J. Chem. Sci. Vol. 125, No. 6, November 2013, pp. 1405–1417.

Reactivity of allenylphosphonates and allenylphosphine oxides toward 9-chloroacridines and acridone– A facile route to new *N*-substituted acridones

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MS received 4 June 2013; revised 16 August 2013; accepted 21 August 2013

Abstract. Base-mediated addition of acridones to allenylphosphonates/allenylphosphine oxides $(OCH_2CMe_2CH_2O)P(O)CH{=}C{=}CR^1R^2$ {$R^1 = R^2 =$ Me (**1**), $R^1 = R^2 = [-CH_2-]_5$ (**2**)}, $Ph_2P(O)C(H){=}C{=}CR^1R^2$ {$R^1 = R^2 =$ Me (**3**), $R^1 = R^2 = [-CH_2-]_5$ (**4**)} and $(EtO)_2P(O)C(H){=}C{=}CMe_2$ (**5**) in DMF results in the regiospecific formation of phosphono-acridones and acridonylphosphine oxides. The acridone addition products were also obtained in the reaction of allenes **1** and **2** with 9-chloroacridine under [Pd]-catalysed conditions, along with (unexpected) α-acridinyl substituted allenes. In contrast, 9-benzyl-6-chloro-purine reacted with **1** affording a β-substituted purinone phosphonate. Allenes **1**–**2** did not react with acridones in the absence of base (CsF), but in the presence of $Pd(OAc)_2$/DMF (or DMA)/pivalic acid rearranged to give 1,3-butadienes probably via [Pd]-allyl complexes. The phosphono-acridones were amenable to Horner–Wadsworth–Emmons (HWE) reaction and led to *N*-substituted acridones. Key products have been characterized by single-crystal X-ray crystallography.

Keywords. Allenylphosphonate/allenylphosphine oxide; acridone; 9-chloroacridine; 9-benzyl-6-chloro-purine; Horner–Wadsworth–Emmons reaction.

1. Introduction

Allenes (or 1,2-dienes) are valuable synthons both industrially and biologically because of the availability of two cumulative double bonds.[1,2] Allenylphosphonates and allenylphosphine oxides (phosphorylated allenes, e.g., **1**–**5**) that constitute a subclass of allenes are also used as versatile building blocks in organic chemistry.[3] Our research group has reported that the nucleophilic addition of amines/nucleobases to allenylphosphonates by using **1** and related allenes resulted in the formation of β-aminophosphonates (e.g., **6**–**8**); here stereochemistry of the products depends on the type of amine used.[4] Recently, rhodium/gold catalysed intermolecular hydroamination of allenes leading to branched allylic amines has been reported independently by Kimber *et al.*,[5a] Breit *et al.*[5b] and Widenhoefer *et al.*[5c] We have previously reported the synthesis of phosphono-benzofurans,[6a,c] pyrazoles,[3c] –chromenes,[6b] –oxindoles,[6d] and indolo-lactones[6e] by [Pd]-catalysed reactions from inexpensive phosphorylated allenes. In most of the [Pd]-catalysed reactions using iodoarenes, we observed that the initial attack occurred at the β-position of the allenes (cf. scheme 1, compound **9**).[6a] One of our initial objectives was to utilize the analogous reactions of allenes with 9-chloroacridine[7] to obtain phosphonoacridines, since substituted acridines [e.g., Amsacrine, a drug used in acute *lymphoblastic leukemia*] are pharmaceutically important.[8] However, in our reactions using allenylphosphonates, we also obtained acridone (formed by hydrolysis of 9-chloroacridine) addition products. Acridone derivatives are important synthetic targets in medicinal chemistry and pharmaceutical industry and exhibit a variety of biological activities.[9a] Recently, Kelly *et al*. have reported an encouraging results with the use of an acridone derivative against drug-resistant malarial parasites both *in vitro* and in mice models.[9b,c] Studies have also shown that *N*-substituted acridone derivatives display high antiviral activity against the hemorrhagic fever causing arenavirus JUNV,[9d] bovine viral diarrhea virus (BVDV);[9e] moreover, these derivatives are antagonists to P2X4 receptors and have the ability for the treatment of neuropathic pain and neurodegenerative diseases.[9f] Acridonium-based fluorescent probes were shown to have the ability of detecting the anions (like F^-, Cl^-, AcO^-, etc.).[9g] Apart from these,

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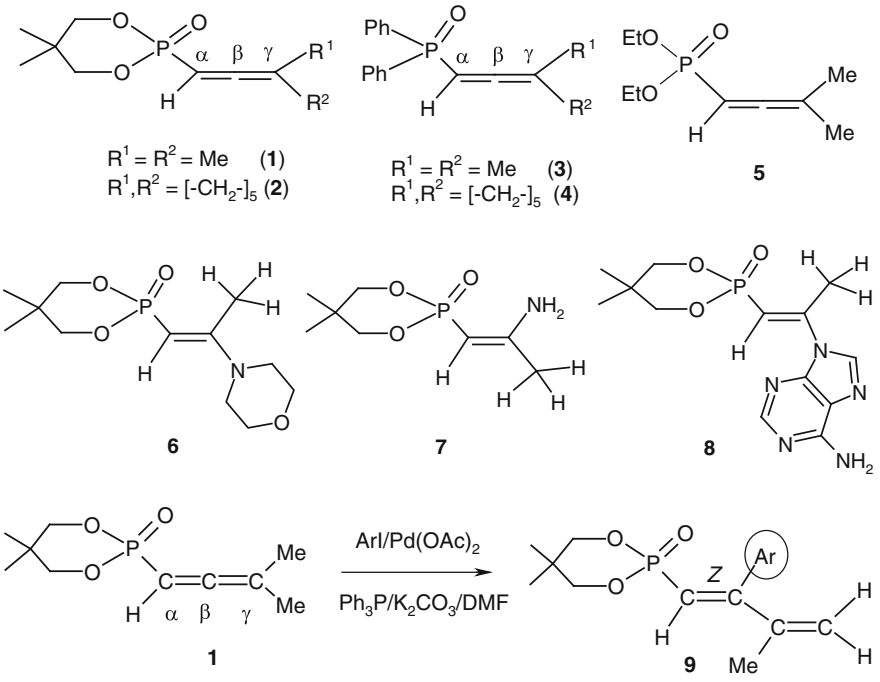


Scheme 1. Palladium catalysed Heck-type arylation showing the attack at the β-position of allenylphosphonate **1**.

10-substituted acridones are used as antipsoriatic agents.[9h] Therefore, there is continuing interest in the development of an efficient and versatile methods to access *N*-substituted acridone derivatives. Thus, in the first part, we report simple base-mediated addition of N–H bond of acridone to phosphorylated allenes **1**–**5** to give the corresponding phosphonoyl acridone and acridonyl phosphine oxide derivatives in good to high yields. Since these products are obtained alongside the acridinyl allene when [Pd]-catalysed reaction of allenes with 9-chloroacridines, this part will be discussed next. This reaction is then compared with that using 9-benzyl-6-chloropurine. In the presence of the [Pd] catalyst, instead of acridone addition, *allene* to *butadiene* rearrangement occurs. This is discussed later. Finally, we have shown that phosphonoyl acridones can be conveniently utilized to prepare *N*-substituted acridones via Horner–Wadsworth–Emmons reaction.[10]

2. Experimental

Solvents were dried according to known methods as appropriate.[11] ^{1}H, ^{13}C, and ^{31}P NMR spectra (^{1}H, 400 MHz; ^{13}C, 100 MHz; ^{31}P, 162 MHz) were recorded using a 400 MHz spectrometer in $CDCl_3$ with shifts referenced to $SiMe_4$ ($\delta = 0$) or 85% H_3PO_4 ($\delta = 0$). IR spectra were recorded on an FTIR 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 LC-MS and HRMS (ESI-TOF) equipment.

Allenylphosphonates **1**–**3** and allenylphosphine oxides **4**–**5** were prepared by literature methods.[12] Acridones **10**–**12** and 9-chloro-acridine were prepared by following a reported method.[13]

2.1 *Representative procedure for the synthesis of acridonyl allylphosphonates/allylphosphine oxides **13**–**23***

A mixture of allene (one among **1**–**5**) (1.0 mmol), acridone (one among **10**–**12**) (1.0 mmol), and CsF (0.303 g, 2.0 mmol) in DMF (5 mL) was heated at 100°C for 4–6 h. When the starting material was consumed fully (^{31}P NMR or TLC), the solvent was removed, reaction mixture quenched with water (5 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic layer was washed with water (2 × 20 mL), brine solution (20 mL), dried (Na_2SO_4) and then the solvent removed to obtain the crude material which was purified by column chromatography using silica gel with ethyl acetate/hexane (3:2) mixture as eluent to afford the corresponding product among **13**–**23**.

2.1a *Compound **13***: Yield 0.35 g (86%, Pale yellow solid) M.p.: 170–172°C; IR (KBr, cm^{-1}) 3069, 2957, 1634, 1601, 1485, 1458, 1264, 1063, 1017. ^{1}H NMR

(400 MHz, $CDCl_3$) δ 0.73 and 0.91 (2 s, 6H, 2 CH_3), 1.52 (d, 3H, J(P-H) = 5.8 Hz, = CCH_3(A)), 2.24 (d, 3H, J(P-H) = 4.5 Hz, = CCH_3(B)), 3.00 (d, 2H, J(P-H) = 21.1 Hz, PCH_2), 3.34 (dd→t, 2H, J(P-H) = J(H-H) ∼ 11.2 Hz, OCH_2), 3.78 (dd→t, 2H, J(P-H) = J(H-H) ∼ 11.6 Hz, OCH_2), 7.32 (t, 2H, J(H-H) = 7.4 Hz, Ar-H), 7.48 (d, 2H, J(H-H) = 8.8 Hz, Ar-H), 7.68–7.72 (m, 2H, Ar-H), 8.56–8.58 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.8, 21.3, 21.4, 27.6 (d, J(P-C) = 135.1 Hz, PCH_2), 32.4 (d, J(P-C) = 6.0 Hz, C(Me)$_2$), 75.4, 75.5, 116.9, 119.6, 121.9, 122.2, 127.6, 133.8, 140.6, 178.2 (C=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.5. LC/MS m/z 412 $[M+1]^+$; Anal.Calcd. for $C_{23}H_{26}NO_4P$: C, 67.14; H, 6.37; N, 3.40. Found: C, 66.95; H, 6.45; N, 3.56.

2.1b *Compound* ***14***: Yield 0.36 g (85%, green solid). M.p.: 172–176°C; IR (KBr, cm^{-1}) 3071, 2973, 1632, 1601, 1495, 1480, 1271, 1059, 1007. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.74 and 0.94 (2 s, 6H, 2 CH_3), 1.52 (d, 3H, J(P-H) = 5.6 Hz, = CCH_3(A)), 2.24 (d, 3H, J(P-H) = 4.4 Hz, = CCH_3(B)), 2.50 (s, 3H, Ar-CH_3), 3.00 (d, 2H, J(P-H) = 20.8 Hz, PCH_2), 3.33–3.38 (m, 2H, OCH_2), 3.35–3.80 (m, 2H, OCH_2), 7.31 (t, 1H, J(H-H) = 7.6 Hz, Ar-H), 7.40 (d, 1H, J(H-H) = 8.8 Hz, Ar-H), 7.46 (d, 1H, J(H-H) = 8.4 Hz, Ar-H), 7.52–7.55 (m, 1H, Ar-H), 7.68–7.71 (m, 1H, Ar-H), 8.37 (br s, 1H, Ar-H), 8.57–8.59 (m, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3 (d, J(P-C) = 3.0 Hz, C=CCH$_3$), 20.7 (d, J(P-C) = 3.0 Hz, C=CCH$_3$), 20.8, 21.2, 21.4, 27.4 (d, J(P-C) = 135.0 Hz, PCH$_2$), 32.3 (d, J(P-C) = 6.0 Hz, C(Me)$_2$), 75.4, 75.5, 116.8 (d, J(P-C) = 12.4 Hz, PCC=CMe$_2$), 119.7, 119.8, 121.6, 122.0 (d, J(P-C) = 2.0 Hz), 126.7, 127.5, 131.5, 133.5, 135.2, 138.6, 140.4, 142.1, 142.2, 178.0 (C=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.5. LC/MS m/z 426 $[M]^+$. Anal. Calcd. for $C_{24}H_{28}NO_4P$: C, 67.75; H, 6.63; N, 3.29. Found: C, 67.85; H, 6.54; N, 3.41.

2.1c *Compound* ***15***: Yield 0.39 g (80%, yellow solid). M.p.: 160–162°C; IR (KBr, cm^{-1}) 2964, 2915, 1633, 1595, 1474, 1458, 1266, 1063, 1019, 811. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.78 and 0.88 (2 s, 6H, 2 CH_3), 1.51 (d, 3H, J(P-H) = 5.8 Hz, = CCH_3(A)), 2.23 (d, 3H, J(P-H) = 4.3 Hz, = CCH_3(B)), 2.92–3.08 (m, 2H, PCH_2), 3.30–3.47 (m, 2H, OCH_2), 3.77–3.87 (m, 2H, OCH_2), 7.34 (t, 1H, J(H-H) = 7.4 Hz, Ar-H), 7.43 (t, 2H, J(H-H) = 8.6 Hz, Ar-H), 7.69–7.76 (m, 2H, Ar-H) 8.56 (d, 1H, J(H-H) = 8.0 Hz, Ar-H), 8.67 (d, 1H, J(H-H) = 1.6 Hz, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.3, 20.7, 21.3, 22.7, 25.3, 27.6 (d, J(P-C) = 135.8 Hz, PCH$_2$), 32.4 (d, J(P-C) = 5.7 Hz, C(Me)$_2$), 75.3 (d, J(P-C) = 5.9 Hz), 75.5 (d, J(P-C) = 6.1 Hz), 115.3, 116.7, 119.2, 119.5 (d, J(P-C) = 10.9 Hz), 122.2 (d, J(P-C) = 9.2 Hz), 123.3, 127.7, 129.8, 134.1, 136.5, 139.4, 140.3, 142.7 (d, J(P-C) = 10.2 Hz), 177.0 (C=O); ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.6; HRMS (ESI) Calcd. for $C_{23}H_{26}BrNO_4P$ $[M^+ + H]$ 490.0784 and 492.0784. Found: 490.0783 and 492.0766.

2.1d *Compound* ***16***: Yield 0.38 g (85%, pale yellow solid). M.p.: 178–180°C; IR (neat, cm^{-1}) 2964, 2926, 2888, 2241, 1671, 1600, 1375, 1266, 1063, 1014, 734. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 and 0.89 (2 s, 6H, 2 CH_3), 1.41 (d, 2H, cyclohexyl-H), 1.59 (br s, 2H, cyclohexyl-H), 1.86 (br s, 4H, cyclohexyl-H), 2.66 (br s, 2H, cyclohexyl-H), 3.01 (d, 2H, J = 21.2 Hz, PCH_2), 3.32–3.37 (m, 2H, OCH_2), 3.75–3.81 (m, 2H, OCH_2), 7.28–7.32 (m, 2H, Ar-H), 7.52–7.55 (d, J = 8.8 Hz, 2H, Ar-H), 7.66–7.70 (m, 2H, Ar-H), 8.56 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3 (d, J(P-C) = 6.3 Hz), 26.0, 26.8, 27.1_8, 27.2_3 (d, J(P-C) = 134.9 Hz, PCH$_2$), 29.9, 31.1, 32.3 (d, J(P-C) = 6.0 Hz, CMe$_2$), 75.3 (d, J(P-C) = 6.2 Hz), 116.1 (d, J(P-C) = 10.8 Hz), 117.0, 121.8, 122.1, 127.4, 133.6, 140.8, 148.8 (d, J(P-C) = 9.8 Hz), 178.1 (C=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8. HRMS (ESI) calcd. for $C_{26}H_{31}NO_4P$ $[M^+ + H]$: 452.1991. Found: 452.1992.

2.1e *Compound* ***17***: Yield 0.41 g (90%, brown solid). M.p.: 168–170°C; IR (KBr, cm^{-1}) 3047, 2959, 2926, 1638, 1600, 1501, 1479, 1337, 1271, 1063, 1019, 816. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.73 and 0.90 (2 s, 6H, 2 CH_3), 1.40–1.41 (m, 2H, cyclohexyl-H), 1.58 (br s, 2H, cyclohexyl-H), 1.85 (br s, 4H, cyclohexyl-H), 2.47 (s, 3H, CH_3), 2.63–2.67 (m, 2H, cyclohexyl-H), 3.01 (d, 2H, J(P-H) = 20.8 Hz, PCH_2), 3.35 (t, J = 11.0 Hz, 2H, OCH_2), 3.77 (m, 2H, J = 11.4 Hz, 2H, OCH_2), 7.28–7.30 (m, 1H, Ar-H), 7.44 (d, J = 8.4 Hz, 1H, Ar-H), 7.51 (d, J = 8.4 Hz, 2H, Ar-H), 7.65–7.69 (m, 1H, Ar-H), 8.34 (s, 1H, Ar-H), 8.55 (dd, J = 1.4 and 8.8 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.8, 21.3 (d, J(P-C) = 10.1 Hz), 26.0, 26.8, 27.1_5 (d, J(P-C) = 134.8 Hz, PCH$_2$), 27.2, 29.9, 31.0, 32.3 (d, J(P-C) = 6.0 Hz, CMe$_2$), 75.4 (d, J(P-C) = 6.0 Hz), 116.2 (d, J(P-C) = 10.8 Hz), 116.9 (d, ^3J(P-C) = 12.0 Hz), 121.5, 122.0, 126.7, 127.4, 131.5, 133.4, 135.1, 138.9, 140.7, 148.7 (d, J(P-C) = 9.9 Hz), 178.0 (C=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8. HRMS (ESI) calcd. for $C_{27}H_{32}NO_4PNa$ $[M^+ + Na]$ 488.1966. Found: 488.1961.

2.1f *Compound* ***18***: Yield 0.48 g (90%, pale yellow solid). M.p.: 176–178°C; IR (KBr, cm^{-1}) 3073, 2937, 2849, 1633, 1600, 1474, 1458, 1255, 1058, 1003, 816. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.79 and 0.91 (2 s, 6H, 2 CH_3), 1.39–1.43 (m, 2H, cyclohexyl-*H*), 1.58–1.60 (m, 2H, cyclohexyl-*H*), 1.83–1.88 (m, 4H, cyclohexyl-*H*), 2.64–2.65 (m, 2H, cyclohexyl-*H*), 2.92 (dd, J = 21.2 and 6.3 Hz, 1H, PCH_AH_B), 3.09 (dd, J = 20.9 and 6.3 Hz, 1H, PCH_AH_B), 3.32–3.47 (m, 2H, OCH_2), 3.79–3.90 (m, 2H, OCH_2), 7.30–7.34 (m, 1H, Ar-H) 7.49 (t, J = 8.6 Hz, 2H, Ar-*H*), 7.68–7.75 (m, 2H, Ar-*H*), 8.52–8.54 (m, 1H, Ar-*H*), 8.65 (d, J = 2.4 Hz, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.3, 25.9, 26.7, 27.1, 27.3 (d, J(P-C) = 135.4 Hz, P*C*H_2), 29.9, 31.0, 32.4 (d, J(P-C) = 5.8 Hz, *C*(Me)$_2$), 75.2 (d, J(P-C) = 6.1 Hz), 75.4 (d, J(P-C) = 6.3 Hz), 115.2, 116.0 (d, J(P-C) = 10.9 Hz), 116.9, 119.4, 122.1, 122.2, 123.2, 127.5, 129.6, 134.0, 136.3, 139.7, 140.6, 149.2 (d, J(P-C) = 10.0 Hz), 176.8 (*C*=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 19.8. HRMS (ESI) calcd. for $C_{26}H_{30}BrNO_4P$ [M^++H] 530.1097 and 532.1097. Found: 530.1098 and 532.1085. This compound was crystallized from ethyl acetate/hexane (1:1) mixture at 25°C. X-ray structure was determined for this compound.

2.1g *Compound* ***19***: Yield 0.39 g (85%, colorless solid). M.p.: 192–194°C; IR (KBr, cm^{-1}) 3057, 2957, 2905, 1634, 1601, 1483, 1433, 1265, 1167, 1117. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.52 (d, 3H, J(P-H) = 4.4 Hz, =CCH_3(A)), 2.24 (d, 3H, J(P-H) = 4.8 Hz, =CCH_3(B)), 3.60 (d, 2H, J(P-H) = 12.8 Hz, PCH_2), 7.10–7.14 (m, 4H, Ar-*H*), 7.18–7.22 (m, 2H, Ar-*H*), 7.25–7.35 (m, 6H, Ar-*H*), 7.43 (d, J(H-H) = 8.4 Hz, 2H, Ar-*H*), 7.56–7.60 (m, 2H, Ar-*H*), 8.36–8.39 (m, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.5, 20.9, 34.0 (d, J(P-C) = 67.7 Hz, P*C*H_2), 117.1, 120.9 (d, J(P-C) = 9.1 Hz, PC*C*=CMe_2), 121.5, 122.1, 127.5, 128.3, 128.4, 131.7, 132.5 (d, J(P-C) = 99.5 Hz, P*C*), 133.6, 140.3, 142.1 (d, J(P-C) = 8.7 Hz), 177.8 (*C*=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.4. LC/MS m/z 464 $[M+1]^+$.Anal.Calcd. for $C_{30}H_{26}NO_2P$: C, 77.74; H, 5.65; N, 3.02. Found: C, 77.63; H, 5.58; N, 3.12; This compound was crystallized from ethyl acetate/hexane (2:1) mixture at 25°C. X-ray structure was determined for this compound.

2.1h *Compound* ***20***: Yield 0.42 g (88%, brown solid). M.p.: 110–112°C; IR (KBr, cm^{-1}) 3058, 2921, 2855, 1638, 1600, 1496, 1441, 1342, 1293, 1189, 1117, 729. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.48 (d, 3H, J(P-H) = 4.3 Hz, =CCH_3(A)), 2.31 (d, 3H, J(P-H) = 3.0 Hz, =CCH_3(B)), 2.42 (s, 3H, Ar-CH_3), 3.54 (d, 2H, J(P-H) = 12.7 Hz, PCH_2), 7.06–7.24 (m, 6H, Ar-*H*), 7.29–7.40 (m, 8H, Ar-*H*), 7.53 (t, J = 7.1 Hz, 1H, Ar-*H*), 8.15 (br s, 1H, Ar-*H*), 8.34 (d, J = 7.9 Hz, 1H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.4, 20.7 (d, J(P-C) = 15.0 Hz, C=C*C*H_3), 29.7, 33.9 (d, J(P-C) = 67.5 Hz, P*C*H_2), 117.0 (d, J(P-C) = 5 Hz, PC*C*=CMe_2), 120.8 (d, J(P-C) = 10.6 Hz), 121.2, 121.8, 126.7, 127.4, 128.2 (d, J(P-C) = 11.5 Hz), 130.0, 131.1, 131.6, 132.5 (d, J(P-C) = 98.0 Hz, P*C*), 132.7, 133.4, 135.0, 138.3, 140.1, 142.0 (d, J(P-C) = 8.2 Hz), 177.6 (*C*=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.6. HRMS (ESI) calcd. for $C_{31}H_{29}NO_2P$ [M^++H] 478.1937. Found: 478.1934.

2.1i *Compound* ***21***: Yield 0.45 g (87%, Yellow solid). M.p.: 140–142°C; IR (KBr, cm^{-1}) 3057, 2926, 2854, 1643, 1594, 1495, 1435, 1336, 1292, 1177, 761. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.39–1.46 (m, 2H, cyclohexyl-*H*), 1.52–1.60 (m, 2H, cyclohexyl-*H*), 1.83–1.87 (m, 4H, cyclohexyl-*H*), 2.42 (s, 3H, Ar-CH_3), 2.77 (br s, 2H, cyclohexyl-*H*), 3.56 (d, 2H, J(P-H) = 12.8 Hz, PCH_2), 7.09–7.16 (m, 5H, Ar-*H*), 7.19–7.36 (m, 7H, Ar-*H*), 7.43–7.54 (m, 3H, Ar-*H*), 8.16 (s, 1H, Ar-*H*), 8.34 (d, J = 8.0 Hz, 1H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 20.7, 22.7, 26.1, 27.0, 27.6, 29.7, 30.1, 31.2, 32.0, 33.3 (d, J(P-C) = 67.6 Hz, P*C*H_2), 36.7, 117.1, 121.2, 121.8, 126.6, 127.3, 128.3 (d, J(P-C) = 11.5 Hz, PC*C*=CMe_2), 130.0, 131.1, 132.3 (d, J(P-C) = 98.5 Hz, P*C*), 132.6, 133.3, 135.0, 138.7, 140.5, 149.0, 177.7 (*C*=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 26.8. HRMS (ESI) calcd. for $C_{34}H_{33}NO_2P$ [M^++H] 518.2249. Found: 518.2247.

2.1j *Compound* ***22***: Yield 0.52 g (90%, pale yellow solid). M.p.: 194–196°C; IR (KBr, cm^{-1}) 3057, 2970, 2926, 2854, 1638, 1479, 1332, 1271, 1167, 1123, 750. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35–1.46 (m, 2H, cyclohexyl-*H*), 1.60–1.62 (m, 2H, cyclohexyl-*H*), 1.83–1.93 (m, 4H, cyclohexyl-*H*), 2.76 (br s, 2H, cyclohexyl-*H*), 3.44 (dd, J = 20.1 and 3.8 Hz, 1H, PCH_AH_B), 3.63 (dd, J = 22.1 and 3.8 Hz, 1H, PCH_AH_B), 7.06–7.10 (m, 2H, Ar-*H*), 7.16–7.20 (m, 2H, Ar-*H*), 7.23–7.32 (m, 5H, Ar-*H*), 7.36–7.46 (m, 4H, Ar-*H*), 7.52–7.55 (m, 1H, Ar-*H*), 7.60–7.63 (m, 1H, Ar-*H*), 8.37–8.40 (m, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.0, 26.9, 27.6, 30.1, 31.3, 33.3 (d, J(P-C) = 67.4 Hz, P*C*H_2), 114.9, 117.0, 120.0, 122.1 (d, J(P-C) = 15.6 Hz, PC*C*=CMe_2), 123.0, 127.6, 128.2, 128.3, 128.4, 128.5, 129.5, 130.0, 131.7, 131.8 (d, J(P-C) = 96.8 Hz, P*C*), 132.5, 133.4, 133.9, 136.0, 139.5, 140.4, 149.4, 176.5 (*C*=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 25.9. HRMS (ESI) calcd. for $C_{33}H_{30}BrNO_2P$ [M^++H] 582.1198 and 584.1198. Found: 582.1193 and 584.1176.

2.1k *Compound* ***23***: Yield 0.35 g (88%, gummy liquid); IR (neat, cm^{-1}) 3069, 2975, 2915, 1638, 1605, 1479, 1458, 1353, 1260, 1030, 767. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (t, J = 7.0 Hz, 6H, 2 CH_3), 1.50 (d, 3H, J(P-H) = 5.6 Hz, = CCH_3(A)), 2.17 (d, 3H, J(P-H) = 4.4 Hz, = CCH_3(B)), 2.96 (d, 2H, J(P-H) = 22.0 Hz, PCH_2), 3.67–3.79 (m, 4H, 2 OCH_2), 7.27–7.31 (m, 2H, Ar-*H*), 7.42 (d, 2H, J = 8.4 Hz, Ar-*H*), 7.65–7.69 (m, 2H, Ar-*H*), 8.54 (d, 2H, J = 1.2 Hz, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.9 (d, J(P-C) = 5.8 Hz, OCH$_2$*C*H$_3$), 20.4 (d, J(P-C) = 21.4 Hz, C=C*C*H$_3$), 29.1 (d, J(P-C) = 141.0 Hz, P*C*H$_2$), 61.7 (d, J(P-C) = 6.2 Hz, O*C*H$_2$CH$_3$), 120.7 (d, J(P-C) = 12.2 Hz, PC*C*=CMe$_2$), 121.7, 122.1, 127.5, 133.5, 140.7, 141.0 (d, J(P-C) = 10.5 Hz), 178.1 (*C*=O). ^{31}P NMR (162 MHz, $CDCl_3$) δ 24.2. HRMS (ESI) calcd. for $C_{22}H_{27}NO_4P$ [M^++H] 400.1678. Found: 400.1680.

2.2 *Synthesis of α-acridinyl allenylphosphonate derivatives* ***24*** *and* ***25***

A mixture of allene (**1** or **2**) (0.216 g, 1.0 mmol), 9-chloroacridine (0.213 g, 1.0 mmol), $Pd(OAc)_2$ (5 mol%) and CsF (0.303 g, 2.0 mmol) in DMF (5 mL) was heated at 100°C for 4–6 h. When the starting material was consumed fully (^{31}P NMR or TLC), the solvent was removed, reaction mixture quenched with water (5 mL) and extracted with ethyl acetate (2 × 30 mL). The combined organic layer was washed with water (2 × 20 mL), brine solution (20 mL), dried (Na_2SO_4) and then the solvent was removed to obtain the crude material which was purified by column chromatography using silica gel with ethyl acetate/hexane (3:2) mixture as eluent to afford the corresponding product **24** or **25**. Reaction using PPh_3/K_2CO_3 in place of CsF did not give these products. *Note*: Along with these, we obtained the corresponding acridone derivatives also. Rest of the allenes (**3**–**5**), when treated with 9-chloroacridine gave only acridone derivatives.

2.2a *Compound* ***24***: Yield 0.08 g [20%, white solid; combined yield of **13**+**24** was > 90%]. Melting point (M.p.): 184–186°C; IR (KBr, cm^{-1}) 2946, 2907, 1958, 1634, 1601, 1485, 1458, 1265, 1061, 1011. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.47 and 0.88 (2 s, 6H, 2 CH_3), 1.91–1.93 (m, 6H, =C(CH_3)$_2$), 3.57–3.61 (m, 2H, OCH_2), 4.12–4.18 (m, 2H, OCH_2), 7.61 (d, 2H, J(H-H) ~ 7.8 Hz, Ar-*H*), 7.82 (d, 2H, J(H-H) ~ 7.8 Hz, Ar-*H*), 8.27 (~t, 2H, J(H-H) ~7.8 Hz, Ar-*H*), 8.38 (~t, 2H, J(H-H) ~7.8 Hz, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 19.0, 19.1, 20.8, 21.3, 32.2 (d, J(P-C) = 6.0 Hz, *C*Me$_2$), 75.7, 75.8, 88.8 (d, J(P-C) = 199.1 Hz, P-*C*=C=C), 99.3 (d, J(P-C) = 16.0 Hz, P-C=C=*C*), 125.2, 125.3, 126.0, 126.5, 129.8, 130.1, 138.5, 148.9, 211.4. ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.7. LC/MS m/z 285 $[M+1]^+$; Anal.Calcd. for $C_{23}H_{24}NO_3P$: C, 70.22; H, 6.15; N, 3.56. Found: C, 70.12; H, 6.10; N, 3.61. This compound was crystallized from ethyl acetate/hexane (1:1) mixture at 25°C. X-ray structure was determined for this compound.

2.2b *Compound* ***25***: Yield 0.09 g (20%, pale brown solid; combined yield of **16**+**25** by ^{31}P NMR was >95%). M.p.: 210–212°C; IR (KBr, cm^{-1}) 2975, 2926, 2849, 1967, 1539, 1457, 1325, 1260, 1057, 1002, 986, 838, 777. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.52 and 0.90 (2 s, 6H, 2 CH_3), 1.42–1.47 (m, 4H, cyclohexyl-*H*), 1.71–1.73 (m, 2H, cyclohexyl-*H*), 2.24–2.29 (m, 2H, cyclohexyl-*H*), 2.43–2.48 (m, 2H, cyclohexyl-*H*), 3.60–3.66 (m, 2H, OCH_2), 4.06–4.11 (m, 2H, OCH_2), 7.58 (t, J = 7.6 Hz, 2H, Ar-*H*), 7.79 (t, J = 7.6 Hz, 2H, Ar-*H*), 8.24 (d, 2H, J = 8.8 Hz, Ar-*H*), 8.36 (d, J = 8.8 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 20.9, 21.3, 25.6, 26.5, 29.7, 32.3 (d, J(P-C) = 6.0 Hz, *C*Me$_2$), 75.9 (d, J(P-C) = 6.0 Hz, P-O-*C*), 88.2 (d, J(P-C) = 197.0 Hz, P-*C*), 105.6 (d, J(P-C) = 15.0 Hz, P-C=C=*C*), 125.3, 126.0, 126.6, 129.6, 130.1, 138.8, 148.8, 208.1. ^{31}P NMR (162 MHz, $CDCl_3$) δ 8.9. HRMS (ESI) calcd. for $C_{26}H_{29}NO_3P$ $[M+H]^+$: 434.1886. Found: 434.1882. This compound was crystallized from ethyl acetate/hexane (1:1) mixture at 25°C. X-ray structure was determined for this compound.

2.3 *Synthesis of phosphono-purine derivative* ***27***

In a 25 mL round-bottomed flask, a mixture of allene (0.098 g, 0.4 mmol), 9-benzyl 6-chloro-purine (0.100 g, 0.4 mmol), $Pd(OAc)_2$ (0.092 g, 0.04 mmol) and K_2CO_3 (0.113 g, 0.81 mmol), PPh_3 (0.032 g, 0.12 mmol) in DMF (2 mL) solvent was heated at 100°C for 12 h. When the starting material was consumed fully (^{31}P NMR or TLC), the solvent was removed, reaction mixture quenched with water (5 mL) and extracted with ethyl acetate (2 × 20 mL). The combined organic layer was washed with water (2 × 10 mL), brine solution (10 mL), dried (Na_2SO_4) and then the solvent was removed to obtain the crude material which was purified by column chromatography using silica gel with ethyl acetate/methanol (9:1) mixture as eluent to afford the product **27**. Yield 0.127 g (67%, white solid). M.p.: 228–230°C; IR (neat, cm^{-1}) 3112, 3063, 3030, 2948, 2849, 1677, 1573, 1540, 1507, 1441, 1358, 1266, 1057, 1008, 816. ^{1}H NMR (400 MHz, $CDCl_3$)) δ 1.00 (s, 6H,

2 CH_3), 1.48–1.60 (m, 4H, cyclohexyl-H), 1.74–1.75 (m, 2H, cyclohexyl-H), 1.90–1.97 (m, 2H, cyclohexyl-H), 2.31–2.47 (m, 2H, cyclohexyl-H), 3.14 (dd, 1H, J = 16.4 and 3.2 Hz, PCH_AH$_B$), 3.37 (dd, J = 16.0 and 3.2 Hz, 1H, PCH$_A$$H_B$), 3.64 (t, J = 11.8 Hz, 1H, OCH_AH$_B$), 3.83 (t, J = 11.8 Hz, 1H, OCH$_A$$H_B$), 4.00 (t, J = 10.8 Hz, 1H, OCH_AH$_B$), 4.14 (t, J = 10.8 Hz, 1H, OCH$_A$$H_B$), 5.32 (s, 2H, C$H_2$Ar), 7.30–7.38 (m, 5H, Ar-H), 7.72 (s, 1H, Ar-H), 7.80 (s, 1H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4 (d, J(P-C) = 11.0 Hz), 26.0, 26.2, 27.1, 27.5, 30.4 (d, J(P-C) = 94.0 Hz), 32.6 (d, J(P-C) = 5.8 Hz, CMe$_2$), 47.6, 75.3 (d, J(P-C) = 6.2 Hz), 75.6 (d, J(P-C) = 6.2 Hz), 118.9 (d, J(P-C) = 12.5 Hz), 124.0, 128.0, 128.6, 129.1, 135.0, 140.0, 144.7 (d, J(P-C) = 11.1 Hz), 148.0, 149.3, 156.6. ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.6. HRMS (ESI) calcd. for $C_{25}H_{31}N_4O_4PNa$ [M$^+$+Na]: 505.1981. Found: 505.2004. X-ray structure was determined for this compound after crystallization from methanol.

2.4 *Synthesis of phosphono-butadienes **28** and **29** by using allenylphosphonates **1** and **2***

To $Pd(OAc)_2$ (0.14 mmol) and allenylphosphonate (**1** or **2**) (1.4 mmol) in a 25 mL RBF, was added dimethylformamide (DMF) [or dimethylacetamide (DMA)]/ pivalic acid mixture (5 mL; 4:1) and then the reaction mixture was gradually heated from room temperature to 120°C in air with the stirring continued for 1 h. The mixture was cooled to 25°C, quenched with water (5 mL) and extracted with EtOAc (3 × 20 mL). The whole organic layer was washed with water (3 × 20 mL), dried (Na_2SO_4), filtered, and filtrate concentrated. The residue was subjected to column chromatography (hexane/ EtOAc; 3:2) to afford the product **28** or **29**.

2.4a *Compound **28***: Yield 0.124 g (62% white solid). M.p.: 90–92°C; IR (KBr, cm^{-1}) 3084, 3002, 2964, 2876, 1632, 1595, 1479, 1375, 1255, 1058, 1003, 866. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.04 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.87 (s, 3H, CH_3), 3.80–3.87 (m, 2H, OCH_2), 4.17–4.23 (m, 2H, OCH_2), 5.34–5.36 (m, 2H, = CH_2), 5.66–5.75 (dd→t, J ∼ 18.0 Hz, 1H, = CH), 7.23–7.27 (m, 1H, = CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 17.7, 21.4, 21.6, 32.5 (d, J(PC) = 5.7 Hz), 75.4 (d, J(PC) = 5.8 Hz), 112.0 (d, J(PC) = 190.1 Hz), 124.7, 140.7 (d, J(PC) = 23.9 Hz), 152.9 (d, J(PC) = 5.9 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.4. HRMS (ESI) calcd. for $C_{10}H_{18}O_3P$ [M$^+$+H]: 217.0993. Found: 217.0993. This compound had been previously prepared in our laboratory; the IR/NMR data are consistent with the ones reported before.[14]

2.4b *Compound **29***: Yield 0.136 g (67% white solid). M.p.: 120–122°C; IR (KBr, cm^{-1}) 3036, 3013, 2926, 2893, 1627, 1589, 1474, 1260, 1052, 1014, 860. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.02 (s, 3H, CH_3), 1.11 (s, 3H, CH_3), 1.59–1.70 (m, 4H, cyclohexenyl-H), 2.12–2.20 (m, 4H, cyclohexenyl-H), 3.78–3.84 (m, 2H, OCH_2), 4.20 (dd→t, J = 10.2 Hz, 2H, OCH_2), 5.55 (dd→t, J ∼ 18.0 Hz, 1H, = CH), 6.15 (br s, 1H, = CH), 7.10–7.20 (dd, J ∼ 18.0, 22.8 Hz, 1H, = CH). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.4, 21.6, 22.0, 23.7, 26.3, 32.4 (d, J(PC) = 5.5 Hz), 75.2 (d, J(PC) = 5.8 Hz), 107.2 (d, J(PC) = 192.0 Hz), 135.2 (d, J(PC) = 23.9 Hz), 139.2, 153.6 (d, J(PC) = 6.2 Hz). ^{31}P NMR (162 MHz, $CDCl_3$) δ 17.1. HRMS (ESI) calcd. for $C_{13}H_{22}O_3P$ [M$^+$+H]: 257.1306. Found: 257.1306.

2.5 *Horner–Wadsworth–Emmons reaction using the acridonyl allylphosphonate **16**: Synthesis of alkenyl-acridone derivatives **30–37***

The phosphonate **16** (0.100 g, 0.22 mmol) was dissolved in dry THF (2 mL) and added drop-wise (10 min) to a suspension of NaH (0.44 mmol) in THF (3 mL) at 0°C with stirring. The mixture was stirred further at this temperature for 0.5 h. Then aldehyde (0.33 mmol) in THF (2 mL) was added and the mixture stirred for 12 h at room temperature. Water (10 mL) was added and the aqueous layer thoroughly extracted with ethyl acetate (3 × 20 mL). The organic layer was collected, dried (Na_2SO_4), filtered and the solvent removed from the filtrate to give a residue that was purified by column chromatography [silica gel, ethyl acetate-hexane (1:4)] to give one of the compounds **30–37**.

2.5a *Compound **30***: Yield 0.082 g (94%, pale yellow solid). M.p.: 210–212°C; IR (KBr, cm^{-1}) 3057, 3030, 2986, 2943, 2849, 1632, 1600, 1490, 1457, 1364, 975, 756. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37–1.40 (m, 2H, cyclohexyl-H), 1.62 (br s, 2H, cyclohexyl-H), 1.81–1.88 (m, 4H, cyclohexyl-H), 2.81 (t, J(H-H) = 6.0 Hz, 2H, cyclohexyl-H), 5.86 (d, J(H-H) = 16 Hz, 1H, CH_A = CH$_B$), 7.16–7.24 (m, 5H, Ar-H), 7.30 (t, J(H-H) = 7.6 Hz, 2H, Ar-H), 7.34–7.36 (m, 2H, Ar-H), 7.44 (d, J(H-H) = 15.6 Hz, 1H, CH$_A$=CH_B), 7.59–7.63 (m, 2H, Ar-H), 8.61 (d, J = 8.0 Hz, 2H, Ar-H).

^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.0, 27.9, 30.4$_5$, 30.5$_2$, 116.6, 119.8, 121.6, 122.0, 126.6, 127.4, 127.7, 128.0, 128.6, 130.0, 133.8, 136.5, 141.8, 146.5, 178.2 (*C*=O). HRMS (ESI) calcd. for $C_{28}H_{26}NO$ [M^++H]: 392.2014. Found: 392.2013.

2.5b *Compound* ***31***: Yield 0.074 g (84%, pale yellow solid). M.p.: 170–172°C; IR (KBr, cm^{-1}) 3063, 2959, 2921, 2855, 1627, 1600, 1479, 1457, 1359, 1293, 1162, 1041, 932, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35–1.37 (m, 2H, cyclohexyl-*H*), 1.61 (br s, 2H, cyclohexyl-*H*), 1.80–1.87 (m, 4H, cyclohexyl-*H*), 2.27 (s, 3H, CH_3), 2.80 (t, *J*(H-H) = 6.2 Hz, 2H, cyclohexyl-*H*), 5.85 (d, *J*(H-H) = 15.6 Hz, 1H, CH_A = CH_B), 7.04 (d, *J*(H-H) = 7.6 Hz, 2H, Ar-*H*), 7.14 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.30 (t, *J*(H-H) = 7.8 Hz, 2H, Ar-*H*), 7.35–7.41 (m, 3H, *C*H$_A$ = C*H*$_B$ + Ar-*H*), 8.01 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 8.62 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 21.2, 26.3, 27.0, 27.9, 30.4, 30.5, 116.7, 118.4, 121.6, 121.9, 126.5, 127.4, 127.8, 129.3, 130.0, 133.8, 138.0. 141.8, 145.6, 178.2 (*C*=O). HRMS (ESI) calcd. for $C_{29}H_{28}NO$ [M^++H]: 406.2171. Found: 406.2172.

2.5c *Compound* ***32***: Yield 0.085 g (91%, pale yellow solid). M.p.: 110–112°C; IR (KBr, cm^{-1}) 3063, 2937, 2855, 1737, 1638, 1600, 1507, 1485, 1457, 1364, 1178, 1030, 942, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.35–1.37 (m, 2H, cyclohexyl-*H*), 1.60 (br s, 2H, cyclohexyl-*H*), 1.78–1.86 (m, 4H, cyclohexyl-*H*), 2.80 (t, *J*(H-H) = 6.0 Hz, 2H, cyclohexyl-*H*), 3.75 (s, 3H, OCH_3), 5.82 (d, *J*(H-H) = 15.6 Hz, 1H, CH_A=CH_B), 6.76 (d, *J*(H-H) = 15.6 Hz, 2H, CH_A = CH_B + Ar-*H*), 7.18 (d, *J*(H-H) = 8.7 Hz, 2H, Ar-*H*), 7.30 (d, *J* = 7.9 Hz, 2H, Ar-H), 7.36 (d, *J* = 8.7 Hz, 2H, Ar-*H*), 7.58–7.62 (m, 3H, Ar-*H*), 8.61 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.0, 27.9, 30.4, 30.5, 55.3, 114.0, 116.7, 117.8, 121.6, 121.9, 127.3, 127.9, 129.3, 129.5, 133.7, 141.8, 145.0, 159.5, 178.2 (*C*=O). HRMS (ESI) calcd. for $C_{29}H_{28}NO_2$ [M^++H]: 422.212. Found: 422.2119.

2.5d *Compound* ***33***: Yield 0.065 g (68%, yellow solid). M.p.: 190–192°C; IR (KBr, cm^{-1}) 3054, 2926, 2849, 1638, 1605, 1512, 1479, 1342, 1293, 1161, 1118, 942, 767. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40–1.43 (m, 2H, cyclohexyl-*H*), 1.61–1.67 (m, 2H, cyclohexyl-*H*), 1.85–1.94 (m, 4H, cyclohexyl-*H*), 2.85 (t, *J*(H-H) = 6.2 Hz, 2H, cyclohexyl-*H*), 5.91 (d, *J*(H-H) = 15.6 Hz, 1H, C*H*$_A$ = CH$_B$), 7.28–7.33 (m, 4H, Ar-*H*), 7.37 (d, *J* = 8.8 Hz, 2H, Ar-*H*), 7.59–7.64 (m, 3H, *C*H$_A$ = C*H*$_B$ + Ar-*H*), 8.01 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 8.61–8.63 (m, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 27.1, 28.0, 30.7$_5$, 30.8$_0$, 116.2, 118.2, 121.6, 121.9, 122.1, 123.9, 124.2, 127.0, 127.4, 127.6, 133.9, 141.6, 143.1, 146.9, 150.6, 178.1 (*C*=O). HRMS (ESI) calcd. for $C_{28}H_{25}N_2O_3$ [M^++H]: 437.1865. Found: 437.1866.

2.5e *Compound* ***34***: Yield 0.096 g (93%, pale yellow solid). M.p.: 192–194°C; IR (KBr, cm^{-1}) 3052, 2964, 2921, 2849, 1638, 1594, 1480, 1364, 1293, 1162, 1074, 937, 674. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (br s, 2H, cyclohexyl-*H*), 1.61 (br s, 2H, cyclohexyl-*H*), 1.80–1.88 (m, 4H, cyclohexyl-*H*), 2.80 (t, *J*(H-H) = 6.0 Hz, 2H, cyclohexyl-*H*), 5.80 (d, *J*(H-H) = 16 Hz, 1H, C*H*$_A$ = CH$_B$), 7.10 (d, *J* = 8.0 Hz, 2H, Ar-*H*), 7.28–7.35 (m, 6H, Ar-*H*), 7.42 (d, *J*(H-H) = 15.6 Hz, 1H, *C*H$_A$ = C*H*$_B$), 7.59–7.63 (m, 2H, Ar-*H*), 8.61 (d, *J* = 7.6 Hz, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.0, 30.0, 30.5, 30.6, 116.5, 120.5, 121.7, 122.0, 127.4, 127.5, 128.1, 128.7, 131.7, 133.8, 135.5, 141.7, 147.3, 178.1 (*C*=O). HRMS (ESI) calcd. for $C_{28}H_{25}BrNO$ [M^++H]: 470.1119 and 472.1119. Found: 470.1116 and 472.1097

2.5f *Compound* ***35***: Yield 0.071 g (77%, pale yellow solid). M.p.: 120–122°C; IR (KBr, cm^{-1}) 3057, 2921, 2849, 1638, 1600, 1479, 1457, 1364, 1293, 1266, 1172, 1085, 937, 762. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37–1.43 (m, 2H, cyclohexyl-*H*), 1.61–1.68 (m, 2H, cyclohexyl-*H*), 1.80–1.91 (m, 4H, cyclohexyl-*H*), 2.80 (t, *J*(H-H) = 6.2 Hz, 2H, cyclohexyl-*H*), 5.81 (d, *J*(H-H) = 16 Hz, 1H, C*H*$_A$ = CH$_B$), 7.15–7.20 (m, 4H, Ar-*H*), 7.27–7.34 (m, 4H, Ar-*H*), 7.40 (d, *J*(H-H) = 15.7 Hz, 1H, *C*H$_A$=C*H*$_B$), 7.59–7.63 (m, 2H, Ar-*H*), 8.61 (d, *J* = 8.0 Hz, 2H, Ar-*H*). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.3, 27.0, 27.9, 30.5, 30.6, 116.5, 120.4, 121.7, 122.0, 127.5, 127.8, 128.6, 128.7, 133.5, 133.8, 135.0, 141.7, 147.2, 178.1 (*C*=O). HRMS (ESI) calcd. for $C_{28}H_{25}ClNO$ [M^++H]: 426.1624. Found: 426.1626.

2.5g *Compound* ***36***: Yield 0.045 g (49 %, pale yellow solid). M.p.: 257–259°C; IR (KBr, cm^{-1}) 3057, 2975, 2926, 2849, 2219, 1638, 1600, 1479, 1457, 1359, 1288, 1178, 937, 745. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.40–1.43 (m, 2H, cyclohexyl-*H*), 1.60–1.63 (m, 2H, cyclohexyl-*H*), 1.84–1.93 (m, 4H, cyclohexyl-*H*), 2.83

(t, J(H-H) = 6.1 Hz, 2H, cyclohexyl-H), 5.86 (d, J(H-H) = 15.7 Hz, 1H, CH_A = CH_B), 7.29–7.33 (m, 6H, Ar-H), 7.50 (d, J = 8.3 Hz, 2H, Ar-H), 7.55 (d, J(H-H) = 15.7 Hz, 1H, CH_A = CH_B), 7.60–7.64 (m, 2H, Ar-H), 8.60–8.63 (m, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.2, 27.0, 28.0, 30.6_8, 30.7_3, 110.8, 116.2, 118.2, 121.8, 122.0, 123.4, 127.0, 127.4, 127.6, 128.0, 132.3, 133.9, 141.1, 141.6, 149.9, 178.1 (C=O). HRMS (ESI) calcd. for $C_{29}H_{25}N_2O$ [M^++H]: 417.1967 Found: 417.1968.

2.5h *Compound* ***37***: Yield 0.063 g (56 %, red solid). M.p.: 190–192°C; IR (KBr, cm^{-1}) 3057, 2931, 2855, 1627, 1606, 1480, 1457, 1359, 1266, 1162, 1107, 1047, 959, 806, 751. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.37 (d, 2H, cyclohexyl-H), 1.61 (br s, 2H, cyclohexyl-H), 1.78–1.86 (m, 4H, cyclohexyl-H), 2.71 (t, 2H, J(H-H) = 5.8 Hz, cyclohexyl-H), 3.85 (s, 5H, ferrocenyl-H), 4.21–4.18 (m, 4H, ferrocenyl-H), 5.58 (d, J(H-H) = 15.2 Hz, 1H, CH_A = CH_B), 6.92 (d, J(H-H) = 15.2 Hz, 1H, CH_A = CH_B), 7.31 (t, J(H-H) = 7.4 Hz, 2H, Ar-H), 7.40 (d, J = 8.4 Hz, 2H, Ar-H), 7.62–7.66 (m, 2H, Ar-H), 8.63 (d, J = 8.0 Hz, 2H, Ar-H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 26.4, 26.9, 27.8, 30.3, 30.4, 67.0, 68.3, 69.1, 69.4, 82.2, 116.5, 116.8, 121.7, 122.0, 127.4, 127.8, 129.4, 133.7, 141.8, 142.8, 178.3 (C=O). HRMS (ESI) calcd. for $C_{32}H_{30}NOFe$ [M^++H]: 500.1674. Found: 500.1675.

2.6 *X-ray structural analysis of* ***18–19, 24–25*** *and* ***27***

Single crystal X-ray diffraction data for compounds **18** and **24** were collected on a Bruker AXS-SMART diffractometer and that for **19**, **25** and **27**·1/2MeOH were collected on an OXFORD diffractometer, using Mo K_α (λ = 0.71073 Å) radiation. The structures were determined and refined by standard methods.[15] In the structure of compound **18**, the bromine at C11 and hydrogen at C17 exchanged positions, leading to partial occupancy at these positions while packing, but the structure was refined well. Full details of the X-ray structure solution and refinement as a CIF file are available as Supplementary Information.

2.6a *Compound* ***18***: pale yellow block, $C_{52}H_{58}Br_2N_2O_8P_2$, M = 1060.76, triclinic, Space group $P\bar{1}$, a = 11.052(6), b = 11.233(6), c = 11.782(6) Å, α = 98.582(8), β = 106.272(7), γ = 112.690(7), V = 1239.5(11) Å^3, Z = 1, μ = 1.755 mm^{-1}, data/restraints/parameters: 4338/0/315, R indices (I > 2σ(I)): R1 = 0.0661, wR2 (all data) = 0.1637. CCDC No. 942493.

2.6b *Compound* ***19***: pale brown block, $C_{30}H_{26}NO_2P$, M = 463.49, Monoclinic, Space group $P2_1/c$, a = 11.072(2), b = 16.360(3), c = 15.858(4) Å, β = 121.423(15), V = 2451.2(9) Å^3, Z = 4, μ = 0.140 mm^{-1}, data/ restraints/parameters: 4301/0/309, R indices (I > 2σ(I)): R1 = 0.0626, wR2 (all data) = 0.1858. CCDC No. 942496.

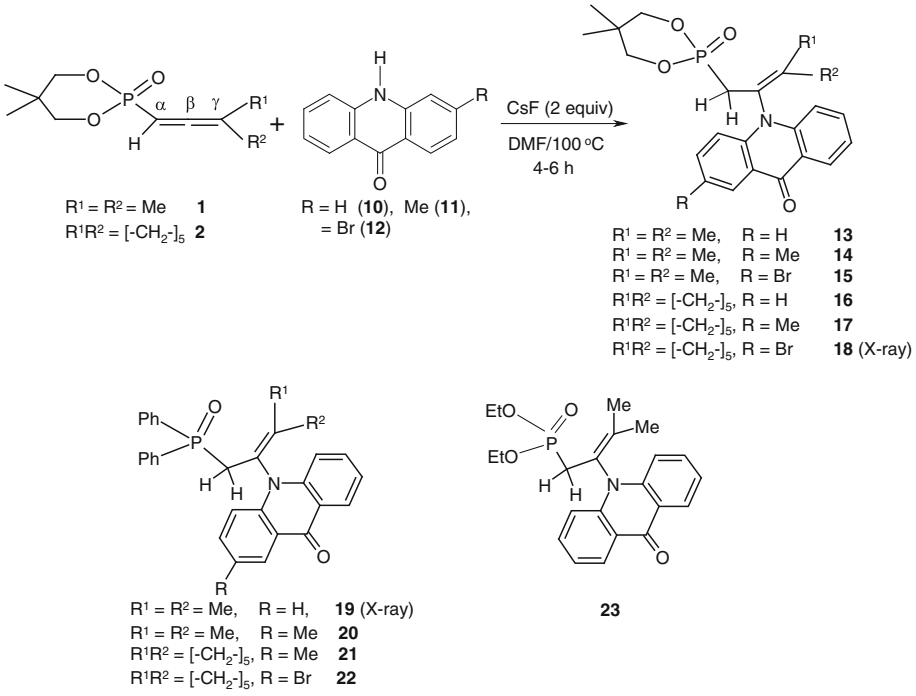
2.6c *Compound* ***24***: colourless block, $C_{23}H_{24}NO_3P$, M = 393.40, Monoclinic, Space group $P2/c$, a = 16.345(7), b = 6.288(3), c = 19.938(8) Å, β = 96.169(7), V = 2037.3(15) Å^3, Z = 4, μ = 0.158 mm^{-1}, data/ restraints/parameters: 3597/0/257, R indices (I > 2σ(I)): R1 = 0.0489, wR2 (all data) = 0.1258. CCDC No. 942494.

2.6d *Compound* ***25***: colourless needles, $C_{26}H_{28}NO_3P$, M = 433.46, Monoclinic, Space group $P2_1/c$, a = 6.3172(7), b = 14.0629(16), c = 27.295(3) Å, β = 108.966(12), V = 2293.2(5) Å^3, Z = 4, μ = 0.147 mm^{-1}, data/restraints/parameters: 3907/0/282, R indices (I > 2σ(I)): R1 = 0.0583, wR2 (all data) = 0.1090. CCDC No. 942495.

2.6e *Compound* ***27***·1/2MeOH: colourless blocks, $C_{51}H_{62}N_8O_9P_2$, M = 993.03, triclinic, Space group $P\bar{1}$, a = 10.0712(12), b = 11.645(2), c = 11.8217(16) Å, α = 85.489(12), β = 67.870(12), γ = 83.492(12), V = 1275.0(3) Å^3, Z = 1, μ = 0.149 mm^{-1}, data/ restraints/parameters: 4473/327, R indices (I > 2σ(I)): R1 = 0.0972, wR2 (all data) = 0.3057. The data quality was only moderate and hence the hydrogen atoms on the solvent were not modelled; however, the basic structure of the molecule was unambiguous. CCDC No. 946920.

3. Results and discussion

The reaction of allenylphosphonates ($OCH_2CMe_2CH_2O$)P(O)CH=C=CR^1R^2 {R^1 = R^2 = Me (**1**), R^1 = R^2 = [−CH_2−]$_5$ (**2**)}, with various substituted acridones (**10–12**) at 100°C in DMF solvent by using CsF as base leads to the formation of acridonyl allylphosphonates **13–18** (scheme 2). Although the reaction worked well even by using one mol equivalent of CsF, more equivalents were used to ensure the completion of reaction in a shorter period. The products were formed quantitatively (^{31}P NMR) and the yields after isolation were >80%. By employing these conditions



Scheme 2. Synthesis of acridonyl allylphosphonates/allylphosphine oxides **13–23**.

to allenylphosphine oxides $Ph_2P(O)C(H)=C=CR^1R^2$ {$R^1 = R^2 =$ Me (**3**), $R^1 = R^2 = [-CH_2-]_5$ (**4**)} and the allenylphosphonate $(EtO)_2P(O)C(H)=C=CMe$ (**5**), we could also obtain acridonyl allylphosphine oxides (**19–22**) and acridonyl allylphosphonate **23**. The reaction did not occur in the absence of CsF (base); this observation is significant since normal amines or nucleobases do not require the presence of CsF.[4] Although we have not investigated this point in detail, it appears that the steric bulk and lower basicity of acridone requires fluoride activation.

In all the above compounds, the ^{1}H NMR spectra show a distinct peak in the region δ 3·0–4·0 [J(P–H) ∼ 21·0 Hz] indicating the presence of PCH_2 group. Further confirmation of the structures is accomplished by the X-ray structure determination for compounds **18–19** (figure 1). The C6–C7 (in **18**) or C13–C14 (in **19**) distances are in the single bond range, as required.

It may be noted that in the above reactions, ^{31}P NMR spectrum of the reaction mixture shows the formation of a single product in each case. The other product (**I**) in

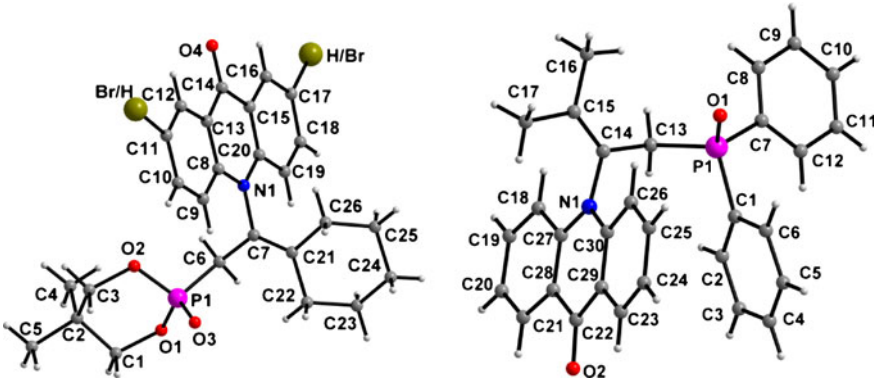
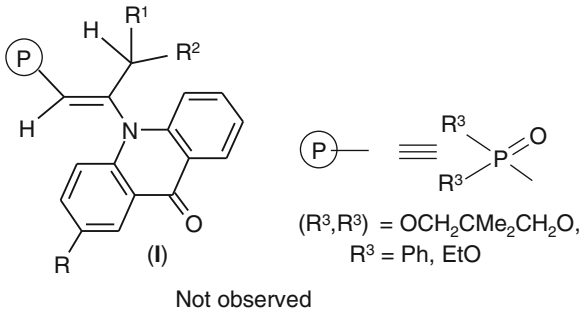


Figure 1. Molecular structures of **18** (left) and **19** (right). Selected bond distances are only given here. Compound **18** P1-C6 1.774(5), C6-C7 1.510(6), N1-C7 1.452(5) Å; compound **19** P1-C13 1.813(3), C13-C14 1.515(4), N1-C14 1.451(4) Å. In the structure of compound **18**, there is Br/H exchange of positions at the carbon atoms C11 and C17.

which the N–H hydrogen is connected to the γ-carbon is not observed. Thus, the hydrogen moves regiospecifically to the carbon with the electron-withdrawing phosphoryl/phosphinoyl group.



Not observed

As mentioned in the Introduction, we initially intended to prepare acridinylphosphonates also by using [Pd]-catalysis. Thus, when compounds **1**–**2** were treated with 9-chloroacridine under the conditions $Pd(OAc)_2$/CsF/DMF, we obtained two products in each case: Compound **13** (or **16**) and the α-substituted allene **24** (or **25**). The products **13**/**16** must have arisen from the *in situ* formed acridone via adventitious moisture as encountered elsewhere.[7] However, isolation of the α-substituted products **24**–**25**, albeit in *ca* 20% yield was a surprise, because as mentioned in the Introduction (cf. scheme 1), the acridinyl residue should have gone to the β-position. Hence, we checked the reaction using 9-benzyl-6-chloropurine (**26**), since the C–Cl bond in this compound is also fairly reactive. Although use of CsF did not work (no product) even after 24 h, Ph_3P/K_2CO_3 as the base combination afforded the β-substituted product **27**.[16] This purinone product must have also formed in a manner similar to the acridone products **13** or **16**. The acridinyl and the acridone products [**13**/**24** or **16**/**25**] had essentially the same R_f value (posing difficulties in isolation) and hence the ^{31}P NMR had to be used as the diagnostic tool during elution.

As regards characterization of substituted *allenylphosphonates* **24**–**25**, ^{13}C NMR is quite useful. A distinct doublet at *ca* $\sim$ δ 88 [^1J(P-C) = 197–199 Hz] is exhibited by the carbon α to the phosphorus. The large value of ^1J(P-C) indicates that the phosphorus is attached to an sp^2 carbon.[6] The ^{31}P NMR chemical shifts are in the region expected for such allenes and are close to those for **1**–**2**. Final confirmation of the structures for **24**–**25** was accomplished by X-ray crystallography (figure 2). The C6-C7 and C7-C8 distances (double bond range) as well as the C6-C7-C8 bond angle clearly prove the allenic structure in both the cases. Steric factors during the formation of the [Pd]-intermediate may be responsible for the formation of the α-substituted products **24**/**25** in the case of reaction using 9-chloroacridne. The *allylphosphonate* **27** is 9-benzyl-purinone addition product with a purine nitrogen connected to β-carbon of the allene, but after the substitution of –Cl by –OH and rearrangement. For this compound, the P-CH_2 protons showed an AM pattern with coupling to phosphorus, thus exhibiting two doublets of doublet. More convincingly, the P–*C* carbon appeared in the aliphatic region [δ 30.4, ^1J(P-C) = 94.0 Hz] which readily shows that this is an aliphatic carbon. The ^{31}P NMR chemical shift [δ 21.6] is also quite far from the precursor *allenylphosphonate* [δ 10.0]; these data are consistent with the structure of **27** as proposed in scheme 3. X-ray structure was determined for **27**·1/2MeOH after crystallization from methanol (figure 3). The P-CH_2 moiety (at C6) and the carbonyl group (at C11) are clearly discernible by the bond parameters associated with these atoms.

In the literature, it is reported that aniline undergoes C–H activation and reacts with alkynes using $Pd(OAc)_2$/pivalic acid under aerobic conditions.[17] Since the nitrogen of the acridone is connected to an aromatic carbon, we wanted to see if acridone can be

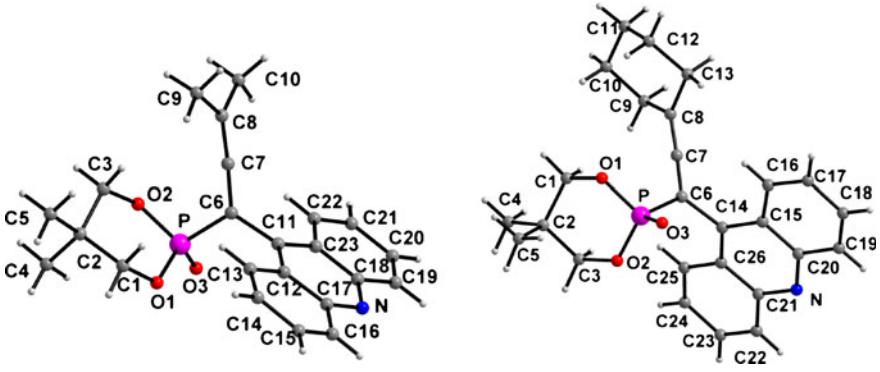
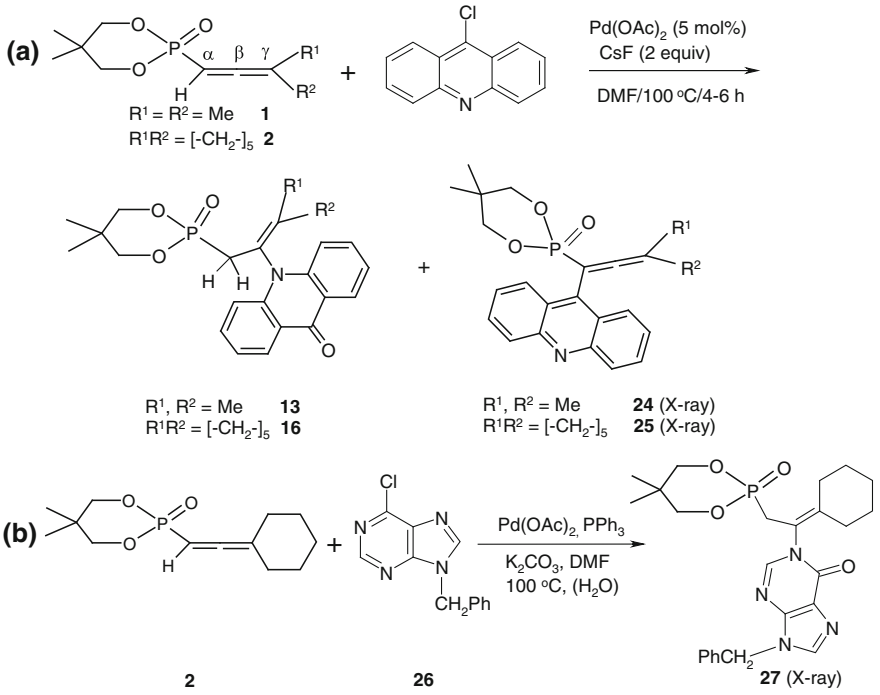


Figure 2. Molecular structures of **24** (left) and **25** (right). Selected bond parameters: Compound **24** P-C6 1.794(2), C6-C7 1.306(3), C7-C8 1.294(3) Å, C6-C7-C8 175.2(2)°; Compound **25** P-C6 1.798(4), C6-C7 1.304(5), C7-C8 1.283(5) Å, C6-C7-C8 173.6(5)°.



Scheme 3. [Pd]-catalysed reaction of allenylphosphonates **1–2** with 9-chloroacridine or 9-benzyl-6-chloropurine.

activated in a similar manner. However, no such activation occurred and acridone also did not add to the allene. Rather the rearranged product, the 1,3-butadiene **28** was obtained probably via an allylic [Pd] intermediate of type **II** (scheme 4); subsequently the strong conjugate base, pivalate anion, will abstract a proton from a terminal methyl group and the [Pd]-catalyst is released to form the product **28**. Although there is a second possible structure for **28–29**, the $^{3}J_{trans}$(HH) value is more consistent with the proposed one. It is also worthwhile to note that in the absence of pivalic acid only traces of the product were observed. In a similar manner, allene **2** gave the 1,3-butadiene **29**. Here acridone is not involved in the reaction and hence it is possible to obtain the 1,3-butadienes **28–29** in the absence of acridone.[14]

Compounds **13–23** possess a P(O)CH_2- group and hence we surmised that these would be attractive precursors for Horner–Wadsworth–Emmons (HWE) reaction.[18] Initially, we used *t*-BuOK for the reaction using allyl acridone **16** but under these conditions, there was no reaction with acridone. Use of NaH as the base afforded the HWE products **30–36** readily in good yields (scheme 5). Even ferrocene carboxaldehyde reacted readily to afford the acridone derivative **37**. Aromatic aldehydes containing electron-releasing [Me, OMe] or electron-withdrawing groups [NO_2, Br,

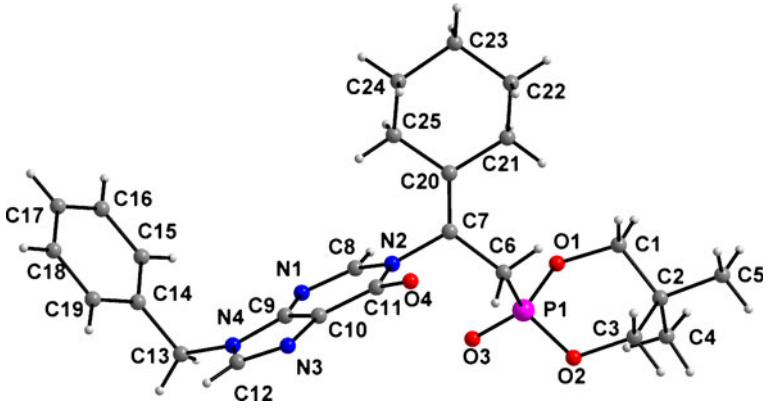
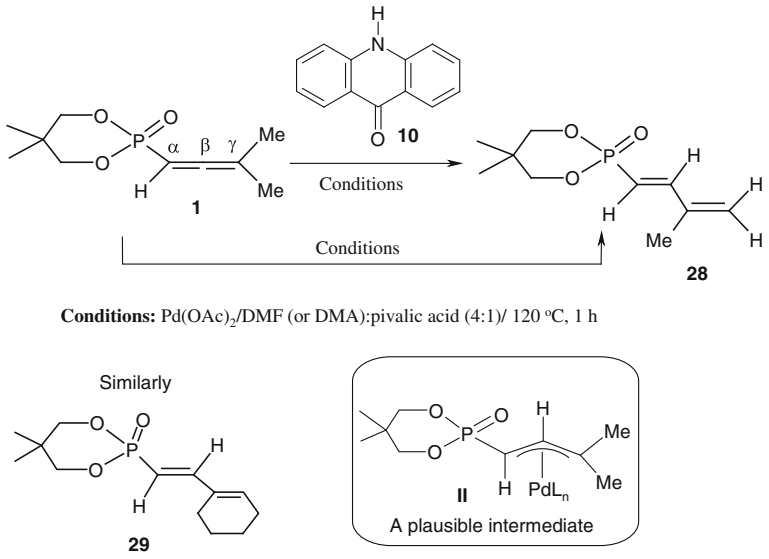
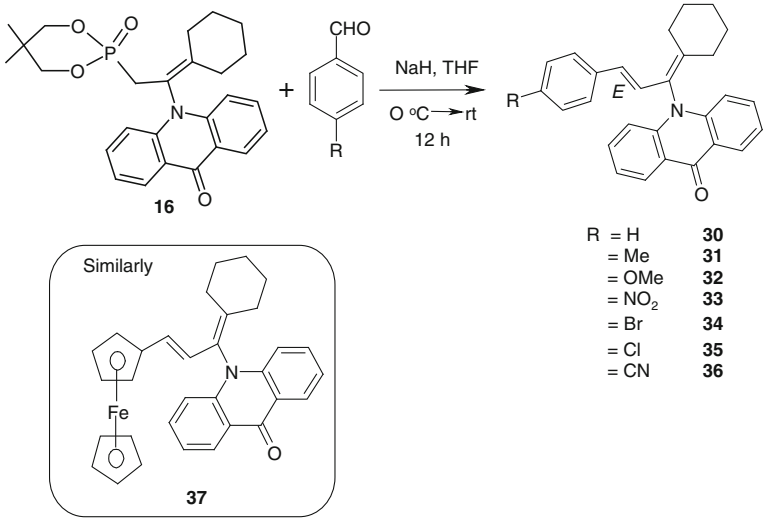


Figure 3. Molecular structure of **27**·1/2MeOH. The solvent molecule is not shown. Selected bond parameters: P1-C6 1.764(5), C6-C7 1.497(7), N2-C7 1.454(5) Å, C6-C7-N2 113.0(4)°.



Scheme 4. [Pd]-catalysed rearrangement of allenylphosphonate **1**–**2** to phosphonobutadienes **28**–**29**.



Scheme 5. Horner–Wadsworth–Emmons reaction of **16** with aldehydes leading to the acridonyl-1,3-butadienes **30**–**37**.

Cl and CN] worked well. The (*E*)-configuration at the newly formed double bond is corroborated by the corresponding ^3J(HH) values as well as the literature.[18]

4. Summary

Simple base-mediated (CsF) addition of acridone to allenylphosphonates/allenylphosphine oxides leads to acridonyl allylphosphonates wherein the nitrogen of the acridone is bonded to the carbon β to phosphorus and the corresponding N–H hydrogen moves to the α-carbon. These compounds are good substrates for HWE reaction and are useful in generating a new class of *N*-substituted acridones. In two examples studied, [Pd]-catalysed reaction of the allenylphosphonates led to the acridonyl allylphosphonates and the rather unexpected α-substituted allenylphosphonates. In the presence of a carboxylic (pivalic) acid and $Pd(OAc)_2$, allenylphosphonates with a terminal $=CR_2$ [R = Me; R_2 = cyclohexyl] group undergo facile rearrangement to 1,3-butadienyl substituted phosphonates.

Supplementary information

The electronic supporting information (CIF file containing the details of crystal structures of compounds reported in this work) can be seen in www.ias.ac.in/chemsci.

Acknowledgements

We thank the Department of Science and Technology (DST), New Delhi for financial support and for setting up of the National Single Crystal Diffractometer Facility at the University of Hyderabad. We also thank University with Potential for Excellence (UPE) programme of the University Grants Commission (UGC), New Delhi for equipment. KCK thanks DST for JC Bose fellowship and ALSK thanks UGC for a fellowship.

References

1. Selected reviews: (a) Hoffmann-Röder A and Krause N 2004 *Angew. Chem. Int. Ed.* **43** 1196; (b) Pacheco M C, Purser S and Gouverneur V 2008 *Chem. Rev.* **108** 1943; (c) Brasholz M, Reissig H-U and Zimmer R 2009 *Acc. Chem. Res.* **42** 45; (d) Alcaide B, Almendros P and Aragoncillo C 2010 *Chem. Soc. Rev.* **39** 783; (e) Yu S and Ma S 2012 *Angew. Chem. Int. Ed.* **51** 3074
2. Selected recent references: (a) Zhou C, Fang Z, Fu C and Ma S 2009 *J. Org. Chem.* **74** 2887; (b) Hirata Y, Inui T, Nakao Y and Hiyama T 2009 *J. Am. Chem. Soc.* **131** 6624; (c) Xu C F, Xu M, Yang L Q and Li C Y 2012 *J. Org. Chem.* **77** 3010; (d) Hossain M L, Ye F, Zhang Y and Wang J 2013 *J. Org. Chem.* **78** 1236
3. (a) Nishimura T, Hirabayashi S and Hayashi T 2006 *J. Am. Chem. Soc.* **126** 2556; (b) Bravo-Altamirano K, Abrunhosa-Thomas I and Montchamp J L 2008 *J. Org. Chem.* **73** 2292; (c) Chakravarty M, Bhuvan Kumar N N, Sajna K V and Kumara Swamy K C 2008 *Eur. J. Org. Chem.* 4500
4. Kumara Swamy K C, Balaraman E and Satish Kumar N 2006 *Tetrahedron* **62** 10152
5. Hydroamination of allenes with amines: (a) Hill A W, Elsegood M R J and Kimber M C 2010 *J. Org. Chem.* **75** 5406; (b) Cooke M L, Xu K and Breit B 2012 *Angew. Chem. Int. Ed.* **51** 10876; (c) Butler K L, Tragni M and Widenhoefer R S 2012 *Angew. Chem. Int. Ed.* **51** 5175
6. (a) Chakravarty M and Kumara Swamy K C 2006 *J. Org. Chem.* **71** 9128; (b) Phani Pavan M, Chakravarty M and Kumara Swamy K C 2009 *Eur. J. Org. Chem.* 5927; (c) Bhuvan Kumar N N, Nagarjuna Reddy M and Kumara Swamy K C 2009 *J. Org. Chem.* **74** 5395; (d) Phani Pavan M and Kumara Swamy K C 2011 *Synlett* 1288; (e) Rama Suresh R and Kumara Swamy K C 2012 *J. Org. Chem.* **77** 6959
7. In the preparation of bisphosphonates bearing an acridine as core moiety by hydrophosphonylation of 9-chloroacridine also, facile formation of acridones was noticed earlier. See: Srinivas V and Kumara Swamy K C 2009 *ARKIVOC* (xii) 31
8. See, for example: (a) Sánchez I, Reches R, Caignard D H, Renard P and Pujol M D 2006 *Eur. J. Med. Chem.* **41** 340; (b) Goodell J R, Ougolkov A V, Hiasa H, Kaur H, Remmel R, Billadeau D D, Ferguson D M 2008 *J. Med. Chem.* **51** 179
9. (a) Kumar R and Kumari M 2011 *J. Chem. Pharm. Res.* **3** 217; (b) Kelly J X, Smilkstein M J, Brun R, Wittlin S, Cooper R A, Lane K D, Janowsky A, Johnson R A, Dodean R A, Winter R, Hinrichs D J and Riscoe M K 2009 *Nature* **459** 270; (c) Kelly J X, Smilkstein M J, Cooper R A, Lane K D, Johnson R A, Janowsky A, Dodean R A, Hinrichs D J, Winter R and Riscoe M 2007 *Antimicrob. Agents Chemother.* **51** 4133; (d) Sepulveda C S, Garcia C C, Fascio M L, D'Accorso N B, Docampo Palacios M L, Pellon R F and Damonte E B 2012 *Antiviral Res.* **93** 62; (e) Tabarrini O, Manfroni G, Fravolini A, Cecchetti V, Sabatini S, Clercq E D, Rozenski J, Canard B, Dutartre H, Paeshuyse J and Neyts J 2006 *J. Med. Chem.* **49** 2621; (f) Hernandez-Olmos V, Abdelrahman A, El-Tayeb A, Freudendahl D, Weinhausen S and Müller C E 2012 *J. Med. Chem.* **55** 9576; (g) Lin Y-C and Chen C-T 2009 *Org. Lett.* **11** 4858; (h) Putic A, Stecher L, Prinz H and Muller K 2010 *Eur. J. Med. Chem.* **45** 5345
10. For another approach to *N*-substituted acridones, see: Singh P, Kaur J, Yadav B and Komath S S 2009 *Bioorg. Med. Chem.* **17** 3973
11. Perrin D D, Armarego W L F and Perrin D 1986 *Purification of laboratory chemicals* (Oxford UK: Pergamon)
12. (a) Guillemin J C, Savignac P and Denis J M 1991 *Inorg. Chem.* **30** 2170; (b) Iorga B, Eymery F, Carmichael D and Savignac P 2000 *Eur. J. Org. Chem.* 3103; (c) Guo H, Qian R, Guo Y and Ma S 2008 *J. Org. Chem.* **73** 7934
13. (a) Allen C F H and McKee G H W 1939 *Org. Synth.* **19** 6; (b) Rouband G, Faure R and Galy J-P 2003 *Magn. Reson. Chem.* **41** 549
14. Phani Pavan M 2010 *New phosphono-heterocycles through allenylphosphonates*, PhD thesis, University of Hyderabad
15. (a) Sheldrick G M 1996 SADABS, *Siemens Area Detector Absorption Correction*, University of Göttingen, Göttingen, Germany; (b) Sheldrick G M 1997 SHELX-97, *A Program for Crystal Structure Solution and Refinement*, University of Göttingen, Göttingen, Germany; (c) Sheldrick G M 1999 *SHELXTL NT Crystal Structure Analysis Package*, Bruker AXS, Analytical X-ray System, Madison WI, version 5.10
16. Use of Ph_3P/K_2CO_3 condition did not work for 9-chloroacridine
17. Shi Z, Zhang C, Li S, Pan D, Ding S, Cui Y and Jiao N 2009 *Angew. Chem. Int. Ed.* **48** 4572
18. See, for example: (a) Abiko A and Masamune S 1996 *Tetrahedron Lett.* **37** 1077; (b) Muthiah C, Praveen Kumar K, Aruna Mani C and Kumara Swamy K C 2000 *J. Org. Chem.* **65** 3733; (c) Chakravarty M, Srinivas B, Muthiah C and Kumara Swamy K C 2003 *Synthesis* 2368