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PAPER

DABCO-catalyzed regioselective cyclization reactions of β,γ-unsaturated α-ketophosphonates or β,γ-unsaturated α-ketoesters with allenic esters†

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Highly efficient DABCO-catalyzed [4 + 2] cycloaddition of β,γ-unsaturated α-ketophosphonates or β,γ-unsaturated α-ketoesters with allenic esters gives the corresponding highly functionalized tetrahydropyran and dihydropyran derivatives in good to excellent yields and moderate to good regioselectivities under mild conditions.

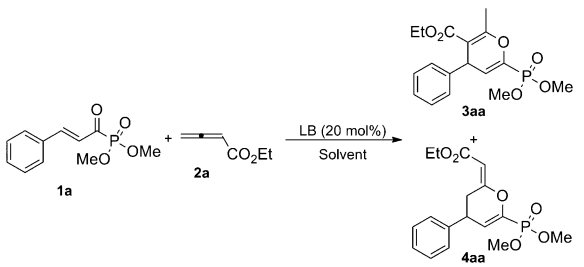
Introduction

Heterocycles are of great value in the design and discovery of new biologically active compounds.[1] The development of efficient processes to construct heterocycles, using metal-free catalysts, has been drawing much attention over the past decades.[2] Recently, nitrogen-containing Lewis base (LB) catalyzed cyclization reactions of allenoates have emerged as powerful synthetic tools in the rapid construction of cyclic molecular complexity.[3] To our surprise, examples of β,γ-unsaturated α-ketophosphonates[4] or β,γ-unsaturated α-ketoesters[5] as the electrophiles were seldom mentioned in the construction of heterocycles. Herein, we wish to report a novel DABCO-catalyzed regioselective [4 + 2] cycloaddition of β,γ-unsaturated α-ketophosphonates or β,γ-unsaturated α-ketoesters with allenic esters to give the corresponding highly functionalized tetrahydropyran and dihydropyran derivatives, which are structural subunits in many natural products and biologically active molecules.[6]

Results and discussion

We initially utilized (*E*)-dimethyl cinnamoylphosphonate **1a** (0.1 mmol, 1.0 equiv) and ethyl 2,3-butadienoate **2a** (0.12 mmol, 1.2 equiv) as the substrates to investigate their cyclization behavior in tetrahydrofuran (THF) at room temperature in the presence of 20 mol% 1,4-diazabicyclo[2,2,2]octane (DABCO). It was found that the desired [4 + 2] cycloaddition reaction took place smoothly to give the corresponding cyclic products **3aa** and **4aa** in 87% combined yield but with low regioselectivity as the ratio of **3aa** : **4aa** was 2 : 1 within 24 h (Table 1, entry 1). Subsequently, we screened various nitrogen-containing Lewis base catalysts for this reaction, and the results are summarized in Table 1 (entries 2–7). 4-*N*,*N*-dimethylpyridine (DMAP) can also efficiently catalyze

Table 1 Optimization of the reaction conditions of (*E*)-dimethyl cinnamoylphosphonate **1a** and ethyl 2,3-butadienoate **2a**[a]



Entry	LB	*T*/°C	Solvent	Yield (%)[b]	**3aa** : **4aa** (%)[c]
1	DABCO	rt	THF	87	2 : 1
2	DMAP	rt	THF	84	1 : 1
3	DBU	rt	THF	NR	—
4	Et_3N	rt	THF	NR	—
5	DIEA	rt	THF	NR	—
6	PPh_3	rt	THF	NR	—
7	PBu_3	rt	THF	NR	—
8	DABCO	rt	DCM	90	3 : 1
9	DABCO	rt	Et_2O	80	1 : 1
10	DABCO	rt	Dioxane	82	2 : 1
11	DABCO	rt	CH_3CN	81	2 : 1
12	DABCO	rt	Toluene	78	1 : 1
13	DABCO	rt	DCE	80	2 : 1
14	DABCO	rt	$CHCl_3$	82	3 : 1
15	DABCO	rt	DMSO	trace	—
16	DABCO	rt	DMF	trace	—
17	DABCO	0	DCM	85	3 : 1
18	DABCO	–20	DCM	85	4 : 1
19	DABCO	–40	DCM	86	5 : 1
20	DABCO	–60	DCM	85	3 : 1

[a] All reactions were carried out using **1a** (0.10 mmol) and **2a** (0.12 mmol) in solvent (1.00 mL) for 24 h. [b] Isolated combined yield. [c] Determined by ^1H NMR spectroscopic data, and these regioisomers can not be easily separated by column chromatography.

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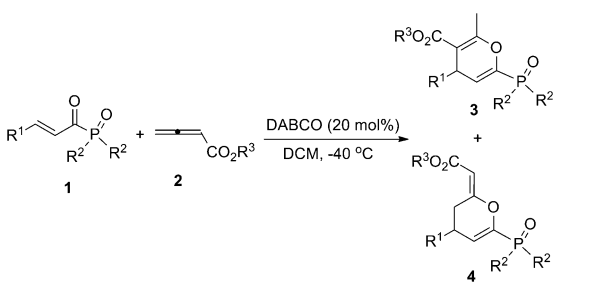
this reaction to give the product mixture of **3aa** and **4aa** in 84% combined yield with a ratio of 1 : 1 (Table 1, entry 2). Other weak nucleophilic nitrogen-containing Lewis base catalysts, such as 1,8-diazabicyclo[5,4,0]-7-undecene (DBU), Et_3N and diisopropylethylamine (DIEA) did not catalyze this reaction (Table 1, entries 3–5). We next attempted to screen phosphane-containing Lewis base catalysts, such as PPh_3 and tributylphosphine (PBu_3), in this reaction, but it was found that no reactions occurred either (Table 1, entries 6 and 7). Of the catalysts examined, DABCO was found to be the best one. Using DABCO as the catalyst, various solvents were examined and dichloromethane (DCM) was found to be the solvent of choice, affording **3aa** and **4aa** in 90% combined yield with the ratio of 3 : 1 (Table 1, entries 8–16). Lowering the reaction temperature to 0 °C or –20 °C, similar results were obtained (Table 1, entries 17 and 18). At –40 °C, the corresponding cyclic adducts **3aa** and **4aa** were obtained in 86% combined yield along with a 5 : 1 ratio of **3aa** : **4aa** (Table 1, entry 19). Further reducing the reaction temperature did not improve the reaction outcomes (Table 1, entry 20). Thus, we have established the optimal reaction conditions for this reaction: using 20 mol % DABCO as a catalyst and DCM as a solvent to perform the reaction at –40 °C.

Under the optimized reaction conditions, the reaction generality was investigated by using various cinnamoylphosphonates **1** in the reaction with several allenic esters **2**, and the results of these experiments are summarized in Table 2. As can be seen from Table 2, changing the ester moiety of allenic esters **2** from OEt to OMe or O^{i}Pr provided similar reaction outcomes, affording the desired products in good combined yields (up to 90%) along with moderate regioselectivities (**3** : **4** = 3 : 1) (Table 2, entries 2 and 3). However, we found that the R^2 substituent in the phosphonate moiety of cinnamoylphosphonates **1** can significantly affect the reaction outcomes, as that R^2 group can improve the regioselectivity of the products (up to **3** : **4** = 10 : 1) if it had a sterically bulky group, such as O^{i}Pr or O^{t}Bu (Table 2, entries 4 and 5). As for substrates **1d**–**1h**, electron-withdrawing or electron-donating substituents at the *meta*- or *para*-positions of the benzene ring of **1** were equally well-tolerated in the reaction, giving the corresponding products **3** and **4** in good combined yields along with high regioselectivities (up to **3** : **4** > 20 : 1) (Table 2, entries 6–10). The substrate **1i**, in which R^1 is a 1-naphthyl group, was also able in this reaction to give the corresponding products in 85% combined yield along with good regioselectivity (**3ia** : **4ia** = 14 : 1) (Table 2, entry 11). When R^1 is an alkyl group (**1j**, R^1 = Me), the reaction also proceeded smoothly to give the desired products **3ja** and **4ja** in 75% combined yield but with moderate regioselectivity (**3ja** : **4ja** = 4 : 1) (Table 2, entry 12). The structures of **3** and **4** were determined by the 2-D NMR spectroscopic data (HMQC, HMBC, DEPT and NOESY spectra) of compounds **3ca** and **4ca** (see the Supporting Information for the details†).

Table 2 Substrate scope of the reactions of phosphonates **1** and allenic esters **2**[a]



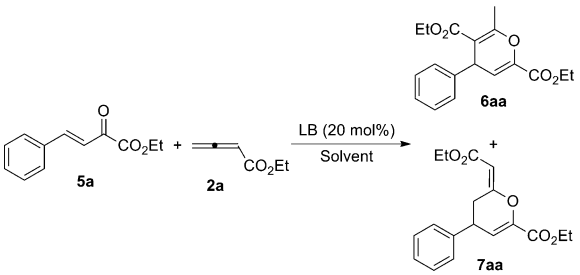
Entry	No	R^1	R^2	R^3 (**2**)	Yield (%)[b]	No	**3** : **4**[c]
1	**1a**	C_6H_5	OMe	Et (**2a**)	86	**3aa** : **4aa**	5 : 1
2	**1a**	C_6H_5	OMe	^{i}Pr (**2b**)	82	**3ab** : **4ab**	3 : 1
3	**1a**	C_6H_5	OMe	Me (**2c**)	90	**3ac** : **4ac**	3 : 1
4	**1b**	C_6H_5	O^{t}Bu	Et (**2a**)	70	**3ba** : **4ba**	9 : 1
5	**1c**	C_6H_5	O^{i}Pr	Et (**2a**)	85	**3ca** : **4ca**	10 : 1
6	**1d**	4-ClC_6H_4	O^{i}Pr	Et (**2a**)	87	**3da** : **4da**	10 : 1
7	**1e**	4-$NO_2C_6H_4$	O^{i}Pr	Et (**2a**)	80	**3ea** : **4ea**	>20 : 1
8	**1f**	4-BrC_6H_4	O^{i}Pr	Et (**2a**)	85	**3fa** : **4fa**	13 : 1
9	**1g**	3-MeC_6H_4	O^{i}Pr	Et (**2a**)	85	**3ga** : **4ga**	10 : 1
10	**1h**	4-$MeOC_6H_4$	O^{i}Pr	Et (**2a**)	75	**3ha** : **4ha**	8 : 1
11	**1i**	1-naphthyl	O^{i}Pr	Et (**2a**)	85	**3ia** : **4ia**	14 : 1
12	**1j**	Me	O^{i}Pr	Et (**2a**)	75	**3ja** : **4ja**	4 : 1

[a] All reactions were carried out using **1** (0.10 mmol) and **2** (0.12 mmol) in DCM (1.00 mL) at –40 °C for 24 h. [b] Isolated combined yield. [c] Determined by ^{1}H NMR spectroscopic data, and these regioisomers cannot be easily separated by column chromatography.

Encouraged by the above results, β,γ-unsaturated α-ketoesters were also examined under the optimal reaction conditions. Initially, we utilized (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate **5a** (0.10 mmol, 1.0 equiv) and ethyl 2,3-butadienoate **2a** (0.12 mmol, 1.2 equiv) as the substrates in DCM (2.00 mL, 0.05 M) at room temperature in the presence of 20 mol% DABCO. We were pleased to find that the reaction proceeded smoothly to give the desired products **6aa** and **7aa** in 82% combined yield along with good regioselectivity (**7aa** : **6aa** = 8 : 1) (Table 3, entry 1), which was contrary to the above results in Table 2. Reducing the concentration to 0.03 M by increasing the amount of solvent (DCM) employed to 3.00 mL can improve the reaction outcome, affording the corresponding products in 85% combined yield along with the 13 : 1 ratio of **7aa** : **6aa** (Table 3, entry 1). Inspired by this result, we next screened various nitrogen-containing Lewis base catalysts for this reaction in the optimized amount of solvent (3.00 mL, 0.03 M). DMAP can efficiently catalyze this reaction as well but with low regioselectivity. However, DBU and DIEA did not catalyze this reaction (Table 3, entries 2–4). Accordingly, DABCO was then used as the best catalyst for further investigation of solvent and temperature effects in this reaction. It was found that THF was the solvent of choice in comparison with those reactions carried out in other organic solvents, such as toluene, Et_2O, 1,2-dichloroethane (DCE), chloroform, 1,4-dioxane, CH_3CN, *N*,*N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) (Table 3, entries 5–13). The low temperature (–10 °C) can improve the combined yield of **6aa** and **7aa** (Table 3, entry 15), but further lowering the reaction temperature to –40 °C reduced the combined yield (Table 3, entry 16). Thus, we have identified the optimal reaction conditions for this reaction: using 20 mol% of DABCO as a catalyst and THF as a solvent to perform the reaction at –10 °C.

Having identified the optimal reaction conditions, we next set out to examine the scope and limitations of the [4 + 2] cycloaddition reaction catalyzed by DABCO using various β,γ-unsaturated α-ketoesters **5** with different substituents on the R^4 group, and the results are summarized in Table 4. As can be seen from Table 4, when R^4 is an aromatic group, whether they have electron-withdrawing or electron-donating substituents at the *ortho*-, *meta*- or *para*-positions on the benzene rings, the

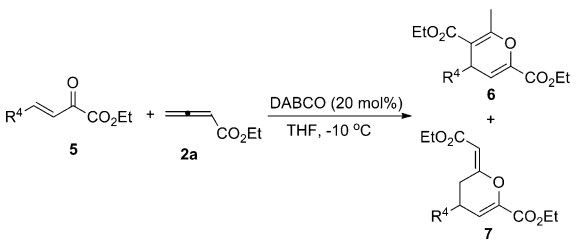
Table 3 Optimization of the reaction conditions of (*E*)-ethyl 2-oxo-4-phenylbut-3-enoate **5a** and ethyl 2,3-butadienoate **2a**[a]



Entry	LB	*T*/°C	Solvent	Yield (%)[b]	**7aa** : **6aa** (%)[c]
1	DABCO	rt	DCM	85 (82)[d]	13 : 1 (8 : 1)[d]
2	DMAP	rt	DCM	80	2 : 1
3	DIEA	rt	DCM	NR	—
4	DBU	rt	DCM	NR	—
5	DABCO	rt	THF	90	>20 : 1
6	DABCO	rt	Toluene	75	5 : 1
7	DABCO	rt	Et_2O	88	13 : 1
8	DABCO	rt	DCE	86	8 : 1
9	DABCO	rt	$CHCl_3$	90	6 : 1
10	DABCO	rt	Dioxane	89	14 : 1
11	DABCO	rt	CH_3CN	50	>20 : 1
12	DABCO	rt	DMSO	trace	—
13	DABCO	rt	DMF	trace	—
14	DABCO	0	THF	91	>20 : 1
15	DABCO	−10	THF	95	>20 : 1
16	DABCO	−40	THF	92	>20 : 1

[a] All reactions were carried out using **5a** (0.10 mmol) and **2a** (0.12 mmol) in solvent (3.00 mL, 0.03 M) for 24 h. [b] Isolated combined yield. [c] Determined by ^{1}H NMR spectroscopic data, and these regioisomers can not be easily separated by column chromatography. [d] The reaction was carried out in DCM (2.00 mL, 0.05 M).

Table 4 Substrate scope of the reactions of β,γ-unsaturated α-ketoesters **5** and ethyl 2,3-butadienoate **2a**[a]



Entry	No	R^1	Yield (%)[b]	No	**7** : **6**[c]
1	**5a**	C_6H_5	95	**7aa** : **6aa**	>20 : 1
2	**5b**	4-ClC_6H_4	86	**7ba** : **6ba**	14 : 1
3	**5c**	4-BrC_6H_4	87	**7ca** : **6ca**	10 : 1
4	**5d**	3-BrC_6H_4	83	**7da** : **6da**	8 : 1
5	**5e**	2-BrC_6H_4	85	**7ea** : **6ea**	8 : 1
6	**5f**	2,4-$Cl_2C_6H_3$	87	**7fa** : **6fa**	7 : 1
7	**5g**	4-MeC_6H_4	85	**7ga** : **6ga**	12 : 1
8	**5h**	2-furyl	60	**7ha** : **6ha**	3 : 1
9	**5i**	2-thiophene	57	**7ia** : **6ia**	6 : 1
10	**5j**	2-naphthyl	82	**7ja** : **6ja**	8 : 1
11	**5k**	cyclopropyl	90	**7ka** : **6ka**	>20 : 1

[a] All reactions were carried out using **5** (0.10 mmol) and **2a** (0.12 mmol) in solvent (3.00 mL, 0.03 M) for 24 h. [b] Isolated combined yield. [c] Determined by ^{1}H NMR spectroscopic data, and these regioisomers can not be easily separated by column chromatography.

reactions proceeded smoothly to give the desired products in good yields along with good regioselectivities (Table 4, entries 2–7). Heterocyclic substrates **5h** and **5l** were also suitable in this reaction to give the corresponding products in moderate combined yields and regioselectivities (Table 4, entries 8 and 9). The substrate **5j**, in which R^4 is a 2-naphthyl group, was also tolerable in this reaction to give the corresponding products in 82% combined yield along with good regioselectivity (**7ja** : **6ja** = 8 : 1) (Table 4, entry 10). For substrate **5k**, in which R^4 is a cyclopropyl group, the reaction also proceeded smoothly to give the desired products in high combined yield (up to 90%) along with high regioselectivity (up to **7ka** : **6ka** = >20 : 1). The structure of **6ea** was unambiguously determined by X-ray diffraction. The ORTEP drawing is shown in Fig. 1 and its CIF data are summarized in the Supporting Information.†[7] The structure of **7** and the *E*-configuration of the double bond were assigned by the 2-D NMR spectroscopic data (HMQC, HMBC, DEPT and NOESY spectra) of compound **7aa** (see the Supporting Information for the details†).

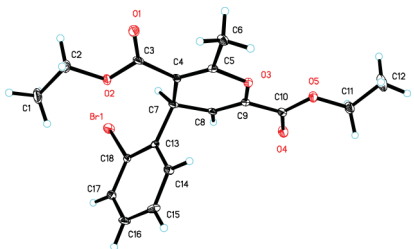
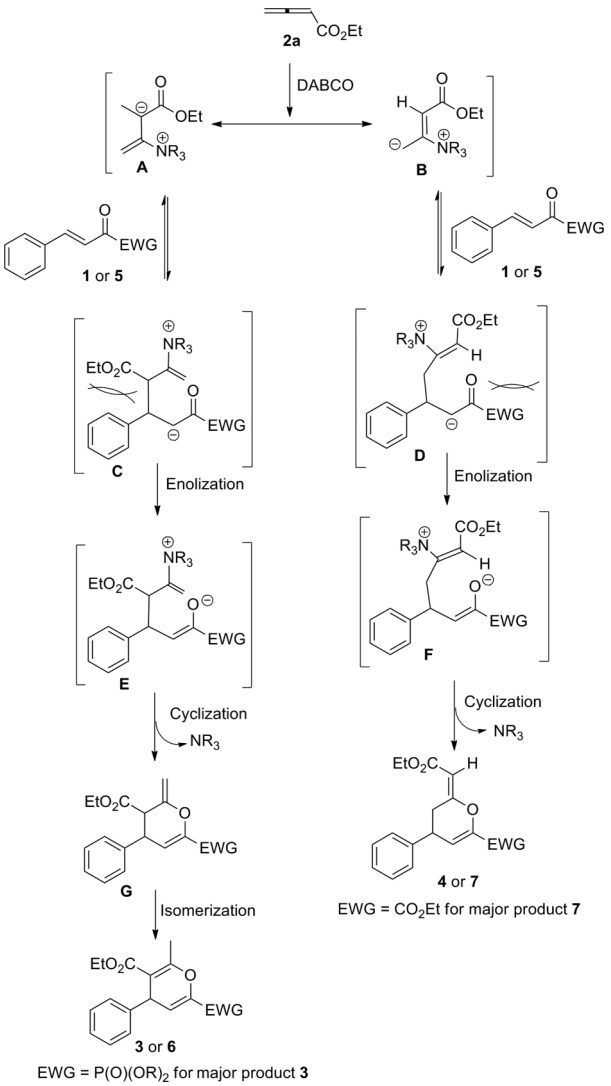


Fig. 1 An ORTEP drawing of **6ea**.

The mechanism for the reactions has not been unequivocally established, but one reasonable explanation is shown in Scheme 1 based on earlier reports and our own investigations. Addition of DABCO to allenoate **2a** delivers zwitterionic intermediate **A**, which coexists with its resonance form **B**.[3a,3c] The zwitterionic intermediate **A** reacts with **1** or **5** to give intermediate **C**, which undergoes enolization to give intermediate **E**. Subsequent cyclization produces cyclic product **G** and regenerates the DABCO catalyst. Finally, **G** isomerizes to give the more stable adducts **3** or **6**. At the same time, the zwitterionic intermediate **B** can also react with **1** or **5** to give intermediate **D**, which undergoes enolization to give intermediate **F**. Subsequent cyclization produces cyclic product **4** or **7** and regenerates the DABCO catalyst. We also assumed that the major products in the reaction might be mainly due to the steric interaction between intermediates **C** and **D**. When EWG = $PO(O^iPr)_2$, which is sterically more bulky than an aromatic ring, the steric repulsion between CO_2Et and EWG is larger than that of CO_2Et and an aromatic ring. Therefore, intermediate **C** is more stable than intermediate **D**, affording **3** as the major product. When EWG = CO_2Et, which is sterically smaller than aromatic ring, the steric repulsion between CO_2Et and EWG is less than that of CO_2Et and aromatic ring. Therefore, intermediate **D** is more stable than intermediate **C**, leading to **7** as the major product.

In conclusion, we have established a novel DABCO-catalyzed [4 + 2] cycloaddition of β,γ-unsaturated α-ketophosphonates or β,γ-unsaturated α-ketoesters with allenic esters to give the corresponding highly functionalized tetrahydropyran and dihydropyran derivatives in good to excellent yields and moderate



Scheme 1 A plausible reaction mechanism.

to good regioselectivities under mild conditions. The obtained multiple functionalized tetrahydropyran and dihydropyran derivatives are useful building blocks in the organic synthesis of biologically useful compounds. A plausible reaction mechanism has been also proposed on the basis of previous literature and our own investigations. Efforts are in progress to elucidate further mechanistic details of these reactions and to understand their scope and limitations.

Experimental section

General remarks

^{1}H NMR spectra were recorded on a Bruker AM-300 or AM-400 spectrometer for solution in $CDCl_3$ with tetramethylsilane (TMS) as internal standard; J-values are in Hz. Mass spectra were recorded with a HP-5989 instrument. All of the compounds reported in this paper gave satisfactory HRMS analytic data. Melting points were determined on a digital melting point apparatus and temperatures were uncorrected. Infrared spectra were recorded on a Perkin-Elmer PE-983 spectrometer with absorption in cm^{-1}. THF, toluene and Et_2O were distilled from sodium (Na) under argon (Ar) atmosphere. CH_3CN, 1,2-dichloroethane and dichloromethane were distilled from CaH_2 under argon (Ar) atmosphere. Commercially obtained reagents were used without further purification. All reactions were monitored by TLC with Huanghai GF254 silica gel coated plates. Flash column chromatography was carried out using 300–400 mesh silica gel at increased pressure. All the β,γ-unsaturated α-ketophosphonates and β,γ-unsaturated α-ketoesters were prepared according to the literature.[4b,8]

General procedure for the preparation of 3 and 4 from the reaction of 1a with 2a using 3aa and 4aa as an example in the presence of DABCO

To a mixture of **1a** (0.10 mmol, 24.0 mg), **2a** (0.12 mmol, 13.6 μL) and DABCO (2.2 mg, 0.02 mmol) was added 2.0 mL of dichloromethane at −40 °C. The reaction solution was monitored by TLC. After the reaction was complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/6) to give the target products **3aa** and **4aa**.

Ethyl 6-(dimethoxyphosphoryl)-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate 3aa. A colorless oil (16.7 mg, 70%); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.09 (t, J = 7.2 Hz, 3H), 2.39 (s, 3H), 3.78 (d, J = 11.2 Hz, 3H), 3.80 (d, J = 11.2 Hz, 3H), 3.96–4.07 (m, 2H), 4.45 (d, J = 5.2 Hz, ^{1}H), 6.12 (dd, J = 10.0 Hz, 5.2 Hz, 1H), 7.19–7.22 (m, 3H), 7.29–7.31 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.8, 19.0, 38.1 (d, J = 10.4 Hz), 53.3 (d, J = 6.7 Hz), 53.4 (d, J = 5.9 Hz), 60.1, 104.8, 122.0 (d, J = 20.9 Hz), 126.9, 127.8, 128.5, 137.4, 139.8, 144.0 (d, J = 2.2 Hz), 159.7 (d, J = 8.2 Hz), 166.6; ^{31}P NMR (161.93 MHz, $CDCl_3$, 85% H_3PO_4): δ 9.734;. IR (CH_2Cl_2) ν 2966, 2902, 1715, 1659, 1473, 1373, 1260, 1176, 1105, 1026, 947, 800, 741, 700 cm^{-1}; MS (ESI) m/z 353.0 (M+H$^+$). HRMS (ESI) Calcd for $C_{17}H_{22}O_6P$ requires (M+H$^+$): 353.1149, found: 353.1156.

(*E*)-Ethyl 2-(6-(dimethoxyphosphoryl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4aa. A colorless oil (5.5 mg, 16%); ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ 1.23 (t, J = 7.2 Hz, 3H), 3.10 (dd, J = 10.4 Hz, 6.8 Hz, 1H), 3.67–3.73 (m, 2H), 3.84 (d, J = 11.2 Hz, 3H), 3.85 (d, J = 11.2 Hz, 3H), 4.08–4.14 (m, 2H), 5.67 (s, 1H), 6.28 (dd, J = 10.4 Hz, 2.8 Hz, 1H), 7.19–7.22 (m, 2H), 7.26–7.28 (m, 1H), 7.31–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 29.8, 35.6 (d, J = 11.9 Hz), 53.39 (d, J = 3.7 Hz), 53.40 (d, J = 6.2 Hz), 59.8, 100.8, 122.0 (d, J = 19.3 Hz), 127.0, 127.2, 128.8, 141.0 (d, J = 11.2 Hz), 143.4, 164.6 (d, J = 9.7 Hz), 166.6; ^{31}P NMR (161.93 MHz, $CDCl_3$, 85% H_3PO_4): δ 9.180; IR (neat) ν 2966, 2902, 1712, 1656, 1494, 1449, 1374, 1261, 1172, 1111, 1026, 824, 764, 700 cm^{-1}; MS (ESI) m/z 353.1 (M+H$^+$); HRMS (ESI) Calcd for $C_{17}H_{22}O_6P$ requires (M+H$^+$): 353.1149, found: 353.1159.

Isopropyl 6-(dimethoxyphosphoryl)-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate 3ab. A slightly yellow liquid (22.0 mg, 60%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.91 (d, J = 6.0 Hz, 3H), 1.16 (d, J = 6.0 Hz, 3H), 2.39 (s, 3H), 3.78 (d, J = 11.2 Hz, 3H), 3.81 (d, J = 11.2 Hz, 3H), 4.44 (d, J = 4.8 Hz, 1H), 4.88 (sept, J = 6.0 Hz, 1H), 6.11 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.18–7.31 (m, 5H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 21.3, 21.8, 38.3 (d, J = 10.6 Hz), 53.29 (d, J = 6.0 Hz), 53.35 (d, J = 6.0 Hz), 67.6, 105.0,

121.9 (d, J = 20.4 Hz), 126.9, 128.0, 128.5, 137.6, 139.9, 144.3, 159.5 (d, J = 9.1 Hz), 166.2; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.795; IR (CH_2Cl_2) ν 3061, 2980, 2902, 1713, 1659, 1628, 1374, 1262, 1177, 1104, 1047, 953, 803, 739, 701 cm^{-1}; MS (ESI) m/z 367.1 (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{23}O_6PNa$ requires (M+Na$^+$): 389.1125, found: 389.1110.

(*E*)-Isopropyl 2-(6-(dimethoxyphosphoryl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ab. A slightly yellow liquid (8.1 mg, 22%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19 (d, J = 6.4 Hz, 3H), 1.22 (d, J = 6.4 Hz, 3H), 3.10 (dd, J = 17.2 Hz, 10.4 Hz, 1H), 3.68–3.72 (m, 2H), 3.84 (d, J = 11.2 Hz, 3H), 3.85 (d, J = 11.2 Hz, 3H), 4.98 (sept, J = 6.4 Hz, 1H), 5.64 (s, 1H), 6.29 (dd, J = 10.0 Hz, 2.8 Hz, 1H), 7.20–7.27 (m, 3H), 7.31–7.34 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.8, 29.9, 35.7 (d, J = 11.9 Hz), 53.4 (d, J = 4.4 Hz), 67.1, 101.4, 121.5 (d, J = 19.3 Hz), 127.1, 127.2, 128.8, 141.1 (d, J = 16.4 Hz), 143.6, 164.4 (d, J = 9.7 Hz), 166.2; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.206; IR (CH_2Cl_2) ν 3062, 2979, 2905, 1706, 1655, 1452, 1374, 1260, 1170, 1100, 1023, 800, 761, 700 cm^{-1}; MS (ESI) m/z 367.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{23}O_6PNa$ requires (M+Na$^+$): 389.1125, found: 389.1112.

Methyl 6-(dimethoxyphosphoryl)-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate 3ac. A slightly yellow liquid (21.6 mg, 64%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 2.39 (s, 3H), 3.57 (s, 3H), 3.78 (d, J = 11.2 Hz, 3H), 3.80 (d, J = 11.2 Hz, 3H), 4.45 (d, J = 4.8 Hz, 1H), 6.13 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.20–7.22 (m, 3H), 7.28–7.32 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 19.1, 38.1 (d, J = 10.4 Hz), 51.3, 53.27 (d, J = 6.0 Hz), 53.34 (d, J = 5.9 Hz), 104.8, 121.9 (d, J = 20.0 Hz), 127.0, 127.8, 128.6, 137.8, 140.2, 144.0, 160.0 (d, J = 8.9 Hz), 167.2; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.654. IR (CH_2Cl_2) ν 3062, 2963, 2904, 1717, 1660, 1627, 1437, 1375, 1262, 1174, 1037, 840, 803, 702 cm^{-1}; MS (ESI) m/z 339.1 (M+H$^+$); HRMS (ESI) Calcd for $C_{16}H_{19}O_6PNa$ requires (M+Na$^+$): 361.0812, found: 361.0801.

(*E*)-Methyl 2-(6-(dimethoxyphosphoryl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ac. (8.8 mg, 26%): a slightly yellow liquid. ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 3.11 (dd, J = 17.6 Hz, 10.4 Hz, 1H), 3.65 (s, 3H), 3.68–3.73 (m, 2H), 3.85 (d, J = 11.2 Hz, 6H), 5.68 (s, 1H), 6.29 (dd, J = 10.4 Hz, 3.2 Hz, 1H), 7.19–7.27 (m, 3H), 7.33–7.35 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.1, 29.9, 35.6 (d, J = 11.9 Hz), 51.1, 53.4 (d, J = 5.2 Hz), 100.4, 122.1 (d, J = 19.4 Hz), 127.1, 127.3, 128.8, 141.1 (d, J = 20.0 Hz), 143.5, 164.5 (d, J = 9.7 Hz), 167.1; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 9.165; IR (CH_2Cl_2) ν 3061, 2963, 2904, 1714, 1655, 1372, 1262, 1168, 1114, 1028, 803, 764, 701, 651 cm^{-1}; MS (ESI) m/z 339.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{16}H_{20}O_6P$ requires (M+H$^+$): 339.1001, found: 339.0992.

Ethyl 6-(di-*tert*-butoxyphosphoryl)-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate 3ba. A slightly yellow liquid (27.5 mg, 63%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.08 (t, J = 7.2 Hz, 3H), 1.46 (s, 9H), 1.51 (s, 9H), 2.40 (s, 3H), 3.96–4.06 (m, 2H), 4.42 (d, J = 4.8 Hz, 1H), 5.99 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.17–7.20 (m, 3H), 7.26–7.29 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.7, 19.2, 29.6–31.0 (m, 6C), 38.2 (d, J = 10.4 Hz), 60.1, 83.5, 104.6, 118.3 (d, J = 21.5 Hz), 126.7, 128.0, 128.3, 142.6, 144.6, 144.9, 160.2 (d, J = 8.2 Hz), 167.1; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ –2.515; IR (CH_2Cl_2) ν 2980, 2902, 2884, 1714, 1659, 1626, 1476, 1372, 1262, 1171, 1108, 1041, 992, 804, 700 cm^{-1}; MS (ESI) m/z 459.3 (M+Na$^+$); HRMS (ESI) Calcd for $C_{23}H_{33}O_6PNa$ requires (M+Na$^+$): 459.1907, found: 459.1919.

(*E*)-ethyl 2-(6-(di-*tert*-butoxyphosphoryl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ba. A slightly yellow liquid (3.1 mg, 7%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.54 (s, 18H), 3.05 (dd, J = 13.6 Hz, 6.8 Hz, 1H), 3.61–3.70 (m, 2H), 4.09–4.14 (m, 2H), 5.65 (s, 1H), 6.19 (dd, J = 11.2 Hz, 2.8 Hz, 1H), 7.19–7.21 (m, 2H), 7.22–7.26 (m, 1H), 7.30–7.33 (m, 2H); ^{31}P NMR ($CDCl_3$, 121 MHz, 85% H_3PO_4) δ –3.003; IR (CH_2Cl_2) ν 2977, 2903, 1713, 1655, 1373, 1261, 1170, 1114, 1042, 1014, 801, 739, 700 cm^{-1}; MS (ESI) m/z 459.2 (M+Na$^+$); HRMS (ESI) Calcd for $C_{23}H_{33}O_6PNa$ requires (M+Na$^+$): 459.1907, found: 459.1915.

Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-phenyl-4*H*-pyran-3-carboxylate 3ca. A slightly yellow liquid (31.4 mg, 77%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.09 (t, J = 6.8 Hz, 3H), 1.31 (d, J = 6.4 Hz, 6H), 1.35 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.40 (s, 3H), 3.97–4.06 (m, 2H), 4.44 (d, J = 4.8 Hz, 1H), 4.65–4.73 (m, 2H), 6.10 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.18–7.22 (m, 3H), 7.28–7.30 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 19.0, 23.60 (d, J = 3.8 Hz), 23.65 (d, J = 4.4 Hz), 23.9 (d, J = 4.5 Hz), 38.2 (d, J = 9.9 Hz), 60.1, 71.8 (d, J = 4.9 Hz), 104.8, 120.7 (d, J = 19.8 Hz), 126.8, 127.9, 128.0, 128.4, 139.7, 142.0, 144.3, 159.9 (d, J = 9.4 Hz), 166.8; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.537; IR (CH_2Cl_2) ν 2982, 2905, 2876, 1769, 1720, 1658, 1376, 1261, 1098, 1009, 800, 701 cm^{-1}; MS (ESI) m/z 409.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{29}O_6PNa$ requires (M+Na$^+$): 431.1594, found: 431.1595.

(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-phenyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ca. A slightly yellow liquid (3.2 mg, 8%); ^{1}H NMR ($CDCl_3$, 300 MHz, TMS) δ 1.23 (t, J = 7.2 Hz, 3H), 1.35 (d, J = 6.3 Hz, 6H), 1.39 (d, J = 6.3 Hz, 6H), 3.10 (dd, J = 16.8 Hz, 9.9 Hz, 1H), 3.64–3.71 (m, 2H), 4.07–4.16 (m, 2H), 4.71–4.80 (m, 2H), 5.65 (s, 1H), 6.27 (dd, J = 10.2 Hz, 6.9 Hz, 1H), 7.19–7.26 (m, 3H), 7.30–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz, TMS) δ 14.2, 23.7 (d, J = 4.6 Hz), 24.0 (d, J = 3.5 Hz), 29.9, 35.6 (d, J = 11.4 Hz), 59.8, 71.9 (d, J = 5.7 Hz), 100.4, 120.6 (d, J = 19.4 Hz), 127.1, 127.2, 128.7, 141.3, 142.8, 145.9, 165.1 (d, J = 9.7 Hz), 166.8; ^{31}P NMR ($CDCl_3$, 121.453 MHz, 85% H_3PO_4) δ 5.107; IR (CH_2Cl_2) ν 3063, 2980, 2937, 2902, 1711, 1654, 1352, 1259, 1170, 1110, 1044, 985, 886, 762, 700 cm^{-1}; MS (ESI) m/z 409.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{29}O_6PNa$ requires (M+Na$^+$): 431.1594, found: 431.1579.

Ethyl 4-(4-chlorophenyl)-6-(diisopropoxyphosphoryl)-2-methyl-4*H*-pyran-3-carboxylate 3da. A slightly yellow liquid (34.9 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.31 (d, J = 6.0 Hz, 6H), 1.36 (d, J = 6.0 Hz, 3H), 1.37 (d, J = 6.0 Hz, 3H), 2.40 (s, 3H), 4.00–4.08 (m, 2H), 4.43 (d, J = 4.8 Hz, 1H), 4.64–4.75 (m, 2H), 6.06 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 7.14 (d, J = 7.2 Hz, 2H), 7.28 (d, J = 7.2 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 19.1, 23.0–24.5 (m, 4C), 37.6 (d, J = 10.4 Hz), 60.2, 71.8 (d, J = 5.2 Hz), 71.9 (d, J = 5.2 Hz), 104.4, 119.9 (d, J = 20.0 Hz), 128.6, 129.2, 132.6, 140.1, 142.4, 142.9, 160.2 (d, J = 8.9 Hz), 166.6; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.175; IR (CH_2Cl_2) ν 2980, 2942, 2904, 1714, 1663, 1625, 1488, 1376, 1259, 1176, 1104, 986, 946, 804, 685 cm^{-1}; MS (ESI) m/z 443.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{28}O_6PNa$ requires (M+Na$^+$): 465.1204, found: 465.1193.

(*E*)-Ethyl 2-(4-(4-chlorophenyl)-6-(diisopropoxyphosphoryl)-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4da. A slightly yellow liquid (3.5 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.34 (d, J = 6.4 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.39 (d, J = 6.0 Hz, 6H); 3.16 (dd, J = 15.2 Hz, 7.6 Hz, 1H), 3.55 (dd, J = 15.2 Hz, 6.0 Hz, 1H); 3.64–3.67 (m, 1H), 4.09–4.13 (m, 2H), 4.73–4.79 (m, 2H), 5.65 (s, 1H), 6.22 (dd, J = 10.0 Hz, 4.0 Hz, 1H), 7.13 (d, J = 8.4 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.723; IR (CH_2Cl_2) ν 2980, 2942, 2902, 1713, 1657, 1492, 1375, 1261, 1172, 1116, 1045, 994, 820, 739, 703 cm^{-1}; MS (ESI) m/z 443.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{28}O_6PNa$ requires (M+Na$^+$): 465.1204, found: 465.1213.

Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-(4-nitrophenyl)-4*H*-pyran-3-carboxylate 3ea. A slightly yellow liquid (36.2 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.32 (d, J = 6.4 Hz, 6H), 1.36 (d, J = 6.4 Hz, 3H), 1.38 (d, J = 6.4 Hz, 3H), 2.43 (s, 3H), 4.00–4.06 (m, 2H), 4.58 (d, J = 4.8 Hz, 1H), 4.67–4.74 (m, 2H), 6.04 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 7.38 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 19.3, 23.7 (d, J = 4.6 Hz), 23.9 (d, J = 2.3 Hz), 38.3 (d, J = 9.9 Hz), 60.5, 72.1 (d, J = 5.3 Hz), 103.8, 118.6 (d, J = 19.5 Hz), 123.9, 128.7 141.1, 143.5, 146.9, 151.6, 161.2 (d, J = 8.3 Hz), 166.3; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.597; IR (CH_2Cl_2) ν 3074, 2981, 2906, 2874, 1715, 1662, 1626, 1521, 1375, 1347, 1176, 1105, 988, 854, 806, 700 cm^{-1}; MS (ESI) m/z 454.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{28}NO_8PNa$ requires (M+Na$^+$): 476.1445, found: 476.1461.

Ethyl 4-(4-bromophenyl)-6-(diisopropoxyphosphoryl)-2-methyl-4*H*-pyran-3-carboxylate 3fa. A slightly yellow liquid (38.3 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 6.8 Hz, 3H), 1.31 (d, J = 6.4 Hz, 6H), 1.35 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.39 (s, 3H), 4.00–4.06 (m, 2H), 4.41 (d, J = 4.8 Hz, 1H), 4.65–4.73 (m, 2H), 6.05 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.61 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 19.1, 23.64 (d, J = 2.3 Hz), 23.68 (d, J = 2.3 Hz), 23.9 (d, J = 3.8 Hz), 37.7 (d, J = 10.6 Hz), 60.3, 71.9 (d, J = 5.3 Hz), 104.4 (d, J = 1.5 Hz), 119.8 (d, J = 19.8 Hz), 120.8, 129.6, 131.6, 140.2, 142.5, 143.5 (d, J = 2.3 Hz), 160.2 (d, J = 8.4 Hz), 166.6; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.165; IR (CH_2Cl_2) ν 2979, 2934, 2906, 1713, 1657, 1488, 1448, 1261, 1170, 1111, 1010, 802, 740, 702, 668 cm^{-1}; MS (ESI) m/z 487.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{28}O_6PBrNa$ requires (M+Na$^+$): 509.0699, found: 509.0705.

(*E*)-Ethyl 2-(4-(4-bromophenyl)-6-(diisopropoxyphosphoryl)-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4fa. A slightly yellow liquid (3.1 mg, 6%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H), 1.39 (d, J = 6.4 Hz, 6H); 3.16 (dd, J = 15.2 Hz, 7.6 Hz, 1H), 3.57 (dd, J = 15.2 Hz, 6.4 Hz, 1H), 3.62–3.66 (m, 1H), 4.09–4.14 (m, 2H), 4.72–4.79 (m, 2H), 5.65 (s, 1H), 6.21 (dd, J = 10.0 Hz, 4.0 Hz, 1H), 7.08 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.697; IR (CH_2Cl_2) ν 2980, 2939, 2902, 1714, 1661, 1626, 1485, 1376, 1260, 1176, 1106, 992, 805, 740, 664 cm^{-1}; MS (ESI) m/z 487.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{21}H_{28}O_6PBrNa$ requires (M+Na$^+$): 509.0699, found: 509.0708.

Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-*m*-tolyl-4*H*-pyran-3-carboxylate 3ga. A slightly yellow liquid (32.6 mg, 77%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.32 (d, J = 6.4 Hz, 6H), 1.35 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.31 (s, 3H), 2.39 (s, 3H), 4.00–4.07 (m, 2H), 4.40 (d, J = 4.8 Hz, 1H), 4.66–4.73 (m, 2H), 6.09 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 7.00–7.02 (m, 3H), 7.17 (t, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 19.0, 21.3, 23.6 (d, J = 5.2 Hz), 23.7 (d, J = 5.9 Hz), 24.0 (d, J = 3.7 Hz), 38.1 (d, J = 9.7 Hz), 60.1, 71.7 (d, J = 5.2 Hz), 104.9, 120.8 (d, J = 20.1 Hz), 125.0, 127.6, 128.3, 128.7, 138.0, 139.7, 142.0, 144.3, 159.8 (d, J = 8.2 Hz), 166.9; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 5.259; IR (CH_2Cl_2) ν 2979, 2901, 2884, 1715, 1660, 1626, 1475, 1376, 1261, 1171, 1107, 1011, 801, 739, 703 cm^{-1}; MS (ESI) m/z 423.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{22}H_{31}O_6PNa$ requires (M+Na$^+$): 445.1751, found: 445.1743.

(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-*m*-tolyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ga. A slightly yellow liquid (3.3 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H), 1.39 (d, J = 6.4 Hz, 6H), 2.33 (s, 3H), 3.03 (dd, J = 15.2 Hz, 8.4 Hz, 1H), 3.62–3.64 (m, 1H), 3.70 (dd, J = 15.2 Hz, 6.0 Hz, 1H), 4.08–4.14 (m, 2H), 4.73–4.79 (m, 2H), 5.64 (s, 1H), 6.26 (dd, J = 10.4 Hz, 3.6 Hz, 1H), 6.99–7.00 (m, 2H), 7.06 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.008; IR (CH_2Cl_2) ν 2979, 2903, 1713, 1656, 1375, 1260, 1175, 1112, 1044, 1013, 800, 739, 703 cm^{-1}; MS (ESI) m/z 423.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{22}H_{31}O_6PNa$ requires (M+Na$^+$): 445.1751, found: 445.1744.

Ethyl 6-(diisopropoxyphosphoryl)-4-(4-methoxyphenyl)-2-methyl-4*H*-pyran-3-carboxylate 3ha. A slightly yellow liquid (29.2 mg, 67%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, J = 7.2 Hz, 3H), 1.30 (d, J = 6.4 Hz, 3H), 1.32 (d, J = 6.4 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 6.4 Hz, 3H), 2.37 (s, 3H), 3.78 (s, 3H), 4.00–4.08 (m, 2H), 4.38 (d, J = 4.8 Hz, 1H), 4.65–4.73 (m, 2H), 6.08 (dd, J = 10.0 Hz, 4.8 Hz, 1H), 6.82 (d, J = 8.0 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 19.0, 23.6 (d, J = 1.4 Hz), 23.7 (d, J = 1.4 Hz), 24.0 (d, J = 4.6 Hz), 37.3 (d, J = 9.9 Hz), 55.2, 60.1, 71.7 (d, J = 5.3 Hz), 105.1 (d, J = 2.3 Hz), 113.8, 120.8 (d, J = 19.8 Hz), 129.0, 136.7 (d, J = 2.3 Hz), 139.6, 141.9, 158.5, 159.6 (d, J = 9.2 Hz), 167.0; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.631; IR (CH_2Cl_2) ν 2980, 2937, 2906, 1714, 1626, 1510, 1376, 1259, 1176, 1106, 1070, 991, 946, 805, 745 cm^{-1}; MS (ESI) m/z 439.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{22}H_{31}O_7PNa$ requires (M+Na$^+$): 461.1700, found: 461.1699.

(*E*)-ethyl 2-(6-(diisopropoxyphosphoryl)-4-(4-methoxyphenyl)-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ha. A slightly yellow liquid (3.7 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (d, J = 6.4 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H), 1.38 (d, J = 6.0 Hz, 6H), 3.11 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 3.57–3.63 (m, 2H), 3.79 (s, 3H), 4.08–4.14 (m, 2H), 4.72–4.78 (m, 2H), 5.64 (s, 1H), 6.24 (dd, J = 10.4 Hz, 4.4 Hz, 1H), 6.85 (d, J = 8.4 Hz, 2H), 7.12 (d, J = 8.4 Hz, 2H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.061; IR (CH_2Cl_2) ν 2968, 2902, 2839, 1713, 1657, 1513, 1474, 1447, 1375, 1172, 1109, 1046, 1016, 803, 738, 702 cm^{-1}; MS

(ESI) *m/z* 439.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{22}H_{31}O_7PNa$ requires (M+Na$^+$): 461.1700, found: 461.1694.

Ethyl 6-(diisopropoxyphosphoryl)-2-methyl-4-(naphthalen-1-yl)-4*H*-pyran-3-carboxylate 3ia. A slightly yellow liquid (36.2 mg, 79%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.74 (t, J = 7.2 Hz, 3H), 1.25 (d, J = 6.4 Hz, 3H), 1.29 (d, J = 5.2 Hz, 3H), 1.30 (d, J = 6.0 Hz, 3H), 1.36 (d, J = 6.4 Hz, 3H), 2.49 (s, 3H), 3.85 (q, J = 7.2 Hz, 2H), 4.53–4.62 (m, 1H), 4.65–4.73 (m, 1H), 5.34 (d, J = 4.8 Hz, 1H), 6.21 (dd, J = 10.4 Hz, 4.8 Hz, 1H), 7.32 (d, J = 6.8 Hz, 1H), 7.42 (t, J = 8.0 Hz, 1H), 7.47–7.56 (m, 2H), 7.71 (d, J = 8.0 Hz, 1H), 7.86 (d, J = 8.0 Hz, 1H), 8.19 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.6, 18.9, 23.5 (d, J = 4.4 Hz), 23.6 (d, J = 5.2 Hz), 23.87 (d, J = 4.4 Hz), 23.91 (d, J = 4.4 Hz), 33.1 (d, J = 10.5 Hz), 60.0, 71.66 (d, J = 5.2 Hz), 71.72 (d, J = 6.0 Hz), 104.3 (d, J = 1.5 Hz), 120.2 (d, J = 21.1 Hz), 122.5, 125.60, 125.61, 126.3, 127.3, 128.7, 130.4, 133.7, 139.5, 140.8 (d, J = 2.2 Hz), 141.8, 160.4 (d, J = 8.2 Hz), 166.8; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.637; IR (CH_2Cl_2) ν 3059, 2980, 2939, 1713, 1665, 1627, 1375, 1327, 1258, 1106, 984, 798, 776, 740, 702 cm^{-1}; MS (ESI) *m/z* 459.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{25}H_{31}O_6PNa$ requires (M+Na$^+$): 481.1751, found: 481.1760.

(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-(naphthalen-1-yl)-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ia. A slightly yellow liquid (2.6 mg, 6%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.16 (t, J = 7.2 Hz, 3H), 1.38 (d, J = 6.0 Hz, 6H), 1.40 (d, J = 6.0 Hz, 6H), 3.22 (dd, J = 15.2 Hz, 8.4 Hz, 1H), 3.87 (dd, J = 15.2 Hz, 5.6 Hz, 1H), 4.00–4.08 (m, 2H), 4.47–4.50 (m, 1H), 4.77–4.84 (m, 2H), 5.68 (s, 1H), 6.38 (dd, J = 10.4 Hz, 3.6 Hz, 1H), 7.32 (d, J = 6.8 Hz, 1H), 7.42 (t, J = 7.6 Hz, 1H), 7.49–7.58 (m, 2H), 7.77 (d, J = 7.6 Hz, 1H), 7.89 (d, J = 7.6 Hz, 1H), 8.04 (d, J = 8.4 Hz, 1H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 3.937; IR (CH_2Cl_2) ν 2981, 2901, 1712, 1657, 1474, 1374, 1261, 1175, 1116, 1046, 1013, 88, 801, 739 cm^{-1}; MS (ESI) *m/z* 459.3 (M+H$^+$); HRMS (ESI) Calcd for $C_{25}H_{31}O_6PNa$ requires (M+Na$^+$): 481.1751, found: 481.1743.

Ethyl 6-(diisopropoxyphosphoryl)-2,4-dimethyl-4*H*-pyran-3-carboxylate 3ja. A slightly yellow liquid (20.8 mg, 60%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.16 (d, J = 6.4 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 1.30 (d, J = 6.0 Hz, 3H), 1.34 (d, J = 6.0 Hz, 3H), 1.36 (d, J = 6.0 Hz, 3H), 1.38 (d, J = 6.0 Hz, 3H), 2.27 (s, 3H), 3.29–3.35 (m, 1H), 4.16–4.26 (m, 2H), 4.64–4.76 (m, 2H), 6.07 (dd, J = 10.0 Hz, 5.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.2, 19.1, 23.4 (d, J = 2.7 Hz), 23.6 (d, J = 4.5 Hz), 24.0 (d, J = 3.8 Hz), 26.7 (d, J = 10.2 Hz), 60.1, 71.6 (d, J = 5.3 Hz), 71.7 (d, J = 5.3 Hz), 106.4, 122.6 (d, J = 20.1 Hz), 140.5, 142.8, 160.0 (d, J = 8.4 Hz), 167.3; ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.672; IR (CH_2Cl_2) ν 2980, 2937, 2905, 2874, 1713, 1665, 1625, 1375, 1259, 1163, 1056, 989, 945, 801, 662, 611 cm^{-1}; MS (ESI) *m/z* 347.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{16}H_{27}O_6PNa$ requires (M+Na$^+$): 369.1438, found: 369.1439.

(*E*)-Ethyl 2-(6-(diisopropoxyphosphoryl)-4-methyl-3,4-dihydro-2*H*-pyran-2-ylidene)acetate 4ja. A slightly yellow liquid (5.2 mg, 15%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.13 (d, J = 7.2 Hz, 3H), 1.28 (t, J = 7.2 Hz, 3H), 1.32 (d, J = 6.4 Hz, 3H), 1.33 (d, J = 6.4 Hz, 3H), 1.37 (d, J = 5.6 Hz, 6H), 2.45–2.92 (m, 1H), 2.68 (dd, J = 14.8 Hz, 8.4 Hz, 1H), 3.44 (dd, J = 14.8 Hz, 5.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 4.66–4.74 (m, 2H), 5.61 (s, 1H), 6.08 (dd, J = 10.4 Hz, 4.0 Hz, 1H); ^{31}P NMR ($CDCl_3$, 161.93 MHz, 85% H_3PO_4) δ 4.380; IR (CH_2Cl_2) ν 2978, 2906, 1713, 1657, 1375, 1351, 1261, 1114, 1048, 1014, 803, 739, 703 cm^{-1}; MS (ESI) *m/z* 347.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{16}H_{27}O_6PNa$ requires (M+Na$^+$): 369.1438, found: 369.1421.

General procedure for the preparation of 6 and 7 from the reaction of 5a with 2a using 6aa and 7aa as an example in the presence of DABCO

To a mixture of **1a** (0.10 mmol, 20.4 mg), **2a** (0.12 mmol, 13.6 μL) and DABCO (2.2 mg, 0.02 mmol) was added 3.0 mL of THF at –10 °C. The reaction solution was monitored by TLC. After the reaction was complete, the solution was concentrated under reduced pressure and the residue was further purified by silica gel column chromatography (EtOAc/PE = 1/6) to give the target products **6aa** and **7aa**.

Diethyl 6-methyl-4-phenyl-4*H*-pyran-2,5-dicarboxylate 6aa. A slightly yellow liquid (2.7 mg, 7%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.08 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 3.99–4.06 (m, 2H), 4.21–4.30 (m, 2H), 4.51 (d, J = 5.2 Hz, 1H), 6.26 (d, J = 5.2 Hz, 1H), 7.20–7.24 (m, 3H), 7.29–7.33 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.9, 14.1, 19.1, 38.9, 60.2, 61.5, 104.6, 116.2, 127.0, 128.1, 128.6, 138.9, 144.4, 159.8, 161.1, 166.9; IR (CH_2Cl_2) ν 2980, 2903, 1736, 1714, 1658, 1448, 1374, 1260, 1118, 1018, 860, 802, 761, 739, 700 cm^{-1}; MS (ESI) *m/z* 317.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{20}O_5Na$ requires (M+Na$^+$): 339.1203, found: 339.1206.

(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-phenyl-3,4-dihydro-2*H*-pyran-6-carboxylate 7aa. A slightly yellow liquid (30.0 mg, 95%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 3.11 (dd, J = 8.0 Hz, 4.8 Hz, 1H), 3.68–3.72 (m, 2H), 4.07–4.14 (m, 2H), 4.28–4.34 (m, 2H), 5.75 (s, 1H), 6.45 (d, J = 4.8 Hz, 1H), 7.20–7.22 (m, 2H), 7.26–7.28 (m, 1H), 7.31–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.7, 35.8, 59.8, 61.6, 101.0, 116.5, 127.2, 128.8, 141.3, 141.7, 161.1, 164.6, 166.9; IR (CH_2Cl_2) ν 2981, 2903, 2875, 1736, 1711, 1660, 1493, 1373, 1258, 1170, 1118, 1046, 1015, 821, 760 cm^{-1}; MS (ESI) *m/z* 317.2 (M+H$^+$). HRMS (ESI) Calcd for $C_{18}H_{20}O_5$ requires (M+Na$^+$): 339.1203, found: 339.1206.

Diethyl 4-(4-chlorophenyl)-6-methyl-4*H*-pyran-2,5-dicarboxylate 6ba. A slightly yellow liquid (2.0 mg, 6%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 4.00–4.08 (m, 2H), 4.22–4.31 (m, 2H), 4.49 (d, J = 4.8 Hz, 1H), 6.21 (d, J = 4.8 Hz, 1H), 7.16 (d, J = 8.8 Hz, 2H), 7.27 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.00, 14.04, 19.2, 38.4, 60.3, 61.6, 104.3, 115.5, 128.7, 129.4, 132.8, 139.1, 142.9, 160.1, 161.0, 166.7; IR (CH_2Cl_2) ν 2981, 2904, 1739, 1715, 1629, 1488, 1372, 1327, 1268, 1106, 1049, 1015, 946, 805, 739 cm^{-1}; MS (ESI) *m/z* 373.2 (M+Na$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}ClNaO_5$ requires (M+Na$^+$): 373.0816, found: 373.0813.

(*E*)-Ethyl 4-(4-chlorophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ba. A slightly yellow liquid (28.1 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 3.18 (dd, J = 15.2 Hz, 7.6 Hz, 1H), 3.57 (dd, J = 15.2 Hz, 6.0 Hz, 1H), 3.68–3.72 (m, 1H), 4.08–4.14 (m, 2H), 4.29–4.35 (m, 2H), 5.75 (s, 1H), 6.40 (d,

J = 4.0 Hz, 1H), 7.14 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.5, 35.2, 59.9, 61.7, 101.3, 115.6, 128.6, 128.9, 133.1, 139.7, 142.0, 161.0, 164.0, 166.8; IR (CH_2Cl_2) ν 2981, 2903, 2875, 1736, 1711, 1660, 1493, 1373, 1258, 1170, 1118, 1046, 1015, 821, 760 cm^{-1}; MS (ESI) m/z 373.2 (M+Na$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}ClO_5$ requires (M+Na$^+$): 373.0813, found: 373.0821.

Diethyl 4-(4-bromophenyl)-6-methyl-4*H*-pyran-2,5-dicarboxylate 6ca. A slightly yellow liquid (3.1 mg, 8%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 3.99–4.08 (m, 2H), 4.23–4.30 (m, 2H), 4.48 (d, J = 5.2 Hz, 1H), 6.21 (d, J = 5.2 Hz, 1H), 7.11 (d, J = 8.8 Hz, 2H), 7.43 (d, J = 8.8 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.2, 38.4, 60.3, 61.6, 104.2, 115.4, 120.9, 129.8, 131.7, 139.1, 143.4, 160.1, 160.9, 166.6; IR (CH_2Cl_2) ν 2979, 2902, 1716, 1660, 1373, 1263, 1173, 1107, 1048, 1013, 803, 762, 738, 703 cm^{-1}; MS (ESI) m/z 395.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, found: 417.0320.

(*E*)-Ethyl 4-(4-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ca. A slightly yellow liquid (31.2 mg, 80%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 3.18 (dd, J = 15.2 Hz, 7.2 Hz, 1H), 3.56 (dd, J = 15.2 Hz, 6.4 Hz, 1H), 3.66–3.71 (m, 1H), 4.09–4.13 (m, 2H), 4.30–4.34 (m, 2H), 5.75 (s, 1H), 6.40 (d, J = 5.2 Hz, 1H), 7.09 (d, J = 8.0 Hz, 2H), 7.45 (d, J = 8.0 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.4, 35.3, 59.9, 61.7, 101.3, 115.4, 121.1, 129.0, 131.9, 140.2, 142.0, 161.0, 164.0, 166.8; IR (CH_2Cl_2) ν 3084, 2982, 2904, 1736, 1711, 1659, 1489, 1394, 1300, 1167, 1117, 1011, 859, 818, 760 cm^{-1}; MS (ESI) m/z 417.2 (M+Na$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, found: 417.0315.

Diethyl 4-(3-bromophenyl)-6-methyl-4*H*-pyran-2,5-dicarboxylate 6da. A slightly yellow liquid (3.6 mg, 9%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.12 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 2.44 (s, 3H), 4.00–4.09 (m, 2H), 4.25–4.30 (m, 2H), 4.48 (d, J = 5.2 Hz, 1H), 6.21 (d, J = 5.2 Hz, 1H), 7.16–7.18 (m, 2H), 7.34–7.26 (m, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.2, 38.7, 60.3, 61.7, 104.1, 115.3, 122.7, 126.8, 130.1, 130.2, 131.2, 139.3, 146.7, 160.4, 160.9, 166.5; IR (CH_2Cl_2) ν 3058, 2980, 2873, 1714, 1627, 1590, 1472, 1328, 1267, 1096, 964, 839, 764, 739, 696 cm^{-1}; MS (ESI) m/z 395.2 (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, found: 417.0315.

(*E*)-Ethyl 4-(3-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate 7da. A slightly yellow liquid (29.2 mg, 74%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.24 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 3.12 (dd, J = 14.8 Hz, 6.8 Hz, 1H), 3.61–3.69 (m, 2H), 4.09–4.14 (m, 2H), 4.29–4.35 (m, 2H), 5.76 (s, 1H), 6.39 (d, J = 3.6 Hz, 1H), 7.13–7.16 (m, 1H), 7.21 (t, J = 8.0 Hz, 1H), 7.35 (s, 1H), 7.39–7.41 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 29.5, 35.6, 59.9, 61.8, 101.4, 115.3, 122.8, 126.0, 130.38, 130.41, 130.5, 142.1, 143.6, 161.0, 164.0, 166.8; IR (CH_2Cl_2) ν 3082, 2981, 2903, 2873, 1710, 1658, 1593, 1475, 1393, 1349, 1256, 1111, 1045, 1021, 855, 790, 676 cm^{-1}; MS (ESI) m/z 419.1 (M+Na$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, found: 417.0307.

Diethyl 4-(2-bromophenyl)-6-methyl-4*H*-pyran-2,5-dicarboxylate 6ea. A white solid (3.7 mg, 9%); m.p. 122–124 °C; ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.00 (t, J = 7.2 Hz, 3H), 1.30 (t, J = 7.2 Hz, 3H), 2.50 (s, 3H), 3.93–4.03 (m, 2H), 4.20–4.29 (m, 2H), 5.06 (d, J = 4.8 Hz, 1H), 6.27 (d, J = 4.8 Hz, 1H), 7.05–7.10 (m, 1H), 7.20 (d, J = 8.0 Hz, 1H), 7.27–7.30 (m, 1H), 7.53 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 14.1, 19.0, 38.3, 60.2, 61.6, 103.6, 114.4, 122.7, 128.2, 128.4, 130.0, 132.7, 139.2, 143.4, 161.0, 161.2, 166.5; IR (CH_2Cl_2) ν 3058, 2980, 2873, 1714, 1627, 1590, 1472, 1328, 1267, 1096, 964, 839, 764, 739, 696 cm^{-1}; MS (ESI) m/z 395.2 (M+H$^+$); HRMS (ESI) Calcd. for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, Found: 417.0315.

(*E*)-Ethyl 4-(2-bromophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ea. A slightly yellow liquid (29.8 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 3.20 (dd, J = 15.6 Hz, 7.6 Hz, 1H), 3.59 (dd, J = 15.6 Hz, 6.4 Hz, 1H), 4.07–4.14 (m, 2H), 4.18–4.23 (m, 1H), 4.29–4.35 (m, 2H), 5.75 (s, 1H), 6.42 (d, J = 4.4 Hz, 1H), 7.13–7.17 (m, 2H), 7.27–7.30 (m, 1H), 7.58 (d, J = 8.0 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.09, 14.14, 28.1, 35.2, 59.9, 61.7, 101.5, 115.1, 124.0, 127.9, 128.4, 128.8, 133.1, 140.0, 142.4, 161.1, 163.8, 166.6; IR (CH_2Cl_2) ν 3060, 2980, 2902, 1711, 1659, 1470, 1372, 1298, 1258, 1197, 1108, 1022, 856, 803, 754, 670 cm^{-1}; MS (ESI) m/z 395.0 (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{19}BrO_5Na$ requires (M+Na$^+$): 417.0308, found: 417.0312.

Diethyl 4-(2,4-dichlorophenyl)-6-methyl-4*H*-pyran-2,5-dicarboxylate 6fa. A slightly yellow liquid (4.2 mg, 11%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.05 (t, J = 7.2 Hz, 3H), 1.31 (t, J = 7.2 Hz, 3H), 2.49 (s, 3H), 3.97–4.03 (m, 2H), 4.22–4.29 (m, 2H), 5.03 (d, J = 4.8 Hz, 1H), 6.22 (d, J = 4.8 Hz, 1H), 7.14 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.37 (s, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 13.8, 14.1, 19.1, 35.1, 60.4, 61.7, 103.0, 113.9, 127.8, 129.1, 130.7, 132.8, 133.2, 139.4, 140.4, 160.8, 161.6, 166.3; IR (CH_2Cl_2) ν 3086, 2982, 2906, 1716, 1630, 1586, 1561, 1372, 1270, 1189, 1172, 1097, 1074, 964, 918, 767 cm^{-1}; MS (ESI) m/z 385.3. (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{18}Cl_2NaO_5$ requires (M+Na$^+$): 407.0424, found: 407.0435.

(*E*)-Ethyl 4-(2,4-dichlorophenyl)-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate 7fa. A slightly yellow liquid (29.2 mg, 76%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 3.30 (dd, J = 15.2 Hz, 6.8 Hz, 1H), 3.47 (dd, J = 15.2 Hz, 6.4 Hz, 1H), 4.07–4.19 (m, 3H), 4.30–4.36 (m, 2H), 5.76 (s, 1H), 6.37 (d, J = 4.4 Hz, 1H), 7.09 (d, J = 8.4 Hz, 1H), 7.22 (d, J = 8.4 Hz, 1H), 7.41 (s, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.11, 14.15, 27.7, 32.2, 60.0, 61.8, 101.8, 114.2, 127.5, 129.1, 129.6, 133.7, 134.1, 136.9, 142.7, 160.9, 163.5, 166.6; IR (CH_2Cl_2) ν 3086, 2982, 2905, 1660, 1587, 1561, 1474, 1372, 1299, 1256, 1170, 1104, 1020, 861, 818, 760 cm^{-1}; MS (ESI) m/z 385.3. (M+H$^+$); HRMS (ESI) Calcd for $C_{18}H_{18}Cl_2NaO_5$ requires (M+Na$^+$): 407.0424, found: 407.0435.

Diethyl 6-methyl-4-p-tolyl-4*H*-pyran-2,5-dicarboxylate 6ga. A slightly yellow liquid (2.2 mg, 7%); ^{1}H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.11 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 2.31 (s, 3H), 2.43 (s, 3H), 3.98–4.07 (m, 2H), 4.21–3.31 (m, 2H), 4.46 (d, J = 4.8 Hz, 1H), 5.74 (s, 1H), 6.25 (d, J = 4.8 Hz, 1H), 7.08–7.13 (m, 4H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.1, 21.0, 38.5, 60.2, 61.5, 104.8, 116.4, 128.0, 129.3, 136.7, 138.9,

141.5, 159.6, 161.2, 167.0; IR (CH_2Cl_2) ν 2979, 2902, 1715, 1659, 1629, 1511, 1446, 1373, 1324, 1263, 1172, 1106, 1021, 865, 803, 739 cm^{-1}; MS (ESI) m/z 353.1 ($M+Na^+$); HRMS (ESI) Calcd for $C_{19}H_{22}O_5Na$ requires ($M+Na^+$): 353.1359, found: 353.1371.

(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-*p*-tolyl-3,4-dihydro-2*H*-pyran-6-carboxylate 7ga. A slightly yellow liquid (25.9 mg, 78%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.23 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 2.33 (s, 3H), 3.06–3.13 (m, 1H), 3.62–3.69 (m, 2H), 4.08–4.14 (m, 2H), 4.27–4.33 (m, 2H), 5.74 (s, 1H), 6.43 (d, J = 4.4 Hz, 1H), 7.09 (d, J = 8.4 Hz, 2H), 7.14 (d, J = 8.4 Hz, 2H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.2, 21.0, 29.7, 35.5, 59.8, 61.6, 100.9, 116.8, 127.1, 129.5, 136.9, 138.3, 141.6, 161.2, 164.8, 166.9; IR (CH_2Cl_2) ν 2980, 2902, 1736, 1712, 1658, 1514, 1373, 1297, 1167, 1113, 1045, 1020, 847, 808, 762 cm^{-1}; MS (ESI) m/z 353.1 ($M+Na^+$); HRMS (ESI) Calcd for $C_{19}H_{22}O_5Na$ requires ($M+Na^+$): 353.1359, found: 353.1371.

Diethyl 4-(furan-2-yl)-6-methyl-4*H*-pyran-2,5-dicarboxylate 6ha. A slightly yellow liquid (4.6 mg, 15%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.18 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 4.06–4.18 (m, 2H), 4.25–4.31 (m, 2H), 4.67 (d, J = 5.2 Hz, 1H), 6.05 (d, J = 5.2 Hz, 1H), 6.28–6.29 (m, 2H), 7.27–7.29 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.06, 14.12, 19.1, 32.3, 60.3, 61.6, 102.2, 106.1, 110.5, 112.9, 140.1, 141.6, 156.1, 160.5, 160.9, 166.7; IR (CH_2Cl_2) ν 2980, 2903, 2857, 1738, 1716, 1660, 1475, 1372, 1266, 1173, 1107, 1048, 1020, 798, 763, 739 cm^{-1}; MS (ESI) m/z 329.1 ($M+Na^+$); HRMS (ESI) Calcd for $C_{16}H_{18}O_6Na$ requires ($M+Na^+$): 329.0996, found: 329.1000.

(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-(furan-2-yl)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ha. A slightly yellow liquid (13.8 mg, 45%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.27 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 3.36 (dd, J = 15.2 Hz, 8.0 Hz, 1H), 3.56 (dd, J = 15.2 Hz, 5.2 Hz, 1H), 3.78–3.83 (m, 1H), 4.15 (q, J = 7.2 Hz, 2H), 4.30 (q, J = 7.2 Hz, 2H), 5.76 (s, 1H), 6.13–6.14 (m, 1H), 6.30–6.31 (m, 1H), 6.45 (d, J = 4.0 Hz, 1H), 7.35–7.36 (m, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.1, 14.3, 26.3, 29.7, 59.9, 61.7, 101.4, 105.7, 110.3, 113.4, 141.8, 142.1, 153.4, 161.1, 164.1, 166.9; IR (CH_2Cl_2) ν 2980, 2906, 2874, 1737, 1712, 1660, 1446, 1373, 1298, 1174, 1120, 1046, 1017, 801, 761, 739 cm^{-1}; MS (ESI) m/z 329.1 ($M+Na^+$); HRMS (ESI) Calcd for $C_{16}H_{18}O_6Na$ requires ($M+Na^+$): 329.0996, found: 329.1007.

Diethyl 6-methyl-4-(thiophen-2-yl)-4*H*-pyran-2,5-dicarboxylate 6ia. A slightly yellow liquid (2.6 mg, 8%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.19 (t, J = 7.2 Hz, 3H), 1.32 (t, J = 7.2 Hz, 3H), 2.41 (s, 3H), 4.07–4.17 (m, 2H), 4.25–4.31 (m, 2H), 4.83 (d, J = 5.2 Hz, 1H), 6.34 (d, J = 5.2 Hz, 1H), 6.86–6.87 (m, 1H), 6.91 (dd, J = 4.8 Hz, 3.2 Hz, 1H), 7.17 (dd, J = 4.8 Hz, 1.2 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.03, 14.1, 19.1, 33.4, 60.4, 61.6, 104.8, 115.1, 124.6, 124.9, 126.9, 139.4, 148.3, 159.7, 161.0, 166.7; IR (CH_2Cl_2) ν 2980, 2903, 2857, 1738, 1716, 1660, 1475, 1372, 1266, 1173, 1107, 1048, 1020, 798, 763, 739 cm^{-1}; MS (ESI) m/z 345.1 ($M+Na^+$); HRMS (ESI) Calcd for $C_{16}H_{18}O_5SNa$ requires ($M+Na^+$): 345.0767, found: 345.0775.

(*E*)-Ethyl 2-(2-ethoxy-2-oxoethylidene)-4-(thiophen-2-yl)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ia. A slightly yellow liquid (15.7 mg, 49%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.25 (t, J = 7.2 Hz, 3H), 1.34 (t, J = 7.2 Hz, 3H), 3.41 (dd, J = 15.2 Hz, 8.0 Hz, 1H), 3.56 (dd, J = 15.2 Hz, 5.2 Hz, 1H), 3.99–4.03 (m, 1H), 4.13 (q, J = 7.2 Hz, 2H), 4.31 (q, J = 7.2 Hz, 2H), 5.77 (s, 1H), 6.48 (d, J = 4.0 Hz, 1H), 6.90 (d, J = 3.6 Hz, 1H), 6.95 (dd, J = 4.8 Hz, 3.6 Hz, 1H), 7.20 (d, J = 4.8 Hz, 1H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.15, 14.24, 29.8, 31.2, 59.9, 61.7, 101.7, 115.7, 124.4, 124.5, 126.9, 141.5, 144.1, 161.2, 163.9, 166.8; IR (CH_2Cl_2) ν 3075, 2966, 2934, 1736, 1713, 1660, 1373, 1259, 1173, 1259, 1119, 1046, 1020, 802, 762, 738, 701 cm^{-1}; MS (ESI) m/z 345.2 ($M+Na^+$); HRMS (ESI) Calcd for $C_{16}H_{18}O_5SNa$ requires ($M+Na^+$): 345.0767, found: 345.0777.

Diethyl 6-methyl-4-(naphthalen-2-yl)-4*H*-pyran-2,5-dicarboxylate 6ja. A slightly yellow liquid (3.3 mg, 9%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.07 (t, J = 7.2 Hz, 3H), 1.29 (t, J = 7.2 Hz, 3H), 2.48 (s, 3H), 3.98–4.00 (m, 2H), 4.24–4.27 (m, 2H), 4.68 (d, J = 5.2 Hz, 1H), 6.31 (d, J = 5.2 Hz, 1H), 7.38 (dd, J = 8.4 Hz, 1.6 Hz, 1H), 7.44–7.47 (m, 2H), 7.65 (s, 1H), 7.78–7.80 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.0, 14.1, 19.2, 39.1, 60.2, 61.6, 104.6, 116.0, 125.8, 126.1, 126.3, 126.9, 127.6, 127.8, 128.3, 132.6, 133.5, 139.0, 141.8, 159.9, 161.1, 166.9; IR (CH_2Cl_2) ν 3057, 2980, 2902, 1715, 1474, 1373, 1262, 1106, 1048, 1021, 956, 859, 801, 746, 702, 667 cm^{-1}; MS (ESI) m/z 389.2 ($M+Na^+$); HRMS (ESI) Calcd for $C_{22}H_{22}O_5Na$ requires ($M+Na^+$): 389.1359, found: 389.1374.

(*E*)-ethyl 2-(2-ethoxy-2-oxoethylidene)-4-(naphthalen-2-yl)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ja. A slightly yellow liquid (26.7 mg, 73%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 1.21 (t, J = 7.2 Hz, 3H), 1.36 (t, J = 7.2 Hz, 3H), 3.27 (dd, J = 14.8 Hz, 8.4 Hz, 1H), 3.71 (dd, J = 14.8 Hz, 5.2 Hz, 1H), 3.86–3.89 (m, 1H), 4.05–4.12 (m, 2H), 4.31–4.36 (m, 2H), 5.76 (s, 1H), 6.54 (d, J = 4.0 Hz, 1H), 7.34 (dd, J = 8.4 Hz, 1.2 Hz, 1H), 7.46–7.49 (m, 2H), 7.64 (s, 1H), 7.78–7.83 (m, 3H); ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 14.17, 14.20, 29.6, 36.0, 59.8, 61.7, 101.3, 116.3, 125.5, 125.8, 125.9, 126.3, 127.6, 127.7, 128.7, 132.6, 133.4, 138.6, 142.0, 161.2, 164.5, 166.9; IR (CH_2Cl_2) ν 3056, 2982, 2904, 1734, 1709, 1659, 1508, 1474, 1445, 1372, 1298, 1254, 1172, 1115, 854, 817, 760 cm^{-1}; MS (ESI) m/z 389.2 ($M+Na^+$); HRMS (ESI) Calcd for $C_{22}H_{22}O_5Na$ requires ($M+Na^+$): 389.1359, found: 389.1364.

(*E*)-Ethyl 4-cyclopropyl-2-(2-ethoxy-2-oxoethylidene)-3,4-dihydro-2*H*-pyran-6-carboxylate 7ka. A slightly yellow liquid (27.3 mg, 90%); ^1H NMR ($CDCl_3$, 400 MHz, TMS) δ 0.23–0.26 (m, 2H), 0.52–0.56 (m, 2H), 0.70–0.76 (m, 1H), 1.28 (t, J = 7.2 Hz, 3H), 1.35 (t, J = 7.2 Hz, 3H), 1.72–1.79 (m, 1H), 2.92 (dd, J = 15.2 Hz, 8.4 Hz, 1H), 3.48 (dd, J = 15.2 Hz, 5.6 Hz, 1H), 4.16 (q, J = 7.2 Hz, 2H), 4.27–4.32 (m, 2H), 5.70 (s, 1H), 6.32 (d, J = 4.0 Hz, 1H). ^{13}C NMR ($CDCl_3$, 100 MHz, TMS) δ 3.2, 3.6, 14.1, 14.3, 15.3, 27.7, 34.9, 59.8, 61.5, 100.4, 117.1, 141.1, 161.3, 165.7, 167.2. IR (CH_2Cl_2) ν 3081, 2982, 2903, 1737, 1713, 1659, 1372, 1335, 1298, 1256, 1120, 1048, 1021, 854, 761, 740 cm^{-1}. MS (ESI) m/z 281.1 ($M+H^+$). HRMS (ESI) Calcd for $C_{15}H_{20}O_5Na$ requires ($M+Na^+$): 303.1203, found: 303.1209.

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7 The crystal data of compound **6ea** have been deposited in CCDC with number 833190. Empirical Formula: $C_{18}H_{19}BrO_5$; Formula Weight: 395.24; Crystal Color, Habit: colorless; Crystal Dimensions: 0.28 × 0.15 × 0.10 mm; Crystal System: Triclinic; Lattice Type: Primitive; Lattice Parameters: a = 8.5579(17) Å, b = 9.7108(19) Å, c = 11.568(3) Å, = 73.985(4)°, β = 68.692(3)°, γ = 73.448(3)°, V = 842.4(3) Å^3; Space group: $P\bar{1}$; Z = 2; D_c = 1.558 g cm^{-3}; F_{000} = 404; Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0438; wR_2 = 0.1321.

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