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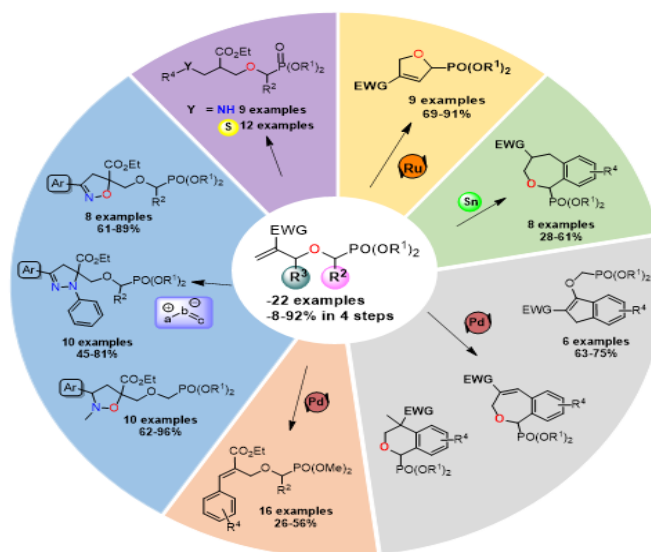
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Exploring the Reactivity of Substituted Allyloxymethylphosphonates in cycloaddition and coupling reactions

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Abstract This paper describes the versatility of substituted allyloxymethylphosphonates to open the way to the synthesis of original phosphonated molecules with heterocyclic architectures. Involved in 1,3-dipolar cycloaddition reactions with nitrile oxides, nitrile imines, and nitrones, these allyloxymethylphosphonates reacted as dipolarophiles to give regioselectively, the corresponding isoxazolines, pyrazolines, and isoxazolidines. Transition metal-catalyzed reactions, including inter- or intramolecular Heck coupling, provided access to cinnamyl- and indenyl-linked moieties and novel phosphonated benzo-fused oxacycles, respectively. Additionally, ring closing metathesis reactions with wisely constructed substrates enabled the synthesis of 2,5-dihydrofurans with the phosphonate group at the anomeric position. In this work, 51 novel phosphorylated heterocyclic compounds have been prepared which could find significance in the pharmaceutical and agrochemical fields.

Key words Organophosphorus Compounds, 1,3-dipolar cycloaddition, Heck coupling reaction, radical cyclization and metathesis.

Although the chemical space within organic chemistry is frequently thought to be thoroughly explored, there is still an acute desire to introduce more molecular diversity due to the already existing arsenal of synthetic techniques and accessible chemicals. Increasing structural diversity is essential to promote innovation, particularly in important areas such as drug discovery. Organophosphorus compounds, particularly those with a phosphonate or phosphonic acid group, have considerable potential for a variety of applications in industrial, agricultural, and medicinal chemistry.¹⁻⁵ In a recent paper, we have described the synthesis of (β -functionalized)allyloxy)methylphosphonates **1** (Scheme 1), and studied their reactivity

towards various nucleophiles such as amines or thiols to prepare linear original phosphonate compounds.⁶

In this work, we investigate the behavior of our substrates **1** in several known reactions, including 1,3-dipolar cycloaddition, Heck coupling, metathesis, and radical coupling reactions, to prepare novel phosphorylated heterocyclic derivatives. The 1,3-dipolar cycloaddition process involving nitrile oxide, nitrile imine, and nitron leads to the formation of 5-membered heterocycles, which are present in a wide range of molecules with specific pharmaceutical and biological activities.^{7,8} Thus, isoxazolines, pyrazolines, and isoxazolidines are nitrogen-containing heterocycles⁹⁻¹¹ found in a vast collection of biologically interesting natural or synthetic compounds (Figure 1).¹²⁻¹⁴

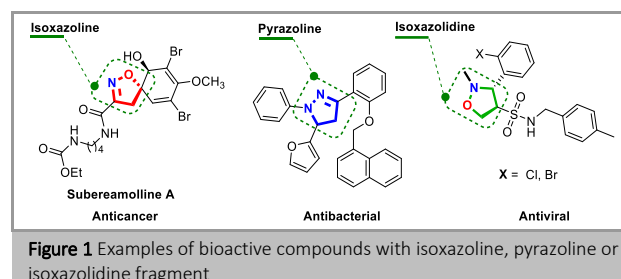
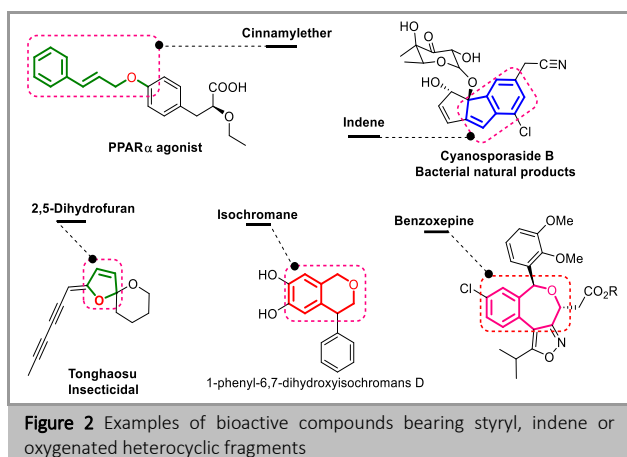


Figure 1 Examples of bioactive compounds with isoxazoline, pyrazoline or isoxazolidine fragment

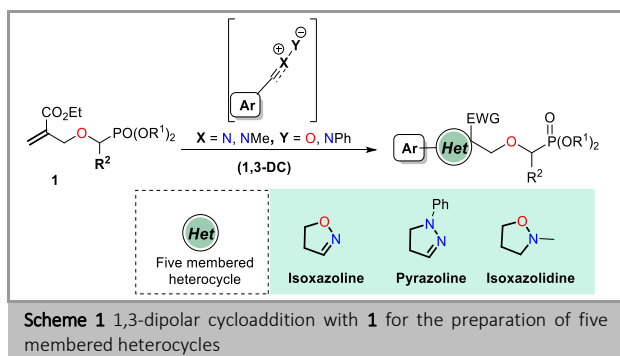
In another point of view, transition metal-catalyzed methodologies are very efficient approaches to construct novel

carbon-carbon bonds in a molecule.^{15,16} When applied to our substrates **1**, they could give access to a wide range of acyclic or cyclic ethers. We could notice that cinnamyl ether, indene, and 2,5-dihydrofuran are structures also found in specific natural and synthetic molecules with biological activities.^{17–19} Benzofused oxacyclic rings are present in natural or synthetic products, such as 1-aryl-6,7-dihydroxyisochromans D extracted from olive oil or benzoxepine derivatives as squalene synthase inhibitors (Figure 2).^{20,21}



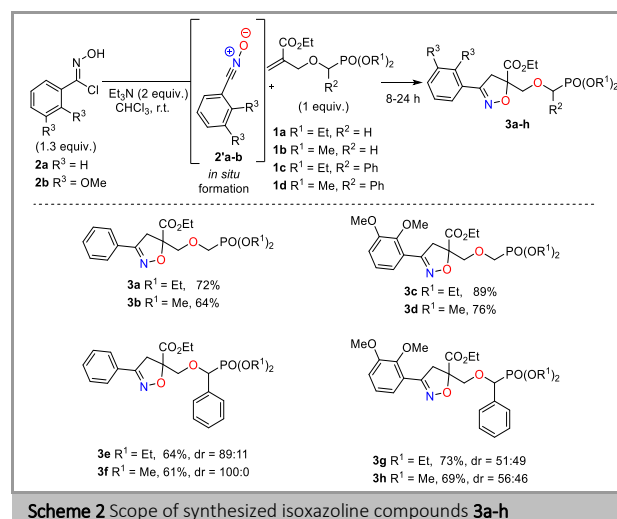
I- 1,3-Dipolar cycloaddition

In a recent study, we have described an efficient synthesis to access to a series of 22 functionalized phosphorylated compounds **1** (Scheme 1).⁶ Because 1,3-dipolar cycloaddition has been increasingly used in organic synthesis to prepare original compounds, we planned to investigate the reactivity of some of our allyloxymethylphosphonate compounds **1** as novel dipolarophiles in 1,3-dipolar cycloaddition involving nitrile oxides, nitrile imines, and nitrones as 1,3-dipoles (Scheme 1).

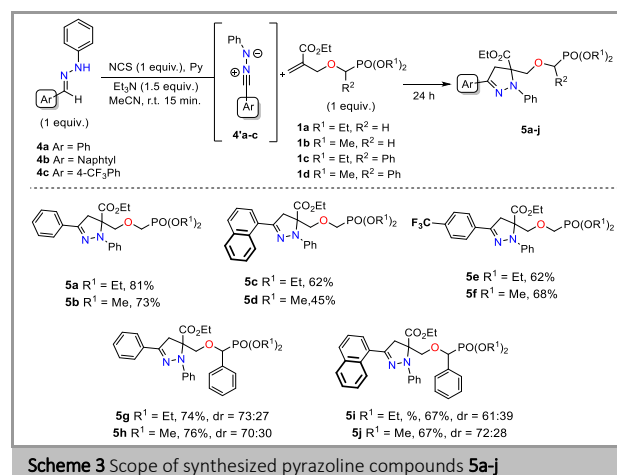


To prepare isoxazolines and pyrazolines derivatives starting from substrates **1**, we first applied the optimized conditions, recently published by our team (Scheme 2).^{22,23} Nitriles oxides **2'a-b** were prepared *in situ* from the corresponding chloroximes **2a-b** in the presence of Et₃N (2 equiv.) in CHCl₃ at room temperature. Those reacted with allyloxymethylphosphonates **1a-d** to give the corresponding isoxazolines **3a-h** in moderate to good yield (61–89%). If such 1,3-dipolar cycloaddition can lead to two regioisomers, as we previously observed²² we only identified the formation of the 5-substituted adducts which

structures could be confirmed by NMR analysis (¹H, ¹³C, and ³¹P). The inseparable isoxazolines **3e-f** were obtained with good to high diastereoselectivity (dr 89:11 to 100:00) which fell down with the isoxazolines **3g-h**, bearing electron-donating methoxy groups on the phenyl ring (dr 51:49 and 56:44 respectively). The electronic effects on the phenyl group of the chloroxime reagent seemed to play an important role in the diastereoselectivity of this cycloaddition (Scheme 2).

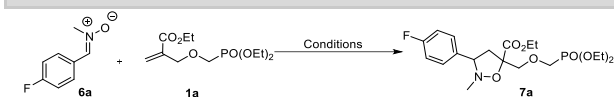


In the same manner, to access to pyrazoline analogs of compounds **5**, our allyloxymethylphosphonates **1** were reacted with chlorohydrazone, in basic conditions, *via* a 1,3-dipolar cycloaddition process (Scheme 3). The nitrile imines **4'a-c** were first synthesized *in situ* after chlorination of hydrazones **4a-c** by NCS, in the presence of a catalytic amount of pyridine, followed by basic treatment with Et₃N (2 equiv.) in MeCN. Then, the addition of allyloxymethylphosphonates **1** (1 equiv.) furnished the expected pyrazolines **5a-j** after 24 hours at room temperature. Therefore, ten pyrazolines were synthesized in moderate to high yields (45–81%). The cycloadducts **5g-j** were obtained with moderate diastereoselectivity, closed to 70:30. Here too, ¹³C NMR analysis confirmed the formation of 5-pyrazoline, with the quaternary carbon C-5 at 71.9 ppm (Scheme 3).²²



We completed these 1,3-dipolar cycloaddition approaches studying the reactivity of our substrates **1a-b** with nitrones **6a-e** to furnish a new series of polyfunctional isoxazolidines **7**. The nitrones **6a-e** were prepared, classically, in one step²⁴, by condensation of neutral *N*-methylhydroxylamine, with aromatic aldehydes in PhMe at 110°C. These reactants **6a-e** were so obtained in moderate yields (49-73%). Optimization of the cyclization reaction conditions was carried out with allyloxymethylphosphonate **1a** and fluorinated nitrone (Table 1). In refluxing THF or MeCN (Entries 1 and 2, table 1), only starting materials were detected and recovered. In PhMe at 80°C (Entry 3, table 1), trace of the desirable compound **7a** was detected and when the temperature was increased to 110°C, the 5-substituted isoxazolidine **7a** could be obtained with 89 % yield after 8 hours in boiling solvent (Entry 4, table 1). The structure of the regioisomer **7a** could be confirmed by ¹³C NMR spectrum analysis, with the specific quaternary carbon signal (C-5) of isoxazolidine located at 84 ppm.

Table 1 Optimization of the reaction conditions for the synthesis of isoxazolidine **7a**

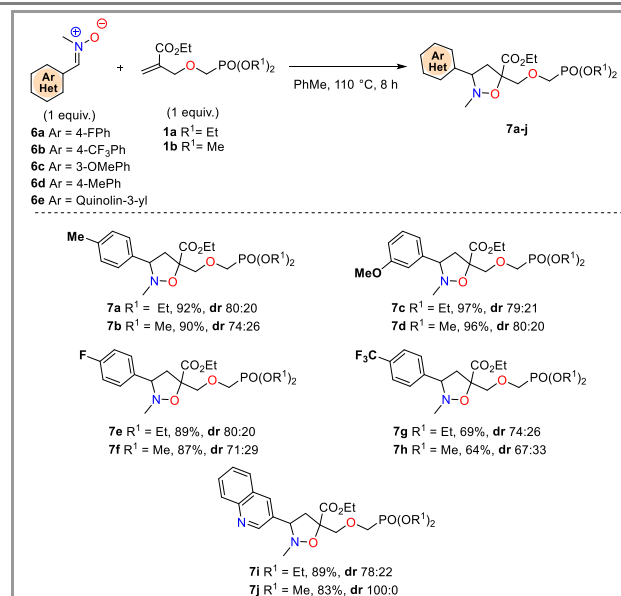


Entry	Solvent	Times (h)	Temp. (°C)	Yield ^(a) (%)
1	THF	24	66	--
2	MeCN	24	80	--
3	PhMe	18	80	Trace
4	PhMe	8	110	89

Reaction conditions: Olefin **1a** (1 mmol), nitrone **6a** (1.2 mmol), Solvent (15 mL).

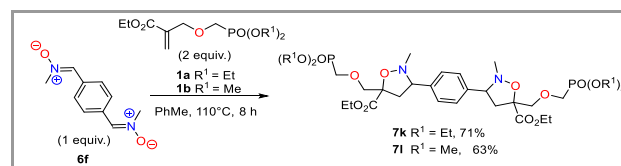
a) Isolated yield after silica gel column chromatography.

With the optimized reaction conditions in hand, a series of ten phosphonated isoxazolidines **7a-j** was obtained in good yield (up to 85%) excepted for **7g-h** (~ 65%) bearing an EWG (-CF₃) on the phenyl moiety. For each compound **7**, an inseparable mixture of diastereoisomers was obtained with low diastereoselectivity around 80:20 excepted for compound **7j** which ³¹P NMR spectrum revealed the presence of a single signal (Scheme 4).



Scheme 4 Scope of synthesized isoxazolidine compounds **7a-j**

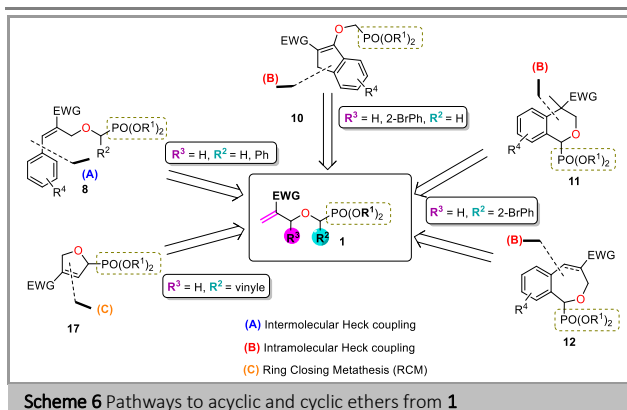
Under the same conditions, we prepared, *in situ*, a bis-nitrone **6f** from the condensation between *N*-methylhydroxylamine (2 equiv.) with terephthalaldehyde in the presence of Et₃N (2 equiv.). The obtained bis-nitrone **6f** was reacted with two equivalents of dialkyl allyloxymethylphosphonate **1a** or **1b** in refluxing PhMe to provide bis-isoxazolidines **7k-l** with acceptable yield (Scheme 5).



Scheme 5 Synthesis of bis-isoxazolidines **7k** and **7l**

II- Study of the allyloxymethylphosphonates reactivity by metallo-catalysis

Subsequently, we examined the behavior of allyloxymethylphosphonates **1** in transition metal-catalyzed reactions, as illustrated in scheme 6. Heck coupling reaction with aryl halides could result in intermolecular C-C bond formation, leading to the cinnamyl ether derivatives **8**. Furthermore, starting from substrates **1** substituted with an *o*-haloaryl moiety (Scheme 6), the intramolecular variation enabled the synthesis of novel analogs such as indenyl ethers **10** (when R³ = *o*-X-Ph, R² = H) and organophosphorus benzoxanes **11** and **12** (when R³ = H, R² = *o*-X-Ph). Additionally, with allyloxymethylphosphonates **1** bearing an unsaturated chain (e.g. R² = vinyl, R³ = H) we could project to generate phosphorylated 2,5-dihydrofuran derivatives **17** through RCM reaction.



Palladium-catalyzed Heck coupling reaction

Intermolecular Heck coupling

Initially, our efforts were focused on the arylation of a selected dimethyl allyloxymethylphosphonate **1b** and **1d** using different aryl iodides, to afford the ethyl cinnamate derivatives **8**, substituted with a methoxymethylphosphonate fragment. A similar Heck coupling reaction was published by our group²⁵ starting from carboxylated allylphosphonates and using Pd(OAc)₂, PPh₃ and *n*-Bu₄NBr in a mixture of DMF/H₂O at 75°C. The expected styryl compounds were obtained in good yields (59-71%).

In a first attempt, we applied the same conditions²⁵ starting with olefin **1b** and iodobenzene (Entry 1, table 2). After 16h at 75 °C, a mixture of two products **8b** and **9b** was obtained with 38% global yield. The NMR data (see SI) allowed us to identify both regioisomers **8b** and **9b** in 79:21 ratio (Entry 1, table 2).

Under the same conditions, but increasing the temperature to 110°C could reduce the reaction time with a slight improvement of the yield (53%) (Entry 2, table 2). No optimization of the yield was observed under Jeffery conditions²⁶ in the absence of phosphine ligand and with NaHCO₃ (2.5 equiv.) as the base (57%). However, in such conditions, the vinyl ether **9b** was obtained as the major product in 42% yield compared to the cinnamyl regioisomer **8b** isolated pure with 15% yield (Entry 3, table 2).

The best yield (81%) was obtained without phosphine ligand, but keeping K₂CO₃ as the base, in a mixture of MeCN/H₂O (9:1) at 80°C (Entry 4, table 2). Thus, cinnamyl derivative **8b** was isolated as the major product (56%) and the enol ether **9b** as the minor regioisomer (25%).

Finally, choosing Ag₂CO₃ as the base (2.5 equiv.) without additive in dry DMF at 110°C, allowed us to obtain a mixture of both regioisomers **8b/9b** in a good yield (75%) and regioisomeric ratio in favor of **8b** (ratio 79:21) (Entry 5, table 2).

It is to be noticed that involving bromobenzene under these different conditions lead to only trace of desired products.

The formation of these regioisomers **8b** and **9b** can be explained by β-H elimination of hydrogen atoms H_a or H_b from the intermediate **1b'** (Scheme 7). In a previous work, and starting with allylphosphonates, our team identified only one regioisomer corresponding to the H_a elimination.²⁵ This selectivity could be explained by the stabilization of the carbopalladate-intermediate with the phosphonate group (DG in scheme 7), controlling the selectivity of the β-H elimination process. In contrast, our starting olefin **1b'** exhibits a longer chain not allowing the phosphonate group to stabilize carbopalladate-intermediate.

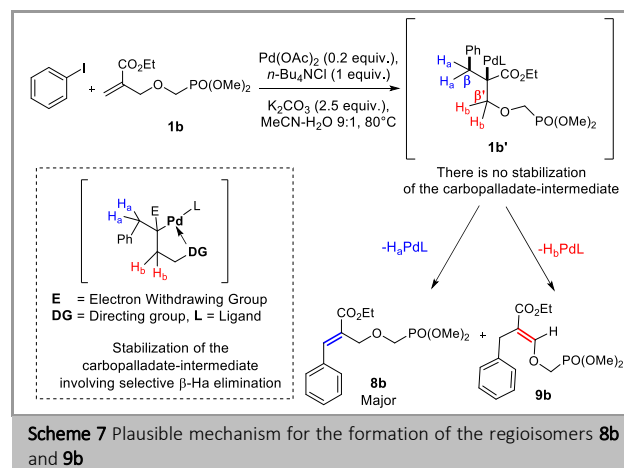


Table 2 Optimization of the intermolecular Heck coupling reaction

Entry	Pd(OAc) ₂ / PPh ₃ (equiv.)	Base (equiv.)	Additive (1 equiv.)	Solvent (temp.)	Times (h)	Results ^(a)			Yield %
						8b	9b	Ratio	
1	0.1/0.2	K ₂ CO ₃ (2)	<i>n</i> -Bu ₄ NBr	DMF-H ₂ O (1:1) 75°C	16	30	8	79:21	38
2	0.1/0.2	K ₂ CO ₃ (2)	<i>n</i> -Bu ₄ NBr	DMF-H ₂ O (1:1) 110°C	6	39	14	74:26	53
3	0.2/--	NaHCO ₃ (2.5)	<i>n</i> -Bu ₄ NCl	DMF 110°C	6	15	42	26:74	57
4	0.2/--	K ₂ CO ₃ (2.5)	<i>n</i> -Bu ₄ NCl	MeCN-H ₂ O (9:1) 80°C	4:30	56	25	69:31	81
5	0.1/0.2	Ag ₂ CO ₃ (2.5)	--	DMF 110°C	16	59	16	79:21	75

Reaction conditions: reaction conducted with an equimolar mixture (0.8 mmol) of the starting olefin **1b** and iodobenzene.

^a Yield of product isolated after purification by column chromatography.

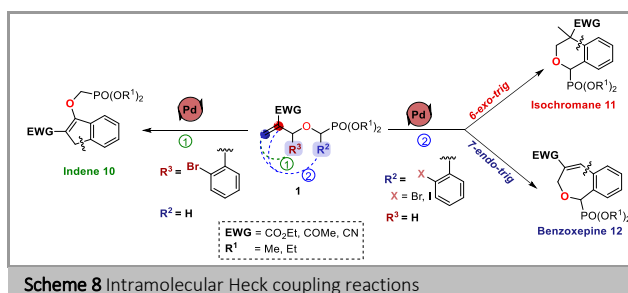
Table 3 Compounds **8** and **9** synthesized via the intermolecular Heck coupling reaction

Entry	R ⁴	R ²	Cinnamylether (yield %)	Vinylether (yield %)	Global yield (%)
1	H	H	8b (56)	9b (25)	81
2		Ph	8c (48)	9c (29)	77
3		H	8d (43)	9d (27)	70
4	<i>p</i> -Me	Ph	8e (46)	9e (14)	60
5	<i>m</i> -Me	H	8f (49)	9f (23)	72
6	<i>o</i> -Me	H	8g (35)	9g (20)	55
7		H	8h (42)	9h (28)	70
8	<i>m</i> -OMe	Ph	8i (38)	9i (23)	61
9		H	8j (32)	9j (27)	59
10	<i>o</i> -OMe	Ph	8k (43)	9k (23)	66
11		H	8l+9l (58) ^(a)		58
12	<i>m</i> -CF ₃	Ph	8m (16)	9m (48)	64
13		H	8n+9n (24) ^(a)		24
14	<i>p</i> -NO ₂	Ph	8o+9o (26) ^(a)		26
15	<i>m</i> -NO ₂	H	8p (26)	9p (10)	36
16	<i>o</i> -NO ₂	H	8q (37)	9q (23)	60

^a Mixture of two regioisomers

Intramolecular Heck coupling reaction

Some of our allyloxymethylphosphonates **1** being substituted with an halogenophenyl group in the α positions of the oxygen ether atom (R² or R³ = *o*-X-Ph, scheme 8), this allowed us to consider intramolecular Heck reactions. Such C-C bond formations could give access to new indenenes **10**, isochromanes **11**, or benzoxepines **12** derivatives (Scheme 8, paths 1 and 2).



So, we started with the optimized conditions that we applied in the precedent intermolecular Heck study, but no expected indene was formed and the starting substrate **1e** was recovered (Entry 1, table 4). Based on literature data²⁷ we changed the conditions to Pd(OAc)₂ (0.1 equiv.), PPh₃ (0.2 equiv.) and Et₃N (2 equiv.) in refluxing MeCN. After 3 hours of reaction, indene **10a** was obtained in 73% yield (Entry 2, table 4).

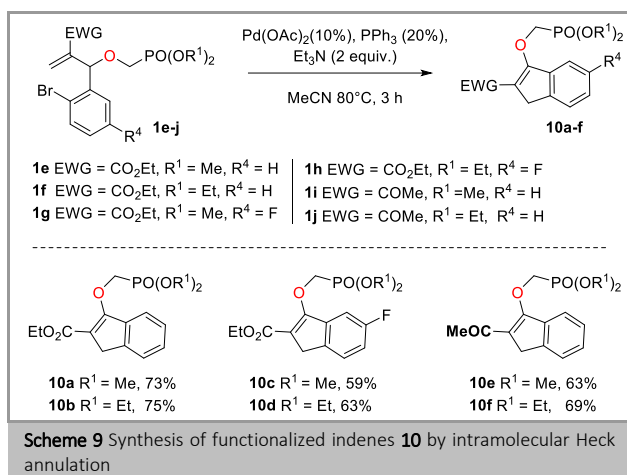
These conditions were then applied to a small series of substrates **1e-j**, to give the expected substituted benzoidenenes **10a-f** with good yields (59-75 %) (Scheme 9). Those could be fully characterized by NMR analysis (¹H, ¹³C, ³¹P), particularly the methylene of the indene ring appeared as a singlet around 3.6 ppm.

Table 4 Optimization of the intramolecular Heck reaction

Entry	Pd(OAc) ₂ (equiv.)	PPh ₃ (equiv.)	Base (equiv.)	Solvent/Temp. °C	<i>n</i> -Bu ₄ NCl (equiv.)	Times (h)	Yield (%)
1	0.2	--	K ₂ CO ₃	MeCN-H ₂ O 80	1	24	--
2	0.1	0.2	Et ₃ N 2	MeCN 80	--	3	73 ^(a)

Reaction conditions: the reaction was conducted with 0.4 mmol of **1e**.

^a Isolated yield after purification by column chromatography



Next, we turned our attention towards the annulation reactions of allyloxymethylphosphonates containing the hetaryl

Table 5 Intramolecular Heck cyclisation assays

Entry	X	Pd(OAc) ₂ (equiv.)	PPh ₃ (equiv.)	Base (equiv.)	Additive (1 equiv.)	Solvent	Temp (°C)
1	Br	0.2	---	K ₂ CO ₃ (2.5)	<i>n</i> -Bu ₄ NCl	MeCN-H ₂ O	80
2	Br	0.1	---	NaHCO ₃ (2.5)	<i>n</i> -Bu ₄ NCl	DMF	80
3	Br	0.1	---	NaHCO ₃ (2.5)	<i>n</i> -Bu ₄ NCl	MeCN	80
4	Br	0.1	---	NaOAc (2.5)	<i>n</i> -Bu ₄ NCl	DMF	80
5	Br	0.1	0.2	Ag ₂ CO ₃ (2.5)	---	DMF	110
6	Br	0.1	0.2	Ag ₂ CO ₃ (2.5)	---	PhMe	110
7	Br	0.1	0.2	K ₂ CO ₃ (2.5)	<i>n</i> -Bu ₄ NBr	DMF-H ₂ O	75
8	Br	0.2	0.4	Et ₃ N (2)	---	MeCN	80
9	Br	0.05	0.1	Et ₃ N (2)	---	MeCN	80
10	I	0.1	---	NaHCO ₃ (2.5)	<i>n</i> -Bu ₄ NCl	MeCN	80
11	I	0.1	0.2	Ag ₂ CO ₃ (2.5)	---	PhMe	110
12	I	0.1	0.2	K ₂ CO ₃ (2.5)	<i>n</i> -Bu ₄ NBr	DMF-H ₂ O	75
13	I	0.2	0.4	Et ₃ N (2)	---	MeCN	80
14	I	0.05	0.1	Et ₃ N (2)	---	MeCN	80

Reaction conditions: The reaction was carried out with 0.8 mmol of substrates **1k** or **1n**.

After unsuccessful outcomes using Heck conditions to prepare oxygenated bicyclic derivatives starting from **1k** or **1n**, we looked towards aryl radical cyclization. This approach has been extensively studied in organic synthesis to give a wide range of carbocycles and heterocycles.^{29,30} Benzoxepine compounds formation in radical conditions has not been so widely studied.^{31–33} Allyloxymethylphosphonate **1k** was treated with *n*-Bu₃SnH (2 equiv.) and AIBN (0.2 equiv.) in degassed benzene at 110°C during 3 hours to give a mixture of vinyl ether **13a**, benzo[*c*]oxepine **14a**, and (tributylstannyl)propanoate **15a**. They could be separated by column chromatography purification and isolated pure with 57%, 20%, and 9% yield

substituent in the α position of the phosphonate function. According to previous results in literature and Baldwin's rules, these allylether chain containing aromatics halides are known to deliver six-membered and seven-membered heterocycles through 6-*exo-trig* and 7-*endo-trig* processes, respectively. To state the reaction conditions, 2-bromophenyl(allyloxymethylphosphonate) **1k** was chosen as the substrate model.

In Jeffery type conditions, with the absence of phosphine ligand (Entries 1-4, table 5) no reaction was observed with bromo-substrate **1k**,²⁸ whatever the base (K₂CO₃, NaHCO₃) or the solvent (MeCN, DMF) chosen for the reaction. No expected bicyclic compounds **11a** or **12a** were also obtained in the presence of phosphine ligand (2 equiv.) with (Entry 7, table 5) or without additive using Ag₂CO₃ (Entries 5-6, table 5) or Et₃N (Entries 8-9, table 5) as the base.

With iodo-substituted substrate **1n**, under different conditions listed in entries 10 to 14 (Table 5), only traces of the expected cyclic compound **12a** were detected by mass spectroscopy.

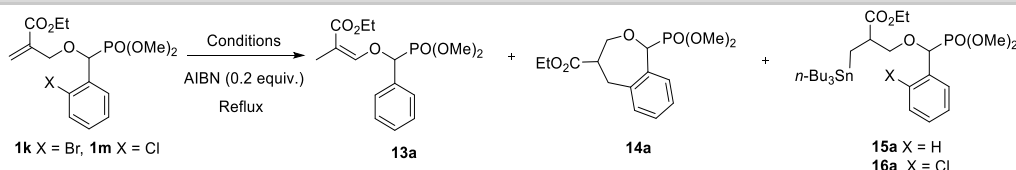
respectively (Entry 1, table 6). With chloro-substituted substrate **1m** under the same conditions, only the stannyl-adduct **16a** was obtained in 55% yield without reduction (Entry 2, table 6). Selecting silane TTMSS instead of stannane *n*-Bu₃SnH to generate aryl radical³⁴ (Entry 3, table 6), only vinyl ether **13a** and benzo[*c*]oxepine **14a** were isolated but in poor yields (26 and 34% respectively). When benzene was replaced by PhMe as the solvent, a similar result was obtained (Entry 4, table 6).

The structures of these products were determined through NMR analysis. The ¹H NMR spectra of compounds **15a** or **16a** clearly indicated the disappearance of ethylene protons and the presence of the *n*-butyl chain of the stannyl group (0.70 and 1.54

ppm). Afterward, the vinyl ether **13a** was confirmed using 135-DEPT NMR by a lone methylene at 60.0 ppm attributed to ester and a novel (-CH₃) signal at 9.3 ppm and a new vinyl CH at 7.29

ppm. The structure of benzoxepine **14a** was also confirmed by confirmed by the appearance of two CH multiplets at 3.10 and 5.13 ppm.

Table 6 Optimization of radical-cyclization conditions



Entry	X	Radical source (equiv.)	Times ^(a) (h)	Solvent ^(b)	Yield ^(c) (%)		
					13a	14a	15a/16a
1	Br	<i>n</i> -Bu ₃ SnH (2)	3	PhH	57	20	9
2	Cl	<i>n</i> -Bu ₃ SnH (2)	3	PhH	--	--	55
3	Br	TTMSS (2)	2	PhH	26	34	--
4	Br	<i>n</i> -Bu ₃ SnH (2)	3	PhMe	59	28	8

Reaction conditions: The reaction was conducted with 0.5 mmol of the **1k** or **1m** in 13 mL of solvent.

(a) Reaction monitored by TLC.

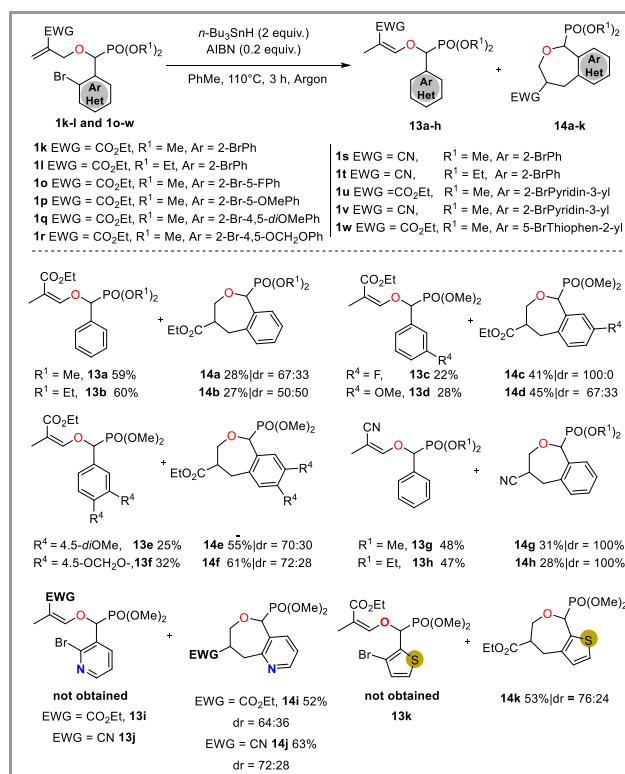
(b) Anhydrous solvent.

(c) Isolated yield after purification by column chromatography.

Our allyloxymethylphosphonates with various (EWG) and/or substituent on the aromatic ring were submitted to the radical reaction conditions in PhMe. With the fluoro **1o** or methoxy substrate **1p-r**, the corresponding benzo[c]oxepine **14c-f** were the major products formed up to 40% yield (41 to 61%, scheme 10) with the corresponding vinyl ether co-products **13c-f** in around 25%.

These conditions were then applied to heteroaromatic substrates **1u-w** to give only the expected bicyclic compounds **14i-k** with acceptable yields (52-63%) (Scheme 10). The corresponding vinyl ether co-products were not observed and this may be explained by the stabilizing effect of a heteroatom on the aryl radical intermediate.³⁵

As a mechanistic point of view, the co-products **13** and **15** were formed from 1,5-HAT radical migration or reduction with *n*-Bu₃SnH respectively (see SI).

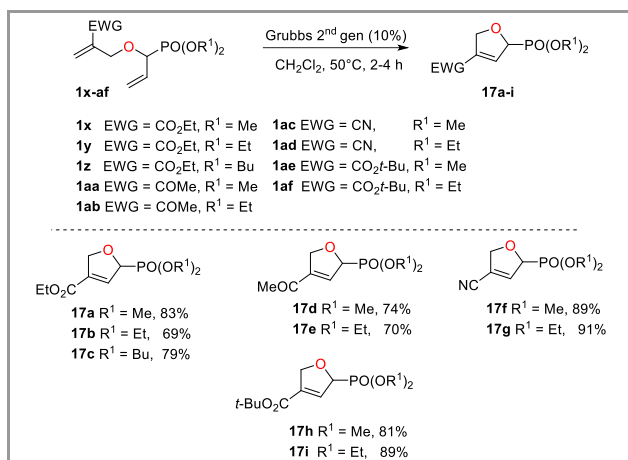


Scheme 10 Synthesis of oxa-cyclic compounds **14** by radical process

Synthesis of phosphono-2,5-dihydrofuran **17** by Ring Closing Metathesis (RCM)

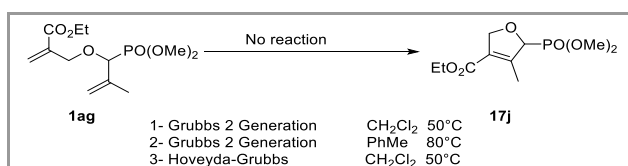
Finally, our efforts were focused on RCM reaction starting from allyloxymethylphosphonates **1x-af** substituted with a vinyl group in the α position of the phosphorus atom. Cyclisation of this specific substrate gave us the opportunity to prepare a series of 2,5-dihydrofuran compounds **17a-i** (Scheme 11). These were obtained in refluxing CH₂Cl₂ at high dilution (0.0025 M) and in the presence of a catalytic amount of Grubbs second generation

(Scheme 11). They were purified by column chromatography with good yields ranging from 69 to 91% and fully characterized by NMR and HRMS analysis.



Scheme 11 Synthesis of 2,5-dihydrofurans **17** by RCM reaction

Unfortunately, with dimethyl [(1-methylvinyl)-allyloxymethyl]phosphonate **1ag** (Scheme 12), no expected 2,5-dihydrofuran **17j** was obtained whatever the catalyst (Grubbs 2nd generation, Hoveyda Grubbs), the solvent (CH₂Cl₂, PhMe) and the temperature tested.



Scheme 12 Toward the synthesis of 4-methyl-2,5-dihydrofuran **17j**

Conclusion

In summary, this study successfully demonstrated the efficacy and versatility of allyloxymethylphosphonates **1** as key precursors in divergent synthetic strategies involving known methodologies, to prepare novel families of linear or cyclic compounds *bis*-functionalized with phosphonate and carboxylate functions. The 1,3-dipolar cycloaddition approaches with nitrile oxide, nitrile imine and nitron allowed for the efficient synthesis of regioselective isoxazolines, pyrazolines, and isoxazolidines. Furthermore, metal-catalyzed processes, such as inter- and intramolecular Heck coupling, facilitated the generation of cinnamyl- and indenyl-linked moieties. While this process failed for the synthesis of phosphonates connected to benzo-fused oxacycles that are obtained through another method, namely, radical arylation cyclization. Finally, ring-closing metathesis methods enabled the synthesis of 2-phosphorylated-2,5-dihydrofurans.

All reagents were obtained from Sigma Aldrich, Alfa Aesar and Acros and used without further purification. Dry EtOH, PhMe, CH₂Cl₂, C₆H₆ and MeCN solvents were commercially available from Sigma Aldrich and were used

as received and after degassing. Reactions were routinely carried out under nitrogen and argon atmosphere with magnetic stirring. All reactions were monitored by TLC on silica gel plates (Fluka Kieselgel 60 F254, Merck) and the series visualized by a 254 nm UV lamp, diode and aqueous potassium permanganate solution. Crude products were purified using high purity grade (Merck grade 9385) pore size 60Å, 230-400 mesh particle size silica gel (Sigma Aldrich). ¹H, ¹³C, ¹⁹F and ³¹P NMR spectra were recorded on a Bruker Avance 300 spectrometer fitted with a 5 mm i.d. BBO probe carefully tuned to the recording frequencies of 300 (¹H), 75 (¹³C) 121 (³¹P) and 282 MHz (¹⁹F), the temperature of the probe was set at r.t. (around 293-294 K), on a Bruker Avance 400 spectrometer fitted with a 5 mm i.d. BBFO+ probe carefully tuned to the recording frequency of 400 (¹H), 101 (¹³C), 376 (¹⁹F) and 162 MHz (³¹P). The spectra are referenced to the solvent in which they were run (7.27 ppm for ¹H CDCl₃ [idem for CDCl₃/CD₃OD 2:1] and 77.16 ppm for ¹³C CDCl₃ [idem for CDCl₃/CD₃OD 2:1]). Chemical shifts (δ) are given in ppm, and coupling constants (*J*) are given in Hz with the following splitting abbreviations: s = singlet, d = doublet, dd = doublets of doublets t = triplet, td = doublet of triplets, q = quartet, dq = doublet of quartet, m = multiplet or massif and br = broad. All assignments were confirmed with the aid of two-dimensional ¹H, ¹H (COSY) and (NOESY) or ¹H, ¹³C (HSQC) experiments using standard pulse programs. High-Resolution Mass Spectrometry (HRMS in Da unit) analyses were recorded on a Xevo-Q-ToF Waters, on CEISAM AMaCC platform. Ionization sources were performed with the available methods among electrospray ionization (ESI⁺ or ESI⁻). Infrared spectroscopic analyses were recorded on an IRTF Bruker Tensor, Spectrophotometer Speac Quest ATK system (samples were neat).

General procedure 1: isoxazolines **3** synthesis

Et₃N (2.0 mmol, 0.20 g, 0.28 mL, 2.0 equiv.) was added dropwise to a solution of olefin **1a-d** (1.0 mmol, 1.0 equiv.) and chloroxime **2a-b** (1.30 mmol, 1.30 equiv.) in CHCl₃ or CH₂Cl₂ (5 mL), the reaction mixture was stirred at r.t. for 16 to 24 h (monitored by TLC). After completion of the reaction, the mixture was washed with H₂O (2 * 20 mL), dried over MgSO₄, filtered and concentrated under reduced pressure. The resulting residue was purified by flash column chromatography on silica gel using (EtOAc-PE, 7:3) as eluent.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate **3a**:

Following general procedure 1 from diethyl allyloxymethylphosphonate **1a** (1.0 mmol, 0.28 g) and chloroxime **2a** (1.30 mmol, 0.20 g), the compound **3a** was obtained in 72% (0.28 g) as a viscous oil. R_f = 0.52 (EtOAc-PE 7:3). IR (neat): 2983 (C-H), 1735 (C=O), 1239 (C-O), 1018 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.68 - 7.65 (m, 2 H), 7.42 - 7.38 (m, 3 H), 4.25 (q, *J* = 7.2 Hz, 2 H), 4.09 (m, 4 H), 3.99 (d, *J* = 1.8 Hz, 2 H), 3.93 (dd, *J* = 8.0, 3.8 Hz, 2 H), 3.69 and 2.83 (syst. AB, *J* = 16.5 Hz, 2 H), 1.32 - 1.21 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.2.

¹³C NMR (100 MHz, CDCl₃): δ = 169.8, 156.5, 130.6, 128.9, 128.9 (2C), 127.0 (2C), 88.5, 74.1 (d, *J* = 10.1 Hz), 66.3 (d, *J* = 165.6 Hz), 62.7 (d, *J* = 3.9 Hz), 62.6 (d, *J* = 3.9 Hz), 62.4, 40.5, 16.5 (d, *J* = 5.6 Hz, 2C), 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₈H₂₇NO₇P: 400.1525; found: 400.1526.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate **3b**:

Following general procedure 1 from dimethyl allyloxymethylphosphonate **1b** (1.0 mmol, 0.25 g) and chloroxime **2a** (1.30 mmol, 0.20 g), the compound **3b** was obtained in 64% (0.24 g) as a yellow solid.

R_f = 0.49 (EtOAc-PE 7:3). Mp = 65 - 70 °C. IR (neat): 2963 (C-H), 1735 (C=O), 1239 (C-O), 1018 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.70 - 7.66 (m, 2 H), 7.44 - 7.41 (m, 3 H), 4.29 (q, *J* = 7.0 Hz, 2 H), 4.02 (s, 2 H), 4.00 (dd, *J* = 8.0, 2.9 Hz, 2 H), 3.77 (d, *J* = 2.1 Hz, 3 H), 3.74 (d, *J* = 2.1 Hz, 3 H), 3.72 and 3.52 (syst. AB, *J* = 16.6 Hz, 2 H), 1.33 (t, *J* = 7.0 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 22.6.

¹³C NMR (100 MHz, CDCl₃): δ = 169.6, 156.4, 130.5, 128.8, 128.7 (2C), 126.8 (2C), 88.4, 74.0 (d, *J* = 10.2 Hz), 65.4 (d, *J* = 165.7 Hz), 62.3, 53.1 (d, *J* = 2.4 Hz), 52.9 (d, *J* = 2.4 Hz), 40.4, 14.0.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₆H₂₂NO₇NaP: 394.1032; found: 394.1027.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-3-(2,3-dimethoxyphenyl)-4,5-dihydroisoxazole-5-carboxylate 3c:

Following general procedure 1 from diethyl allyloxymethylphosphonate **1a** (1.0 mmol, 0.28 g) and chloroxime **2b** (1.30 mmol, 0.28 g), the compound **3c** was obtained in 89% (0.41 g) as a viscous oil.

*R*_f = 0.51 (EtOAc-PE 7:3). IR (neat): 2925 (C-H), 1735 (C=O), 1260 (C-O), 1025 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.32 (dd, *J* = 7.9, 1.5 Hz, 1 H), 7.05 (t, *J* = 8.0 Hz, 1 H), 6.96 (dd, *J* = 8.2, 1.6 Hz, 1 H), 4.32 - 4.08 (m, 6 H), 3.95 (s, 2 H), 3.89 (d, *J* = 7.9 Hz, 2 H), 3.87 (s, 3 H), 3.78 (s, 4 H), 3.65 (d, *J* = 17.9 Hz, 1 H), 1.34 - 1.27 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.2.

¹³C NMR (100 MHz, CDCl₃): δ = 170.1, 155.5, 153.3, 147.9, 124.3, 123.3, 120.9, 114.3, 88.4, 74.3 (d, *J* = 10.0 Hz), 66.2 (d, *J* = 165.3 Hz), 62.6 (d, *J* = 4.7 Hz), 62.6 (d, *J* = 4.7 Hz), 62.2, 61.2, 56.0, 42.8, 16.5 (d, *J* = 5.6 Hz, 2C), 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₀H₃₀NNaO₉P: 482.1556; found: 482.1576.

Ethyl 3-(2,3-dimethoxyphenyl)-5-(((dimethoxyphosphoryl)-methoxy)methyl)-4,5-dihydroisoxazole-5-carboxylate 3d:

Following general procedure 1 from dimethyl allyloxymethylphosphonate **1b** (1.0 mmol, 0.25 g) and chloroxime **2b** (1.30 mmol, 0.28 g), the compound **3d** was obtained in 67% (0.29 g) as a viscous oil.

*R*_f = 0.51 (EtOAc-PE 7:3). IR (neat): 2924 (C-H), 1733 (C=O), 1259 (C-O), 1020 (C-O) cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.32 (dd, *J* = 7.9, 1.6 Hz, 1 H), 7.05 (t, *J* = 8.0 Hz, 1 H), 6.97 (dd, *J* = 8.1, 1.6 Hz, 1 H), 4.32 - 4.21 (m, 2 H), 4.00 (t, *J* = 4.0 Hz, 2 H), 3.90 - 3.86 (m, 4 H), 3.84 (s, 3 H), 3.83 - 3.79 (m, 2 H), 3.78 (s, 3 H), 3.75 (s, 3 H), 3.65 (d, *J* = 17.9 Hz, 1 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 22.8.

¹³C NMR (100 MHz, CDCl₃): δ = 170.1, 155.5, 155.3, 147.9, 124.4, 123.3, 120.9, 114.3, 88.4, 74.3 (d, *J* = 10.3 Hz), 65.6 (d, *J* = 165.5 Hz), 62.3, 61.3, 56.0, 53.2, 42.9 (d, *J* = 6.5 Hz, 2C), 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₈H₂₆NNaO₉P: 454.1243; found: 454.1248.

Ethyl 5-(((diethoxyphosphoryl)(phenyl)methoxy)methyl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate 3e:

Following general procedure 1 from diethyl allyloxymethylphosphonate **1d** (1.0 mmol, 0.35 g) and chloroxime **2a** (1.30 mmol, 0.20 g), the compound **3e** was obtained in 64% (0.30 g) as a viscous oil.

*R*_f = 0.53 (EtOAc-PE 7:3). IR (neat): 2981 (C-H), 1728 (C=O), 1018 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.73 - 7.67 (m, 2 H), 7.45 - 7.33 (m, 8 H), 4.84 (d, *J* = 15.2 Hz, 1 H), 4.19 (qd, *J* = 7.1, 2.3 Hz, 2 H), 4.04 - 3.92 (m, 4 H), 3.87 - 3.78 (m, 3 H), 3.74 (d, *J* = 7.4 Hz, 1 H), 1.24 (t, *J* = 7.2 Hz, 3 H), 1.13 (t, *J* = 7.0 Hz, 6 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.1.

¹³C NMR (100 MHz, CDCl₃): δ = 169.8, 156.7, 134.2, 130.6 (2C), 129.0, 128.9 (2C), 128.8, 128.6 (2C), 128.4, 127.0 (2C), 88.7, 79.7 (d, *J* = 160.7 Hz), 71.0 (d, *J* = 18.0 Hz), 63.3 (d, *J* = 7.1 Hz), 63.2 (d, *J* = 6.9 Hz), 62.4, 40.3, 16.4 (d, *J* = 5.1 Hz), 16.3 (d, *J* = 5.0 Hz), 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₄H₃₁NO₇P: 476.1838; found: 476.1833.

Ethyl 5-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-phenyl-4,5-dihydroisoxazole-5-carboxylate 3f:

Following general procedure 1 from dimethyl allyloxymethylphosphonate **1c** (1.0 mmol, 0.32 g) and chloroxime **2a** (1.3 mmol, 0.20 g), the compound **3f** was obtained in 61% (0.27 g) as a yellow solid.

*R*_f = 0.50 (EtOAc-PE 7:3). Mp = 65 - 70 °C. IR (neat): 2925 (C-H), 1733 (C=O), 1259 (C-O), 1020 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.64 (dd, *J* = 7.7, 1.9 Hz, 2H), 7.46 - 7.33 (m, 8H), 4.85 (d, *J* = 15.2 Hz, 1 H), 4.30 (q, *J* = 7.1 Hz, 2 H), 3.95 and 3.89 (syst. AB, *J* = 10.2 Hz, 2 H), 3.69 (d, *J* = 10.5 Hz, 3 H), 3.62 (d, *J* = 10.5 Hz, 3 H), 3.60 (m, 2 H), 1.34 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.1.

¹³C NMR (100 MHz, CDCl₃): δ = 169.9, 156.3, 133.9, 130.5, 128.9, 128.7 (2C), 128.7, 128.1 (2C), 128.0 (2C), 126.9 (2C), 88.3, 79.8 (d, *J* = 168.6 Hz), 72.2 (d, *J* = 13.4 Hz), 62.5, 54.0 (d, *J* = 7.0 Hz), 53.8 (d, *J* = 6.7 Hz), 41.0, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₂H₂₆NO₇NaP: 470.1345; found: 470.1356.

Ethyl 5-(((diethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(2,3-dimethoxyphenyl)-4,5-dihydroisoxazole-5-carboxylate 3g:

Following general procedure 1 from diethyl allyloxymethylphosphonate **1c** (1.0 mmol, 0.35 g) and chloroxime **2b** (1.30 mmol, 0.28 g), mixture of two inseparables diastereoisomers **3g** was obtained in 73% (0.38 g) as a viscous oil.

*R*_f = 0.49 (EtOAc-PE 7:3). IR (neat): 2924 (C-H), 1733 (C=O), 1259 (C-O), 1020 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.47 - 7.32 (m, 6 H), 7.15 - 6.90 (m, 2 H), 4.82 (d, *J* = 14.8 Hz, 1 H), 4.20 (q, *J* = 7.1 Hz, 2 H), 4.05 - 3.90 (m, 6 H), 3.89 (s, 3 H), 3.86 (s, 3 H), 3.70 (m, 2 H), 1.34 - 1.16 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 17.9.

¹³C NMR (100 MHz, CDCl₃): δ_{diast1} = 170.0, 155.2, 153.1, 147.7, 134.1, 128.6 - 128.0 (5C), 134.1, 124.2, 123.2, 120.7, 114.1, 88.1, 79.6 (d, *J* = 160.7 Hz), 71.2 (d, *J* = 18.0), 63.0 (d, *J* = 6.0 Hz), 63.3 (d, *J* = 6.0 Hz), 62.1, 61.1, 55.9, 42.5, 16.3 (2C), 14.0.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.47 - 7.32 (m, 6 H), 7.15 - 6.90 (m, 2 H), 4.83 (d, *J* = 15.2 Hz, 1 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 4.05 - 3.90 (m, 6 H), 3.89 (s, 3 H), 3.86 (s, 3 H), 3.70 (m, 2 H), 1.34 - 1.16 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 18.0.

¹³C NMR (100 MHz, CDCl₃): δ_{diast2} = 170.0, 155.5, 153.2, 147.8, 134.1, 128.6 - 128.0 (5C), 124.2, 123.2, 120.7, 114.1, 88.2, 79.6 (d, *J* = 160.7 Hz), 72.0, 63.0 (d, *J* = 6.0 Hz), 63.3 (d, *J* = 6.0 Hz), 62.1, 61.2, 55.9, 43.0, 16.4 (2C), 14.1.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₆H₃₄NO₉NaP: 558.1869; found: 558.1875.

Ethyl 3-(2,3-dimethoxyphenyl)-5-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-4,5-dihydroisoxazole-5-carboxylate 3h:

Following general procedure 1 from dimethyl allyloxymethylphosphonate **1d** (1.0 mmol, 0.35 g) and chloroxime **2b** (1.30 mmol, 0.28 g), mixture of two inseparables diastereoisomers **3h** was obtained in 69% (0.31 g) as a viscous oil.

*R*_f = 0.50 (EtOAc-PE 7:3). IR (neat): 2925 (C-H), 1733 (C=O), 1259 (C-O), 1020 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.47 – 7.26 (m, 6 H), 7.11 – 6.95 (m, 2 H), 4.88 (d, *J* = 15.0 Hz, 1 H), 4.28 (qd, *J* = 7.0, 1.3 Hz, 2 H), 4.01 – 3.83 (m, 2 H), 3.88 (s, 3 H), 3.81 (s, 3 H), 3.72 – 3.57 (m, 8 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 20.2.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 170.0, 155.1, 153.1, 147.7, 133.8, 128.5 (2C), 128.0, 127.9 (2C), 124.2, 123.1, 120.8, 114.1, 88.1, 79.4 (d, *J* = 168.1 Hz), 72.0 (d, *J* = 13.0 Hz), 62.1, 61.1, 55.9, 53.9 (d, *J* = 7.0 Hz, 2C), 43.1, 14.0.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.47 – 7.26 (m, 6 H), 7.11 – 6.95 (m, 2 H), 4.89 (d, *J* = 15.4 Hz, 1 H), 4.21 (qd, *J* = 7.0, 1.0 Hz, 2 H), 4.01 – 3.83 (m, 2 H), 3.87 (s, 3 H), 3.81 (s, 3 H), 3.72 – 3.57 (m, 8 H), 1.26 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 20.3.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 170.0, 155.5, 153.2, 147.8, 133.8, 128.5 (2C), 128.1, 127.9 (2C), 124.3, 123.3, 120.8, 114.1, 88.3, 79.3 (d, *J* = 168.1 Hz), 71.0 (d, *J* = 13.0 Hz), 62.1, 61.2, 55.9, 53.6 (d, *J* = 7.0 Hz, 2C), 42.5, 14.0.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₄H₃₀N₂O₆NaP: 530.1556; found: 530.1564.

General procedure 2: pyrazolines 5 synthesis

Under nitrogen atmosphere, NCS (1.0 mmol, 0.13 g, 1.0 equiv.) was added to solution at 0°C of the appropriate hydrazone **4a-c** (1.0 mmol, 1.0 equiv.) and pyridine (two drops) in MeCN (15 mL). After 20 min, dialkyl allyloxymethylphosphonate **1a-d** (1.0 mmol, 1.0 equiv.) and, then Et₃N (1.50 mmol, 0.15 g, 0.20 mL) was added to the mixture. The solution was allowed to reach at r.t. and stirred for 24 h. Then, the solvent was removed under reduced pressure and the resulting residue was dissolved in CH₂Cl₂ (40 mL), washed twice with H₂O (20 mL) and dried over MgSO₄. The solvent was evaporated, and the residue was purified by column chromatography on silica gel using (PE–EtOAc 7:3) as eluent.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5a:

Following the general procedure 2, using hydrazone **4a** (1.0 mmol, 0.20 g) and diethyl allyloxymethylphosphonate **1a** (1.0 mmol, 0.28 g), the pyrazoline **5a** was obtained in 81% (0.38 g) as a red brown oil.

R_f = 0.53 (EtOAc 100%). IR (neat): 2956 (C-H), 1723 (C=O), 1495 (C=C), 1232 (C-O and C-N), 1028 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.76 – 7.70 (m, 2 H), 7.40 – 7.32 (m, 3 H), 7.29 – 7.23 (m, 2 H), 7.14 – 7.13 (m, 2 H), 6.93 – 6.86 (m, 1 H), 4.25 – 4.12 (m, 4 H), 4.00 – 3.95 (m, 4 H), 3.83 – 3.60 (m, 4 H), 1.23 – 1.10 (m, 9 H).

³¹P NMR (121 MHz, CDCl₃): δ = 19.9.

¹³C NMR (75 MHz, CDCl₃): δ = 171.5, 146.0, 143.4, 132.1, 128.9 (2C), 128.7, 128.5 (2C), 125.7 (2C), 120.4, 115.0 (2C), 72.3 (d, *J* = 10.5 Hz), 71.7, 65.7 (d, *J* = 164.6 Hz), 62.5 (d, *J* = 6.5 Hz), 62.3 (d, *J* = 6.5 Hz), 61.9, 43.4, 16.2 (d, *J* = 4.6 Hz, 2C), 13.9.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₄H₃₂N₂O₆P: 475.1998; found: 475.2001.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5b:

Following the general procedure 2, using hydrazone **4a** (1.0 mmol, 0.20 g) and dimethyl allyloxymethylphosphonate **1b** (1.0 mmol, 0.25 g), the pyrazoline **5b** was obtained in 73% (0.32 g) as a red brown oil.

R_f = 0.54 (EtOAc 100%). IR (neat): 2955 (C-H), 1726 (C=O), 1493 (C=C), 1251 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 7.96 – 7.76 (m, 2 H), 7.44 – 7.30 (m, 3 H), 7.29 – 7.21 (m, 2 H), 7.16 – 7.11 (m, 2 H), 6.89 (tt, *J* = 7.4, 1.1 Hz, 1 H), 4.28 – 4.08 (m, 4 H), 3.86 – 3.70 (m, 4 H), 3.61 (d, *J* = 3.4 Hz, 3 H), 3.58 (d, *J* = 3.4 Hz, 3 H), 1.14 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 22.6.

¹³C NMR (101 MHz, CDCl₃): δ = 171.5, 146.2, 143.5, 132.1, 129.0 (2C), 128.8, 128.5 (2C), 125.8 (2C), 120.5, 115.0 (2C), 72.4 (d, *J* = 10.6 Hz), 71.7, 65.1 (d, *J* = 164.9), 62.0, 53.0 (d, *J* = 6.6 Hz), 52.8 (d, *J* = 6.6 Hz), 43.4, 13.9.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₂H₂₇N₂O₆NaP: 469.1504; found: 469.1497.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5c:

Following the general procedure 2, using hydrazone **4b** (1.0 mmol, 0.25 g) and diethyl allyloxymethylphosphonate **1a** (1.0 mmol, 0.28 g), the pyrazoline **5c** was obtained in 62% (0.31 g) as a red brown oil.

R_f = 0.55 (EtOAc 100%). IR (neat): 3060 (C-H), 1720 (C=O), 1494 (C=C), 1255 cm⁻¹ (C-O and C-N).

¹H NMR (300 MHz, CDCl₃): δ = 8.22 – 8.10 (m, 1 H), 7.90 – 7.77 (m, 4 H), 7.55 – 7.47 (m, 2 H), 7.32 – 7.15 (m, 4 H), 6.93 (t, *J* = 7.2 Hz, 1 H), 4.32 – 4.14 (m, 4 H), 4.05 – 3.92 (m, 5 H), 3.85 – 3.70 (m, 3 H), 1.18 (t, *J* = 7.1 Hz, 3 H), 1.17 (t, *J* = 7.1 Hz, 3 H), 1.11 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 20.0.

¹³C NMR (75 MHz, CDCl₃): δ = 171.7, 146.2, 143.4, 133.5, 133.3, 129.9, 129.1, 129.0, 128.3, 128.2, 127.9, 126.6, 126.5, 125.2, 123.5, 120.6, 115.1 (2C), 72.5 (d, *J* = 10.6 Hz), 71.9, 65.9 (d, *J* = 164.6 Hz), 62.6 (d, *J* = 6.5 Hz), 62.4 (d, *J* = 6.5 Hz), 62.1, 43.5, 16.4 (d, *J* = 2.7 Hz, 2C), 14.0.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₈H₃₄N₂O₆P: 525.2154; found: 525.2159.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5d:

Following the general procedure 2, using hydrazone **4b** (1.0 mmol, 0.25 g) and dimethyl allyloxymethylphosphonate **1b** (1.0 mmol, 0.25 g), the pyrazoline **5d** was obtained in 45% (0.22 g) as a red brown oil.

R_f = 0.53 (EtOAc 100%). IR (neat): 2955 (C-H), 1727 (C=O), 1495 (C=C), 1230 cm⁻¹ (C-O and C-N).

¹H NMR (300 MHz, CDCl₃): δ = 8.13 (dd, *J* = 8.6, 1.7, 1 H), 7.88 – 7.81 (m, 3 H), 7.54 – 7.47 (m, 2 H), 7.34 – 7.14 (m, 5 H), 7.01 – 6.90 (m, 1 H), 4.29 – 4.17 (m, 4 H), 3.99 – 3.72 (m, 4 H), 3.60 (d, *J* = 10.7 Hz, 6 H), 1.18 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 22.5.

¹³C NMR (75 MHz, CDCl₃): δ = 171.5, 146.2, 143.3, 133.4, 133.5, 129.7, 129.0 (2C), 128.9, 128.2, 127.8, 126.5, 126.5, 125.1, 123.4, 120.6, 115.0 (2C), 72.4 (d, *J* = 10.6), 71.8, 65.1, 62.0, 53.0 (d, *J* = 6.6 Hz), 52.8 (d, *J* = 6.6 Hz), 13.9, 43.3.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₆H₃₀N₂O₆P: 497.1841; found: 497.1840.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate 5e:

Following the general procedure 2, using hydrazone **4c** (1.0 mmol, 0.26 g) and diethyl allyloxymethylphosphonate **1a** (1.0 mmol, 0.28 g), the pyrazoline **5e** was obtained in 62% (0.33 g) as a red brown oil.

R_f = 0.56 (EtOAc 100%). IR (neat): 2920 (C-H), 1731 (C=O), 1322 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 7.73 (dd, *J* = 8.7, 0.7 Hz, 2 H), 7.61 – 7.51 (m, 2 H), 7.27 – 7.12 (m, 2 H), 7.01 – 7.10 (m, 2 H), 6.85 (tt, *J* = 7.5, 1.1 Hz, 1 H), 4.20 – 4.01 (m, 4 H), 3.93 – 3.83 (m, 4 H), 3.74 and 3.56 (syst. AB, *J* = 16.9 Hz, 2 H), 3.81 – 3.50 (m, 2 H), 1.17 – 1.01 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.0.

¹³C NMR (101 MHz, CDCl₃): δ = 171.2, 144.4, 142.9, 135.6, 130.1 (d, *J* = 32.6 Hz), 129.0 (2C), 128.9 (2C), 125.7 (2C), 125.4 (d, *J* = 3.9 Hz), 121.1, 115.2 (2C), 72.3 (d, *J* = 10.1 Hz), 72.1, 65.7 (d, *J* = 165.1 Hz), 62.5 (d, *J* = 6.5 Hz), 62.3 (d, *J* = 6.4 Hz), 43.0, 62.1, 17.7 – 15.5 (2C), 13.9.

¹⁹F NMR (377 MHz, CDCl₃): δ = -62.6.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₅H₃₁N₂O₆F₃P: 543.1872; found: 543.1871.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-1-phenyl-3-(4-(trifluoromethyl)phenyl)-4,5-dihydro-1H-pyrazole-5-carboxylate 5f:

Following the general procedure 2, using hydrazone **4c** (1.0 mmol, 0.26 g) and dimethyl allyloxymethylphosphonate **1b** (1.0 mmol, 0.25 g), the pyrazoline **5f** was obtained in 68% (0.34 g) as a red brown oil.

R_f = 0.55 (EtOAc 100%). IR (neat): 2957 (C-H), 1730 (C=O), 1321 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 7.82 (d, *J* = 8.1 Hz, 2 H), 7.65 (d, *J* = 8.2 Hz, 2 H), 7.33 – 7.26 (m, 2 H), 7.19 – 7.13 (m, 2 H), 6.95 (t, *J* = 7.3 Hz, 1 H), 4.28 – 4.11 (m, 4 H), 3.84 – 3.76 (m, 4 H), 3.63 (d, *J* = 1.3 Hz, 3 H), 3.60 (d, *J* = 1.3 Hz, 3 H), 1.17 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 22.5.

¹³C NMR (101 MHz, CDCl₃): δ = 171.2, 144.5, 142.9, 135.5, 130.1 (d, *J* = 32.5 Hz), 129.0 (2C), 125.8 (2C), 125.7 (2C), 125.4 (d, *J* = 3.8 Hz), 121.1, 115.2 (2C), 72.3 (d, *J* = 10.1 Hz), 72.1, 65.1 (d, *J* = 165.2 Hz), 62.1, 52.9 (d, *J* = 6.6 Hz), 52.7 (d, *J* = 6.6 Hz), 43.0, 13.9.

¹⁹F NMR (282 MHz, CDCl₃): δ = -62.6.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₃H₂₇N₂O₆PF₃: 515.1559; found: 515.1560.

Ethyl 5-(((diethoxyphosphoryl)(phenyl)methoxy)methyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5g:

Following the general procedure 2, using hydrazone **4a** (1.0 mmol, 0.20 g) and diethyl allyloxymethylphosphonate **1c** (1.0 mmol, 0.35 g), mixture of two diastereoisomers **5g** was obtained in overall yield 74% (0.40 g) as a red brown oil.

Diastereoisomer 1 was obtained in 54% (0.29 g) as a major product.

R_f = 0.61 (EtOAc 100%). IR (neat): 2980 (C-H), 1715 (C=O), 1493 (C=C), 1249 cm⁻¹ (C-O and C-N).

¹H NMR (300 MHz, CDCl₃): δ = 7.78 – 7.70 (m, 2 H), 7.47 – 7.33 (m, 3 H), 7.32 – 7.19 (m, 7 H), 7.14 – 7.01 (m, 2 H), 6.93 – 6.83 (m, 1 H), 4.57 (d, *J* = 15.1 Hz, 1 H), 4.20 – 4.09 (m, 2 H), 4.15 and 4.00 (syst. AB, *J* = 11.5 Hz, 2 H), 3.90 – 3.56 (m, 4 H), 3.83 and 3.61 (syst. AB, *J* = 16.9 Hz, 2 H), 1.09 (t, *J* = 7.1 Hz, 3 H), 1.04 – 0.96 (m, 6 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.8.

¹³C NMR (101 MHz, CDCl₃): δ = 171.6, 146.0, 143.4, 134.1 (d, *J* = 2.0 Hz), 132.2, 128.7 (2C), 129.0, 128.5 (2C), 128.3 (2C), 128.2 (2C), 128.1, 125.8 (2C), 120.3, 114.7 (2C), 79.3 (d, *J* = 167.8 Hz), 71.7, 69.2 (d, *J* = 13.5 Hz), 63.3 (d, *J* = 7.1 Hz), 62.8 (d, *J* = 6.7 Hz), 61.9, 43.6, 16.2 (t, *J* = 5.7 Hz, 2C), 13.8.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₃₀H₃₆N₂O₆P: 551.2311; found: 551.2316.

Diastereoisomer 2 was obtained in 20% (0.11 g) as a minor product.

R_f = 0.53 (EtOAc 100%). IR (neat): 2981 (C-H), 1724 (C=O), 1494 (C=C), 1249 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 7.62 – 7.68 (m, 2 H), 7.35 – 7.25 (m, 4 H), 7.14 – 7.08 (m, 3 H), 7.02 – 6.92 (m, 5 H), 6.84 – 6.77 (m, 1 H), 4.56 (d, *J* = 15.5 Hz, 1 H), 4.16 – 4.10 (m, 3 H), 3.90 – 3.58 (m, 6 H), 3.51 (d, *J* = 12.0 Hz, 1 H), 1.09 (t, *J* = 7.1 Hz, 3 H), 0.99 (td, *J* = 7.0 Hz, 0.4 Hz, 3 H), 0.97 – 0.93 (m, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.2.

¹³C NMR (101 MHz, CDCl₃): δ = 171.7, 145.7, 143.3, 133.8 (d, *J* = 2.3 Hz), 132.2, 128.9, 128.6 (2C), 128.5 (2C), 128.1, 128.1 (2C), 127.4 (2C), 125.7 (2C), 120.2, 114.9 (2C), 79.8 (d, *J* = 167.7 Hz), 71.5, 70.3 (d, *J* = 13.9 Hz), 63.1 (t, *J* = 6.3 Hz, 2C), 62.0, 43.9, 16.2 (t, *J* = 5.7 Hz, 2C), 13.9.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₃₀H₃₅N₂O₆NaP: 573.2130; found: 573.2133.

Ethyl 5-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-1,3-diphenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5h:

Following the general procedure 2, using hydrazone **4a** (1.0 mmol, 0.20 g) and dimethyl allyloxymethylphosphonate **1d** (1.0 mmol, 0.33 g), mixture of two diastereoisomers **5h** was obtained in overall yield 76% (0.39 g) as a red brown solid.

Diastereoisomer 1 was obtained in 53% (0.27 g) as a major product.

R_f = 0.60 (EtOAc 100%). Mp = 105 – 114 °C. IR (neat): 2955 (C-H), 1724 (C=O), 1493 (C=C), 1256 cm⁻¹ (C-O and C-N).

¹H NMR (300 MHz, CDCl₃): δ = 7.79 – 7.70 (m, 2 H), 7.45 – 7.33 (m, 3 H), 7.44 – 7.19 (m, 7 H), 7.14 – 7.08 (m, 2 H), 6.94 – 6.85 (m, 1 H), 4.61 (d, *J* = 15.4 Hz, 1 H), 4.20 – 3.96 (m, 4 H), 3.83 and 3.62 (syst. AB, *J* = 16.9 Hz, 2 H), 3.44 (d, *J* = 10.5 Hz, 3 H), 3.36 (d, *J* = 10.5 Hz, 3 H), 1.09 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.3.

¹³C NMR (75 MHz, CDCl₃): δ = 177.9, 171.5, 146.0, 143.3, 133.8 (d, *J* = 2.0 Hz), 128.6 (2C), 128.5, 128.4 (2C), 128.2 (2C), 128.1 (2C), 125.7 (2C), 120.2 (2C), 114.5 (2C), 78.6 (d, *J* = 169.3), 71.5, 68.8 (d, *J* = 13.9 Hz), 61.9, 53.8 (d, *J* = 7.0 Hz), 53.2 (d, *J* = 6.8 Hz), 43.6, 13.8.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₈H₃₂N₂O₆P: 523.1998; found: 523.2003.

Diastereoisomer 2 was obtained in 23% (0.12 g) as a minor product.

R_f = 0.53 (EtOAc 100%). Mp = 137 – 144 °C. IR (neat): 2955 (C-H), 1722 (C=O), 1254 cm⁻¹ (C-O and C-N).

¹H NMR (300 MHz, CDCl₃): δ = 7.77 – 7.72 (m, 2 H), 7.45 – 7.35 (m, 3 H), 7.30 – 7.22 (m, 7 H), 7.10 (dd, *J* = 8.8, 1.0 Hz, 1 H), 6.89 (t, *J* = 7.3 Hz, 1 H), 4.60 (d, *J* = 15.4 Hz, 1 H), 4.20 – 3.96 (m, 4 H), 3.84 and 3.62 (syst. AB, *J* = 16.9 Hz, 3 H), 3.44 (d, *J* = 10.5 Hz, 3 H), 3.37 (d, *J* = 10.5 Hz, 3 H), 1.10 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 20.7.

¹³C NMR (75 MHz, CDCl₃): δ = 171.7, 145.9, 143.3, 133.5, 133.5 (d, *J* = 2.4 Hz), 132.1 (2C), 128.9 (2C), 128.7, 128.5, 128.0, 127.9, 127.3, 127.3, 125.7 (2C), 120.3, 114.9 (2C), 79.6 (d, *J* = 167.9 Hz), 71.5, 70.3 (d, *J* = 14.2 Hz), 62.0, 53.7 (d, *J* = 6.7 Hz), 53.5 (d, *J* = 6.7 Hz), 44.0, 13.9.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₂₈H₃₁N₂O₆PNa: 545.1817; found: 545.1816.

Ethyl 5-(((diethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1H-pyrazole-5-carboxylate 5i:

Following the general procedure 2, using hydrazone **4b** (1.0 mmol, 0.25 g) and diethyl allyloxymethylphosphonate **1c** (1.0 mmol, 0.35 g), mixture of two diastereoisomers **5i** was obtained in overall yield 67% (0.39 g) as a red brown oil.

Diastereoisomer 1 was obtained in 41% (0.24 g) as a major product.

R_f = 0.59 (EtOAc 100%). IR (neat): 2980 (C-H), 1710 (C=O), 1495 (C=C), 1246 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 8.16 (dd, *J* = 8.8, 1.6 Hz, 1 H), 7.91 – 7.81 (m, 4 H), 7.55 – 7.51 (m, 2 H), 7.38 – 7.11 (m, 9 H), 6.99 – 6.88 (m, 1 H), 4.61 (d, *J* = 15.0 Hz, 1 H), 4.27 – 4.05 (m, 2 H), 4.22 and 4.07 (syst. AB, *J* = 11.0 Hz, 2 H), 3.96 and 3.76 (syst. AB, *J* = 16.8 Hz, 2 H), 4.02 – 3.69 (m, 4 H), 1.13 (t, *J* = 7.1 Hz, 3 H), 1.00 (q, *J* = 6.8 Hz, 6 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.7.

¹³C NMR (101 MHz, CDCl₃): δ = 171.5, 146.1, 143.3, 134.1, 133.5, 133.3, 129.9, 129.0, 128.5 – 127.8 (10 C), 126.5, 126.4, 125.1, 123.5, 120.4, 114.8, 79.3 (d, *J* = 167.9 Hz), 71.8, 69.4, 63.2 (d, *J* = 7.0 Hz), 62.8 (d, *J* = 6.8 Hz), 61.9, 43.5, 16.2 (2C), 13.9.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₃₄H₃₈N₂O₆P: 601.2467; found: 601.2475.

Diastereoisomer 2 was obtained in 26% (0.15 g) as a minor product.

R_f = 0.51 (EtOAc 100%). IR (neat): 2920 (C-H), 1727 (C=O), 1595 (C=C), 1246 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 8.12 (dd, *J* = 8.7, 1.6 Hz, 1 H), 7.93 – 7.80 (m, 4 H), 7.56 – 7.46 (m, 2 H), 7.33 – 6.96 (m, 9 H), 6.96 – 6.86 (m, 1 H), 4.68 (d, *J* = 15.7 Hz, 1 H), 4.42 – 4.19 (m, 3 H), 4.15 – 4.05 (m, 1 H), 4.02 – 3.88 (m, 3 H), 3.90 – 3.79 (m, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H), 1.05 (t, *J* = 7.1 Hz, 3 H), 0.98 (t, *J* = 7.0 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.2.

¹³C NMR (101 MHz, CDCl₃): δ = 171.7, 145.9, 143.2, 133.8 – 133.3 (8C), 129.9, 129.0, 128.1 (2C), 128.0 (2C), 127.7, 127.4 (2C), 127.3, 126.5, 126.4, 125.1, 123.4, 120.4, 114.9, 79.8 (d, *J* = 167.7 Hz), 71.6, 70.3 (d, *J* = 13.9 Hz), 63.1 (d, *J* = 6.7 Hz, 2C), 62.0, 43.9, 16.1 (d, *J* = 5.8 Hz, 2C), 13.9.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₃₄H₃₈N₂O₆P: 601.2467; found: 601.2471.

Ethyl 5-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(naphthalen-1-yl)-1-phenyl-4,5-dihydro-1*H*-pyrazole-5-carboxylate 5j:

Following the general procedure 2, using hydrazone **4b** (1.0 mmol, 0.25 g) and dimethyl allyloxymethylphosphonate **1d** (1.0 mmol, 0.33 g), mixture of two diastereoisomers **5j** was obtained in overall yield 67% (0.38 g) as a red brown oil.

Diastereoisomer 1 was obtained in 48% (0.27 g) as a major product.

R_f = 0.60 (EtOAc 100%). IR (neat): 2954 (C-H), 1719 (C=O), 1446 (C=C), 1260 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 8.17 (dd, *J* = 8.7, 1.5 Hz, 1 H), 7.88 (dd, *J* = 8.2, 3.4 Hz, 4 H), 7.53 (dd, *J* = 6.5, 2.9 Hz, 2 H), 7.33 – 7.24 (m, 7 H), 7.17 (dd, *J* = 8.8, 1.0 Hz, 2 H), 6.94 (t, *J* = 7.3 Hz, 1 H), 4.63 (d, *J* = 15.4 Hz, 1 H), 4.20 – 4.17 (m, 2 H), 4.23 and 4.07 (syst. AB, *J* = 11.3 Hz, 2 H), 3.98 and 3.77 (syst. AB, *J* = 16.8 Hz, 2 H), 3.43 (d, *J* = 10.5 Hz, 3 H), 3.38 (d, *J* = 10.5 Hz, 3 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.3.

¹³C NMR (101 MHz, CDCl₃): δ = 171.5, 146.1, 143.2, 133.9, 133.5, 133.3, 129.9, 129.1, 128.6 – 128.1 (9C), 127.8, 126.5, 126.5, 125.1, 123.4, 120.4, 114.7, 78.7 (d, *J* = 168.5 Hz), 71.7, 68.8, 61.9, 53.8 (d, *J* = 7.1 Hz), 53.2 (d, *J* = 6.7 Hz), 43.6, 13.9.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₃₂H₃₄N₂O₆P: 573.2154; found: 573.2161.

Diastereoisomer 2 was obtained in 19% (0.11 g) as a minor product.

R_f = 0.53 (EtOAc 100%). IR (neat): 2953 (C-H), 1719 (C=O), 1461 (C=C), 1247 cm⁻¹ (C-O and C-N).

¹H NMR (400 MHz, CDCl₃): δ = 8.11 (dd, *J* = 8.6, 1.7 Hz, 1 H), 7.92 – 7.38 (m, 4 H), 7.54 – 7.50 (m, 2 H), 7.29 – 7.03 (m, 4 H), 6.95 – 6.90 (m, 1 H), 4.70 (d, *J* = 15.5 Hz, 1 H), 4.28 – 4.20 (m, 4 H), 4.06 and 3.85 (syst. AB, *J* = 16.8 Hz, 2 H), 3.50 (d, *J* = 9.5 Hz, 3 H), 3.48 (d, *J* = 9.4 Hz, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.7.

¹³C NMR (101 MHz, CDCl₃): δ = 171.7, 146.0, 143.3, 133.6, 133.5, 133.4, 133.3, 129.9, 129.0 (2C), 128.3 – 128.1 (5C), 127.8, 127.4, 127.4, 126.5, 126.4, 125.1, 123.4, 120.5, 115.0, 79.7 (d, *J* = 168.0 Hz), 71.7, 70.4 (d, *J* = 14.0 Hz), 62.0, 53.7 (d, *J* = 7.2 Hz), 53.5 (d, *J* = 6.6 Hz), 43.9, 13.9.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₃₂H₃₄N₂O₆P: 573.2154; found: 573.2155.

General procedure 3: isoxazolidines synthesis

An equimolecular amount of the nitron **6a-e** and olefin **1a-b** (0.70 mmol, 1.0 equiv.) was dissolved in anhydrous PhMe (10 mL) and was refluxed at

110 °C under argon atmosphere for various time. After completion of the reaction, monitored by TLC, the mixture was cooled to r.t., evaporation of the solvent. Then, the crude product was purified by flash column chromatography on silica gel using EtOAc (100%) as eluent.

Following general procedure 3, from diethyl allyloxymethylphosphonate **1a** (0.70 mmol, 0.20 g) and nitron **6a** (0.70 mmol, 0.10 g), mixture of two inseparables diastereoisomers **7a** was obtained in 92% (0.27 g) as a viscous oil.

R_f = 0.5 (EtOAc 100%). IR (neat): 2983 (C-H), 1733 (C=O), 1223 (C-O), 1020 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ_{diast1} = 7.27 – 7.19 (m, 2 H), 7.16 (t, *J* = 6.4 Hz, 2 H), 4.36 – 4.25 (m, 2 H), 4.24 – 4.12 (m, 4 H), 4.09 – 3.95 (m, 2 H), 3.93 – 3.85 (syst. AB, *J* = 10.6 Hz, 2 H), 3.63 – 3.46 (m, 1 H), 2.91 – 2.57 (m, 2 H), 2.60 (s, 3 H), 2.35 (s, 3 H), 1.44 – 1.30 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 20.6.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.3, 137.9, 134.6, 129.4 (2C), 127.7 (2C), 84.0, 75.3 (d, *J* = 9.7 Hz), 73.2, 66.1 (d, *J* = 165.0 Hz), 62.5 (d, *J* = 5.6 Hz, 2C), 61.6, 45.1, 42.9, 21.1, 16.5 (d, *J* = 5.5 Hz, 2C), 14.2.

¹H NMR (400 MHz, CDCl₃): δ_{diast2} = 7.27 – 7.19 (m, 2 H), 7.16 (t, *J* = 6.4 Hz, 2 H), 4.36 – 4.25 (m, 2 H), 4.24 – 4.12 (m, 4 H), 4.09 – 3.95 (m, 2 H), 3.93 – 3.85 (syst. AB, *J* = 10.6 Hz, 2 H), 3.63 – 3.46 (m, 1 H), 2.91 – 2.57 (m, 2 H), 2.64 (s, 3 H), 2.35 (s, 3 H), 1.44 – 1.30 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 20.9.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 171.2, 138.0, 134.3, 129.5 (2C), 127.5 (2C), 83.9, 75.7 (d, *J* = 9.3 Hz), 73.0, 65.9 (d, *J* = 164.2 Hz), 62.4 (d, *J* = 5.6 Hz, 2C), 61.6, 45.9, 43.1, 21.1, 16.5 (d, *J* = 5.5 Hz, 2C), 14.1.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₀H₃₃N₃O₇P: 430.1995; found: 430.1992.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-2-methyl-3-(*p*-tolyl)isoxazolidine-5-carboxylate 7b:

Following general procedure 3, from dimethyl allyloxymethylphosphonate **1b** (0.70 mmol, 0.17 g) and nitron **6a** (0.70 mmol, 0.10 g), mixture of two inseparables diastereoisomers **7b** was obtained in 90% (0.25 g) as a viscous oil.

R_f = 0.52 (EtOAc 100%). IR (neat): 2958 (C-H), 1731 (C=O), 1242 (C-O), 1024 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.22 – 7.18 (m, 2 H), 7.16 – 7.09 (m, 2 H), 4.36 – 4.22 (m, 2 H), 4.09 – 3.90 (m, 4 H), 3.74 – 3.86 (m, 6 H), 3.48 (s, 1 H), 2.58 – 2.86 (m, 2 H), 2.57 (s, 3 H), 2.31 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 23.0.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.2, 137.8, 134.6, 129.3 (2C), 127.6 (2C), 84.0, 75.4 (d, *J* = 10.0 Hz), 73.1, 65.4 (d, *J* = 165.0 Hz), 61.6, 53.0 (d, *J* = 6.5 Hz, 2C), 45.1, 42.9, 21.1, 14.1.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.22 – 7.18 (m, 2 H), 7.16 – 7.09 (m, 2 H), 4.36 – 4.22 (m, 2 H), 4.09 – 3.90 (m, 4 H), 3.74 – 3.86 (m, 6 H), 3.48 (s, 1 H), 2.58 – 2.86 (m, 2 H), 2.61 (s, 3 H), 2.32 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 23.2.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 171.1, 137.9, 134.3, 129.4 (2C), 127.5 (2C), 83.9, 75.7, 72.0, 65.2 (d, *J* = 164.3 Hz), 61.6, 53.0 (d, *J* = 6.5 Hz, 2C), 45.9, 43.1, 21.0, 14.1.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₁₈H₂₉N₃O₇P: 402.1682; found: 402.1699.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-3-(3-methoxyphenyl)-2-methyl isoxazolidine-5-carboxylate 7c:

Following general procedure 3, from diethyl allyloxymethylphosphonate **1a** (0.70 mmol, 0.20 g) and nitron **6b** (0.70 mmol, 0.11 g), mixture of two

inseparables diastereoisomers **7c** was obtained in 69% (0030 g) as a viscous oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2983 (C-H), 1733 (C=O), 1239 (C-O), 1019 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ_{diast1} = 7.25 (m, 1 H), 7.02 – 6.86 (m, 2 H), 6.83 (dd, *J* = 7.4, 1.9 Hz, 1 H), 4.34 – 4.14 (m, 6 H), 3.97 (d, *J* = 7.9 Hz, 2 H), 3.92 and 3.85 (syst. AB, *J* = 10.6 Hz, 2 H), 3.80 (s, 3 H), 3.54 – 3.47 (m, 1 H), 2.93 – 2.71 (m, 2 H), 2.62 (s, 3 H), 1.42 – 1.31 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 20.6.

¹³C NMR (101 MHz, CDCl₃): δ_{diast1} = 172.2, 159.9, 139.6, 129.6, 120.2, 113.5, 113.1, 84.1, 75.2 (d, *J* = 9.7 Hz), 73.2, 66.1 (d, *J* = 165.0 Hz), 62.4 (d, *J* = 6.3 Hz, 2C), 61.6, 55.2, 45.0, 43.1, 16.5 (d, *J* = 5.7 Hz, 2C), 14.2.

¹H NMR (400 MHz, CDCl₃): δ_{diast2} = 7.25 (m, 1 H), 7.02 – 6.86 (m, 2 H), 6.83 (dd, *J* = 7.4, 1.9 Hz, 1 H), 4.34 – 4.14 (m, 6 H), 3.97 (d, *J* = 7.9 Hz, 2 H), 3.92 and 3.85 (syst. AB, *J* = 10.6 Hz, 2 H), 3.80 (s, 3 H), 3.54 – 3.47 (m, 1 H), 2.93 – 2.71 (m, 2 H), 2.66 (s, 3 H), 1.42 – 1.31 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 20.8.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 171.1, 159.9, 139.3, 129.7, 119.6, 113.6, 113.2, 83.9, 75.7 (d, *J* = 7.6 Hz), 72.0, 66.0 (d, *J* = 164.2 Hz), 62.4 (d, *J* = 6.3 Hz, 2C), 61.5, 55.2, 45.0, 43.3, 16.4 (2C), 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₀H₃₃NO₈P: 446.1944; found: 446.1954.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-3-(3-methoxyphenyl)-2-methyl isoxazolidine-5-carboxylate **7d**:

Following general procedure 3, from dimethyl allyloxymethylphosphonate **1b** (0.70 mmol, 0.17 g) and nitrone **6b** (0.70 mmol, 0.11 g), mixture of two inseparables diastereoisomers **7d** was obtained in 97% (0.28 g) as a viscous oil.

R_f = 0.52 (EtOAc 100%). IR (neat): 2959 (C-H), 1731 (C=O), 1242 (C-O), 1025 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.28 – 7.15 (m, 1 H), 6.91 – 6.85 (m, 2 H), 6.83 – 6.77 (m, 1 H), 4.33 – 4.17 (m, 2 H), 3.98 (d, *J* = 7.7 Hz, 2 H), 3.86 – 3.69 (m, 11 H), 3.59 – 3.37 (m, 1 H), 2.82 – 2.65 (m, 2 H), 2.58 (s, 3 H), 1.30 (td, *J* = 7.1, 1.8 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 23.0.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.1, 159.8, 139.4, 129.6, 120.1, 113.3, 113.1, 84.1, 75.3 (d, *J* = 10.0 Hz), 65.4 (d, *J* = 165.0 Hz), 73.2, 61.6, 55.1, 53.0 (d, *J* = 6.4 Hz, 2C), 45.1, 43.1, 14.2.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.28 – 7.15 (m, 1 H), 6.91 – 6.85 (m, 2 H), 6.83 – 6.77 (m, 1 H), 4.33 – 4.17 (m, 2 H), 3.98 (d, *J* = 7.7 Hz, 2 H), 3.86 – 3.69 (m, 11 H), 3.59 – 3.37 (m, 1 H), 2.82 – 2.65 (m, 2 H), 2.66 (s, 3 H), 1.30 (td, *J* = 7.1, 1.8 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 23.2.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 171.0, 159.8, 139.1, 129.7, 119.8, 113.4, 83.9, 113.0, 75.7 (d, *J* = 9.8 Hz), 72.1, 65.2 (d, *J* = 164.4 Hz), 61.6, 55.1, 53.0 (d, *J* = 6.4 Hz, 2C), 45.9, 43.2, 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₈H₂₉NO₈P: 418.1631; found: 418.1642.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-3-(4-fluorophenyl)-2-methyl isoxazolidine-5-carboxylate **7e**:

Following general procedure 3, from diethyl allyloxymethylphosphonate **1a** (0.70 mmol, 0.20 g) and nitrone **6c** (0.70 mmol, 0.10 g), mixture of two inseparables diastereoisomers **7e** was obtained in 89% (0.27 g) as a viscous oil.

R_f = 0.51 (EtOAc 100%). IR (neat) ν 2983 (C-H), 1732 (C=O), 1222 (C-O), 1020 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.28 – 7.12 (m, 2 H), 7.07 – 6.88 (m, 2 H), 4.36 – 4.17 (m, 2 H), 4.17 – 4.05 (m, 4 H), 4.00 – 3.87 (m, 2 H), 3.87 and

3.73 (syst. AB, *J* = 10.8, 2 H), 3.46 (t, *J* = 8.2, 1 H), 2.79 – 2.62 (m, 2 H), 2.50 (s, 3 H), 1.35 – 1.22 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 20.6.

¹³C NMR (101 MHz, CDCl₃): δ_{diast1} = 172.1, 162.5 (d, *J* = 246.6), 133.6, 129.5 (d, *J* = 8.1, 2C), 115.4 (d, *J* = 21.4, 2C), 84.1, 75.0 (d, *J* = 9.7), 72.6, 66.2 (d, *J* = 165.2), 62.4 (d, *J* = 6.2, 2C), 61.6, 45.0, 42.9, 16.5 (d, *J* = 5.6, 2C), 14.2.

¹⁹F NMR (377 MHz, CDCl₃): δ_{diast1} = -114.1.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.28 – 7.12 (m, 2 H), 7.07 – 6.88 (m, 2 H), 4.36 – 4.17 (m, 2 H), 4.17 – 4.05 (m, 4 H), 4.00 – 3.87 (m, 2 H), 3.87 and 3.73 (syst. AB, *J* = 10.8, 2 H), 3.46 (t, *J* = 8.2, 1 H), 2.79 – 2.62 (m, 2 H), 2.55 (s, 3 H), 1.35 – 1.22 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 20.8.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 171.0, 162.5 (d, *J* = 246.6), 133.3, 129.2 (d, *J* = 7.8, 2C), 115.6 (d, *J* = 21.4, 2C), 83.9, 75.0 (d, *J* = 9.7), 71.6, 66.0 (d, *J* = 164.6), 62.4 (d, *J* = 6.6, 2C), 61.6, 45.0, 43.1, 16.5 (2C), 14.1.

¹⁹F NMR (377 MHz, CDCl₃): δ_{diast2} = -113.9.

HRMS (ESI⁺): for C₁₉H₃₀FNO₇P [M+H]⁺ calcd. 434.1744 found 434.1744

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-3-(4-fluorophenyl)-2-methyl isoxazolidine-5-carboxylate **7f**:

Following general procedure 3, from dimethyl allyloxymethylphosphonate **1b** (0.70 mmol, 0.17 g) and nitrone **6c** (0.70 mmol, 0.10 g), mixture of two inseparables diastereoisomers **7f** was obtained in 87% (0.24 g) as a viscous oil.

R_f = 0.5 (EtOAc 100%). IR (neat): 2959 (C-H), 1731 (C=O), 1222 (C-O and C-N), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ_{disat1} = 7.26 (d, *J* = 1.9 Hz, 2 H), 6.94 (td, *J* = 8.6, 4.9 Hz, 2 H), 4.24 – 4.11 (m, 2 H), 4.09 – 3.79 (m, 4 H), 3.76 – 3.69 (m, 6 H), 3.58 – 3.39 (m, 1 H), 2.78 – 2.54 (m, 2 H), 2.50 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ_{disat1} = 22.8.

¹⁹F NMR (377 MHz, CDCl₃): δ_{disat1} = -113.9.

¹³C NMR (101 MHz, CDCl₃): δ_{disat1} = 172.0, 162.4 (d, *J* = 246.5 Hz), 133.6, 129.4 (d, *J* = 8.1 Hz, 2C), 115.5 (d, *J* = 21.4, 2C), 84.0, 75.1 (d, *J* = 10.0 Hz), 72.4, 65.4, 61.6, 52.9 (dd, *J* = 6.5, 2.9 Hz, 2C), 45.0, 42.8, 14.1.

¹H NMR (400 MHz, CDCl₃): δ_{diast2} = 7.26 (d, *J* = 1.9 Hz, 2 H), 6.94 (td, *J* = 8.6, 4.9 Hz, 2 H), 4.24 – 4.11 (m, 2 H), 4.09 – 3.79 (m, 4 H), 3.76 – 3.69 (m, 6 H), 3.58 – 3.39 (m, 1 H), 2.78 – 2.54 (m, 2 H), 2.54 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 23.1.

¹⁹F NMR (377 MHz, CDCl₃): δ_{diast2} = -114.1.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 170.9, 162.4 (d, *J* = 246.5 Hz), 133.2 (d, *J* = 3.1 Hz), 129.1 (d, *J* = 8.0 Hz, 2C), 115.5 (d, *J* = 21.4 Hz, 2C), 83.9, 75.6 (d, *J* = 9.8 Hz), 71.5, 65.2 (d, *J* = 164.5 Hz), 61.6, 52.9 (d, *J* = 6.4 Hz, 2C), 45.8, 43.0, 14.0.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₇H₂₆FNO₇P: 406.1431; found: 406.1420.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-2-methyl-3-(4(trifluoromethyl)phenyl) isoxazolidine-5-carboxylate **7g**:

Following general procedure 3, from diethyl allyloxymethylphosphonate **1a** (0.70 mmol, 0.20 g) and nitrone **6d** (0.70 mmol, 0.14 g), mixture of two inseparables diastereoisomers **7g** was obtained in 69% (0.23 g) as a viscous oil.

R_f = 0.54 (EtOAc 100%). IR (neat): 2984 (C-H), 1734 (C=O), 1254 (C-O and C-N), 1019 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.66 – 7.56 (m, 2 H), 7.56 – 7.44 (m, 2 H), 4.31 (m, 2 H), 4.19 (q, *J* = 7.1 Hz, 4 H), 3.97 – 3.91 (m, 2 H), 3.89 and 3.83 (syst. AB, *J* = 10.7 Hz, 2 H), 3.61 (t, *J* = 8.4 Hz, 1 H), 2.58 (s, 3 H), 3.01 – 2.27 (m, 2 H), 1.41 – 1.31 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 20.5.

¹³C NMR (101 MHz, CDCl₃): δ_{diast1} = 171.9, 142.4, 130.5 (q, *J* = 32.4 Hz), 128.1 (2C), 126.6 (q, *J* = 258.1 Hz), 125.6 (2C), 84.3, 74.8 (d, *J* = 9.8 Hz), 72.6, 66.1 (d, *J* = 165.4 Hz), 62.4 (d, *J* = 3.1 Hz), 62.3 (d, *J* = 3.0 Hz), 61.7, 44.9, 43.0, 16.4 (d, *J* = 5.6 Hz, 2C), 14.1.

¹⁹F NMR (377 MHz, CDCl₃): δ_{diast1} = -62.7.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.66 – 7.56 (m, 2 H), 7.56 – 7.44 (m, 2 H), 4.31 (m, 2 H), 4.19 (q, *J* = 7.1 Hz, 4 H), 3.97 – 3.91 (m, 2 H), 3.89 and 3.83 (syst. AB, *J* = 10.7 Hz, 2 H), 3.61 (t, *J* = 8.4 Hz, 1 H), 2.62 (s, 3 H), 3.01 – 2.27 (m, 2 H), 1.41 – 1.31 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 20.8.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 165.5, 136.5, 130.5 (q, *J* = 32.4 Hz), 127.9 (2C), 126.6 (q, *J* = 258.1 Hz), 125.6 (2C), 84.1, 72.6, 71.2 (d, *J* = 12.5 Hz), 64.7 (d, *J* = 166.9 Hz), 62.4 (d, *J* = 3.1 Hz), 62.3 (d, *J* = 3.0 Hz), 60.7, 44.9, 43.3, 16.3 (2C), 14.1.

¹⁹F NMR (377 MHz, CDCl₃): δ_{diast2} = -62.7.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₀H₃₀F₃N₇O₇P: 484.1712; found: 484.1712.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-2-methyl-3-(4-(trifluoromethyl)phenyl)isoxazolidine-5-carboxylate 7h:

Following general procedure 3, from dimethyl allyloxymethylphosphonate **1b** (0.70 mmol, 0.17 g) and nitrone **6d** (0.70 mmol, 0.14 g), the compound **7h** was obtained in 64% (0.20 g) as a viscous oil.

R_f = 0.55 (EtOAc 100%). IR (neat): 2921 (C-H), 1727 (C=O), 1324 (C-N), 1022 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.52 (d, *J* = 8.1 Hz, 2 H), 7.39 (d, *J* = 8.1 Hz, 2 H), 4.28 – 4.13 (m, 2 H), 3.93 (d, *J* = 7.9 Hz, 2 H), 3.85 – 3.66 (m, 8 H), 3.61 – 3.51 (m, 1 H), 2.70 (d, *J* = 8.6 Hz, 2 H), 2.54 (s, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H).

¹⁹F NMR (282 MHz, CDCl₃): δ = -62.6.

³¹P NMR (121 MHz, CDCl₃): δ = 22.9.

¹³C NMR (75 MHz, CDCl₃): δ = 171.9, 142.2, 130.3 (d, *J* = 32.4 Hz), 128.1 (2C), 126.5, 125.6 (d, *J* = 3.7 Hz, 2C), 84.3, 75.0 (d, *J* = 10.0 Hz), 72.6, 65.4 (d, *J* = 165.3 Hz), 61.7, 56.4 (2C), 45.0, 43.1, 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₈H₂₆F₃N₇O₇P: 456.1399; found: 456.1389.

Ethyl 5-(((diethoxyphosphoryl)methoxy)methyl)-2-methyl-3-(quinolin-3-yl)isoxazolidine-5-carboxylate 7i:

Following general procedure 3, from diethyl allyloxymethylphosphonate **1a** (0.70 mmol, 0.20 g) and nitrone **6e** (0.70 mmol, 0.13 g), mixture of two inseparables diastereoisomers **7i** was obtained in 89% (0.29 g) as a viscous oil.

R_f = 0.48 (EtOAc 100%). IR (neat): 2983 (C-H), 1732 (C=O), 1224 (C-O and C-N), 1019 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 8.81 (s, 1 H), 8.07 (s, 1 H), 8.04 (d, *J* = 8.4 Hz, 1 H), 7.94 – 7.68 (m, 1 H), 7.72 – 7.53 (m, 1 H), 7.72 – 7.46 (m, 1 H), 4.29 – 4.18 (m, 2 H), 4.18 – 4.06 (m, 4 H), 3.98 – 3.70 (m, 4 H), 3.75 (t, *J* = 8.3 Hz, 1 H), 3.15 – 2.73 (m, 2 H), 2.60 (s, 3 H), 1.28 (m, 9 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 20.4.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 171.8, 150.2, 147.8, 134.9 (d, *J* = 17.8 Hz), 130.9, 129.7, 129.0, 127.8, 127.7, 127.0, 84.3, 74.8 (d, *J* = 9.7 Hz), 70.8, 66.1, 62.4, 61.7 (d, *J* = 165.3 Hz), 44.8, 43.1 (d, *J* = 4.3 Hz, 2C), 16.4 (d, *J* = 5.4 Hz, 2C), 14.1.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 8.81 (s, 1 H), 8.07 (s, 1 H), 8.04 (d, *J* = 8.4 Hz, 1 H), 7.94 – 7.68 (m, 1 H), 7.72 – 7.53 (m, 1 H), 7.72 – 7.46 (m, 1 H), 4.29 – 4.18 (m, 2 H), 4.18 – 4.06 (m, 4 H), 3.98 – 3.70 (m, 4 H), 3.75 (t, *J* = 8.3 Hz, 1 H), 3.15 – 2.73 (m, 2 H), 2.63 (s, 3 H), 1.28 (m, 9 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 20.6.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 170.8, 149.9, 147.8, 134.9 (d, *J* = 17.8 Hz), 130.6, 129.7, 129.0, 127.8, 127.7, 127.0, 84.1, 75.5 (d, *J* = 9.4 Hz), 70.0, 65.9 (d, *J* = 164.5 Hz), 62.4 (d, *J* = 4.3 Hz, 2C), 61.7, 45.6, 43.3, 16.3 (2C), 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₃₂N₂O₇P: 467.1963; found: 467.1969.

Ethyl 5-(((dimethoxyphosphoryl)methoxy)methyl)-2-methyl-3-(quinolin-3-yl)isoxazolidine-5-carboxylate 7j:

Following general procedure 3, from dimethyl allyloxymethylphosphonate **1b** (0.70 mmol, 0.17 g) and nitrone **6e** (0.70 mmol, 0.13 g), the compound **7j** was obtained in 83% (0.25 g) as a viscous oil.

R_f = 0.52 (EtOAc 100%). IR (neat): 2959 (C-H), 1729 (C=O), 1226 (C-O and C-N), 1025 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 8.85 (s, 1 H), 8.13 (d, *J* = 1.7 Hz, 1 H), 8.11 (dd, *J* = 12.0, 5.1 Hz, 1 H), 7.80 (d, *J* = 8.1 Hz, 1 H), 7.75 – 7.66 (m, 1 H), 7.54 (t, *J* = 7.5 Hz, 1 H), 4.35 – 4.24 (m, 2 H), 4.01 (d, *J* = 7.8 Hz, 2 H), 3.95 and 3.87 (syst. AB, *J* = 10.7 Hz, 2 H), 3.84 (d, *J* = 1.5 Hz, 3 H), 3.80 (d, *J* = 1.5 Hz, 3 H), 3.78 – 3.76 (m, 1 H), 2.87 (dd, *J* = 8.6, 5.0 Hz, 2 H), 2.65 (s, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 22.9.

¹³C NMR (75 MHz, CDCl₃): δ = 171.9, 150.4, 148.1, 134.9, 130.8, 129.6, 129.2, 127.8, 127.7, 126.9, 84.3, 75.0 (d, *J* = 10.0 Hz), 70.9, 65.4 (d, *J* = 165.4 Hz), 61.8, 53.0 (d, *J* = 2.3 Hz), 53.0 (d, *J* = 2.2 Hz), 45.0, 43.1, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₀H₂₈N₂O₇P: 439.1634; found: 439.1627.

Diethyl 3,3'-(1,4-phenylene)bis(5-(((diethoxyphosphoryl)methoxy)methyl)-2-methylisoxazolidine-5-carboxylate) 7k:

Following general procedure 3, from diethyl allyloxymethylphosphonate **1a** (1.40 mmol, 0.40 g) and nitrone **6f** (0.70 mmol, 0.13 g), mixture of two inseparables diastereoisomers **7k** was obtained in 71% (0.36 g) as a viscous oil.

R_f = 0.32 (EtOAc 100%). IR (neat): 2983 (C-H), 1732 (C=O), 1223 (C-O and C-N), 1019 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ_{diast1} = 7.22 (dd, *J* = 10.8, 5.9 Hz, 4 H), 4.28 – 4.16 (m, 4 H), 4.15 – 4.05 (m, 8 H), 4.01 – 3.86 (m, 4 H), 3.84 – 3.77 (syst. AB, *J* = 10.7 Hz, 4 H), 3.62 – 3.43 (m, 2 H), 2.88 – 2.21 (m, 4 H), 2.52 (s, 6 H), 1.35 – 1.22 (m, 18 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 20.5.

¹³C NMR (101 MHz, CDCl₃): δ_{diast1} = 172.1 (2C), 138.0 (2C), 137.5 (2C), 127.9 (2C), 84.2 (2C), 75.0 (d, *J* = 9.0 Hz, 2C), 72.7 (2C), 66.1 (d, *J* = 165.1 Hz, 2C), 62.4 (d, *J* = 6.4 Hz, 4C), 61.6 (2C), 44.8 (2C), 43.0 (2C), 16.5 (d, *J* = 5.5 Hz, 4C), 14.2 (2C).

¹H NMR (400 MHz, CDCl₃): δ_{diast2} = 7.22 (dd, *J* = 10.8, 5.9 Hz, 4 H), 4.28 – 4.16 (m, 4 H), 4.15 – 4.05 (m, 8 H), 4.01 – 3.86 (m, 4 H), 3.84 – 3.77 (syst. AB, *J* = 10.7 Hz, 4 H), 3.51 – 3.60 (m, 2 H), 2.88 – 2.21 (m, 4 H), 2.55 (s, 6 H), 21.35 – 1.22 (m, 18 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 20.8.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 171.1 (2C), 138.0 (2C), 137.6 (2C), 128.2 (2C), 84.0 (2C), 75.6 (2C), 71.8 (2C), 65.7 (2C), 62.3 (d, *J* = 6.5 Hz, 4C), 61.6 (2C), 45.8 (2C), 43.2 (2C), 16.4 (4C), 14.1 (2C).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₃₂H₅₅N₂O₁₄P₂: 753.3129; found: 753.3125.

Dimethyl 3,3'-(1,4-phenylene)bis(5-(((dimethoxyphosphoryl)methoxy)methyl)-2-methylisoxazolidine-5-carboxylate) 7l:

Following general procedure 3, from dimethyl allyloxymethylphosphonate **1b** (1.40 mmol, 0.35 g) and nitrone **6f** (0.70

mmol, 0.13 g), mixture of two inseparable diastereoisomers **71** was obtained in 63% (0.30 g) as a viscous oil.

$R_f = 0.3$ (EtOAc 100%). IR (neat): 2959 (C-H), 1731 (C=O), 1241 (C-o and C-N), 1022 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta_{\text{diast1}} = 7.22$ (d, $J = 6.0$ Hz, 4 H), 4.31 – 4.11 (m, 4 H), 3.92 (dd, $J = 7.9, 2.4$ Hz, 4 H), 3.86 – 3.70 (m, 16 H), 3.45 (s, 2 H), 2.96 – 2.16 (m, 4 H), 2.51 (s, 6 H), 1.25 (t, $J = 7.1$ Hz, 6 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta_{\text{diast1}} = 22.9$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta_{\text{diast1}} = 172.1$ (2C), 137.8 (2C), 128.2 (d, $J = 5.9$ Hz, 4C), 84.1 (2C), 75.2 (d, $J = 9.9$ Hz, 2C), 72.9 (2C), 65.4 (d, $J = 165.2$ Hz, 2C), 61.6 (2C), 52.9 (dd, $J = 6.4, 2.6$ Hz, 4C), 45.0 (2C), 43.0 (2C), 14.1 (2C).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta_{\text{diast2}} = 7.22$ (d, $J = 6.0$ Hz, 4 H), 4.31 – 4.11 (m, 4 H), 3.92 (dd, $J = 7.9, 2.4$ Hz, 4 H), 3.86 – 3.70 (m, 16 H), 3.45 (s, 2 H), 2.96 – 2.16 (m, 4 H), 2.53 (s, 6 H), 1.25 (t, $J = 7.1$ Hz, 6 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta_{\text{diast2}} = 23.2$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta_{\text{diast2}} = 171.0$ (2C), 137.9 (2C), 127.9 (4C), 84.0 (2C), 75.7 (d, $J = 9.9$ Hz, 2C), 71.9 (2C), 65.3 (d, $J = 164.5$ Hz, 2C), 61.6 (2C), 52.9 (d, $J = 6.4$ Hz, 4C), 45.6 (2C), 43.2 (2C), 14.1 (2C).

HRMS (ESI⁺): m/z [M + H]⁺ calcd for $\text{C}_{28}\text{H}_{47}\text{N}_2\text{O}_{14}\text{P}_2$: 697.2503; found: 697.2505.

General procedure 4: intermolecular Heck coupling:

A mixture of the dimethyl allyloxymethylphosphonate **1** (0.80 mmol, 1.0 equiv.), iodobenzene derivatives (0.80 mmol, 1.0 equiv.), K_2CO_3 (0.27 g, 2.0 mmol, 2.50 equiv.), and $n\text{-Bu}_4\text{NCl}$ (0.22 mg, 0.80 mmol, 1.0 equiv.) in mixture of MeCN/ H_2O (9:1, 24 mL) was stirred at r.t. for 15 min. Pd(OAc)₂ (36 mg, 0.16 mmol, 0.20 equiv.) was added and the mixture was stirred at 80 °C for 24 h. The solvent was removed under reduced pressure, and the resulting residue was dissolved in EtOAc (40 mL), washed with saturated aqueous NaHCO_3 and brine solutions. The organic phase was dried, filtered and concentrated. The resulting residue was purified by column chromatography on silica gel using EtOAc as eluent to afford two regioisomers **8b** and **9b**.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-phenylacrylate **8b** and Ethyl (*E*)-2-benzyl-3-(((dimethoxyphosphoryl)methoxy)acrylate **9b**:

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and iodobenzene (0.80 mmol, 0.16 g, 0.085 mL) gave regioisomer **8b** in 56% (0.15 g) as a colorless oil and regioisomer **9b** in 25% (0.80 g) as a colorless oil.

$R_f = 0.59$ (EtOAc 100%). IR (neat): 2960 (C-H), 1702 (C=O), 1643 (C=C), 1027 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.96$ (s, 1 H), 7.55 – 7.53 (m, 2 H), 7.52 – 7.38 (m, 3 H), 4.44 (s, 2 H), 4.30 (q, $J = 7.1$ Hz, 2 H), 3.94 (d, $J = 8.6$ Hz, 2 H), 3.80 (d, $J = 10.7$ Hz, 6 H), 1.36 (t, $J = 7.1$ Hz, 3 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 23.6$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 167.4, 145.2, 134.5, 129.9$ (2C), 129.6, 128.6 (2C), 128.0, 67.3 (d, $J = 13.1$ Hz), 63.8 (d, $J = 166.0$ Hz), 61.1, 53.0 (d, $J = 6.5$ Hz, 2C), 14.3.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for $\text{C}_{15}\text{H}_{22}\text{O}_6\text{P}$: 329.1154; found: 329.1156.

$R_f = 0.60$ (EtOAc 100%). IR (neat): 2957 (C-H), 1703 (C=O), 1633 (C=C), 1023 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.38$ (s, 1 H), 7.30 – 7.09 (m, 5 H), 4.31 (d, $J = 8.0$ Hz, 2 H), 4.14 (q, $J = 7.1$ Hz, 2 H), 3.78 (dd, $J = 10.8, 0.6$ Hz, 6 H), 3.61 (s, 2 H), 1.23 (td, $J = 7.1, 0.4$ Hz, 3 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 20.0$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 167.5, 157.4$ (d, $J = 7.5$ Hz), 140.2, 128.6 (2C), 128.1 (2C), 125.8, 112.6, 66.8 (d, $J = 166.5$ Hz), 60.2, 53.3 (d, $J = 6.6$ Hz, 2C), 29.7, 14.2.

HRMS (ESI⁺): m/z [M + NH₄]⁺ calcd for $\text{C}_{15}\text{H}_{25}\text{NO}_6\text{P}$: 346.1419; found: 346.1422.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-phenylacrylate **8c** and Ethyl (*E*)-2-benzyl-3-(((dimethoxyphosphoryl)(phenyl)methoxy)acrylate **9c**:

Following general procedure 4, from compound **1d** (0.80 mmol, 0.26 g) and iodobenzene (0.80 mmol, 0.16 g, 0.085 mL) gave regioisomer **8c** in 48% (0.16 g) as a colorless oil and regioisomer **9c** in 29% (0.09 g) as a colorless oil.

$R_f = 0.58$ (EtOAc 100%). IR (neat): 2921 (C-H), 1700 (C=O), 1644 (C=C), 1026 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.93$ (s, 1 H), 7.55 – 7.52 (m, 4 H), 7.50 – 7.30 (m, 6 H), 4.81 (d, $J = 16.4$ Hz, 1 H), 4.43 (d, $J = 10.2$ Hz, 1 H), 4.30 – 4.15 (m, 3 H), 3.72 (d, $J = 10.5$ Hz, 3 H), 3.64 (d, $J = 10.5$ Hz, 3 H), 1.32 (t, $J = 7.1$ Hz, 3 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 21.1$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 167.3, 145.2, 134.3, 134.6, 134.2, 129.9, 129.4$ (2C), 128.6 (2C), 128.5 (2C), 128.4, 128.3 (2C), 78.7 (d, $J = 166.5$ Hz), 65.2 (d, $J = 15.4$ Hz), 61.0, 54.0 (d, $J = 6.9$ Hz), 53.4 (d, $J = 6.8$ Hz), 14.2.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for $\text{C}_{21}\text{H}_{26}\text{O}_6\text{P}$: 405.1467; found: 405.1469.

$R_f = 0.6$ (EtOAc 100%). IR (neat): 2956 (C-H), 1706 (C=O), 1023 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.37$ (d, $J = 4.9$ Hz, 6 H), 7.34 – 7.29 (m, 2 H), 7.28 – 7.22 (m, 2 H), 7.20 – 7.13 (m, 1 H), 5.18 (d, $J = 14.0$ Hz, 1 H), 4.20 – 4.03 (m, 2 H), 3.73 (m, 2 H), 3.66 (d, $J = 2.4$ Hz, 3 H), 3.64 (d, $J = 2.4$ Hz, 3 H), 1.19 (t, $J = 7.1$ Hz, 3 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 18.4$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 167.5, 156.4$ (d, $J = 12.0$ Hz), 140.3, 133.1, 128.8, 128.6, 128.1 (2C), 127.6 (2C), 127.5 (2C), 125.8, 112.9, 81.3 (d, $J = 169.3$ Hz), 60.2, 54.1 (d, $J = 6.9$ Hz), 53.7 (d, $J = 6.9$ Hz), 30.0, 14.2.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for $\text{C}_{21}\text{H}_{25}\text{NaO}_6\text{P}$: 427.1286; found: 427.1281.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(*p*-tolyl)acrylate **8d** and Ethyl (*E*)-3-(((dimethoxyphosphoryl)methoxy)-2-(4-methylbenzyl)acrylate **9d**:

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 1-iodo-4-methylbenzene (0.80 mmol, 0.17 g) gave regioisomer **8d** in 43% (0.12 g) as a colorless oil and **9d** in 27% (0.07 g) as a colorless oil.

$R_f = 0.59$ (EtOAc 100%). IR (neat): 2957 (C-H), 1699 (C=O), 1642 (C=C), 1024 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.93$ (s, 1 H), 7.46 (d, $J = 8.1$ Hz, 2 H), 7.22 (d, $J = 8.0$ Hz, 2 H), 4.45 (s, 2 H), 4.29 (q, $J = 7.1$ Hz, 2 H), 3.94 (d, $J = 8.6$ Hz, 2 H), 3.81 (d, $J = 10.7$ Hz, 6 H), 2.38 (s, 3 H), 1.36 (t, $J = 7.1$ Hz, 3 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 23.7$.

$^{13}\text{C NMR}$ (101 MHz, CDCl_3): $\delta = 167.5, 145.4, 140.0, 131.7, 130.1$ (2C), 129.4 (2C), 127.0, 67.4 (d, $J = 13.3$ Hz), 63.7 (d, $J = 166.0$ Hz), 61.1, 53.0 (d, $J = 6.5$ Hz, 2C), 21.4, 14.3.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for $\text{C}_{16}\text{H}_{24}\text{O}_6\text{P}$: 343.1310; found: 343.1308.

$R_f = 0.61$ (EtOAc 100%). IR (neat): 2957 (C-H), 1701 (C=O), 1024 cm^{-1} (C-O).

$^1\text{H NMR}$ (400 MHz, CDCl_3): $\delta = 7.35$ (s, 1 H), 7.15 (d, $J = 8.0$ Hz, 2 H), 7.04 (d, $J = 7.8$ Hz, 2 H), 4.30 (d, $J = 8.0$ Hz, 2 H), 4.14 (q, $J = 7.1$ Hz, 2 H), 3.80 (d, $J = 10.8$ Hz, 6 H), 2.28 (s, 3 H), 3.56 (s, 2 H), 1.23 (t, $J = 7.1$ Hz, 3 H).

$^{31}\text{P NMR}$ (162 MHz, CDCl_3): $\delta = 20.0$.

¹³C NMR (101 MHz, CDCl₃): δ = 167.5, 157.3 (d, *J* = 7.6 Hz), 137.2, 135.2, 128.8 (2C), 128.4 (2C), 112.8, 66.8 (d, *J* = 166.4 Hz), 60.1, 53.3 (d, *J* = 6.6 Hz, 2C), 29.3, 20.9, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₆H₂₃NaO₆P: 365.1130; found: 365.1125.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(*p*-tolyl)acrylate **8e and Ethyl (*E*)-3-(((dimethoxyphosphoryl)(phenyl)methoxy)-2-(4-methylbenzyl)acrylate **9e**:**

Following general procedure 4, from compound **1d** (0.80 mmol, 0.26 g) and 1-iodo-4-methylbenzene (0.80 mmol, 0.17 g) gave regioisomer **8e** in 46% (0.15 g) as a colorless oil and regioisomer **9e** in 14% (0.05 g) as a colorless oil.

R_f = 0.58 (EtOAc 100%). IR (neat): 2958 (C-H), 1701 (C=O), 1643 (C=C), 1026 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.91 (s, 1 H), 7.56 – 7.44 (m, 4 H), 7.42 – 7.31 (m, 3 H), 7.19 – 7.17 (d, *J* = 6.2 Hz, 2 H), 4.82 (d, *J* = 16.4 Hz, 1 H), 4.45 (d, *J* = 10.2 Hz, 1 H), 4.29 – 4.20 (m, 3 H), 3.72 (d, *J* = 10.5 Hz, 3 H), 3.64 (d, *J* = 10.5 Hz, 3 H), 2.37 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.4.

¹³C NMR (75 MHz, CDCl₃): δ = 167.5, 145.4, 139.8, 134.3, 131.7, 130.0 (2C), 129.3 (2C), 128.6, 128.3 (2C), 128.2 (2C), 127.2, 78.5 (d, *J* = 168.8 Hz), 65.2 (d, *J* = 15.5 Hz), 60.9, 54.0 (d, *J* = 6.9 Hz), 53.4 (d, *J* = 6.8 Hz), 21.4, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₈O₆P: 419.1624; found: 419.1615.

R_f = 0.59 (EtOAc 100%). IR (neat): 2955 (C-H), 1704 (C=O), 1023 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.42 – 7.36 (m, 6 H), 7.22 – 7.19 (d, *J* = 5.2 Hz, 2 H), 7.07 – 7.05 (d, *J* = 5.2 Hz, 2 H), 5.18 (d, *J* = 14.0 Hz, 1 H), 4.09 (qd, *J* = 7.1, 3.0 Hz, 2 H), 3.73 – 3.61 (m, 8 H), 2.30 (s, 3 H), 1.19 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.4.

¹³C NMR (75 MHz, CDCl₃): δ = 167.5, 156.3 (d, *J* = 12.2 Hz), 137.2, 135.2, 133.1, 129.1 (2C), 128.5 (2C), 128.7 (2C), 128.5, 127.5 (2C), 113.1, 81.2 (d, *J* = 169.3 Hz), 60.1, 54.2 (d, *J* = 6.9 Hz), 53.7 (d, *J* = 6.9 Hz), 29.5, 21.0, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₂H₂₇NaO₆P: 441.1443; found: 441.1444.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(*m*-tolyl)acrylate **8f and Ethyl (*E*)-3-(((dimethoxyphosphoryl)methoxy)-2-(3-methylbenzyl)acrylate **9f**:**

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 3-iodotoluene (0.80 mmol, 0.17 g, 0.1 mL) gave regioisomer **8f** in 49% (0.13 g) as a colorless oil and **9f** in 23% (0.06 g) as a colorless oil.

R_f = 0.55 (EtOAc 100%). IR (neat): 2957 (C-H), 1698 (C=O), 1642 (C=C), 1025 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 1.36 (t, *J* = 7.1 Hz, 3 H), 2.39 (s, 3 H), 3.79 (s, 3 H), 3.82 (s, 3 H), 3.94 (d, *J* = 8.6 Hz, 2 H), 4.29 (q, *J* = 7.1 Hz, 2 H), 4.43 (s, 2, CH₂O), 7.39 – 7.15 (m, 4 H), 7.93 (s, 1 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.6.

¹³C NMR (101 MHz, CDCl₃): δ = 167.3, 145.4, 138.2, 134.4, 130.5, 135.3, 128.5, 127.8, 126.9, 67.4 (d, *J* = 13.4 Hz), 63.8 (d, *J* = 166.0 Hz), 61.0, 52.9 (d, *J* = 6.5 Hz, 2C), 21.3, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₄O₆P: 343.1310; found: 343.1315.

R_f = 0.56 (EtOAc 100%). IR (neat): 2957 (C-H), 1702 (C=O), 1461 (C=C), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.39 (s, 1 H), 7.08 (m, 4 H), 4.33 (d, *J* = 8.0 Hz, 2 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 3.59 (s, 2 H), 2.32 (s, 3 H), 1.26 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.0.

¹³C NMR (101 MHz, CDCl₃): δ = 167.5, 157.3 (d, *J* = 7.6 Hz), 140.1, 137.6, 129.3, 128.0, 126.6, 125.5, 112.6, 66.8 (d, *J* = 166.4 Hz), 60.1, 53.2 (d, *J* = 6.6 Hz, 2C), 29.6, 21.3, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₄O₆P: 343.1340; found: 343.1313.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(*o*-tolyl)acrylate **8g and Ethyl (*E*)-3-(((dimethoxyphosphoryl)methoxy)-2-(2-methylbenzyl)acrylate **9g**:**

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 2-iodotoluene (0.80 mmol, 0.17 g, 0.1 mL) gave regioisomer **8g** in 35% (0.09 g) as a colorless oil and **9g** in 20% (0.05 g) as a colorless oil.

R_f = 0.56 (EtOAc 100%). IR (neat): 2958 (C-H), 1699 (C=O), 1642 (C=C), 1024 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.96 (s, 1 H), 7.20 – 7.12 (m, 4 H), 4.28 – 4.18 (m, 4 H), 3.81 (d, *J* = 8.5 Hz, 2 H), 3.74 (s, 3 H), 3.70 (s, 3 H), 2.24 (s, 3 H), 1.29 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.6.

¹³C NMR (101 MHz, CDCl₃): δ = 167.1, 143.8, 137.1, 133.7, 130.1, 130.0, 129.3, 128.9, 125.9, 67.6 (d, *J* = 12.9 Hz), 64.0 (d, *J* = 165.6 Hz), 61.0, 52.9 (d, *J* = 6.5 Hz, 2C), 19.9, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₃NaO₆P: 365.1130; found: 365.1119.

R_f = 0.57 (EtOAc 100%). IR (neat): 2957 (C-H), 1704 (C=O), 1461 (C=C), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.46 (s, 1 H), 7.20 – 7.05 (m, 4 H), 4.31 (d, *J* = 7.9 Hz, 2 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 3.78 (s, 3 H), 3.76 (s, 3 H), 3.60 (s, 2 H), 2.37 (s, 3 H), 1.24 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.9.

¹³C NMR (101 MHz, CDCl₃): δ = 167.6, 157.6, 137.7, 136.1, 129.8, 128.0, 125.8, 125.6, 111.7, 66.8, 60.2, 53.2 (d, *J* = 6.6 Hz, 2C), 26.8, 19.6, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₄O₆P: 343.1310; found: 343.1312.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(3-methoxyphenyl)acrylate **8h and Ethyl (*E*)-3-(((dimethoxyphosphoryl)methoxy)-2-(3-methoxybenzyl)acrylate **9h**:**

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 3-methoxyiodobenzene (0.80 mmol, 0.19 g) gave regioisomer **8h** in 42% (0.12 g) as a colorless oil and **9h** in 28% (0.08 g) as a colorless oil.

R_f = 0.57 (EtOAc 100%). IR (neat): 2957 (C-H), 1698 (C=O), 1643 (C=C), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.94 (s, 1 H), 7.34 (t, *J* = 8.2 Hz, 1 H), 7.20 – 7.10 (m, 1 H), 6.98 – 6.94 (m, 2 H), 4.45 (m, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 3.96 (d, *J* = 8.7 Hz, 2 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 3.80 (s, 3 H), 1.38 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.5.

¹³C NMR (101 MHz, CDCl₃): δ = 167.3 (d, *J* = 13.7 Hz), 163.1 (d, *J* = 166.1 Hz), 145.2, 135.8, 129.5, 128.2, 122.3, 115.5, 114.9, 67.3 (d, *J* = 6.5 Hz, 2C), 55.3, 61.1, 63.8 (d, *J* = 166.1 Hz), 52.9 (d, *J* = 6.5 Hz, 2C), 14.3.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₄O₇P: 359.1260; found: 359.1246.

R_f = 0.58 (EtOAc 100%). IR (neat): 2956 (C-H), 1704 (C=O), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.30 (s, 1 H), 7.07 (t, *J* = 7.9 Hz, 1 H), 6.80 – 6.71 (m, 2 H), 6.63 (ddd, *J* = 8.2, 2.6, 0.7 Hz, 1 H), 4.24 (d, *J* = 8.0 Hz, 2 H), 4.08 (q, *J* = 7.1 Hz, 2 H), 3.74 (s, 3 H), 3.70 (d, *J* = 2.1 Hz, 6 H), 3.51 (s, 2 H), 1.17 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.9.

¹³C NMR (101 MHz, CDCl₃): δ = 167.4, 159.5, 157.4 (d, *J* = 7.6 Hz), 141.8, 129.0, 121.0, 114.4, 112.4, 111.1, 66.8 (d, *J* = 166.4 Hz), 60.2, 55.0, 53.2 (d, *J* = 6.5 Hz, 2C), 29.7, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₄O₇P: 359.1260; found: 359.1247.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(3-methoxyphenyl) acrylate **8i and Ethyl (*E*)-3-(((dimethoxyphosphoryl)(phenyl)methoxy)-2-(3-methoxybenzyl)acrylate **9i**:**

Following general procedure 4, from compound **1d** (0.80 mmol, 0.26 g) and 3-methoxyiodobenzene (0.80 mmol, 0.19 g) gave regioisomer **8i** in 38% (0.13 g) as a colorless oil and **9i** in 23% (0.08 g) as a colorless oil.

*R*_f = 0.53 (EtOAc 100%). IR (neat): 2881 (C-H), 1698 (C=O), 1486 (C=C) 1023 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.91 (s, 1 H), 7.51 – 7.47 (m, 2 H), 7.39 – 7.29 (m, 4 H), 7.27 – 7.09 (m, 2 H), 6.95 – 6.91 (dd, *J* = 5.2, 2.6 Hz, 1 H), 4.84 (d, *J* = 16.2 Hz, 1 H), 4.44 (d, *J* = 10.2 Hz, 1 H), 4.27 – 4.25 (m, 3 H), 3.83 (s, 3 H), 3.72 (d, *J* = 10.5 Hz, 3 H), 3.64 (d, *J* = 10.5 Hz, 3 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 21.1.

¹³C NMR (75 MHz, CDCl₃): δ = 167.3, 159.6, 145.0, 135.8, 134.2, 129.5, 128.5, 128.4, 128.3 (2C), 128.2 (2C), 122.2, 115.2, 115.0, 78.5 (d, *J* = 165.9 Hz), 65.0 (d, *J* = 15.5 Hz), 61.0, 55.3, 54.0 (d, *J* = 6.9 Hz), 53.4 (d, *J* = 6.8 Hz), 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₈O₇P: 435.1573; found: 135.1569

*R*_f = 0.55 (EtOAc 100%). IR (neat): 2955 (C-H), 1706 (C=O), 1453 (C=C), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.37 – 7.27 (m, 6 H), 7.13 – 7.02 (m, 1 H), 6.78 – 6.90 (m, 2 H), 6.64 (ddd, *J* = 18.2, 7.5, 5.7 Hz, 1 H), 5.11 (d, *J* = 13.9 Hz, 1 H), 4.10 – 3.95 (m, 2 H), 3.69 (s, 3 H), 3.61 – 3.57 (m, 8 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.4.

¹³C NMR (101 MHz, CDCl₃): δ = 167.4, 159.6, 156.5, 141.8, 133.1, 129.1, 129.0 (2C), 128.7, 127.5 (2C), 121.1, 114.2, 112.7, 111.4, 81.3 (d, *J* = 169.3 Hz), 60.2, 55.0, 54.1 (d, *J* = 7.0 Hz), 53.7 (d, *J* = 6.9 Hz), 30.0, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₈O₇P: 435.1573; found: 435.1559.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(2-methoxyphenyl)acrylate **8j and Ethyl (*E*)-3-(((dimethoxyphosphoryl)-methoxy)-2-(2-methoxybenzyl)acrylate **9j**:**

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 2-methoxyiodobenzene (0.80 mmol, 0.18 g) gave regioisomer **8j** in 32% (0.09 g) as a colorless oil and regioisomer **9j** in 27% (0.08 g) as a colorless oil.

*R*_f = 0.58 (EtOAc 100%). IR (neat): 2958 (C-H), 1699 (C=O), 1643 (C=C), 1022 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 8.15 (s, 1 H), 7.61 – 6.84 (m, 4 H), 4.39 (s, 2 H), 4.30 (q, *J* = 7.1 Hz, 2 H), 3.92 (d, *J* = 8.5 Hz, 2 H), 3.86 (s, 3 H), 3.81 (d, *J* = 10.7 Hz, 6 H), 1.36 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.7.

¹³C NMR (101 MHz, CDCl₃): δ = 167.3, 157.8, 141.0, 131.1, 130.7, 127.8, 123.7, 120.5, 110.4, 67.9 (d, *J* = 13.1 Hz), 63.8 (d, *J* = 165.6 Hz), 61.0, 55.5, 52.9 (d, *J* = 6.5 Hz, 2C), 14.3.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₄O₇P: 359.1260; found: 359.1258.

*R*_f = 0.60 (EtOAc 100%). IR (neat): 2956 (C-H), 1704 (C=O), 1460 (C=C), 1021, 756 and 558 cm⁻¹.

¹H NMR (300 MHz, CDCl₃): δ = 7.44 (s, 1 H), 7.16 – 7.05 (m, 2 H), 6.89 – 6.80 (m, 2 H), 4.28 (d, *J* = 8.0 Hz, 2 H), 4.14 (q, *J* = 7.1 Hz, 2 H), 3.82 (s, 3 H), 3.74 (d, *J* = 10.7 Hz, 6 H), 3.61 (s, 2 H), 1.22 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.8.

¹³C NMR (101 MHz, CDCl₃): δ = 167.7, 157.8 (d, *J* = 7.6 Hz), 157.4, 128.6, 127.9, 126.8, 120.2, 111.4, 110.1, 66.9 (d, *J* = 166.0 Hz), 60.1, 55.3, 53.3 (d, *J* = 6.6 Hz, 2C), 23.7, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₆H₂₃NaO₇P: 381.1079; found: 381.1074.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(2-methoxyphenyl)- acrylate **8k and Ethyl (*E*)-3-(((dimethoxyphosphoryl)(phenyl)methoxy)-2-(2-methoxybenzyl)-acrylate **9k**:**

Following general procedure 4, from compound **1d** (0.80 mmol, 0.26 g) and 2-methoxyiodobenzene (0.80 mmol, 0.18 g) gave regioisomer **8k** in 43% (0.15 g) as a colorless oil and **9k** in 23% (0.08 g) as a colorless oil.

*R*_f = 0.57 (EtOAc 100%). IR (neat): 2956 (C-H), 1699 (C=O), 1641 (C=C), 1023 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 8.13 (s, 1 H), 7.62 (dd, *J* = 7.6 Hz, 1.3, 1 H), 7.49 (dt, *J* = 7.7, 1.8 Hz, 2 H), 7.42 – 7.26 (m, 4 H), 6.96 – 6.83 (m, 2 H), 4.80 (d, *J* = 16.4, 1 H), 4.40 (d, *J* = 10.1 Hz, 1 H), 4.31 – 4.06 (m, 3 H), 3.82 (s, 3 H), 3.73 (d, *J* = 10.5 Hz, 3 H), 3.64 (d, *J* = 10.5 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 21.2.

¹³C NMR (101 MHz, CDCl₃): δ = 167.3, 157.8, 141.0, 134.3, 131.0 (2C), 129.0, 128.7 (2C), 128.3, 128.2, 128.0, 123.7, 120.4, 110.3, 78.6 (d, *J* = 168.4 Hz), 65.7 (d, *J* = 15.4 Hz), 60.9, 55.4, 54.0 (d, *J* = 6.9 Hz), 53.4 (d, *J* = 6.8 Hz), 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₇O₇P: 435.1573; found: 435.1562.

*R*_f = 0.59 (EtOAc 100%). IR (neat): 2956 (C-H), 1702 (C=O), 1459 (C=C), 1022 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.41 (s, 1 H), 7.34 – 7.32 (m, 5 H), 7.19 – 7.09 (m, 2 H), 6.83 (d, *J* = 7.7 Hz, 2 H), 5.16 (d, *J* = 14.2 Hz, 1 H), 4.17 – 4.02 (m, 2 H), 3.83 (s, 3 H), 3.73 (s, 2 H), 3.63 (d, *J* = 10.6 Hz, 3 H), 3.58 (d, *J* = 10.6 Hz, 3 H), 1.18 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.2.

¹³C NMR (101 MHz, CDCl₃): δ = 167.8, 157.4, 156.8 (d, *J* = 12.4 Hz), 133.3 (d, *J* = 2.2 Hz), 129.0, 128.9, 128.7, 128.6 (2C), 127.5 (2C), 126.9, 120.2, 111.2, 110.1, 81.4 (d, *J* = 169.0 Hz), 60.1, 55.3, 54.2 (d, *J* = 6.9 Hz), 53.7 (d, *J* = 6.9 Hz), 23.9, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₈O₇P: 435.1573; found: 435.1563.

Ethyl (*E*)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(3-(trifluoromethyl) phenyl) acrylate **8l and Ethyl (*E*)-3-(((dimethoxyphosphoryl)methoxy)-2-(3-(trifluoromethyl)benzyl)-acrylate **9l**:**

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 1-iodo-3-(trifluoromethyl)benzene (0.80 mmol, 0.22 g) gave a mixture of two regioisomers **8l** (65%) and **9l** (35%) in 58% (0.18 g) as a colorless oil.

*R*_f = 0.62 (EtOAc 100%). IR (neat): 2959 (C-H), 1704 (C=O), 1644 (C=C), 1025 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.95 (s, 1 H), 7.84 – 7.24 (m, 4 H), 4.40 (s, 2 H), 4.32 (q, *J* = 7.1 Hz, 2 H), 3.95 (d, *J* = 8.7 Hz, 2 H), 3.81 (d, *J* = 10.7 Hz, 6 H), 1.37 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.2.

¹⁹F NMR (377 MHz, CDCl₃): δ = -62.8.

¹³C NMR (101 MHz, CDCl₃): δ = 167.3, 143.4, 120.8 – 136.6 (8C), 67.1 (d, *J* = 13.2 Hz), 64.1 (d, *J* = 166.3 Hz), 61.4, 53.0 (d, *J* = 6.5 Hz, 2C), 14.2.

R_f = 0.62 (EtOAc 100%).

¹H NMR (400 MHz, CDCl₃): δ = 7.41 (s, 1 H), 7.81 – 7.27 (m, 4 H), 4.33 (d, *J* = 8.0 Hz, 2 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 3.80 (d, *J* = 10.8 Hz, 6 H), 3.65 (s, 2 H), 1.24 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.9.

¹⁹F NMR (377 MHz, CDCl₃): δ = -62.5.

¹³C NMR (101 MHz, CDCl₃): δ = 166.9, 157.9 (d, *J* = 7.2 Hz), 143.4 – 122.7 (7C), 111.8, 66.7 (d, *J* = 166.5 Hz), 60.4, 53.3 (d, *J* = 6.6 Hz, 2C), 29.7, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₁F₃O₆P: 397.1028; found: 397.1018.

Ethyl (E)-2-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(3-(trifluoromethyl)phenyl)acrylate 8m and Ethyl (E)-3-(((dimethoxyphosphoryl)(phenyl)methoxy)-2-(3-(trifluoromethyl)benzyl) acrylate 9m:

Following general procedure 4, from compound **1d** (0.80 mmol, 0.26 g) and 1-iodo-3-(trifluoromethyl)benzene (0.80 mmol, 0.22 g) gave regioisomer **8m** in 48% (0.18 g) as a colorless oil and **9m** in 16% (6 mg) as a colorless oil.

R_f = 0.61 (EtOAc 100%). IR (neat): 2958 (C-H), 1700 (C=O), 1642 (C=C), 1450 (C=C), 1025 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.92 (s, 1 H), 7.79 – 7.72 (m, 2 H), 7.66 – 7.56 (m, 1 H), 7.49 (dd, *J* = 8.0, 2.2 Hz, 3 H), 7.39 – 7.29 (m, 2 H), 4.83 (d, *J* = 16.0 Hz, 1 H), 4.43 – 4.16 (m, 2 H), 4.27 (qd, *J* = 7.1, 1.5 Hz, 2 H), 3.72 (dd, *J* = 10.5, 1.6 Hz, 3 H), 3.64 (dd, *J* = 10.6, 1.7 Hz, 3 H), 1.33 (td, *J* = 7.1 Hz, 1.8, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.9.

¹⁹F NMR (377 MHz, CDCl₃): δ = -62.7.

¹³C NMR (101 MHz, CDCl₃): δ = 166.9, 143.0, 129.5 – 140.3 (14C), 78.9 (d, *J* = 168.9 Hz), 64.9 (d, *J* = 15.4 Hz), 61.3, 53.9 (d, *J* = 7.0 Hz), 53.5 (d, *J* = 6.8 Hz), 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₅F₃O₆P: 473.1341; found: 473.1331.

R_f = 0.62 (EtOAc 100%). IR (neat): 2958 (C-H), 1707 (C=O), 1442 (C=C), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.58 (s, 1 H), 7.52 (d, *J* = 7.6 Hz, 1 H), 7.46 – 7.33 (m, 8 H), 5.20 (d, *J* = 13.9 Hz, 1 H), 4.16 – 4.07 (m, 2 H), 3.76 (d, *J* = 9.1 Hz, 2 H), 3.67 (s, 3 H), 3.65 (s, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.3.

¹⁹F NMR (377 MHz, CDCl₃): δ = -62.7.

¹³C NMR (101 MHz, CDCl₃): δ = 167.2, 156.9 (d, *J* = 11.9 Hz), 141.4 – 121.8 (13C), 112.1, 81.4 (d, *J* = 169.5), 60.3, 54.1 (d, *J* = 7.0 Hz), 53.7 (d, *J* = 6.9 Hz), 29.9, 14.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₂H₂₅F₃O₆P: 473.1341; found: 473.1335.

Ethyl (E)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(4-nitrophenyl)acrylate 8n and Ethyl (E)-3-(((dimethoxyphosphoryl)methoxy)-2-(4-nitrobenzyl)acrylate 9n:

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 4-nitroiodobenzene (0.80 mmol, 0.20 g) gave a mixture of two regioisomers **8n** (73%) and **9n** (27%) in 24% (0.07 g) as a colorless oil.

R_f = 0.51 (EtOAc 100%).

¹H NMR (300 MHz, CDCl₃): δ = 8.28 (d, *J* = 8.7 Hz, 2 H), 7.96 (s, 1 H), 7.73 (d, *J* = 8.4 Hz, 2 H), 4.41 (s, 2 H), 4.38 – 4.28 (m, 2 H), 3.96 (d, *J* = 8.4 Hz, 2 H), 3.85 (s, 3 H), 3.81 (s, 3 H), 1.39 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.4.

¹³C NMR (101 MHz, CDCl₃): δ = 166.5, 148.1, 142.2, 140.7, 130.6 (2C), 129.4, 123.7 (2C), 67.0 (d, *J* = 12.2 Hz), 64.2 (d, *J* = 166.5 Hz), 61.6, 52.9 (d, *J* = 6.5 Hz, 2C), 14.2.

R_f = 0.51 (EtOAc 100%).

¹H NMR (300 MHz, CDCl₃): δ = 8.11 (d, *J* = 8.8 Hz, 2 H), 7.43 (d, *J* = 7.4 Hz, 2 H), 7.28 (s, 1 H), 4.38 – 4.28 (m, 2 H), 4.16 (q, *J* = 7.1 Hz, 2 H), 3.84 (s, 3 H), 3.81 (s, 3 H), 3.70 (s, 2 H), 1.29 – 1.22 (m, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.9.

¹³C NMR (101 MHz, CDCl₃): δ = 166.9, 158.1 (d, *J* = 6.7 Hz), 148.1, 131.3, 129.4 (2C), 123.4 (2C), 111.1, 67.7 (d, *J* = 162.8 Hz), 60.4, 53.2 (d, *J* = 6.6 Hz, 2C), 29.8, 14.3.

IR (neat): 2922 (C-H), 1703 (C=O), 1519 (C-NO₂), 1023 cm⁻¹ (C-O).

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₅H₂₀NNaO₈P: 396.0824; found: 396.0816.

Ethyl (E)-2-(((dimethoxyphosphoryl)(phenyl)methoxy)methyl)-3-(4-nitrophenyl)acrylate 8o and Ethyl (E)-3-(((dimethoxyphosphoryl)(phenyl)methoxy)-2-(4-nitrobenzyl)acrylate 9o:

Following general procedure 4, from compound **1d** (0.80 mmol, 0.26 g) and 4-nitroiodobenzene (0.80 mmol, 0.20 g) gave a mixture of two regioisomers **8o** (57 %) and **9o** (47 %) in 36% (0.13 g) as a colorless oil.

R_f = 0.53 (EtOAc 100%).

¹H NMR (300 MHz, CDCl₃): δ = 8.21 (d, *J* = 8.7, 2 H), 7.93 (s, 1 H), 7.54 – 7.34 (m, 7 H), 4.79 (d, *J* = 16.2 Hz, 1 H), 4.28 (m, 4 H), 3.75 (d, *J* = 10.6 Hz, 3 H), 3.64 (d, *J* = 10.5 Hz, 3 H), 1.33 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 20.9.

¹³C NMR (75 MHz, CDCl₃): δ = 166.4, 148.1, 142.3, 140.8, 133.8, 132.7, 131.4, 130.5 (2C), 129.5, 128.8 (d, *J* = 2.2 Hz, 2C), 128.2 (d, *J* = 6.0 Hz, 2C), 123.6, 78.8 (d, *J* = 169.4 Hz), 64.8, 61.5, 54.0 (2C), 14.1.

R_f = 0.54 (EtOAc 100%).

¹H NMR (300 MHz, CDCl₃): δ = 8.12 (d, *J* = 8.8 Hz, 2 H), 7.71 (d, *J* = 8.5 Hz, 2 H), 7.54 – 7.35 (m, 6 H), 5.20 (d, *J* = 13.7 Hz, 1 H), 4.12 (qd, *J* = 7.1, 2.6 Hz, 2 H), 3.80 (m, 2 H), 3.70 (d, *J* = 10.7 Hz, 3 H), 3.65 (d, *J* = 10.6 Hz, 3 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 18.4.

¹³C NMR (75 MHz, CDCl₃): δ = 167.0, 157.1 (d, *J* = 11.5 Hz), 146.4, 133.8, 131.4, 129.5 (2C), 128.5 (d, *J* = 2.0 Hz, 2C), 127.6 (d, *J* = 5.8 Hz, 2C), 123.4 (2C), 111.4, 81.3 (d, *J* = 169.9 Hz), 60.4, 53.6 (d, *J* = 6.8 Hz, 2C), 30.0, 14.2.

IR (neat): 2956 (C-H), 1703 (C=O), 1518 (C-NO₂), 1023 cm⁻¹ (C-O).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₂₁H₂₅NO₈P: 450.1318; found: 450.1306.

Ethyl (E)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(3-nitrophenyl)acrylate 8p and Ethyl (E)-3-(((dimethoxyphosphoryl)methoxy)-2-(3-nitrobenzyl)acrylate 9p:

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 3-nitroiodobenzene (0.8 mmol, 0.20 g) gave regioisomer **8p** in 26% (0.08 g) as a colorless oil and **9p** in 10% (0.03 g) as a colorless oil.

R_f = 0.54 (EtOAc 100%). IR (neat): 2958 (C-H), 1698 (C=O), 1643 (C=C), 1526 (C-NO₂), 1023 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 8.33 (d, *J* = 1.7 Hz, 1 H), 8.23 – 8.13 (m, 1 H), 7.89 (s, 1 H), 7.83 (dd, *J* = 7.7, 0.6 Hz, 1 H), 7.55 (t, *J* = 8.0 Hz, 1 H), 4.35 (s, 2 H), 4.26 (q, *J* = 7.1 Hz, 2 H), 3.91 (d, *J* = 8.6 Hz, 2 H), 3.77 (s, 3 H), 3.74 (s, 3 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 23.1.

¹³C NMR (75 MHz, CDCl₃): δ = 166.5, 148.4, 142.2, 136.0, 135.6, 130.7, 129.7, 124.5, 124.0, 66.9 (d, *J* = 13.0 Hz), 64.1 (d, *J* = 166.2 Hz), 61.5, 53.0 (d, *J* = 6.5 Hz, 2C), 14.2.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₁₅H₂₁NO₈P: 374.1005; found: 374.1009.

R_f = 0.55 (EtOAc 100%). IR (neat): 2958 (C-H), 1707 (C=O), 1529 (C-NO₂), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 8.12 (t, J = 1.8 Hz, 1 H), 8.05 (ddd, J = 8.2, 2.3, 1.0 Hz, 1 H), 7.64 (dd, J = 7.6, 0.5 Hz, 1 H), 7.43 - 7.41 (m, 2 H), 4.36 (d, J = 7.9 Hz, 2 H), 4.18 (q, J = 7.1 Hz, 2 H), 3.85 (s, 3 H), 3.83 (s, 3 H), 3.71 (s, 2 H), 1.27 (t, J = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.8.

¹³C NMR (101 MHz, CDCl₃): δ = 167.0, 158.1 (d, J = 7.1 Hz), 147.7, 142.3, 135.0, 128.9, 123.4, 121.1, 111.2, 66.8 (d, J = 166.7 Hz), 60.4, 53.2 (d, J = 6.6 Hz, 2C), 29.5, 14.2.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₁₅H₂₁NO₈P: 374.1005; found: 374.1009.

Ethyl (E)-2-(((dimethoxyphosphoryl)methoxy)methyl)-3-(2-nitrophenyl)acrylate 8q **Ethyl (E)-3-(((dimethoxyphosphoryl)methoxy)-2-(2-nitrobenzyl)acrylate 9q**:

Following general procedure 4, from compound **1b** (0.80 mmol, 0.20 g) and 2-nitroiodobenzene (0.80 mmol, 0.20 g) gave regioisomer **8q** in 37% (0.11 g) as a colorless oil and **9q** in 23% (0.07 g) as a colorless oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2922 (C-H), 1699 (C=O), 1644 (C=C), 1524 (C-NO₂), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 8.12 - 8.07 (m, 2 H), 7.65 - 7.58 (m, 1 H), 7.57 - 7.51 (m, 1 H), 7.50 - 7.48 (m, 1 H), 4.25 (q, J = 7.1 Hz, 2 H), 4.19 (s, 2 H), 3.77 (t, J = 6.1 Hz, 2 H), 3.71 (s, 3 H), 3.69 (s, 3 H), 1.30 (t, J = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 23.4.

¹³C NMR (101 MHz, CDCl₃): δ = 166.3, 147.5, 141.3, 133.7, 131.8, 130.6, 129.8, 129.7, 124.8, 67.5 (d, J = 12.4 Hz), 64.1 (d, J = 166.0 Hz), 61.4, 52.9 (d, J = 6.5 Hz, 2C), 14.2.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₁₅H₂₁NO₈P: 374.1005; found: 374.0996.

R_f = 0.54 (EtOAc 100%). IR (neat): 2922 (C-H), 1710 (C=O), 1523 (C-NO₂), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.42 - 7.37 (m, 2 H), 7.33 - 7.14 (m, 3 H), 4.21 (d, J = 7.7 Hz, 2 H), 4.05 (q, J = 7.1 Hz, 2 H), 3.88 (s, 2 H), 3.72 (s, 3 H), 3.70 (s, 3 H), 1.12 (t, J = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 19.7.

¹³C NMR (101 MHz, CDCl₃): δ = 167.1, 158.5 (d, J = 6.1 Hz), 149.8, 134.6, 132.5, 130.6, 126.7, 124.1, 110.4, 66.8 (d, J = 165.8 Hz), 60.4, 53.2 (d, J = 6.6 Hz, 2C), 25.9, 14.1.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₅H₂₀NNaO₈P: 396.0824; found: 396.0819.

General procedure 5: Intramolecular Heck coupling, indenenes synthesis:

A stirred solution of dialkyl allyloxymethylphosphonate derivatives **1** (1.0 equiv.), Pd(OAc)₂ (0.10 equiv.), PPh₃ (0.20 equiv.) and Et₃N (2.0 equiv.) in MeCN (5 mL) was heated at reflux under argon atmosphere for 3 h. The reaction mixture was allowed to cool to room temperature, quenched with H₂O (10 mL) and extracted with Et₂O (30 mL × 3). The combined organic layers were washed with dilute HCl solution, brine, dried over MgSO₄, and concentrated under vacuum. The residue was purified by column chromatography on silica gel using EtOAc as eluent to afford the desired compounds.

Ethyl 3-(((dimethoxyphosphoryl)methoxy)-1H-indene-2-carboxylate 10a:

Followig general procedure 5, from compound **1e** (0.40 mmol, 0.17 g), Pd(OAc)₂ (0.04 mmol, 0.01 g), PPh₃ (0.08 mmol, 0.02 g) and Et₃N (0.80

mmol, 0.08 g, 0.11 mL), the indene **10a** was obtained in 73% (0.096 g) as a yellow oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2958 (C-H), 1699 (C=O), 1023 cm⁻¹ (C-O)

¹H NMR (300 MHz, CDCl₃): δ = 7.65 - 7.60 (m, 1 H), 7.45 - 7.37 (m, 3 H), 4.95 (d, J = 7.9 Hz, 2 H), 4.29 (q, J = 7.1 Hz, 2 H), 3.88 (d, J = 10.8 Hz, 6 H), 3.69 (s, 2 H), 1.37 (t, J = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 21.7.

¹³C NMR (75 MHz, CDCl₃): δ = 164.1, 164.0, 141.6, 139.3, 128.7, 126.8, 124.2, 120.8, 111.4, 66.3 (d, J = 165.9 Hz), 60.2, 53.2 (d, J = 6.4 Hz, 2C), 36.3, 14.3.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₅H₁₉NaO₆P: 349.0817; found: 349.0815.

Ethyl 3-(((diethoxyphosphoryl)methoxy)-1H-indene-2-carboxylate 10b:

Followig general procedure 5, from compound **1f** (0.46 mmol, 0.20 g), Pd(OAc)₂ (0.046 mmol, 0.01 g), PPh₃ (0.092 mmol, 0.024 g) and Et₃N (0.92 mmol, 0.092 g, 1.3 mL), the indene **10b** was obtained in 75% (0.12 g) as a yellow oil.

R_f = 0.49 (EtOAc 100%). IR (neat): 2982 (C-H), 1699 (C=O), 1017 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.66 - 7.62 (m, 1 H), 7.41 (m, 3 H), 4.92 (d, J = 7.7 Hz, 2 H), 4.32 - 4.19 (m, 6 H), 3.69 (s, 2 H), 1.40 - 1.32 (m, 9 H).

³¹P NMR (121 MHz, CDCl₃): δ = 19.2.

¹³C NMR (75 MHz, CDCl₃): δ = 164.3, 164.1, 141.6, 139.5, 128.7, 126.7, 124.1, 120.9, 111.1, 67.0 (d, J = 165.6 Hz), 62.6 (d, J = 6.3 Hz, 2C), 60.2, 36.3, 16.4 (d, J = 5.8 Hz, 2C), 14.4.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₇H₂₃NaO₆P: 377.1130; found: 377.1127.

Ethyl 3-(((dimethoxyphosphoryl)methoxy)-5-fluoro-1H-indene-2-carboxylate 10c:

Followig general procedure 5, from compound **1g** (0.23 mmol, 0.10 g), Pd(OAc)₂ (0.023 mmol, 0.05 g), PPh₃ (0.046 mmol, 0.024 g) and Et₃N (0.46 mmol, 0.046 g, 0.06 mL), the indene **10c** was obtained in 59% (0.047 g) as a colorless oil.

R_f = 0.54 (EtOAc 100%). IR (neat): 2958 (C-H), 1691 (C=O), 1575 (C=C) 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.31 - 7.26 (m, 1 H), 7.23 - 7.18 (m, 1 H), 7.01 (ddd, J = 9.3, 8.2, 2.5 Hz, 1 H), 4.85 (d, J = 7.8 Hz, 2 H), 4.21 (q, J = 7.1 Hz, 2 H), 3.79 (d, J = 10.8 Hz, 6 H), 3.57 (s, 2 H), 1.28 (t, J = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 21.5.

¹⁹F NMR (377 MHz, CDCl₃): δ = -115.4.

¹³C NMR (101 MHz, CDCl₃): δ = 163.8, 163.7, 162.3 (d, J = 243.3 Hz), 141.2 (d, J = 10.5 Hz), 136.7, 125.2 (d, J = 8.7 Hz), 115.9 (d, J = 23.4 Hz), 113.2, 107.6, 66.4 (d, J = 166.0 Hz), 60.4, 53.1 (d, J = 6.4 Hz, 2C), 35.8, 14.3.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₅H₁₈FN₂O₆P: 367.0723; found: 367.0722.

Ethyl 3-(((diethoxyphosphoryl)methoxy)-5-methoxy-1H-indene-2-carboxylate 10d:

Followig general procedure 5, from compound **1h** (0.22 mmol, 0.10 g), Pd(OAc)₂ (0.022 mmol, 0.05 g), PPh₃ (0.044 mmol, 0.012 g) and Et₃N (0.44 mmol, 0.048 g, 0.06 mL), the indene **10d** was obtained in 63% (0.051 g) as a yellow oil.

R_f = 0.52 (EtOAc 100%). IR (neat): 2982 (C-H), 1694 (C=O), 1360, (C=C), 1018 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.37 (dd, J = 8.2, 4.7 Hz, 1 H), 7.30 (dd, J = 8.4, 2.4 Hz, 1 H), 7.09 (ddd, J = 9.3, 8.3, 2.5 Hz, 1 H), 4.90 (d, J = 7.6 Hz, 2 H),

4.33 – 4.27 (m, 2 H), 4.27 – 4.18 (m, 4 H), 3.65 (s, 2 H), 1.39 – 1.33 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.1.

¹⁹F NMR (377 MHz, CDCl₃): δ = -115.5.

¹³C NMR (101 MHz, CDCl₃): δ = 163.8, 163.2, 162.3, 141.4, 136.7, 125.2, 115.9, 113.0, 107.7, 67.1 (d, *J* = 164.4 Hz), 62.6 (d, *J* = 6.4 Hz, 2C), 60.4, 35.8, 16.4 (d, *J* = 5.4 Hz, 2C), 14.3.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₇H₂₃O₆FP: 373.1216; found: 373.1214.

Dimethyl (((2-acetyl-5-methoxy-1*H*-inden-3-yl)oxy)methyl)phosphonate 10e:

Followig general procedure 5, from compound **1i** (0.53 mmol, 0.20 g), Pd(OAc)₂ (0.053 mmol, 0.012 g), PPh₃ (0.10 mmol, 0.027 g) and Et₃N (1.0 mmol, 0.10 g, 0.15 mL), the indene **10e** was obtained in 63% (0.093 g) as a yellow oil.

R_f = 0.48 (EtOAc 100%).

IR (neat): 2955 (C-H), 1622 (C=O), 1339 (C=C), 1029 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.62 – 7.57 (m, 1 H), 7.45 – 7.32 (m, 3 H), 4.71 (d, *J* = 8.9 Hz, 2 H), 3.81 (d, *J* = 10.8 Hz, 6 H), 3.58 (s, 2 H), 2.46 (s, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 21.0.

¹³C NMR (75 MHz, CDCl₃): δ = 194.7, 162.8 (d, *J* = 11.5 Hz), 142.5, 138.1, 132.1 (d, *J* = 9.9 Hz), 127.0, 125.0, 123.2, 121.6, 65.5 (d, *J* = 168.4 Hz), 53.2 (d, *J* = 6.4 Hz, 2C), 35.4, 29.8.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₄H₁₇NaO₅P: 319.0711; found: 319.0725.

Diethyl (((2-acetyl-1*H*-inden-3-yl)oxy)methyl)phosphonate 10f:

Followig general procedure 5, from compound **1j** (0.50 mmol, 0.20 g), Pd(OAc)₂ (0.05 mmol, 0.011 g), PPh₃ (0.10 mmol, 0.026 g) and Et₃N (1.0 mmol, 0.10 g, 0.14 mL), the indene **10f** was obtained in 69% (0.10 g) as a yellow oil.

R_f = 0.49 (EtOAc 100%). IR (neat): 2984 (C-H), 1707 (C=O), 1018 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.71 – 7.63 (m, 1 H), 7.50 – 7.35 (m, 3 H), 4.75 (d, *J* = 8.8 Hz, 2 H), 4.35 – 4.11 (m, 4 H), 3.64 (s, 2 H), 2.55 (s, 3 H), 1.36 (t, *J* = 7.1 Hz, 6 H).

³¹P NMR (121 MHz, CDCl₃): δ = 18.4.

¹³C NMR (75 MHz, CDCl₃): δ = 194.7, 163.0, 142.6, 138.0, 132.0 (d, *J* = 9.9 Hz), 128.9, 126.9, 125.0, 121.7, 66.1 (d, *J* = 168.1 Hz), 62.8 (d, *J* = 6.4 Hz, 2C), 35.2, 29.8, 16.4 (d, *J* = 5.8 Hz, 2C).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₆H₂₂O₅P: 325.1205; found: 325.1207.

General procedure 6, radical reaction:

n-Bu₃SnH (0.30 g, 0.27 mL, 1.0 mmol, 2.0 equiv.) was added dropwise by syringe to a solution of AIBN (16 mg, 0.10 mmol, 0.20 equiv.) and (2-halophenyl)(dimethoxyphosphoryl) methoxy)methyl)acrylate **1** (0.50 mmol, 1.0 equiv.) in PhMe (13 mL). The mixture was heated at reflux under argon atmosphere for 3 h. After cooling the mixture, the solvent was then evaporated under reduced pressure and the residue was purified by column chromatography on silica gel using EtOAc (100%) as eluent.

Ethyl 3-((2-chlorophenyl)(dimethoxyphosphoryl)methoxy)-2-((tributylstannyl)methyl)propanoate 16a:

Following general procedure 6, from olefin **1m** (0.18 g, 0.5 mmol), compound **16a** was obtained in 55% (0.18 g) as a colorless oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2923 (C-H), 1730 (C=O), 1185 (C-O), 1028 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.58 (ddt, *J* = 28.9, 7.7, 2.1 Hz, 1 H), 7.38 – 7.16 (m, 3 H), 5.20 (dd, *J* = 16.0, 1.3 Hz, 1 H), 4.09 – 3.96 (m, 2 H), 3.71 (dd, *J* = 10.6, 8.9 Hz, 3 H), 3.63 – 3.51 (m, 4 H), 3.45 – 3.26 (m, 1 H), 2.84 – 2.67 (m, 1 H), 1.39 – 1.28 (m, 6 H), 1.24 – 1.13 (m, 9 H), 0.85 – 0.66 (m, 17 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.2.

¹³C NMR (101 MHz, CDCl₃): δ = 175.3, 175.0, 132.5 (d, *J* = 13.3 Hz), 129.9, 129.6, 129.3, 127.1, 74.9 (dd, *J* = 171.1, 15.3 Hz), 74.7 (dd, *J* = 13.8, 9.6 Hz), 60.5, 53.7 (dd, *J* = 31.3, 21.1 Hz, 2C), 43.7 (d, *J* = 17.8 Hz), 29.0 (d, *J* = 3.4 Hz, 3C), 27.3 (d, *J* = 1.8 Hz, 3C), 14.1, 13.6 (3C), 9.2 (3C), 7.8 (C-5).

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₂₇H₄₈ClNaO₆PSn116: 673.1792; found: 673.1796.

Ethyl (Z)-3-((dimethoxyphosphoryl)(phenyl)methoxy)-2-methylacrylate 13a and Ethyl 1-(dimethoxyphosphoryl)-1,3,4,5-tetrahydrobenzo[*c*]oxepine-4-carboxylate 14a and Ethyl 3-((dimethoxyphosphoryl)(phenyl)methoxy)-2-((tributylstannyl)methyl)propanoate 15a:

Following general procedure 8, from olefin **1k** (0.20 g, 0.50 mmol) gave compound **13a** in 59% (95.0 mg) as a colorless oil, compound **14a** in 28% (46.0 mg) as a colorless oil and a mixture of two inseparable diastereoisomers of compound **15a** in 14% (43.0 mg) as a colorless oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2957 (C-H), 1700 (C=O), 1648 (C=C), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.40 – 7.29 (m, 5 H), 7.29 (d, *J* = 1.3 Hz, 1 H), 5.07 (d, *J* = 14.0 Hz, 1 H), 4.02 – 4.10 (m, 2 H), 3.66 (d, *J* = 7.2 Hz, 3 H), 3.64 (d, *J* = 7.2 Hz, 3 H), 1.88 (d, *J* = 1.4 Hz, 3 H), 1.16 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 18.6.

¹³C NMR (101 MHz, CDCl₃): δ = 168.1, 155.6 (d, *J* = 12.1 Hz), 133.2 (d, *J* = 2.1 Hz), 129.0 (d, *J* = 2.9 Hz), 128.7 (d, *J* = 2.2 Hz, 2C), 127.5 (d, *J* = 5.6 Hz, 2C), 108.9, 81.0 (d, *J* = 169.3 Hz), 60.0, 54.1 (d, *J* = 6.9 Hz), 53.8 (d, *J* = 6.9 Hz), 14.2, 9.4.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₅H₂₁NaO₆P: 351.0973; found: 351.0959.

R_f = 0.49 (EtOAc 100%). IR (neat): 2956 (C-H), 1724 (C=O), 1178 (C-O), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.25 – 7.07 (m, 4 H), 5.13 (d, *J* = 15.6 Hz, 1 H), 4.23 (ddd, *J* = 12.5, 7.1, 2.4 Hz, 1 H), 4.08 – 3.93 (m, 2 H), 3.80 – 3.71 (m, 2 H), 3.68 (d, *J* = 10.5 Hz, 3 H), 3.64 (d, *J* = 10.6 Hz, 3 H), 3.17 – 3.04 (m, 1 H), 2.95 (dd, *J* = 14.0, 3.6 Hz, 1 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 21.3.

¹³C NMR (101 MHz, CDCl₃): δ = 172.1, 137.0 (d, *J* = 7.1 Hz), 132.3 (d, *J* = 3.2 Hz), 131.1 (d, *J* = 2.0 Hz), 128.6, 128.5, 126.9 (d, *J* = 2.4 Hz), 80.7 (d, *J* = 169.0 Hz), 67.9 (d, *J* = 13.4 Hz), 60.5, 53.7 (d, *J* = 7.0 Hz), 53.4 (d, *J* = 6.9 Hz), 44.1, 32.5, 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₅H₂₂O₆P: 329.1154; found: 329.1156.

R_f = 0.59 (EtOAc 100%). IR (neat): 2923 (C-H), 1730 (C=O), 1185 (C-O), 1028 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.49 – 7.30 (m, 5 H), 4.67 (d, *J* = 15.5 Hz, 1 H), 4.20 – 4.07 (m, 2 H), 3.78 – 3.42 (m, 8 H), 2.98 – 2.76 (m, 1 H), 1.54 – 1.21 (m, 15 H), 1.00 – 0.75 (m, 17 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.6.

¹³C NMR (101 MHz, CDCl₃): δ_{diast1} = 175.1, 134.3, 128.4 (d, *J* = 2.3 Hz, 2C), 128.0 (d, *J* = 5.9), 127.8 (d, *J* = 5.8 Hz, 2C), 78.2 (d, *J* = 168.1 Hz), 74.5 (d, *J* = 14.7 Hz), 60.5, 53.8 (d, *J* = 7.0 Hz), 53.6 (d, *J* = 6.7 Hz), 43.7, 29.0 (d, *J* = 3.6 Hz, 3C), 27.3 (3C), 14.1, 13.6 (3C), 9.2 (3C), 7.9.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 175.1, 134.3, 128.4 (d, *J* = 2.3 Hz, 2C), 128.0 (d, *J* = 5.9 Hz), 127.8 (d, *J* = 5.8 Hz, 2C), 79.4 (d, *J* = 168.4 Hz), 74.7 (d, *J* = 13.1 Hz), 60.5, 54.2 (d, *J* = 6.7 Hz), 53.4 (d, *J* = 6.8 Hz), 43.8, 29.0 (d, *J* = 3.6 Hz, 3C), 27.3 (3C), 14.1, 13.5 (3C), 9.2 (3C), 8.1.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₂₇H₄₉NaO₆PSn116: 639.2182; found: 639.2186.

Ethyl (Z)-3-((diethoxyphosphoryl)(phenyl)methoxy)-2-methylacrylate 13b, Ethyl 1-(diethoxyphosphoryl)-1,3,4,5-tetrahydrobenzo[c]oxepine-4-carboxylate 14b and Ethyl 3-((diethoxyphosphoryl)(phenyl)methoxy)-2-((tributylstannyl)-methyl)propanoate 15b.

Following general procedure 6, from olefin **11** (0.21 g, 0.50 mmol) gave, compound **13b** in 60% (0.11 g) as a colorless oil, compound **14b** in 27% (48.0 mg) as a colorless oil and a mixture of two inseparable diastereoisomers of compound **15b** in 9% (29.0 mg) as a colorless oil.

R_f = 0.50 (EtOAc 100%). IR (neat): 2956 (C-H), 1723 (C=O), 1241 (C-O), 1019 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.48 – 7.28 (m, 6 H), 5.13 (d, J = 13.9 Hz, 1 H), 4.28 – 4.02 (m, 6 H), 1.87 (d, J = 1.3 Hz, 3 H), 1.30 – 1.21 (m, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ = 16.2.

¹³C NMR (101 MHz, CDCl₃): δ = 168.2, 155.9 (d, J = 11.6 Hz), 133.5, 128.9 (d, J = 2.8 Hz), 128.5 (2C), 127.5 (d, J = 5.5 Hz, 2C), 108.7, 81.3 (d, J = 168.7 Hz), 63.6 (d, J = 7.0 Hz), 63.3 (d, J = 6.9 Hz), 60.0, 16.3 (d, J = 5.4 Hz), 16.3 (d, J = 5.4 Hz), 14.3, 9.4.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₁₇H₂₆O₆P: 357.1458; found: 357.1467.

R_f = 0.49 (EtOAc 100%). IR (neat): 2957 (C-H), 1726 (C=O), 1245 (C-O), 1021 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.24 – 7.20 (m, 1 H), 7.16 – 7.09 (m, 3 H), 5.08 (d, J = 15.7 Hz, 1 H), 4.22 (ddd, J = 12.5, 7.1, 2.4 Hz, 1 H), 4.15 – 3.91 (m, 6 H), 3.96 – 3.80 (m, 2 H), 3.16 – 3.10 (m, 1 H), 2.93 (dd, J = 14.0, 3.6 Hz, 1 H), 1.21 (t, J = 7.1 Hz, 6 H), 1.13 (t, J = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.0.

¹³C NMR (101 MHz, CDCl₃): δ = 172.2, 137.0 (d, J = 7.1 Hz), 132.6 (d, J = 3.1 Hz), 131.0 (d, J = 1.9 Hz), 128.6 (d, J = 5.2 Hz), 128.3 (d, J = 2.9 Hz), 126.7 (d, J = 2.4 Hz), 81.0 (d, J = 168.7 Hz), 67.9 (d, J = 13.4 Hz), 63.1 (d, J = 6.9 Hz), 62.8 (d, J = 6.9 Hz), 60.5, 44.1, 32.5, 16.3 (d, J = 4.6 Hz, 2C), 14.1.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₁₇H₂₆O₆P: 357.1467; found: 357.1465.

R_f = 0.59 (EtOAc 100%). IR (neat): 2958 (C-H), 1726 (C=O), 1254 (C-O), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.51 – 7.31 (m, 5 H), 4.64 (d, J = 15.4 Hz, 1 H), 4.18 – 3.99 (m, 6 H), 3.71 (t, J = 8.9 Hz, 0.5 H), 3.58 (t, J = 8.9 Hz, 0.5 H), 3.44 (td, J = 8.8, 5.0 Hz, 1 H), 2.93 – 2.80 (m, 1 H), 1.54 – 1.34 (m, 8 H), 1.33 – 1.19 (m, 15 H), 1.02 – 0.76 (m, 15 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.5.

¹³C NMR (101 MHz, CDCl₃): δ_{diast1} = 175.2, 134.6 (d, J = 1.6 Hz), 128.2 (d, J = 2.3 Hz, 2C), 128.1 (d, J = 5.9 Hz), 127.9 (d, J = 5.7 Hz, 2C), 79.3 (d, J = 167.9 Hz), 74.7, 63.0 (d, J = 8.0 Hz), 62.8 (d, J = 6.8 Hz), 60.4, 43.7, 29.0 (3C), 27.3 (3C), 16.3 (d, J = 2.7 Hz, 2C), 14.1, 13.6 (3C), 9.2 (3C), 8.0.

³¹P NMR (162 MHz, CDCl₃): δ = 18.4.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 175.5, 134.6, 128.3 (d, J = 2.4 Hz, 2C), 128.2 (d, J = 2.3 Hz), 127.9 (d, J = 5.7 Hz, 2C), 79.5 (d, J = 168.1 Hz), 74.4, 63.1 (d, J = 8.0 Hz), 62.8 (d, J = 6.8 Hz), 60.4, 43.8, 29.0 (3C), 27.3 (3C), 16.4 (d, J = 1.9 Hz, 2C), 14.1, 13.6 (3C), 9.2 (3C), 8.2.

HRMS (ESI⁺): m/z [M + H]⁺ calcd for C₂₉H₅₄O₆ PSn112: 641.2706; found: 641.2699.

Ethyl (Z)-3-((dimethoxyphosphoryl)(3-fluorophenyl)methoxy)-2-methylacrylate 13c and Ethyl 1-(dimethoxyphosphoryl)-8-fluoro-1,3,4,5-tetrahydrobenzo[c]oxepine-4-carboxylate 14c:

Following general procedure 6, from olefin **10** (0.21 g, 0.50 mmol) gave compound **13c** in 22% (38.0 mg) as a colorless oil and compound **14c** in 41% (71.0 mg) as a colorless oil.

R_f = 0.53 (EtOAc 100%). IR (neat): 2958 (C-H), 1701 (C=O), 1648 (C=C), 1025 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.30 (td, J = 7.9, 6.1 Hz, 1 H), 7.18 – 6.84 (m, 4 H), 5.06 (d, J = 14.5 Hz, 1 H), 4.27 – 3.98 (m, 2 H), 3.81 – 3.50 (m, 6 H), 1.80 (d, J = 1.4 Hz, 3 H), 1.17 (t, J = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.9.

¹⁹F NMR (377 MHz, CDCl₃): δ = -111.7.

¹³C NMR (101 MHz, CDCl₃): δ = 171.9, 162.5 (d, J = 247.5 Hz), 155.3 (d, J = 11.8 Hz), 135.8, 130.3 (dd, J = 8.2, 2.2 Hz), 130.3 (dd, J = 8.2, 2.2 Hz), 116.0 (dd, J = 21.2, 2.9 Hz), 114.5 (dd, J = 23.0, 5.2 Hz), 109.4, 80.4 (d, J = 169.2 Hz), 60.1, 54.3 (d, J = 6.9 Hz), 53.8 (d, J = 6.9 Hz), 14.3, 9.4 (CH₃).

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₅H₂₀FN₂O₆P: 369.0879; found: 369.0874.

R_f = 0.52 (EtOAc 100%). IR (neat): 2957 (C-H), 1725 (C=O), 1249 (C-O), 1023 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.07 (dd, J = 8.3, 5.6 Hz, 1 H), 6.94 (dt, J = 9.5, 2.3 Hz, 1 H), 6.84 (tt, J = 8.3, 2.3 Hz, 1 H), 5.06 (d, J = 15.9 Hz, 1 H), 4.24 (ddd, J = 12.5, 7.2, 2.4 Hz, 1 H), 4.06 – 3.95 (m, 2 H), 3.76 – 3.72 (m, 1 H), 3.71 (d, J = 10.6 Hz, 3 H), 3.67 (d, J = 10.6 Hz, 3 H), 3.67 – 3.66 (m, J = 10.5, 4.3, 2.6 Hz, 1 H), 3.14 – 3.05 (m, 1 H), 2.93 (dd, J = 14.1, 3.6 Hz, 1 H), 1.13 (t, J = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 20.4.

¹⁹F NMR (377 MHz, CDCl₃): δ = -115.6.

¹³C NMR (101 MHz, CDCl₃): δ = 172.0, 160.7 (d, J = 245.8 Hz), 134.4 (d, J = 10.9 Hz), 132.7 (d, J = 7.1, 3.5 Hz), 132.6 (dd, J = 7.9, 2.0 Hz), 115.1 (dd, J = 20.8, 2.8 Hz), 115.5 (dd, J = 22.9, 5.2 Hz), 80.4 (d, J = 169.3 Hz), 68.1 (d, J = 13.6 Hz), 60.6, 53.9 (d, J = 6.9 Hz), 53.4 (d, J = 6.9 Hz), 44.1, 31.7, 14.1.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for C₁₅H₂₀O₆FNaP: 369.0879; found: 369.0875.

Ethyl (Z)-3-((dimethoxyphosphoryl)(3-methoxyphenyl)methoxy)-2-methylacrylate 13d and Ethyl 1-(dimethoxyphosphoryl)-8-methoxy-1,3,4,5-tetrahydrobenzo[c]oxepine-4-carboxylate 14d:

Following general procedure 6, from olefin **1p** (0.22 g, 0.50 mmol) gave compound **13d** in 28% (50.0 mg) as a colorless oil and compound **14d** in 45% (80.0 mg) as a colorless oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2957 (C-O), 1700 (C=O), 1647 (C=C), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 7.24 (t, J = 7.9 Hz, 1 H), 7.18 (d, J = 1.1 Hz, 1 H), 6.90 – 6.94 (m, 2 H), 6.86 – 6.79 (m, 1 H), 5.04 (d, J = 14.2 Hz, 1 H), 4.05 (q, J = 7.2 Hz, 2 H), 3.75 (s, 3 H), 3.67 (d, J = 8.9 Hz, 3 H), 3.64 (d, J = 8.9 Hz, 3 H), 1.96 (s, 3 H), 1.18 (t, J = 7.2 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.5.

¹³C NMR (101 MHz, CDCl₃): δ = 168.1, 159.8 (d, J = 2.2 Hz), 155.6 (d, J = 12.5 Hz), 134.7 (d, J = 2.0 Hz), 129.7 (d, J = 2.1 Hz), 119.8 (d, J = 5.7 Hz), 114.6 (d, J = 2.8 Hz), 113.1 (d, J = 5.4 Hz), 109.0, 81.0 (d, J = 169.4 Hz), 60.2, 55.3, 54.2 (d, J = 6.9 Hz), 53.8 (d, J = 6.8 Hz), 14.3, 9.4.

HRMS (ESI⁺): m/z [M + Na]⁺ calcd for ¹⁶H₂₃NaO₇P: 381.1079; found: 381.1079.

R_f = 0.48 (EtOAc 100%). IR (neat): 2956 (C-H), 1724 (C=O), 1254 (C-O), 1022 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.01 (d, J = 8.3 Hz, 1 H), 6.76 – 6.62 (m, 2 H), 5.08 (d, J = 15.5 Hz, 1 H), 4.21 (ddd, J = 12.5, 7.2, 2.4 Hz, 1 H), 4.12 – 3.91 (m, 2 H), 3.80 – 3.73 (m, 3 H), 3.71 (s, 3 H), 3.69 (d, J = 5.0 Hz, 3 H), 3.63 – 3.56 (m, 1 H), 3.08 (dtd, J = 10.4, 7.0, 3.4 Hz, 1 H), 2.88 (dd, J = 14.1, 3.4 Hz, 1 H), 1.14 (t, J = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 21.2.

¹³C NMR (75 MHz, CDCl₃): δ = 172.3, 158.3 (d, J = 2.6 Hz), 133.3 (d, J = 3.5 Hz), 132.1 (d, J = 2.2 Hz), 129.0 (d, J = 6.9 Hz), 114.3 (d, J = 5.2 Hz), 113.6

(d, *J* = 3.0 Hz), 80.7 (d, *J* = 168.8 Hz), 67.9 (d, *J* = 13.7 Hz), 60.5, 55.2, 53.8 (d, *J* = 7.0 Hz), 53.4 (d, *J* = 7.0 Hz), 44.3, 31.5, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₆H₂₃NaO₇P: 381.1079; found: 381.1073.

Ethyl (Z)-3-((3,4-dimethoxyphenyl)(dimethoxyphosphoryl)methoxy)-2-methylacrylate 13e and Ethyl 1-(dimethoxyphosphoryl)-7,8-dimethoxy-1,3,4,5-tetrahydrobenzo[*c*]oxepine-4-carboxylate 14e:

Following general procedure 6, from olefin **1q** (0.36 g, 0.77 mmol) gave compound **13e** in 25% (75.0 mg) as a colorless oil a mixture of tow inseparables diastereoisomers of compound **14e** in 55% (0.16 g) as a colorless oil.

R_f = 0.44 (EtOAc 100%). IR (neat): 2956 (C=O), 1699 (C=O), 1247 (C-O), 1023 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.19 (dt, *J* = 1.6, 0.8 Hz, 1 H), 6.93 – 6.89 (m, 2 H), 6.82 (d, *J* = 1.0 Hz, 1 H), 4.99 (d, *J* = 13.7 Hz, 1 H), 4.14 – 4.00 (m, 2 H), 3.84 (s, 3 H), 3.82 (s, 3 H), 3.70 (d, *J* = 10.6 Hz, 3 H), 3.62 (d, *J* = 10.6 Hz, 3 H), 1.78 (d, *J* = 1.3 Hz, 3 H), 1.16 (td, *J* = 7.1, 1.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 18.9.

¹³C NMR (75 MHz, CDCl₃): δ = 168.2, 155.5 (d, *J* = 13.2 Hz), 149.7 (d, *J* = 3.0 Hz), 149.1 (d, *J* = 3.0 Hz), 125.3, 120.5 (d, *J* = 7.0 Hz), 110.9 (d, *J* = 1.6 Hz), 110.5 (d, *J* = 5.1 Hz), 108.9, 80.7 (d, *J* = 172.1 Hz), 60.1, 55.9, 55.8, 54.2 (d, *J* = 6.9 Hz), 53.7 (d, *J* = 6.8 Hz), 14.3, 9.5.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₇H₂₅NaO₈P: 411.1185; found: 411.1177.

R_f = 0.42 (EtOAc 100%). IR (neat): 2955 (C-H), 1723 (C=O), 1249 (C-O), 1018 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 6.72 (d, *J* = 2.0 Hz, 1 H), 6.61 (s, 1 H), 5.06 (d, *J* = 14.6 Hz, 1 H), 4.21 (ddd, *J* = 12.5, 7.3, 2.4 Hz, 1 H), 4.13 – 3.94 (m, 3 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.68 (d, *J* = 2.2 Hz, 3 H), 3.65 (d, *J* = 2.0 Hz, 3 H), 3.17 – 3.02 (m, 1 H), 2.86 (dd, *J* = 14.1, 3.3 Hz, 1 H), 2.77 – 2.64 (m, 1 H), 1.14 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 21.5.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.2, 148.4 (d, *J* = 3.3 Hz), 147.3 (d, *J* = 2.8 Hz), 129.5 (d, *J* = 7.5 Hz), 123.5 (d, *J* = 3.7 Hz), 114.1 (d, *J* = 2.5 Hz), 111.7 (d, *J* = 4.9 Hz), 80.3 (d, *J* = 170.0 Hz), 67.5 (d, *J* = 13.4 Hz), 60.5, 55.9, 55.8, 53.8 (d, *J* = 7.0 Hz), 53.4 (d, *J* = 6.9 Hz), 44.3, 31.8, 14.2.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 6.72 (d, *J* = 2.0 Hz, 1 H), 6.61 (s, 1 H), 5.06 (d, *J* = 14.6 Hz, 1 H), 4.21 (ddd, *J* = 12.5, 7.3, 2.4 Hz, 1 H), 4.13 – 3.94 (m, 3 H), 3.80 (s, 3 H), 3.79 (s, 3 H), 3.68 (d, *J* = 2.2 Hz, 3 H), 3.65 (d, *J* = 2.0 Hz, 3 H), 3.17 – 3.02 (m, 1 H), 2.86 (dd, *J* = 14.1, 3.3 Hz, 1 H), 2.77 – 2.64 (m, 1 H), 1.21 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 20.9.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 173.3, 148.5 (d, *J* = 3.6 Hz), 147.3 (d, *J* = 2.9 Hz), 130.2 (d, *J* = 6.3 Hz), 123.7 (d, *J* = 4.3 Hz), 113.6 (d, *J* = 2.5 Hz), 112.0 (d, *J* = 5.0 Hz), 80.8 (d, *J* = 168.8 Hz), 67.3 (d, *J* = 13.5 Hz), 60.8, 56.0, 55.9, 53.9 (d, *J* = 7.1 Hz), 53.6 (d, *J* = 7.1 Hz), 45.4, 31.7, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₇H₂₅NaO₈P: 411.1185; found: 411.1194.

Ethyl (Z)-3-(benzo[*d*][1,3]dioxol-5-yl(dimethoxyphosphoryl)methoxy)-2-methylacrylate 13f and Ethyl 5-(dimethoxyphosphoryl)-5,7,8,9-tetrahydro-[1,3]dioxolo[4',5':4,5]benzo[1,2-*c*]oxepine-8-carboxylate 14f:

Following general procedure 6, from olefin **1r** (0.15 g, 0.33 mmol) gave compound **13f** in 23% (28.0 mg) as a colorless oil and a mixture of tow inseparables diastereoisomers of compound **14f** in 64% (75.0 mg) as a colorless oil.

R_f = 0.45 (EtOAc 100%). IR (neat): 2956 (C-H), 1699 (C=O), 1647 (C=C), 1023, cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.24 (d, *J* = 1.5 Hz, 1 H), 7.01 – 6.92 (m, 1 H), 6.94 – 6.84 (m, 1 H), 6.84 (d, *J* = 0.6 Hz, 1 H), 6.00 (s, 2 H), 5.04 (d, *J* = 13.6 Hz, 1 H), 4.27 – 4.08 (m, 2 H), 3.79 (d, *J* = 10.6 Hz, 3 H), 3.73 (d, *J* = 10.6 Hz, 3 H), 1.85 (d, *J* = 1.4 Hz, 3 H), 1.25 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 18.6.

¹³C NMR (75 MHz, CDCl₃): δ = 168.1, 155.4 (d, *J* = 13.0 Hz), 148.4 (d, *J* = 2.9 Hz), 148.1 (d, *J* = 1.8 Hz), 126.8 (d, *J* = 2.5 Hz), 121.7 (d, *J* = 7.1 Hz), 108.4 (d, *J* = 2.4 Hz), 108.0 (d, *J* = 4.9 Hz), 107.4 (d, *J* = 2.1 Hz), 101.4, 80.8 (d, *J* = 172.3 Hz), 60.1, 54.2 (d, *J* = 6.9 Hz), 53.8 (d, *J* = 6.9 Hz), 14.3, 9.4.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₆H₂₁NaO₈P: 395.0872; found: 395.0869.

R_f = 0.40 (EtOAc 100%).

IR (neat): 2955 (C-H), 1723 (C=O), 1249 (C-O), 1018 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 6.70 – 6.62 (m, 1 H), 6.75 (dd, *J* = 6.0, 1.7 Hz, 1 H), 5.99 – 5.88 (m, 2 H), 5.08 (d, *J* = 14.9 Hz, 1 H), 4.26 (ddd, *J* = 12.4, 7.2, 2.4 Hz, 1 H), 4.24 – 4.00 (m, 2 H), 3.87 – 3.81 (m, 1 H), 3.78 (d, *J* = 8.9 Hz, 3 H), 3.74 (d, *J* = 9.0 Hz, 3 H), 3.74 – 3.65 (m, 1 H), 3.13 (dtd, *J* = 10.5, 7.1, 3.5 Hz, 1 H), 2.90 (dd, *J* = 14.2, 3.5 Hz, 1 H), 1.32 – 1.18 (m, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 21.2,

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.2, 147.5 (d, *J* = 3.3 Hz), 146.4 (d, *J* = 2.1 Hz), 130.9 (d, *J* = 8.0 Hz), 124.9 (d, *J* = 3.7 Hz), 111.3 (d, *J* = 2.4 Hz), 108.9 (d, *J* = 5.0 Hz), 101.2, 80.3 (d, *J* = 170.9 Hz), 67.6 (d, *J* = 13.4 Hz), 60.6, 53.8 (d, *J* = 7.0 Hz), 53.4 (d, *J* = 7.0 Hz), 44.1, 32.1, 14.2.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 6.70 – 6.62 (m, 1 H), 6.75 (dd, *J* = 6.0, 1.7 Hz, 1 H), 5.99 – 5.88 (m, 2 H), 5.09 (d, *J* = 14.9 Hz, 1 H), 4.43 (dt, *J* = 12.7, 2.0 Hz, 1 H), 4.24 – 4.00 (m, 2 H), 3.87 – 3.81 (m, 1 H), 3.78 (d, *J* = 8.9 Hz, 3 H), 3.74 (d, *J* = 9.0 Hz, 3 H), 3.74 – 3.65 (m, 1 H), 3.13 (dtd, *J* = 10.5, 7.1, 3.5 Hz, 1 H), 2.81 – 2.66 (m, 1 H), 1.32 – 1.18 (m, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 20.7.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 173.2, 147.6 (d, *J* = 4.6 Hz), 146.4 (d, *J* = 2.3 Hz), 131.6 (d, *J* = 6.7 Hz), 125.0 (d, *J* = 4.6 Hz), 110.8 (d, *J* = 2.7 Hz), 109.1 (d, *J* = 5.1 Hz), 101.3, 80.9 (d, *J* = 170.1 Hz), 67.2 (d, *J* = 13.6 Hz), 60.8, 54.0 (d, *J* = 7.1 Hz), 53.6 (d, *J* = 7.1 Hz), 45.2, 31.8, 14.2.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₆H₂₁NaO₈P: 395.0862; found: 395.0862.

Dimethyl (Z)-(((2-cyanoprop-1-en-1-yl)oxy)(phenyl)methyl)phosphonate 13g and Dimethyl (4-cyano-1,3,4,5-tetrahydrobenzo[*c*]oxepin-1-yl)phosphonate 14g:

Following general procedure 6, from olefin **1s** (0.20 g, 0.56 mmol) gave compound **13g** in 48% (75.0 mg) as a colorless oil and a mixture of tow inseparables diastereoisomers of compound **14g** in 31% (49.0 mg) as a colorless oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2956 (C-H), 2360 (C≡N), 1446 (C=C), 1241 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.40 – 7.31 (m, 5 H), 6.73 – 6.71 (m, 1 H), 5.04 (d, *J* = 13.6 Hz, 1 H), 3.68 (d, *J* = 10.7 Hz, 3 H), 3.64 – 3.54 (m, 3 H), 1.81 (d, *J* = 1.4 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.0.

¹³C NMR (75 MHz, CDCl₃): δ = 157.0 (d, *J* = 12.2 Hz), 132.3 (d, *J* = 2.4 Hz), 129.6 (d, *J* = 2.8 Hz), 128.9 (d, *J* = 2.0 Hz, 2C), 127.7 (d, *J* = 5.7 Hz, 2C), 119.6, 89.9, 81.1 (d, *J* = 170.4 Hz), 54.1 (d, *J* = 7.0 Hz), 53.9 (d, *J* = 6.9 Hz), 11.5.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₃H₁₆NNaO₄P: 304.0715; found: 304.0715.

R_f = 0.49 (EtOAc 100%). IR (neat): 3957 (C-H), 2361 (C≡N), 1442 (C=C), 1021 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.28 – 7.18 (m, 4 H), 5.15 (d, *J* = 15.4 Hz, 1 H), 4.28 – 4.17 (m, 1 H), 4.01 – 3.92 (m, 1 H), 3.73 – 3.65 (m, 4 H), 3.57 (d, *J* = 10.6 Hz, 3 H), 3.31 – 3.21 (m, 1 H), 2.80 – 2.70 (m, 1 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast1} = 20.5.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 134.5 (d, *J* = 5.6 Hz), 131.6 (d, *J* = 4.2 Hz), 131.3 (d, *J* = 2.7 Hz), 129.3 (d, *J* = 3.3 Hz), 129.1 (d, *J* = 5.8 Hz), 127.9 (d, *J* = 2.5 Hz), 119.0, 81.0 (d, *J* = 169.0 Hz), 66.3 (d, *J* = 13.0 Hz), 53.8 (d, *J* = 7.0 Hz), 53.6 (d, *J* = 6.9 Hz), 32.7, 30.3.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.28 – 7.18 (m, 4 H), 5.14 (d, *J* = 15.9 Hz, 1 H), 4.28 – 4.17 (m, 1 H), 4.01 – 3.92 (m, 1 H), 3.73 – 3.65 (m, 4 H), 3.57 (d, *J* = 10.6 Hz, 3 H), 3.31 – 3.21 (m, 1 H), 2.80 – 2.70 (m, 1 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 20.0.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 135.3 (d, *J* = 6.1 Hz), 132.3 (d, *J* = 3.7 Hz), 130.6 (d, *J* = 2.5 Hz), 129.3 (d, *J* = 3.3 Hz), 129.1 (d, *J* = 5.8 Hz), 127.9 (d, *J* = 2.5 Hz), 120.8, 81.2 (d, *J* = 168.6 Hz), 67.4 (d, *J* = 13.3 Hz), 54.1 (d, *J* = 6.8 Hz), 53.8 (d, *J* = 7.0 Hz), 33.4, 31.3.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₃H₁₇NO₄P: 282.0895; found: 282.0899.

Diethyl (Z)-((2-cyanoprop-1-en-1-yl)oxy)(phenyl)methylphosphonate 13h and Diethyl (4-cyano-1,3,4,5-tetrahydrobenzo[*c*]oxepin-1-yl)phosphonate 14h:

Following general procedure 6, from olefin **1t** (0.20 g, 0.51 mmol) gave compound **13h** in 47% (74.0 mg) as a colorless oil and compound **14h** in 28% (44.0 mg) as a colorless oil.

R_f = 0.51 (EtOAc 100%). IR (neat): 2955 (C-H), 2240 (C≡N), 1446 (C=C), 1019 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.61 – 7.18 (m, 6 H), 5.08 (d, *J* = 13.4 Hz, 1 H), 4.44 – 3.96 (m, 4 H), 1.88 (d, *J* = 1.4 Hz, 3 H), 1.29 (td, *J* = 7.1, 0.5 Hz, 3 H), 1.23 (td, *J* = 7.1, 0.5 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 15.7.

¹³C NMR (75 MHz, CDCl₃): δ = 157.3 (d, *J* = 11.7 Hz), 132.6 (d, *J* = 2.3 Hz), 129.4 (d, *J* = 2.8 Hz), 128.8 (d, *J* = 2.0 Hz, 2C), 127.7 (d, *J* = 5.6 Hz, 2C), 119.7, 89.6, 81.4 (d, *J* = 169.8 Hz), 63.7 (d, *J* = 6.9 Hz), 63.5 (d, *J* = 6.9 Hz), 16.4 (d, *J* = 5.7 Hz), 16.3 (d, *J* = 5.7 Hz), 11.5.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₅H₂₀NNaO₄P: 332.1028; found: 332.1029.

R_f = 0.49 (EtOAc 100%). IR (neat): 2957 (C-H), 2362 (C≡N), 1442 (C=C), 1021 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ = 7.28 – 7.18 (m, 4 H), 5.11 (d, *J* = 15.5 Hz, 1 H), 4.31 – 4.21 (m, 1 H), 4.15 – 3.93 (m, 4 H), 3.91 – 3.78 (m, 1 H), 3.64 (ddd, *J* = 12.2, 10.2, 1.1 Hz, 1 H), 3.36 – 3.21 (m, 1 H), 2.72 (dd, *J* = 14.1, 2.7 Hz, 1 H), 1.22 (t, *J* = 7.1 Hz, 3 H), 1.19 – 1.14 (m, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ = 18.3.

¹³C NMR (75 MHz, CDCl₃): δ = 134.5 (d, *J* = 5.6 Hz), 131.9 (d, *J* = 4.1 Hz), 131.2 (d, *J* = 2.7 Hz), 129.3 (d, *J* = 5.7 Hz), 129.2 (d, *J* = 3.3 Hz), 127.7 (d, *J* = 2.5 Hz), 119.1, 81.4 (d, *J* = 168.6 Hz), 66.4 (d, *J* = 13.0 Hz), 63.2 (d, *J* = 6.9 Hz), 63.1 (d, *J* = 6.9 Hz), 32.7, 30.4, 16.4 (d, *J* = 5.6 Hz), 16.3 (d, *J* = 5.5 Hz).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₅H₂₁NO₄P: 310.1208; found: 310.1211.

Ethyl 5-(dimethoxyphosphoryl)-5,7,8,9-tetrahydrooxepino[4,3-*b*]pyridine-8-carboxylate 14i:

Following general procedure 6, from olefin **1u** (0.20 g, 0.50 mmol) gave a mixture of two inseparables diastereoisomers of compound **14i** in 52% (90.0 mg) as a viscous oil.

R_f = 0.45 (EtOAc 100%). IR (neat): 2959 (C-H), 1724 (C=O), 1181 (C-O), 1022 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ_{diast1} = 8.46 – 8.36 (m, 1 H), 7.60 (ddd, *J* = 22.6, 7.9, 4.8 Hz), 7.11 (dt, *J* = 7.8, 5.2 Hz, 1 H), 5.04 (d, *J* = 17.2 Hz, 1 H), 4.33 (ddd, *J* = 12.5, 6.3, 1.9 Hz, 1 H), 4.09 – 4.00 (m, 2 H), 3.89 (dd, *J* = 12.4, 10.0 Hz, 1 H), 3.77 – 3.72 (m, 1 H), 3.75 (d, *J* = 2.7 Hz, 3 H), 3.72 (d, *J* = 2.6 Hz, 3 H), 3.29 (dd, *J* = 14.3, 5.8 Hz, 1 H), 3.12 – 3.05 (m, 1 H), 1.14 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 20.3.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.0, 157.3 (d, *J* = 9.8 Hz), 148.7 (d, *J* = 2.1 Hz), 136.0 (d, *J* = 4.7 Hz), 129.3, 121.7 (d, *J* = 1.3 Hz), 78.4 (d, *J* = 169.7 Hz), 70.7 (d, *J* = 13.2 Hz), 60.8, 54.0 (d, *J* = 7.0 Hz), 53.4 (d, *J* = 6.9 Hz), 43.1, 37.1, 14.1.

¹H NMR (400 MHz, CDCl₃): δ_{diast2} = 8.46 – 8.36 (m, 1 H), 7.60 (ddd, *J* = 22.6, 7.9, 4.8 Hz, 1 H), 7.11 (dt, *J* = 7.8, 5.2 Hz, 1 H), 5.05 (d, *J* = 16.6 Hz, 1 H), 4.45 (dt, *J* = 12.8, 2.2 Hz, 1 H), 4.12 (qd, *J* = 7.1, 1.0 Hz, 2 H), 3.84 – 3.77 (m, 1 H), 3.75 (d, *J* = 10.6 Hz, 3 H), 3.73 – 3.69 (m, 1 H), 3.67 (d, *J* = 10.5 Hz, 3 H), 3.17 (dd, *J* = 13.7, 4.8 Hz, 1 H), 2.88 – 2.77 (m, 1 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 19.8.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 172.9, 157.0 (d, *J* = 6.3 Hz), 148.8 (d, *J* = 3.4 Hz), 136.5 (d, *J* = 4.9 Hz), 129.3, 121.7 (d, *J* = 2.3 Hz), 79.2 (d, *J* = 168.0 Hz), 68.4 (d, *J* = 13.9 Hz), 60.9, 53.8 (d, *J* = 7.1 Hz), 53.4 (d, *J* = 6.9 Hz), 43.5, 35.3, 14.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₄H₂₁NO₆P: 330.1106; found: 330.1104.

Dimethyl (8-cyano-5,7,8,9-tetrahydrooxepino[4,3-*b*]pyridin-5-yl)phosphonate 14j:

Following general procedure 6, from olefin **1v** (0.17 g, 0.47 mmol) gave compound **14j** in two separables diastereoisomers: **Diastereoisomer 1** was obtained in 18% (24.0 mg) as a colorless oil and **Diastereoisomer 2** was obtained in 45% (60.0 mg) as a colorless oil.

R_f = 0.50 (EtOAc 100%). IR (neat): 2956 (C-H), 2332 (C≡N), 1019 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 8.48 (dt, *J* = 4.8, 1.6 Hz, 1 H), 7.61 (dt, *J* = 7.8, 1.5 Hz, 1 H), 7.19 (dd, *J* = 7.8, 4.9 Hz, 1 H), 5.07 (d, *J* = 17.0 Hz, 1 H), 4.39 (ddd, *J* = 12.4, 6.6, 2.0 Hz, 1 H), 3.94 (ddd, *J* = 13.9, 5.0, 1.8 Hz, 1 H), 3.78 – 3.71 (m, 1 H), 3.73 (d, *J* = 10.7 Hz, 3 H), 3.68 (d, *J* = 10.7 Hz, 3 H), 3.29 – 3.16 (m, 2 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 19.5.

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 154.7 (d, *J* = 7.3 Hz), 149.4 (d, *J* = 2.8 Hz), 136.7 (d, *J* = 5.1 Hz), 128.8 (d, *J* = 2.0 Hz), 122.5 (d, *J* = 1.8 Hz), 118.5, 78.8 (d, *J* = 168.6 Hz), 68.4 (d, *J* = 12.8 Hz), 54.1 (d, *J* = 7.0 Hz), 53.6 (d, *J* = 6.9 Hz), 36.4, 29.2.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₂H₁₆N₂O₄P: 283.0848; found: 283.0849.

R_f = 0.47 (EtOAc 100%). IR (neat): 2957 (C-H), 2323 (C≡N), 1021 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ_{diast2} = 8.44 – 8.41 (m, 1 H), 7.60 (dt, *J* = 7.8, 1.5 Hz, 1 H), 7.17 (dd, *J* = 7.8, 4.9 Hz, 1 H), 5.05 (d, *J* = 16.9 Hz, 1 H), 4.32 (dt, *J* = 12.9, 2.0 Hz, 1 H), 3.92 (ddd, *J* = 13.6, 11.5, 2.0 Hz, 1 H), 3.79 (ddd, *J* = 12.9, 5.2, 0.9 Hz, 1 H), 3.76 (d, *J* = 4.5 Hz, 3 H), 3.73 (d, *J* = 4.4 Hz, 3 H), 3.36 – 3.21 (m, 1 H), 3.00 (dtd, *J* = 11.7, 5.0, 2.0 Hz, 1 H).

³¹P NMR (162 MHz, CDCl₃): δ_{diast2} = 19.1.

¹³C NMR (101 MHz, CDCl₃): δ_{diast2} = 154.7 (d, *J* = 7.1 Hz), 149.2 (d, *J* = 2.9 Hz), 136.8 (d, *J* = 5.0 Hz), 129.0 (d, *J* = 2.9 Hz), 122.6 (d, *J* = 1.9 Hz), 120.2, 79.1 (d, *J* = 168.8 Hz), 68.6 (d, *J* = 13.3 Hz), 54.2 (d, *J* = 7.0 Hz), 53.8 (d, *J* = 7.0 Hz), 36.5, 29.9.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₂H₁₆N₂O₄P: 283.0848; found: 283.0853.

Ethyl 8-(dimethoxyphosphoryl)-4,5,6,8-tetrahydrothieno[2,3-*c*]oxepine-5-carboxylate 14k:

Following general procedure 6, from olefin **1w** (0.20 g, 0.48 mmol) gave a mixture of two inseparables diastereoisomers of compound **14k** in 53% (85.0 mg) as a viscous oil.

R_f = 0.41 (EtOAc 100%). IR (neat): 2956 (C-H), 1723 (C=O), 1459 (C=C), 1020 cm⁻¹ (C-O).

¹H NMR (300 MHz, CDCl₃): δ_{diast1} = 7.10 (dd, *J* = 4.8, 1.7 Hz, 1 H), 6.77 (dd, *J* = 5.1, 0.9 Hz, 1 H), 5.14 (dd, *J* = 16.6, 1.1 Hz, 1 H), 4.51 – 4.36 (m, 1 H), 4.15 – 3.91 (m, 3 H), 3.76 (d, *J* = 3.9 Hz, 3 H), 3.72 (d, *J* = 3.9 Hz, 3 H), 3.32 (dt, *J* = 13.4, 3.6 Hz, 1 H), 3.10 – 2.80 (m, 2 H), 1.13 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast1} = 19.8,

¹³C NMR (75 MHz, CDCl₃): δ_{diast1} = 172.4, 138.9, 138.7, 130.1 (d, *J* = 2.4 Hz), 124.5 (d, *J* = 3.0 Hz), 75.8 (d, *J* = 172.7 Hz), 70.7 (d, *J* = 12.5 Hz), 60.7, 53.9 (d, *J* = 7.1 Hz), 53.6 (d, *J* = 6.8 Hz), 44.3 (d, *J* = 2.0 Hz), 27.9, 14.1.

¹H NMR (300 MHz, CDCl₃): δ_{diast2} = 7.10 (dd, *J* = 4.8, 1.7 Hz, 1 H), 6.77 (dd, *J* = 5.1, 0.9 Hz, 1 H), 5.15 (dd, *J* = 16.2, 0.8 Hz, 1 H), 4.51 – 4.36 (m, 1 H), 4.15 – 3.91 (m, 3 H), 3.76 (d, *J* = 3.9 Hz, 3 H), 3.72 (d, *J* = 3.9 Hz, 3 H), 3.32 (dt, *J* = 13.4, 3.6 Hz, 1 H), 3.10 – 2.80 (m, 2 H), 1.20 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (121 MHz, CDCl₃): δ_{diast2} = 19.5.

¹³C NMR (75 MHz, CDCl₃): δ_{diast2} = 172.7, 138.9 (d, *J* = 6.3 Hz), 138.8 (d, *J* = 7.6 Hz), 130.0 (d, *J* = 3.1 Hz), 124.6 (d, *J* = 2.8 Hz), 75.6 (d, *J* = 171.1 Hz), 70.5 (d, *J* = 11.7 Hz), 60.9, 53.9 (d, *J* = 6.9 Hz), 53.7 (d, *J* = 6.9 Hz), 45.0 (d, *J* = 2.5 Hz), 28.0, 14.1.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₃H₁₉NaO₆PS: 357.0538; found: 357.0540.

General procedure 7, 2,5-dihydrofuran synthesis by RCM:

Grubbs second-generation catalyst (0.10 equiv.) in dry CH₂Cl₂ (4 mL) was added to a stirred solution of the corresponding *bis*-olefin **1** (1.0 equiv.) in CH₂Cl₂ (25 mL). The reaction mixture was stirred at 50 °C under argon atmosphere until TLC analysis indicated that the starting material was consumed. The reaction mixture was then filtered over a pad of Celite® previously washed with CH₂Cl₂ and concentrated under reduced pressure to afford a crude residue which was purified by flash column chromatography on silica gel using EtOAc as eluent.

Ethyl 5-(dimethoxyphosphoryl)-2,5-dihydrofuran-3-carboxylate **17a**:

Following general procedure 7, from Grubbs 2nd generation (0.072 mmol, 0.06 mg) and *bis*-olefin **1x** (0.72 mmol, 0.20 mg), the 2,5-DHF **17a** was obtained in 84% (0.15 g) as a colorless oil.

R_f = 0.31 (EtOAc 100%). IR (neat): 2958 (C-H), 1712 (C=O), 1183 (C-O), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.80 (quint, *J* = 2.3 Hz, 1 H), 5.27 (dddd, *J* = 7.7, 6.4, 4.1, 2.1 Hz, 1 H), 4.99 – 4.89 (m, 2 H), 4.25 (q, *J* = 7.1 Hz, 2 H), 3.86 (d, *J* = 3.1 Hz, 3 H), 3.84 (d, *J* = 3.0 Hz, 3 H), 1.32 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.0.

¹³C NMR (101 MHz, CDCl₃): δ = 161.7, 135.3 (d, *J* = 11.1 Hz), 133.8 (d, *J* = 5.7 Hz), 83.0 (d, *J* = 167.5 Hz), 75.5, 61.0, 53.8 (d, *J* = 7.2 Hz), 53.4 (d, *J* = 7.1 Hz), 14.1.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₉H₁₅NaO₆P: 273.0504; found: 273.0508.

Ethyl 5-(diethoxyphosphoryl)-2,5-dihydrofuran-3-carboxylate **17b**:

Following general procedure 7, from Grubbs 2nd generation (0.032 mmol, 0.028 g) and *bis*-olefin **1y** (0.32 mmol, 0.01 mg), the 2,5-DHF **17b** was obtained in 69% (0.061 g) as a colorless oil.

R_f = 0.30 (EtOAc 100%). IR (neat): 2958 (C-H), 1712 (C=O), 1644 (C=C), 1182 (C-O), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.83 – 6.76 (m, 1 H), 5.27 – 5.19 (m, 1 H), 4.92 – 4.82 (m, 2 H), 4.27 – 4.15 (m, 6 H), 1.39 – 1.32 (m, 6 H), 1.31 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 16.8.

¹³C NMR (101 MHz, CDCl₃): δ = 161.8 (d, *J* = 3.4 Hz), 135.1 (d, *J* = 11.1 Hz), 134.2 (d, *J* = 5.7 Hz), 83.3 (d, *J* = 167.3 Hz), 75.4, 63.2 (d, *J* = 7.1 Hz), 62.9 (d, *J* = 7.1 Hz), 60.9, 16.4 (d, *J* = 5.4 Hz, 2C), 14.1.

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₁H₁₉NaO₆P: 301.0817; found: 301.0815.

Ethyl 5-(dibutoxyphosphoryl)-2,5-dihydrofuran-3-carboxylate **17c**:

Following general procedure 7, from Grubbs 2nd generation (0.04 mmol, 0.034 g) and *bis*-olefin **1z** (0.40 mmol, 0.015 g), the 2,5-DHF **17c** was obtained in 79% (0.015 g) as a colorless oil.

R_f = 0.48 (EtOAc 100%). IR (neat): 2961 (C-H), 1719 (C=O), 1463 (C=C), 1246 (C-O), 1018 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.72 (quint, *J* = 2.2 Hz, 1 H), 5.18 – 5.13 (m, 1 H), 4.91 – 4.97 (m, 2 H), 4.17 (q, *J* = 7.1 Hz, 2 H), 4.10 – 4.02 (m, 4 H), 1.65 – 1.54 (m, 4 H), 1.39 – 1.26 (m, 4 H), 1.24 (t, *J* = 7.1 Hz, 3 H), 0.87 (t, *J* = 7.4 Hz, 3 H), 0.86 (td, *J* = 7.4, 4.9 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 16.8.

¹³C NMR (101 MHz, CDCl₃): δ = 161.8, 134.9 (d, *J* = 28.1 Hz), 134.3 (d, *J* = 5.7 Hz), 83.3 (d, *J* = 167.1 Hz), 75.4, 66.9 (d, *J* = 7.3 Hz), 66.6 (d, *J* = 7.3 Hz), 60.9, 32.6 (d, *J* = 3.5 Hz, 2C), 18.6 (d, *J* = 1.7 Hz, 2C), 14.1, 13.5 (2C).

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₅H₂₇NaO₆P: 357.1443; found: 357.1454.

Dimethyl (4-acetyl-2,5-dihydrofuran-2-yl)phosphonate **17d**:

Following general procedure 7, from Grubbs 2nd generation (0.04 mmol, 0.034 g) and *bis*-olefin **1aa** (0.40 mmol, 0.01 g), the 2,5-DHF **17d** was obtained in 74% (0.065 g) as a colorless oil.

R_f = 0.28 (EtOAc 100%). IR (neat): 1734 (C=O), 1241 (C-O), 1024 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.63 (dd, *J* = 4.6, 2.2 Hz, 1 H), 5.25 (dtd, *J* = 8.3, 4.1, 2.0 Hz, 1 H), 4.97 – 4.82 (m, 2 H), 3.79 (d, *J* = 5.6 Hz, 3 H), 3.76 (d, *J* = 5.6 Hz, 3 H), 2.32 (s, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 18.9.

¹³C NMR (101 MHz, CDCl₃): δ = 193.4, 143.3, 133.8 (d, *J* = 5.9 Hz), 83.3 (d, *J* = 166.7 Hz), 75.8, 53.9 (d, *J* = 7.2 Hz), 53.4 (d, *J* = 7.3 Hz), 27.1.

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₈H₁₃O₅P: 219.0422; found: 219.0432.

Diethyl (4-acetyl-2,5-dihydrofuran-2-yl)phosphonate **17e**:

Following general procedure 7, from Grubbs 2nd generation (0.032 mmol, 0.027 g) and *bis*-olefin **1ab** (0.32 mmol, 0.09 g), the 2,5-DHF **17e** was obtained in 70% (0.055 g) as a colorless oil.

R_f = 0.29 (EtOAc 100%). IR (neat): 2959 (C-H), 1670 (C=O), 1240 (C-O), 1021 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.66 – 6.63 (m, 1 H), 5.24 – 5.19 (m, 1 H), 4.89 – 4.84 (m, 2 H), 4.33 – 4.05 (m, 4 H), 2.32 (s, 3 H), 1.30 (t, *J* = 7.0 Hz, 3 H), 1.25 (t, *J* = 7.0 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 16.6.

¹³C NMR (101 MHz, CDCl₃): δ = 193.5, 143.1 (d, *J* = 7.0 Hz), 134.2 (d, *J* = 9.6 Hz), 83.2 (d, *J* = 102.2 Hz), 75.8, 63.3 (d, *J* = 5.1 Hz), 63.0 (d, *J* = 7.3 Hz), 27.1, 16.5 (d, *J* = 4.0 Hz), 16.4 (d, *J* = 4.2 Hz).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₁₀H₁₈O₅P: 249.0892; found: 249.0901.

Dimethyl (4-cyano-2,5-dihydrofuran-2-yl)phosphonate **17f**:

Following general procedure 7, from Grubbs 2nd generation (0.04 mmol, 0.034 g) and *bis*-olefin **1ac** (0.40 mmol, 0.01 mg), the 2,5-DHF **17f** was obtained in 89% (0.071 g) as a colorless oil.

R_f = 0.34 (EtOAc 100%). IR (neat): 2960 (C-H), 2231 (C≡N), 1246 (C-O), 1019 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 5.22 – 5.17 (m, 1 H), 6.76 – 6.58 (m, 1 H), 4.88 – 4.73 (m, 2 H), 3.79 (d, *J* = 10.7 Hz, 3 H), 3.76 (d, *J* = 10.7 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.5.

¹³C NMR (101 MHz, CDCl₃): δ = 139.6 (d, *J* = 5.7 Hz), 113.8 (d, *J* = 12.0 Hz), 112.1 (d, *J* = 5.4 Hz), 83.2 (d, *J* = 168.4 Hz), 76.1, 53.9 (d, *J* = 7.1 Hz), 53.6 (d, *J* = 7.2 Hz).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₇H₁₁NO₄P: 204.0426; found: 204.0432.

Diethyl (4-cyano-2,5-dihydrofuran-2-yl)phosphonate **17g**:

Following general procedure 7, from Grubbs 2nd generation (0.06 mmol, 0.05 g) and *bis*-olefin **1ad** (0.60 mmol, 0.16 g), the 2,5-DHF **17g** was obtained in 91% (0.012 g) as a colorless oil.

R_f = 0.35 (EtOAc 100%). IR (neat): 2986 (C-H), 2231 (C≡N), 1239 (C-O), 1013 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.79 – 6.76 (m, 1 H), 5.26 – 5.20 (m, 1 H), 4.95 – 4.80 (m, 2 H), 4.25 – 4.16 (m, 4 H), 1.37 (t, *J* = 7.0 Hz, 3 H), 1.36 (t, *J* = 7.0 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 15.3.

¹³C NMR (101 MHz, CDCl₃): δ = 140.1 (d, *J* = 5.7 Hz), 113.6 (d, *J* = 12.0 Hz), 112.2 (d, *J* = 5.2 Hz), 83.5 (d, *J* = 168.1 Hz), 76.1, 63.5 (d, *J* = 7.1 Hz), 63.2 (d, *J* = 7.1 Hz), 16.5 (d, *J* = 3.6 Hz), 16.4 (d, *J* = 3.9 Hz).

HRMS (ESI⁺): *m/z* [M + H]⁺ calcd for C₉H₁₅NO₄P: 232.0739; found: 232.0743.

Tert-butyl 5-(dimethoxyphosphoryl)-2,5-dihydrofuran-3-carboxylate **17h**:

Following general procedure 7, from Grubbs 2nd generation (0.036 mmol, 0.03 g) and *bis*-olefin **1ae** (0.36 mmol, 0.11 g), the 2,5-DHF **17h** was obtained in 81% (0.089 g) as a colorless oil.

R_f = 0.33 (EtOAc 100%). IR (neat): 2980 (C-H), 1709 (C=O), 1244 (C-O), 1017 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.68 (quint, *J* = 2.3 Hz, 1 H), 5.27 – 5.22 (m, 1 H), 4.97 – 4.81 (m, 2 H), 3.86 (d, *J* = 10.5 Hz, 3 H), 3.85 (d, *J* = 10.5 Hz, 3 H), 1.51 (s, 9 H).

³¹P NMR (162 MHz, CDCl₃): δ = 19.2.

¹³C NMR (101 MHz, CDCl₃): δ = 161.0 (d, *J* = 3.3 Hz), 136.9 (d, *J* = 11.3 Hz), 132.7 (d, *J* = 5.7 Hz), 83.0 (d, *J* = 167.6 Hz), 81.8, 75.6, 53.8 (d, *J* = 7.1 Hz), 53.3 (d, *J* = 7.1 Hz), 28.0 (3C).

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₁H₁₉NaO₆P: 301.0817; found: 301.0816.

Tert-butyl 5-(diethoxyphosphoryl)-2,5-dihydrofuran-3-carboxylate **17i**:

Following general procedure 7, from Grubbs 2nd generation (0.045 mmol, 0.038 g) and *bis*-olefin **1af** (0.45 mmol, 0.15 g), the 2,5-DHF **17i** was obtained in 89% (0.115 g) as a colorless oil.

R_f = 0.32 (EtOAc 100%). IR (neat): 2959 (C-H), 1707 (C=O), 1247 (C-O), 1021 cm⁻¹ (C-O).

¹H NMR (400 MHz, CDCl₃): δ = 6.69 (quint, *J* = 2.3 Hz, 1 H), 5.25 – 5.15 (m, 1 H), 4.99 – 4.80 (m, 2 H), 4.26 – 4.15 (m, 4 H), 1.50 (s, 9 H), 1.37 (t, *J* = 7.1 Hz, 3 H), 1.34 (t, *J* = 7.1 Hz, 3 H).

³¹P NMR (162 MHz, CDCl₃): δ = 17.0.

¹³C NMR (101 MHz, CDCl₃): δ = 161.1 (d, *J* = 3.5 Hz), 136.7 (d, *J* = 11.1 Hz), 133.1 (d, *J* = 5.7 Hz), 83.3 (d, *J* = 167.3 Hz), 81.7, 75.5, 63.2 (d, *J* = 7.1 Hz), 62.8 (d, *J* = 7.1 Hz), 28.0 (3C), 16.4 (d, *J* = 5.5 Hz, 2C).

HRMS (ESI⁺): *m/z* [M + Na]⁺ calcd for C₁₃H₂₃NaO₆P: 329.1130; found: 329.1129.

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