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$FeCl_3$ catalysed regioselective allylation of phenolic substrates with (α-hydroxy)allylphosphonates

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Abstract. Electrophilic allylation of phenolic substrates including salicylaldehydes with (α-hydroxy) allylphosphonates is presented. It is observed that catalytic $FeCl_3$ is sufficient to accomplish the allylation. Interestingly, the reaction led to the formation of *allylphosphonates* in addition to *vinylphosphonates*, depending upon the substituent. The vinylphosphonates obtained here are *E*-isomers. More importantly, the reaction occurred regioselectively with respect to the phenolic substrates. Substituted allylphosphonates are formed when salicylaldehyde or (2-hydroxy-phenyl)arylmethanones are used. Conclusive proof for the formation of allylphosphontates as well as vinylphosphonates has been provided by single crystal X-ray crystallography.

Keywords. Allylation; electrophilic aromatic substitution; phosphorus; phenols; vinylphosphonates; allylphosphonates.

1. Introduction

Friedel-Crafts type arylation[1] involving allyl alcohols is an efficient route to construct new C-C and C-X bonds and hence is of enormous significance in organic synthesis.[2] Phosphono-allylic alcohols can also undergo analogous reactions leading to substituted vinylphosphonates, which themselves are valuable synthons for organic transformations.[3] The latter compounds have been utilised for the synthesis of natural products such as enterolactone (**I**),[3a] turmerone (**II**),[3b] cyclopostin phosphonate analogues (**III**),[3c] and oxylipids from brown algae (**IV**) (Chart 1).[3f] A regiospecific fluorination using DAST leading to γ-fluoro-vinylphosphonates has been reported by Sanders and Hammond several years ago.[3g] Palladium-catalysed decarboxylative rearrangement of nonracemic phosphono allylic acetoacetates (that are also vinylphosphonates) has been utilised to prepare a diverse class of cyclopentenones.[4] In a recent report, the same group of Spilling has also explored the relay cross metathesis of vinylphosphonates.[5] There have been a few earlier reviews on the synthesis and utility of vinylphosphonates.[6] An excellent exhaustive review on Michael addition of vinylphosphonates has been presented recently by Janecki et al.[7] Later, the same group has developed a simple and effective protocol for activated vinylphosphonates from 3-methoxy-2-diethoxyphosphorylacrylate.[8] Several interesting routes to vinylphosphonates have also been reported recently.[9] Polymerization of vinylphosphonates to poly(diethyl vinylphosphonates) is also an active area of study.[10] An oxa-Michael addition of various alcohols to diethyl vinylphosphonate is reported.[11] An efficient organocatalytic enantioselective conjugate addition of 3-substituted oxindoles to activated vinylphosphonates has been established.[12] Despite many reports on vinylphosphonates, studies on the corresponding allylphosphonates, are rare.

Since organophosphonates have diverse applications in organic synthesis [e.g., Horner-Wadsworth- Emmons reaction], pharmaceutical industry [e.g., clodronic acid for osteoporosis], materials science as well as polymer chemistry [e.g. flame retardants], it is of great interest to expand the synthetic routes to functionalised phosphonates.[13,14] During the course of our study on α-hydroxyphosphonates,[15,16] we came across a recent report in which Chakravarty and co-workers have utilised such phosphonates for arylation/alkylation of α-hydroxyphosphonates and isolated vinyl- or γ-ketophosphonates.[17] In most of these reactions a stoichiometric amount of Lewis acid ($FeCl_3$) was utilized. In this context, we were interested in the reactivity and utility of (α-hydroxy)allylphosphonates (phosphono-allylic alcohols).[15b] Thus in pursuance of our work on organophosphonate chemistry,[18] and α-hydroxyphosphonates in particular,[14a–c] we were interested in the phosphono-allylic alcohol **1** that can be readily prepared by the addition of H-phosphonate $(OCH_2CMe_2CH_2O)P(O)H$ to cinnamaldehyde.[19] The main advantage of using this

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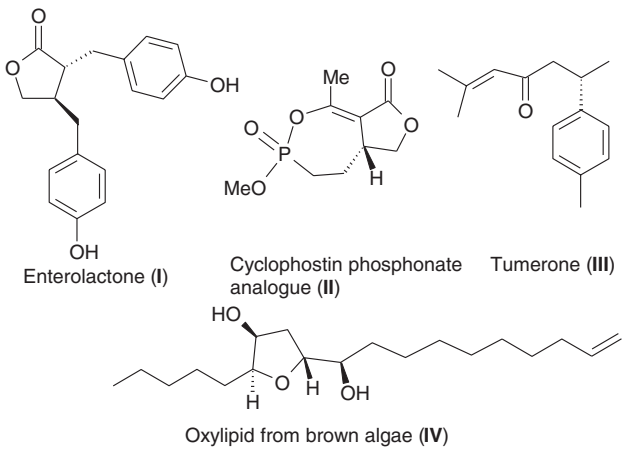


Chart 1. Selected products obtained using vinylphosphonates.

cyclic phosphonate is that in general, it leads to solid crystalline products. Removal of α-OH by a Lewis acid (LA) can lead to allyl cation **V** which is in resonance with **VI**. Hence if arylation is accomplished, we can get either an allylphosphonate (**VII**) or a vinylphosphonate (**VIII**). The second point is related to functionalised arenes like phenolic substrates. We were interested in the regiospecificity of such reactions since that part was not addressed before.

2. Experimental

Solvents were dried according to known methods as appropriate.[20] ^{1}H, ^{13}C and ^{31}P NMR spectra (^{1}H-400 MHz or 500 MHz, ^{13}C-100 MHz or 125 MHz and ^{31}P-162 MHz) were recorded using a 400 MHz or 500 MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ ($\delta = 0$). IR spectra were recorded on an FTIR spectrophotometer. Melting points were determined by using a local hot-stage melting point apparatus and are uncorrected. High resolution mass spectra (HR-MS) were performed using a BRUKER-MAXIS mass spectrometer with ESI-QTOF-II method. Synthesis of the precursor **1** is described in the supplementary material.

2.1 *General procedure for the allylation of arenes with phosphonoallylic alcohol **1***

To phosphonoallylic alcohol **1** (0.282 g, 1 mmol) and $FeCl_3$ (0.016 g, 0.1 mmol) in nitromethane (3 mL) was added 4-methoxyphenol (0.620 g, 5 mmol). The mixture was stirred at 80°C for 6 h. After the starting material **1** was consumed completely, solvent was removed under vacuum. Crude product was purified by column chromatography using silica gel with ethyl acetate/ hexane (1:1) mixture as the eluent.

2.1a *Compound **2a***: Yield 0.330 g (85%, white solid). M.p.: 184–186°C; IR (KBr, cm^{-1}) 3260, 2969, 1638, 1597, 1510, 1431, 1372, 1244, 1213, 1053, 997, 822, 806, 698, 498. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33–7.18 (m, 6H, Ar*H* + PCH = C*H*), 6.76 (d, ^3J(H-H) ~8.4 Hz, 1H, Ar*H*), 6.67 (d, ^3J(H-H) ~8.4 Hz, 1H, Ar-*H*), 6.57 (s, 1H, Ar-*H*), 5.59 (dd, ^2J(P-H) = 20.4 and ^3J(H-H) = 18.4 Hz, 1H, PC*H* = CH), 5.30-5.60 (br (?), 1H, -O*H*), 5.21 (br, 1H, =CHC*H*Ar), 4.17 (dd→t, ^3J(P-H) = ^2J(H-H) ~10.6 Hz, 2H, OCH_2), 3.82 (dd→t, ^3J(P-H) = ^2J(H-H) ~11.8 Hz, 2H, OCH_2), 3.70 (s, 3H, OCH_3), 1.06 and 1.04 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.2, 153.4, 148.0, 140.1, 128.9, 128.7, 128.5, 127.0, 116.8, 116.0 (d, ^1J(P-C) = 185.9 Hz, P*C* = C), 115.7, 112.8, 75.7 and 75.6 (2s, O*C*H$_2$), 55.7, 49.0 (d, ^3J(P-C) = 22.0 Hz, =CH*C*HAr), 32.5 (d, ^3J(P-C) = 5.8 Hz, *C*(CH$_3$)$_2$), 21.6 and 21.5 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.5. LC/MS m/z389 [M+1]$^+$. Anal. Calcd. for $C_{21}H_{25}O_5P$: C, 64.94; H, 6.49. Found: C, 65.10; H, 6.41.

2.1b *Compound **3a***: This compound was prepared by following a procedure similar to that for **2a**, using 2,4-dimethylphenol (0.611 g, 5 mmol). Yield 0.302 g (92%, white solid). M.p.: 192–194°C; IR (KBr, cm^{-1}) 3245, 2965, 2917, 1626, 1597, 1485, 1260, 1190, 1061, 1009, 830, 706, 515. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.37-7.18 (m, 6H, Ar*H* + PCH = *CH*), 6.85 (s, 1H, Ar*H*), 6.70 (s, 1H, Ar*H*), 5.62-5.52 (~dd, 1H, ^2J(P-H) = 22.0 and ^3J(H-H) = 17.2 Hz, PC*H* = CH), 5.21 (d, 1H, ^3J(H-H) = 2.8 Hz, CHC*H*Ph), 4.99 (br, 1H, O*H*), 4.16 (dd→t, ^3J(P-H) = ^2J(H-H) ~10.6 Hz, 2H, OCH_2), 3.80 (dd→t, ^3J(P-H) = ^2J(H-H) ~12.2 Hz, 2H, OCH_2), 2.21 and 2.19 (2s, 6H, ArCH_3), 1.06 and 1.03 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.3, 156.2, 149.5, 140.3, 130.5, 129.7, 128.8$_3$, 128.8, 127.7, 127.2, 127.1, 124.1, 116.4 (d, ^1J(P-C) = 185.9, P*C*), 75.5 and 75.4 (2 s, O*C*H$_2$), 49.1 (d, ^3J(P-C) = 22.0 Hz, =CH*C*HAr), 32.5 (d, ^3J(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 21.7 and 21.5 (2s, C(*C*H$_3$)$_2$), 20.7 and 16.1 (2s, Ar*C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.5. LC/MS m/z: 387 [M+1]$^+$. Anal.Calcd. for $C_{22}H_{27}O_4P$: C, 68.38; H, 7.04. Found: C, 68.25; H, 7.12.

2.1c *Compound **4a***: This compound was prepared by following a procedure similar to that for **2a**, using 4-cresol (0.541 g, 5 mmol). Yield 0.335 g (90%, white solid). M.p.: 190–192°C; IR (KBr, cm^{-1}) 3482, 2915, 1624, 1512, 1456, 1372, 1240, 1057, 1005, 872, 505, 469, 421. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.32–7.18

(m, 6H, Ar*H* + PCH = *CH*), 6.92-6.89 (∼dd, ^3J(H-H) = 8.0 Hz, ^4J(H-H) ∼2.0 Hz 1H, Ar*H*), 6.81 (s, 1H, Ar-*H*), 6.72 (d, ^3J(H-H) = 8.0 Hz, 1H, Ar*H*), 5.88 (br, 1H, O*H*), 5.63-5.52 (dd→m, ^2J(P-H) ∼20.4 and ^3J(H-H) ∼18.0 Hz, 1H, PC*H* = CH), 5.21-5.20 (br, 1H, C*H*Ph), 4.16 (dd→t, ^3J(P-H) = ^2J(H-H) ∼12.0 Hz, 2H, OCH_2), 3.84-3.78 (m, 2H, OCH_2), 2.22 (s, 3H, ArCH_3), 1.06 and 1.02 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.4, 156.3, 151.4, 140.3, 130.1, 128.9, 128.8, 128.7, 127.2, 127.0, 116.2 (d, ^1J(P-C) = 187.7, P*C* = C), 116.0, 75.6 and 75.5 (2s, O*C*H$_2$), 49.0 (d, ^3J(P-C) = 22.1 Hz, =CH*C*HAr), 32.6 (d, ^3J(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 21.7 and 21.5 (2s, C(*C*H$_3$)$_2$), 20.7 (s, Ar*C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 14.8. LC/MS *m*/*z*: 373 [M+1]$^+$. Anal. Calcd. for $C_{21}H_{25}O_4P$: C, 67.73; H, 6.77. Found: C, 67.85; H, 6.71.

2.1d *Compound* ***5a***: This compound was prepared by following a procedure similar to that for **2a**, using 4-*t*-butyl phenol (0.490 g, 5 mmol). Yield 0.370 g (80%, white Solid). M.p.: 170–172°C; IR (KBr, cm^{-1}) 3400 (br), 2958, 2882, 2356, 1627, 1501, 1457, 1413, 1375, 1254, 1205, 1112, 1057, 1008, 882, 821, 695, 493, 482. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.30–7.18 (m, 6H, Ar*H* + PCH =*CH*), 7.09 (dd, ^3J(H-H) = 8.4 Hz, ^4J(H-H) ∼1.6 Hz, 1H, Ar*H*), 6.99 (d, ^3J(H-H) = 1.6 Hz, 1H, Ar-*H*), 6.82 (d, ^3J(H-H) = 8.4 Hz, 1H, Ar*H*), 5.59 (dd, ^3J(P-H) = 22.4 Hz, ^2J(H-H) = 17.2 Hz, 1H, PC*H* = CH), 5.26 (br, 1H, =CHC*H*Ar), 4.11-4.05 (m, 2H, OCH_2), 3.81 (dd, ^3J(P-H) ∼21.4 Hz, ^2J(H-H) = 10.6 Hz, 2H, OCH_2), 1.23 (s, 9H, C(CH_3)$_3$) and 1.00 (s, 6H, C(CH_3)$_2$). The O*H* peak was broad. Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 156.8, 151.9, 142.4, 140.5, 128.8, 128.5, 126.7, 126.4, 124.9, 115.5$_1$ (d, ^1J(P-C) = 180.0 Hz, P*C* = C), 115.5$_0$, 75.7 (2d→t, ^2J(P-C) ∼7.0 Hz, O*C*H$_2$), 49.2 (d, ^3J(P-C) = 29.0 Hz, = CH*C*HAr), 34.1 (s, *C*(CH$_3$)$_3$), 32.4 (d, ^3J(P-C) = 3.0 Hz, *C*(CH$_3$)$_2$), 31.5 (s, C(*C*H$_3$)$_3$) and 21.4 (s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.1. HRMS (ESI): Calcd. for $C_{24}H_{31}O_4PNa$ [M$^+$+Na] *m*/*z*: 437.1858 Found: 437.1857.

2.1e *Compound* ***6a***: This compound was prepared by following a procedure similar to that for **2a**, using 4-hydroxy benzaldehyde (0.611 g, 5 mmol). Yield 0.324 g (84%, White solid). M.p.: 188-190°C; IR (KBr, cm^{-1}) 3360, 3059, 3030, 2969, 1690, 1601, 1474, 1373, 1246, 1161, 1059, 1009, 830, 702, 615. ^{1}H NMR (400 MHz, $CDCl_3$) δ 9.73 (s, 1H, ArC*H*O), 9.40 (br, 1H, ArO*H*), 7.61–7.03 (m, 9H, Ar*H* + PCH = *CH*), 5.61 (dd→t, ^2J(P-H) = ^3J(H-H) = 20.0 Hz, 1H, PC*H* = CH), 5.25 (br, 1H, =CHC*H*Ar), 4.16 (dd→t, ^3J(P-H) = ^2J(H-H) ∼10.0 Hz, 2H, OCH_2), 3.88 (dd→t, ^3J(P-H) = ^2J(H-H) ∼10.0 Hz, 2H, OCH_2), 1.08 (s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 191.1 (s, Ar*C*HO), 161.1, 156.2, 139.6, 131.6, 128.8, 128.3, 127.2, 116.4, 115.7 (d, ^1J(P-C) = 186.0 Hz, P*C* = C), 76.2 and 76.1 (2 s, O*C*H$_2$), 48.9 (d, ^3J(P-C) = 23.0 Hz, =CH*C*HAr), 32.6 (d, ^3J(P-C) = 4.0 Hz, *C*(CH$_3$)$_2$), 21.5$_1$ and 21.5$_0$ (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 15.0. LC/MS *m*/*z*: 387 [M+1]$^+$. Anal.Calcd. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.41; H, 5.93.

2.1f *Compound* ***7a***: This compound was prepared by following a procedure similar to that for **2a**, using *o*-vanillin (0.761 g, 5 mmol). Mixture of products were formed, from which **7a** only was separated. Yield 0.125 g (30%, white solid). M.p.: 130–132°C; IR (KBr, cm^{-1}) 3300 (br), 2971, 1649, 1474, 1401, 1059, 1011, 870, 830, 739. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.08 (s, 1H, ArO*H*), 9.86 (s, 1H, ArC*H*O), 7.40-7.16 (m, 6H, Ar*H* + PCH = *CH*), 6.96 (s, 1H, Ar*H*), 6.87 (s, 1H, Ar*H*), 5.64 (dd→t, ^2J(P-H) = ^3J(H-H) ∼19.2 Hz, 1H, PC*H* = CH), 4.90 (s, 1H, =CHC*H*Ar), 4.25 (dd→t, ^3J(P-H) = ^2J(H-H) ∼9.4 Hz, 2H, OCH_2), 3.85 (s, 3H, OCH_3), 3.83-3.77 (m, 2H, OCH_2), 1.12 and 1.01 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6 (s, Ar*C*HO), 155.6 (d, ^3J(P-C) = 5.8 Hz, P*C*), 150.9, 148.7, 140.1, 132.4, 129.0, 128.6, 127.5, 123.8, 120.4, 118.6, 117.7 (d, ^1J(P-C) = 187.1 Hz, P*C* = C), 75.3 (d, ^2J(P-C) = 5.6 Hz, O*C*H$_2$), 56.4 (s, O*C*H$_3$), 54.4 (d, ^3J(P-C) = 22.0 Hz, =CH*C*HAr), 32.6 (d, ^3J(P-C) = 5.5 Hz, *C*(CH$_3$)$_2$), 21.8 and 21.4 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13. LC/MS *m*/*z*: 417 [M+1]$^+$. Anal. Calcd. for $C_{22}H_{25}O_6P$: C, 63.46; H, 6.05. Found: C, 63.32; H, 6.15.

2.1g *Compounds* ***8a–b***: These compounds were prepared by following a procedure similar to that for **2a**, using 2-hydroxy-4-octyloxy benzophenone (0.490 g, 5 mmol). Mixture of isomers was formed. The isomers were separated successfully by column chromatography using silica gel with ethyl acetate-hexane (1:1) mixture as eluent. **Compound 8a:** Yield 0.372 g (50%, yellow gummy liquid). IR (KBr, cm^{-1}) 3400 (br), 2926, 2849, 2350, 1627, 1594, 1572, 1484, 1463, 1347, 1265, 1189, 1112, 1057, 1002, 942, 926, 816. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.75 (s, 1H, ArO*H*), 7.50 -7.16 (m, 12H, Ar*H* + PCH = *CH*), 6.49 (s, 1H, Ar*H*)), 5.50 (dd, ^3J(P-H) ∼20.4 Hz, ^3J(H-H) ∼18.0 Hz, 1H, PC*H* = CH), 5.14 (br, 1H, =CHC*H*Ar), 4.16 (dd, ^3J(P-H) = 10.8 Hz, ^2J(H-H) = 8.8 Hz, 2H, OCH_2), 3.70 (t, ^3J(H-H) = 6.6 Hz, 2H, ArOCH_2(CH$_2$)$_6$CH$_3$), 4.03-3.94 (m, 2H,

OCH_2), 1.27 (m, 10H, (CH_2)$_5$CH$_3$), 1.72 (m, 2H, -CH_2(CH$_2$)$_5$CH$_3$), 1.02 and 0.99 (2s, 6H, C(CH$_3$)$_2$), 0.89 (t, ^3J(H-H) = 7.0 Hz, 3H, -CH$_2$CH_3). Assignment for PCH = *CH* protons is tentative. ^{13}C NMR (100 MHz, CDCl$_3$): δ 199.5, 165.7, 162.9, 155.8 (d, ^3J(P-C) = 6.0 Hz, P*C*), 140.2, 137.8, 134.7, 131.6, 129.1, 128.6, 128.3, 126.9, 121.1, 116.7 (d, ^1J(P-C) = 188.0 Hz, P*C*=C), 112.2, 100.3, 75.1 (2d→t, ^2J(P-C) = 5.5 Hz, O*C*H$_2$), 68.8, 47.8 (^3J(P-C) = 22.0 Hz, =CH*C*HAr), 32.5 (d, ^3J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 31.8, 29.3, 29.2, 28.8, 25.9, 22.7, 21.7, 21.3 and 14.2. ^{31}P NMR (162 MHz, CDCl$_3$) δ 14.4. HRMS (ESI): Calcd. for C$_{35}H_{44}$O$_6$P [M$^+$+H] *m/z*: 591.2875. Found: 591.2874. **Compound 8b:** Yield 0.182 g (30%, white solid). M.p.: 136-138°C; IR (KBr, cm^{-1}) 3400 (br), 2947, 2926, 2854, 1616, 1572, 1490, 1473, 1441, 1369, 1342, 1276, 1238, 1189, 1112, 1057, 1013, 980, 920, 827, 734, 695. ^{1}H NMR (400 MHz, CDCl$_3$) δ 12.71 (s, 1H, ArO*H*), 7.94-7.21 (m, 11H, Ar*H* + PhC*H* = CH), 6.54 (s, 1H, Ar*H*), 6.51 (s, 1H, Ar*H*), 6.35-6.27 (m, 1H, -C*H*=CHPh), 4.67 (dd, 1H, ^2J(P-H) = 24.4 Hz, ^3J(H-H) = 8.4 Hz, PC*H*), 4.24-4.05 (m, 4H, OCH_2), 3.79 (m, 2H, OCH_2(CH$_2$)$_6$CH$_3$), 1.86 (t, 2H, -CH_2(CH$_2$)$_5$CH$_3$), 1.62-1.30 (m, 10H, -(CH_2)$_5$CH$_3$), 0.99 (d, 6H, C(CH_3)$_2$), 0.90 (t, ^3J(H-H) = 5.8 Hz, 3H, -CH$_2$CH_3). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, CDCl$_3$) δ 199.7, 165.5, 137.9, 135.5, 133.9, 133.8, 131.9, 129.5, 128.5, 128.4, 128.3, 127.8, 126.4, 123.7, 123.6, 100.4, 75.3 and 75.1 (2d, ^2J(P-C) ~6.6 Hz, O*C*H$_2$), 69.0, 37.9 (d, ^1J(P-C) = 136.0 Hz, P*C*CH), 32.7 (d, ^3J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 31.8, 29.3, 29.2, 29.1, 26.1, 22.7, 21.6 and 21.5 (2s, C(*C*H$_3$)$_2$), 14.1. ^{31}P NMR (162 MHz, CDCl$_3$) δ 21.9; HRMS (ESI): Calcd. for C$_{35}H_{44}$O$_6$P [M$^+$+H] *m/z*: 591.2875. Found: 591.2876.

2.1h *Compounds **9a-b***: These compounds were prepared by following a procedure similar to that for **2a**, using 2,6-dimethylphenol (0.611 g, 5 mmol). Mixture of isomers was formed. They were separated successfully by column chromatography using silica gel with ethyl acetate-hexane (1:1) mixture as the eluent. **Compound 9a:** Yield 0.270 g (70%, white solid). M.p.: 190-192°C; IR (KBr, cm^{-1}) 3308, 2971, 1734, 1622, 1489, 1372, 1237, 1200, 1148, 1059, 1007, 824, 702, 615. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.62-7.14 (m, 8H, Ar*H* + ArO*H*), 6.75 (s, 1H, PCH = *CH*), 5.58 (dd→t, ^2J(P-H) = ^3J(H-H) ~19.0 Hz, 1H, PC*H* = CH), 4.76 (br, 1H, =CHC*H*Ar), 4.20 (dd→t, ^3J(P-H) = ^2J(H-H) ~9.6 Hz, 2H, OCH_2), 3.80 (dd→t, ^3J(P-H) = ^2J(H-H) = 12.0 Hz, 2H, OCH_2), 2.20 (s, 6H, ArCH_3), 1.08 and 1.02 (2s, 6H, C(CH_3)$_2$). The spectrum was not very clear, assignment of PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, CDCl$_3$) δ 157.0, 151.4, 141.4, 132.3, 128.7$_2$, 128.7, 128.6, 126.9, 123.5, 116.2 (d, ^1J(P-C) = 186.0 Hz, P*C*=C), 75.3 (s, O*C*H$_2$), 54.6 (d, ^3J(P-C) = 22.0 Hz, =CH*C*HAr), 32.5 (d, ^3J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 21.7 and 21.4 (2s, C(*C*H$_3$)$_2$), 16.1 (s, Ar*C*H$_3$). ^{31}P NMR (162 MHz, CDCl$_3$) δ 14.5; LC/MS *m/z*: 387 [M+1]$^+$. **Compound 9b:** Yield 0.085 g (22%, white solid). M.p.: 196−198°C; IR (KBr, cm^{-1}) 3339, 2961, 2917, 1487, 1256, 1184, 1057, 1003, 982, 833, 812, 694, 473. ^{1}H NMR (400 MHz, CDCl$_3$) δ 7.38-7.22 (m, 6H, Ar*H*),7.03 (s, 2H, Ar*H* + Ar-O*H* (?)), 6.75-6.48 (m, 2H, C*H* = *CH*Ar), 4.27-4.20 (m, 2H, OCH_2), 3.99 (dd, ^2J(P-H) = 24.4 Hz,^3J(H-H) = 8.0 Hz, 1H, PC*H*), 3.82-3.75 (m, 2H, OCH_2), 2.20 (s, 6H, ArCH_3), 1.06 and 0.96 (2s, 6H, C(CH_3)$_2$). Assignment of PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, CDCl$_3$) δ 152.0, 136.8, 133.8, 133.6, 129.1 (d, ^3J(P-C) = 7.1 Hz, Ar-*C*), 128.6, 127.7, 126.6, 125.9, 124.4 (d, ^2J(P-C) = 9.0 Hz, Ar-*C*), 123.9, 75.3 and 75.2 (2 s, O*C*H$_2$), 47.2 (d, ^1J(P-C) = 134.5 Hz, P*C*CH), 32.8 (s, *C*(CH$_3$)$_2$), 21.8 and 21.5 (2s, C(*C*H$_3$)$_2$), 16.1 (s, Ar*C*H$_3$). ^{31}P NMR (162 MHz, CDCl$_3$) δ 21.9. LC/MS *m/z*: 387 [M+1]$^+$. Anal. Calcd. for C$_{22}H_{27}$O$_4$P: C, 68.38; H, 7.04. Found: C, 68.25; H, 7.12.

2.1i *Compounds **10a-b***: These compounds were prepared by following a procedure similar to that for **2a**, using 2'-hydroxy benzophenone (0.611 g, 5 mmol). Mixture of isomers was formed. They were separated successfully in column chromatography using silica gel with ethyl acetate-hexane (1:1) mixture as eluent. **Compound 10a:** Yield 0.069 g (15%, white solid). M.p.: 136–138°C; IR (KBr, cm^{-1}) 3300 (br), 2967, 2930, 1630, 1601, 1480, 1244, 1061, 1009, 826, 737, 700. ^{1}H NMR (400 MHz, CDCl$_3$) δ 11.96 (s, 1H, ArO*H*), 7.58 -7.04 (m, 14 H, Ar*H* + PCH = *CH*), 5.59 (dd→t, ^2J(P-H) = ^3J(H-H) ~18.6 Hz, 1H, PC*H* = CH), 4.83 (br, 1H, =CHC*H*Ar), 4.21 (dd→t, ^3J(P-H) = ^2J(H-H) ~9.4 Hz, 2H, OCH_2), 3.76 (dd→t, ^3J(P-H) = ^2J(H-H) ~12.8 Hz, 2H, OCH_2), 1.07 and 1.01 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, CDCl$_3$) δ 201.2 (s, Ar*C*OPh), 162.3, 155.9, 140.4, 137.5, 136.6, 133.6, 132.2, 131.1, 129.4, 128.9, 128.6, 128.5, 127.3, 119.0, 118.9, 117.4 (d, ^1J(P-C) = 188.0 Hz, P*C* = C), 75.3 (2s, O*C*H$_2$), 54.1 (d, ^3J(P-C) = 22.0 Hz, =CH*C*HAr), 32.5 (d, ^3J(P-C) = 5.0 Hz, *C*(CH$_3$)$_2$), 21.8 and 21.4 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, CDCl$_3$) δ 13.8. LC/MS *m/z*: 463 [M+1]$^+$. Anal. Calcd. for C$_{27}H_{27}$O$_5$P: C, 70.12; H, 5.88. Found: C, 70.06; H, 5.93. **Compound 10b:** Yield 0.347 g (75%, white solid). M.p.: 140–142°C; IR (KBr, cm^{-1}) 3300 (br), 2963, 2926, 1707, 1630, 1601, 1480, 1449, 1335, 1258, 1059, 1007, 828, 758, 700. ^{1}H NMR (400

MHz, $CDCl_3$) δ 11.98 (s, 1H, ArO*H*), 7.73 m, 13H, Ar*H* + PCH = *CH*), 6.59–6.43 (m, 2H, ArH + CH = *CH*Ph), 4.26 (br, 2H, OCH_2), 4.05 (dd, ^2J(P-H) ~24.6 Hz and ^3J(H-H) ~7.8 Hz, 1H, PC*H*), 3.80–3.74 (m, 2H, OCH_2), 1.02 and 0.95 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 201.1 (s, Ar*C*OPh), 162.5, 137.6, 137.0, 136.4, 134.6 (d, ^2J(P-C) = 14.0 Hz, Ar-*C*), 134.2 (d, ^3J(P-C) = 7.0 Hz, Ar-*C*), 132.3, 129.6, 128.6, 128.4, 128.0, 126.5, 125.4, 123.1, 123.0, 119.1, 118.9, 75.2 and 75.1 (2d, ^2J(P-C) = 6.0 Hz and 7.0 Hz respectively, O*C*H$_2$), 46.7 (d, ^1J(P-C) = 136.0 Hz, P*C*CH), 32.7 (d, ^3J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 21.8 and 21.4 (2 s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.1. LC/MS *m/z*: 463 [M+1]$^+$. Anal. Calcd. for $C_{27}H_{27}O_5P$: C, 70.12; H, 5.88. Found: C, 70.25; H, 5.76.

2.1j *Compound* ***11b***: This compound was prepared by following a procedure similar to that for **2a**, using salicylaldehyde (0.611 g, 5 mmol). Mixture of products was formed, from which **11b** was only separated from the reaction mixture. Yield 0.116 g (30%, white solid). M.p.: 188-190°C; IR (KBr, cm^{-1}) 3401, 2967, 2915, 1665, 1586, 1482, 1258, 1057, 1009, 831, 787, 756, 694, 480. ^{1}H NMR (400 MHz, $CDCl_3$) δ 11.00 (s, 1H, ArO*H*), 9.92 (s, 1H, ArC*H*O), 7.70-7.27 (m, 7H, Ar*H* + PCH = *CH*), 7.01 (d, ^3J(H-H) = 8.8 Hz, 1H, Ar*H*), 6.60-6.52 (m, 2H, Ar*H* + *CH* = *CH*Ph), 4.31–4.24 (m, 2H, OCH_2), 4.16-4.08 (~dd, ^2J(P-H) ~24.8 Hz and ^3J(H-H) ~8.0 Hz, 1H, PC*H*), 3.82-3.78 (m, 2H, OCH_2), 1.05 and 0.96 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 196.6 (s, Ar*C*HO), 161.1, 137.9 (d, ^3J(P-C) = 3.9 Hz, Ar-*C*), 136.3, 134.8(d, ^2J(P-C) = 13.6 Hz, Ar-*C*), 134.1 (d, ^3J(P-C) = 7.1 Hz, Ar-*C*), 128.7, 128.2, 126.6, 123.0 (d, ^3J(P-C) = 9.3 Hz, Ar-*C*), 120.8, 118.3, 75.3 (dd→t, ^2J(P-C) ~6.8 Hz, O*C*H$_2$), 46.7 (d, ^1J(P-C) = 135.7 Hz, P*C*CH), 32.8 (d, ^3J(P-C) = 5.6 Hz, *C*(CH$_3$)$_2$), 21.8 and 21.4 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.8. LC/MS *m*/z: 387 [M+1]$^+$. Anal.Calcd. for $C_{21}H_{23}O_5P$: C, 65.28; H, 6.00. Found: C, 65.14; H, 6.08.

2.1k *Compound* ***12b***: This compound was prepared by following a procedure similar to that for **2a**, using 2'-hydroxy acetophenone (0.681 g, 5 mmol). Mixture of isomers was formed, from which **12b** only was separated from the reaction mixture. Yield 0.264 g (66%, white solid). M.p.: 170–172°C; IR (KBr, cm^{-1}) 3400 (br), 2966, 1724, 1643, 1483, 1370, 1261, 1060, 1009, 914, 826, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ 12.26 (s, 1H, ArO*H*), 7.86 (m, 7H, Ar*H* + PCH = *CH*), 7.00 (d, ^3J(H-H) = 8.4 Hz, 1H, Ar*H*), 6.62–6.49 (m, 2H, Ar*H* + CH = *CH*Ph), 4.31-4.24 (m, 2H, OCH_2), 4.09 (dd, ^2J(P-H) = 20.8 Hz,^3J(H-H) = 7.8 Hz, 1H, PC*H*), 3.84–3.75 (m, 2H, OCH_2), 2.67 (s, 3H, ArCOCH_3), 1.05 and 0.96 (2s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 204.6 (s, Ar*C*OMe), 161.8, 137.3, 136.3, 134.6 (d, ^2J(P-C) = 13.4 Hz, Ar-*C*), 131.4, 128.7, 128.1, 126.6, 123.2 (d, ^3J(P-C) = 9.2 Hz, Ar-*C*), 119.9, 119.0, 75.3 and 75.2 (2s, O*C*H$_2$), 46.9 (d, ^1J(P-C) = 135.5 Hz, P*C*CH), 32.8 (s,*C*(CH$_3$)$_2$), 26.9 (s, CO*C*H$_3$), 21.8 and 21.4 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 21.1. LC/MS *m/z*: 401 [M+1]$^+$.

2.11 *Compound* ***13a***: This compound was prepared by following a procedure similar to that for **2a**, using 2-*t*-butyl-4-methyl phenol (0.804 g, 5.0 mmol). Yield 0.363 g (70%, white solid). M.p.: 178–180°C; IR (KBr, cm^{-1}) 3391, 3084, 3063, 3019, 2997, 2964, 2942, 2909, 2860, 1632, 1473, 1441, 1358, 1249, 1216, 1167, 1057, 1013, 975, 920, 876, 832, 695, 668, 536. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36-7.20 (m, 6H, Ar*H* + PCH = *CH*), 7.03 (s, 1H, Ar-*H*), 6.74 (s, 1H, Ar*H*), 5.57 (dd, ^2J(P-H) ~21.0 Hz, ^3J(H-H) ~17.8 Hz, 1H, PC*H* = CH), 5.12 (br, 1H, PhC*H*), 4.87 (br, 1H, ArO*H*), 4.16 (dd→t, ^3J(P-H) = ^2J(H-H) ~10.0 Hz, 2H, OCH_2), 3.81 (dd→t, ^3J(P-H) = ^2J(H-H) ~12.0 Hz, 2H, OCH_2), 2.25 (s, 3H, Ar-CH_3), 1.36 (s, 9H, C(CH_3)$_3$), 1.04 (s, 6H, C(CH_3)$_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.5, 150.0, 139.3, 137.2, 129.5, 129.1, 128.0, 127.7, 127.5, 126.8, 116.9 (d, ^1J(P-C) = 185.0 Hz, P*C* = C), 75.5 (d, ^2J(P-C) = 6.0 Hz, O*C*H$_2$), 49.6 (d, ^3J(P-C) = 22.0 Hz, =CH*C*HAr), 34.4 (s, *C*(CH$_3$)$_3$), 32.5 (d, ^3J(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 30.0 (s, C(*C*H$_3$)$_3$), 21.4 and 21.5 (2s, C(*C*H$_3$)$_2$), 21.1 (s, Ar*C*H$_3$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.9. HRMS (ESI): Calcd. for $C_{25}H_{34}O_4P$ [M$^+$+H] *m/z*: 429.2194. Found: 429.2192.

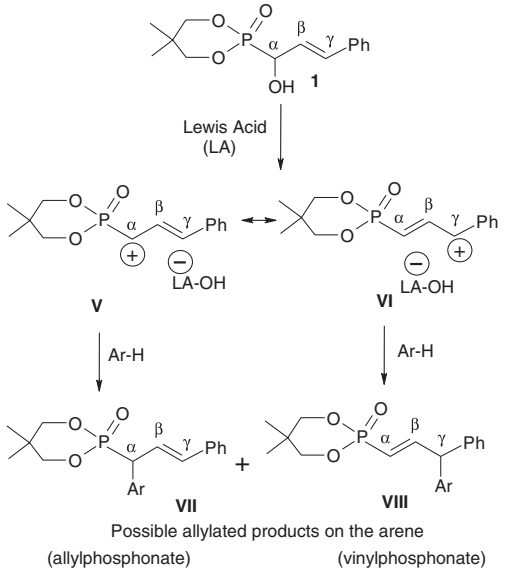
2.1m *Compounds* ***14a*** *and* ***14b***: These compounds were prepared by following a procedure similar to that for **2a**, using 2,6-dichlorophenol (0.813 g, 5 mmol). Mixture of isomers was formed. Isomers were separated successfully by column chromatography using silica gel with ethyl acetate-hexane (1:1) mixture as the eluent. **Compound 14a:** Yield 0.269 g (70%, light yellow solid). M.p.: 140-142°C; IR (KBr, cm^{-1}) 3431, 2917, 2847, 1624, 1489, 1413, 1259, 1156, 1055, 1004, 833, 702. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36–7.20 (m, 7H, Ar*H*), 7.04 (s, 2H, PCH = *CH* + ArO*H*), 5.67-5.57 (m, 1H, PC*H* = CH), 4.79 (br d, ^3J(H-H) ~6.0 Hz, 1H, =CHC*H*Ph), 4.24 (dd→t, ^3J(P-H) = ^2J(H-H) ~9.7 Hz, 2H, OCH_2), 3.81 (dd, ^3J(P-H) ~14.2 Hz, ^2J(H-H) ~11.0 Hz, 2H, OCH_2), 1.11 and 1.02 (2s, 6H,

$C(CH_3)_2$). Assignment for PC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 155.1, 155.0, 147.3, 139.7, 134.0, 129.0, 128.5, 128.3, 127.5, 121.6, 117.6 (d, ^1J(P-C) = 187.0 Hz, P*C* = C), 75.4 and 75.3 (2d, ^2J(P-C) = 19.0 Hz, O*C*H$_2$), 53.8 (d, ^3J(P-C) = 23.0 Hz, =CH*C*HAr), 32.5 (d, ^3J(P-C) = 5.0 Hz, *C*(CH$_3$)$_2$), 21.7 and 21.3 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 13.6. LC/MS *m*/*z* : 427 [M+1]$^+$. Anal. Calcd. for $C_{20}H_{21}Cl_2O_4P$: C, 56.22; H, 4.95 Found: C, 56.32; H, 4.98. **Compound 14b:** Yield 0.116 g (30%, white solid). M.p.: 196-198°C; IR (KBr, cm^{-1}) 3454, 2924, 2847, 1652, 1556, 1488, 1403, 1238, 1172, 1055, 1008, 983, 915, 836, 757, 692. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40–7.28 (m, 7H, Ar*H*), 6.62-6.39 (m, 2H, C*H* = *CH*Ar), 6.23 (s, 1H, ArO*H*), 4.37–4.22 (m, 2H, OC*H*$_2$), 4.01 (dd, ^2J(P-H) = 19.6 Hz, ^3J(H-H) = 6.8 Hz, 1H, PC*H*), 3.86–3.79 (m, 2H, OC*H*$_2$), 1.07 and 0.97 (2 s, 6H, C(C*H*$_3$)$_2$). Assignment for PhC*H* = *CH* protons is tentative. ^{13}C NMR (100 MHz, $CDCl_3$) δ 147.5, 147.4, 136.1, 134.9, 134.8, 129.0, 128, 128.6, 128.4, 128.3, 128.1, 126.5 (d,^3J(P-C) ~2.0 Hz, Ar-*C*), 122.5, 122.4, 121.5, 121.4 (d,^2J(P-C) = 2.1 Hz, Ar-*C*), 75.3 and 75.2 (2d, ^2J(P-C) = 5.0 Hz and 6.0 Hz respectively, O*C*H$_2$), 46.7 (d, ^1J(P-C) = 109.0 Hz, P*C*CH), 32.7 (d, ^3J(P-C) = 5.0 Hz, *C*(CH$_3$)$_2$), 21.7 and 21.3 (2s, C(*C*H$_3$)$_2$). ^{31}P NMR (162 MHz, $CDCl_3$) δ 20.3. LC/MS *m*/*z*: 427 [M+1]$^+$. Anal.Calcd. for $C_{20}H_{21}Cl_2O_4P$: C, 56.22; H, 4.95 Found: C, 56.12; H, 4.91.

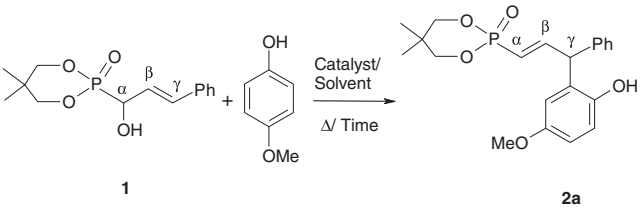
2.2 *X-ray structural analysis of compounds **7a**, **9a** and **11b***

Single crystal X-ray diffraction data were collected on OXFORD diffractometer using Mo-K$_\alpha$ (λ = 0.71073 Å) radiation. The structures were solved and refined by standard methods.[21]

2.2a *Crystal data **7a***: colorless block, $C_{26}H_{25}O_6P$, *M* = 416.39, Monoclinic, Space group *C2/C*, *a* = 21.054(3), *b* = 10.8878(14), *c* = 20.100(3) Å, β = 113.955(2), *V* = 4210.7(10) Å^3, *Z* = 8, μ = 0.166 mm^{-1}, data/restraints/parameters: 3693/0/266, R indices (I > 2σ(I)): R1 = 0.0583, *w*R2 (all data) = 0.1572. **9a**: colorless block, $C_{25}H_{33}O_4P(C_{22}H_{27}O_4P+0.5(C_6H_{12}))$, *M* = 428.48, Triclinic, Space group *P-1*, *a* = 9.0851(11), *b* = 10.4186(17), *c* = 14.7018(18) Å, α = 85.515(3), β = 79.025(2), γ = 64.209(2)°, *V* = 1230.0(3) Å^3, *Z* = 2, μ = 0.138 mm^{-1}, data/restraints/parameters: 4325/0/276, R indices (I > 2σ(I)): R1 = 0.0649, *w*R2 (all data) = 0.1659. **11b**: colorless block, $C_{21}H_{23}O_5P$, *M* = 386.36, Monoclinic, Space group *P*2(1)/n, *a* = 9.572(2), *b* = 11.076(2), *c* = 18.809(4) Å, β = 97.60(3°), *V* = 1976.6(7) Å^3, *Z* = 4, μ = 0.168 mm^{-1}, data/restraints/parameters: 3475/0/247, R indices (I > 2σ(I)): R1 = 0.0761, *w*R2 (all data) = 0.2373.



Scheme 1. Formation and reactivity of phosphono-allyl cations.



Scheme 2. Reaction of allylphosphonate **1** with 4-methoxyphenol.

3. Results and Discussion

We envisioned that electron rich functionalised arenes could be allylated fairly easily in Friedel-Crafts allylic alkylation of arenes and hence started probing with 4-methoxyphenol in the presence of catalytic $FeCl_3$. Two products, allylphosphonate **VII** and vinylphosphonate **VIII** can be formed (cf. scheme 1). Thus phosphono-allyl alcohol **1** along with the phenolic substrate was stirred with 10 mol % $FeCl_3$ at 80°C (oil bath) in nitromethane. After 6 h, the substrate **1** was completely consumed (scheme 2). The reaction mixture showed a major peak in the ^{31}P NMR at δ 15.7 corresponding to the allylated product (vinylphosphonate) **2a** which was isolated in good yield (85%). This product is formed regioselectively. Delighted by this result, we then checked with different catalysts and solvents for the optimization of the product **2a**. Use of 2 equivalents

Table 1. Effect of catalyst/solvent in the optimization of **2a** in the allylation of the arene.

Entry	Catalyst (10 mol %)	Solvent	Temp (°*C*)[a]/ Time (h)	Yield of **2a**[b] (%)
1	$FeCl_3$	CH_3NO_2	80/ 6	84
2	$FeCl_3$	CH_3NO_2	80/ 12	22[c,d]
3	$Sc(OTf)_3$	CH_3NO_2	80/ 12	0[c]
4	$TiCl_4$	CH_3NO_2	80/ 12	0[c]
5	$InCl_3$	CH_3NO_2	80/ 12	0[c]
6	$BF_3.Et_2O$	CH_3NO_2	80/ 12	0[c]
7	$AuCl_3$	CH_3NO_2	80/ 12	Trace[c]
8	$FeCl_3$	DCE	80/ 12	65[c]
9	$FeCl_3$	THF	80/ 12	0[c]
10	$FeCl_3$	Dioxane	80/ 12	80[c]
11	$BiCl_3$	CH_3NO_2	80/ 12	0[c]
12	Triflic acid	CH_3NO_2	80/ 12	Other[e]

[a]Oil bath temperature, [b]Yield of the isolated products, [c]Starting material remained, [d]2 mol equivalents of phenol was used. [e]Other products were formed, but could not be isolated.

of arene with $FeCl_3$ led to 22% of **2a** only. The starting material remained when lower catalyst loading (5%) was used. The performance of other catalysts such as $Sc(OTf)_3$, $TiCl_4$, $InCl_3$, $BF_3.Et_2O$, $AuCl_3$ and $BiCl_3$ was poor (or none) in this reaction whereas in the presence of $FeCl_3$, solvents DCE and dioxane led to lower yields. Use of triflic acid did not afford the expected products, although the starting material was consumed; we were not successful in isolating a pure product. Hence it is clear that $FeCl_3$ in nitromethane is the best optimized condition for this kind of allylation. Details on the allylation of arenes are shown in table 1.

To ascertain the effectiveness of the catalytic system ($FeCl_3$/ nitromethane) in allylation on arenes, various substrates were used. In all the cases, the starting material **1** had completely reacted. In most cases, vinylphosphonates **2a-14a** with regioselectivity on arene, were formed (table 2). In the case of reactions using 2-hydroxy-4-octyloxy benzophenone, 2,6-dimethylphenol, 2'-hydroxy

Table 2. Details on allylation of arenes using $FeCl_3$.

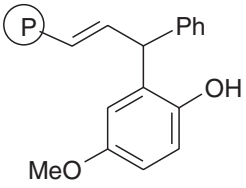
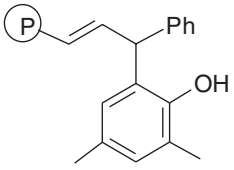
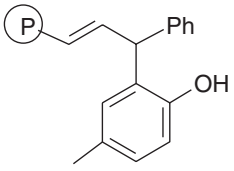
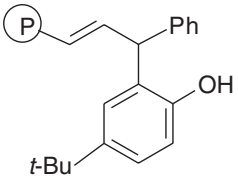
Entry	Arene	Vinylphosphonate[a]/Yield[b]	Allylphosphonate[a]/Yield[b]
1	4-Methoxyphenol	 **2a**/85%	Not observed
2	2,4-Dimethylphenol	 **3a**/92%	Not observed
3	*p*-Cresol	 **4a**/90%	Not observed
4	4-*t*-Butyl phenol	 **5a**/80%	Not observed

Table 2. *continued*

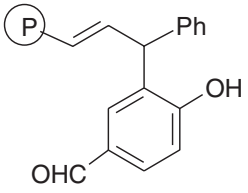
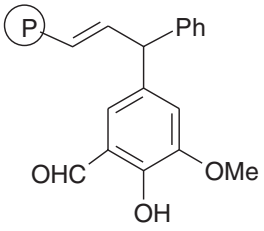
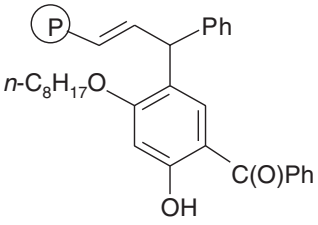
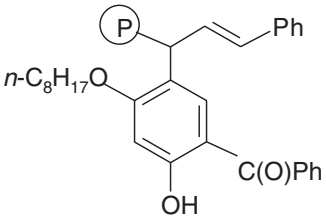
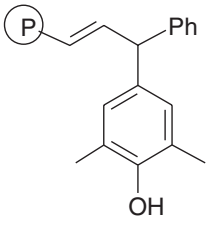
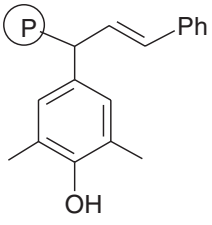
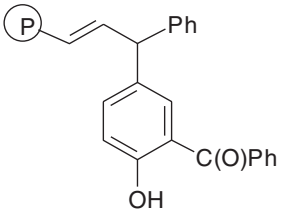
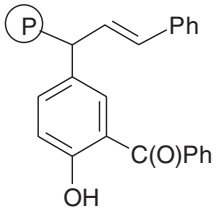
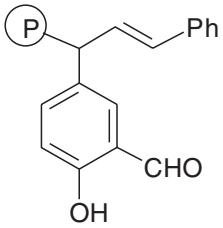
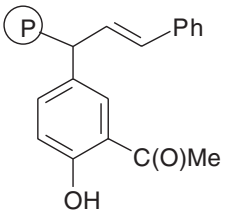
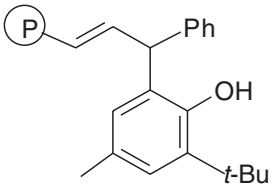
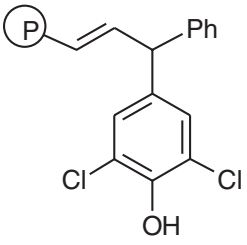
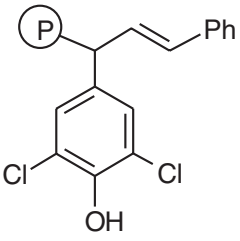
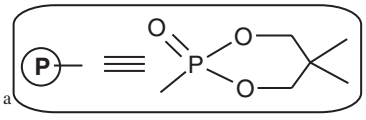
Entry	Arene	Vinylphosphonate[a]/Yield[b]	Allylphosphonate[a]/Yield[b]
5	4-Hydroxy benzaldehyde	 **6a**/84%	Not observed
6	*o*-Vanillin	 **7a** (X-ray)/30%	Formed but not isolated
7	2-Hydroxy-4-octyloxy benzophenone	 **8a**/50%	 **8b**/30%
8	2,6-Dimethylphenol	 **9a** (X-ray)/70%	 **9b**/22%
9	2'-Hydroxy benzophenone	 **10a**/15%	 **10b**/75%
10	Salicylaldehyde	Formed but not isolated[c]	 **11b** (X-ray)/30%

Table 2. *continued*

Entry	Arene	Vinylphosphonate[a]/Yield[b]	Allylphosphonate[a]/Yield[b]
11	2'-Hydroxy acetophenone	Formed but not isolated[c]	 **12b**/66%
12	2-*t*-Butyl-4-methyl phenol	 **13a**/70%	Not observed
13	2,6-Dichlorophenol	 **14a**/70%	 **14b**/30%



[a]

[b] Yields of isolated products.

[c] In these cases both the products were formed but we could isolate only one of them in pure form.

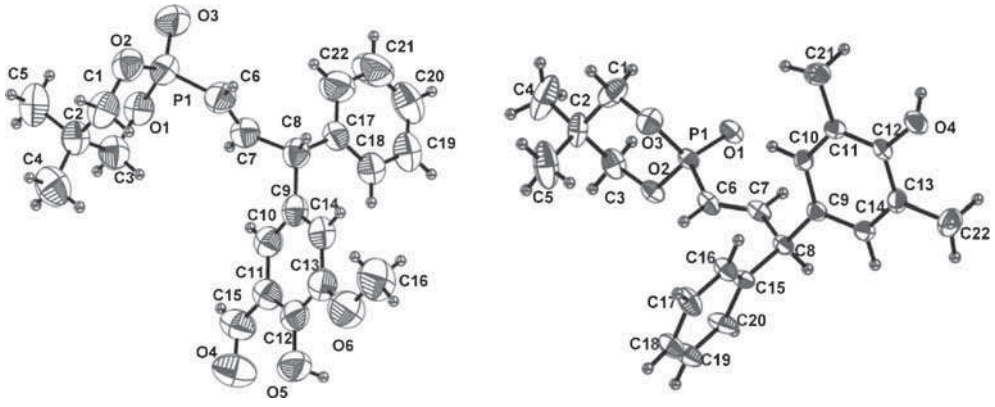


Figure 1. Molecular structures of **7a** (left) and **9a.**1/2C_6H_{12} (right, solvent molecule is omitted). Selected bond lengths [Å] with esds are given in parentheses. **7a**: P1-C6 1.757 (3), C6-C7 1.305(4), C7-C8 1.504(4), C8-C9 1.524(4). **9a.**1/2C_6H_{12}: P1-C6 1.740 (3), C7-C6 1.309(4), C8-C7 1.489(4), C9-C8 1.523(4).

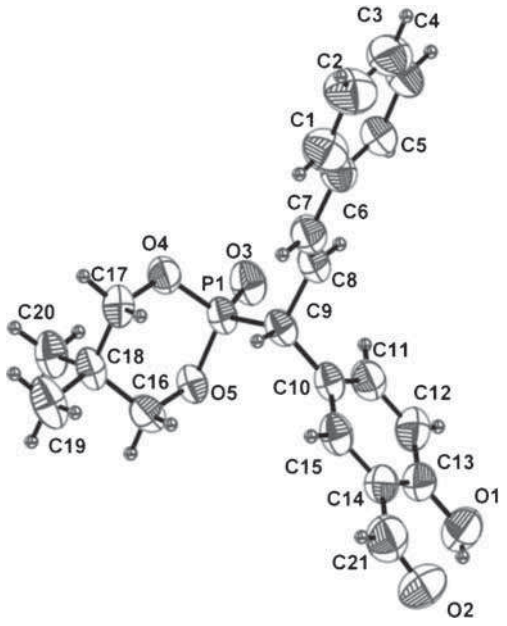


Figure 2. Molecular structure of **11b**. Selected bond lengths [Å] with esds are given in parentheses: P1-C9 1.816(4),C6-C7 1.475(2), C7-C8 1.307(6), C8-C9 1.513(5).

benzophenone and 2,6-dichlorophenol that led to vinylphosphonates **8a**–**10a** and **14a**, allylphosphonates **8b**–**10b** and **14b** (entries 7–9 and 13) were also formed and isolated successfully. Allylphosphonates **11b** and **12b** were only isolated due to the close R_f values in the case of salicylaldehyde and 2'-hydroxy-acetophenone albeit other isomers (vinylphosphonates **12a** and **13a**) were also formed [^{31}P NMR evidence]. The structures of vinylphosphonates **7a** and **9a** and the allylphosphonate **11b** were confirmed by X-ray crystallography (figures 1 and 2).

4. Conclusions

In summary, regioselective allylation of phenolic substrates using phosphono-allyl alcohols was achieved by using even catalytic amounts of $FeCl_3$. Both vinylphosphonates and allylphosphonates were obtained, the ratio depending upon the substrate. This is in contrast to a previous report on the reaction wherein only non-functionalised arenes were used and no allylphosphonate products were observed. Conclusive proof for the results is provided by structurally characterising both types of products.

Supplementary Information

Crystallographic data for the structure **7a**, **9a** and **11b** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication number CCDC 1028043-1028045. Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: +44(1223) 336033 or e-mail: deposit@ccdc.cam.ac.uk]. Copies of ^{1}H/^{13}C/ ^{31}P NMR spectra are available at www.ias.ac.in/chemsci.

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