A New and Convenient Route to Optically Active 2-Phosphoryl-3-oxo-5-alkyl/-aryltetrahydrofurans and Their Reactions[‡]

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The two enantiomers of 4-hydroxy-2-oxo-4-alkyl/-arylalkylphosphonates were prepared chemoenzymatically and converted to chiral 2-phosphoryl-3-oxo-5-alkyl/-aryl tetrahydrofurans using an intramolecular O–H insertion reaction catalyzed by rhodium(II) acetate. The potential biological activity of the resulting tetrahydrofurans is of much interest. The presence of the β-ketophosphonate skeleton in these heterocycles allowed their use as substrate in the cyclic Horner–Wadsworth–Emmons reaction with aldehydes or ketones furnishing chiral α,β-unsaturated ketones – a new class of building block in organic synthesis.

1. Introduction

Functionalized tetrahydrofurans make up a class of compounds with potential biological activity and synthetic utility.[1] For example, racemic 2-carboxy-3-oxo-5-aryl tetrahydrofurans have been used to form C-nucleosides that are potential anticancer and anti-HIV agents.[2] Consequently, the chemical and biological behavior of tetrahydrofuran derivatives aroused our interest, and we also noted that there have been very few reports regarding substituted tetrahydrofurans.[3]

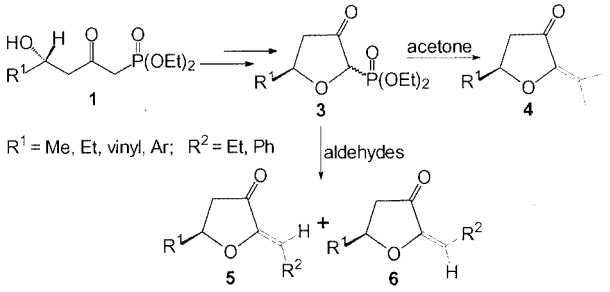
However, Calters and coworkers prepared chiral 2-ethoxycarbonyl-3-oxo-5-phenyltetrahydrofurans using a diazo-ketone-aldol/O−H insertion reaction.[3a,3b] This synthetic strategy attracted our attention since it is interesting to examine the possibility of obtaining optically active tetrahydrofurans bearing a phosphoryl moiety. Nevertheless, the introduction of a phosphoryl group to heterocycles by direct C−P bond formation is not an easy task. It is noteworthy that the Horner−Wadsworth−Emmons (HWE) reaction of β-ketophosphonates allows the formation of cyclic chiral α,β-unsaturated ketones that could be considered as a new type of building block for the synthesis of complex molecules.

The phosphoryl group is contained in many natural products and living organisms, and several compounds bearing this group have shown significant biological activity.[4] From a synthetic point of view, it is interesting to examine the reactivity of these β-carbonyl cyclic phosphonates under HWE reaction conditions.[5]

Thus, diethyl 4-hydroxy-2-oxo-4-aryl/-alkylbutylphosphonates gave α,β-unsaturated ketones[6a] and were transformed into 2-oxo-3-alkenylphosphonates. These 2-oxo-3-alkenylphosphonates were reacted further with vinyl ethers via hetero-Diels−Alder reactions, leading to 5-substituted-2-phosphoryl-2-cyclohexen-1-ones.[7]

The starting diethyl (4*S*)-4-hydroxy-2-oxoalkylphosphonates and diethyl (4*R*)-4-hydroxy-2-oxo-4-arylbutylphosphonates were prepared using *Candida antarctica* lipase B (*CALB*) and *Candida rugosa* lipase (*CRL*) enzymatic catalysis.[6a]

In this report, optically active 4-hydroxy-2-oxoalkylphosphonates **1a**−**k** were transformed into compounds **3a**−**k**. This process involved the introduction of a phosphoryl group to the α-position of substituted tetrahydrofurans followed by cyclization via an intramolecular O−H insertion reaction catalyzed by rhodium(II) acetate.[8] The presence of the β-ketophosphonate moiety in the cyclic systems allowed subsequent HWE reactions with aldehydes or ketones. (Scheme 1)



Scheme 1

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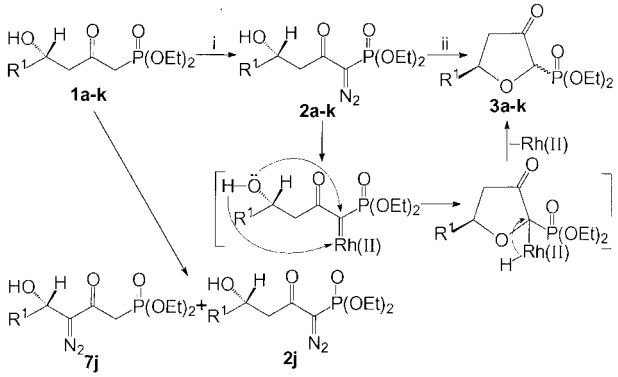
2. Results and Discussion

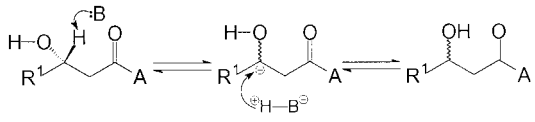
The optically active compounds **1a**−**k**[6a] were converted into the corresponding α-diazo compounds **2a**−**k**, which were then cyclized into compounds **3a**−**k** in the presence of 1mol % rhodium (II) acetate followed by an intramolecular



Scheme 2. **a**: R^1 = Me; **b**: R^1 = Et; **c**: R^1 = vinyl; **d**: R^1 = C_6H_5; **e**: R^1 = 4-MeC_6H_4; **f**: R^1 = 4-EtC_6H_4; **g**: R^1 = 4-$MeOC_6H_4$; **h**: R^1 = 2-furyl; **i**: R^1 = 2-BrC_6H_4; **j**: R^1 = 4-FC_6H_4; **k**: R^1 = 2,4-$Cl_2C_6H_3$ (i) $TosN_3/K_2CO_3/CNCH_3$, 0 °C (ii) 1 mol% $Rh_2(OAc)_4$/benzene, reflux

O−H insertion reaction as shown in Scheme 2 and Table 1.

We found that if harsh reaction conditions are applied, i.e. higher reaction temperature and longer reaction time, the *ee* values of optically active compounds **1a**−**k** are reduced dramatically in reactions under basic conditions. Partial or complete racemization during the reaction can be rationalized as shown in Scheme 3.

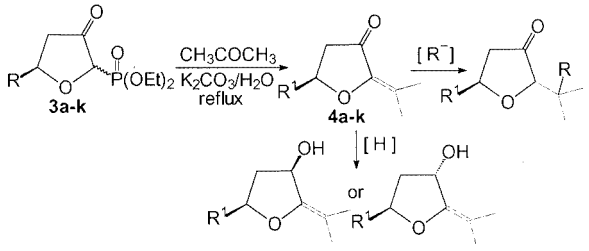


Scheme 3. R^1 = Ar; A = $CH_2P(O)(OEt)_2$ or $C(N_2)P(O)(OEt)_2$

Because of this situation, we carefully optimized the conversion of compounds **1a**−**k** to compounds **3a**−**k**. Compounds **1a**−**k** were converted smoothly to the corresponding diazo derivatives **2a**−**k**, in yields up to 80%, by use of tosyl azide in the presence of an equimolar amount of potassium carbonate in acetonitrile at 0 °C for less than 2 h. If an excess of potassium carbonate was present then the γ-diazo compound **7** was also obtained (Scheme 2). If an organic base such as triethylamine was used, the yields of compounds **2a**−**k** were reduced dramatically to less than 40% after 4 h. The resulting α-diazo compounds **2a**−**k** were converted into substituted tetrahydrofurans **3a**−**k** by an intramolecular O−H insertion reaction, catalyzed by rhodium(II) acetate. Compounds **3a**−**k** existed in rapid equilibrium between *cis* and *trans* isomers whose ratio was about 1:1 as shown by ^{31}P and ^1H NMR spectroscopy.

Although the synthesis of substituted tetrahydrofurans has been reported by Calter and Zhu,[3a] in that work, a carboxy group rather than a phosphoryl group was introduced at the tetrahydrofuran α-position. Undoubtedly, substituted tetrahydrofurans containing a phosphoryl group should offer much more potential for use in organic synthesis. β-Ketophosphonates that react with aldehydes or ketones in the HWE reaction have been used extensively for the synthesis of complex molecules and natural products.[9]

Since substituted tetrahydrofurans **3a**−**k** contain a phosphoryl group at the α-position in addition to a carbonyl group at the β-position of the ring system, it is interesting to observe their reactivity towards aldehydes and ketones under HWE reaction conditions. Although the HWE reaction has been used in organic synthesis for many years, reactions involving ketones or cyclic systems are relatively rare.[10] Initially, we performed the reaction with ketones. We found that compounds **3a**−**k** reacted with acetone under reflux in the presence of excess potassium carbonate and water, and α,β-unsaturated ketones **4a**−**k** were obtained in satisfactory yields and excellent enantiomeric excesses. The resulting α,β-unsaturated ketones **4a**−**k** should have some uses, such as by reduction of the carbonyl group to a hydroxy group or in the Michael reaction etc. (see Scheme 4 and Table 2).



Scheme 4

Attempts to carry out the HWE reaction of compounds **3a**−**k** with benzaldehyde in aqueous potassium carbonate

Table 1. The synthesis of 2-phosphoryl-3-oxo-5-alkyl/-aryltetrahydrofurans **3a**−**k**

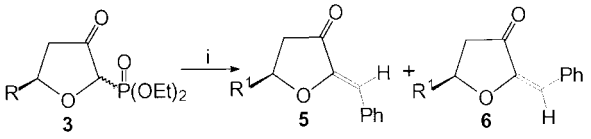
Substrate	Time (h)		R^1	Yield (%)		Substrate	Time (h)		R^1	Yield (%)	
	2	**3**		**2**	**3**		**2**	**3**		**2**	**3**
a	1.5	0.5	Me	82	94	**g**	1.5	0.5	4-$MeOC_6H_4$	84	96
b	1.5	0.5	Et	84	94	**h**	1.5	0.5	2-furyl	86	97
c	1.5	0.5	vinyl	84	95	**i**	1.5	0.5	2-BrC_6H_4	86	95
d	1.5	0.5	C_6H_5	81	96	**j**	1.5	0.5	4-FC_6H_4	85	96
e	1.5	0.5	4-MeC_6H_4	80	97	**k**	1.5	0.5	2,4-$Cl_2C_6H_4$	87	94
f	1.5	0.5	4-EtC_6H_4	81	93						

Table 2. HWE reaction of compounds **3a**−**k** with acetone

Substrate	Time (h)	R^1	Yield (%) **4**	*ee* (%)[a]	Substrate	Time (h)	R^1	Yield (%) **4**	*ee* (%)[a]
3a	2.0	Me	66	99	**3g**	2.0	4-$MeOC_6H_4$	60	>99
3b	2.0	Et	68	>99	**3h**	2.0	2-C_4H_3O	70	94
3c	2.0	−CH=CH_2	67	99	**3i**	2.0	2-BrC_6H_4	63	>99
3d	2.0	C_6H_5	67	>99	**3j**	2.0	4-FC_6H_4	67	>99
3e	2.0	4-MeC_6H_4	59	>99	**3k**	2.0	2,4-$Cl_2C_6H_3$	64	>99
3f	2.0	4-EtC_6H_4	59	>99					

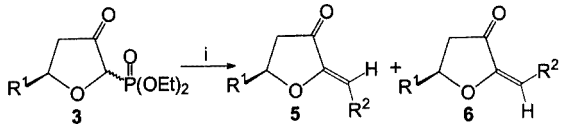
[a] The *ee* values were determined by chiral HPLC.

solution failed.[6a] However, sodium hydride was found to be a suitable base[10] for reaction of compounds **3a**−**k** with benzaldehyde at low temperatures around −30 to ca. −20 °C. The products of these reactions were mixtures of (*Z*) and (*E*) isomers (see Scheme 5).



Scheme 5. (i) PhCHO/NaH/THF, −20 ... −30 °C; R^1 = Ph, 4-$MeOC_6H_4$, vinyl

Because the reaction conditions are so delicate and compounds **3a**−**k** decomposed at room temperature in sodium hydride solution, modification of the method seemed necessary. We observed that compounds **3a**−**k** reacted smoothly with aldehydes in THF/H_2O solution in the presence of excess K_2CO_3 as base and at room temperature for about 2.5 h to give the expected products. The resulting mixture of (*Z*) and (*E*) isomers could be isolated by careful TLC. These two isomers could be differentiated easily by ^1H NMR spectroscopy (Figure 1). The products from reaction of α,β-unsaturated ketones **5** and **6** could also be employed in other reactions (see Scheme 6 and Table 3).



Scheme 6. R^1 = Et, vinyl, Ph, 4-$MeOC_6H_4$, 4-FC_6H_4; R^2 = Et, Ph. (i) $R^2CHO/K_2CO_3/THF/H_2O$, r.t.

3. Conclusion

In summary, the enzyme catalyzed products, compounds **1a**−**k**, were successfully transformed to functionalized tetrahydrofurans **3a**−**k** with high enantioselectivity. As expected, these tetrahydrofurans bearing the β-ketophosphonate moiety underwent the HWE reaction with aldehydes or ketones to provide optically active α,β-unsaturated ketones, which constitute a new class of chiral building blocks with potential application in organic synthesis.

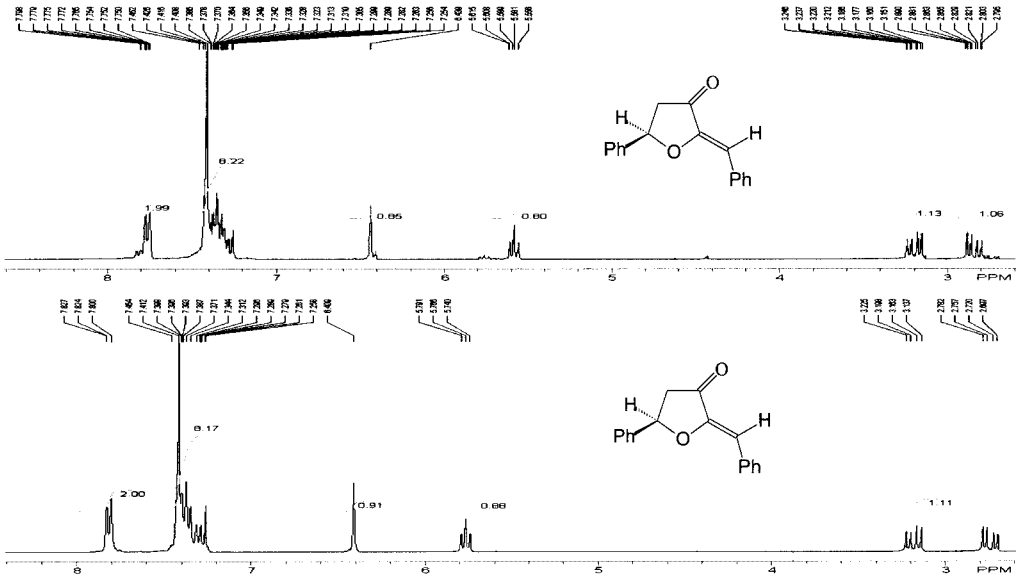


Figure 1. ^1H NMR spectrum of (5*R*)-2-[(*Z*)-benzylidene]-3-oxo-5-phenyltetrahydrofuran (**5d′**) and (5*R*)-2-[(*E*)-benzylidene]-3-oxo-5-phenyltetrahydrofuran (**6d′**)

Table 3. HWE reaction of compounds **3a**−**k** with aldehydes

Substrate	Time (h)	R^1	R^2	Yield (%) **5**	*ee* (%)[a]	Yield (%) **6**	*ee* (%)[a]
3b	2.5	Et	Ph	41	98	18	99
3c	2.5	−CH=CH_2	Et	30	−[b]	29	−[b]
	2.5		Ph	39	>99	21	99
3d	2.5	C_6H_5	Et	31	98	29	99
	2.5		Ph	41	>99	21	99
3g	2.5	4-$MeOC_6H_4$	Et	33	−[c]	29	90
	2.5		Ph	38	>99	16	95
3j	2.5	4-FC_6H_4	Et	35	>99	34	>99
	2.5		Ph	42	>99	24	>99

[a] The *ee* values were determined by chiral HPLC. [b] The *ee* values could not be determined by chiral HPLC. [c] This compound decompose during chiral HPLC.

4. Experimental Section

IR spectra were recorded with a Shimadzu IR-440 spectrometer. EI mass spectra (MS) were run with an HP-5989A mass spectrometer. ^{1}H NMR spectra were recorded in $CDCl_3$ with a Bruker AMX-330 (300 MHz) spectrometer and downfield chemical shifts (ppm) are reported relative to TMS (internal standard). ^{13}C NMR spectra were recorded in $CDCl_3$ on the same spectrometer and downfield chemical shifts (ppm) are reported relative to TMS (internal standard). ^{31}P NMR spectra were taken on the same spectrometer using 80% phosphorus acid as external standard. Melting points are uncorrected.

The chiral liquid chromatography system was constructed from the following components: Waters 515 HPLC pump; UV Waters 2487 Dual λ Absorbance Detector operating at 254 nm; Penelson Network chromatography interface NCI 900, Turbochrom Navigator data station software; column dimensions: 0.46 cm × 25 cm; the flow rate: 0.7 mL/min; eluent: hexane/2-propanol, 9:1−8:2 (v/v).

General Procedure for Preparation of Optically Active Diethyl 4-Hydroxy-2-oxoalkylphosphonates 1[6a]

Diethyl (4*R*)-4-(4-Ethylphenyl)-4-hydroxy-2-oxobutylphosphonate (1f): Colorless oil; yield: 43%. $[\alpha]_D^{25}$ = +42.3 (*c* = 1.3, $CHCl_3$). IR (film): ṽ = 3380, 2968, 2933, 2911, 2875, 1715, 1249, 1025, 971 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.28 (d, *J* = 7.8 Hz, 2 H, ArC*H*), 7.17 (2 H, d, *J* = 8.4 Hz, ArC*H*), 5.16−5.12 (m, 1 H, ArC*H*), 4.18−4.08 (m, 4 H, OCH_2CH_3), 3.13 (d, *J* = 22.8 Hz, 2 H, CH_2P), 3.16−2.92 (m, 2 H, $CHCH_2$), 2.63 (q, *J* = 7.8 Hz, 2 H, $ArCH_2CH_3$), 1.33 (t, *J* = 7.2 Hz, 6 H, OCH_2CH_3), 1.22 (t, *J* = 7.5 Hz, 3 H, $ArCH_2CH_3$) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 19.561 ppm. EI-MS: *m*/*z* = 328 (6.56) [M$^+$], 311 (96.86), 195 (64.16), 194 (59.13), 152 (55.50), 133 (100.00), 125 (87.55), 91 (51.40), 79 (64.14). HR-MS calcd. for $C_{16}H_{25}O_5P$ [M$^+$]: 328.1440; found: 328.1406.

General Procedure for Preparation of Diethyl 1-Diazo-4-hydroxy-2-oxo-4-aryl(or -alkyl)alkylphosphonates 2: Compound **1** (1 mmol), tosyl azide[11] (236 mg, 1.2 mmol), and acetonitrile (8 mL) were mixed in a 25 mL flask and cooled to 0 °C. Then K_2CO_3 (166 mg, 1.2 mmol) was added to this mixture. After stirring at 0 °C for 1.5 h, the mixture was filtered. The solvent was removed under reduced pressure and the residue was subjected to flash chromatography to furnish the corresponding compound **2**.

Diethyl (4*S*)-1-Diazo-4-hydroxy-2-oxopentylphosphonate (2a): Colorless oil; yield: 82%. $[\alpha]_D^{25}$ = +30.2 (*c* = 1.1, $CHCl_3$). IR (film): ṽ = 3427, 2982, 2935, 2911, 2379, 2123, 1655, 1290, 1263, 1194, 1015, 979 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.31−4.10 (m, 5 H, OCH_2CH_3, $CHCH_3$), 3.30 (s, 1 H, O*H*), 2.77 (dd, *J* = 3.3, 16.8 Hz, 1 H, $CHCH_2CO$), 2.65 (dd, *J* = 8.7, 16.5 Hz, 1 H, $CHCH_2CO$), 1.46−1.37 (m, 6 H, OCH_2CH_3), 1.24 (d, *J* = 6.3 Hz, 3 H, $CHCH_3$) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 11.23 ppm. EI-MS: *m*/*z* = 265 (100.00) [M$^+$ + 1], 237 (27.63), 236 (15.59), 219 (34.95), 181 (42.23), 163 (46.22), 138 (35.45), 111 (34.89), 82 (40.76), 65 (43.46), 45 (52.53). $C_9H_{17}N_2O_5P$ (264.22): calcd. C 40.91, H 6.49, N 10.60; found C 40.97, H 6.58, N 10.45.

Diethyl (4*S*)-1-Diazo-4-hydroxy-2-oxo-hexylphosphonate (2b): Colorless oil; yield: 84%. $[\alpha]_D^{25}$ = +28.9 (*c* = 1.3, $CHCl_3$). IR (film): ṽ = 3431, 2980, 2937, 2880, 2123, 1654, 1263, 1191, 1164, 1016, 980 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.29−4.15 (m, 4 H, OCH_2CH_3), 4.02−3.95 (m, 1 H, $HOCHCH_2$), 2.77 (dd, *J* = 3.3, 16.5 Hz, 1 H, $CHCH_2CO$), 2.67 (dd, *J* = 8.7, 16.5 Hz, 1 H, $CHCH_2CO$), 1.60−1.47 (m, 2 H, $CHCH_2CH_3$), 1.39 (6 H, dt *J* = 1.5, 6.9 Hz, OCH_2CH_3), 0.97 (t, *J* = 7.2 Hz, 3 H, $CHCH_2CH_3$) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 13.79 ppm. EI-MS: *m*/*z* = 250 (6.04) [M$^+$ − N_2] , 221 (4.05), 179 (16.47), 165 (20.12), 137 (39.42), 123 (45.12), 109 (61.00), 93 (48.39), 82 (63.67), 65 (100.00), 55 (79.02). $C_{10}H_{19}N_2O_5P$ (278.24): calcd. C 43.17, H 6.88, N 10.07; found C 42.95, H 6.87, N 9.97.

Diethyl (4*R*)-1-Diazo-4-hydroxy-2-oxo-5-hexenylphosphonate (2c): Colorless oil; yield: 84%. $[\alpha]_D^{25}$ = +27.3 (*c* = 1.2, $CHCl_3$). IR (film): ṽ = 3409, 2986, 2936, 2910, 2124, 1655, 1269, 1019, 980 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 5.95−5.83 (m, 1 H, CH=CH_2), 5.33 (d, *J* = 17.1 Hz, 1 H, CH_2=CH), 5.16 (d, *J* = 10.5 Hz, 1 H, CH_2=CH), 4.64−4.58 (m, 1 H, $HOCHCH_2$), 4.29−4.15 (m, 4 H, OCH_2CH_3), 3.05 (s, 1 H, O*H*), 3.08 (d, *J* = 5.4 Hz, 2 H, $CHCH_2CO$), 1.39 (t, *J* = 6.9 Hz, 6 H, OCH_2CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 13.62 ppm. EI-MS: *m*/*z* = 277 (0.18) [M$^+$ + 1], 220 (6.01), 191 (7.26), 175 (10.35), 163 (16.49), 146 (21.77), 135 (35.11), 121 (37.53), 109 (65.53), 93 (40.03), 81 (66.70), 65 (100.00), 57 (61.22), 55 (58.39). $C_{10}H_{17}N_2O_5P$ (276.23): calcd. C 43.48, H 6.20, N 10.14; found C 43.26, H 6.37, N 9.98.

Diethyl (4*R*)-1-Diazo-4-hydroxy-2-oxo-4-phenylbutylphosphonate (2d): Colorless oil; yield: 81%. $[\alpha]_D^{25}$ = +52.3 (*c* = 0.8, $CHCl_3$). IR (film): ṽ = 3400, 2986, 2124, 1656, 1268, 1018, 979 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.39−7.28 (m, 5 H, Ar*H*), 5.29 (dd, *J* = 2.7, 9.0 Hz, 1 H ArC*H*), 4.24−4.11 (m, 4 H, OCH_2CH_3), 3.41 (s, 1 H, O*H*), 3.04 (dd, *J* = 9.0, 16.2 Hz, 1 H, $CHCH_2CO$), 2.90 (dd, *J* = 3.0, 16.8 Hz, 1 H, $CHCH_2CO$), 1.44−1.26 (m, 6 H, OCH_2CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 6.13ppm. EI-MS: *m*/*z* =

298 (2.33) [$M^+ - N_2$], 270 (15.46), 254 (13.48), 220 (26.20), 196 (31.53), 179 (11.57), 160 (25.24), 136 (33.12), 123 (39.34), 109 (65.15), 105 (90.28), 79 (81.12), 77 (100.00), 65 (54.19). HR-MS calcd. for $C_{14}H_{19}O_5P$ [$M - N_2$]$^+$: 298.0970; found 298.0997.

Diethyl (4*R*)-1-Diazo-4-hydroxy-4-(4-methylphenyl)-2-oxobutylphosphonate (2e): Colorless oil; yield: 80%. $[\alpha]_D^{25} = +48.7$ ($c = 1.0$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3406, 2986, 2123, 1656, 1268, 1018, 979 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 7.9 Hz, 2 H, Ar*H*), 7.16 (d, J = 7.9 Hz, 2 H, Ar*H*), 5.15 (dd, J = 2.7, 9.1 Hz, 1 H, ArC*H*), 4.24−4.13 (m, 4 H, OCH_2CH$_3$), 3.03 (dd, J = 9.2, 16.2 Hz, 1 H, CHCH_2CO), 2.90 (dd, J = 3.2, 16.3 Hz, 1 H, CHCH_2CO), 2.34 (s, 3 H, ArCH_3), 1.65−1.34 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 15.03 ppm. EI-MS: *m*/*z* = 312 (6.59) [$M^+ - N_2$], 284 (35.55), 220 (19.65), 174 (24.26), 137 (24.95), 130 (49.55), 119 (100.00), 109 (43.24), 93 (48.67), 91 (76.02), 77 (41.80), 65 (45.39). HR-MS calcd. for $C_{15}H_{21}O_5P$ [$M - N_2$]$^+$: 312.1127; found 312.1121.

Diethyl (4*R*)-1-Diazo-4-(4-ethylphenyl)-4-hydroxy-2-oxobutylphosphonate (2f): Colorless oil; yield: 81%. $[\alpha]_D^{25} = +49.8$ ($c = 1.0$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3405, 2969, 2934, 2875, 2123, 1656, 1268, 1017, 979 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.24 (d, J = 8.1 Hz, 2 H, Ar*H*), 7.20 (d, J = 8.1 Hz, 2 H Ar*H*), 5.16 (dd, J = 3.0, 9.0 Hz, 1 H, ArC*H*), 4.25−4.10 (m, 4 H, OCH_2CH$_3$), 3.04 (dd, J = 9.3, 16.2 Hz, 1 H, CHCH_2CO), 2.90 (dd, J = 3.0, 15.9 Hz, 1 H, CHCH_2CO), 2.64 (dd, J = 7.5 Hz, 2 H, ArCH_2CH$_3$), 1.43−1.34 (m, 6 H, OCH$_2$CH_3), 1.23 (t, J = 7.5 Hz, 3 H, ArCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 11.10 ppm. EI-MS: *m*/*z* = 355 (0.84) [$M^+ + 1$], 337 (29.39), 326 (12.44), 298 (51.31), 280 (12.85), 253 (14.82), 224 (20.79), 188 (27.41), 144 (59.18), 133 (100.00), 123 (29.88), 109 (40.90), 91 (47.04), 79 (75.53), 65 (43.01). HR-MS calcd. for $C_{16}H_{23}O_5N_2PNa^+$ [$M + Na$]$^+$: 377.1242; found 377.1237.

Diethyl (4*R*)-1-Diazo-4-hydroxy-4-(4-methoxyphenyl)-2-oxobutylphosphonate (2g): Colorless oil; yield: 84%. $[\alpha]_D^{25} = +43.9$ ($c = 1.0$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3403, 2986, 2937, 2839, 2124, 1654, 1514, 1249, 1019, 980 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.30 (d, J = 6.6 Hz, 2 H, Ar*H*), 6.88 (d, J = 6.6 Hz, 2 H, Ar*H*), 5.14 (dd, J = 3.6, 9.0 Hz, 1 H, ArC*H*), 4.22−4.14 (m, 4 H, OCH_2CH$_3$), 3.80 (s, 3 H OCH_3), 3.03 (dd, J = 9.3, 16.2 Hz, 1 H, CHCH_2CO), 2.88 (dd, J = 3.3, 16.2 Hz, 1 H, CHCH_2CO), 1.40−1.34 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 6.15 ppm. EI-MS: *m*/*z* = 328 (2.16) [$M^+ - N_2$], 300 (13.13), 220 (7.03), 190 (8.41), 150 (22.81), 146 (42.92), 137 (47.61), 135 (100.00), 123 (20.87), 109 (49.39), 94 (23.28), 77 (38.87), 65 (36.51) ppm. $C_{15}H_{21}N_2O_6P$ (356.31): calcd. C 50.56, H 5.94, N 7.86; found C 50.60, H 5.88, N 7.69.

Diethyl (4*R*)-1-Diazo-4-(2-furyl)-4-hydroxy-2-oxobutylphosphonate (2h): Colorless oil; yield: 86%. $[\alpha]_D^{25} = +34.0$ ($c = 0.9$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3389, 2987, 2911, 2125, 1656, 1253, 1017, 981 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.38−7.37 (m, 1 H, Ar*H*), 7.35−7.33 (m, 1 H, Ar*H*), 6.30−6.28 (m, 1 H, Ar*H*), 5.21 (dd, J = 3.0, 8.1 Hz, 1 H ArC*H*), 4.28−4.14 (m, 4 H, OCH_2CH$_3$), 3.62 (d, J = 5.1 Hz, 1 H, O*H*), 3.22 (dd, J = 8.7, 16.5 Hz, 1 H, CHCH_2CO), 3.02 (dd, J = 3.6, 16.5 Hz, 1 H, CHCH_2CO), 1.42−1.36 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 11.43 ppm. EI-MS: *m*/*z* = 299 (0.50) [$M^+ - OH$], 288 (6.70), 259 (36.41), 244 (34.97), 231 (22.72), 214 (33.16), 203 (40.79), 186 (44.39), 179 (22.96), 151 (42.09), 135 (25.66), 123 (100.00), 106 (70.22), 97 (79.20), 81 (48.16), 65 (56.14). $C_{12}H_{17}N_2O_6P$ (316.25): calcd. C 45.58, H 5.42, N 8.86; found C 45.51, H 5.51, N 8.80.

Diethyl (4*R*)-4-(2-Bromophenyl)-1-diazo-4-hydroxy-2-oxobutylphosphonate (2i): Colorless oil; yield: 86%. $[\alpha]_D^{25} = +96.3$ ($c = 0.9$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3384, 2986, 2909, 2125, 1656, 1266, 1046, 1019, 980 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.63 (d, J = 7.5 Hz, 1 H, Ar*H*), 7.52 (d, J = 7.5 Hz, 1 H, Ar*H*), 7.37 (t, J = 7.5 Hz, 1 H, Ar*H*), 7.16 (t, J = 7.2 Hz, 1 H, Ar*H*), 5.49 (d, J = 8.4 Hz, 1 H ArC*H*), 4.24−4.11 (m, 4 H, OCH_2CH$_3$), 3.09 (dd, J = 1.5, 16.8 Hz, 1 H, CHCH_2CO), 2.81 (dd, J = 9.3, 17.1 Hz, 1 H, CHCH_2CO), 1.40−1.34 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 10.85 ppm. EI-MS: *m*/*z* = 408 (0.88) [M^+], 325 (10.20), 297 (28.31), 269 (24.59), 241 (36.54), 223 (36.52), 195 (16.92), 185 (26.38), 159 (15.92), 137 (30.38), 123 (26.08), 109 (52.23), 91 (41.31), 77 (100.00), 65 (69.04). $C_{14}H_{18}BrN_2O_5P$ (405.18): calcd. C 41.50, H 4.48, N 6.91; found C 41.76, H 4.56, N 6.63.

Diethyl (4*R*)-1-Diazo-4-(2-fluorophenyl)-4-hydroxy-2-oxobutylphosphonate (2j): Colorless oil; yield: 85%. $[\alpha]_D^{25} = +51.4$ ($c = 0.9$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3400, 2987, 2911, 2125, 1653, 1511, 1266, 1018, 980 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40−7.38 (m, 2 H, Ar*H*), 7.15−7.00 (m, 2 H, Ar*H*), 5.16 (dd, J = 3.3, 9.0 Hz, 1 H, ArC*H*), 4.25−4.08 (m, 4 H, OCH_2CH$_3$), 3.84 (s, 1 H, O*H*), 3.01 (dd, J = 9.3, 16.5 Hz, 1 H, CHCH_2CO), 2.86 (dd, J = 3.6, 16.5 Hz, 1 H, CHCH_2CO), 1.44−1.33 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 10.98 ppm. EI-MS: *m*/*z* = 316 (6.97) [$M^+ - N_2$], 288 (11.16), 272 (29.50), 244 (10.31), 216 (15.96), 179 (27.08), 165 (100.00), 133 (52.18), 123 (87.38), 109 (70.50), 95 (27.27), 65 (19.49). HR-MS calcd. for $C_{14}H_{18}FO_5P$ [$M - N_2$]$^+$: 316.0876; found 316.0864.

Diethyl (4*R*)-1-Diazo-4-(2,4-dichlorophenyl)-4-hydroxy-2-oxobutylphosphonate (2k): Colorless oil; yield: 87%. $[\alpha]_D^{25} = +96.0$ ($c = 0.7$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3379, 2986, 2910, 2125, 1656, 1265, 1048, 1018, 979 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.58 (d, J = 8.4 Hz, 1 H, Ar*H*), 7.35−7.28 (m, 2 H, Ar*H*), 5.47 (dd, J = 2.4, 9.0 Hz, 1 H, ArC*H*), 4.23−4.13 (m, 4 H, OCH_2CH$_3$), 3.06 (dd, J = 2.4, 17.1 Hz, 1 H, CHCH_2CO), 2.28 (dd, J = 9.3, 17.1 Hz, 1 H, CHCH_2CO), 1.43−1.34 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 10.80 ppm. EI-MS: *m*/*z* = 395 (0.50) [$M^+ + 1$] [M^+], 359 (16.44), 331 (19.13), 303 (44.75), 275 (31.71), 257 (24.13), 220. (87.73), 175 (63.92), 137 (66.52), 111 (100.00), 109 (88.16), 93 (30.53), 65 (52.47), 65 (54.19). $C_{14}H_{17}Cl_2N_2O_5P$ (395.18): calcd. C 42.55, H 4.34, N 7.09; found C 42.50, H 4.55, N 7.32.

General Procedure for Preparation of 2-Diethoxylphosphoryl-3-oxo-5-aryl(or -alkyl)tetrahydrofurans 3: To a suspension of $Rh_2(OAc)_4$ (1 mg) in refluxing benzene (10 mL) was added compound **2** (1 mmol) in benzene (3 mL) over a 5 min period. After an additional 30 min at reflux, the mixture was cooled to room temperature. After concentration and flash chromatography, the corresponding compound **3** was obtained.

(5*S*)-2-Diethoxyphosphoryl-5-methyl-3-oxotetrahydrofuran (3a): Colorless oil; yield: 94%. $[\alpha]_D^{25} = +26.2$ ($c = 1.0$, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2983, 2934, 2913, 1762, 1255, 1048, 1023, 974 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.83−4.76 (m, 0.5 H, OC*H*CH$_2$), 4.41−4.34 (m, 1 H, OC*H*CH$_2$, OC*H*CO), 4.29−4.17 (m, 4.5 H, OCH_2CH$_3$, OC*H*CO), 2.79−2.58 (m, 1 H, CHCH_2CO), 2.41−2.16 (m, 1 H, CHCH_2CO), 1.51 (d, J = 5.4 Hz, 1.5 H, CHCH_3), 1.43 (d, J = 5.4 Hz, 1.5 H, CHCH_3), 1.37 (t, J = 7.2 Hz, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 14.79, 13.82 ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 209.4 (J = 35.3 Hz), 79.1 (J = 44.7 Hz), 74.7 (J = 30.4 Hz), 63.5 (J = 19.3 Hz), 44.8 (J = 40.2 Hz), 21.0, 16.4 ppm. EI-MS: *m*/*z* = 236

(7.58) [M$^+$], 179 (15.56), 167 (34.17), 138 (58.41), 127 (39.82), 111 (90.29), 138 (35.45), 99 (73.88), 81 (87.57), 65 (43.58), 43 (100.00). $C_9H_{17}O_5P$ (236.20): calcd. C 45.77, H 7.25; found C 45.72, H 7.35.

(5*S*)-2-Diethoxyphosphoryl-5-ethyl-3-oxotetrahydrofuran (3b): Colorless oil; yield: 94%. $[\alpha]_D^{25}$ = +14.5 (c = 2.1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2980, 2937, 2883, 1763, 1255, 1050, 1024, 974 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.63−4.58 (m, 0.5 H), 4.36 (d, J = 14.4 Hz, 0.5 H, OC*H*CO), 4.29−4.18 (m, 5 H, OCH_2CH$_3$, OC*H*CH$_2$, OC*H*CO), 2.76−2.55 (m, 1 H, CHCH_2CO), 2.44−2.22 (m, 1 H, CHCH_2CO), 1.90−1.67 (m, 2 H, CHCH_2CH$_3$), 1.40−1.34 (m, 6 H, OCH$_2$CH_3), 1.05−0.97 (m, 3 H, CHCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 17.17, 16.34 ppm. EI-MS: m/z = 250 (6.97) [M$^+$], 221 (11.57), 179 (23.15), 167 (80.49), 139 (50.49), 127 (42.92), 111 (100.00), 99 (57.57), 81 (85.61), 65 (65.79), 41 (79.70). $C_{10}H_{19}O_5P$ (250.23): calcd. C 48.00, H 7.65; found C 48.15, H 7.94.

(5*R*)-2-Diethoxyphosphoryl-3-oxo-5-vinyltetrahydrofuran (3c): Colorless oil; yield: 95%. $[\alpha]_D^{25}$ = +21.2 (c = 1.0, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2897, 2914, 1761, 1254, 1048, 1023, 975 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.12−5.87 (m, 1 H, C*H*=CH$_2$), 5.44−5.27 (m, 2 H, CH_2=CH), 5.18−5.09 (m, 0.5 H, OC*H*CH$_2$), 4.80−4.50 (m, 0.5 H, OC*H*CH$_2$), 4.38 (d, J = 14.4 Hz, 0.5 H, OC*H*CO), 4.30−4.20 (m, 4.5 H, OCH_2CH$_3$, OC*H*CO), 2.88−2.37 (m, 2 H, CHCH_2CO), 1.40−1.34 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 16.81, 15.99 ppm. EI-MS: m/z = 248 (4.77) [M$^+$], 220 (13.18), 179 (23.47), 167 (74.60), 139 (59.01), 111 (100.00), 99 (54.38), 81 (59.43), 65 (50.03), 54 (76.59). $C_{10}H_{17}O_5P$ (248.21): calcd. C 48.39, H 6.90; found C 48.10, H7.20.

(5*R*)-2-Diethoxyphosphoryl-3-oxo-5-phenyltetrahydrofuran (3d): Colorless oil; yield: 96%. $[\alpha]_D^{25}$ = +66.3 (c = 1.5, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2986, 2914, 1763, 1252, 1048, 1023, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.52−7.28 (m, 5 H, Ar*H*), 5.71 (dd, J = 6.9, 6.9 Hz, 0.5 H, ArC*H*), 5.25 (dd, J = 5.7, 6.0 Hz, 0.5 H, ArC*H*), 4.55 (d, J = 14.1 Hz, 0.5 H, OC*H*CO), 4.40 (d, J = 13.8 Hz, 0.5 H, OC*H*CO), 4.32−4.21 (m, 4 H, OCH_2CH$_3$), 3.09−2.56 (m, 2 H, CHCH_2CO), 1.46−1.29 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 14.24, 13.45 ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 208.5 (J = 39.4 Hz), 139.7 (J = 17.7 Hz), 128.8, 126.4, 126.1, 80.1 (J = 10.4 Hz), 79.3 (J = 19.3 Hz), 63.7 (J = 13.4 Hz), 45.1 (J = 74.9 Hz), 16.5 ppm. EI-MS: m/z = 298 (1.35) [M$^+$], 242 (3.48), 179 (20.94), 160 (32.23), 144 (30.04), 123 (18.21), 105 (89.00), 104 (100.00), 77 (30.67). $C_{14}H_{19}O_5P$ (298.27): calcd. C 56.38, H 6.42; found C 56.10, H 6.62.

(5*R*)-2-Diethoxyphosphoryl-5-(4-methylphenyl)-3-oxotetrahydrofuran (3e): Colorless oil; yield: 97%. $[\alpha]_D^{25}$ = +64.3 (c = 1.1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2985, 2916, 1761, 1251, 1048, 1023, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81−7.22 (m, 4 H, Ar*H*), 5.66 (dd, J = 6.9, 8.6 Hz, 0.5 H, ArC*H*), 5.19 (dd, J = 5.1, 6.0 Hz, 0.5 H, ArC*H*), 4.50 (d, J = 14.4 Hz, 0.5 H, OC*H*CO), 4.36 (d, J = 13.9 Hz, 0.5 H, OC*H*CO), 4.26−4.21 (m, 4 H, OCH_2CH$_3$), 3.03−2.03 (m, 2 H, CHCH_2CO), 2.40 (s, 3 H, ArCH_3), 1.39−1.24 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 18.23, 17.38 ppm. EI-MS: m/z = 312 (4.65) [M$^+$], 179 (20.13), 174 (37.94), 158 (17.23), 119 (100.00), 118 (70.45), 105 (19.48), 91 (52.37). HR-MS Calcd. for $C_{15}H_{21}O_5PNa$ ([M + Na]$^+$): 335.1024; found 335.1019.

(5*R*)-2-Diethoxyphosphoryl-5-(4-ethylphenyl)-3-oxotetrahydrofuran (3f): Colorless oil; yield: 93%. $[\alpha]_D^{25}$ = +66.5 (c = 1.1, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2969, 2933, 2914, 2875, 1761, 1253, 1048, 1022, 976 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.4 Hz, 1 H, Ar*H*), 7.31 (d, J = 8.4 Hz, 1 H, Ar*H*), 7.27−7.21 (m, 2 H, Ar*H*), 5.67 (dd, J = 6.9, 7.5 Hz, 0.5 H, ArC*H*), 5.21 (dd, J = 6.0, 6.3 Hz, 0.5 H, ArC*H*), 4.53 (d, J = 14.7 Hz, 0.5 H, OC*H*CO), 4.38 (d, J = 13.8 Hz, 0.5 H, OC*H*CO), 4.31−4.20 (m, 4 H, OCH_2CH$_3$), 3.02 (dd, J = 6.8, 18.3 Hz, 0.5 H, CHCH_2CO), 2.84−2.77 (m, 1 H, CHCH_2CO), 2.70−2.57 (m, ArCH_2CH$_3$, 2.5 H, CHCH_2CO), 1.41−1.32 (m, 6 H, OCH$_2$CH_3), 1.24 (t, J = 7.5 Hz, 3 H, ArCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 14.26, 13.47 ppm. EI-MS: m/z = 326 (10.09) [M$^+$], 256 (4.65), 188 (41.93), 179 (18.16), 151 (12.07), 133 (100.00), 132 (80.17), 117 (54.39), 105 (23.05), 91 (26.64), 65 (13.72). $C_{16}H_{23}O_5P$ (326.33): calcd. C 58.90, H 7.10; found C 58.79, H 7.19.

(5*R*)-2-Diethoxyphosphoryl-5-(4-methoxyphenyl)-3-oxotetrahydrofuran (3g): Colorless oil; yield: 96%. $[\alpha]_D^{25}$ = +64.0 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2985, 2935, 2913, 2841, 1761, 1517, 1251, 1027, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43 (d, J = 8.7 Hz, 1 H, Ar*H*), 7.32 (d, J = 9.0 Hz, 1 H, Ar*H*), 6.93 (dd, J = 2.1, 8.7 Hz, 2 H, Ar*H*), 5.65 (dd, J = 6.6, 6.9 Hz, 0.5 H, ArC*H*), 5.19 (dd, J = 6.3, 6.6 Hz, 0.5 H, ArC*H*), 4.52 (d, J = 14.7 Hz, 0.5 H, OC*H*CO), 4.37 (d, J = 13.8 Hz, 0.5 H, OC*H*CO), 4.30−4.20 (m, 4 H, OCH_2CH$_3$), 3.82 (s, 3 H, OCH_3), 3.00 (dd, J = 6.8, 18.3 Hz, 0.5 H, CHCH_2CO), 2.83−2.76 (m, 1 H, CHCH_2CO), 2.64 (dd, J = 6.6, 18.3 Hz, 0.5 H, CHCH_2CO), 1.44−1.26 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 3.93, 8.59 ppm. EI-MS: m/z = 328 (22.97) [M$^+$], 258 (3.11), 191 (22.27), 190 (23.03), 179 (10.03), 150 (15.57), 135 (100.00), 134 (54.28), 121(33.01), 91 (18.39). $C_{15}H_{21}O_6P$ (328.30): calcd. C 54.88, H 6.45; found C 54.58, H 6.74.

(5*R*)-2-Diethoxyphosphoryl-5-(2-furyl)-3-oxotetrahydrofuran (3h): Colorless oil; yield: 97%. $[\alpha]_D^{25}$ = −6.0 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2987, 1763, 1253, 1046, 1021, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.46−7.28 (m, 1 H, Ar*H*), 6.49−6.37 (m, 2 H, Ar*H*), 5.66 (t, J = 7.4 Hz, 0.5 H, ArC*H*), 5.28 (dd, J = 6.0, 6.3 Hz, 0.5 H, ArC*H*), 4.45 (t, J = 13.8 Hz, 0.5 H, OC*H*CO), 4.36 (d, J = 13.5 Hz, 0.5 H, OC*H*CO), 4.29−4.18 (m, 4 H, OCH_2CH$_3$), 3.16−2.75 (m, 2 H, CHCH_2CO), 1.41−1.31 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 12.57, 12.46 ppm. EI-MS: m/z = 288 (7.96) [M$^+$], 218 (32.87), 179 (27.44), 151 (29.32), 123 (43.04), 109 (17.42), 95 (30.74), 94 (100.00), 81 (54.58), 65 (29.32). $C_{12}H_{17}O_6P$ (288.23): calcd. C 50.00, H 5.94; found C 49.86, H 6.05.

(5*R*)-5-(2-Bromophenyl)-2-diethoxyphosphoryl-3-oxotetrahydrofuran (3i): Colorless oil; yield: 95%. $[\alpha]_D^{25}$ = +87.4 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2985, 2932, 2912, 1763, 1254, 1047, 1021, 976 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.84 (d, J = 8.4 Hz, 1 H, Ar*H*), 7.60−7.53 (m, 1.5 H, Ar*H*), 7.42−7.35 (m, 1 H, Ar*H*), 7.24−7.20 (m, 1 H, Ar*H*), 5.93 (t, J = 8.1 Hz, 0.5 H, ArC*H*), 5.58 (dd, J = 5.4, 5.7 Hz, 0.5 H, ArC*H*), 4.63 (d, J = 14.4 Hz, 0.5 H, OC*H*CO), 4.43 (d, J = 14.7 Hz, 0.5 H, OC*H*CO), 4.33−4.23 (m, 4 H, OCH_2CH$_3$), 3.31 (dd, J = 6.9, 18.6 Hz, 0.5 H, CHCH_2CO), 3.13 (dd, J = 6.0, 18.6 Hz, 0.5 H, CHCH_2CO), 2.51−2.37 (m, 1 H, CHCH_2CO), 1.43−1.36 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 14.21, 13.34 ppm. EI-MS: m/z = 377 (0.84) [M$^+$], 348 (11.56), 306 (14.13), 297 (88.21), 269 (25.33), 241 (22.23), 184 (68.51), 167 (62.78), 123 (36.20), 111 (49.96), 103 (100.00), 77 (80.38), 65 (35.96). $C_{14}H_{18}BrO_5P$ (377.17): calcd. C 44.58, H 4.81; found C 44.79, H 4.75.

(5*R*)-2-Diethoxyphosphoryl-5-(4-fluorophenyl)-3-oxotetrahydrofuran (3j): Colorless oil; yield: 96%. $[\alpha]_D^{25}$ = +71.9 (c = 1.3, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2987, 2914, 1762, 1514, 1252, 1048, 1023, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.53−7.48 (m, 1 H, Ar*H*), 7.41−7.37 (m, 1 H, Ar*H*), 7.13−7.07 (m, 2 H, Ar*H*), 5.70 (dd, J = 6.9, 6.9 Hz, 0.5 H, ArC*H*), 5.25 (dd, J = 6.0, 6.0 Hz, 0.5 H, ArC*H*),

4.55 (d, J = 14.4 Hz, 0.5 H, OC*H*CO), 4.40 (d, J = 13.8 Hz, 0.5 H, OC*H*CO), 4.33−4.10 (m, 4 H, OCH_2CH$_3$), 3.05 (dd, J = 6.9, 18.0 Hz, 0.5 H, CHCH_2CO), 2.89 (dd, J = 5.8, 17.7 Hz, 0.5 H, CHCH_2CO), 2.74 (dd, J = 11.4, 17.4 Hz, 0.5 H, CHCH_2CO), 2.57 (dd, J = 9.3, 18.0 Hz, 0.5 H, CHCH_2CO), 1.44−1.25 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 14.09, 14.39 ppm. EI MS: m/z = 316 (1.70) [M$^+$], 179 (30.10), 178 (24.11), 162 (27.72), 151 (21.61), 133 (17.40), 123 (86.52), 122 (100.00), 109 (29.54), 81 (21.25), 65 (10.87). $C_{14}H_{18}FO_5P$ (316.26): calcd. C 53.17, H 5.74; found C 53.06, H 5.89.

(5*R*)-5-(2,4-Dichlorophenyl)-2-diethoxyphosphoryl-3-oxotetrahydrofuran (3k): Colorless oil; yield: 94%. $[\alpha]_D^{25}$ = +91.0 (c = 1.2, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2985, 2913, 1764, 1253, 1048, 1022, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (d, J = 8.7 Hz, 1 H, Ar*H*), 7.56 (d, J = 8.7 Hz, 0.5 H, Ar*H*), 7.41−7.28 (m, 2 H, Ar*H*), 5.91 (dd, J = 7.2, 7.5 Hz, 0.5 H, ArC*H*), 5.58 (dd, J = 6.0, 6.3 Hz, 0.5 H, , ArC*H*), 4.61 (d, J = 14.1 Hz, 0.5 H, OC*H*CO), 4.42 (d, J = 13.8 Hz, 0.5 H, OC*H*CO), 4.33−4.14 (m, 4 H, OCH_2CH$_3$), 3.26 (dd, J = 7.1, 18.3 Hz, 0.5 H, CHCH_2CO), 3.11 (dd, J = 6.1, 17.7 Hz, 0.5 H, CHCH_2CO), 2.54−2.35 (m, 1 H, CHCH_2CO), 1.45−1.34 (m, 6 H, OCH$_2$CH_3) ppm. ^{31}P NMR (120 MHz, $CDCl_3$): δ = 14.01, 13.23 ppm. EI-MS: m/z = 366 (2.54) [M$^+$], 338 (29.32), 332 (29.79), 331 (87.52), 303 (20.27), 296 (41.90), 275 (12.98), 212 (36.26), 179 (62.28), 174 (67.78), 167 (61.54), 151 (36.26), 137 (54.01), 123 (37.71), 111 (38.74), 102 (37.24), 91 (29.20), 65 (21.63). $C_{14}H_{17}Cl_2O_5P$ (367.16): calcd. C 45.80, H 4.67; found C 46.02, H 4.82.

General Procedure for Preparation of 2-(1-Methylethylidene)-3-oxo-5-aryl(or -alkyl)tetrahydrofurans 4: A solution of compound **3** (0.5 mmol), K_2CO_3 (0.2 g, 1.5 mmol), acetone (2 mL) and H_2O (2 mL) was refluxed for 2 h. The mixture was cooled to room temperature and the solvents evaporated in vacuo. Brine (5 mL) was added to the residue which was then extracted with ethyl acetate (3×5 mL). The combined extracts were dried, the solvents evaporated under reduced pressure and the residue subjected to flash chromatography to furnish the corresponding compound **4**.

(5*S*)-5-Methyl-2-(1-methylethylidene)-3-oxotetrahydrofuran (4a): Colorless oil; yield: 66%. $[\alpha]_D^{25}$ = −14.2 (c = 0.9, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2978, 2912, 1724, 1646, 1275, 1153 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.56−4.49 (m, 1 H, OC*H*CH$_2$), 2.75 (dd, J = 7.1, 17.4 Hz, 1 H, CHCH_2CO), 2.30 (dd, J = 7.9, 17.7 Hz, 1 H, CHCH_2CO), 2.08 (s, 3 H, C=CCH_3), 1.81 (s, 3 H, C=CCH_3), 1.41 (d, J = 6.0 Hz, 3 H, CHCH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 199.5, 143.6, 120.5, 72.1, 45.2, 22.0, 19.8, 17.0 ppm. EI-MS: m/z = 140 (1.94) [M$^+$], 109 (10.33), 87 (9.40), 82 (9.96), 73 (14.02), 70 (65.59), 69 (80.44), 59 (39.75), 43 (73.41), 42 (10.00), 41 (42.15). HR-MS Calcd. for $C_8H_{12}O_2$ [M$^+$]: 140.0837; found 140.0830.

(5*S*)-5-Ethyl-2-(1-methylethylidene)-3-oxotetrahydrofuran (4b): Colorless oil; yield: 68%. $[\alpha]_D^{25}$ = −25.0 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2966, 2930, 1726, 1647, 1276, 1208, 1152 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 4.35−4.31 (m, 1 H, OC*H*CH$_2$), 2.72 (dd, J = 7.2, 17.7 Hz, 1 H, CHCH_2CO), 2.33 (dd, J = 7.2, 18.0 Hz, 1 H, CHCH_2CO), 2.07 (s, 3 H, C=CCH_3), 1.81 (s, 3 H, C=CCH_3), 1.78−1.59 (m, 2 H, CH_2CH$_3$), 1.02 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 154 (8.09) [M$^+$], 125 (5.00), 111 (7.62), 97 (11.92), 85 (20.45), 83 (30.98), 71 (43.73), 70 (41.08), 57 (100.00), 55 (42.68), 43 (75.76), 41 (66.62). HR-MS calcd. for $C_9H_{14}O_2$ [M$^+$]: 154.0994; found 154.1008.

(5*R*)-2-(1-Methylethylidene)-3-oxo-5-vinyltetrahydrofuran (4c): Colorless oil; yield: 67%. $[\alpha]_D^{25}$ = −6.8 (c = 0.9, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2990, 2985, 2870, 1726, 1645, 1273, 1208, 1150 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00−5.88 (m, 1 H, C*H*=CH$_2$), 5.47 (dt, J = 0.9, 17.1 Hz, 1 H, CH=CH_2), 5.26 (dt, J = 0.9, 10.2 Hz, 1 H, CH=CH_2), 4.90−4.83 (m, 1 H, OC*H*CH$_2$), 2.83 (dd, J = 7.8, 17.7 Hz, 1 H, CHCH_2CO), 2.48 (dd, J = 7.7, 18.0 Hz, 1 H, CHCH_2CO), 2.09 (s, 3 H, C=CCH_3), 1.84 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 152 (5.92) [M$^+$], 145 (0.89), 82 (7.65), 81 (6.48), 70 (37.39), 59 (8.17), 55 (10.39), 54 (100.00), 43 (26.91), 42 (28.70). HR-MS calcd. for $C_9H_{12}O_2$ [M$^+$]: 152.0837; found 152.0806.

(5*R*)-2-(1-Methylethylidene)-3-oxo-5-phenyltetrahydrofuran (4d): Colorless oil; yield: 67%. $[\alpha]_D^{25}$ = +135.7 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3034, 2913, 2855, 1726, 1647, 1274, 1215, 1201, 1147 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.40−7.26 (m, 5 H, Ar*H*), 5.43 (t, J = 8.1 Hz, 1 H, ArC*H*), 3.06 (dd, J = 7.5, 17.7 Hz, 1 H, CHCH_2CO), 2.68 (dd, J = 8.2, 17.7 Hz, 1 H, CHCH_2CO), 2.13 (s, 3 H, C=CCH_3), 1.88 (s, 3 H, C=CCH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 198.4, 143.6, 141.2, 128.8, 128.3, 125.7, 121.5, 77.6, 45.9, 20.0, 17.1 ppm. EI-MS: m/z = 202 (39.8) [M$^+$], 184 (5.09), 131 (5.41), 118 (2.64), 105 (8.39), 104 (47.88), 103 (18.75), 78 (15.52), 77 (15.80), 70 (100.00), 51 (10.47), 42 (33.37), 41 (19.29). $C_{13}H_{14}O_2$ (202.25): calcd. C 77.20, H 6.98; found C 77.34, H 7.26.

(5*R*)-2-(1-Methylethylidene)-5-(4-methylphenyl)-3-oxotetrahydrofuran (4e): Colorless oil; yield: 59%. $[\alpha]_D^{25}$ = +100.6 (c = 0.5, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2924, 2856, 1726, 1647, 1274, 1209, 1199, 1147 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.26 (d, J = 7.5 Hz, 2 H, Ar*H*), 7.20 (d, J = 7.9 Hz, 2 H, Ar*H*), 5.39 (t, J = 7.8 Hz, 1 H, ArC*H*), 3.03 (dd, J = 7.7, 17.8 Hz, 1 H, CHCH_2CO), 2.68 (dd, J = 8.0, 17.8 Hz, 1 H, CHCH_2CO), 2.36 (3 H,s, ArCH_3), 2.18 (s, 3 H, C=CCH_3), 1.86 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 216 (46.88) [M$^+$], 201 (5.59), 183 (4.12), 173 (4.60), 145 (10.15), 132 (10.33), 118 (100.00), 117 (44.46), 105 (9.50), 91 (16.49), 70 (42.94), 42 (19.71). $C_{14}H_{16}O_2$ (216.28): calcd. C 77.75, H 7.46; found C 77.45, H 7.62.

(5*R*)-5-(4-Ethylphenyl)-2-(1-methylethylidene)-3-oxotetrahydrofuran (4f): Colorless oil; yield: 59%. $[\alpha]_D^{25}$ = +115.2 (c = 0.5, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2967, 2931, 2912, 2875, 1726, 1647, 1274, 1203, 1147 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.1 Hz, 2 H, Ar*H*), 7.22 (d, J = 7.8 Hz, 2 H, Ar*H*), 5.93 (t, J = 8.1 Hz, 1 H, ArC*H*), 3.03 (dd, J = 7.7, 18.0 Hz, 1 H, CHCH_2CO), 2.74−2.62 (m, 3 H, CHCH_2CO, ArCH_2CH$_3$), 2.12 (s, 3 H, C=CCH_3), 1.86 (s, 3 H, C=CCH_3), 1.24 (t, J = 8.1 Hz, 3 H, ArCH$_2$CH_3) ppm. EI-MS: m/z = 230 (47.56) [M$^+$], 201 (6.83), 183 (5.59), 160 (8.05), 132 (89.90), 117 (100.00), 103 (6.17), 91 (21.35), 77 (10.54), 70 (67.64), 42 (56.93), 41 (56.01). $C_{15}H_{18}O_2$ (230.31): calcd. C 78.23, H 7.88; found C 78.40, H 7.97.

(5*R*)-5-(4-Methoxyphenyl)-2-(1-methylethylidene)-3-oxotetrahydrofuran (4g): Colorless oil; yield: 60%. $[\alpha]_D^{25}$ = +82.5 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3003, 2958, 2911, 2839, 1724, 1646, 1516, 1274, 1251, 1201, 1146 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.22 (d, J = 9.0 Hz, 2 H, Ar*H*), 6.84 (d, J = 8.7 Hz, 2 H, Ar*H*), 5.29 (t, J = 7.8 Hz, 1 H, ArC*H*), 3.74 (s, 3 H, OCH_3), 2.93 (dd, J = 7.7, 18.0 Hz, 1 H, CHCH_2CO), 2.61 (dd, J = 8.1, 17.7 Hz, 1 H, CHCH_2CO), 2.05 (s, 3 H, C=CCH_3), 1.78 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 232 (17.30) [M$^+$], 161 (5.63), 134 (100.00), 121 (20.23), 119 (21.51), 91 (20.69), 77 (5.77), 70 (17.08), 65 (11.66), 42 (15.60), 41 (15.78). $C_{14}H_{16}O_3$ (232.28): calcd. C 72.39, H 6.94; found C 72.23, H 7.21.

(5*S*)-5-(2-Furyl)-2-(1-methylethylidene)-3-oxotetrahydrofuran (4h): Colorless oil; yield: 70%. $[\alpha]_D^{25}$ = +39.7 (c = 0.7, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2912, 1725, 1647, 1274, 1204, 1146 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (s, 1 H, Ar*H*), 6.40−6.37 (m, 2 H, Ar*H*), 5.42 (t,

J = 7.5 Hz, 1 H, ArC*H*), 2.95 (t, J = 2.7 Hz, 2 H, 7.5 Hz, CHCH_2CO), 2.10 (s, 3 H, C=CCH_3), 1.81 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 192 (15.70) [M^+], 174 (3.74), 164 (8.56), 121 (5.31), 94 (100.00), 81 (5.34), 70 (20.98), 66 (14.16), 42 (11.91). HR-MS calcd. for $C_{11}H_{12}O_3$ [M^+]:192.0786; found 192.0779.

(5*R*)-5-(2-Bromophenyl)-2-(1-methylethylidene)-3-oxotetrahydrofuran (4i): Colorless oil; yield: 63%. $[\alpha]_D^{25}$ = +172.3 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3069, 2988, 2911, 2854, 1726, 1647, 1441, 1274, 1214, 1198, 1147, 1027 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.56 (d, J = 7.8 Hz, 1 H, Ar*H*), 7.49 (d, J = 6.9 Hz, 1 H, Ar*H*), 7.36 (t, J = 6.9 Hz, 1 H, 8.4 Hz, Ar*H*), 7.18 (d, J = 7.8 Hz, 1 H, Ar*H*), 5.70 (t, J = 7.8 Hz, 1 H, ArC*H*), 3.29 (dd, J = 8.3, 18.0 Hz, 1 H, CHCH_2CO), 2.51 (dd, J = 7.1, 18.0 Hz, 1 H, CHCH_2CO), 2.15 (s, 3 H, C=CCH_3), 1.93 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 282 (15.63 [M^+]), 280 (16.08) [M^+], 201 (5.24), 184 (8.08), 182 (7.97), 103 (17.60), 102 (8.81), 98 (4.52), 77 (15.44), 70 (100.00), 51 (7.95), 42 (25.87). $C_{13}H_{13}BrO_2$ (281.15): calcd. C 55.54, H 4.66; found C 55.83, H 4.81.

(5*R*)-5-(4-Fluorophenyl)-2-(1-methylethylidene)-3-oxotetrahydrofuran (4j): Colorless oil; yield: 67%. $[\alpha]_D^{25}$ = +89.9 (c = 0.7, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2913, 2856, 1726, 1647, 1513, 1274, 1235, 1222, 1200, 1146 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.34 (dd, J = 5.7 Hz, 2 H, Ar*H*), 7.08 (t, J = 8.4 Hz, 2 H, Ar*H*), 5.41 (t, J = 7.8 Hz, 1 H, ArC*H*), 3.05 (dd, J = 7.5, 18.0 Hz, 1 H, CHCH_2CO), 2.65 (dd, J = 8.1, 17.7 Hz, 1 H, CHCH_2CO), 2.13 (s, 3 H, C=CCH_3), 1.87 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 220 (82.69) [M^+], 202 (10.27), 174 (6.24), 149 (6.86), 122 (63.90), 121 (20.57), 101 (15.74), 96 (14.67), 75 (8.56), 70 (100.00), 42 (27.53). HR-MS calcd. for $C_{13}H_{13}FO_2$ [M^+]: 220.0900; found 220.0895.

(5*R*)-5-(2,4-Dichlorophenyl)-2-(1-methylethylidene)-3-oxotetrahydrofuran (4k): Colorless oil; yield: 64%. $[\alpha]_D^{25}$ = +144.4 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2962, 2928, 1724, 1647, 1278, 1201, 1138, 1059 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.45 (d, J = 8.1 Hz, 1 H, Ar*H*), 7.40 (d, J = 2.1 Hz, 1 H, Ar*H*), 7.29 (dd, J = 1.8, 8.4 Hz, 2 H, Ar*H*), 5.68 (t, J = 7.5 Hz, 1 H, ArC*H*), 3.24 (dd, J = 8.3, 18.0 Hz, 1 H, CHCH_2CO), 2.49 (dd, J = 7.2, 18.3 Hz, 1 H, CHCH_2CO), 2.14 (s, 3 H, C=CCH_3), 1.91 (s, 3 H, C=CCH_3) ppm. EI-MS: m/z = 272 (29.26) [M^+], 270 (36.02) [M^+], 235 (10.17), 181 (6.16), 137 (13.65), 102 (10.63), 101 (10.72), 75 (7.60), 65 (11.66), 70 (100.00), 42 (21.92), 41 (11.37). $C_{13}H_{12}Cl_2O_2$ (271.14): calcd. C 57.59, H 4.46; found C 57.77, H 4.71.

General Procedure for Preparation of 2-[(*Z*)-Benzylidene(or -propylidene)]-3-oxo-5-aryl(or -alkyl)tetrahydrofurans 5 and 2-[(*E*)-Benzylidene(or -propylidene)]-3-oxo-5-aryl (or -alkyl)tetrahydrofurans 6: A solution of **3** (0.5 mmol), K_2CO_3 (0.2 g, 1.5 mmol), THF (2 mL), H_2O (2 mL) and aldehyde (1 mmol) was stirred for 2.5 h. Then brine (5 mL) was added to the mixture and it was extracted with ethyl acetate. The organic phase was dried and the solvents evaporated under reduced pressure. The residue was subjected to flash chromatography giving compounds **5** and **6**.

(5*S*)-2-[(*Z*)-Benzylidene]-5-ethyl-3-oxotetrahydrofuran (5b): Colorless oil; yield: 41%. $[\alpha]_D^{25}$ = +6.3 (c = 0.7, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2970, 2937, 2881, 1769, 1731, 1243, 1222, 1170 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.5 Hz, 2 H, Ar*H*), 7.38−7.25 (m, 3 H, Ar*H*), 6.30 (s, 1 H, C=C*H*Ar), 4.55−4.45 (m, 1 H, OC*H*CH$_2$), 2.86 (dd, J = 7.2, 18.0 Hz, 1 H, CHCH_2CO), 2.48 (dd, J = 7.2, 18.6 Hz, 1 H, CHCH_2CO), 1.86−1.69 (m, 2 H, CH_2CH$_3$), 1.03 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 202 (56.46) [M^+], 173 (2.62), 147 (4.33), 119 (15.61), 118 (100.00), 107 (15.07), 105 (13.84), 90 (49.91), 89 (29.00), 77 (5.65), 56 (7.16). HR-MS calcd. for $C_{13}H_{14}O_2$ [M^+]: 202.0994; found 202.0986.

(5*R*)-2-[(*E*)-Benzylidene]-5-ethyl-3-oxotetrahydrofuran (6b): Colorless oil; yield: 18%. $[\alpha]_D^{25}$ = +19.5 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3065, 2969, 2936, 2881, 1734, 1635, 1243, 1190, 1180 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.77 (d, J = 8.1 Hz, 2 H, Ar*H*), 7.30−7.25 (m, 3 H, Ar*H*), 6.28 (s, 1 H, C=C*H*Ar), 4.74−4.65 (m, 1 H, OC*H*CH$_2$), 2.83 (dd, J = 7.8, 18.6 Hz, 1 H, CHCH_2CO), 2.41 (dd, J = 6.8, 18.3 Hz, 1 H, CHCH_2CO), 1.93−1.75 (m, 2 H, CH_2CH$_3$), 1.10 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 202 (64.61) [M^+], 173 (2.69), 147 (4.42), 119 (14.88), 118 (100.00), 90 (38.07), 89 (38.07), 63 (3.01). HR-MS calcd. for $C_{13}H_{14}O_2$ [M^+]: 202.0994; found 202.0992.

(5*R*)-3-Oxo-2-[(*Z*)-propylidene]-5-vinyltetrahydrofuran (5c): Colorless oil; yield: 30%. $[\alpha]_D^{25}$ = −11.3 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2970, 2935, 2880, 1770, 1192, 1192,983, 935 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00−5.88 (m, 1 H, C*H*=CH$_2$), 5.51−5.26 (m, 3 H, CH=CH_2, C=C*H*), 4.93−4.84 (m, 1 H, OC*H*CH$_2$), 2.88 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO), 2.60−2.45 (m, 3 H, C=CHCH_2CH$_3$, CHCH_2CO), 1.02 (t, J = 7.8 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 152 (28.01) [M^+], 117 (7.02), 110 (3.57), 98 (12.13), 82 (11.19), 70 (46.19), 57 (23.01), 55 (83.31), 54 (100.00), 42 (16.28). HR-MS calcd. for $C_9H_{12}O_2$ [M^+]: 152.0837; found 152.0835.

(5*R*)-3-Oxo-2-[(*E*)-propylidene]-5-vinyltetrahydrofuran (6c): Colorless oil; yield: 29%. $[\alpha]_D^{25}$ = −8.5 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2967, 2929, 2878, 2856, 1730, 1655, 1461, 1189, 1122, 1037, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 6.00−5.88 (m, 1 H, C*H*=CH$_2$), 5.49 (t, J = 7.8 Hz, 1 H, C=C*H*), 5.42−5.27 (m, 2 H, CH=CH_2), 4.99−4.92 (m, 1 H, OC*H*CH$_2$), 2.83 (dd, J = 7.4, 18.3 Hz, 1 H, CHCH_2CO), 2.46 (dd, J = 7.1, 18.0 Hz, 1 H, CHCH_2CO), 2.26−2.16 (m, 2 H, C=CHCH_2CH$_3$), 1.06 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 152 (24.00) [M^+], 151 (85.52), 137 (19.95), 123 (17.54), 110 (15.70), 99 (38.32), 95 (58.52), 83 (74.51), 70 (90.05), 69 (80.17), 57 (91.76), 55 (100.00), 43 (39.41), 41 (33.40). HR-MS calcd. for $C_9H_{12}O_2$ [M^+]: 152.0837; found 152.0831.

(5*R*)-2-[(*Z*)-Benzylidene]-3-oxo-5-vinyltetrahydrofuran (5c′): Colorless oil; yield 39%. $[\alpha]_D^{25}$ = +50.5 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2924, 1769, 1731, 1220, 1167 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.71 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.44−7.26 (m, 3 H, Ar*H*), 6.36 (s, 1 H, ArC*H*), 6.04−5.95 (m, 1 H, C*H*=CH$_2$), 5.48−4.99 (m, 3 H, CH=CH_2, C=C*H*), 2.96 (dd, J = 7.5, 18.0 Hz, 1 H, CHCH_2CO), 2.62 (dd, J = 7.7, 18.0 Hz, 1 H, CHCH_2CO) ppm. EI-MS: m/z = 200 (40.82) [M^+], 172 (0.96), 119 (9.57), 118 (100.00), 105 (13.73), 90 (62.19), 82 (9.61), 77 (7.54), 54 (28.33). HR-MS calcd. for $C_{13}H_{12}O_2$ [M^+]: 200.0837; found 200.0804.

(5*R*)-2-[(*E*)-Benzylidene]-3-oxo-5-vinyltetrahydrofuran (6c′): Colorless oil; yield: 21%. $[\alpha]_D^{25}$ = +64.3 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3065, 3027, 2926, 2856, 1726, 1627, 1257, 1177 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.8 Hz, 2 H, Ar*H*), 7.40−7.26 (m, 3 H, Ar*H*), 6.33 (s, 1 H, ArC*H*), 6.08−5.97 (m, 1 H, C*H*=CH$_2$), 5.46 (d, J = 16.5 Hz, 1 H, CH=CH_2), 5.33 (d, J = 10.2 Hz, 1 H, CH=CH_2), 5.22−5.15 (m, 1 H, OC*H*CH$_2$), 2.93 (dd, J = 8.1, 18.3 Hz, 1 H, CHCH_2CO), 2.54 (dd, J = 7.0, 18.3 Hz, 1 H, CHCH_2CO) ppm. EI-MS: m/z = 200 (24.13) [M^+], 172 (2.94), 143 (7.30), 128 (4.80), 118 (100.00), 105 (14.46), 91 (20.70), 90 (51.11), 89 (22.43), 81 (19.75), 77 (24.39), 53 (13.03). HRMS calcd. for $C_{13}H_{12}O_2$ [M^+]: 200.0837; found 200.0844.

(5*R*)-3-Oxo-5-phenyl-2-[(*Z*)-propylidene]tetrahydrofuran (5d): Colorless oil; yield: 31%. $[\alpha]_D^{25}$ = +24.3 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2965, 2928, 1717, 1261, 977 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43−7.34 (m, 5 H, Ar*H*), 5.51−5.42 (m, 2 H, C=C*H*, OC*H*CH$_2$), 3.07 (dd, J = 7.5, 18.0 Hz, 1 H, CHCH_2CO),

2.75−2.57 (m, 3 H, CHCH_2CO, CH_2CH$_3$), 1.04 (t, J = 7.8 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 199.8, 146.5, 140.5, 128.9, 128.4, 125.7, 115.5, 77.6, 45.4, 18.0, 14.5 ppm. EI-MS: m/z = 202 (6.96) [M$^+$], 178 (3.14), 160 (4.23), 131 (16.61), 121 (11.93), 107 (24.43), 105 (26.31), 104 (100.00), 86 (13.59), 84 (58.87), 77 (23.54), 59 (10.80). HR-MS calcd. for $C_{13}H_{14}O_2$ [M$^+$]: 202.0994; found 202.0994.

(5*R*)-3-Oxo-5-phenyl-2-[(*E*)-propylidene]tetrahydrofuran (6d): Colorless oil; yield: 29%. $[\alpha]_D^{25}$ = +32.0 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2961, 2924, 2852, 1741, 1261 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.43−7.26 (m, 5 H, Ar*H*), 5.60−5.51 (m, 2 H, C=C*H*, OC*H*CH$_2$), 3.09 (dd, J = 7.9, 18.3 Hz, 1 H, CHCH_2CO), 2.67 (dd, J = 7.4, 18.3 Hz, 1 H, CHCH_2CO), 2.31−2.20 (m, 2 H, CH_2CH$_3$), 1.08 (t, J = 7.2 Hz, 3 H, CH$_2$CH_3) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 198.4, 148.0, 140.7, 128.9, 128.4, 125.6, 109.8, 78.0, 43.8, 29.6, 13.4 ppm. EI-MS: m/z = 202 (14.06) [M$^+$], 160 (4.52), 149 (4.02), 131 (7.55), 107 (8.11), 104 (100.00), 85 (5.57), 77 (12.57), 55 (11.09). HR-MS calcd. for $C_{13}H_{14}O_2$ [M$^+$]: 202.0994; found 202.0988.

(5*R*)-2-[(*Z*)-Benzylidene]-3-oxo-5-phenyltetrahydrofuran (5d′): Colorless oil; yield 41%. $[\alpha]_D^{25}$ = +66.7 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3085, 3033, 2925, 1731, 1608, 1220, 1166, 1029, 915 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, J = 6.9 Hz, 2 H, Ar*H*), 7.45−7.26 (m, 8 H, Ar*H*), 6.44 (s, 1 H, C=C*H*Ar), 5.59 (t, J = 7.8 Hz, 1 H, OC*H*CH$_2$), 3.20 (dd, J = 7.8, 18.0 Hz, 1 H, CHCH_2CO), 2.84 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 198.7, 148.0, 133.1, 130.0, 128.7, 128.5, 128.2, 128.0, 125.7, 125.5, 113.8, 78.7, 62.5 ppm. EI-MS: m/z = 250 (23.86) [M$^+$], 180 (5.94), 131 (17.69), 118 (100.00), 104 (23.44), 90 (44.70), 84 (26.18), 77 (23.08). HR-MS calcd. for $C_{17}H_{14}O_2$ [M$^+$]: 250.0994; found 250.1006.

(5*R*)-2-[(*E*)-Benzylidene]-3-oxo-5-phenyltetrahydrofuran (6d′): Colorless oil; yield: 21%. $[\alpha]_D^{25}$ = +112.0 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3033, 2920, 2850, 1719, 1625, 1247, 1183, 1190, 1015, 971 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.81 (2 H,d, J = 7.5 Hz, Ar*H*), 7.46−7.26 (m, 8 H, Ar*H*), 6.41 (s, 1 H, C=C*H*Ar), 5.77 (t, J = 7.5 Hz, 1 H, OC*H*CH$_2$), 3.18 (dd, J = 8.1, 18.0 Hz, 1 H, CHCH_2CO), 2.74 (dd, J = 7.4, 18.3 Hz, 1 H, CHCH_2CO) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$): δ = 200.2, 147.4, 141.1, 139.5, 133.8, 128.7, 128.4, 127.3, 125.3, 115.1, 105.8, 78.8, 63.5 ppm. EI-MS: m/z = 250 (31.91) [M$^+$], 180 (5.11), 131 (12.25), 118 (100.00), 104 (8.56), 90 (43.89), 89 (19.04), 77(5.80). HR-MS calcd. for $C_{17}H_{14}O_2$ [M$^+$]: 250.0994; found 250.1018.

(5*R*)-5-(4-Methoxyphenyl)-3-oxo-2-[(*Z*)-propylidene]tetrahydrofuran (5g): Colorless oil; yield: 33%. $[\alpha]_D^{25}$ = +64.5 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2968, 2937, 2840, 1739, 1613, 1515, 1254, 1175 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.23 (d, J = 6.9 Hz, 2 H, Ar*H*), 6.86 (d, J = 7.2 Hz, 2 H, Ar*H*), 5.40−5.30 (m, 2 H, C=C*H*, OC*H*CH$_2$), 3.76 (s, 3 H, CH_3), 2.95 (dd, J = 7.5, 18.0 Hz, 1 H, CHCH_2CO), 2.64 (dd, J = 8.1, 18.0 Hz, 1 H, CHCH_2CO), 2.56−2.50 (m, 2 H, CH_2CH$_3$), 0.97 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 232 (3.52) [M$^+$], 161 (30.04), 137 (37.96), 135 (100.00), 119 (15.79), 109 (6.10), 91 (12.84), 77 (11.13). HR-MS calcd. for $C_{14}H_{16}O_3$ [M$^+$]: 232.1099; found 232.1088.

(5*R*)-5-(4-Methoxyphenyl)-3-oxo-2-[(*E*)-propylidene]tetrahydrofuran (6g): Colorless oil; yield: 29%. $[\alpha]_D^{25}$ = +80.0 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2968, 2936, 2879, 2840, 1735, 1516, 1255, 1177, 1033, 833 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.29 (d, J = 8.4 Hz, 2 H, Ar*H*), 6.93 (d, J = 9.0 Hz, 2 H, Ar*H*), 5.57−5.44 (m, 2 H, C=C*H*, OC*H*CH$_2$), 3.82 (s, 3 H, CH_3), 3.03 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO), 2.66 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO), 2.28−2.17 (m, 2 H, CH_2CH$_3$), 1.07 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 232 (18.60) [M$^+$], 203 (7.02), 190 (2.72), 162 (8.22), 134 (100.00), 119 (16.94), 119 (15.79), 91 (12.56), 77 (4.61), 65 (5.81), 55 (7.38). HR-MS calcd. for $C_{14}H_{16}O_3$ [M$^+$]: 232.1099; found 232.1094.

(5*R*)-2-[(*Z*)-Benzylidene]-5-(4-methoxyphenyl)-3-oxotetrahydrofuran (5g′): Colorless oil; yield: 38%. $[\alpha]_D^{25}$ = +26.7 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2932, 2839, 1730, 1613, 1515, 1251, 1172, 1031 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.75 (d, J = 7.5 Hz, 2 H, Ar*H*), 7.37−7.25 (m, 5 H, Ar*H*), 6.94 (d, J = 7.2 Hz, 2 H, Ar*H*), 6.40 (s, 1 H, C=C*H*Ar), 5.52 (t, J = 7.8 Hz, 1 H, OC*H*CH$_2$), 3.82 (s, 3 H, OCH_3), 3.14 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO), 2.84 (dd, J = 7.8, 18.0 Hz, 1 H, CHCH_2CO) ppm. EI-MS: m/z = 280 (23.49) [M$^+$], 210 (9.77), 161 (34.19), 134 (100.00), 118 (31.82), 105 (14.71), 90 (21.72), 86 (45.09) 84 (70.90), 77 (18.38). HR-MS calcd. for $C_{18}H_{16}O_3$ [M$^+$]: 280.1099; found 280.1096.

(5*R*)-2-[(*E*)-Benzylidene]-5-(4-methoxyphenyl)-3-oxotetrahydrofuran (6g′): Colorless oil; yield: 16%. $[\alpha]_D^{25}$ = +327.5 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2956, 2929, 2837, 1727, 1623, 1516, 1249,1178, 1031 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.79 (d, J = 7.2 Hz, 2 H, Ar*H*), 7.38−7.25 (m, 5 H, Ar*H*), 6.94 (d, J = 8.7 Hz, 2 H, Ar*H*), 6.39 (s, 1 H, C=C*H*Ar), 5.69 (t, J = 7.8 Hz, 1 H, OC*H*CH$_2$), 3.82 (s, 3 H, OCH_3), 3.13 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO), 2.73 (dd, J = 7.5, 18.3 Hz, 1 H, CHCH_2CO) ppm. EI-MS: m/z = 280 (28.61) [M$^+$], 210 (10.87), 161 (29.31), 134 (100.00), 118 (33.94), 90 (23.13), 77 (5.49), 65 (8.68). HR-MS calcd. for $C_{18}H_{16}O_3$ [M$^+$]: 280.1099; found 280.1095.

(5*R*)-5-(4-Fluorophenyl)-3-oxo-2-[(*Z*)-propylidene]tetrahydrofuran (5j): Colorless oil; yield: 35%. $[\alpha]_D^{25}$ = +64.5 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2970, 2934, 2877, 1734, 1514, 1228, 1190, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.41−7.33 (m, 2 H, Ar*H*), 7.13−7.17 (m, 2 H, Ar*H*), 5.51−5.44 (m, 2 H, C=C*H*, OC*H*CH$_2$), 3.07 (dd, J = 7.5, 18.0 Hz, 1 H, CHCH_2CO), 2.72−2.58 (m, 3 H, CHCH_2CO, CH_2CH$_3$), 1.05 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 220 (8.83) [M$^+$], 178 (3.12), 149 (7.68), 122 (100.00), 101 (7.22), 96 (7.44), 75 (2.57), 69 (3.67), 55 (3.78). HR-MS calcd. for $C_{13}H_{13}FO_2$ [M$^+$]: 220.0900; found 220.0913.

(5*R*)-5-(4-Fluorophenyl)-3-oxo-2-[(*E*)-propylidene]tetrahydrofuran (6j): Colorless oil; yield: 34%. $[\alpha]_D^{25}$ = +28.5 (c = 0.6, $CHCl_3$). IR (film): $\tilde{\nu}$ = 2970, 2935, 2878, 1737, 1659, 1513, 1228, 838 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.37−7.28 (m, 2 H, Ar*H*), 7.13−7.06 (m, 2 H, Ar*H*), 5.61−5.49 (m, 2 H, C=C*H*, OC*H*CH$_2$), 3.08 (dd, J = 8.1, 18.3 Hz, 1 H, CHCH_2CO), 2.63 (dd, J = 7.5, 18.0 Hz, 1 H, CHCH_2CO), 2.30−2.20 (m, 2 H, CH_2CH$_3$), 1.09 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3) ppm. EI-MS: m/z = 220 (5.66) [M$^+$], 191 (1.54), 178 (2.37), 149 (6.46), 122 (100.00), 101 (7.31), 96 (8.20), 75 (2.84), 55 (2.91). HR-MS calcd. for $C_{13}H_{13}FO_2$ [M$^+$]: 220.0900; found 220.0874.

(5*R*)-2-[(*Z*)-Benzylidene]-5-(4-fluorophenyl)-3-oxotetrahydrofuran (5j′): Colorless oil; yield 42%. $[\alpha]_D^{25}$ = +66.8 (c = 0.8, $CHCl_3$). IR (film): $\tilde{\nu}$ = 3068, 3033, 2928, 2855, 1754, 1730, 1608, 1513, 1226, 1158 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.76 (d, J = 7.8 Hz, 2 H, Ar*H*), 7.40−7.29 (m, 5 H, Ar*H*), 7.10 (t, J = 8.4 Hz, 2 H, Ar*H*), 6.43 (s, 1 H, C=C*H*Ar), 5.55 (t, J = 7.8 Hz, 1 H, OC*H*CH$_2$), 3.17 (dd, J = 7.5, 18.3 Hz, 1 H, CHCH_2CO), 2.79 (dd, J = 7.8, 18.3 Hz, 1 H, CHCH_2CO) ppm. EI-MS: m/z = 268 (2.33) [M$^+$], 178 (3.67), 149 (27.74), 122 (100.00), 118 (63.17), 107 (44.14), 101 (31.60), 90 (58.45), 77 (70.99), 63 (15.51), 57 (24.71), 51 (23.89). HR-MS calcd. for $C_{17}H_{13}O_2F$ [M$^+$]: 268.0900; found 268.0889.

(5*R*)-2-[(*E*)-Benzylidene]-5-(4-fluorophenyl)-3-oxotetrahydrofuran (6j′): Colorless oil; yield: 24%. $[\alpha]_D^{25}$ = +240.5 (c = 0.6, $CHCl_3$).

IR (film): $\tilde{\nu}$ = 3058, 2958, 2927, 2856, 1733, 1636, 1513, 1237, 1187, 837 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ = 7.80 (d, *J* = 7.5 Hz, 2 H, Ar*H*), 7.41−7.26 (m, 5 H, Ar*H*), 7.11 (t, *J* = 8.1 Hz, 2 H, Ar*H*), 6.41 (s, 1 H, C=C*H*Ar), 5.74 (t, *J* = 7.5 Hz, 1 H, OC*H*CH_2), 3.17 (dd, *J* = 7.5, 18.0 Hz, 1 H, CHC*H*$_2$CO), 2.70 (dd, *J* = 7.5, 18.0 Hz, 1 H, CHC*H*$_2$CO) ppm. EI-MS: *m*/*z* = 268 (4.43) [M^+], 198 (2.62), 149 (5.15), 122 (23.93), 118 (100.00), 101 (11.28), 96 (11.60), 90 (78.15), 89 (48.92), 63 (14.12). HR-MS calcd. for $C_{17}H_{13}O_2F$ [M^+]: 268.0900; found 268.0910.

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