DOI: 10.1002/ejoc.201101398

(*E*)-Dimethyl 2-Oxopent-3-enylphosphonate: An Excellent Substrate for Cross-Metathesis – Easy Access to Functionalized Heterocycles

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Keywords: Phosphorus / Heterocycles / Metathesis / Michael addition / Tandem reaction

Simple and efficient access to tetrahydrofurans, tetrahydropyrans, and pyrrolidines through a tandem cross-metathesis/1,4-addition process from (*E*)-dimethyl 2-oxopent-3-enylphosphonate and *N*-protected ω-unsaturated amines or alcohols under microwave irradiation is described. As the Grubbs–Hoveyda catalyst is highly chemoselective, a diversity of functionalized heterocycles were synthesized. Furthermore, an additional functionalization can be performed due to the presence of a side chain that possesses a ketophosphonate at the C2 position of the heterocycle.

Introduction

Nowadays, cross-metathesis (CM) is considered as an atom economical reaction that allows the construction of di- and trisubstituted C=C bonds under mild conditions.[1] Due to the development of active and stable catalysts such as [Ru]-**I**,[2] [Ru]-**II**,[3] [Ru]-**III**,[4] and [Ru]-**IV**[5] (Figure 1) and due to the chemoselectivity of these catalysts, the olefin partners can be substituted by a variety of functional groups such as a hydroxy, a ketone, an ester, an amide, an ether, or a protected amine. Furthermore, the ruthenium catalysts, either by themselves or by in situ modification, can induce tandem reactions.[6] One-pot sequential reactions[7] can also take place due to the compatibility of the ruthenium catalysts with other catalysts and/or reagents.[8]

During the past decade, some examples of tandem CM/1,4-addition have been described. Hex-1-enols have been coupled with enones to obtain tetrahydropyran skeletons by using catalyst [Ru]-**III**.[9,10] It has also been reported that ω-unsaturated protected amines,[11] sulfinylamines,[12] pyrroles,[13] and indoles[14] can be involved in a tandem CM/aza-Michael sequence. However, in most cases the presence of additives such as $BF_3{\cdot}OEt_2$, $Ti(OiPr)_4$, or phosphoric acid was required to induce an aza-Michael reaction.[11,12,14]

Here, we report that a CM can be performed between γ,δ-unsaturated β-ketophosphonate **1** and functionalized olefins **A** to produce enones **B**. Furthermore, heterocycles of type **E** can be obtained from **1** and suitable olefins **D**, according to a tandem CM/1,4-addition without any additive (Scheme 1). It is worth noting that β-ketophosphonates **B** and **E** can be involved in a Horner–Wadsworth–Emmons reaction (HWE) for further functionalization to produce unsymmetrical dienones **C** or heterocycles **F** that can be useful precursors to synthesize a variety of products.

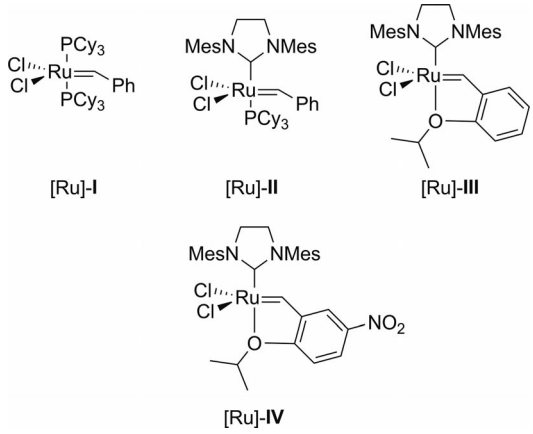

Figure 1. Ruthenium catalysts.

Results and Discussion

The synthesis of the known phosphonate **1** was achieved, according to the described literature procedure, by treatment of dimethyl methylphosphonate (2 equiv.) with *n*BuLi (2.2 equiv., THF, –78 °C) followed by the addition of (*E*)-methyl but-2-enoate (1 equiv., –78 °C → r.t., 16 h).[15] The resulting γ,δ-unsaturated β-ketophosphonate **1** was isolated in 90–94% yield (Scheme 2).

The CM reaction involving **1** was performed with different ω-unsaturated alcohols and *N*-protected ω-unsaturated amines. When but-3-en-1-ol (**2a**) (1 equiv.) was treated with [Ru]-**II** (5 mol-%) at room temperature for 16 h in the

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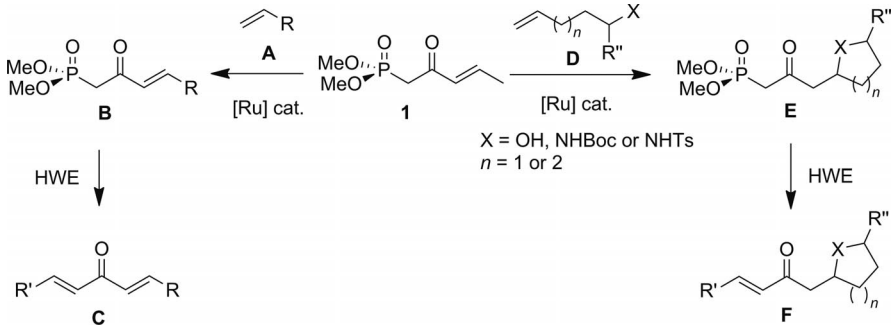
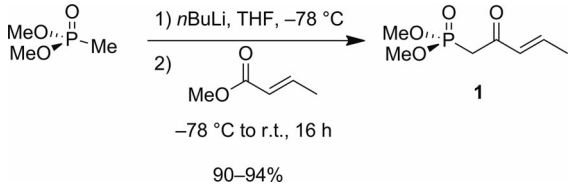
Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/ejoc.201101398.



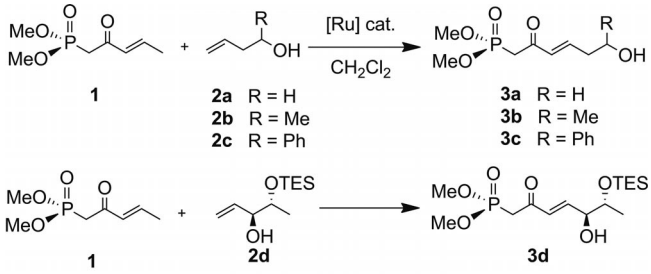
Scheme 1. General scheme.



Scheme 2. Preparation of **1**.

presence of **1** (3 equiv.), CM product **3a** was obtained in 10% yield (Table 1, Entry 1). Increasing the amount of catalyst to 10 mol-% and heating the reaction at 40 °C allowed the isolation of **3a** in 70% yield (Table 1, Entry 2). When a stoichiometric amount of **1** and **2a** was treated with [Ru]-**III** (5 mol-%) at room temperature for 16 h only trace amounts of **3a** were observed (Table 1, Entry 3). Increasing the amount of **1** to 3 equiv. and performing the reaction at room temperature for 16 h furnished **3a** in 75% yield (Table 1, Entry 4). Under these latter conditions, substituted butenol **2b** was converted into **3b** in 14% yield and no trace amounts of CM product **3c** were observed from 1-phenyl-but-3-enol (**2c**) (Table 1, Entries 5 and 6). These conditions furnished cross-metathesis product **3d** in only 15% yield from monoprotected diol **2d**; however, when the CM between **1** and **2d** was performed under microwave irradiation (100 °C, 2 × 15 min) and after two consecutive additions of 5 mol-% of [Ru]-**III** catalyst,[16] **3d** was isolated in 53% yield (Table 1, Entries 7 and 8). It is worth noting that when the CM was performed between **1** and 1-methyl- or 1-phenylprop-2-en-1-ol, only homodimers of the allylic alcohols were formed, even under microwave irradiation.

Table 1. CM with homoallylic alcohols.

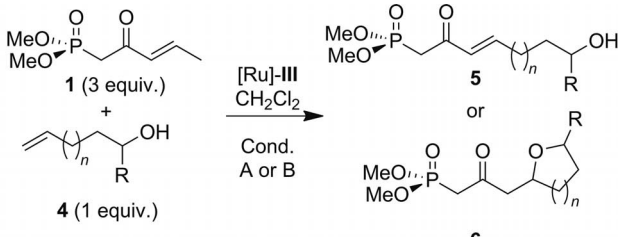


Entry	1 (equiv.)	2 (1 equiv.)	Cat. (mol-%)	*T*, t	Product (% yield)
1	3	**2a**	[Ru]-**II** (5)	r.t., 16 h	**3a** (10)
2	3	**2a**	[Ru]-**II** (10)	40 °C, 4 h	**3a** (70)
3	1	**2a**	[Ru]-**III** (5)	r.t., 16 h	**3a** (trace)
4	3	**2a**	[Ru]-**III** (5)	r.t., 16 h	**3a** (75)
5	3	**2b**	[Ru]-**III** (5)	r.t., 16 h	**3b** (14)
6	3	**2c**	[Ru]-**III** (5)	rt, 16 h	**3c** (0)
7	3	**2d**	[Ru]-**III** (5)	r.t., 16 h	**3d** (15)
8	3	**2d**	[Ru]-**III** (2 x 5)	100 °C μW 2 x 15 min	**3d** (53)

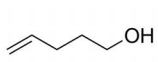
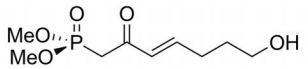
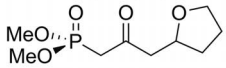
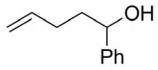
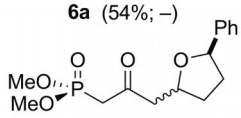
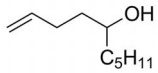
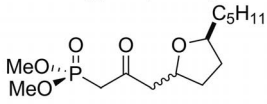
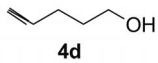
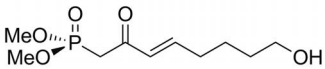
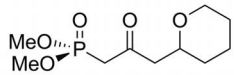
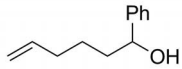
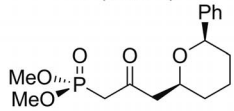
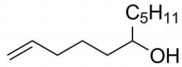
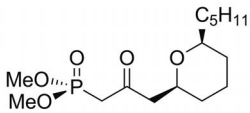
When a CM was achieved between pent-1-en-5-ol (**4a**) and **1** in the presence of [Ru]-**III** (5 mol-%) in CH_2Cl_2 at room temperature for 16 h (conditions A), **5a** was isolated in only 15% yield (Table 2, Entry 1). By forcing the conditions, for example, by performing the reaction at 100 °C under microwave irradiation for 30 min with two successive additions of [Ru]-**III** (2 × 5 mol-%) every 15 min (conditions B), functionalized tetrahydrofuran **6a** was isolated in 54% yield (Table 2, Entry 2). The formation of this product can be explained by a CM/oxa-Michael cascade sequence, probably due to the activation of the unsaturated ketone either by the ruthenium intermediate [Ru]-**III**′,[11] which can act as a Lewis acid, or by a ruthenium hydride species resulting from the thermal decomposition of [Ru]-**III**′ (Scheme 3).[9,17] This cascade reaction is general, as **6b** and **6c** were formed from **4b** and **4c**, respectively, in good yields (77% to quant.); however, the diastereoselectivity was poor (*dr* ≈ 1:1–1.5:1; Table 2, Entries 3 and 4). As for but-3-en-1-ol (**4a**), when hex-5-en-1-ol (**4d**) was engaged in a CM, the obtained products were enone **5d** (20%) under conditions A and tetrahydropyran **6d** (46%) under conditions B (Table 2, Entries 5 and 6). Thus, when α-substituted hexenols **4e** and **4f** (Table 2, Entries 7 and 8) were engaged in a CM under conditions B, the corresponding disubstituted tetrahydropyrans **6e** and **6f** were isolated in excellent yield (90% and 80%) with excellent diastereoselectivities (>98:2) in favor of the *cis*-isomers.

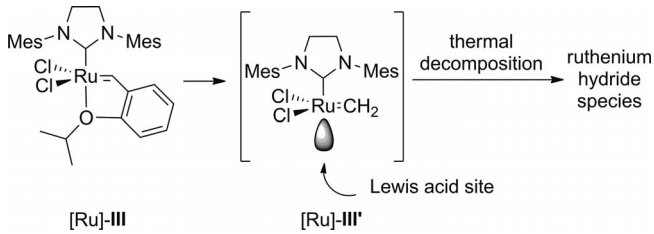
As the ruthenium catalyst [Ru]-**III** can induce a CM/1,4-addition cascade, the reactivity of ω-unsaturated *N*-protected amines **7a**–**g** was examined to synthesize function-

Table 2. CM with pent-4-en-1-ols and hex-5-en-1-ols.



Cond. A = [Ru]-**III** (5 mol-%), CH_2Cl_2, r.t., 16 h
Cond. B = [Ru]-**III** (2 x 5 mol-%), CH_2Cl_2, 100 °C μW, 2 x 15 min

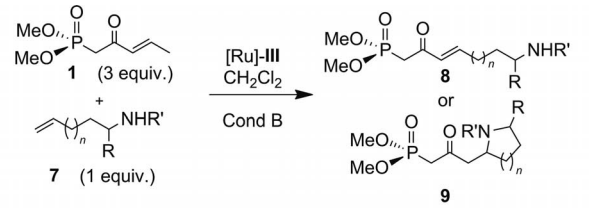
Entry	Alcohol	Conditions	Product (Yield; *dr*)
1	 **4a**	A	 **5a** (15%; –)
2	**4a**	B	 **6a** (54%; –)
3	 **4b**	B	 **6b** (quant.; 60:40)
4	 **4c**	B	 **6c** (77%; 1:1)
5	 **4d**	A	 **5d** (20%; –)
6	**4d**	B	 **6d** (46%; –)
7	 **4e**	B	 **6e** (90%; >98:2)
8	 **4f**	B	 **6f** (80%; >98:2)

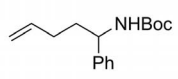
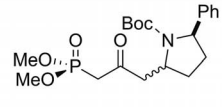
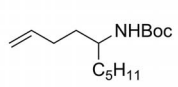
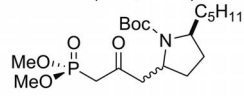
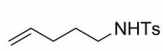
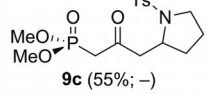
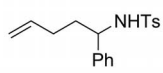
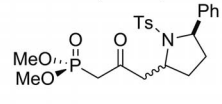
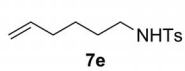
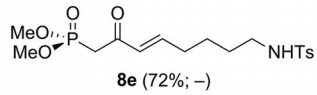
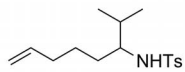
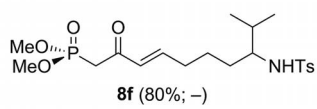
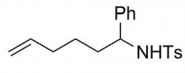
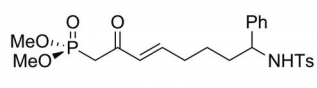


Scheme 3. Possible catalysts for the 1,4-addition.

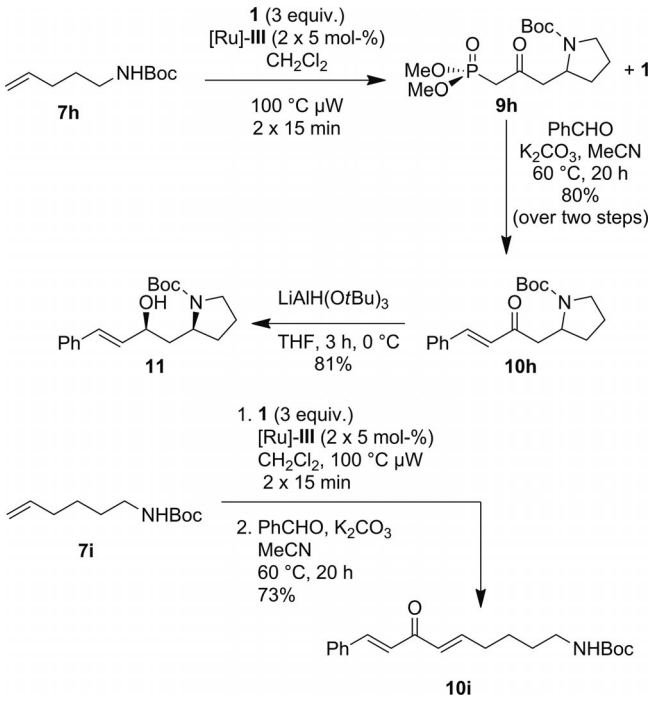
alized pyrrolidines and piperidines. When ω-unsaturated *tert*-butylcarbamates such as **7a** and **7b** were involved in a CM reaction with **1** {[Ru]-**III** (2 × 5 mol-%), CH_2Cl_2, 100 °C, μW, 2 × 15 min}, they were converted into pyrrolidines **9a** and **9b**, respectively, in moderate yields and selectivities (65–43%; *dr* = 70:30; Table 3, Entries 1 and 2). When ω-unsaturated *N*-tosylamine **7c** was involved in CM with **1**, pyrrolidine **9c** was isolated in 55% yield and substituted *N*-tosylamine **7d** was converted into **9d** (60%) with a good diastereomeric ratio of 80:20 (Table 3, Entries 3 and 4). Again, the overall process was efficient and provided substituted pyrrolidines in good yields with good diastereoselectivities. Unfortunately, when *N*-tosyl-hex-5-enamines **7e**–**g** were used, only CM products **8e**–**g** were obtained in good yield (72–88%) and no trace amounts of the corresponding cyclized products were detected (Table 3, Entries 5–7).

Table 3. CM with unsaturated *N*-protected amines.



Entry	Amine	Product (Yield; *dr*)
1	 **7a**	 **9a** (65%; 70:30)
2	 **7b**	 **9b** (43%; 70:30)
3	 **7c**	 **9c** (55%; –)
4	 **7d**	 **9d** (60%; 80:20)
5	 **7e**	 **8e** (72%; –)
6	 **7f**	 **8f** (80%; –)
7	 **7g**	 **8g** (88%; –)

It is worth noting that for compound **7h** (Scheme 4), pyrrolidine **9h** was formed but, as its polarity was similar to that of phosphonate **1**, **9h** could not be separated from the excess amount of phosphonate **1** (Scheme 4). In order to achieve the purification of **9h**, a HWE reaction was performed on the mixture of **1**/CM product by using benzaldehyde. Thus, **7h** was engaged in the CM/1,4-addition cascade and after chromatography on silica gel, the isolated mixture, constituted by **1** and **9h**, was engaged in a HWE reaction to produce enone **10h** in 80% yield from **7h** over the two-step sequence (Scheme 4). Compound **10h** can be diastereoselectively reduced by using $LiAlH(OtBu)_3$[18] to produce hydroxypyrrolidine **11**, which can be a useful building block to access natural products and/or biologically active compounds.[19]



Scheme 4. CM with ω-unsaturated carbamates.

ω-Unsaturated carbamate **7i** was also engaged in this two-step process. As for *N*-tosyl-hex-5-enamines, the formation of the desired piperidine was not observed and the CM product was the only product formed that gave, after a HWE reaction, unsymmetrical divinyl ketone **10i** in 73% yield.

Conclusions

In summary, we have developed a CM reaction involving γ,δ-unsaturated β-ketophosphonate **1** catalyzed by [Ru]-**III**. Depending on the olefinic partners and conditions, a CM/1,4-addition sequence can take place without any additives to furnish functionalized tetrahydrofurans, tetrahydropyrans, and pyrrolidines. These functionalized heterocycles are interesting building blocks that can be involved in the synthesis of natural products and/or bioactive compounds.

Experimental Section

General Remarks: Infrared (IR) spectra were recorded with a Bruker Tensortm 27 (IRFT) on an ATR plate. NMR was performed with a Bruker Avance-1 400 instrument. ^1H NMR spectra were recorded at 400 MHz in $CDCl_3$ and data are reported as follows: chemical shift in ppm from tetramethylsilane as an internal standard, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, quint. = quintuplet, m = multiplet or overlap of non-equivalent resonances, br. = broad), integration. ^{13}C NMR spectra were recorded at 100 MHz in $CDCl_3$ and data are reported as follows: chemical shift in ppm from tetramethylsilane with the solvent as an internal indicator ($CDCl_3$, δ = 77.16 ppm), multiplicity, with respect to proton (deduced from DEPT experiments, s = quaternary C, d = CH, t = CH_2, q = CH_3). High-resolution mass spectra (HRMS) were performed by the Groupe de Spectrométrie de Masse de l'Université Pierre et Marie Curie (Paris-France). Optical rotations were measured with a Perkin–Elmer model 343 polarimeter with a 1-dm path length. TLC was performed on Merck 60F254 silica gel plates with UV and Hanessian stain or *para*-anisaldehyde. CH_2Cl_2 was distilled from CaH_2, and Et_2O and THF were distilled from sodium/benzophenone. Phosphonate **1**[15] and olefins **2c**,[20] **4b**,[21] **4c**,[22] **4e**,[21] **4f**,[23] **7a**,[22] **7c**,[22] **7d**,[24] **7e**,[25] **7f**,[26] **7g**,[26] **7h**,[27] and **7i**[28] were obtained following existing procedures. Other reagents were obtained from commercial suppliers and used as received. Flash column chromatography was performed on silica gel (230–400 mesh). Diastereomeric ratios were measured by examination of the ^1H NMR spectrum of the crude material. All reactions were performed under an argon atmosphere.

General Procedure for CM Reactions

Method A: To a solution of phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.) and olefin (0.2 mmol, 1 equiv.), in anhydrous CH_2Cl_2 (1.5 mL) at room temperature was added catalyst [Ru]-**II** (6 mg, 5 mol-%) or [Ru]-**III** (6 mg, 5 mol-%) in one portion. After 16 h at room temperature, the reaction mixture was evaporated and purified by flash chromatography on silica gel to afford the title compound. In some cases, a second purification by medium-pressure liquid chromatography (MPLC, AcOEt) was required to separate the products.

Method B: To a solution of phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.) and olefin (0.2 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (1.5 mL), in a microwave vial at room temperature was added catalyst [Ru]-**III** (6 mg, 5 mol-%) in one portion. The vial was sealed and heated under microwave irradiation. After 15 min at 100 °C, a second portion of [Ru]-**III** (6 mg, 5 mol-%) was added, and the reaction was heated for 15 min at 100 °C. Evaporation of the volatiles and purification by flash chromatography afforded the title compound. In some cases, a second purification by medium-pressure liquid chromatography (MPLC, AcOEt) was required to separate the products.

Method C: To a solution of phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.) and olefin (0.2 mmol, 1 equiv.) in anhydrous CH_2Cl_2 (1 mL) at room temperature was added catalyst [Ru]-**II** (12 mg, 10 mol-%) in one portion. After 4 h at 40 °C, the reaction mixture was evaporated and purified by flash chromatography on silica gel to afford the title compound.

(3*S*,4*R*)-4-Triethylsilyloxypent-1-en-3-ol and (3*R*,4*R*)-4-Triethylsilyloxypent-1-en-3-ol (2d): To a solution of (*R*)-isobutyl lactate (7.02 g, 48 mmol, 1 equiv.) in DMF (50 mL) at room temperature was added imidazole (3.88 g, 57 mmol, 1.2 equiv.) and TESCl (8.5 mL, 50 mmol, 1.1 equiv.). After 1.5 h of stirring, the reaction

was quenched with H_2O (20 mL). The aqueous layer was extracted with Et_2O (4 × 50 mL), and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated under reduced pressure to afford isobutyl (2*R*)-2-(triethylsilyloxy)propionate (**2d**-1; 12.48 g, 47.8 mmol) as a colorless oil. Yield: 99%. $[\alpha]_D^{20}$ = +25.3 (*c* = 0.04, $CHCl_3$). IR: $\tilde{\nu}$ = 2957, 2878, 2360, 2341, 1757, 1459, 1143, 1002 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.34 (q, *J* = 6.7 Hz, 1 H), 3.90 (dd_{systAB}, *J* = 10.4, 6.8 Hz, 1 H), 3.86 (dd_{systAB}, *J* = 10.4, 6.7 Hz, 1 H), 1.96 ($nonuplet_{app}$, *J* = 6.8 Hz, 1 H), 1.41 (d, *J* = 6.7 Hz, 3 H), 0.99 (m, 15 H), 0.63 (q, *J* = 7.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 174.1 (s), 70.8 (t), 68.1 (d), 27.7 (d), 21.5 (q), 19.0 (q, 2 C), 6.6 (q, 3 C), 4.6 (t, 3 C) ppm. MS (EI): *m*/*z* (%) = 246 (1) $[M - Me]^+$, 217 (100), 189 (86), 161 (48), 133 (23), 105 (26), 94 (14), 80 (25), 66 (27), 59 (20). HRMS (ESI): calcd. for $C_{13}H_{28}O_3NaSi$ $[M + Na]^+$ 283.1700 found 283.1692. To a solution of **2d**-1 (2.6 g, 10 mmol, 1 equiv.) in anhydrous Et_2O (40 mL) at –78 °C was added DIBAL-H (1 M in hexanes, 15 mL, 15 mmol, 1.5 equiv.), and the reaction mixture was warmed to room temperature. After 1.5 h, the reaction was quenched with H_2O (20 mL), and the precipitate was dissolved in Et_2O (20 mL). The aqueous layer was then extracted with Et_2O (3 × 30 mL), and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated under vacuum. Purification by flash chromatography (PE to PE/Et_2O = 10:1) afforded (2*R*)-2-triethylsilyloxypropionaldehyde (**2d**-2; 1.35 g, 7.2 mmol) as a colorless oil. Yield: 72%. Spectral data match those previously described in the literature for (2*S*)-**2d**-2.[29] $[\alpha]_D^{20}$ = +10 (*c* = 1.56, $CHCl_3$) {ref.[29] for *ent*-**2d**-2: $[\alpha]_D^{20}$ = –11.5 (*c* = 1.55, $CHCl_3$)}. IR: $\tilde{\nu}$ = 2957, 2878, 1739, 1459, 1415, 1375, 1240, 1134, 1096, 1007 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 9.63 (d, *J* = 1.6 Hz, 1 H), 4.09 (qd, *J* = 6.8, 1.6 Hz, 1 H), 1.29 (d, *J* = 6.8 Hz, 3 H), 0.98 (t, *J* = 7.9 Hz, 9 H), 0.64 (q, *J* = 7.9 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 204.3 (s), 73.5 (d), 18.6 (q), 6.7 (q, 3 C), 4.7 (t, 3 C) ppm. MS (EI): *m*/*z* (%) = 189 (1), 159 (76), 132 (11), 131 (100), 129 (11), 115 (46), 113 (13), 103 (29), 101 (19), 87 (69), 75 (23), 59 (38), 58 (12), 57 (11). HRMS (ESI): calcd. for $C_{10}H_{24}O_3NaSi$ $[M + Na + MeOH]^+$ 243.1387; found 243.1388. To a solution of vinylmagnesium chloride (1.6 M in THF, 4 mL, 6.4 mmol, 1.2 equiv.) in anhydrous THF (7.5 mL) at –60 °C was added a solution of **2d**-2 (1 g, 5.3 mmol, 1 equiv.) in THF (7.5 mL) by cannula, and the reaction was warmed to room temperature. After 2 h the reaction was quenched with aqueous saturated NH_4Cl (10 mL) and H_2O was added (10 mL). The aqueous layer was extracted with Et_2O (3 × 40 mL), and the combined organic layers were dried with $MgSO_4$, filtered, and concentrated under vacuum to afford **2d** (0.92 g, 4.2 mmol) as a mixture of *syn*/*anti*-diastereoisomers in a 1:4 ratio. Yield: 80%. IR: $\tilde{\nu}$ = 3445, 2955, 2877, 1458, 1415, 1378, 1238, 1129, 1088, 1003 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, *anti* diastereoisomer): δ = 5.75 (br. ddd, *J* = 17.3, 10.6, 6.0 Hz, 1 H), 5.23 (dt, *J* = 17.5, 1.6 Hz, 1 H), 5.12 (dt, *J* = 10.7, 1.6 Hz, 1 H), 3.98 (m, 1 H), 3.79 (qd, *J* = 6.4, 3.6 Hz, 1 H), 2.27 (br. s, 1 H), 1.02 (d, *J* = 6.3 Hz, 3 H), 0.90 (t, *J* = 7.9 Hz, 9 H), 0.55 (q, *J* = 7.6 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, *anti* diastereoisomer): δ = 136.8 (d), 116.6 (t), 76.9 (d), 71.3 (d), 17.7 (q), 7.0 (q, 3 C), 5.2 (t, 3 C) ppm. ^1H NMR (400 MHz, $CDCl_3$, *syn* diastereoisomer): δ = 5.75 (br. ddd, *J* = 17.3, 10.6, 6.0 Hz, 1 H), 5.23 (dt, *J* = 17.5, 1.6 Hz, 1 H), 5.12 (dt, *J* = 10.7, 1.6 Hz, 1 H), 3.73 (m, 1 H), 3.61 ($quint._{app}$, *J* = 6.2 Hz, 1 H), 2.58 (br. s, 1 H), 1.09 (d, *J* = 6.2 Hz, 3 H), 0.90 (t, *J* = 7.9 Hz, 9 H), 0.55 (q, *J* = 8.0 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, *syn*): δ = 137.7 (d), 117.1 (t), 77.2 (d), 71.9 (d), 20.2 (q), 7.0 (q, 3 C), 5.2 (t, 3 C) ppm. MS (EI): *m*/*z* (%) = 187 (85) $[M - Et]^+$, 169 (10), 159 (67), 115 (72), 103 (100), 87 (55), 75 (62), 59 (21). HRMS (ESI): calcd. for $C_{11}H_{24}O_2NaSi$ $[M + Na]^+$ 239.1438; found 239.1438.

Dimethyl [(*E*)-6-Hydroxy-2-oxohex-3-en-1-yl]phosphonate (3a)

Method A: But-3-en-1-ol (**2a**; 14 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**II** (6 mg, 5 mol-%) led to **3a** (5 mg, 0.024 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 95:5), as a brown oil. Yield: 10%.

Method A: But-3-en-1-ol (**2a**; 14 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (6 mg, 5 mol-%) led to **3a** (34 mg, 0.15 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 95:5) as a brown oil. Yield: 75%.

Method C: But-3-en-1-ol (**2a**; 14 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**II** (6 mg, 5 mol-%) led to **3a** (22 mg, 0.10 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 95:5) as a brown oil. Yield: 70%. IR: $\tilde{\nu}$ = 3378, 2853, 1691, 1663, 1624, 1447, 1406, 1239, 1183, 1020 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.94 (dt, *J* = 16.0, 7.2 Hz, 1 H), 6.23 (br. d, *J* = 16.0 Hz,1 H), 3.76 (t_{app}, *J* = 6.0 Hz, 2 H), 3.73 (d, $^3J_{H,P}$ = 11.3 Hz, 6 H), 3.12 (d, $^2J_{H,P}$ = 22.6 Hz, 2 H), 3.00 (br. s, 1 H), 2.46 (br. q_{app}, *J* = 6.5 Hz, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0 (s, $^2J_{C,P}$ = 6.0 Hz), 148.2 (d), 131.8 (d), 60.6 (t), 53.1 (q, $^2J_{C,P}$ = 6.8 Hz, 2 C), 38.8 (t, $^1J_{C,P}$ = 128.3 Hz), 35.9 (t) ppm. HRMS (ESI): calcd. for $C_8H_{15}O_5PNa$ $[M + Na]^+$ 245.0549; found 245.0542.

Dimethyl [(*E*)-6-Hydroxy-2-oxohept-3-enyl]phosphonate (3b): According to method A, 1-phenylbut-3-enol (**2b**; 30 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (6 mg, 5 mol-%) led to **3b** (6.6 mg, 0.028 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 95:5) as a brown oil. Yield: 14%. IR: $\tilde{\nu}$ = 3408, 2961, 2925, 2854, 1691, 1667, 1626, 1251, 1029 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.97 (ddd, *J* = 16.0, 7.6, 6.8 Hz, 1 H), 6.19 (dt_{app}, *J* = 5.9, 1.4 Hz, 1 H), 3.99 ($sext._{app}$, *J* = 5.9 Hz, 1 H), 3.75 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.74 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.26 (t_{app}, $^2J_{H,P}$ = $^1J_{H,P}$ = 22.8 Hz, 1 H), 3.22 (t_{app}, $^2J_{H,P}$ = $^1J_{H,P}$ = 22.8 Hz, 1 H), 2.47–2.28 (m, 3 H), 1.24 (d, *J* = 6.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2 (s, $^2J_{C,P}$ = 6.0 Hz), 148.2 (d), 132.5 (d), 67.0 (d), 53.4 (q, $^2J_{C,P}$ = 7.0 Hz, 2 C), 42.6 (t), 39.3 (t, $^1J_{C,P}$ = 127.4 Hz), 23.4 (q) ppm. HRMS (ESI): calcd. for $C_9H_{17}O_5PNa$ $[M + Na]^+$ 259.0706; found 259.0701.

Dimethyl [(*E*)-(5*S*,6*R*)-5-Hydroxy-2-oxo-6-(*tert*-butyldimethyl-silyloxy)hept-3-enyl]phosphonate (3d)

Method A: Alcohol **2d** (43 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (12 mg, 10 mol-%) led to **3d** (6 mg, 0.03 mmol) after purification on silica gel (EP/AcOEt = 40:60) as a brown oil. Yield: 15%.

Method B: Alcohol **2d** (43 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **3d** (39 mg, 0.11 mmol) after purification on silica gel (EP/AcOEt = 40:60) as a brown oil. Yield: 53% IR: $\tilde{\nu}$ = 3372, 2956, 2919, 2877, 2359, 1693, 1667, 1629, 1459, 1413, 1377, 1242, 1031 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.84 (dd, *J* = 15.8, 4.5 Hz, 1 H), 6.48 (dd, *J* = 15.8, 1.5 Hz, 1 H), 4.29 (br. td_{app}, *J* = 6.2, 3.9 Hz, 1 H), 3.96 (dq, *J* = 6.2, 3.9 Hz, 1 H), 3.77 (d, *J* = 11.3 Hz, 6 H), 3.23 (d, *J* = 22.0 Hz, 2 H), 2.60 (m, 1 H), 1.10 (d, *J* = 6.3 Hz, 3 H), 0.96 (t, *J* = 7.9 Hz, 9 H), 0.61 (q, *J* = 7 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.8 (s, $^2J_{C,P}$ = 7.0 Hz), 146.6 (d), 129.2 (d), 75.0 (d), 70.5 (d) 53.1 (q, $^2J_{C,P}$ = 6.0 Hz, 2 C), 39.7 (t, $^1J_{C,P}$ = 128.8 Hz), 17.9 (q), 6.7 (q, 3 C), 4.9 (t, 3 C) ppm. MS (EI): *m*/*z* (%) = 322 (1), 304 (100), 303 (79), 289 (13), 158 (13). HRMS (ESI): calcd. for $C_{15}H_{31}O_6PSiNa$ $[M + Na]^+$ 389.1520; found 389.1523.

Dimethyl [(*E*)-7-Hydroxy-2-oxohept-3-en-1-yl]phosphonate (5a): According to method A, alcohol **4a** (17 mg, 0.2 mmol, 1 equiv.), phos-

phonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (6 mg, 5 mol-%) led to **5a** (7 mg, 0.03 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 90:10) as a brown oil. Yield: 15%. IR: $\tilde{\nu}$ = 3417, 2957, 2923, 1715, 1692, 1665, 1625, 1449, 1406, 1250, 1029 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.95 (m, 1 H), 6.24 (m, 1 H), 3.75 (m, 6 H), 3.66 (br. t, J = 6.4 Hz, 2 H), 3.20 (d, $^2J_{H,P}$ = 22.8 Hz, 2 H), 2.35 (br. q_{app}, J = 7.3 Hz, 2 H), 1.75 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0 (s), 150.1 (d), 130.4 (d), 61.9 (t), 53.1 (q, $^2J_{C,P}$ = 6.3 Hz, 2 C), 39.2 (t, $^1J_{C,P}$ = 129.0 Hz), 30.9 (t), 29.2 (t) ppm. MS (EI): *m*/*z* (%) = 193 (22), 166 (19), 151 (63), 127 (11), 126 (67), 124 (100), 119 (18), 111 (44), 109 (68), 95 (10), 94 (76), 85 (23), 79 (53), 71 (62), 55 (12). HRMS (ESI): calcd. for $C_9H_{17}O_5NaP$ $[M + Na]^+$ 259.0706; found 259.0711.

Dimethyl [(*E*)-8-Hydroxy-2-oxooct-3-en-1-yl]phosphonate (5d): According to method A, alcohol **4d** (20 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (6 mg, 5 mol-%) led to **5d** (10 mg, 0.4 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 90:10) as a brown oil slightly polluted by the cyclic product. Yield: 20%. IR: $\tilde{\nu}$ = 3421, 2925, 2854, 1716, 1691, 1664, 1625, 1457, 1405, 1250, 1028 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 6.95 (dt, J = 16.0, 6.8 Hz, 1 H), 6.24 (br. dt, J = 16.0, 1.4 Hz, 1 H), 3.78 (d, $^3J_{H,P}$ = 11.2 Hz, 6 H), 3.65 (br. t, J = 5.6 Hz, 2 H), 3.22 (d, $^2J_{H,P}$ = 22.4 Hz, 2 H), 2.34–2.24 (m, 2 H), 1.63–1.58 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.1 (s), 150.6 (d), 130.4 (d), 62.4 (t), 53.2 (q, $^2J_{C,P}$ = 6.7 Hz, 2 C), 39.3 (t, $^1J_{C,P}$ = 129.0 Hz), 32.4 (t), 32.1 (t), 29.2 (t) ppm. MS (EI): *m*/*z* (%) = 232 (5), 166 (20), 151 (83), 140 (87), 135 (12), 125 (52), 124 (100), 122 (10), 119 (19), 111 (16), 109 (76), 99 (22), 98 (13), 95 (11), 94 (67), 93 (11), 85 (27), 79 (47), 67 (18), 57 (21), 55 (33). HRMS (ESI): calcd. for $C_{10}H_{19}O_5PNa$ $[M + Na]^+$ 273.0862; found 273.0861.

Dimethyl [2-Oxo-3-(tetrahydrofuran-2-yl)propyl]phosphonate (6a): According to method B, alcohol **4a** (17 mg, 0.2 mmol, 1 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **6a** (25 mg, 0.11 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 90:10) as a brown oil. Yield: 54%. IR: $\tilde{\nu}$ = 2956, 2926, 2855, 1714, 1462, 1385, 1253, 1185, 1025 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 4.23 (m, 1 H), 3.86 (m, 1 H), 3.81–3.67 (m, 7 H), 3.25–3.08 (m, 2 H), 2.88 (dd_{systAB}, J = 16.1, 7.4 Hz,1 H), 2.77 (dd_{systAB}, J = 16.1, 5.4 Hz, 1 H), 2.10 (m, 1 H), 1.96–1.83 (m, 2 H), 1.50 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5 (s), 74.8 (d), 66.0 (t), 53.1 (q, $^2J_{C,P}$ = 6.0 Hz, 2 C), 49.8 (t), 42.0 (t, $^1J_{C,P}$ = 128.2 Hz), 31.5 (t), 25.5 (t) ppm. MS (EI): *m*/*z* (%) = 218 (1), 193 (18), 166 (17), 151 (68), 126 (69), 124 (100), 119 (16), 111 (53), 109 (67), 94 (76), 85 (24), 79 (45), 71 (58), 55 (11). HRMS (ESI): calcd. for $C_9H_{17}O_5PNa$ $[M + Na]^+$ 259.0706; found 259.0702.

Dimethyl [2-Oxo-3-(5-phenyltetrahydrofuran-2-yl)propyl]phosphonate (6b): According to method B, alcohol **4b** (32 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **6b** (63 mg, 0.2 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: quant. as a mixture of 2 diastereomers in a 60:40 ratio. IR: $\tilde{\nu}$ = 2957, 1714, 1453, 1255, 1026 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, major diastereomer): δ = 7.34–7.21 (m, 5 H), 4.87 (t_{app}, ^3J = 7.4 Hz, 1 H), 4.43 (m, 1 H), 3.78 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.77 (d, $^3J_{H,P}$ = 10.8 Hz, 3 H), 3.29–3.15 (m, 2 H), 3.08 (dd_{systAB}, ^2J = 16.2, 7.0 Hz, 1 H), 2.88 (dd_{systAB}, ^2J = 16.2, 5.8 Hz, 1 H), 1.93–1.78 (m, 2 H), 1.75–1.63 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major diastereomer): δ = 200.3 (s, $^2J_{C,P}$ = 6.3 Hz), 142.8 (s), 128.3 (d, 2 C), 127.3 (d), 125.8 (d, 2 C), 81.2 (d), 75.4 (d), 53.0 (q, $^2J_{C,P}$ = 6.0 Hz, 2 C), 50.1 (t), 42.0 (t, $^1J_{C,P}$ = 127.0 Hz), 34.0 (t), 31.4 (t) ppm. ^1H NMR (400 MHz, $CDCl_3$, minor diastereomer): δ = 7.34–7.21 (m, 5 H), 5.02 (dd, ^3J = 8.4, 6.4 Hz, 1 H), 4.61 (m, 1 H), 3.79 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.78 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.29–3.15 (m, 2 H), 3.02 (dd_{systAB}, ^2J = 16.0, 7.2 Hz, 1 H), 2.83 (dd_{systAB}, ^2J = 16.0, 5.6 Hz, 1 H), 2.42–2.16 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, minor diastereomer): δ = 200.5 (s, $^2J_{C,P}$ = 6.4 Hz), 143.3 (s), 128.3 (d, 2 C), 127.2 (d), 125.5 (d, 2 C), 80.5 (d), 75.6 (d), 53.1 (q, $^2J_{C,P}$ = 5.9 Hz, 2 C), 50.5 (t), 42.1 (t, $^1J_{C,P}$ = 127.0 Hz), 35.0 (t), 32.4 (t) ppm. MS (EI, diastereomer one): *m*/*z* (%) = 208 (73), 193 (22), 166 (27), 151 (100), 129 (26), 124 (89), 117 (26), 111 (23), 109 (69), 105 (25), 94 (43), 91 (68), 77 (51), 55 (17). MS (EI, diastereomer two): *m*/*z* (%) = 208 (4), 194 (12), 193 (65), 151 (100), 135 (23), 124 (48), 109 (59), 105 (42), 95 (21), 94 (55), 91 (65), 79 (41), 77 (45). HRMS (ESI): calcd. for $C_{15}H_{21}O_5PNa$ $[M + Na]^+$ 335.1019; found 335.1008.

Dimethyl [2-Oxo-3-(5-pentyltetrahydrofuran-2-yl)propyl]phosphonate (6c): According to method B, alcohol **4c** (31 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **6c** (47 mg, 0.15 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: 77%. IR: $\tilde{\nu}$ = 2956, 2929, 2857, 1714, 1461, 1377, 1257, 1186, 1029 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$, equimolar mixture of *cis*/*trans* diastereoisomers): δ = 4.34 ($quint._{app}$, J = 7.0 Hz, 0.5 H), 4.20 ($quint._{app}$, J = 7.0 Hz, 0.5 H), 3.94 ($quint._{app}$, J = 7.0 Hz, 0.5 H), 3.79 (d, $^3J_{H,P}$ = 11.2 Hz, 6 H), 3.79 (m, 0.5 H), 3.28–3.10 (m, 2 H), 2.89 (dd_{systAB}, J = 16.0, 7.0 Hz, 1 H), 2.75 (dd_{systAB}, J = 16.0, 5.6 Hz, 0.5 H), 2.72 (dd_{systAB}, J = 16.0, 5.8 Hz, 0.5 H), 2.18–1.91 (m, 2 H), 1.62–1.20 (m, 10 H), 0.88 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, equimolar mixture of *cis*/*trans* diastereoisomers): δ = 201.0, 200.9 (s, $^2J_{C,P}$ = 6.8 Hz), 80.1, 79.3 (d), 74.9, 74.4 (d), 53.2 (q, $^3J_{C,P}$ = 12.7 Hz, 2 C), 50.5, 50.3 (t, 2 C), 42.1 (t, $^1J_{C,P}$ = 127.0 Hz), 36.2, 36.0 (t), 32.4, 32.1 (t), 31.9 (t), 31.4, 31.0 (t), 26.0 (t), 22.8 (t), 14.2 (q) ppm. MS (EI): *m*/*z* (%) = 235 (47) $[M - C_5H_{11}]^+$, 208 (56), 193 (27), 189 (11), 167 (20), 166 (25), 151 (100), 124 (34), 109 (37), 94 (16), 79 (15), 55 (19). HRMS (ESI): calcd. for $C_{14}H_{27}O_5PNa$ $[M + Na]^+$ 329.1488; found 329.1477.

Dimethyl [2-Oxo-3-(tetrahydro-2*H*-pyran-2-yl)propyl]phosphonate (6d): According to method B, alcohol **4d** (20 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **6d** (23 mg, 0.09 mmol) after purification on silica gel (AcOEt to AcOEt/MeOH = 90:10) as a brown oil. Yield: 46%. IR: $\tilde{\nu}$ = 2935, 2856, 1714, 1456, 1403, 1253, 1026 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 3.90 (m, 1 H), 3.82–3.70 (m, 7 H), 3.44 (m, 1 H), 3.28–3.01 (m, 2 H), 2.92–2.59 (m, 2 H), 1.96–1.44 (m, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8 (s), 74.3 (d), 68.7 (t), 53.2 (q, $^2J_{C,P}$ = 6.4 Hz, 2 C), 50.8 (t), 42.0 (t, $^1J_{C,P}$ = 127.8 Hz), 31.9 (t), 25.7 (t), 23.5 (t) ppm. MS (EI): *m*/*z* (%) = 250 (1) $[M]^{+\cdot}$, 166 (18), 151 (83), 140 (88), 135 (10), 125 (49), 124 (100), 119 (17), 111 (14), 109 (75), 99 (21), 98 (11), 95 (10), 94 (66), 85 (26), 79 (43), 67 (18), 57 (18), 55 (26). HRMS (ESI): calcd. for $C_{10}H_{19}O_5NaP$ $[M + Na]^+$ 273.0862; found 273.0864.

Dimethyl [2-Oxo-3-(6-phenyltetrahydro-2*H*-pyran-2-yl)propyl]phosphonate (6e): According to method B, alcohol **4e** (35 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **6e** (59 mg, 0.18 mmol) after purification on silica gel (AcOEt/EP = 98:2) as a brown oil. Yield: 90%. IR: $\tilde{\nu}$ = 2935, 2854, 1714, 1453, 1256, 1187, 1024 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.32–7.21 (m, 5 H), 4.38 (dd, J = 11.2, 2.4 Hz, 1 H), 4.00 (m, 1 H), 3.75 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.74 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.17 (dq, $^2J_{H,P}$ = 22.6 Hz, J = 13.8 Hz,

2 H), 2.93 (dd, ^2J = 15.6 Hz, ^3J = 8.0 Hz, 1 H), 2.72 (dd, ^2J = 15.6 Hz, ^3J = 5.1 Hz, 1 H), 1.93 (m, 1 H), 1.83 (m, 1 H), 1.78–1.65 (m, 2 H), 1.48 (m, 1 H), 1.35 (m, 1 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.8 (s, $^2J_{C,P}$ = 6.3 Hz), 143.0 (s), 128.2 (d, 2 C), 127.2 (d), 125.8 (d, 2 C), 79.9 (d), 74.7 (d), 53.0 (q, $^2J_{C,P}$ = 6.2 Hz, 2 C), 50.6 (t), 42.2 (t, $^1J_{C,P}$ = 127.8 Hz), 33.2 (t), 31.0 (t), 23.7 (t) ppm. MS (EI): *m*/*z* (%) = 308 (11), 221 (18), 193 (12), 179 (11), 166 (22), 151 (99), 124 (100), 117 (24), 104 (57), 94 (45), 79 (53), 65 (11), 55 (15). HRMS (ESI): calcd. for $C_{16}H_{23}O_5PNa$ [M + Na]$^+$ 349.1181; found 349.1173.

Dimethyl [2-Oxo-3-(6-pentyltetrahydro-2*H*-pyran-2-yl)propy]phosphonate (6f): According to method B, alcohol **4f** (34 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **6f** (51 mg, 0.16 mmol) after purification on silica gel (AcOEt/EP = 98:2) as a brown oil. Yield: 80%. IR: $\tilde{\nu}$ = 2931, 2858, 1716, 1458, 1375, 1346, 1258, 1197, 1029 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 3.75 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.74 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.71 (m, 1 H), 3.25–3.06 (m, 3 H), 2.76 (dd$_{systAB}$, J = 15.2, 8.4 Hz, 1 H), 2.57 (dd$_{systAB}$, J = 15.2, 4.4 Hz, 1 H), 1.81–1.73 (m, 1 H), 1.58–1.04 (m, 13 H), 0.83 (t, J = 7.0 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 201.2 (s, $^2J_{C,P}$ = 6.0 Hz), 78.2 (d), 74.5 (d), 53.1 (q, $^2J_{C,P}$ = 6.7 Hz, 2 C), 50.7 (t), 42.2 (t, $^1J_{C,P}$ = 128.3 Hz), 36.5 (t), 32.0 (t), 31.6 (t), 31.4 (t), 25.4 (t), 23.6 (t), 22.8 (t), 14.2 (q) ppm. MS (EI): *m*/*z* (%) = 302 (5), 221 (14), 210 (14), 208 (18), 193 (11), 167 (41), 166 (24), 151 (100), 135 (17), 124 (54), 119 (11), 111 (13), 109 (54), 100 (24), 95 (19), 94 (26), 93 (11), 81 (15), 79 (25), 69 (10), 57 (10), 54 (10). HRMS (ESI): calcd. for $C_{15}H_{29}O_5NaP$ [M + Na]$^+$ 343.1641; found 343.1645.

***tert*-Butyl Dec-1-en-5-ylcarbamate (7b):** 2,2,6,6-Tetramethyl-1-piperidinyloxyl (TEMPO; 30 mg, 0.2 mmol, 0.2 equiv.) and [bis(acetoxy)iodo]benzene (BAIB; 370 mg, 1.15 mmol, 1.15 equiv.) were added to a stirred solution of alcohol **4c** (155 mg, 1 mmol, 1 equiv.) in CH_2Cl_2 (4 mL), and the mixture was stirred at room temperature until complete conversion of alcohol was observed, as monitored by TLC and GC–MS. After 20 h, $NaBH_3CN$ (414 mg, 2 mmol, 2 equiv.), methanol (2 mL), and ammonium formate (630 mg, 10 mmol, 5 equiv.) were added to the reaction mixture. After 20 h, the mixture was quenched carefully with aq. NaOH (10 mol-%, 10 mL) and extracted with Et_2O (3 × 20 mL). The crude material was then diluted in CH_2Cl_2 (2 mL) and Et_3N (0.29 mL, 2 mmol, 2 equiv.) was added. The reaction was cooled to 0 °C and Boc_2O (240 mg, 1.1 mmol, 1.1 equiv.) was added. After 16 h at room temperature, the reaction was diluted with CH_2Cl_2 (20 mL), and the organic layer was washed with 10% HCl (10 mL) and $NaHCO_3$ (10 mL). The organic layer was dried with $MgSO_4$, filtered, and evaporated to afford after purification on silica gel (EP/AcOEt = 98:2 to 90:10) **7b** (144 mg, 0.56 mmol) as a colorless oil. Yield: 56%. IR: $\tilde{\nu}$ = 3338, 2930, 2858, 1685, 1522, 1453, 1390, 1365, 1246, 1171 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 5.78 (ddt, J = 17.1, 10.2, 6.7 Hz, 1 H), 5.02–4.88 (m, 2 H), 4.13 (br. d, J = 8.4 Hz, 1 H), 3.53 (m, 1 H), 2.13–1.97 (m, 2 H), 1.57–1.44 (m, 2 H), 1.45–1.35 (m, 11 H), 1.33–1.17 (m, 6 H), 0.84 (br. t, J = 6.8 Hz, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.8 (s), 138.5 (d), 114.8 (t), 79.0 (s), 50.5 (d), 35.7 (t), 35.0 (t), 31.9 (t), 30.4 (t), 28.6 (q, 3 C), 25.7 (t), 22.8 (t), 14.2 (q) ppm. MS (EI): *m*/*z* (%) = 201 (1), 144 (22), 128 (26), 100 (36), 84 (42), 67 (13), 59 (10), 57 (100), 55 (14). HRMS (ESI): calcd. for $C_{15}H_{29}NO_2$ [M + Na]$^+$ 278.2090; found 278.2097.

Dimethyl [(*E*)-8-(4-Methylphenylsulfonamido)-2-oxooct-3-en-1-yl]-phosphonate (8e): According to method B, amine **7e** (51 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **8e** (58 mg, 0.14 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: 72%. IR: $\tilde{\nu}$ = 3163, 2953, 2858, 1691, 1664, 1624, 1451, 1325, 1246, 1155, 1026 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (d, J = 8.2 Hz, 2 H), 7.30 (d, J = 8.8 Hz, 2 H), 6.89 (dt, J = 16.0, 7.2 Hz, 1 H), 6.19 (dt$_{app}$, J = 15.6, 1.3 Hz, 1 H), 5.42 (br. t, J = 6.0 Hz, 1 H), 3.78 (d, $^3J_{H,P}$ = 11.2 Hz, 6 H), 3.23 (d, $^2J_{H,P}$ = 22.8 Hz, 2 H), 2.91 (q$_{app}$, J = 6.3 Hz, 2 H), 2.43 (s, 3 H), 2.23 (m, 2 H), 1.53–1.50 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2 (s, $^3J_{C,P}$ = 5.9 Hz), 150.3 (d), 143.4 (s), 137.2 (s), 130.5 (d), 129.8 (d, 2 C) 127.2 (d, 2 C), 53.3 (q, $^2J_{C,P}$ = 6.8 Hz, 2 C), 42.9 (t), 39.1 (t, $^1J_{C,P}$ = 128.6 Hz), 31.9 (t), 28.7 (t), 24.7 (t), 21.7 (q) ppm. HRMS (ESI): calcd. for $C_{17}H_{26}NO_6PSNa$ [M + Na]$^+$ 426.1111; found 426.1101.

Dimethyl [(*E*)-9-Methyl-8-(4-methylphenylsulfonamido)-2-oxodec-3-en-1-yl]phosphonate (8f): According to method B, amine **7f** (59 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **8f** (71 mg, 0.16 mmol) after purification on silica gel (AcOEt) as a brown oil. Yield: 80%. IR: $\tilde{\nu}$ = 3174, 2957, 2873, 1718, 1691, 1664, 1624, 1598, 1455, 1246, 1156, 1026 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.75 (br. d, J = 8.0 Hz, 2 H), 7.28 (d, J = 8.0 Hz, 2 H), 6.83 (dt, J = 16.0, 6.8 Hz, 1 H), 6.16 (dt, J = 16.0, 1.4 Hz, 1 H), 5.17 (d, J = 8.8 Hz, 1 H), 3.80 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.77 (d, $^3J_{H,P}$ = 11.2 Hz, 3 H), 3.38–3.06 (m, 3 H), 2.42 (s, 3 H), 2.24–2.04 (m, 2 H), 1.67 (m, 1 H), 1.49–1.23 (m, 4 H), 0.76 (t, J = 6.8 Hz, 6 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.2 (s, $^2J_{C,P}$ = 6.3 Hz), 150.6 (d), 143.1 (s), 139.1 (s), 130.4 (d), 129.6 (d, 2 C), 127.0 (d, 2 C), 59.3 (d), 53.3 (q, $^2J_{C,P}$ = 6.3 Hz, 2 C), 39.2 (t, $^1J_{C,P}$ = 128.5 Hz), 32.2 (t), 31.9 (d), 30.6 (t), 24.1 (t), 21.6 (q), 18.1 (q, 2 C) ppm. HRMS (ESI): calcd. for $C_{20}H_{32}NO_6PSNa$ [M + Na]$^+$ 468.1580; found 468.1572.

Dimethyl [(*E*)-8-(4-Methylphenylsulfonamido)-2-oxo-8-phenyloct-3-en-1-yl]phosphonate (8g): According to method B, amine **7g** (66 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **8g** (81 mg, 0.17 mmol) after purification on silica gel (AcOEt) as a brown oil. Yield: 88%. IR: $\tilde{\nu}$ = 3258, 2925, 2854, 1664, 1624, 1494, 1456, 1323, 1244, 1155, 1026 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.49 (br. d, J = 8.4 Hz, 2 H), 7.12–7.07 (m, 3 H), 7.05 (d, J = 8.4 Hz, 2 H), 7.03–6.98 (m, 2 H), 6.86 (dt, J = 16.0, 6.8 Hz, 1 H), 6.17 (br. dt, J = 16.0, 1.4 Hz, 1 H), 6.04 (d, J = 8.4 Hz, 1 H), 4.25 (m, 1 H), 3.79 (d, $^2J_{H,P}$ = 11.6 Hz, 3 H), 3.76 (d, $^2J_{H,P}$ = 11.6 Hz, 3 H), 3.35–3.10 (m, 2 H), 2.32 (s, 3 H), 2.29–2.10 (m, 2 H), 1.85–1.38 (m, 4 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 191.0 (s, $^2J_{C,P}$ = 5.9 Hz), 150.2 (d), 142.6 (s), 141.2 (s), 138.1 (s), 130.5 (d), 129.1 (d, 2 C), 128.4 (d, 2 C), 127.2 (d), 126.9 (d, 2 C), 126.4 (d, 2 C), 58.2 (d), 53.2 (q, $^2J_{C,P}$ = 6.3 Hz, 2 C), 39.0 (t, $^1J_{C,P}$ = 128.8 Hz), 36.7 (t), 31.7 (t), 24.1 (t), 21.4 (q) ppm. HRMS (ESI): calcd. for $C_{23}H_{30}NO_6PSNa$ [M + Na]$^+$ 502.1424; found 502.1407.

***tert*-Butyl 2-[3-(Dimethoxyphosphoryl)-2-oxopropyl]-5-phenylpyrrolidine-1-carboxylate (9a):** According to method B, amine **7a** (52 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **9a** (53 mg, 0.13 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: 65% as a mixture of two diastereomers in a 70:30 ratio. IR: $\tilde{\nu}$ = 2972, 1707, 1683, 1452, 1393, 1375, 1258, 1169, 1036 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers = 70:30): δ = 7.32–7.18 (m, 3 H), 7.11–7.07 (m, 2 H), 4.98 (br. d, J = 8.0 Hz, 0.3 H), 4.83 (br. d, J = 8.0 Hz, 0.7 H), 4.59–4.45 (m, 1 H), 3.80 (2 d, ^3J = 11.2 Hz, 6 H), 3.32–3.02 (m, 3 H), 2.80 (dd$_{systAB}$, J = 16.8, 9.2 Hz, 1 H), 2.33 (m, 1 H), 2.20 (m,1 H), 1.74 (m, 1 H), 1.62 (m, 1 H),

1.61, 1.43, 1.12 (3s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major diastereomer): δ = 200.5 (s, $^2J_{C,P}$ = 5.9 Hz), 153.9 (s), 144.9 (s), 128.1 (d, 2 C), 126.5 (d), 125.2 (d, 2 C), 79.5 (s), 61.7 (d), 54.1 (d), 53.1 (q, $^2J_{C,P}$ = 6.8 Hz, 2 C), 47.8 (t), 41.5 (t, $^1J_{C,P}$ = 126.6 Hz), 32.5 (t), 28.0 (s, 3 C), 27.6 (t) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, minor diastereomer): δ = 200.3 (s, $^2J_{C,P}$ = 6.9 Hz), 153.3 (s), 143.5 (s), 128.4 (d, 2 C), 126.3 (d), 125.0 (d, 2 C), 80.0 (s), 61.0 (d), 53.6 (d), 52.9 (q, $^2J_{C,P}$ = 6.8 Hz, 2 C), 48.4 (t), 41.5 (t, $^1J_{C,P}$ = 126.6 Hz), 31.7 (t), 28.4 (s, 3 C), 28.0 (t) ppm. HRMS (ESI): calcd. for $C_{20}H_{30}NO_6PNa$ [M + Na]$^+$ 434.1703; found 434.1704.

***tert*-Butyl 2-[3-(Dimethoxyphosphoryl)-2-oxopropyl]-5-pentylpyrrolidine-1-carboxylate (9b):** According to method B, amine **7b** (51 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **9b** (34 mg, 0.09 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: 43% as a mixture of two diastereomers in a 70:30 ratio. IR: $\tilde{\nu}$ = 2957, 2928, 2857, 1713, 1684, 1456, 1391, 1367, 1254, 1171, 1110, 1025 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, mixture of diastereomers = 70:30): δ = 4.24–4.25 (m, 1 H), 3.79 (d, $^3J_{H,P}$ = 11.0 Hz, 6 H), 3.73 (m, 0.3 H), 3.64 (m, 0.7 H), 3.25–3.02 (m, 3 H), 2.66–2.59 (m, 1 H), 2.12–2.01 (m, 1 H), 1.91–1.80 (m, 1 H), 1.68–1.55 (m, 3 H), 1.45 (s, 9 H), 1.36–1.18 (m, 7 H), 0.90–0.86 (m, 3 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major diastereomer): δ = 200.6 (s), 153.8 (s), 79.3 (s), 57.8 (d), 53.1 (q, $^2J_{C,P}$ = 6.9 Hz, 2 C), 47.5 (d), 41.5 (t, $^1J_{C,P}$ = 127.4 Hz), 33.8 (t), 31.7 (t), 28.5 (q, 3 C), 28.7 (t), 28.1 (t), 27.3 (t), 26.3 (t), 22.6 (t), 14.0 (q) ppm. HRMS (ESI): calcd. for $C_{19}H_{36}NO_6PNa$ [M + Na]$^+$ 428.2172; found 428.2175.

Dimethyl [2-Oxo-3-(1-tosylpyrrolidin-2-yl)propy]phosphonate (9c): According to method B, amine **7c** (48 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **9c** (43 mg, 0.11 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: 55%. IR: $\tilde{\nu}$ = 2957, 1713, 1598, 1451, 1402, 1374, 1253, 1198, 1157, 1023 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.71 (br. d, J = 8.2 Hz, 2 H), 7.33 (d, J = 7.9 Hz, 2 H), 3.96 (m, 1 H), 3.80 (d, $^3J_{H,P}$ = 11.3 Hz, 6 H), 3.44 (m, 1 H), 3.30 (dd$_{systAB}$, J = 18.1, 3.8 Hz, 1 H), 3.26–3.03 (m, 3 H), 2.94 (dd$_{systAB}$, J = 18.1, 9.2 Hz, 1 H), 2.44 (s, 3 H), 1.84–1.71 (m, 2 H), 1.61–1.43 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 200.5 (s, $^2J_{C,P}$ = 6.3 Hz), 143.8 (s), 134.0 (s), 129.9 (d, 2 C), 127.7 (d, 2 C), 55.9 (d), 53.3 (q, $^2J_{C,P}$ = 6.4 Hz), 53.1 (q, $^2J_{C,P}$ = 6.4 Hz), 51.1 (t), 49.3 (t), 42.4 (t, $^1J_{C,P}$ = 126.7 Hz), 32.1 (t), 24.0 (t), 21.7 (q) ppm. HRMS (ESI): calcd. for $C_{16}H_{24}NO_6PSNa$ [M + Na]$^+$ 412.0954; found 412.0939.

Dimethyl [2-Oxo-3-(5-phenyl-1-tosylpyrrolidin-2-yl)propyl]phosphonate (9d): According to method B, amine **7d** (63 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to **9d** (43 mg, 0.12 mmol) after purification on silica gel (AcOEt) followed by MPLC (AcOEt/MeOH = 99:1) as a brown oil. Yield: 60% as a mixture of diastereomers in a 80:20 ratio. IR: $\tilde{\nu}$ = 2956, 2853, 1712, 1598, 1495, 1454, 1337, 1258, 1155, 1028 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, major diastereomer): δ = 7.20–6.80 (m, 9 H), 5.01 (d, J = 8.4 Hz, 1 H), 4.54 (m, 1 H), 3.82 (d, $^3J_{H,P}$ = 11.2 Hz, 6 H), 3.66 (m, 1 H), 3.30–2.97 (m, 3 H), 2.43–2.32 (m, 2 H), 2.33 (s, 3 H), 1.80–1.71 (m, 2 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, major diastereomer): δ = 200.6 (s, $^2J_{C,P}$ = 6.3 Hz), 142.7 (s), 141.4 (s), 138.0 (s), 129.1 (d, 2 C), 128.3 (d, 2 C), 127.2 (d), 127.1 (d, 4 C), 64.2 (d), 56.5 (d), 53.4 (q, $^2J_{C,P}$ = 6.3 Hz), 53.2 (q, $^2J_{C,P}$ = 6.3 Hz), 50.3 (t), 42.1 (t, $^1J_{C,P}$ = 127.5 Hz), 32.9 (t), 30.6 (t), 21.6 (q) ppm. ^{1}H NMR (400 MHz, $CDCl_3$, minor diastereomer): δ = 7.40–6.91 (m, 9 H), 4.65 (d, J = 8.4 Hz, 1 H), 4.14 (m, 1 H), 3.81 (d, $^3J_{H,P}$ = 11.2 Hz, 6 H), 3.77 (m, 1 H), 3.30–2.97 (m, 3 H), 2.44 (s, 3 H), 2.43–2.32 (m, 2 H), 1.80–1.71 (m, 2 H) ppm. HRMS (ESI): calcd. for $C_{22}H_{28}NO_6PSNa$ [M + Na]$^+$ 488.1267; found 488.1256.

***tert*-Butyl 2-[(*E*)2-Oxo-4-phenylbut-3-en-1-yl]pyrrolidine-1-carboxylate (10h):** According to method B, amine **7h** (37 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to, after purification on silica gel (AcOEt), **9h** as an inseparable mixture with phosphonate **1**. The mixture was then dissolved in MeCN (5 mL), K_2CO_3 (221 mg, 0.8 mmol, 2 equiv.) was added, and the mixture was stirred at room temperature. After 30 min, benzaldehyde (85 mg, 0.8 mmol, 2 equiv.) was added, and the mixture was heated at reflux for 16 h. The volatiles were removed under reduced pressure, and the crude material was dissolved in AcOEt (10 mL). The organic layer was washed with water (5 mL) and brine (5 mL), and the organic layers phases were combined, dried with $MgSO_4$, filtered, and evaporated to afford after purification on silica gel (EP/AcOEt = 95:5 to 80:20) enone **10h** (50 mg, 16 mmol) as a slightly yellow oil. Yield: 80% (over two steps). IR: $\tilde{\nu}$ = 2973, 2877, 1686, 1610, 1450, 1394, 1366, 1167, 1115 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$, equimolar ratio of two rotamers): δ = 7.72–7.52 (m, 3 H), 7.40 (br. s, 3 H), 6.73 (d, J = 16.0 Hz, 1 H), 4.26 (m, 1 H), 3.48–3.12 (m, 3 H), 2.63 (m, 1 H), 2.05 (s, 1 H), 1.86 (m, 2 H), 1.75 (m, 1 H), 1.48 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$, equimolar ratio of two rotamers): δ = 199.3, 198.7 (s), 154.4, 154.3 (d), 143.3, 142.9 (d), 134.6, 134.4 (s), 130.6, 130.4 (d), 129.0–126.5 (d, 5 C), 79.6, 79.2 (s), 54.3, 54.0 (d), 46.7, 46.2, 45.9, 44.9 (t, 2 C), 31.4, 30.4 (t), 28.6 (q, 3 C), 23.6, 22.9 (t) ppm. MS (EI): m/z (%) = 260 (3), 214 (10), 131 (51), 110 (10), 103 (30), 83 (24), 77 (22), 70 (44), 69 (11), 68 (16), 57 (100), 56 (13). HRMS (ESI): calcd. for $C_{19}H_{25}NO_3Na$ [M + Na]$^+$ 338.1727; found 338.1724.

***tert*-Butyl [(5*E*,8*E*)-7-Oxo-9-phenylnona-5,8-dien-1-yl]carbamate (10i):** According to method B, amine **7i** (40 mg, 0.2 mmol, 3 equiv.), phosphonate **1** (117 mg, 0.6 mmol, 3 equiv.), and [Ru]-**III** (2 × 6 mg, 2 × 5 mol-%) led to, after purification on silica gel (AcOEt), **9i** as an inseparable mixture with phosphonate **1**. The mixture was then dissolved in MeCN (3 mL), K_2CO_3 (221 mg, 0.8 mmol, 2 equiv.) was added, and the mixture was stirred at room temperature. After 30 min, benzaldehyde (85 mg, 0.8 mmol, 2 equiv.) was added, and the mixture was heated at reflux for 16 h. The volatiles were removed under reduced pressure, and the crude material was dissolved in AcOEt (10 mL). The organic layer was washed with water (5 mL) and brine (5 mL), dried with $MgSO_4$, filtered, and evaporated to afford, after purification on silica gel (EP/AcOEt = 95:5 to 80:20), enone **10i** (46 mg, 14 mmol) as a slightly yellow oil. Yield: 73% (over two steps). IR: $\tilde{\nu}$ = 3353, 2975, 2931, 2863, 1694, 1660, 1629, 1600, 1517, 1450, 1365, 1275, 1251, 1170 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.65 (d, J = 16.0 Hz, 1 H), 7.60–7.56 (m, 2 H), 7.42–7.37 (m, 3 H), 7.02–6.94 (m, 2 H), 6.45 (dt, J = 15.6, 1.6 Hz, 1 H), 4.53 (br. s, 1 H), 3.15 (br. m, 2 H), 2.31 (m, 2 H), 1.57–1.52 (m, 4 H), 1.45 (s, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 189.2 (s), 156.0 (s), 147.5 (d), 143.1 (d), 134.8 (s), 130.4 (d), 129.5 (d), 128.9 (d, 2 C), 128.3 (d, 2 C), 124.9 (d), 79.2 (s), 40.3 (t), 32.3 (t), 29.7 (t), 28.4 (q, 3 C), 25.4 (t) ppm. HRMS (ESI): calcd. for $C_{20}H_{27}NO_3Na$ [M + Na]$^+$ 352.1883; found 352.1885.

***tert*-Butyl 2-[(*E*)-2-Hydroxy-4-phenylbut-3-en-1-yl]pyrrolidine-1-carboxylate (11):** To a solution of **9h** (57 mg, 0.18 mmol, 1 equiv.) in THF (5 mL) at 0 °C was added $LiAlH(OtBu)_3$ (1 M in THF, 186 μL, 0.186 mmol, 1.03 equiv.). After 3 h at 0 °C, the reaction was quenched by addition of a few drops of cold water and AcOEt

and stirred for 1 h. The mixture was filtered through Celite to afford **11** (44 mg, 0.14 mmol) as a slightly yellow oil. Yield: 81%. IR: $\tilde{\nu}$ = 3670, 3408, 2973, 1670, 1405, 1250, 1168, 1111, 1067 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.15 (m, 5 H), 6.60 (d, J = 16.1 Hz, 1 H), 6.24 (dd, J = 16.0, 5.6 Hz, 1 H), 4.40 (br. s, 1 H), 4.10 (br. s, 1 H), 3.31 (m, 2 H), 2.03–1.84 (m, 4 H), 1.71–1.50 (m, 2 H), 1.48–1.43 (m, 9 H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.6 (s), 137.2 (s), 133.0 (d), 128.8 (d), 128.5 (d, 2 C), 127.3 (d), 126.4 (d, 2 C), 79.9 (s), 70.7 (d), 55.0 (d), 46.4 (t), 43.6 (t), 32.1 (t), 28.5 (q, 3 C), 23.8 (t) ppm. MS (EI): *m/z* (%) = 243 (1), 129 (11), 115 (14), 114 (44), 91 (14), 85 (18), 70 (100), 57 (87), 56 (20), 55 (15). HRMS (ESI): calcd. for $C_{19}H_{27}NO_3Na$ $[M + Na]^+$ 340.1883; found 340.1884.

Supporting Information (see footnote on the first page of this article): Copies of the ^1H and ^{13}C NMR spectra for all new compounds.

Acknowledgments

Edelris s.a.s. is greatly acknowledged for financial support (grant to T. C.).

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Received: September 24, 2011
Published Online: December 5, 2011

