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Assembly of Dimethyl Acetylenedicarboxylate and Phosphanes with Aldehydes Leading to γ-Lactones Bearing α-Phosphorus Ylides as Wittig Reagents

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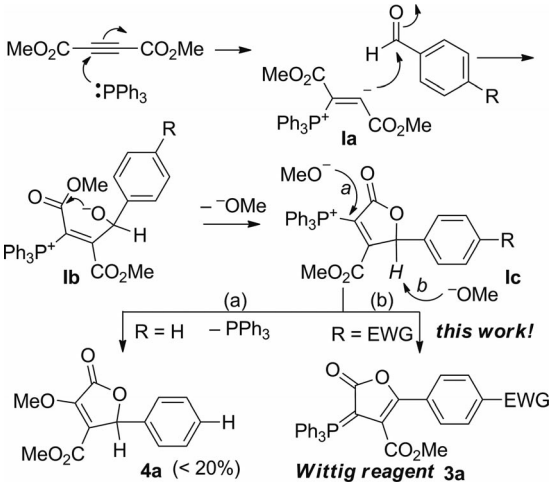
We report herein a convenient route to the synthesis of aryl-substituted γ-lactones bearing an α-phosphorus ylide moiety through the assembly of dimethyl acetylenedicarboxylate (DMAD), electron-deficient aldehydes, and triaryl- or trialkylphosphanes in moderate to good yields. The formation of γ-lactones is highly dependent on the reaction time, the phosphane nucleophile, and the molar ratio of DMAD, aldehyde, and phosphane. We found that reactions with a DMAD/aldehyde/tri-*p*-tolylphosphane molar ratio of 3:1:6 and more electron-deficient aldehydes, such as 4-nitrobenzaldehyde and 4-chloro-3-nitrobenzaldehyde, gave good yields. The isolated ylides reacted with aldehydes as Wittig reagents to give olefins in moderate yields.

Introduction

1,3-Dipolar cycloaddition is a convenient synthetic methodology for the construction of cyclic molecular structures in synthetic chemistry.[1] In this context, nucleophilic carbenoid species generated in situ from phosphanes and electron-deficient acetylenes have received considerable attention due to their application in the construction of heterocyclic molecules.[2] Organophosphanes have been found to mediate such reactions catalytically,[3] and asymmetric versions of the phosphane catalysis and their synthetic applications have also been studied.[4] In recent years, versatile reactions using phosphane catalysis have also been demonstrated for the synthesis of useful heterocycles.[5] Important nucleophilic reagents other than phosphanes, such as pyridines,[6] isoquinolines,[7] and alkyl isocyanides,[8] have also been used with electron-deficient alkynes to promote the formation of 1,3-dipoles. In a previous study, Winterfeldt and Dillinger explored the reactions of aldehydes with a 1,3-dipole **Ia**, generated from dimethyl acetylenedicarboxylate (DMAD) and PPh_3, and they isolated dephosphanated lactone **4a** in low yield (<20%) in the 1960s (Scheme 1).[9] The formation of **4a** was proposed to occur by a dephosphanation step, the methoxide anion generated during the reaction attacking the *P*-substituted sp^2 carbon atom of intermediate **Ic** (pathway *a*; R = H).



Scheme 1. Mechanism for the formation of putative **3a** and **4a**.

We became interested in developing a new synthetic methodology for the total synthesis of dehydrocrotonin (DHC) analogues,[10] which have been used for the treatment of gastrointestinal, kidney, and liver disorders, and have also shown anti-ulcerogenic and anti-tumor activities.[11] Thus, we have investigated whether a putative molecule **3a** could become available or survive as a short-lived intermediate for subsequent Wittig reactions. We envisaged that the methine proton of **Ic** could become acidic enough for deprotonation through the inductive effect of the phenyl ring.

In our recent studies we found that an electron-withdrawing group (EWG) on the phenyl ring will make the methine C–H more acidic,[12] and the methoxide released during the reaction will remove the more acidic C–H proton

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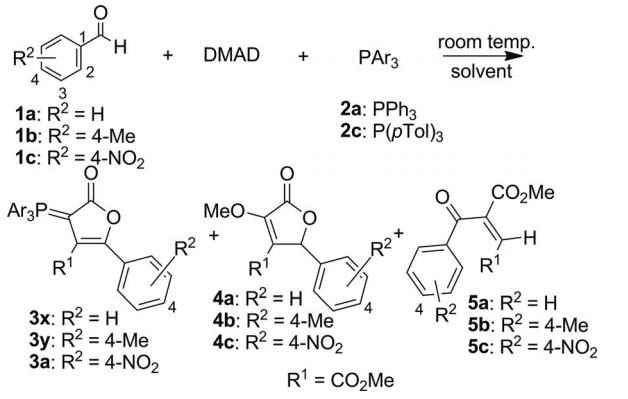
(pathway *b*; R = EWG). Herein we wish to report our synthesis of γ-lactones featuring an α-phosphorus ylide moiety by multicomponent reactions (MCRs) of DMAD, phosphanes, and electron-poor aldehydes in various molar ratios and explore their reactivities as Wittig reagents.

Results and Discussion

We started our investigation by revisiting the parent reaction explored by Winterfeldt and Dillinger[9] to confirm the previously observed low-yielding formation of dephosphanated compound **4a** and the absence of phosphane-containing compounds. We then investigated the use of more electron-poor aldehydes as electrophiles and other triarylphosphanes as nucleophiles to explore the scope of the reaction (Table 1).

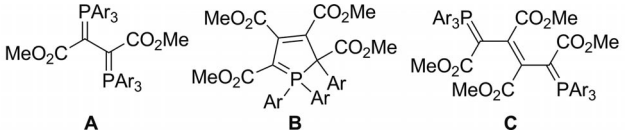
Table 1. Reactions of DMAD with phosphanes **2a** and **2c** and aldehydes **1a**–**c**.[a]



Entry	**1**	**2**	*t* [h]	**3**; yield [%][b]	**4**; Yield [%][b,c]	**5**; Yield [%][b,d]
1	**1a**	**2a**	0.5	**3x**; <2	**4a**; <2	**5a**; 0
2	**1a**	**2a**	24	**3x**; 0	**4a**; 0	**5a**; 0
3	**1b**	**2a**	0.5	**3y**; <2	**4b**; <2	**5b**; <2
4	**1a**	**2c**	0.5	**3x**; 0	**4a**; 0	**5a**; 0
5	**1a**	**2c**	24	**3x**; 0	**4a**; 0	**5a**; 0
6	**1b**	**2c**	0.5	**3y**; 0	**4b**; 0	**5b**; 0
7	**1c**	**2a**	0.5	**3a**; 29 (39)	**4c**; 15 (20)	**5c**; 15 (21)
8	**1c**	**2a**	3	**3a**; 26 (36)	**4c**; 20 (27)	**5c**; 18 (25)
9[e]	**1c**	**2a**	24	**3a**; 19 (26)	**4c**; 22 (30)	**5c**; 23 (31)
10	**1c**	**2a**	48	**3a**; 21 (27)	**4c**; 24 (30)	**5c**; 18 (22)
11	**1c**	**2a**	72	**3a**; 21 (26)	**4c**; 24 (29)	**5c**; 28 (34)
12[f]	**1c**	**2a**	0.5	**3a**; 25 (32)	**4c**; 12 (16)	**5c**; 8 (10)
13[g]	**1c**	**2a**	0.5	**3a**; 29 (44)	**4c**; 16 (25)	**5c**; 10 (15)
14[h]	**1c**	**2a**	0.5	**3a**; 30 (32)	**4c**; 27 (29)	**5c**; 26 (28)
15[i]	**1c**	**2a**	0.5	**3a**; 27	**4c**; 29	**5c**; 32
16[j]	**1c**	**2a**	0.5	**3a**; 21 (34)	**4c**; 13 (20)	**5c**; 15 (24)

[a] All reactions were performed with DMAD (0.500 mmol), **1** (0.500 mmol), and **2** (0.500 mmol) at room temp. in anhydrous CH_2Cl_2 unless otherwise noted. [b] Determined by ^1H NMR spectroscopy using mesitylene as internal standard; the yields in parentheses are based on converted aldehyde. [c] See refs.[9,18] for the known structures **4a**–**c**. [d] See refs.[17,21] for the known structures **5a**–**c**. [e] Reaction was carried out on the 1.0 mmol scale. [f] Reaction was carried out in anhydrous THF. [g] Reaction was carried out in anhydrous 1,2-dichlorobenzene (ODCB). [h] Molar ratio of DMAD/**1**/**2** = 1.5:1:1. [i] Molar ratio of DMAD/**1**/**2** = 3:1:1. [j] Reaction was performed with 1 equiv. of H_2O as an additive.

Entries 1–6 show the absence of γ-lactones **3x**,**y** and **4a**,**b** when benzaldehyde or *p*-tolualdehyde was used as the π electrophile for *t* = 24 h; neither were the products obtained by using more nucleophilic phosphanes. In addition, we only detected trace amounts of **3x**,**y** and **4a**,**b** for *t* = 0.5 h (Entries 1 and 3). We then explored the reactions with the more reactive 4-nitrobenzaldehyde, which produced **3a** under various conditions. We found that **3a** was formed in 29% yield (39% based on converted aldehyde), accompanied by 15% **4c** (20% based on converted aldehyde) and 15% of the side-product **5c** (21% based on converted aldehyde) in anhydrous CH_2Cl_2 (Entry 7). Prolonged reaction times (Entries 7–11) gave lower chemical yields of **3a** (21–29% for *t* = 0.5–72 h) and more of **4c** (15–24% for *t* = 0.5–72 h) and **5c** (15–28% for *t* = 0.5–72 h). We noticed that **3a** was initially formed and then slowly transformed into other species. We also found that THF (Entry 12) and ODCB (Entry 13) were also suitable solvents for this reaction despite the yields of **3a** being slightly lower; the reaction with THF as solvent, however, gave better selectivity. The yield of **3a** did not increase significantly with larger amounts of DMAD (molar ratio of DMAD/**1**/**2** = 1.5:1:1 and 3:1:1, respectively; Entries 14 and 15). We noted that the reactions were moisture-sensitive, because addition of 1 equiv. of water led to a poorer reaction performance (Entry 16). In addition, we also noticed that the fast addition of DMAD, that is, in one portion, caused the formation of other side-products. These side-products were structurally the same as those investigated by Tebby and co-workers, who noted that the 1,3-dipoles generated from DMAD and phosphanes, in competition with aldehydes, reacted to form 1:2 (**A**), 2:1 (**B**), or 1:1 (**C**) adducts of DMAD/phosphanes.[13]



We next evaluated the scope of this reaction by employing a variety of phosphanes **2a**–**i** bearing either electron-donating or -withdrawing groups (EDG or EWG) on their aryl rings or monoalkyl(diaryl)phosphanes (Table 2). We observed that triarylphosphanes bearing electron-releasing groups afforded γ-lactones **3a**–**c** in higher yields based on converted aldehyde (Table 2, Entries 1–3, 39–66%). However, the more nucleophilic phosphane P(4-MeOPh)$_3$ (**2d**) gave a lower yield and selectivity (Entry 4, 16%). Alkyl-substituted phosphane **2e** led to a higher selectivity, but a lower reaction yield (Entry 5, 12%). We observed that the isolated product **3e** was relatively labile. In addition, we attempted to obtain lactone **3** by using phosphites such as P(O*n*Pr)$_3$ and P(O*n*Bu)$_3$ in this three-component reaction instead of triarylphosphanes; however, complex mixtures were formed. These mixtures formed a stripe of spots on TLC plates and could not be separated by silica gel or aluminium oxide column chromatography. However, we isolated stable **3f**, obtained from P(*c*Hex)$_3$ (**2f**), in 18% yield

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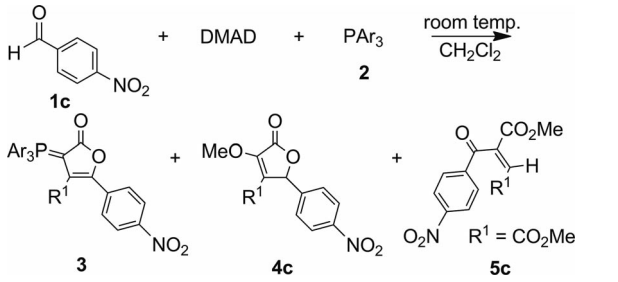
(31% based on converted **1c**) for characterization, which has been attributed to the bulkier tricyclohexyl groups sterically protecting the ylidic moiety (Entry 6). Reactions with phosphanes bearing 4-haloaryl groups, such as $P(4\text{-}ClPh)_3$ and $P(4\text{-}FPh)_3$, also provided the corresponding products (**3g** and **3h**, respectively) in moderate yields of 31 and 30% (68 and 54% based on converted **1c**; Entries 7 and 8), respectively, with less **4c**. The reaction with electron-withdrawing tri-2-thienylphosphane (**2i**) gave a much lower yield and selectivity (Entry 9) with larger amounts of **4c** and **5c** being produced. To summarize, we found that the reaction with tri-*p*-tolylphosphane (**2c**) as nucleophile performed best among the investigated phosphanes with a compromise between yield and selectivity.

Table 2. Reactions of phosphanes **2a**–**i** with DMAD and 4-nitrobenzaldehyde (**1c**).[a]



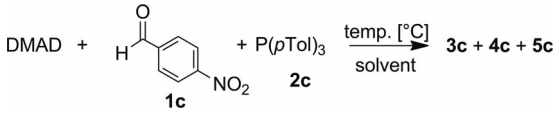
Entry	**2**: PAr_3	**3**; yield [%][b]	**4c**; yield [%][b]	**5c**; yield [%][b]
1	**2a**; PPh_3	**3a**; 29 (39)	15 (20)	15 (21)
2	**2b**; $PPh_2(p\text{Tol})$	**3b**; 29 (47)	12 (19)	12 (19)
3	**2c**; $P(p\text{Tol})_3$	**3c**; 31 (66)	4 (8)	7 (15)
4	**2d**; $P(4\text{-}MeOC_6H_4)_3$	**3d**; 16 (21)	17 (22)	4 (5)
5	**2e**; $PMePh_2$	**3e**; 12 (30)	0	3 (7)
6	**2f**; $P(c\text{Hex})_3$	**3f**; 18 (31)	0	2 (4)
7	**2g**; $P(4\text{-}ClC_6H_4)_3$	**3g**; 31 (68)	2 (5)	12 (26)
8	**2h**; $P(4\text{-}FC_6H_4)_3$	**3h**; 30 (54)	9 (16)	15 (28)
9	**2i**; $P(2\text{-thienyl})_3$	**3i**; 10 (16)	30 (46)	21 (33)

[a] All reactions were performed with DMAD (0.500 mmol), **1c** (0.500 mmol), and **2** (0.500 mmol) in CH_2Cl_2 at room temp.. [b] Determined by ^1H NMR spectroscopy using mesitylene as internal standard; the yields in parentheses are based on converted aldehyde.

Because electron-releasing phosphanes outperform electron-withdrawing phosphanes on selectivities and yields, we chose tri-*p*-tolylphosphane (**2c**) to carry out further optimizations of the reaction (Table 3). We found that the reaction carried out in THF at 0 °C gave a higher yield and selectivity than that performed in CH_2Cl_2 [27 (66) vs. 33% (81%); Entries 1 and 2]. Reactions with higher molar ratios of DMAD (1.5 equiv. with respect to **1c** and **2c**) or with a prolonged reaction time (4 h) did not improve the yield significantly (Entries 3–5); unreacted aldehydes were recovered under these conditions. Parallel increments of DMAD and **2c**, to give a molar ratio of DMAD/**1c**/**2c** = 2:1:2, resulted in less recovered aldehyde and higher yields of **3c** (33% for t = 0.5 h and 50% for t = 3 h; Entries 6 and 7). It was interesting that the reaction carried out at –60 °C (Entry 8) gave a lower yield than that carried out at 0 °C, and a large amount of **4c** (26%) was observed under these conditions. Adjustment of the molar ratio of DMAD/**1c**/**2c** to 2:1:4 exclusively provided **3c** in 66% yield for t = 3 h (Entry 9); however, for t = 6 h, **3c** was obtained in a lower yield of 56% and was accompanied by **4c** in 31% yield (Entry 10). We finally obtained **3c** in up to 86% yield selectively with a molar ratio of DMAD/**1c**/**2c** = 3:1:6 (Entry 11); these reaction conditions were found to be quite reproducible giving yields of 76–86%.

With the optimized conditions in hand, we further explored the reaction scope by using other electron-deficient aldehydes in a DMAD/aldehyde/phosphane molar ratio of 3:1:6 (Table 4). We found that aldehydes such as 3- and 2-nitrobenzaldehydes (**1d** and **1e**) gave 65 and 43% yields of

Table 3. Optimization of the reaction conditions.[a]



Entry	Molar ratio of DMAD/**1c**/**2c**	Temp.[°C]	Time [min]	**3c**; yield [%][b]	**4c**; yield [%][b]	**5c**; yield [%][b]
1[c]	1:1:1	r.t.	30	27 (66)	4 (8)	7 (15)
2	1:1:1	0	30	33 (81)	0	4 (10)
3	1.5:1:1	0	30	31 (72)	0	5 (12)
4	1.5:1:1	0	240[d]	35 (69)	1 (2)	4 (8)
5	1.5:1:1	0	240[e]	28 (71)	0	4 (11)
6	2:1:2	0	30	33 (62)	0	5 (8)
7	2:1:2	0	180	50	23	0
8	2:1:2	–60	180[f]	35	26	13
9	2:1:4	0	180	66 (77)	0	0
10	2:1:4	0	360	56	31	0
11	3:1:6	0	180	86	0	0

[a] All reactions were carried out in THF under nitrogen unless otherwise noted. The reaction time included the initial 10 min injection time of a DMAD solution. [b] Determined by ^1H NMR spectroscopy using mesitylene as internal standard; the yields in parentheses are based on converted aldehyde. [c] The reaction was carried out in CH_2Cl_2. [d] DMAD in THF (10 mL) was added through a syringe pump over 3 h and the mixture stirred for 1 h. [e] DMAD in THF (20 mL) was added through a syringe pump over 3 h and and the mixture stirred for 1 h. [f] DMAD in THF (10 mL) was added at –60 °C in one portion and the mixture stirred at room temp. for 3 h.

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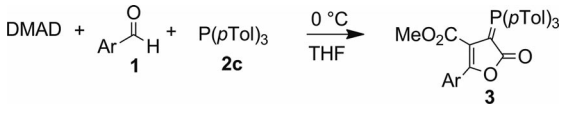
3j and **3k**, respectively (72 and 56% based on converted **1d** and **1e**; Entries 2 and 3); some unreacted aldehyde was recovered in each case. We noted that compound **3k** is relatively unstable upon isolation. Disubstituted benzaldehydes such as 4-chloro-3-nitro- and 4-fluoro-3-nitrobenzaldehydes (**1f** and **1g**; Entries 4 and 5) gave moderate to good yields (78 and 52%, respectively, 84% based on converted **1g**). This indicates that the aryl ring of the 4-fluoro-substituted aldehyde is more electron-rich than that of the 4-chloro-substituted aldehyde. Finally, reactions with 4-cyano and 4-pyridyl aldehydes as electrophiles gave lower yields (49 and 37%, respectively), but moderate to good yields based on converted aldehyde (60 and 62%, Entries 6 and 7, respectively). This is likely due to their lower reactivities. In summary, this study of reaction scope provided reaction yields in the range of 37–86% (56–86% based on converted aldehyde).

Table 4. Reaction of DMAD and **2c** with aldehydes **1c**–**i**.[a]



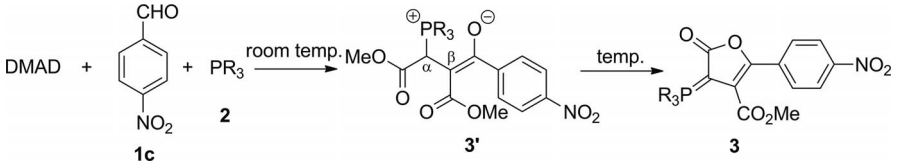
Entry	**1**; Ar	**3**; yield [%][b]
1	**1c**; 4-$O_2NC_6H_4$	**3c**; 86
2	**1d**; 3-$O_2NC_6H_4$	**3j**; 65 (72)
3	**1e**; 2-$O_2NC_6H_4$	**3k**; 43 (56)
4	**1f**; 4-Cl-3-$O_2NC_6H_3$	**3l**; 78
5	**1g**; 4-F-3-$O_2NC_6H_3$	**3m**; 52 (84)
6	**1h**; 4-NCC_6H_4	**3n**; 49 (60)
7	**1i**; 4-pyridyl	**3o**; 37 (62)

[a] All reactions were performed with DMAD (0.500 mmol), DMAD (0.167 mmol), and **2c** (1.000 mmol; DMAD/**1**/**2c** = 3:1:6) at 0 °C; DMAD in THF (10 mL) was added through a syringe pump over 10 min and the mixture stirred for 3 h. [b] Determined by ^{1}H NMR spectroscopy using mesitylene as internal standard; the yields in parentheses are based on converted aldehyde.

We also evaluated the reactions yielding ylides incorporating trialkylphosphanes **2j**–**m** (Table 5). To our surprise, we isolated zwitterionic intermediates **3p′**–**3s′** in 60–64% yields, which are precursors to the ylides **3p**–**3s**; in these reactions, only trace amounts of **3p**–**3s** were observed. Intermediates of type **3p′**–**3s′** have recently been discovered by Kwon and co-workers.[14] The transformation of intermediates **3p′**–**3s′** into ylides **3p**–**3s** requires an initial C_α–C_β bond rotation (structure **3′** in Table 5) for subsequent intramolecular lactonization. We observed that intermediate **3p′** bearing tri-*n*-butylphosphane (**2j**) was transformed into reddish ylide **3p** on slightly acidic silica gel at room temperature over 2 d (60%, Entry 1). However, the lactonization of **3q′**–**3s′** is less effective as these intermediates have shorter alkyl chains. We found that intermediates **3r′** and **3s′** are quite stable and can be isolated in yields of 61 and 64%, respectively (Entries 3 and 4, respectively), accompanied by lactones **3r** and **3s** as side-products (13 and 10%, respectively). To obtain **3r** and **3s** more efficiently, we heated the intermediates **3r′** and **3s′** to give **3r** and **3s** in moderate to good yields (81 and 53%, Entries 3 and 4). This reflects the fact that intermediates with bulkier substituents such as the *n*-butyl group are less stable due to steric hindrance and that with methyl or ethyl groups they are more stable at room temperature due to stronger intramolecular bonding between the charged oxygen and phosphorus groups in intermediates **3r′** and **3s′**.

We characterized the γ-lactones **3a**–**3s** by IR and ^{1}H, ^{31}P, and ^{13}C NMR spectroscopy, ESI-MS, and X-ray crystallography. All MS data corresponded to the expected formulae of the isolated γ-lactones. In the IR spectra, the C=O stretching band next to the ylidic carbanion appears at around 1669–1704 cm^{-1}, lower than that of a normal C=O stretching frequency because of resonance effects. In the ^{31}P NMR spectrum of compound **3o** as an example, we observed a signal at δ = 13.9 ppm corresponding to a typical α-ylidic γ-lactone. Its ^{1}H NMR spectrum displays singlets

Table 5. Reactions of DMAD with alkylphosphanes **2j**–**m** and aldehyde **1c**.[a]



Entry	**2**; R	**3′**; yield [%][b]	**3′** to **3**; yield [%][c]
1	**2j**; *n*Bu	**3p′**; 62 (82)	**3p**; 60[d]
2	**2k**; *n*Pr	**3q′**; 60 (72)	**3q**; 56[d]
3	**2l**; Et	**3r′**; 61 (75)	**3r**; 81[e]
4	**2m**; Me	**3s′**; 64[f]	**3s**; 53[e]

[a] All reactions were performed with a DMAD/**1c**/**2** molar ratio of 1:1:1 under anhydrous conditions at room temp. unless otherwise noted; phosphane **2** in THF was added through a syringe pump over 10 min and the mixture stirred for 50 min. [b] Determined by ^{1}H NMR spectroscopy using mesitylene as internal standard; the yields in parentheses are based on converted aldehyde. [c] Determined by ^{1}H NMR spectroscopy using mesitylene as internal standard. [d] Upon completion of the reaction, solvents were removed under reduced pressure, and ethyl acetate was added followed by further stirring at room temp. for 72 h (two-step yield). [e] The pure intermediates **3r′**–**s′** were first isolated by flash column chromatography, and then **3r′**–**s′** (0.300 mmol) was heated at 80 °C for 12 h to obtain **3r**–**s**. [f] Molar ratio of DMAD/**1c**/**2** = 1:3:1.

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at δ = 2.44 and 2.94 ppm corresponding to methyl and methoxy groups. The two signals in the ^{13}C NMR spectrum at δ = 164.2 and 169.0 ppm ($^2J_{PC}$ = 18.0 Hz) correspond to ester and lactone carbonyl resonances. The signal of the ylidic carbon atom (C2, Figure 1) appears at δ = 54.7 ppm with one-bond coupling to P1 ($^1J_{PC}$ = 135.6 Hz). We found that these isolated ylide compounds tend to crystallize by slow concentration of their chloroform solutions. We determined the crystal structure of compound **3o** by X-ray diffraction (Figure 1).[15] The phosphorus atom P1 is clearly bonded to C2 with a bond length of 1.7480(3) Å. The skeleton of the lactone ring is slightly distorted from planarity, as evidenced from the torsional angle for C2–C1–O1–C4 of –3.1(3)°. Owing to the delocalization of negative charge from the ylidic carbon atom C2 to the carbonyl π bond (C1–O2), the C1–C2 bond is shorter [1.4070(5) Å] than a normal C–C single bond.

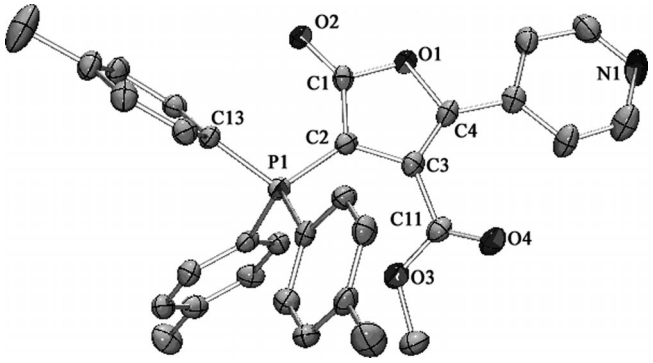
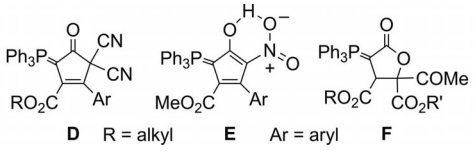


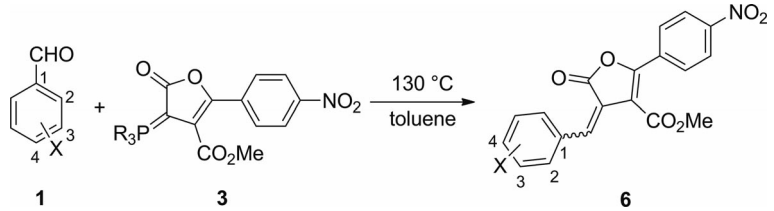
Figure 1. X-ray crystal structure of compound **3o**.

The reactions of DMAD, triarylphosphanes, and aldehydes have previously been investigated by Nozaki,[16] Shi,[17] and Bayat[18] and their co-workers. However, such lactones bearing α-phosphorus ylides were not isolated, likely due to longer reaction times (24 h) or lower loadings of phosphanes in their investigations. We noted that the reactivity of DMAD with phosphanes is higher than that of an enyne; this difference was observed by the slow progress of the reactions of enynes with phosphanes at room temperature.[12a] The efficiency is lower due to the formation of highly polar and non-eluable dark material. However, we isolated lactone ylides **3** in yields of up to 86% under our conditions. The independent work of Nair, Alizadeh, and Yavari and their co-workers[19] resulted in the isolation of cyclopentenylphosphoranes (**D**),[19a] cyclopentadienylphosphoranes (**E**),[19b] or phosphorus lactone (**F**) through the reactions of triphenylphosphane, DMAD, and electron-deficient dicyanostyrenes, 2-(nitroethenyl)benzene, or alkyl 2-chloroacetoacetates.[19f] To the best of our knowledge, these are the first γ-lactones featuring an α-phosphorus ylide moiety to be obtained under our new conditions from the reaction of DMAD, phosphanes, and aldehydes.[20] Our work has provided a convenient and direct route to γ-lactones possessing an α-phosphorus ylide moiety from commercially available reagents in one step, namely by multicomponent reactions (MCRs).



The reactions of these isolated α-ylidic lactones as Wittig reagents with aldehydes were interesting. We found that both **3a** and **3c** reacted with aldehyde **1c** to give only trace amounts of a yellowish mixture of (*E*)- and (*Z*)-**6a** (<1% yield; Table 6, Entries 1 and 2). After prolonging the reaction time from 3 to 21 d, only 3% of (*E*)- and (*Z*)-**6a** was observed (6% based on converted ylide **3a**; Entry 3). However, their synthetic potential becomes notable when these ylides bear alkylphosphanes. The ylides bearing *n*-butyl, *n*-

Table 6. Wittig reaction of ylides with aldehydes.[a]



Entry	**1**; X	**3**; R	Molar ratio of **1**/**3**	Time	**6**; yield [%][b]
1	**1c**; 4-O_2N	**3a**; Ph	1:1	72 h	**6a**; <1
2	**1c**; 4-O_2N	**3c**; *p*Tol	1:1	72 h	**6a**; 1 (2)
3	**1c**; 4-O_2N	**3c**; *p*Tol	1:1	21 d	**6a**; 3 (6)
4	**1c**; 4-O_2N	**3p**; *n*Bu	1:1	72 h	**6a**; 8 (11)
5	**1c**; 4-O_2N	**3q**; *n*Pr	1:1	72 h	**6a**; 13 (22)
6	**1c**; 4-O_2N	**3r**; Et	1:1	72 h	**6a**; 9 (35)
7	**1c**; 4-O_2N	**3s**; Me	1:1	72 h	**6a**; 30 (43)
8	**1d**; 3-O_2N	**3s**; Me	1:1	72 h	**6c**; 39 (74)
9	**1f**; 4-Cl-3-O_2N	**3s**; Me	1:1	72 h	**6b**; 18 (24)
10	**1d**; 3-O_2N	**3s**; Me	1:3	72 h	**6c**; 48 (51)

[a] All reactions were performed in anhydrous toluene in a sealed tube under argon at 130 °C. [b] Determined by ^1H NMR spectroscopy using mesitylene as internal standard; the yields in parentheses are based on converted **3**.

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propyl, ethyl, and methyl groups (**3p**–**s**, respectively) reacted with aldehyde **1c**, with a molar ratio of 1:1, to afford yields of 8–30% (11–43% based on converted aldehyde) at 130 °C in a sealed tube over 3 d (Entries 4–7). We also investigated the reaction of ylide **3s** with aldehyde **1d** and found that this Wittig reaction occurred in higher yield (39%, 74% based on converted aldehyde; Entry 8). By comparing the results of the reactions of the ylides **1c**, **1d**, and **1f** with the less hindered alkylphosphanes **3p**–**s** (Entries 4–9), we concluded that the Wittig reaction between aldehyde **1d** and ylide **3s** gave the highest yield (39%, 74% based on converted aldehyde; Entry 8). A further increment in the molar ratio of **3s** relative to **1d** provided a higher yield of **6c** (48%; 51% based on converted aldehyde; Entry 10). Although the outcome of this Wittig reaction is promising, we found that the most reactive ylide **3s** is unreactive towards ketones such as 4′-nitroacetophenone. A higher reaction temperature does not assist the Wittig reaction with ketones, because decomposition of ylide **3s** becomes notable above 150 °C.

Compound **6a** exhibits an (*E*)/(*Z*) isomeric ratio of 3:1 (based on the crude HPLC chromatogram), and the ratio changed to nearly 1:1 upon exposure to light for a few days. We found that the (*E*) and (*Z*) isomers of **6a**–**c** could not be separated by flash column chromatography (SiO_2); however, one of them, (*E*)- and (*Z*)-**6a**, could be separated by recycling HPLC on the seventh cycle, as shown in the HPLC chromatogram in Figure 2. Owing to the poor solubility of **6b** and **6c**, we could only obtain ^{1}H NMR spectrometric data for the separated (*E*) and (*Z*) isomers of **6a** (see the Supporting Information).

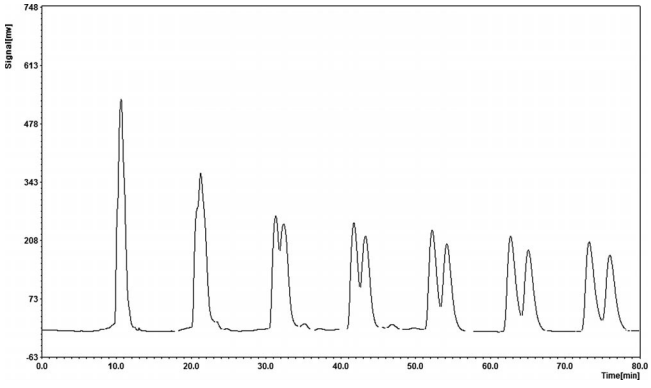

Figure 2. Recycling HPLC chromatogram of (*E*)- and (*Z*)-**6a** (preparative Buckyprep column; 2 cm × 25 cm, eluent: toluene, 50 °C); compound (*E*)-**6a** (shorter retention time) was eluted prior to (*Z*)-**6a**.

Conclusions

We have demonstrated that γ-lactones bearing an α-phosphorus ylide moiety can be efficiently prepared through multicomponent reactions (MCRs) of DMAD, phosphanes, and electron-deficient aldehydes in one step. Tri-*p*-tolylphosphane was found to be the most appropriate phosphane nucleophile for giving the γ-lactone products in good yields. The application of this synthesis could lead to a variety of versatile aryl-substituted γ-lactones. Furthermore, the γ-lactone bearing the trimethylphosphorus ylide moiety reacts with aldehydes to give olefinic compounds in moderate yields. This methodology provides a new tool for use in the synthesis of α-olefinic lactones via γ-lactone ylides prepared in a single pot.

Experimental Section

General Methods: All reactions were performed under nitrogen. Anhydrous CH_2Cl_2 was distilled from CaH_2 under argon. Anhydrous THF was distilled from sodium/benzophenone under argon. The chemical shifts in the ^{31}P NMR spectra are given with 85% of H_3PO_4 in D_2O as reference and those in the ^{1}H and ^{13}C NMR spectra are referenced to TMS or $CHCl_3$. Mesitylene was added to the products isolated by column chromatography to determine their quantity by ^{1}H NMR spectroscopy. After spectroscopic measurement, the isolated products were dissolved in a minimum amount of $CHCl_3$ and precipitated with hexanes in a centrifuge tube. Pure solids were obtained by centrifuge followed by removal of trace solvents under vacuum. NMR, FT-IR and mass data were recorded with Bruker DRX-300, Digilab Excalibur HE series FTS 3100 and Varian 901-MS spectrometers, respectively.

Typical Procedure for the Synthesis of Compound 3a in CH_2Cl_2: DMAD (0.0710 g, 0.500 mmol) in CH_2Cl_2 (10 mL) was added to an anhydrous dichloromethane solution of 4-nitrobenzaldehyde (**1c**; 0.0760 g, 0.500 mmol) and triphenylphosphane (**2a**; 0.1310 g, 0.5000 mmol) through a digital syringe pump in 10 min. The mixture was then stirred at room temp. for 30 min. Upon completion of the reaction, CH_2Cl_2 was removed under vacuum. The mixture was then subjected to flash chromatography. Elution with hexanes/ethyl acetate (EA) (1:1) gave product **3a** (Entry 7, Table 1).

Typical Procedure for the Synthesis of Compound 3c in THF: DMAD (0.0710 g, 0.500 mmol) in THF (10 mL) was added to an anhydrous THF solution (5 mL) containing molecular sieves (4 Å), 4-nitrobenzaldehyde (**1c**; 0.0250 g, 0.170 mmol), and tri-*p*-tolylphosphane (**2c**; 0.3040 g, 1.000 mmol) through a digital syringe pump at 0 °C over 10 min. The mixture was then stirred at 0 °C for 3 h. Upon completion of the reaction, THF was removed under vacuum. The mixture was then subjected to flash chromatography. Elution with hexanes/EA (1:1) gave product **3c** (Entry 11, Table 3).

Typical Procedure for the Synthesis of (*E*)- and (*Z*)-6c: A pressure-affordable reaction tube containing ylide **3s** (0.1000 g, 0.2640 mmol), aldehyde **1d** (0.0130 g, 0.0880 mmol), and a stirring bar in dry toluene (15 mL) was stirred vigorously at 130 °C for 72 h. After completion of the reaction, the reaction mixture was subjected to column chromatography with hexanes/dichloromethane (DCM) (1:3) as eluent to obtain a mixture of (*E*)- and (*Z*)-**6c** (0.0160 g) in 48% yield (51% based on unreacted **1d**) and hexanes/DCM (1:2) as eluent for the recovery of unreacted **1d** (0.0010 g, 8%).

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(triphenyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3a): Red solid. M.p. 214–216 °C. R_f = 0.20 (EA/hexanes, 1:1). Isolated yield 29% (0.0759 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.93 (s, OCH_3), 7.53–7.59 (m, 6 H, Ar-H), 7.63–7.76 (m, 9 H, Ar-H), 7.95 (d, J = 9.2 Hz, 2 H, Ar-H), 8.16 (d, J = 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 50.7 (O*C*H$_3$), 54.0 [d, ^1J(C,P) = 135.9 Hz], 117.2 [d, ^2J(C,P) = 11.5 Hz], 123.4, 123.6 [d, ^1J(C,P) = 95.0 Hz], 127.0,

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128.9 [d, ^3J(C,P) = 12.8 Hz], 133.0 [d, ^4J(C,P) = 2.9 Hz], 133.8 [d, ^2J(C,P) = 10.5 Hz], 136.0, 141.4 [d, ^3J(C,P) = 12.5 Hz], 145.9, 164.0 (C=O), 169.0 [d, ^2J(C,P) = 18.3 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 14.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1685, 1716 cm^{-1}. HRMS (ESI^+): calcd. for $C_{30}H_{22}NO_6P$ $[M]^+$ 523.1165; found 523.1185.

Methyl 4-[Diphenyl(*p*-tolyl)-λ^5-phosphanylidene]-2-(4-nitrophenyl)-5-oxo-4,5-dihydrofuran-3-carboxylate (3b): Orange solid. M.p. 194 °C. R_f = 0.18 (EA/hexanes, 1:1). Isolated yield 29% (0.0779 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.45 (s, CH_3), 2.93 (s, OCH_3), 7.36 (dd, J = 2.9, J = 8.2 Hz, 2 H, Ar-H), 7.52–7.76 (m, 12 H, Ar-H), 7.94 (d, J = 9.1 Hz, 2 H, Ar-H), 8.16 (d, J = 9.2 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.6 [d, ^5J(C,P) = 1.4 Hz, *C*H$_3$], 50.7 (O*C*H$_3$), 54.4 [d, ^1J(C,P) = 135.6 Hz], 117.4 [d, ^2J(C,P) = 11.6 Hz], 119.9 [d, ^1J(C,P) = 97.4 Hz], 123.4, 123.9 [d, ^1J(C,P) = 95.0 Hz], 126.9, 128.9 [d, ^3J(C,P) = 12.9 Hz], 129.7 [d, ^3J(C,P) = 13.3 Hz], 132.9 [d, ^4J(C,P) = 3 Hz], 133.8 [d, ^3J(C,P) = 10.3 Hz], 133.9 [d, ^3J(C,P) = 10.3 Hz], 136.1, 141.1 [d, ^3J(C,P) = 12.2 Hz], 144.0 [d, ^4J(C,P) = 2.9 Hz], 145.8, 164.1 (C=O), 169.0 [d, ^2J(C,P) = 18.2 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 14.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 1685, 1717 cm^{-1}. HRMS (ESI^+): calcd. for $C_{31}H_{24}NO_6P$ $[M]^+$ 537.1341; found 537.1339.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3c): Orange solid. M.p. 216–218 °C. R_f = 0.29 (EA/hexanes, 1:1). Isolated yield 86% (0.0826 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 CH_3), 2.93 (s, OCH_3), 7.33–7.36 (m, 6 H, Ar-H), 7.56–7.63 (m, 6 H, Ar-H), 7.93 (d, J = 9.0 Hz, 2 H, Ar-H), 8.14 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.6 [d, ^5J(C,P) = 1.0 Hz, *C*H$_3$], 50.6 (O*C*H$_3$), 55.3 [d, ^1J(C,P) = 135.2 Hz], 117.8 [d, ^2J(C,P) = 11.6 Hz], 120.3 [d, ^1J(C,P) = 97.4 Hz], 123.3, 126.6, 129.6 [d, ^3J(C,P) = 13.3 Hz], 133.7 [d, ^2J(C,P) = 10.9 Hz], 136.1, 140.6 [d, ^3J(C,P) = 12.3 Hz], 143.7 [d, ^4J(C,P) = 2.9 Hz], 145.6, 164.2 (C=O), 169.0 [d, ^2J(C,P) = 18.1 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1691, 1721 cm^{-1}. HRMS (ESI^+): calcd. for $C_{33}H_{28}NO_6P$ $[M]^+$ 565.1654; found 565.1648.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-[tris(4-methoxyphenyl)-λ^5-phosphanylidene]-4,5-dihydrofuran-3-carboxylate (3d): Red solid. M.p. 80–82 °C. R_f = 0.29 (EA/hexanes, 2:1). Isolated yield 16% (0.0491 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.00 (s, OCH_3), 3.87 (s, 3 OCH_3), 7.04 (dd, J = 2.3, J = 9.0 Hz, 6 H, Ar-H), 7.62 (dd, J = 8.8, J = 12.5 Hz, 6 H, Ar-H), 7.89 (d, J = 9.0 Hz, 2 H, Ar-H), 8.14 (d, J = 9.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 50.9 (O*C*H$_3$), 55.4 (O*C*H$_3$), 56.6 [d, ^1J(C,P) = 135.5 Hz], 114.4 [d, ^2J(C,P) = 14.0 Hz], 114.5 [d, ^1J(C,P) = 102.4 Hz], 118.1 [d, ^2J(C,P) = 11.8 Hz], 123.4, 126.3, 135.6 [d, ^2J(C,P) = 12.2 Hz], 136.1, 140.0 [d, ^3J(C,P) = 12.2 Hz], 145.5, 163.1 [d, ^4J(C,P) = 2.9 Hz], 164.4 (C=O), 169.1 [d, ^2J(C,P) = 18.1 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 12.3 ppm. FTIR (KBr): $\tilde{\nu}$ = 1685, 1717 cm^{-1}. HRMS (ESI^+): calcd. for $C_{33}H_{28}NO_9P$ $[M]^+$ 613.1502; found 613.1498.

Methyl 4-[Methyl(diphenyl)-λ^5-phosphanylidene]-2-(4-nitrophenyl)-5-oxo-4,5-dihydrofuran-3-carboxylate (3e): Orange solid. M.p. 180 °C. R_f = 0.18 (EA/hexanes, 3:1). Isolated yield 12% (0.0277 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.54 (d, J = 13.7 Hz, CH_3), 3.10 (s, OCH_3), 7.57–7.77 (m, 10 H, Ar-H), 7.94 (d, J = 9.1 Hz, 2 H, Ar-H), 8.17 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 13.0 [d, ^1J(C,P) = 62.9 Hz, *C*H$_3$], 50.9 (O*C*H$_3$), 55.1 [d, ^1J(C,P) = 134.5 Hz], 116.5 [d, ^2J(C,P) = 10.9 Hz], 123.3, 125.4 [d, ^1J(C,P) = 94.3 Hz], 127.5, 129.2 [d, ^3J(C,P) = 13.0 Hz], 132.0 [d, ^2J(C,P) = 10.9 Hz], 133.0 [d, ^4J(C,P) = 2.9 Hz], 136.0, 141.5 [d, ^3J(C,P) = 12.2 Hz], 146.1, 163.8 (C=O), 169.7 [d, ^2J(C,P) = 19.2 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 11.3 ppm. FTIR (KBr): $\tilde{\nu}$ = 1682, 1721 cm^{-1}. HRMS (ESI^+): calcd. for $C_{25}H_{20}NO_6P$ $[M]^+$ 461.1028; found 461.1030.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(tricyclohexyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3f): Orange solid. M.p. 233–235 °C. R_f = 0.38 (EA/hexanes, 1:1). Isolated yield 18% (0.0487 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.21–1.92 (m, 15 CH_2), 3.03 (q, J = 12.6 Hz, 3 C*H*), 3.77 (s, OCH_3), 7.55 (d, J = 9.0 Hz, 2 H, Ar-H), 8.15 (d, J = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 25.82 (*C*H$_2$), 27.0 [d, ^3J(C,P) = 12.5 Hz, *C*H$_2$], 27.3 [d, ^2J(C,P) = 3.0 Hz, *C*H$_2$], 31.6 [d, ^1J(C,P) = 40.2 Hz, *C*H], 52.1 (O*C*H$_3$), 52.8 [d, ^1J(C,P) = 110.4 Hz], 118.1 [d, ^2J(C,P) = 9.7 Hz], 123.4, 126.1, 136.5, 139.2 [d, ^3J(C,P) = 10.6 Hz], 145.4, 166.4 (C=O), 170.2 [d, ^2J(C,P) = 15.1 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 27.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1669, 1717 cm^{-1}. HRMS (ESI^+): calcd. for $C_{30}H_{40}NO_6P$ $[M]^+$ 541.2593; found 541.2592.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-[tris(4-chlorophenyl)-λ^5-phosphanylidene]-4,5-dihydrofuran-3-carboxylate (3g): Yellow solid. M.p. 118–120 °C. R_f = 0.40 (EA/hexanes, 1:1.5). Isolated yield 31% (0.0969 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.10 (s, OCH_3), 7.53–7.65 (m, 12 H, Ar-H), 7.93 (d, J = 8.8 Hz, 2 H, Ar-H), 8.18 (d, J = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 51.0 (O*C*H$_3$), 52.2 [d, ^1J(C,P) = 138.6 Hz], 115.9 [d, ^2J(C,P) = 11.4 Hz], 121.8 [d, ^1J(C,P) = 98.3 Hz], 123.2, 127.6, 129.5 [d, ^3J(C,P) = 13.7 Hz], 134.9 [d, ^2J(C,P) = 11.6 Hz], 135.7, 140.3 [d, ^4J(C,P) = 3.8 Hz], 142.5 [d, ^3J(C,P) = 12.8 Hz], 146.2, 163.6 (C=O), 168.7 [d, ^2J(C,P) = 19.6 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 1686, 1716 cm^{-1}. HRMS (ESI^+): calcd. for $C_{30}H_{19}Cl_3NO_6P$ $[M]^+$ 625.0016; found 625.0015.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-[tris(4-fluorophenyl)-λ^5-phosphanylidene]-4,5-dihydrofuran-3-carboxylate (3h): Yellow solid. M.p. 112–114 °C. R_f = 0.19 (EA/hexanes, 1:2). Isolated yield 30% (0.0866 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.09 (s, OCH_3), 7.24–7.31 (m, 6 H, Ar-H), 7.67–7.75 (m, 6 H, Ar-H), 7.91 (d, J = 9.1 Hz, 2 H, Ar-H), 8.16 (d, J = 9.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 50.9 (O*C*H$_3$), 53.2 [d, ^1J(C,P) = 138.2 Hz], 116.2 [d, ^2J(C,P) = 11.5 Hz], 116.5 [dd, ^3J(C,P) = 10.6, ^2J(C,F) = 21.9 Hz], 119.3 [dd, ^4J(C,F) = 3.4, ^1J(C,P) = 100.0 Hz], 123.3, 127.4, 135.8, 136.3 [dd, ^3J(C,F) = 9.2, ^2J(C,P) = 12.3 Hz], 142.1 [d, ^3J(C,P) = 12.4 Hz], 146.2, 163.8 (C=O), 165.6 [dd, ^4J(C,P) = 3.2, ^1J(C,F) = 257.4 Hz], 168.8 [d, ^2J(C,P) = 18.8 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.1 [d, ^5J(P,F) = 1.5 Hz] ppm. FTIR (KBr): $\tilde{\nu}$ = 1686, 1717 cm^{-1}. HRMS (ESI^+): calcd. for $C_{30}H_{19}F_3NO_6P$ $[M]^+$ 577.0902; found 577.0899.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(tri-2-thienyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3i): Red solid. M.p. 180 °C. R_f = 0.29 (EA/hexanes, 2:1). Isolated yield 10% (0.0270 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.14 (s, OCH_3), 7.29–7.33 (m, 3 H, Ar-H), 7.76–7.80 (m, 3 H, Ar-H), 7.91–7.95 (m, 3 H, Ar-H), 7.98 (d, J = 9.1 Hz, 2 H, Ar-H), 8.18 (d, J = 9.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 50.9 (O*C*H$_3$), 56.5 [d, ^1J(C,P) = 150.0 Hz], 116.1 [d, ^2J(C,P) = 13.6 Hz], 123.3, 125.6 [d, ^1J(C,P) = 119.4 Hz], 127.4, 129.0 [d, ^3J(C,P) = 16.1 Hz], 135.9, 136.5 [d, ^4J(C,P) = 5.8 Hz], 139.5 [d, ^2J(C,P) = 12.0 Hz], 141.8 [d, ^3J(C,P) = 13.8 Hz], 146.1, 163.7 (C=O), 168.2 [d, ^2J(C,P) = 20.3 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ =

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–8.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1688 cm^{-1}. HRMS (ESI^+): calcd. for $C_{24}H_{16}NO_6PS_3$ $[M]^+$ 540.9877; found 540.9876.

Methyl 2-(3-Nitrophenyl)-5-oxo-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3j): Orange solid. M.p. 196 °C. R_f = 0.23 (EA/hexanes, 1:1). Isolated yield 65% (0.0625 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 CH_3), 2.98 (s, OCH_3), 7.33 (m, 6 H, Ar-H), 7.48 (t, J = 8.1 Hz, 1 H, Ar-H), 7.58 (m, 6 H, Ar-H), 8.06 (dd, J = 1.5, J = 8.1 Hz, 1 H, Ar-H), 8.11, (d, J = 8.0 Hz, 1 H, Ar-H), 8.76 (t, J = 1.8 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.6 [d, ^5J(C,P) = 1.1 Hz, CH_3], 50.5 (OCH_3), 53.1 [d, ^1J(C,P) = 136.4 Hz], 115.5 [d, ^3J(C,P) = 11.4 Hz], 120.9 [d, ^1J(C,P) = 102.6 Hz], 121.5, 122.1, 128.7, 129.5 [d, ^3J(C,P) = 13.3 Hz], 131.9, 132.8, 133.7 [d, ^2J(C,P) = 10.8 Hz], 141.6 [d, ^3J(C,P) = 12.2 Hz], 143.5 [d, ^4J(C,P) = 3.1 Hz], 147.9, 164.0 (C=O), 169.1 [d, ^2J(C,P) = 18.1 Hz, C=] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.5 ppm. FTIR (KBr): $\tilde{\nu}$ = 1688 (br) cm^{-1}. HRMS (ESI^+): calcd. for $C_{33}H_{28}NO_6P$ $[M]^+$ 565.1654; found 565.1660.

Methyl 2-(2-Nitrophenyl)-5-oxo-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3k): Red solid. M.p. 96–98 °C. R_f = 0.28 (EA/hexanes, 1.5:1). Isolated yield 43% (0.0413 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.42 (s, 3 CH_3), 2.94 (s, OCH_3), 7.31 (dd, J = 2.8, J = 8.2 Hz, 6 H, Ar-H), 7.44 (dt, J = 1.5, J = 8.2 Hz, 1 H, Ar-H), 7.53–7.60 (m, 7 H, Ar-H), 7.69 (dd, J = 1.4, J = 7.8 Hz, 1 H, Ar-H), 7.97 (dd, J = 1.2, J = 8.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (75.48 MHz, $CDCl_3$, 25 °C): δ = 21.6 [d, ^5J(C,P) = 1.3 Hz, CH_3], 50.0 [d, ^1J(C,P) = 137.1 Hz], 50.3 (OCH_3), 114.2 [d, ^2J(C,P) = 10.5 Hz], 121.6 [d, ^1J(C,P) = 98.1 Hz], 124.2, 126.5, 128.8, 129.4 [d, ^3J(C,P) = 13.3 Hz], 132.1, 132.3, 133.7 [d, ^2J(C,P) = 10.8 Hz], 141.6 [d, ^3J(C,P) = 12.6 Hz], 143.2 [d, ^4J(C,P) = 3.0 Hz], 148.7, 163.1 (C=O), 169.6 [d, ^2J(C,P) = 18.8 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.8 ppm. FTIR (KBr): $\tilde{\nu}$ = 1699 (br) cm^{-1}. HRMS (ESI^+): calcd. for $C_{33}H_{28}NO_6P$ $[M]^+$ 565.1654; found 565.1636.

Methyl 2-(4-Chloro-3-nitrophenyl)-5-oxo-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3l): Orange solid. M.p. 188 °C. R_f = 0.18 (EA/hexanes, 1:1). Isolated yield 78% (0.0794 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.42 (s, 3 CH_3), 2.92 (s, OCH_3), 7.32 (dd, J = 2.7, J = 8.1 Hz, 6 H, Ar-H), 7.42 (d, J = 6.0 Hz, 1 H, Ar-H), 7.53–7.60 (m, 6 H, Ar-H), 7.97 (dd, J = 2.1, J = 8.7 Hz, 1 H, Ar-H), 8.47 (d, J = 2.1 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.5 [d, ^5J(C,P) = 1.1 Hz, CH_3], 50.4 (OCH_3), 53.5 [d, ^1J(C,P) = 136.0 Hz], 116.1 [d, ^2J(C,P) = 11.4 Hz], 120.6 [d, ^1J(C,P) = 97.7 Hz], 123.7, 124.2, 129.5 [d, ^3J(C,P) = 13.4 Hz], 130.1, 130.9, 131.0, 133.5 [d, ^2J(C,P) = 10.8 Hz], 140.3 [d, ^3J(C,P) = 12.2 Hz], 143.5 [d, ^4J(C,P) = 2.9 Hz], 147.4, 163.7 (C=O), 168.7 [d, ^2J(C,P) = 18.4 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 14.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 1695 (br) cm^{-1}. HRMS (ESI^+): calcd. for $C_{33}H_{27}ClNO_6P$ $[M]^+$ 599.1265; found 599.1257.

Methyl 2-(4-Fluoro-3-nitrophenyl)-5-oxo-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3m): Yellow solid. M.p. 208–210 °C. R_f = 0.19 (EA/hexanes, 1:1). Isolated yield 52% (0.0516 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 CH_3), 2.94 (s, OCH_3), 7.21 (t, J = 9.4 Hz, 1 H, Ar-H), 7.34 (dd, J = 2.6, J = 8.0 Hz, 6 H, Ar-H), 7.55–7.62 (m, 6 H, Ar-H), 8.09–8.14 (m, 1 H, Ar-H), 8.68 (dd, J = 2.2, J = 7.3 Hz, 1 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.5 [d, ^5J(C,P) = 1.1 Hz, CH_3], 50.3 (OCH_3), 52.7 [d, ^1J(C,P) = 136.6 Hz], 115.2 [d, ^2J(C,P) = 11.1 Hz], 117.6 [d, J(C,F) = 21.1 Hz], 120.7 [d, ^1J(C,P) = 97.7 Hz], 124.6 [d, J(C,F) = 2.8 Hz], 127.5 [d, J(C,F) = 4.2 Hz], 129.4 [d, ^3J(C,P) = 13.3 Hz], 133.5 [d, ^4J(C,P) = 10.7 Hz], 133.9 [d, J(C,F) = 8.4 Hz], 136.7 [d, J(C,F) = 7.8 Hz], 140.8 [d, ^3J(C,P) = 12.4 Hz], 143.4 [d, ^4J(C,P) = 3.0 Hz], 153.9 [d, ^1J(C,F) = 265.7 Hz], 163.7 (C=O), 168.8 [d, ^2J(C,P) = 18.5 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.6 ppm. FTIR (KBr): $\tilde{\nu}$ = 1704 (br) cm^{-1}. HRMS (ESI^+): calcd. for $C_{33}H_{27}FNO_6P$ $[M]^+$ 583.1560; found 583.1568.

Methyl 2-(4-Cyanophenyl)-5-oxo-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3n): Yellow solid. M.p. 182–184 °C. R_f = 0.19 (EA/hexanes, 1:1). Isolated yield 49% (0.0454 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 CH_3), 2.91 (s, OCH_3), 7.32–7.35 (m, 6 H, Ar-H), 7.55–7.62 (m, 8 H, Ar-H), 7.90 (d, J = 6.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.5 (CH_3), 50.5 (OCH_3), 54.2 [d, ^1J(C,P) = 136.0 Hz], 109.6, 116.6 [d, ^2J(C,P) = 11.4 Hz], 119.3, 120.6 [d, ^1J(C,P) = 97.5 Hz], 126.9, 129.6 [d, ^3J(C,P) = 13.3 Hz], 131.6, 133.7 [d, ^2J(C,P) = 10.9 Hz], 136.1, 141.4 [d, ^3J(C,P) = 12.4 Hz], 143.6 [d, ^4J(C,P) = 2.9 Hz], 164.2 (C=O), 169.1 [d, ^2J(C,P) = 18.1 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 1702, 1719 cm^{-1}. HRMS (ESI^+): calcd. for $C_{34}H_{28}NO_4P$ $[M]^+$ 545.1756; found 545.1779.

Methyl 5-Oxo-2-pyridin-4-yl-4-(tri-*p*-tolyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3o): Orange solid. M.p. 216–218 °C. R_f = 0.28 (EA/hexanes, 3:1). Isolated yield 37% (0.0328 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.44 (s, 3 CH_3), 2.94 (s, OCH_3), 7.33 (dd, J = 2.9, J = 8.2 Hz, 6 H, Ar-H), 7.58 (dd, J = 8.2, J = 12.9 Hz, 6 H, Ar-H), 7.65 (dd, J = 1.5, J = 4.8 Hz, 2 H, Ar-H), 8.51 (dd, J = 1.5, J = 4.8 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 21.6 [d, ^5J(C,P) = 1.1 Hz, CH_3], 50.6 (OCH_3), 54.7 [d, ^1J(C,P) = 135.6 Hz], 117.7 [d, ^2J(C,P) = 11.7 Hz], 120.0, 120.4 [d, ^1J(C,P) = 97.4 Hz], 129.5 [d, ^3J(C,P) = 13.3 Hz], 133.7 [d, ^2J(C,P) = 10.9 Hz], 137.0, 139.8 [d, ^3J(C,P) = 12.3 Hz], 143.6 [d, ^4J(C,P) = 2.9 Hz], 149.3, 164.2 (C=O), 169.0 [d, ^2J(C,P) = 18.0 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 13.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 1684, 1717 cm^{-1}. HRMS (ESI^+): calcd. for $C_{32}H_{28}NO_4P$ $[M]^+$ 521.1756; found 521.1753.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(tri-*n*-butyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3p): Orange oil. R_f = 0.48 (EA/hexanes, 2:1). Isolated yield (from two steps) 60% (0.1390 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.95 (t, J = 6.9 Hz, 3 CH_3), 2.28 (m, 9 CH_2), 3.77 (s, OCH_3), 7.79 (d, J = 9.0 Hz, 2 H, Ar-H), 8.18 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 13.4 (CH_3), 21.2 [d, ^1J(C,P) = 55.3 Hz, CH_2], 23.8 [d, ^3J(C,P) = 15.8 Hz, CH_2], 23.9 [d, ^2J(C,P) = 3.9 Hz, CH_2], 51.6 (OCH_3), 54.1 [d, ^1J(C,P) = 119.4 Hz], 115.8 [d, ^2J(C,P) = 9.6 Hz], 123.0, 128.2, 136.6, 141.9 [d, ^3J(C,P) = 10.7 Hz], 146.0, 165.1 (C=O), 169.5 [d, ^2J(C,P) = 16.7 Hz] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 20.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 1683 (br) cm^{-1}. HRMS (ESI^+): calcd. for $C_{24}H_{34}NO_6P$ $[M]^+$ 463.2124; found 463.2128.

(Z)-4-Methoxy-2-(methoxycarbonyl)-1-(4-nitrophenyl)-4-oxo-3-(tributylphosphonio)but-1-en-1-olate (3p′): Orange oil. R_f = 0.35 (EA). Isolated yield 62% (0.1535 g). ^1H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 0.97 (t, J = 6.5 Hz, 3 CH_3), 1.45–1.63 (m, 6 CH_2), 2.18–2.39 (m, 3 CH_2), 3.37 (s, OCH_3), 3.75 (s, OCH_3), 5.48 (d, J = 16.0 Hz, 1 H, CH), 7.48 (d, J = 8.5 Hz, 2 H, Ar-H), 8.17 (d, J = 7.9 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 13.3 (CH_3), 19.5 [d, ^1J(C,P) = 45.9 Hz, CH_2], 23.8 [d, ^3J(C,P) = 10.9 Hz, CH_2], 24.0 (CH_2), 40.2 [d, ^1J(C,P) = 60.6 Hz], 49.4 (OCH_3), 52.5 (OCH_3), 84.8, 122.3, 127.3, 146.3, 152.0, 168.6 (C=O), 170.9 [d, ^2J(C,P) = 6.3 Hz, C=O], 184.0 (C=O) ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 35.2 ppm. FTIR (KBr): $\tilde{\nu}$ = 1674, 1720 cm^{-1}.

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HRMS (ESI$^+$): calcd. for $C_{25}H_{38}NO_7P$ [M]$^+$ 495.2386; found 495.2385.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(tri-*n*-propyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3q): Orange solid. M.p. 129–131 °C. R_f = 0.25 (EA/hexanes, 2:1). Isolated yield (from two steps) 56% (0.1179 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.09 (t, J = 6.8 Hz, 3 CH_3), 1.53–1.64 (m, 3 CH_2), 2.24–2.34 (m, 3 CH_2), 3.80 (s, OCH_3), 7.81 (d, J = 9.0 Hz, 2 H, Ar-H), 8.18 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 15.87 [d, ^3J(C,P) = 16.6 Hz, *C*H$_3$], 16.3 [d, ^2J(C,P) = 3.8 Hz, *C*H$_2$], 24.2 [d, ^1J(C,P) = 54.9 Hz, *C*H$_2$], 52.1 (O*C*H$_3$), 54.6 [^1J(C,P) = 118.9 Hz], 116.4 [d, ^2J(C,P) = 9.7 Hz], 123.4, 128.6, 137.1, 142.2 [d, ^3J(C,P) = 10.6 Hz], 146.4, 165.5 (C=O), 169.8 [d, ^2J(C,P) = 16.5 Hz] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 19.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 1590, 1678 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{21}H_{38}NO_6P$ [M]$^+$ 421.1654; found 421.1655.

(*Z*)-4-Methoxy-2-(methoxycarbonyl)-1-(4-nitrophenyl)-4-oxo-3-(tripropylphosphonio)but-1-en-1-olate (3q′): Orange oil. R_f = 0.10 (EA). Isolated yield 60% (0.1360 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.08–1.13 (m, 3 CH_3), 1.64–1.75 (m, 3 CH_2), 2.16–2.37 (m, 3 CH_2), 3.37 (s, OCH_3), 3.74 (s, OCH_3), 5.48 (d, J = 16.0 Hz, 1 H, C*H*), 7.46 (t, J = 8.6 Hz, 2 H, Ar-H), 8.17 (d, J = 8.7 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 15.2 [d, ^3J(C,P) = 16.1 Hz, *C*H$_3$], 15.7 [d, ^2J(C,P) = 4.5 Hz, *C*H$_2$], 21.5 [d, ^1J(C,P) = 45.5 Hz, *C*H$_2$], 39.9 [d, ^1J(C,P) = 60 Hz], 49.2 (O*C*H$_3$), 52.3 (O*C*H$_3$), 84.6, 122.1, 127.1, 146.1, 151.9, 168.4 (C=O), 170.6 [d, ^1J(C,P) = 6.2 Hz, C=O], 183.7 (C=O) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 34.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 1633, 1722 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{22}H_{32}NO_7P$ [M]$^+$ 453.1916; found 453.1916.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(triethyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3r): Orange oil. R_f = 0.28 (EA/MeOH, 15:1). Isolated yield 81% (0.0921 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.14–1.28 (m, 3 CH_3), 2.29–2.41 (m, 3 CH_2), 3.78 (s, OCH_3), 7.80 (d, J = 9.0 Hz, 2 H, Ar-H), 8.18 (d, J = 9.0 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 6.0 [d, ^2J(C,P) = 4.8 Hz, *C*H$_3$], 14.16 [d, ^1J(C,P) = 56.5 Hz, *C*H$_2$], 51.6 (O*C*H$_3$), 52.7 [d, ^1J(C,P) = 120.0 Hz], 115.6 [d, ^2J(C,P) = 9.5 Hz], 122.9, 128.4, 136.6, 142.3 [d, ^3J(C,P) = 10.7 Hz], 146.1, 165.0 (C=O), 169.8 [d, ^2J(C,P) = 16.4 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 26.9 ppm. FTIR (KBr): $\tilde{\nu}$ = 1590, 1678 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{18}H_{22}NO_6P$ [M]$^+$ 379.1185; found 379.1183.

(*Z*)-4-Methoxy-2-(methoxycarbonyl)-1-(4-nitrophenyl)-4-oxo-3-(triethylphosphonio)but-1-en-1-olate (3r′): Orange oil. R_f = 0.15 (EA/MeOH, 15:1). Isolated yield 61% (0.1254 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.27–1.38 (m, 3 CH_3), 2.23–2.49 (m, 3 CH_2), 3.36 (s, OCH_3), 3.75 (s, OCH_3), 5.48 (d, J = 16.0 Hz, 1 H, C*H*), 7.49 (d, J = 8.3 Hz, 2 H, Ar-H), 8.16 (d, J = 8.3 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 5.9 [d, ^2J(C,P) = 5.4 Hz, *C*H$_3$], 12.5 [d, ^1J(C,P) = 47.5 Hz, *C*H$_2$], 39.3 [d, ^1J(C,P) = 60.0 Hz], 49.3 (O*C*H$_3$), 52.4 (O*C*H$_3$), 84.4, 122.2, 127.2, 146.1, 151.9, 168.4 (C=O), 170.5 [d, ^2J(C,P) = 6.2 Hz, C=O], 183.8 (C=O) ppm. ^{31}P NMR (242 MHz, $CDCl_3$, 25 °C): δ = 40.1 ppm. FTIR (KBr): $\tilde{\nu}$ = 1627, 1721 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{19}H_{26}NO_7P$ [M]$^+$ 411.1447; found 411.1448.

Methyl 2-(4-Nitrophenyl)-5-oxo-4-(trimethyl-λ^5-phosphanylidene)-4,5-dihydrofuran-3-carboxylate (3s): Red solid. M.p. 105–108 °C. R_f = 0.43 (EA/MeOH, 5:1). Isolated yield 53% (0.0536 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 2.00 (d, J = 13.8 Hz, 3 CH_3), 3.79 (s, OCH_3), 7.82 (d, J = 9.1 Hz, 2 H, Ar-H), 8.19 (d, J = 9.1 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75.5 MHz, $CDCl_3$, 25 °C): δ = 13.8 [d, ^1J(C,P) = 62.6 Hz, *C*H$_3$], 51.7 (O*C*H$_3$), 57.9 [d, ^1J(C,P) = 129.4 Hz], 115.2 [d, ^2J(C,P) = 10.1 Hz], 123.0, 128.8, 136.6, 142.6 [d, ^3J(C,P) = 11.3 Hz], 146.4, 164.9 (C=O), 168.5 [d, ^2J(C,P) = 18.7 Hz, C=O] ppm. ^{31}P NMR (242.5 Hz, $CDCl_3$, 25 °C): δ = 6.3 ppm. FTIR (KBr): $\tilde{\nu}$ = 1591, 1684 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{15}H_{16}NO_6P$ [M]$^+$ 337.0715; found 337.0717.

(*Z*)-4-Methoxy-2-(methoxycarbonyl)-1-(4-nitrophenyl)-4-oxo-3-(trimethylphosphonio)but-1-en-1-olate (3s′): Yellow oil. R_f = 0.14 (EA/MeOH, 5:1). Isolated yield 64% (0.1181 g). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 1.95 (d, J = 13.8 Hz, 3 CH_3), 3.35 (OCH_3), 3.76 (OCH_3), 5.30 (d, J = 16.1 Hz, 1 H, C*H*), 7.49 (d, J = 8.4 Hz, 2 H, Ar-H), 8.15 (d, J = 8.5 Hz, 2 H, Ar-H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$, 25 °C): δ = 8.8 [d, ^1J(C,P) = 54.3 Hz, *C*H$_3$], 42.2 [d, ^1J(C,P) = 65.2 Hz], 48.9 (O*C*H$_3$), 52.0 (O*C*H$_3$), 84.2, 121.8, 127.0, 145.7, 151.6, 167.8 (C=O), 170.0 [d, ^2J(C,P) = 4.8 Hz, C=O], 183.3 [d, ^2J(C,P) = 2.3 Hz, C=O] ppm. ^{31}P NMR (242.5 MHz, $CDCl_3$, 25 °C): δ = 27.4 ppm. FTIR (KBr): $\tilde{\nu}$ = 1635, 1718 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{16}H_{20}NO_7P$ [M]$^+$ 369.0977; found 369.0978.

Methyl 4-(4-Nitrobenzylidene)-2-(4-nitrophenyl)-5-oxo-4,5-dihydrofuran-3-carboxylate (6a): Isolated yield 30% (0.0314 g).

Spectral Data of Compound (*Z*)-6a: Yellow solid. M.p. 230–232 °C. R_f = 0.31 (DCM/hexanes, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.88 (s, OCH_3), 7.98 (d, J = 9.0 Hz, 2 H, Ar-H), 8.15 (d, J = 7.6 Hz, 2 H, Ar-H), 8.22 (s, C*H*), 8.35–8.29 (m, 4 H, Ar-H) ppm. FTIR (KBr): $\tilde{\nu}$ = 1718, 1733 cm^{-1}. HRMS (EI): calcd. for $C_{19}H_{22}N_2O_8$ [M]$^+$ 396.0594; found 396.0589. Owing to poor solubility, ^{13}C NMR spectroscopic data were not obtained.

Spectral Data of Compound (*E*)-6a: Yellow solid. M.p. 209–210 °C. R_f = 0.31 (DCM/hexanes, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.34 (s, OCH_3), 7.53 (d, J = 8.9 Hz, 2 H, Ar-H), 7.61 (s, C*H*), 8.16–8.10 (d, J = 9.0 Hz, 2 H, Ar-H), 8.35–8.29 (m, 4 H, Ar-H) ppm. FTIR (KBr): $\tilde{\nu}$ = 1718, 1733 cm^{-1}. HRMS (EI): calcd. for $C_{19}H_{22}N_2O_8$ [M]$^+$ 396.0594; found 396.0589. Owing to poor solubility, ^{13}C NMR spectroscopic data were not obtained.

Methyl 4-(4-Chloro-3-nitrobenzylidene)-2-(4-nitrophenyl)-5-oxo-4,5-dihydrofuran-3-carboxylate (6b): Isolated yield 18% (0.0204 g).

Spectral Data of Compound (*Z*)-6b: Yellow solid mixture. R_f = 0.32 (DCM/hexanes, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.88 (s, OCH_3), 7.97 (d, J = 9.0 Hz, 2 H, Ar-H), 8.13 (s, C*H*), 8.24 (dd, J = 1.8, J = 9.0 Hz, 1 H, Ar-H), 8.32–8.35 (m, 2 H, Ar-H), 8.32–8.35 (m, 1 H, Ar-H), 8.59 (d, J = 2.1 Hz, 1 H, Ar-H) ppm. FTIR (KBr): $\tilde{\nu}$ = 1718, 1792 cm^{-1}. HRMS (EI$^+$): calcd. for $C_{19}H_{11}ClN_2O_8$ [M]$^+$ 430.0204; found 430.0200. Only data for (*Z*)-**6b** is given as the trace of (*E*)-**6b** is uncharacterizable. Owing to poor solubility, ^{13}C NMR spectroscopic data were not obtained.

Methyl 4-(3-Nitrobenzylidene)-2-(4-nitrophenyl)-5-oxo-4,5-dihydrofuran-3-carboxylate (6c): Isolated yield 48% (0.0160 g).

Spectral Data of Compound (*Z*)-6c: Yellow solid mixture. R_f = 0.20 (DCM/hexanes, 3:1). ^{1}H NMR (300 MHz, $CDCl_3$, 25 °C): δ = 3.89 (s, OCH_3), 7.67 (t, J = 8.0 Hz, 1 H, Ar-H), 7.98 (d, J = 8.9 Hz, 2 H, Ar-H), 8.22 (s, C*H*), 8.31–8.40 (m, 4 H, Ar-H), 8.84 (s, 1 H, Ar-H) ppm. FTIR (KBr): $\tilde{\nu}$ = 1722, 1780 cm^{-1}. HRMS (ESI$^+$): calcd. for $C_{19}H_{12}N_2O_8$ [M]$^+$ 396.0594; found 396.0596. Only data for (*Z*)-**6c** is given as the trace of (*E*)-**6c** is uncharacterizable. Owing to poor solubility, ^{13}C NMR spectroscopic data were not obtained.

Supporting Information (see footnote on the first page of this article): ^{1}H and ^{13}C NMR data for all new compounds, X-ray crystallographic data for compound **3o**.

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[15] X-ray crystallographic data for compound **3o**: orange bricks, 0.18 × 0.15 × 0.01 mm, $C_{64}H_{62}N_2O_{11}P_2$, monoclinic, space group $P1c1$, ρ = 1.310 mg/m^3, V = 2780.82(14) Å^3, a = 11.3365(3), b = 9.8027(3), c = 27.0395(8) Å, β = 112.265(2)°, R_1 = 0.0452, R_w = 0.1214. CCDC-888077 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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