Base-Promoted One-Pot Sequential Phosphite Addition and 5-*exo*-dig Cyclization of Enynals: A Facile Route to Trisubstituted Furans

Anasuyamma Uravakilli, Ramesh Kotikalapudi, K. C. Kumara Swamy*

School of Chemistry, University of Hyderabad, Hyderabad 500 046, A. P., India
E-mail: kckssc@uohyd.ac.in; E-mail: kckssc@yahoo.com; Fax +91(40)23012460

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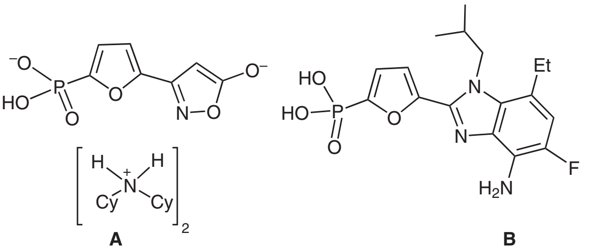
Abstract: An easy route for the synthesis of trisubstituted furans has been demonstrated. One-pot sequential phosphite (H-phosphonate) addition to alkynylaldehydes (enynals) promoted by tripotassium phosphate leads to trisubstituted furans (phosphono-furans) via 5-*exo*-dig cyclization of the phosphono-alkynol intermediates. In contrast, in the presence of silver(I) tetrafluoroborate, the reaction using the same substrates leads to a diene product.

Key words: nucleophilic addition, enynals, cyclization, isomerization, furans, phosphorus

The furan ring system is an important skeleton and hence it is a much sought after target in synthetic chemistry.[1] 3-Alkynylcinnamaldehydes/alcohols have been utilized for the construction of various carbocyclic, furan, and pyran ring systems.[2] Diverse phosphono-isobenzofurans[3] and -isochromenes[4] are also synthesized using *o*-alkynylbenzaldehydes. Organophosphonates, due to their enormous application in medicinal chemistry are interesting scaffolds in the field of organic synthesis.[5–7] As a subclass of organophosphonates, phosphono-heterocycles have also found many bio-related applications. For example, two drugs containing a furylphosphonic acid moiety that can be used for the treatment of hyperlipidemia and type 2 diabetes mellitus are shown in Figure 1.[8] It is always challenging to introduce a phosphonate moiety on to an aromatic ring from the synthetic perspective of arylphosphonates.[9] Our recent investigation of the synthesis of phosphono-furans utilizing 2-alkynylcinnamaldehydes[10] resulted in the construction of phosphorus-substituted heterocycles[11] and this prompted us to find new and facile routes for the synthesis of phosphono-furans (furylphosphonates). We envisaged that phosphite (H-phosphonate) addition to 3-alkynylaldehydes followed by cyclization in one pot could lead to phosphono-furans. Herein we report an easy route for the construction of trisubstituted phosphono-furans using 3-alkynylcinnamaldehydes via one-pot sequential phosphite (H-phosphonate) addition and cyclization.

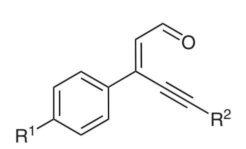
Initially, diverse 3-alkynylaldehydes **1a**–**k** were synthesized from the corresponding 3-bromoacrylaldehydes and terminal acetylenes (Figure 2).[2f,12] Different H-phosphonates and diphenylphosphine oxide were also used in this study.



A
potent AMPK activator

B
[5-(4-amino-7-ethyl-5-fluoro-1-isobutyl-1*H*-benzoimidazol-2-yl)furan-2-yl]-phosphonic acid

Figure 1 Drugs containing a furylphosphonic acid moiety



1a R^1 = H, R^2 = Ph
1b R^1 = H, R^2 = 4-MeC_6H_4
1c R^1 = H, R^2 = 4-$MeOC_6H_4$
1d R^1 = H, R^2 = 4-ClC_6H_4
1e R^1 = H, R^2 = 2-$O_2NC_6H_4$
1f R^1 = H, R^2 = 1-cyclohexenyl
1g R^1 = H, R^2 = 3-FC_6H_4
1h R^1 = OMe, R^2 = Ph
1i R^1 = OMe, R^2 = 4-MeC_6H_4
1j R^1 = F, R^2 = Ph
1k R^1 = F, R^2 = 4-MeC_6H_4

2a R–R = $-CH_2C(Me_2)CH_2$
2b R = Et
2c R = *i*-Pr
2d

Figure 2 Precursors used in this study

At the outset, the reaction of 3-alkynylaldehyde **1a** and phosphite **2a** was conducted in the presence of one mole equivalent of triethylamine in tetrahydrofuran at 50 °C (Scheme 1, Table 1, entry 1). Interestingly, the reaction provided furylphosphonate **3** in 65% yield. The use of diisopropylamine, potassium carbonate, and cesium carbonate led to moderate yields of furan **3a** (entries 2–4) even after 12 hours. However, tripotassium phosphate in tetrahydrofuran led to the furan **3a** in 81% yield at 50 °C for four hours (entry 5). Sodium methoxide and amine bases such as DBU, 4-(dimethylamino)pyridine, and pyridine did not give an improved yield of **3a** (entries 6–9). Even in the presence of tripotassium phosphate, solvents such as dioxane, toluene, and 1,2-dichloroethane gave moderate yields of phosphono-furans **3a** only (entries 10–12). Thus the best conditions used one mole equivalent of tripotassium phosphate in tetrahydrofuran as the solvent at

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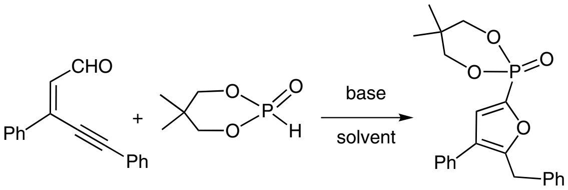
50 °C to accomplish the best yields of phosphono-furans via this route.



Scheme 1 Reaction of **1a** and **2a** to form the trisubstituted phosphono-furan **3**

Table 1 Optimization for the Formation of Trisubstituted Furan **3**[a]

Entry	Base	Solvent	Temp (°C)	Time (h)	Yield[b] (%)
1	Et_3N	THF	50	5	65[c]
2	i-Pr_2NH	THF	50	5	67
3	K_2CO_3	THF	50	8	68[c]
4	Cs_2CO_3	THF	50	5	70
5	K_3PO_4	THF	50	4	81
6	NaOMe	THF	50	5	69
7	DBU	THF	50	6	64[c]
8	DMAP	THF	50	6	71
9	pyridine	THF	50	5	68
10	K_3PO_4	dioxane	50	5	73
11	K_3PO_4	toluene	50	5	72
12	K_3PO_4	DCE	50	5	76

[a] Conditions: **1a** (0.5 mmol), **2a** (0.6 mmol), base (0.6 mmol), solvent (2 mL), 50 °C.
[b] Yield of the isolated product.
[c] Starting material remained.

To generalize this protocol for the synthesis of diverse phosphorus-containing furans, with the optimized conditions in hand, various 3-alkynylcinnamaldehydes **1a**–**k** and phosphites (H-phosphonates) **2a**–**c** were utilized. In all the cases furylphosphonates **3**–**15** were obtained in good to excellent yields (Table 2). Diphenylphosphine oxide (**2d**) was also used in this study to explore the reactivity of 3-alkynylcinnamaldehydes **1e** and **1g**, which further led to phosphinoylfurans **16** and **17**, respectively in good yields (entries 14 and 15). The structure of 2-furylphosphonate **3** was confirmed by X-ray crystallography (Figure 3).[13]

A probable pathway for the formation of phosphonofurans on the basis of available literature[3] is shown in Scheme 2. Initially, the base abstracts a proton from the phosphite (H-phosphonate) followed by nucleophilic addition to the aldehyde group of 3-alkynylcinnamaldehyde via the Pudovik reaction[14] leading to the intermediate **I**. Species **I** undergoes sequential 5-*exo*-dig cyclization and isomerization to lead to the furan derivative. This reaction proceeds in one pot to afford the final product.

Table 2 Synthesis of Diverse Phosphorus-Containing Trisubstituted Furans

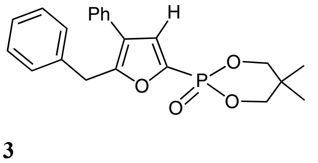
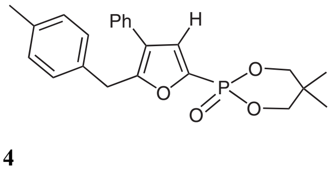
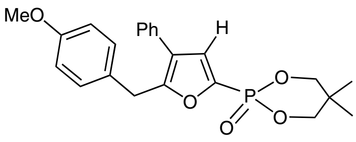
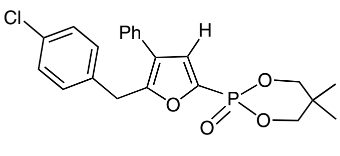
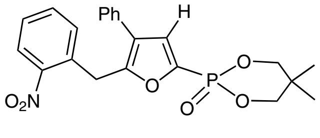
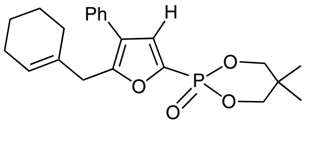
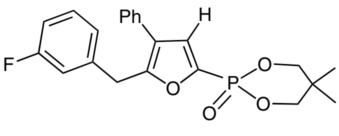
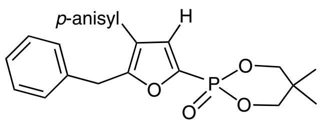
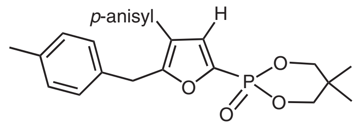
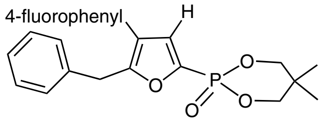
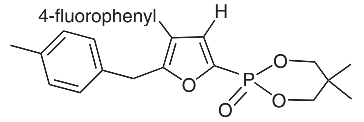
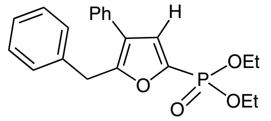
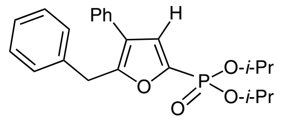
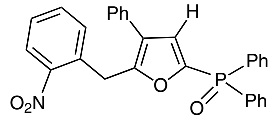
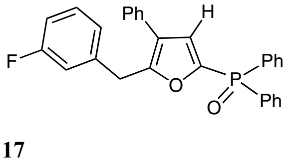
Entry	Alk-3-ynal + Phosphite	Furylphosphonate	Yield[a] (%)
1	**1a** + **2a**	 **3**	72
2	**1b** + **2a**	 **4**	64
3	**1c** + **2a**	 **5**	62
4	**1d** + **2a**	 **6**	81
5	**1e** + **2a**	 **7**	84
6	**1f** + **2a**	 **8**	72
7	**1g** + **2a**	 **9**	92
8	**1h** + **2a**	 **10**	75

Table 2 Synthesis of Diverse Phosphorus-Containing Trisubstituted Furans (continued)

Entry	Alk-3-ynal + Phosphite	Furylphosphonate	Yield[a] (%)
9	**1i** + **2a**	 **11**	72
10	**1j** + **2a**	 **12**	89
11	**1k** + **2a**	 **13**	88
12	**1a** + **2b**	 **14**	70
13	**1a** + **2c**	 **15**	69
14	**1e** + **2d**	 **16**	69
15	**1g** + **2d**	 **17**	78

[a] Yield of the isolated product.

There is a precedent for the metal-catalyzed reaction of alkynylaldehydes and phosphites leading to pyran derivatives.[4a] Hence reaction of **1a** with **2a** was performed in the presence of catalytic silver(I) tetrafluoroborate (Scheme 3). The reaction leads to the phosphono-diene **18** (X-ray,[13] Figure 4); it is likely that the initially formed pyran **IV** undergoes ring opening to form the diene **18**.

In conclusion, a new and facile synthetic route to trisubstituted furans with phosphono- or phosphinoyl-substituents has been demonstrated. This reaction involves the one-pot synthesis of diverse trisubstituted furans in good yields starting from 3-alkynylaldehydes and H-phosphonates.

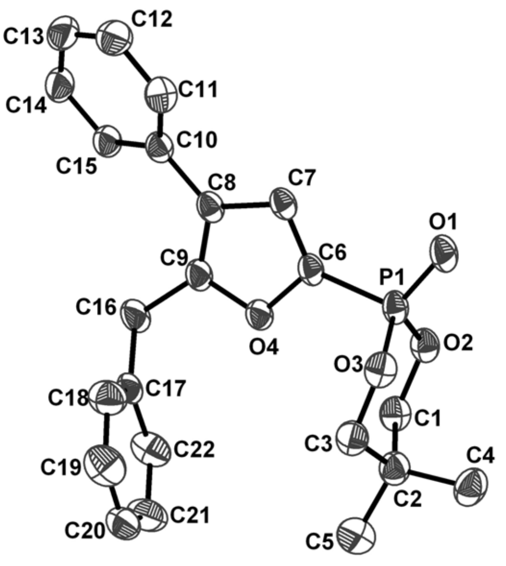
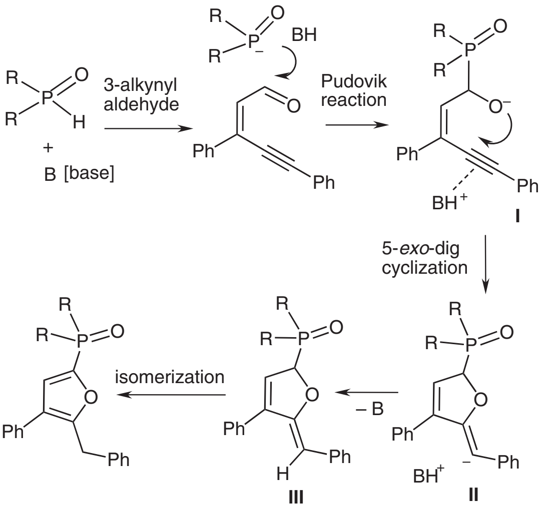
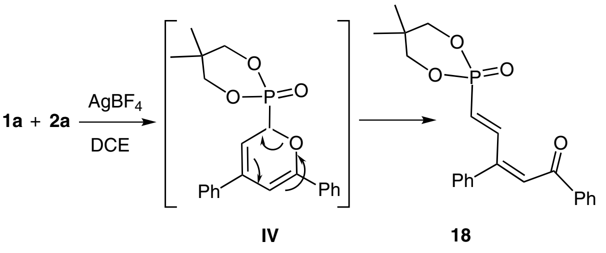


Figure 3 ORTEP of compound **3**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1–C6 1.775(2), C6–C7 1.343(3), C7–C8 1.430(3), C8–C9 1.344(3), and C9–C16 1.494(3).



Scheme 2 Plausible pathway for the formation of furans



Scheme 3 Formation of phosphono diene

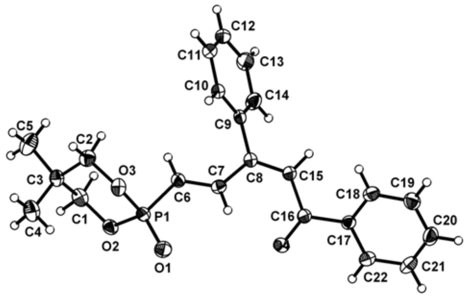


Figure 4 ORTEP of compound **18**. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å): P1–C6 1.774(2), C6–C7 1.334(3), C7–C8 1.464(3), C8–C15 1.349(3), and C15–C16 1.476(3).

Solvents were dried according to known methods as appropriate.[15] ^{1}H, ^{13}C, and ^{31}P NMR spectra (^{1}H: 400 MHz or 500 MHz; ^{13}C: 100 MHz or 125 MHz; ^{31}P: 162 MHz) were recorded using a 400 MHz or 500 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to TMS (δ = 0 ppm) or 85% H_3PO_4 (δ = 0 ppm). IR spectra were recorded on an FT-IR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. Elemental analyses were carried out on a CHN analyzer. Mass spectra were recorded using an LCMS instrument. HRMS were performed using a mass spectrometer Bruker-maXis with ESI-QTOF-II method. Single crystal X-ray diffraction was collected on Oxford diffractometer using MoKα (l = 0.71073 Å) radiation. The structure was solved and refined by standard methods.[15]

3-Bromoacrylaldehydes were synthesized by following a literature procedure.[12]

(*Z*)-3,5-Diarylpent-2-en-4-ynals 1a–k; General Procedure

These precursors were synthesized by slightly modifying a literature procedure.[2f] To a stirred solution of (*Z*)-3-aryl-3-bromoacrylaldehyde[11] (5.00 mmol) in MeCN (16 mL) were added Et_3N (1 mL), $PdCl_2$ (0.026 g, 0.15 mmol), Ph_3P (0.079 g, 0.30 mmol), CuI (0.057 g, 0.30 mmol), and terminal acetylene (6.00 mmol) at r.t. and the mixture was stirred for a further 1 h. After completion of the reaction, sat. NH_4Cl soln (30 mL) was added and the mixture was extracted with Et_2O (3 × 50 mL). The combined organic layers were stripped of volatiles under vacuum. The crude product was purified by column chromatography (silica gel, hexane–EtOAc, 10:1). Compound **1a** is known but **1b**–**k** are new; spectroscopic data for **1a** are identical to that known in the literature.[2f]

(*Z*)-5-(4-Methylphenyl)-3-phenylpent-2-en-4-ynal (1b)

Orange liquid; yield: 109 mg (89%).

IR (neat): 3419, 1764, 1666 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.42 (d, J = 8.0 Hz, 1 H), 7.88–7.86 (m, 2 H), 7.52–7.48 (m, 5 H), 7.24 and 7.22 (2 br s, 2 H), 6.80 (d, J = 8.0 Hz, 1 H), 2.42 (s, 3 H, $ArCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.4, 142.9, 140.4, 135.7, 132.0, 131.1, 130.7, 129.5, 128.9, 127.2, 118.6, 102.8, 83.9, 21.7.

LC-MS: m/z = 247 [M + 1]$^+$.

Anal. Calcd for $C_{18}H_{14}O$: C, 87.78; H, 5.73. Found: C, 87.69; H, 5.78.

(*Z*)-5-(4-Methoxyphenyl)-3-phenylpent-2-en-4-ynal (1c)

Orange gummy liquid; yield: 114 mg (87%).

IR (neat): 3386, 3063, 1770, 1720, 1665 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.41 (d, J = 7.6 Hz, 1 H), 7.87–7.85 (m, 2 H), 7.57–7.48 (m, 5 H), 6.95 and 6.93 (2 br s, 2 H), 6.78 (d, J = 8.4 Hz, 1 H), 3.90 (s, 3 H, $ArOCH_3$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.3, 160.9, 143.0, 135.9, 133.7, 131.0, 130.3, 128.9, 127.2, 114.4, 113.7, 102.9, 83.6, 55.4.

LC-MS: m/z = 263 [M + 1]$^+$.

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38. Found: C, 82.31; H, 5.45.

(*Z*)-5-(4-Chlorophenyl)-3-phenylpent-2-en-4-ynal (1d)

Orange gummy liquid; yield: 109 mg (82%).

IR (neat): 3408, 3057, 1719, 1659 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.40 (d, J = 8.0 Hz, 1 H), 7.85–7.83 (m, 2 H), 7.55–7.39 (m, 7 H), 6.82 (d, J = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.1, 142.3, 136.1, 135.6, 133.2, 131.2, 129.8, 129.1, 128.9, 127.2, 120.1, 100.9, 85.1.

LC-MS: m/z = 267, 269 [M]$^+$ [M + 2]$^+$.

Anal. Calcd for $C_{17}H_{11}OCl$: C, 76.55; H, 4.16. Found: C, 76.65; H, 4.23.

(*Z*)-5-(2-Nitrophenyl)-3-phenylpent-2-en-4-ynal (1e)

Yellow solid; yield: 126 mg (91%); mp 95–97 °C.

IR (KBr): 3063, 1720, 1659, 1555 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.45 (m, J = 6.8 Hz, 1 H), 8.22 (d, J = 8.0 Hz, 1 H), 7.92–7.27 (m, 8 H), 6.89 (m, J = 6.8 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.0, 149.1, 141.5, 135.2, 135.0, 133.4, 132.6, 131.3, 130.2, 127.3, 125.2, 117.4, 96.3, 91.1.

LC-MS: m/z = 278 [M + 1]$^+$.

Anal. Calcd for $C_{17}H_{11}O_3N$: C, 73.64; H, 4.00; N, 5.05. Found: C, 73.48; H, 4.08; N, 5.12.

(*Z*)-5-Cyclohex-1-enyl-3-phenylpent-2-en-4-ynal (1f)

Yellow oil; yield: 96 mg (82%).

IR (neat): 3413, 3063, 1725, 1665 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.29 (d, J = 8.0 Hz, 1 H), 7.80–7.78 (m, 2 H), 7.45–7.44 (m, 3 H), 6.72 (d, J = 8.0 Hz, 1 H), 6.41 (s, 1 H, $H_{cyclohexenyl}$), 2.28 and 2.20 (2 br s, 4 H), 1.72–1.60 (m, 4 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.5, 143.1, 138.9, 135.8, 130.9, 130.2, 128.8, 127.1, 120.2, 104.7, 82.1, 28.8, 26.0, 22.1, 21.2.

LC-MS: m/z = 237 [M + 1]$^+$.

Anal. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.82. Found: C, 86.27; H, 6.71.

(*Z*)-5-(3-Fluorophenyl)-3-phenylpent-2-en-4-ynal (1g)

Yellow solid; yield: 117 mg (89%); mp 146–148 °C.

IR (KBr): 3057, 1657, 1579, 1221 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.40 (d, J = .8.0 Hz, 1 H), 7.85–7.83 (m, 2 H), 7.50–7.15 (m, 7 H), 6.83 (d, J = 8.0 Hz, 1 H).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 193.6, 163.2, 159.5, 143.4, 135.3, 132.2, 131.6, 130.7, 130.1, 129.6, 129.1, 128.6, 128.5, 122.6, 115.7, 99.3, 85.5.

LC-MS: m/z = 249 [M + 1]$^+$.

Anal. Calcd for $C_{17}H_{11}OF$: C, 81.59; H, 4.43. Found: C, 81.46; H, 4.51.

(*Z*)-3-(4-Methoxyphenyl)-5-phenylpent-2-en-4-ynal (1h)

Bright yellow solid; yield: 115 mg (88%); mp 68–70 °C.

IR (KBr): 3287, 2860, 1668, 1569 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 10.41 (d, J = 7.6 Hz, 1 H), 7.87–7.85 (m, 2 H), 7.57–7.47 (m, 5 H), 6.95–6.93 (m, 2 H), 6.78 (d, J = 8.4 Hz, 1 H), 3.90 (s, 3 H, OCH_3).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 193.2, 161.0, 143.0, 135.9, 133.7, 131.0, 130.3$_3$, 130.3$_{0,}$ 128.9, 127.2, 114.4, 103.0, 83.6, 55.4.

LC-MS*:* *m*/*z* = 263 [M + 1]$^+$.

Anal. Calcd for $C_{18}H_{14}O_2$: C, 82.42; H, 5.38.Found: C, 82.56; H, 5.31.

(*Z*)-3-(4-Methoxyphenyl)-5-(4-methylphenyl)pent-2-en-4-ynal (1i)

Yellow gummy solid; yield: 120 mg (86%); mp 72–74 °C.

IR (KBr): 3030, 2997, 1660, 1594 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.40 (m, *J* = 6.0 Hz, 1 H), 7.50–7.38 (m, 5 H), 7.24–7.21 (m, 2 H), 7.03 (d, *J* = 8.0 Hz, 1 H), 6.78 (m, *J* = 5.6 Hz, 1 H), 3.90 (s, 3 H, OCH$_3$), 2.40 (s, 3 H, CH$_3$).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 193.3, 159.9, 142.6, 140.4, 137.1, 132.0, 130.8, 129.5, 119.7, 116.7, 112.7, 102.7, 83.9, 55.4, 21.7.

LC-MS*:* *m*/*z* = 277 [M + 1]$^+$.

Anal. Calcd for $C_{19}H_{16}O_2$: C, 82.58; H, 5.84. Found: C, 82.41; H, 5.81.

(*Z*)-3-(4-Fluorophenyl)-5-phenylpent-2-en-4-ynal (1j)

Yellow solid; yield: 111 mg (89%); mp 145–147 °C.

IR (KBr): 3063, 1659, 1572, 1183 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.40 (d, *J* = 8 Hz, 1 H), 7.88–7.84 (m, 2 H), 7.62–7.59 (m, 2 H), 7.47–7.40 (m, 3 H), 7.19–7.15 (m, 2 H), 6.75 (d, *J* = 8 Hz, 1 H).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 193.6, 163.2, 159.5, 143.4, 135.3, 132.7, 131.6, 130.1, 129.3, 128.6, 122.7, 122.5, 115.8, 99.3, 85.5.

LC-MS*:* *m*/*z* = 249 [M + 1]$^+$.

Anal. Calcd for $C_{17}H_{11}OF$: C, 81.59; H, 4.43. Found: C, 81.42; H, 4.38.

(*Z*)-3-(4-Fluorophenyl)-5-(4-methylphenyl)pent-2-en-4-ynal (1k)

Orange gummy liquid; yield: 114 mg (72%).

IR (neat): 3047, 1671, 1600, 1342 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 10.39 (d, *J* = 8.0 Hz, 1 H), 7.88–7.84 (m, 2 H), 7.50–7.49 (m, 2 H), 7.27–7.14 (m, 4 H), 6.73 (d, *J* = 8.0 Hz, 1 H), 2.41 (s, 3 H, CH$_3$).

^{13}C NMR (100 MHz, CDCl$_3$): δ = 193.2, 164.5, 141.6, 140.6, 132.0, 131.9, 131.8, 130.3, 129.5, 129.4, 129.3, 118.4, 116.0, 103.0, 83.6, 21.7.

LC-MS*:* *m*/*z* = 265 [M + 1]$^+$.

Anal. Calcd for $C_{18}H_{13}OF$: C, 81.80; H, 4.96. Found: C, 81.68; H, 4.85.

2,3-Disubstituted 5-Phosphono- or 5-Phosphinoylfurans 3–17; General Procedure

To a stirred solution of H-phosphonate (0.6 mmol) and K_3PO_4 (0.6 mmol) in THF (1 mL) was added 3-alkynylcinnamaldehyde (0.5 mmol) in THF (1 mL) under a N_2 atmosphere. The solution was stirred at 50 °C until the starting material had been consumed. Solvent was removed under vacuum and the crude product was purified by column chromatography (silica gel, hexane–EtOAc, 1:1).

2-Benzyl-5-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-phenylfuran (3)

Pale yellow solid; yield: 137 mg (72%); mp 168–170 °C.

IR (KBr): 3084, 3052, 3030, 2964, 2899, 2866, 1605, 1518, 1496, 1282, 1244, 1151, 1101, 1052, 1008, 975, 773, 729, 548 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.43–7.22 (m, 11 H, H$_{Ar}$), 4.21 (s, 2 H, PhC*H*$_2$), 4.11–4.05 (m, 4 H, OCH$_2$), 1.25 and 0.95 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 155.0 (d, $^3J_{P\text{-}C}$ = 9.0 Hz, PCO*C*), 142.5 (d, $^1J_{P\text{-}C}$ = 242.0 Hz, PC), 137.1, 132.2, 128.8, 128.7, 128.5, 127.9, 127.4, 126.7, 124.4 (d, $^2J_{P\text{-}C}$ = 25.0 Hz, PC=*C*), 123.4 (d, $^3J_{P\text{-}C}$ = 11.0 Hz, PC=C-*C*), 77.0 (s, OCH$_2$), 33.3 (s, Ph*C*H$_2$), 32.3 [d, $^3J_{P\text{-}C}$ = 6.8 Hz, *C*(CH$_3$)$_2$], 21.8 and 20.8 [2 s, C(*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.10.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{22}H_{24}O_4P$: 383.1411; found: 383.1412.

5-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-2-(4-methylbenzyl)-3-phenylfuran (4)

Pale yellow solid; yield: 126 mg (64%); mp 170–172 °C.

IR (KBr): 3123, 3052, 2964, 2888, 1605, 1578, 1534, 1468, 1348, 1277, 1112, 1058, 1008, 986, 833, 767, 707, 553, 477 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.42–7.11 (m, 10 H, H$_{Ar}$), 4.15 (s, 2 H, PhC*H*$_2$), 4.10–4.01 (m, 4 H, OCH$_2$), 2.32 (s, 3 H, ArC*H*$_3$), 1.24 and 0.95 [2 s, 6 H, C (CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 155.4 (d, $^3J_{P\text{-}C}$ = 10.0 Hz, PCO*C*), 142.4 (d, $^1J_{P\text{-}C}$ = 242.0 Hz, PC), 136.3, 132.3, 132.2, 129.4, 129.1, 128.4, 127.9, 127.4, 124.4 (d, $^2J_{P\text{-}C}$ = 27.0 Hz, PC=*C*), 123.2 (d, $^3J_{P\text{-}C}$ = 12.0 Hz, PC=C-*C*), 77.1 (s, OCH$_2$), 32.9 (s, Ph*C*H$_2$), 32.3 [d, $^3J_{P\text{-}C}$ = 7.0 Hz, *C*(CH$_3$)$_2$], 21.8, 21.0 and 20.7 [3 s, C(*C*H$_3$)$_2$ + Ar*C*H$_3$].

^{31}P NMR: δ = –2.91.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{26}O_4P$: 397.1569; Found: 397.1569.

5-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-2-(4-methoxybenzyl)-3-phenylfuran (5)

Pale yellow solid; yield: 128 mg (62%); mp 150–152 °C.

IR (KBr): 2959, 2932, 2827, 1742, 1611, 1507, 1277, 1244, 1178, 1101, 1058, 1003, 838, 784, 701, 542 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.43–6.85 (m, 10 H, H$_{Ar}$), 4.12–4.08 (m, 6 H, OCH$_2$ + PhC*H*$_2$), 3.81 (s, 3 H, OCH$_3$), 1.26 and 0.98 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 158.4 (*C*-OCH$_3$), 155.6 (d, $^3J_{P\text{-}C}$ = 9.0 Hz, PCO*C*), 142.3 (d, $^1J_{P\text{-}C}$ = 252.0 Hz, PC), 132.2, 129.5, 129.1, 128.4, 127.8, 127.4, 124.5 (d, $^2J_{P\text{-}C}$ = 25.0 Hz, PC=*C*), 123.1 (d, $^3J_{P\text{-}C}$ = 12.0 Hz, PC=C-*C*), 114.1, 77.1 (s, OCH$_2$), 55.3 (s, OCH$_3$), 32.4 (s, Ph*C*H$_2$), 32.3 [d, $^3J_{P\text{-}C}$ = 7.0 Hz, *C*(CH$_3$)$_2$], 21.8 and 20.8 [2 s, C(*C*H$_3$)$_2$].

^{31}P NMR: δ = –2.90.

HRMS (ESI): *m*/*z* [M + H]$^+$ calcd for $C_{23}H_{26}O_5P$: 413.1519; found: 413.1519.

2-(4-Chlorobenzyl)-5-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-phenylfuran (6)

Pale yellow solid; yield: 170 mg (81%); mp 110–112 °C.

IR (KBr): 3107, 3052, 2964, 2888, 1742, 1600, 1490, 1282, 1058, 1014, 816, 784, 690, 548 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.43–7.13 (m, 10 H, H$_{Ar}$), 4.16 (s, 2 H, PhC*H*$_2$), 4.13–4.06 (m, 4 H, OCH$_2$), 1.23 and 0.97 [2 s, 6 H, C (CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 154.4 (d, $^3J_{P\text{-}C}$ = 7.0 Hz, PCO*C*), 142.5 (d, $^1J_{P\text{-}C}$ = 194.0 Hz, PC), 135.5, 132.6, 132.0, 129.8, 128.9, 128.8, 127.8, 127.5, 124.5 (d, $^2J_{P\text{-}C}$ = 19.0 Hz, PC=*C*), 123.6 (d, $^3J_{P\text{-}C}$ = 8.0 Hz, PC=C-*C*), 77.0$_5$ and 77.0$_0$ (2 s, OCH$_2$), 32.7 (s, Ph*C*H$_2$), 32.3 [d, $^3J_{P\text{-}C}$ = 6.0 Hz, *C*(CH$_3$)$_2$], 21.8 and 20.8 [2 s, *C*(*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.02.

HRMS (ESI): *m*/*z* [M + H]$^+$ and [M + 2 + H]$^+$ calcd for $C_{22}H_{23}O_4ClP$: 417.1023; found: 417.1021 and 419.0997.

5-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-2-(2-nitrobenzyl)-3-phenylfuran (7)

Pale yellow solid; yield: 180 mg (84%); mp 108–110 °C.

IR (KBr): 2959, 1611, 1529, 1342, 1266, 1112, 1052, 1008, 975, 833, 789, 729, 701, 553 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.02–7.17 (m, 10 H, H$_{Ar}$), 4.58 (s, 2 H, PhCH_2), 4.11–4.00 (m, 4 H, OCH$_2$), 1.24 and 0.94 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 152.8 (d, $^{3}J_{P-C}$ = 7.0 Hz, PCO*C*), 149.0, 143.2 (d, $^{1}J_{P-C}$ = 193.0 Hz, PC), 133.5, 132.0, 131.8, 131.7, 128.9, 128.1, 127.8, 127.7, 125.0, 124.5$_2$ (d, $^{2}J_{P-C}$ = 20.0 Hz, PC=*C*), 124.5$_0$ (s, PC=C-*C*), 77.2 and 77.1 (2 s, OCH$_2$), 32.3 [d, $^{3}J_{P-C}$ = 6.0 Hz, *C*(CH$_3$)$_2$], 30.7 (s, Ph*C*H$_2$), 21.8 and 20.7 [2 s, C(*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.60.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for C$_{22}$H$_{23}$O$_6$PN: 428.1266; found: 428.1263.

2-(Cyclohex-1-enylmethyl)-5-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-phenylfuran (8)

Pale yellow solid; yield: 137 mg (72%); mp 140–142 °C.

IR (KBr): 2921, 1611, 1468, 1364, 1293, 1249, 1096, 1008, 832, 783, 706, 542 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.43–7.32 (m, 6 H, H$_{Ar}$), 5.47 (s, 1 H, =CH), 4.25–4.11 (m, 4 H, OCH$_2$), 3.45 (s, 2 H, CH$_2$), 2.00–1.93 and 1.62–1.56 (m, 8 H, H$_{cyclohexenyl}$), 1.28 and 1.06 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 155.7 (d, $^{3}J_{P-C}$ = 8.0 Hz, PCO*C*), 141.8 (d, $^{1}J_{P-C}$ = 194.0 Hz, PC), 133.7, 132.5, 128.7, 127.9, 127.2, 124.4 ($^{2}J_{P-C}$ = 20.0 Hz, PC=*C*), 124.1, 123.4 (d, $^{3}J_{P-C}$ = 9.0 Hz, PC=C-*C*), 77.1 (s, OCH$_2$), 35.7 (s, CH$_2$), 32.4 [d, $^{3}J_{P-C}$ = 5.0 Hz, *C*(CH$_3$)$_2$], 28.6, 25.3, 22.8, 22.2, 21.9 and 20.9 [6 s, C(*C*H$_3$)$_2$, C$_{cyclohexenyl}$].

^{31}P NMR: δ = –2.40.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for C$_{22}$H$_{28}$O$_4$P: 387.1726; found: 387.1723.

5-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-2-(3-fluorobenzyl)-3-phenylfuran (9)

Bright yellow solid; yield: 185 mg (92%); mp 122–124 °C.

IR (KBr): 3107, 3052, 2975, 2899, 1616, 1589, 1512, 1490, 1441, 1375, 1288, 1244, 1129, 1101, 1047, 1003, 866, 827, 784, 712, 613, 553 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.45–6.92 (m, 10 H, H$_{Ar}$), 4.19 (s, 2 H, PhCH_2), 4.11 and 4.08 (2 br s, 4 H, OCH$_2$), 1.24 and 0.98 [2 s, 6 H, C (CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 162.9 (d, $^{1}J_{F-C}$ = 245.0 Hz, FC), 154.2 (d, $^{3}J_{P-C}$ = 10.0 Hz, PCO*C*), 142.7 (d, $^{1}J_{P-C}$ = 242.0 Hz, PC), 139.6 (d, $^{3}J_{F-C}$ = 8.0 Hz, FC=*C*), 132.0, 130.2 (d, $^{3}J_{F-C}$ = 9.0 Hz, FC=*C*), 128.9, 127.9, 127.6, 124.5 (d, $^{2}J_{P-C}$ = 25.0 Hz, PC=*C*), 124.2$_2$, 124.20, 123.7 (d, $^{3}J_{P-C}$ = 11.0 Hz, PC=C-*C*), 115.5 and 113.7 (2 d, $^{2}J_{F-C}$ = 21.0 Hz each, FC=*C*), 77.3 and 77.1 (2 s, OCH$_2$), 33.0 (s, Ph*C*H$_2$), 32.3 [d, $^{3}J_{P-C}$ = 7.0 Hz, *C*(CH$_3$)$_2$], 21.8 and 20.8 [2 s, C(*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.10.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for C$_{22}$H$_{23}$O$_4$FP: 401.1319; found: 401.1320.

2-Benzyl-5-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-(4-methoxyphenyl)furan (10)

Yellow solid; yield: 155 mg (75%); mp 94–96 °C.

IR (KBr): 3101, 2959, 2893, 1770, 1600, 1468, 1392, 1288, 1255, 1058, 1014, 948, 795, 723, 706, 559, 482 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.35–6.87 (m, 10 H, H$_{Ar}$), 4.20 (s, 2 H, PhCH_2), 4.12–4.01 (m, 4 H, OCH$_2$), 3.77 (s, 3 H, OCH$_3$), 1.23 and 0.91 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.9, 155.2 (d, $^{3}J_{P-C}$ = 9.0 Hz, PCO*C*), 142.5 (d, $^{1}J_{P-C}$ = 241.5 Hz, PC), 137.1, 133.5, 129.9, 128.7, 128.5, 126.7, 124.4 (d, $^{2}J_{P-C}$ = 24.4 Hz, PC=*C*), 123.3 (d, $^{3}J_{P-C}$ = 11.0 Hz, PC=C-*C*), 120.2, 113.4, 113.1, 77.1 (s, OCH$_2$), 55.2 (s, OCH$_3$), 33.4 (s, Ph*C*H$_2$), 32.3 [d, $^{3}J_{P-C}$ = 6.7. Hz, *C*(CH$_3$)$_2$], 21.8 and 20.8 [2 s, C(*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.10.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for C$_{23}$H$_{26}$O$_5$P: 413.1519; found: 413.1520.

5-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-(4-methoxyphenyl)-2-(4-methylbenzyl)furan (11)

Pale yellow gummy solid; yield: 155 mg (72%).

IR (neat): 2967, 1764, 1605, 1573, 1512, 1463, 1430, 1367, 1282, 1216, 1162, 1058, 1008, 838, 789 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.35–6.86 (m, 9 H, H$_{Ar}$), 4.17–4.02 (m, 6 H, OCH$_2$, PhCH_2), 3.80 (s, 3 H, OCH$_3$), 2.32 (s, 3 H, CH$_3$), 1.25 and 0.95 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 159.9, 155.5 (d, $^{3}J_{P-C}$ = 9.1 Hz, PCO*C*), 142.4 (d, $^{1}J_{P-C}$ = 241.8 Hz, PC), 136.4, 134.1, 133.7, 129.9, 129.4, 128.5, 124.4 (d, $^{2}J_{P-C}$ = 24.5 Hz, PC=*C*), 123.1 (d, $^{3}J_{P-C}$ = 11.1 Hz, PC=C-*C*), 120.3, 113.5, 113.1, 77.1 (s, OCH$_2$), 55.3 (s, OCH$_3$), 33.0 (s, Ph*C*H$_2$), 32.3 [d, $^{3}J_{P-C}$ = 6.7.Hz, *C*(CH$_3$)$_2$], 21.9 (s, CH$_3$), 21.1 and 20.8 [2 s, C (*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.0.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for C$_{24}$H$_{28}$O$_5$P: 427.1675; found: 427.1676.

2-Benzyl-5-(5,5-dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-(4-fluorophenyl)furan (12)

Bright yellow solid; yield: 178 mg (89%); mp 140–142 °C.

IR (KBr): 3112, 3058, 2970, 2893, 1600, 1578, 1518, 1501, 1375, 1282, 1227, 1123, 1063, 1014, 953, 920, 833, 773, 718, 603, 548 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.34–7.08 (m, 10 H, H$_{Ar}$), 4.16 (s, 2 H, PhCH_2), 4.09–4.05 (m, 4 H, OCH$_2$), 1.24 and 0.95 [2 s, 6 H, C (CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 162.2 (d, $^{1}J_{F-C}$ = 245.0 Hz, FC), 155.0 (d, $^{3}J_{P-C}$ = 9.0 Hz, PCO*C*), 142.6 (d, $^{1}J_{P-C}$ = 242.0 Hz, PC), 137.0, 129.6 (d, $^{3}J_{F-C}$ = 8.0 Hz, FC=*C*), 128.8, 128.5, 128.3, 128.2, 126.9, 124.3 (d, $^{2}J_{P-C}$ = 24.0 Hz, PC=*C*), 122.5 (d, $^{3}J_{P-C}$ = 11.0 Hz, PC=C-*C*), 115.8 (d, $^{2}J_{F-C}$ = 22.0 Hz, FC=*C*), 77.1$_4$ and 77.1$_0$ (2 s, OCH$_2$), 33.2 (s, Ph*C*H$_2$), 32.3 [d, $^{3}J_{P-C}$ = 7.0 Hz, *C*(CH$_3$)$_2$], 21.8 and 20.8 [2 s, C(*C*H$_3$)$_2$].

^{31}P NMR: δ = –3.20.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for C$_{22}$H$_{23}$FO$_4$P: 401.1319; found: 401.1317.

5-(5,5-Dimethyl-2-oxo-1,3,2-dioxaphosphinan-2-yl)-3-(4-fluorophenyl)-2-(4-methylbenzyl)furan (13)

Bright yellow solid; yield: 186 mg (88%); mp 128–130 °C.

IR (KBr): 3090, 2964, 2926, 2893, 1600, 1583, 1523, 1495, 1468, 1375, 1287, 1227, 1145, 1112, 1063, 1013, 980, 958, 920, 827, 778, 602, 542, 482 cm^{-1}.

^{1}H NMR (400 MHz, CDCl$_3$): δ = 7.34–7.07 (m, 9 H, H$_{Ar}$), 4.11–4.03 (m, 6 H, OCH$_2$, PhCH_2), 2.33 (s, 3 H, CH$_3$), 1.25 and 0.96 [2 s, 6 H, C(CH$_3$)$_2$].

^{13}C NMR (100 MHz, CDCl$_3$): δ = 162.2 (d, $^{1}J_{F-C}$ = 197.0 Hz, FC), 155.3 (d, $^{3}J_{P-C}$ = 7.0 Hz, PCO*C*), 142.5 (d, $^{1}J_{P-C}$ = 193.0 Hz, PC), 136.4, 133.9, 129.5 (d, $^{3}J_{F-C}$ = 7.0 Hz, FC=*C*), 129.4, 128.3, 124.3 (d, $^{2}J_{P-C}$ = 19.0 Hz, PC=*C*), 122.3 (d, $^{3}J_{P-C}$ = 9.0 Hz, PC=C-*C*), 115.8 (d, $^{2}J_{\text{F-C}}$ = 17.0 Hz, FC=*C*), 77.0 (s, OCH_2), 32.8 (s, Ph*C*H_2), 32.3 [d, $^{3}J_{\text{P-C}}$ = 7.0 Hz, *C*$(CH_3)_2$], 21.8 (s, CH_3), 21.0 and 20.8 [2 s, C(*C*$H_3)_2$].

^{31}P NMR: δ = –3.10.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{23}H_{25}O_4FP$: 415.1475; found: 415.1472.

Diethyl 5-Benzyl-4-phenylfuran-2-ylphosphonate (14)

Light yellow gummy liquid; yield: 130 mg (70%).

IR (neat): 3057, 3030, 2975, 2926, 2904, 1764, 1600, 1490, 1452, 1392, 1255, 1101, 1019, 975, 767, 729, 696 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.18 (m, 11 H, H_{Ar}), 4.19–4.12 (m, 6 H, OCH_2, PhC*H*$_2$), 1.31 (t, $^{3}J_{\text{H-H}}$ = 7.0 Hz, 6 H, C*H*$_3CH_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 155.2 (d, $^{3}J_{\text{P-C}}$ = 9.2 Hz, PCO*C*), 142.3 (d, $^{1}J_{\text{P-C}}$ = 241.1 Hz, PC), 137.4, 132.4, 128.8, 128.6, 128.3, 127.8, 127.4, 126.7, 124.6 (d, $^{2}J_{\text{P-C}}$ = 24.2 Hz, PC=*C*), 123.6 (d, $^{3}J_{\text{P-C}}$ = 10.7 Hz, PC=C-*C*), 62.9 (d, $^{2}J_{\text{P-C}}$ = 5.1 Hz, OCH), 33.1 (s, Ph*C*H_2), 16.2 (d, $^{3}J_{\text{P-C}}$ = 6.4 Hz, *C*H_3CH_2).

^{31}P NMR: δ = 4.31.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{21}H_{24}O_4P$: 371.1413; found: 371.1410.

Diisopropyl 5-Benzyl-4-phenylfuran-2-ylphosphonate (15)

Pale yellow gummy liquid; yield: 138 mg (69%).

IR (neat): 3057, 3024, 2980, 2931, 1757, 1605, 1495, 1457, 1391, 1260, 1100, 986, 772, 728, 690 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40–7.18 (m, 11 H, H_{Ar}), 4.72–4.67 (m, 2 H, OCH), 4.18 (s, 2 H, PhC*H*$_2$), 1.36 and 1.23 (2 d, each $^{4}J_{\text{P-H}}$ = 7.2 Hz, 12 H, CH_3).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 154.9 (d, $^{3}J_{\text{P-C}}$ = 9.0 Hz, PCO*C*), 143.5 (d, $^{1}J_{\text{P-C}}$ = 241.0 Hz, PC), 137.5, 132.5, 128.8, 128.6, 128.3, 127.8, 127.2, 126.6, 124.1 (d, $^{2}J_{\text{P-C}}$ = 24.0 Hz, PC=*C*), 123.5 (d, $^{3}J_{\text{P-C}}$ = 11.0 Hz, PC=C-*C*), 71.8 (d, $^{2}J_{\text{P-C}}$ = 5.0, OCH), 33.1 (s, Ph*C*H_2), 24.0 and 23.7 [2 d, each $^{3}J_{\text{P-C}}$ = 4.0 Hz, C(*C*$H_3)_2$].

^{31}P NMR: δ = 2.00.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{25}H_{28}O_4P$: 399.1726; found: 399.1726.

[5-(2-Nitrobenzyl)-4-phenylfuran-2-yl]diphenylphosphine Oxide (16)

Orange solid; yield: 165 mg (69%); mp 170–172 °C.

IR (KBr): 3408, 3063, 2964, 2921, 2849, 1605, 1529, 1436, 1348, 1200, 1118, 860, 762, 724, 701 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.99–7.09 (m, 20 H, H_{Ar}), 4.56 (s, 2 H, ArC*H*$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 153.5 (d, $^{3}J_{\text{P-C}}$ = 5.0 Hz, PCO*C*), 148.9, 147.3 (d, $^{1}J_{\text{P-C}}$ = 103.0 Hz, PC), 133.3, 132.4, 131.6 (d, $^{3}J_{\text{P-C}}$ = 8.0 Hz, PC=*C*), 131.4, 131.0, 130.9, 128.9, 128.5 (d, $^{2}J_{\text{P-C}}$ = 10.0 Hz, PC=C-*C*), 127.9, 127.7, 127.6, 125.1, 125.0, 124.9, 124.8, 30.8 (s, Ar*C*H_2).

^{31}P NMR: δ = 15.8.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{29}H_{23}O_4NP$: 480.1365; found: 480.1365.

[5-(3-Fluorobenzyl)-4-phenylfuran-2-yl]diphenylphosphine Oxide (17)

Pale yellow gummy solid; yield: 175 mg (78%).

IR (neat): 3051, 2920, 2843, 1747, 1616, 1588, 1484, 1440, 1254, 1205, 1117, 766, 723, 695 cm^{-1}.

^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.79–6.83 (m, 20 H, H_{Ar}), 4.14 (s, 2 H, ArC*H*$_2$).

^{13}C NMR (100 MHz, $CDCl_3$): δ = 162.9 (d, $^{1}J_{\text{F-C}}$ = 196.0 Hz, FC), 155.2 (d, $^{3}J_{\text{P-C}}$ = 5.0 Hz, PCO*C*), 146.8 (d, $^{1}J_{\text{P-C}}$ = 108.0 Hz, PC), 139.9 (d, $^{3}J_{\text{F-C}}$ = 6.0 Hz, FC=*C*), 133.0, 132.9, 132.8, 132.4, 132.3, 132.2, 131.9, 131.8, 131.7, 131.6, 131.5, 131.0, 130.1 (d, $^{3}J_{\text{F-C}}$ = 6.0 Hz, FC=*C*), 128.9, 128.8, 128.6 (d, $^{3}J_{\text{P-C}}$ = 11. 0 Hz, PC=*C*), 128.0, 127.9, 127.5, 124.9 (d, $^{2}J_{\text{P-C}}$ = 14.0 Hz, PC=C-*C*), 124.1, 124.0, 115.3 and 113.6 (2 d, each $^{2}J_{\text{F-C}}$ = 17.0 Hz, FC=*C*), 32.8 (s, ArCH_2).

^{31}P NMR: δ = 16.00.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{29}H_{23}O_2FP$: 453.1420; found: 453.1418.

5,5-Dimethyl-2-[(*E*,*E*)-5-oxo-3,5-diphenylpentyl]-1,3,2-dioxaphosphinan-2-one (18)

A mixture of the H-phosphonate **2a** (0.5 mmol), 3-alkynylcinnamaldehyde **1a** (g, 0.5 mmol), and $AgBF_4$ (0.05 mmol, 10 mol%) in DCE (2 mL) was stirred overnight at r.t. under a N_2 atmosphere. After completion of the reaction, the mixture was quenched with H_2O (2 mL) and extracted with EtOAc. Solvent was removed under vacuum and the crude product **18** was purified by column chromatography (silica gel, hexane–EtOAc, 1:1) to give a bright yellow solid; yield: 180 mg (95%); mp 128–130 °C.

IR (KBr): 3030, 2975, 2937, 2877, 1655, 1605, 1551, 1474, 1441, 1359, 1277, 1222, 1058, 1008, 942, 838, 778, 701, 619, 553 cm^{-1}.

^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.19 (dd→t, $^{2}J_{\text{P-H}} \sim {}^{3}J_{\text{H-H}}$ = 20.0 Hz, 1 H, P-CH), 7.98 (m, 2 H), 7.60–7.45 (m, 8 H), 7.13 (s, 1 H), 5.93 (dd→t, $^{3}J_{\text{P-H}} \sim {}^{3}J_{\text{H-H}}$ = 19.0 Hz, 1 H, PC=CH), 4.12–4.08 (m, 4 H), 1.24 and 1.03 [2 s, 6 H, C $(CH_3)_2$].

^{13}C NMR (100 MHz, $CDCl_3$): δ = 190.7, 155.7 (d, $^{2}J_{\text{P-C}}$ = 20.0 Hz, PC*C*H), 145.5 (d, $^{3}J_{\text{P-C}}$ = 6.0 Hz, PCC*C*H), 138.3, 133.3, 129.1, 128.9, 128.8, 128.7, 128.6, 127.3, 123.1 (d, $^{1}J_{\text{P-C}}$ = 144.0 Hz, PC), 77.3 and 77.1 (2 s, OCH_2), 32.6 [d, $^{3}J_{\text{P-C}}$ = 5.0 Hz, *C*$(CH_3)_2$], 21.9 and 21.1 [2 s, C(*C*$H_3)_2$].

^{31}P NMR: δ = 11.70.

HRMS (ESI): *m/z* [M + H]$^+$ calcd for $C_{22}H_{24}O_4P$: 383.1411; found: 383.1413.

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