gel, PE:EA 90:10, 80:20, 50:50) to give 370 mg (1.15 mmol, 50%) of product (S)-5b.
Colourless liquid. $^1$H-NMR (400 MHz, CDCl$_3$): $\delta = 0.62$ (q, $^3J_{2,1} = 8.0$ Hz, 6 H, 2-H), 0.96 (t, $^3J_{1,2} = 8.0$ Hz, 9 H, 1-H), 1.42 (d, $^3J_{7,6} = 6.4$ Hz, 3 H, 7-H), 4.38 (m, 2 H, 3-H), 5.55 (ddt, $^3J_{5,4} = 10.8$ Hz, $^4J_{6,5} = 8.8$ Hz, $^4J_{3,2} = 1.6$ Hz, 1 H, 5-H), 5.68 (ddt, $^3J_{4,5} = 10.8$ Hz, $^2J_{4,3} = 6.0$ Hz, $^4J_{6,4} = 0.8$ Hz, 1 H, 4-H), 5.86 (m, 1 H, 6-H), 7.43 (m, 2 H, 11-H), 7.54 (m, 1 H, 12-H), 8.03 (m, 1 H, 10-H). $^{13}$C-NMR (100 MHz, CDCl$_3$): $\delta = 4.4$ (t, C-2), 6.7 (q, C-1), 20.9 (q, C-7), 59.2 (t, C-3), 67.6 (d, C-6), 128.3 (d, C-11), 129.6 (d, C-10), 129.7 (d, C-5), 130.6 (s, C-9), 132.5 (d, C-4), 132.8 (d, C-12), 165.8 (s, C-8). HRMS (CI) calcd for C$_{18}$H$_{29}$O$_3$Si [M+H]$^+$: 321.1880, found: 321.1894. Optical rotation: $[\alpha]_D^{20} = +84.6^\circ$ (c = 1.00, CHCl$_3$, >99% ee).


To a solution of 469 mg (2.17 mmol) [(S)-4] in 11 mL abs. dichloromethane were added 220 μL (203 mg, 2.39 mmol) 3,4-Dihydro-2H-pyran (99%) and 53.2 mg (0.217 mmol) lanthanum (III) chloride and the reaction was stirred at room temperature overnight. Catalytical amounts of pyridinium p-toluenesulfonate and 180 μL (166 mg, 1.95 mmol) 3,4-Dihydro-2H-pyran (99%) were added at room temperature and the reaction was stirred for two days at rt. For workup, water was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane and the combined organic layers were dried over Na$_2$SO$_4$. The crude product was purified by column chromatography (silica gel, PE:EA 90:10, 80:20, 50:50) to give 402 mg (1.34 mmol, 62%) product [(S)-5c] as a mixture of diastereomers (ratio 1:1).

$^1$H-NMR (400 MHz, CDCl$_3$): major diastereomer: $\delta = 0.61$ (q, $^3J_{2,1} = 8.0$ Hz, 6 H, 2-H), 0.96 (t, $^3J_{1,2} = 8.0$ Hz, 9 H, 1-H), 1.19 (d, $^3J_{7,6} = 6.4$ Hz, 3 H, 7-H), 1.52 (m, 4 H, 9-Ha, 10-Ha, 11-H), 1.69 (m, 1 H, 9-Hb), 1.83 (m, 1 H, 10-Hb), 3.46 (m, 1 H, 12-Ha), 3.90 (m, 1 H, 12-Hb), 4.26 (m, 2 H, 3-H), 4.54 (m, 2 H, 6-H, 8-H), 5.30 (ddt, $^3J_{5,4} = 11.6$ Hz, $^4J_{6,5} = 9.4$ Hz, $^4J_{3,2} = 1.7$ Hz, 1 H, 5-H), 5.68 (ddt, $^3J_{4,5} = 11.6$ Hz, $^2J_{4,3} = 5.7$ Hz, $^4J_{6,4} = 2.3$ Hz, 1 H, 4-H). minor diastereomer: $\delta = 1.25$ (d, $^3J_{2,1} = 6.4$ Hz, 6 H, 2-H), 4.62 (m, 1 H, 6-H), 4.71 (m, 1 H, 8-H), 5.54 (m, 2 H, 4-H, 5-H). $^{13}$C-NMR (100 MHz, CDCl$_3$): major diastereomer: $\delta = 4.4$ (t, C-2), 6.7 (q, C-1), 19.6 (t, C-10), 20.6 (q, C-7), 25.5 (t, C-11), 30.9 (t, C-9), 59.2 (t, C-3), 62.3 (t, C-12), 68.1 (d, C-6), 95.9 (d, C-8), 132.0 (d, C-5), 132.3 (d, C-4). minor diastereomer: $\delta = 4.8$ (t, C-2), 6.7 (q, C-1), 20.1 (t, C-10), 21.6 (q, C-7), 25.5 (t, C-11), 31.0 (t, C-9), 58.9 (t, C-3), 63.0 (t, C-12), 66.5 (d, C-6), 96.4 (d, C-8), 129.7 (d, C-4, C-5), 132.9 (d, C-4, C-5). HRMS (CI) calcd for C$_{16}$H$_{32}$O$_3$Si [M$^+$]: 300.2121, found: 300.2116.

**((R,Z)-5-[(Diethoxyphosphoryl)oxy]pent-3-en-2-yl]oxy)acetate [(R)-6a]**

365 mg (1.41 mmol) [(R)-5a] were dissolved in 15 mL MeOH and 15.0 mg (77.3 μmol) p-toluenesulfonic acid monohydrate (98%) were added at rt. After one hour, sat. NaHCO$_3$ solution was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane and the combined organic layers were dried over Na$_2$SO$_4$. The corresponding crude alcohol was dissolved in 7.5 mL abs. dichloromethane and was reacted with 0.31 mL (307 mg, 3.88 mmol) pyridine, 19.0 mg (0.156 mmol) 4-dimethylaminopyridine (99%) and 0.28 mL (336 mg, 1.89 mmol) diethyl chlorophosphate (97%) at 0°C. The reaction
mixture was allowed to warm to room temperature overnight and was hydrolyzed with water. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na₂SO₄. After purification by column chromatography (silica gel, PE:EA 80:20, 50:50) 341 mg (1.22 mmol, 87% over two steps) product (R)-6a were obtained.

![Diagram of compound R-6a]

Colourless oil. ¹H-NMR (400 MHz, CDCl₃): δ = 1.29 (d, ³J₃,₄ = 6.0 Hz, 3 H, 3-H), 1.32 (m, 6 H, 9-H), 2.01 (s, 3 H, 1-H), 4.10 (m, 4 H, 8-H), 4.68 (m, 2 H, 7-H), 5.53 (m, 2 H, 4-H, 5-H), 5.65 (m, 1 H, 6-H). ¹³C-NMR (100 MHz, CDCl₃): δ = 16.1 (dq, ³J₉,p = 7.3 Hz, C-9), 20.5 (q, C-3), 21.2 (q, C-1), 63.0 (dt, ²J₇,p = 5.1 Hz, C-7), 63.8 (dt, ²J₈,p = 5.8 Hz, C-8), 66.6 (d, C-4), 126.8 (dd, ³J₆,p = 6.6 Hz, C-6), 133.1 (d, C-5), 170.1 (s, C-2). HRMS (CI) calcd for C₁₁H₂₂O₆P [M+H]⁺: 281.1149, found: 281.1157. Optical rotation: [α]⁺D = −23.2° (c = 1.05, CHCl₃, >99% ee).

(S,Z)-5-[(Diethoxyphosphoryl)oxy]pent-3-en-2-yl acetate [(S-6a)]

A solution of 429 mg (1.66 mmol) (S)-5a in 8 mL MeOH was reacted with 16.1 mg (82.9 μmol) p-toluenesulfonic acid monohydrate (98%) for one hour at rt. Sat. NaHCO₃ solution was added and the layers were separated. The aqueous phase was extracted three times with dichloromethane and the combined organic layers were dried over Na₂SO₄. The crude alcohol was dissolved in 8 mL abs. dichloromethane and 0.34 mL (333 mg, 4.21 mmol) pyridine, 20.5 mg (166 μmol) 4-dimethylaminopyridine (99%) and 0.30 mL (360 mg, 2.02 mmol) diethyl chlorophosphate (97%) were added at 0°C. The reaction was allowed to warm to room temperature and was hydrolyzed with water. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na₂SO₄. Purification by column chromatography (silica gel, PE:EA 80:20, 50:50) gave 309 mg (1.10 mmol, 66% over two steps) product (S)-6a.

![Diagram of compound S-6a]

Colourless oil. ¹H-NMR (400 MHz, CDCl₃): δ = 1.30 (d, ³J₃,₄ = 6.4 Hz, 3 H, 3-H), 1.33 (t, ³J₉,g = 7.0 Hz, 6 H, 9-H), 2.01 (s, 3 H, 1-H), 4.11 (m, 4 H, 8-H), 4.69 (m, 2 H, 7-H), 5.55 (m, 2 H, 4-H, 5-H), 5.67 (m, 1 H, 6-H). ¹³C-NMR (100 MHz, CDCl₃): δ = 16.1 (dq, ²J₉,p = 6.5 Hz, C-9), 20.6 (q, C-3), 21.2 (q, C-1), 63.1 (dt, ²J₇,p = 5.1 Hz, C-7), 63.8 (dt, ²J₈,p = 5.9 Hz, C-8), 66.6 (d, C-4), 126.8 (dd, ³J₆,p = 6.5 Hz, C-6), 133.1 (d, C-5), 170.1 (s, C-2). HRMS (CI) calcd for C₁₁H₂₂O₆P [M+H]⁺: 281.1149, found: 281.1197. Optical rotation: [α]⁺D = +30.9° (c = 1.00, CHCl₃, >99% ee).

(S,Z)-5-Hydroxypent-3-en-2-yl benzoate [(S)-6’b]

356 mg (1.11 mmol) (S)-5b were dissolved in 5.5 mL MeOH and 11.3 mg (58.2 μmol) p-toluenesulfonic acid monohydrate (98%) were added at rt. The solvent was evaporated in
and the crude product was purified by column chromatography (silica gel, PE:EA 80:20, 50:50) to give 181 mg (0.878 mmol, 79%) product \(\text{(S-6'b)}\).

Colourless oil. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.46 \text{ (d, } ^3J_{6,7} = 6.4 \text{ Hz, } 3 \text{ H, } 6-\text{H})\), 2.72 (bs, 1 H, OH), 4.13 (ddd, \(^2J_{10a,10b} = 13.2 \text{ Hz}, ^3J_{10a,9} = 6.0 \text{ Hz}, ^4J_{10a,8} = 0.9 \text{ Hz, } 1 \text{ H, } 10-\text{H}a)\), 4.52 (dd, \(^2J_{10b,10a} = 13.2 \text{ Hz}, ^3J_{10b,8} = 8.0 \text{ Hz}, ^4J_{10b,9} = 1.3 \text{ Hz, } 1 \text{ H, } 10-\text{H}b\) ), 5.53 (dt, \(^3J_{8,9} = 11.0 \text{ Hz, } ^3J_{8,8} = 9.6 \text{ Hz}, ^4J_{8,10} = 1.2 \text{ Hz, } 1 \text{ H, } 8-\text{H})\), 5.82 (ddddd, \(^3J_{9,8} = 11.0 \text{ Hz}, ^3J_{9,10b} = 8.0 \text{ Hz}, ^3J_{9,10a} = 6.0 \text{ Hz}, ^4J_{9,7} = 0.9 \text{ Hz, } 1 \text{ H, } 9-\text{H})\), 5.92 (dqdd, \(^3J_{7,8} = 9.6 \text{ Hz, } ^3J_{7,9} = 6.4 \text{ Hz, } ^3J_{7,8} = 0.9 \text{ Hz, } 1 \text{ H, } 7-\text{H})\), 7.43 (m, 2 H, 2-H), 7.56 (m, 1 H, 1-H), 8.02 (m, 2 H, 3-H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 20.6 \text{ (q, C-6)}, 58.5 \text{ (t, C-10)}, 67.5 \text{ (d, C-7)}, 128.3 \text{ (d, C-2)}, 129.6 \text{ (d, C-3)}, 130.3 \text{ (s, C-4)}, 131.2 \text{ (d, C-8, C-9)}, 131.6 \text{ (d, C-8, C-9)}, 133.0 \text{ (d, C-1)}, 166.4 \text{ (s, C-5)}\).

\((S,Z)-5\)-[(Diethoxyphosphoryl)oxy]pent-3-en-2-yl benzoate \([\text{(S-6b)}]\)

165 mg (0.800 mmol) \(\text{(S-6'b)}\) were dissolved in 4.0 mL abs. dichloromethane and 162 \(\mu\)L (158 mg, 2.00 mmol) pyridine, 9.9 mg (80.2 \(\mu\)mol) 4-dimethylaminopyridine (99%) and 142 \(\mu\)L (171 mg, 0.960 mmol) diethyl chlorophosphate (97%) were added at 0°C. The reaction mixture was allowed to warm to room temperature overnight and was hydrolyzed with water. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na\(_2\)SO\(_4\). Purification by column chromatography (silica gel, PE:EA 80:20, 50:50) gave 262 mg (0.765 mmol, 96%) product \(\text{(S-6b)}\).

Colourless oil. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): \(\delta = 1.33 \text{ (m, } 6 \text{ H, } 12-\text{H})\), 1.45 (d, \(^3J_{6,7} = 6.4 \text{ Hz, } 3 \text{ H, } 6-\text{H})\), 4.12 (m, 4 H, 11-H), 4.78 (m, 2 H, 10-H), 5.75 (m, 3 H, 7-H, 8-H, 9-H), 7.43 (m, 2 H, 2-H), 7.56 (m, 1 H, 1-H), 8.02 (m, 2 H, 3-H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): \(\delta = 16.1 \text{ (dq, } ^3J_{12,P} = 6.6 \text{ Hz, C-12)}, 20.7 \text{ (q, C-6)}, 63.1 \text{ (dt, } ^2J_{10,P} = 5.8 \text{ Hz, C-10)}, 63.8 \text{ (dt, } ^2J_{11,P} = 5.9 \text{ Hz, C-11)}, 67.2 \text{ (d, C-7)}, 127.1 \text{ (dd, } ^3J_{9,P} = 6.5 \text{ Hz, C-9)}, 128.3 \text{ (d, C-2)}, 129.5 \text{ (d, C-3)}, 130.3 \text{ (s, C-4)}, 132.9 \text{ (d, C-1)}, 133.1 \text{ (d, C-8)}, 165.7 \text{ (s, C-5)}\). HRMS (CI) calcd for C\(_9\)H\(_{18}\)O\(_4\)P [M-OBz]\(^+\): 221.0943, found: 221.0948. Optical rotation: \([\alpha]_D^{22} = +93.7^\circ \text{ (c = 1.00, CHCl}_3\text{, >99\% ee)}\).


381 mg (1.27 mmol) \(\text{(S-5c)}\) in 2.0 mL abs. THF were reacted with 1.59 mL (1.59 mmol) TBAF solution (1.0 M in THF) and stirred for 5 minutes at rt. After hydrolysis with water, the aqueous phase was extracted three times with dichloromethane and the combined organic layers were dried over Na\(_2\)SO\(_4\). The corresponding crude alcohol was dissolved in 6.0 mL abs. dichloromethane and 0.26 mL (251 mg, 3.17 mmol) pyridine and 15.6 mg (0.126 mmol) 4-dimethylaminopyridine (99%) were added. The reaction mixture was cooled to 0°C before...
0.23 mL (276 mg, 1.55 mmol) diethyl chlorophosphate (97%) were added dropwise. The reaction was allowed to warm to room temperature overnight and was hydrolyzed with water. The layers were separated and the aqueous phase was extracted three times with dichloromethane. The combined organic layers were dried over Na2SO4. Purification by column chromatography (silica gel, PE:EA 80:20, 50:50) gave 375 mg (1.16 mmol, 91% over two steps) product \((S)-6c\) as a mixture of diastereomers (ratio 1:1).

Colourless oil. \(^1\)H-NMR (400 MHz, CDCl3): major diastereomer: \(\delta = 1.26\) (d, \(^3\)J\(_{6,7} = 6.8\) Hz, 3 H, 6-H), 1.33 (t, \(^3\)J\(_{12,11} = 7.0\) Hz, 6 H, 12-H), 1.54 (m, 4 H, 2-H, 3-H\(_{as}\), 4-H\(_{a}\)), 1.68 (m, 1 H, 4-H\(_b\)), 1.81 (m, 1 H, 3-H\(_b\)), 3.46 (m, 1 H, 1-H\(_a\)), 3.84 (m, 1 H, 1-H\(_b\)), 4.11 (m, 4 H, 11-H), 4.62 (m, 4 H, 5-H, 7-H, 10-H), 5.47 (dd, \(^3\)J\(_{8,9} = 11.4\) Hz, \(^3\)J\(_{8,7} = 9.2\) Hz, 1 H, 8-H), 5.73 (dt, \(^3\)J\(_{9,8} = 11.4\) Hz, \(^3\)J\(_{9,10} = 6.8\) Hz, 1 H, 9-H). minor diastereomer: \(\delta = 1.17\) (d, \(^3\)J\(_{6,7} = 6.4\) Hz, 3 H, 6-H), 5.58 (dt, \(^3\)J\(_{9,8} = 11.1\) Hz, \(^3\)J\(_{9,10} = 6.0\) Hz, 1 H, 9-H), 5.67 (m, 1 H, 8-H). \(^13\)C-NMR (100 MHz, CDCl3): major diastereomer: \(\delta = 16.1\) (dq, \(^3\)J\(_{12,P} = 6.5\) Hz, C-12), 19.8 (t, C-3), 21.5 (q, C-6), 25.4 (t, C-2), 30.8 (t, C-4), 62.7 (t, C-1), 63.0 (dt, \(^2\)J\(_{10,P} = 5.1\) Hz, C-10), 63.8 (dt, \(^2\)J\(_{11,P} = 5.9\) Hz, C-11), 66.0 (d, C-7), 95.7 (d, C-5), 126.9 (dd, \(^2\)J\(_{9,P} = 6.6\) Hz, C-9), 135.5 (d, C-8), minor diastereomer: \(\delta = 19.6\) (t, C-3), 20.6 (q, C-6), 25.4 (t, C-2), 30.9 (t, C-4), 62.5 (t, C-1), 63.3 (dt, \(^2\)J\(_{10,P} = 5.1\) Hz, C-10), 63.7 (dt, \(^2\)J\(_{11,P} = 5.9\) Hz, C-11), 68.2 (d, C-7), 96.9 (d, C-5), 124.1 (d, C-9), 136.5 (d, C-8). HRMS (CI) calcd for C\(_{14}\)H\(_{28}\)O\(_6\)P [M+H]\(^+\): 323.1618, found: 323.1617.

**tert-Butyl (6R,Z)-6-acetoxy-2-(2,2,2-trifluoroacetamido)hept-4-enolate [(R)-7a]**

Preparation according to the general procedure for Ru-catalyzed allylic alkylation (1.75 mmol scale). Purification by column chromatography (silica gel, PE:EA 90:10, 70:30) gave 526 mg (1.49 mmol, >98% Z, 85%) product \((R)-7a\) as a mixture of diastereomers (ratio 7:3). Furthermore, 67 mg (0.215 mmol, 12%) of the deacetylated product were obtained.

Colourless oil. \(^1\)H-NMR (400 MHz, CDCl3): major diastereomer: \(\delta = 1.29\) (d, \(^3\)J\(_{3,4} = 6.2\) Hz, 3 H, 3-H), 1.47 (s, 9 H, 13-H), 2.02 (s, 3 H, 1-H), 2.65 (m, 1 H, 7-H\(_a\)), 2.88 (m, 1 H, 7-H\(_b\)), 4.44 (m, 1 H, 8-H), 5.44 (m, 3 H, 4-H, 5-H, 6-H), 7.51 (d, \(^3\)J\(_{NH,8} = 6.8\) Hz, 1 H, NH). minor diastereomer: \(\delta = 1.28\) (d, \(^3\)J\(_{3,4} = 6.2\) Hz, 3 H, 3-H), 1.48 (s, 9 H, 13-H), 2.01 (s, 3 H, 1-H), 4.52 (m, 1 H, 8-H). \(^13\)C-NMR (100 MHz, CDCl3): major diastereomer: \(\delta = 20.2\) (q, C-3), 21.1 (q, C-1), 27.9 (q, C-13), 29.5 (t, C-7), 52.7 (d, C-8), 66.7 (d, C-4), 82.8 (s, C-12), 127.3 (d, C-6), 132.8 (d, C-5), 157.4 (q, \(^2\)J\(_{9,F} = 38.0\) Hz, C-9), 169.2 (s, C-11), 171.6 (s, C-2). Signal of C-10
could not be observed.

**Minor diastereomer:** \(\delta = 27.9\) (q, C-13), 52.5 (d, C-8), 66.8 (d, C-4).

HRMS (Cl) calcd for \(C_{15}H_{23}F_{3}NO_{5}\) [M+H]: 354.1523, found: 354.1534. GC (\(L\)-Chirasil-Val, 80°C, 10 min, 80°C → 180°C (1°C/min), 40 min): \(t_{R}[(2S,6R)] = 55.69\) min (70%), \(t_{R}[(2R,6S)] = 58.85\) min (30%).

**tert-Butyl (6S,Z)-6-acetoxy-2-(2,2,2-trifluoroacetamido)hept-4-enoate [(S)-7a]**

Preparation according to the general procedure for Ru-catalyzed allylic alkylation (0.978 mmol scale). After purification by column chromatography (silica gel, PE:EA 90:10, 80:20, 50:50) 275 mg (0.778 mmol, >98% Z, 80%) product (S)-7a were obtained as a mixture of diastereomers (ratio 69:31). Furthermore, 21 mg (0.067 mmol, 5%) of the deacetylated product were isolated.

Colourless oil. \(^1\)H-NMR (400 MHz, CDCl\(_3\)): major diastereomer: \(\delta = 1.29\) (d, \(3J_{3,4} = 6.0\) Hz, 3 H, 3-H), 1.48 (s, 9 H, 13-H), 2.52 (m, 3 H, 1-H), 2.65 (m, 1 H, 7-H\(_a\)), 2.86 (m, 1 H, 7-H\(_b\)), 4.45 (m, 1 H, 8-H), 5.44 (m, 3 H, 4-H, 5-H, 6-H), 7.50 (d, \(3J_{NH,8} = 6.8\) Hz, 1 H, NH). minor diastereomer: \(\delta = 1.28\) (d, \(3J_{3,4} = 6.4\) Hz, 3 H, 3-H), 1.48 (s, 9 H, 13-H), 2.01 (s, 3 H, 1-H), 4.52 (m, 1 H, 8-H). \(^{13}\)C-NMR (100 MHz, CDCl\(_3\)): major diastereomer: \(\delta = 20.2\) (q, C-3), 21.1 (q, C-1), 27.9 (q, C-13), 29.5 (t, C-7), 52.7 (d, C-8), 66.7 (d, C-4), 82.8 (s, C-12), 127.3 (d, C-6), 132.8 (d, C-5), 169.2 (s, C-11), 171.6 (s, C-2). Signals of the TFA-group could not be observed. minor diastereomer: \(\delta = 20.4\) (q, C-3), 21.1 (q, C-1), 27.9 (q, C-13), 52.5 (d, C-8), 66.8 (d, C-4), 83.3 (s, C-12), 125.0 (d, C-6), 133.8 (d, C-5). HRMS (Cl) calcd for \(C_{15}H_{22}F_{3}NO_{5}\) [M]: 353.1450, found: 353.1434. GC (\(L\)-Chirasil-Val, 80°C, 10 min, 80°C → 180°C (1°C/min), 10 min): \(t_{R}[(2R,6S)] = 54.27\) min (69%), \(t_{R}[(2S,6S)] = 61.33\) min (31%).

**\((2S,Z)-7-(\text{tert-Butoxy})-7-oxo-6-(2,2,2-trifluoroacetamido)hept-3-en-2-yl benzoate [(S)-7b]**

Preparation according to the general procedure for Ru-catalyzed allylic alkylation (0.508 mmol scale). After purification by column chromatography (silica gel, PE:EA 90:10) 198 mg (0.477 mmol, >98% Z, 94%) product (S)-7a were obtained as a mixture of diastereomers (ratio 74:26).
Colourless oil. 1H-NMR (400 MHz, CDCl3): major diastereomer: $\delta = 1.45$ (d, $^3J_{6,7} = 6.4$ Hz, 3 H, 6-H), 1.50 (s, 9 H, 16-H), 1.52 (m, 4 H, 2-H, 4-Ha, 4-Hb), 1.68 (m, 1 H, 4-Hb), 1.82 (m, 1 H, 3-Hb), 2.57 (m, 1 H, 10-H), 2.74 (m, 1 H, 7-H), 3.47 (m, 2 H, 1-H), 4.49 (m, 3 H, 5-H, 7-H, 11-H), 5.49 (m, 1 H, 9-H), 5.64 (m, 1 H, 8-H), 7.93 (d, $^3J_{NH,11} = 6.8$ Hz, 1 H, NH). minor diastereomer: $\delta = 1.21$ (d, $^3J_{6,7} = 6.4$ Hz, 1 H, 6-H), 1.25 (d, $^3J_{6,7} = 6.0$ Hz, 1 H, 6-H), 1.26 (d, $^3J_{6,7} = 6.4$ Hz, 1 H, 6-H), 1.48 (s, 9 H, 16-H), 1.49 (s, 9 H, 16-H), 1.50 (s, 9 H, 16-H), 2.66 (m, 1 H, 10-Hb), 2.87 (m, 1 H, 10-Hb), 3.63 (m, 2 H, 1-H), 3.76 (m, 2 H, 1-H), 3.83 (m, 2 H, 1-H), 4.00 (m, 2 H, 1-H), 4.73 (m, 1 H, 5-H), 5.28 (m, 1 H, 9-H), 5.35 (m, 2 H, 8-H, 9-H), 5.43 (m, 1 H, 8-H), 7.18 (d, $^3J_{NH,11} = 5.2$ Hz, 1 H, NH), 7.62 (d, $^3J_{NH,11} = 7.6$ Hz, 1 H, NH), 8.08 (d, $^3J_{NH,11} = 6.0$ Hz, 1 H, NH). 13C-NMR (100 MHz, CDCl3): major diastereomer: $\delta = 21.1$ (t, C-3), 21.4 (q, C-6), 24.9 (t, C-2), 27.9 (q, C-16), 29.3 (t, C-10), 31.2 (t, C-4), 52.7 (d, C-11), 64.8 (t, C-1), 68.3 (d, C-7), 82.5 (s, C-15), 99.7 (d, C-5), 125.6 (d, C-9), 135.8 (d, C-8), 169.6 (s, C-14). Signals of the TFA-group could not be observed. minor diastereomer: $\delta = 18.1$ (t, C-3), 19.3 (t, C-3), 19.7 (q, C-6), 20.5 (q, C-6), 20.9 (t, C-3), 21.4 (q, C-6), 25.3 (t, C-2), 25.3 (t, C-2), 25.4 (t, C-2), 27.7 (q, C-16), 27.9 (q, C-16), 28.0 (q, C-16), 29.3 (t, C-10), 29.5 (t, C-10), 29.5 (t, C-10), 30.4 (t, C-4), 31.0 (t, C-4), 52.6 (d, C-11), 52.7 (d, C-11), 53.1 (d, C-11), 60.9 (t, C-1), 62.0 (t, C-1), 62.5 (t, C-1), 64.4 (d, C-7), 65.5 (d, C-7), 69.5 (d, C-7), 82.7 (s, C-15), 82.9 (s, C-15), 83.3 (s, C-15), 92.7 (d, C-5), 94.7 (d, C-5), 97.9 (d, C-5), 122.2 (d, C-9), 125.2 (d, C-9), 128.0 (d, C-9), 134.3 (d, C-8), 135.5 (d, C-8), 137.2 (d, C-8), 169.1

**tert-Butyl (6S,7Z)-6-[(tetrahydro-2H-pyran-2-yl)oxy]-2-(2,2,2-trifluoroacetamido)hept-4-enoate [(S)-7c]**

Preparation according to the general procedure for Ru-catalyzed allylic alkylation (0.642 mmol scale). After purification by column chromatography (silica gel, PE:EA 90:10, 80:20) 167 mg (0.422 mmol, >98% Z, 66%) product [(S)-7c] were isolated as a mixture of diastereomers (ratio 65:35).
Compound $2g$ was prepared either via Ru-catalyzed allylic alkylation or following previously reported procedures starting from $2c$.\[7\]

**tert-Butyl 1-(2,2,2-trifluoroacetyl)-1,2,3,6-tetrahydropyridine-2-carboxylate ($8c$)**

179 mg (0.602 mmol) of alcohol $2g$ were dissolved in 13 mL abs. THF and added dropwise to a solution of 254 mg (0.959 mmol) triphenylphosphine (99%) and 196 μL (204 mg, 0.958 mmol) di-iso-propyl azodicarboxylate (95%) in 33 mL abs. THF at 0°C. The reaction was allowed to warm to room temperature overnight. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, PE:EE 90:10). 148 mg (0.530 mmol, 88%) of the desired product were obtained as a mixture of rotamers (ratio 55:45).

Colourless oil. $^1$H-NMR (400 MHz, CDCl$_3$): major rotamer: δ = 1.43 (s, 9 H, 10-H), 2.49 (m, 1 H, 4-H$_a$), 2.73 (m, 1 H, 4-H$_b$), 3.86 (m, 1 H, 1-H$_a$), 4.19 (m, 1 H, 1-H$_b$), 5.33 (dd, \(J_{5,4a} = 6.6\) Hz, \(J_{5,4b} = 1.4\) Hz, 1 H, 5-H), 5.64 (m, 1 H, 2-H), 5.83 (m, 1 H, 3-H); minor rotamer: δ = 4.35 (m, 1 H, 1-H$_a$), 4.70 (d, \(J_{5,4x} = 6.0\) Hz, 1 H, 5-H), 5.73 (m, 1 H, 2-H). $^{13}$C-NMR (100 MHz, CDCl$_3$): major rotamer: δ = 25.8 (t, C-4), 27.8 (q, C-10), 42.1 (t, C-1), 51.3 (d, C-5), 82.6 (s, C-9), 122.2 (d, C-2), 123.4 (d, C-3), 168.3 (s, C-8). Signals of the TFA-group could not be observed. minor rotamer: δ = 26.8 (t, C-4), 27.8 (q, C-10), 42.5 (t, C-1), 54.3 (d, C-5), 82.9 (s, C-9), 121.9 (d, C-2), 122.9 (d, C-3), 168.4 (s, C-8). Elementary analysis calcd for
C_{12}H_{16}F_{3}NO_{3}: C 51.61, H 5.78, N 5.02, found: C 51.76, H 5.67, N 4.98. HRMS (CI) calcd for C_{12}H_{17}F_{3}NO_{3} [M+H]^+: 280.1155, found: 280.1159.

tert-Butyl (6R,Z)-6-hydroxy-2-(2,2,2-trifluoroacetamido)hept-4-enoate (8’a)

To a solution of 76 mg (0.215 mmol) (R)-7a in 1.5 mL abs. MeOH was added a solution of 192 mg (2.16 mmol) magnesium methylate (97%) in 1.0 mL abs. MeOH at rt. The reaction was stirred for one hour before 1 M KHSO₄ solution and EA were added. The layers were separated and the aqueous phase was extracted three times with EA. The combined organic phases were dried over Na₂SO₄. After purification by column chromatography (silica gel, PE:EA 80:20) 66.6 mg (0.214 mmol, 99%) product 8’a were isolated as a mixture of diastereomers (ratio 7:3).

Colourless oil. ¹H-NMR (400 MHz, CDCl₃): major diastereomer: δ = 1.29 (d, 3 J₁,₂ = 6.4 Hz, 3 H, 1-H), 1.48 (s, 9 H, 11-H), 1.77 (bs, 1 H, OH), 2.71 (m, 2 H, 5-H), 4.37 (td, 3 J₆,₅ = 6.3 Hz, ³J₆,NH = 6.3Hz, 1 H, 6-H), 4.58 (m, 1 H, 2-H), 5.38 (m, 1 H, 4-H), 5.66 (m, 1 H, 3-H), 7.72 (bs, 1 H, NH). minor diastereomer: δ = 4.48 (m, 1 H, 6-H), 7.56 (bs, 1 H, NH). ¹³C-NMR (100 MHz, CDCl₃): major diastereomer: δ = 23.9 (q, C-1), 27.9 (q, C-11), 29.6 (t, C-5), 52.7 (d, C-6), 63.4 (d, C-2), 83.2 (s, C-10), 125.3 (d, C-4), 137.6 (d, C-3), 169.4 (s, C-9). Signals of the TFA-group could not be observed. minor diastereomer: δ = 23.8 (q, C-1), 29.4 (t, C-5), 52.5 (d, C-6), 63.6 (d, C-2), 83.3 (s, C-10) 124.1 (d, C-4), 138.0 (d, C-3) 169.1 (s, C-9). HRMS (CI) calcd for C_{13}H_{21}F_{3}NO_{4} [M+H]^+: 312.1417, found: 312.1389.

tert-Butyl (6S)-6-methyl-1-(2,2,2-trifluoroacetyl)-1,2,3,6-tetrahydropyridine-2-carboxylate (8a)

A solution of 322 mg (1.03 mmol) 8’a were dissolved in 30 mL abs. THF and added to a solution of 438 mg (1.65 mmol) triphenylphosphine (99%) and 333 μL (341 mg, 1.60 mmol) di-iso-propyl azodicarboxylate (95%) in 70 mL abs. THF at 0°C. The reaction was allowed to warm to room temperature overnight. The solvent was evaporated and the crude product was purified by column chromatography (silica gel, PE:EA 90:10) to give 242 mg (0.825 mmol, 80%) product 8a as a mixture of diastereomers (ratio 7:3).

Colourless oil. ¹H-NMR (400 MHz, CDCl₃): major diastereomer: δ = 1.36 (d, 3 J₁,₂ = 6.8 Hz, 3 H, 1-H), 1.45 (s, 9 H, 11-H), 2.36 (m, 1 H, 5-Hₐ), 2.77 (m, 1 H, 5-Hₖ), 4.65 (m, 2 H, 2-H, 6-H), 5.64 (m, 1 H, 3-H), 5.82 (m, 1 H, 4-H). minor diastereomer: δ = 1.48 (s, 9 H, 11-H), 1.75
(m, 3 H, 1-H), 4.22 (m, 1 H, 6-H), 4.51 (m, 1 H, 2-H), 5.34 (m, 1 H, 6-H), 5.49 (m, 1 H, 3-H).

$^{13}$C-NMR (100 MHz, CDCl$_3$): major diasteromer: $\delta = 19.3$ (q, C-1), 25.6 (t, C-5), 27.8 (q, C-11), 49.2 (d, C-2), 53.6 (d, C-6), 82.9 (s, C-10), 121.4 (d, C-4), 128.5 (d, C-3), 168.6 (s, C-9).

Signals of the TFA-group could not be observed. minor diastereomer: $\delta = 26.5$ (t, C-5), 27.9 (q, C-11), 50.0 (d, C-2). HRMS (Cl) calcd for C$_{13}$H$_{19}$F$_{3}$NO$_{3}$ [M+H]$^+$: 294.1312, found: 294.1310.
3) Copies of nmr spectra
Chemical Shift (ppm)

Normalized Intensity

CHLOROFORM-d

OSi

OH

3
(S)-4

**Chemical Shift (ppm)**

- CHLOROFORM-d
  - 7.260
  - 5.617
  - 5.603
  - 5.589
  - 5.575
  - 5.562
  - 5.547
  - 5.545
  - 5.542
  - 5.517
  - 4.646
  - 4.630
  - 4.614
  - 4.597
  - 4.329
  - 4.324
  - 4.312
  - 4.290
  - 4.279
  - 4.225
  - 4.215
  - 4.194

**Normalized Intensity**

- S22
  - 6.05
  - 9.00
  - 2.80
  - 0.71
  - 0.95
  - 1.10
  - 0.92
  - 1.77

**OHO**

- CHLOROFORM-d
  - 135.607
  - 129.774
  - 77.000
  - 63.927
  - 59.056
  - 23.314
  - 6.676
  - 4.357
4) References


