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Hydrophosphonylation of activated alkenes and alkynes via fluoride ion activation in ionic liquid medium

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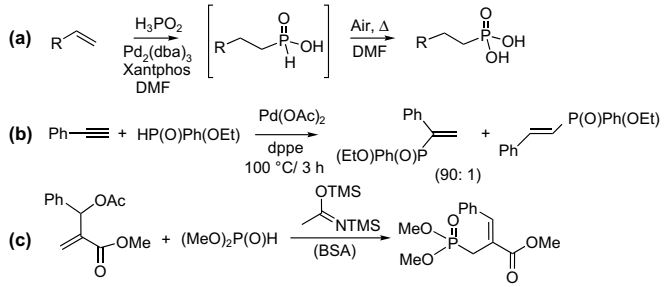
ABSTRACT

A simple transition metal-free hydro/hydrothiophosphonylation of Baylis–Hillman adducts, substituted allyl bromides, allenylphosphonates and alkynes, promoted by fluoride ion in ionic liquid, is described. Clear-cut evidence for fluoride activation of the phosphite via pentacoordinate phosphorus is provided for the first time. Also, in a comparative reaction, the product obtained was different from that from the palladium catalyzed one. Structures of key products are proven by X-ray crystallography.

1. Introduction

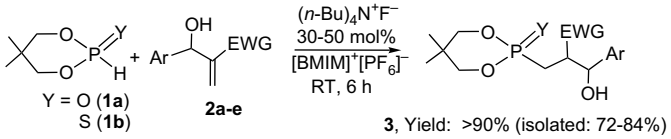
Hydrophosphonylation of organic unsaturated systems is an important reaction that leads to versatile organophosphonates of great synthetic utility and diverse biological activities.[1–3] This reaction is often promoted by transition metal catalysts, radical initiators, strong bases or Lewis acid-microwave (MW) assistance.[1,2] Many of these routes work well only at high temperature or with low selectivity and (except while using MW) volatile organic solvents are used as reaction media. Some recent examples wherein better success has been achieved are shown in Scheme 1.[2n–p] In this paper, we disclose that activation of P(X)H (X=O, S) group via pentacoordinate phosphorus[4] works efficiently for a variety of substrates at room temperature in an ionic liquid medium and leads to stereoselective products. X-ray structures of key compounds (**3ba**, **6ab**, **8** and **18**; Supplementary data) have been determined. Higher reactivity of hypervalent (pentacoordinate) silicon compared to tetracoordinate species is put to wide practical synthesis, but similar chemistry by activation of tetra- to pentacoordinate phosphorus as utilized here is rather scarce.[5,6] This is also one of the points we wish to highlight in the present article.



Scheme 1.

2. Results and discussion

The reaction of cyclic phosphites **1a**–**b** with various Baylis–Hillman adducts **2a**–**e** in the presence of $(n\text{-Bu})_4N^+F^-$ (TBAF) in $[bmim]^+[PF_6]^-$ leads selectively to γ-hydroxyphosphonates **3aa**–**3ac**, **3ae** and **3ba**–**3be** (Scheme 2, Table 1). The choice of these cyclic phosphites used here was dictated by our desire to obtain well-defined and stable crystalline products.[4g] In contrast, (a) the



Scheme 2.

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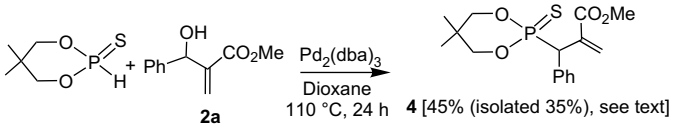
Table 1
Details on the yields of γ-hydroxyphosphonates (**3aa–3ac**, **3ae**, **3ba–be**)

Entry	Y	Baylis–Hillman adduct		Product	Yield[a] (%)
		Ar	EWG		
1	**O**	Ph	CO_2Me	**3aa**	82
2	**O**	4-MeO-C_6H_4	CO_2Me	**3ab**	72
3	**O**	4-O_2N-C_6H_4	CO_2Me	**3ac**	76
4	**O**	Ph	CN	**3ae**	80
5	**S**	Ph	CO_2Me	**3ba (X-ray)**	75
6	**S**	4-MeO-C_6H_4	CO_2Me	**3bb**	84
7	**S**	4-O_2N-C_6H_4	CO_2Me	**3bc**	80
8	**S**	1-C_4H_3O (furfuryl)	CO_2Et	**3bd**	73
9	**S**	Ph	CN	**3be**	79

[a] Isolated yields.

corresponding reaction of **1a–b** with Baylis–Hillman acetates affords P-CH_2 allylphosphonates with the elimination of acetic acid,[7] and (b) the $Pd_2(dba)_3$ catalyzed reaction of **1b** with the Baylis–Hillman alcohol **2a** [Ar=Ph][8] leads to the α-phenyl allylphosphonate **4** as a major product while **1a** gave a mixture of several products in low yields (Scheme 3).



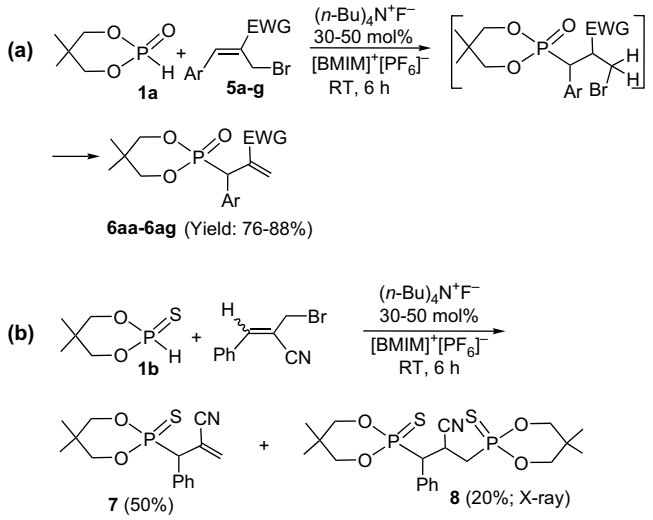
Scheme 3.

Later, we treated cyclic phosphite (**1a**) with allyl bromide (**5a**) in the presence of $(n\text{-Bu})_4N^+F^-$ to give α-aryl allylphosphonate **6aa**. We optimized the reaction conditions for **6aa** in different solvents (Table 2). Although DMF works slightly better, $[bmim]^+[PF_6]^-$ offers the advantage that it is readily recovered. In fact, we could use the same medium in the synthesis of **6aa** for at least two consecutive reactions. Use of DMF required removal of solvent by distillation which was incomplete; hence an additional subsequent water-wash was also required. Isolation using ionic liquid as the medium was much simpler and easier in our hands. Under optimized conditions, we have conducted the reactions of a variety of allyl bromides (**5a–g**) with cyclic phosphites (**1a–b**) for the synthesis of different α-aryl allylphosphonates **6–7** (Scheme 4, Table 3). The reaction is regioselective for **6aa–6ag**. The crude reaction mixture corresponding to **3aa–3ba** showed only one diastereomer (^{31}P and ^1H NMR); we did not observe the other diastereomer under these reaction conditions. It is important to note that the synthesis of these by Arbuzov rearrangement of phosphites $(OCH_2CMe_2CH_2O)POCH_2C(EWG)=CHAr$ is difficult.[9] The more reactive **1b** leads to double phosphonylation product **8** also under these conditions.[10]

Table 2
Details on the yield of **6aa** under different reaction conditions[a]

Entry	Solvent	Temp (°C)	Yield[a] (%)
1	THF	65	78
2	Acetonitrile	65	60
3	Dichloroethane	70	66
4	Dichloromethane	RT	68
5	Toluene	110	60
6	DMF	RT	90[b]
7	1,4-Dioxane	80	73
8	PEG	RT	72
9	$[bmim]^+[PF_6]^-$	RT	84[b]
10	Water	80	—

[a] There was no reaction in the absence of TBAF; yields were based on ^1H NMR spectra.
[b] Although yields were better in DMF, work-up was much easier using the ionic liquid.



Scheme 4.

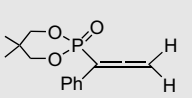
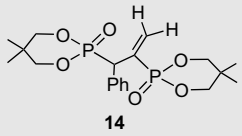
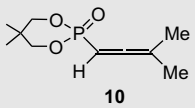
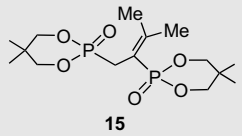
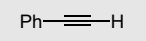
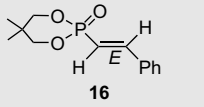
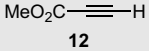
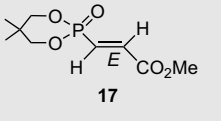
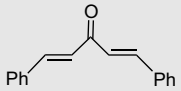
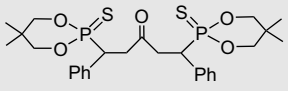
Table 3
Details on the yields of α-aryl allylphosphonates **6aa–6ag**

Entry	Baylis–Hillman adduct		Product	Yield[a] (%)
	Ar	EWG		
1	Ph	CO_2Me	**6aa**	84
2	4-Me–C_6H_4	CO_2Me	**6ab (X-ray)**	85
3	4-Cl–C_6H_4	CO_2Me	**6ac**	78
4	4-O_2N–C_6H_4	CO_2Me	**6ad**	88
5	Ph	CN	**6ae**	76
6	4-Me–C_6H_4	CN	**6af**	78
7	4-Cl–C_6H_4	CN	**6ag**	78

[a] Isolated yields.

The above procedure is fairly general and as shown in Table 4, reactions of cyclic phosphites **1a–b** with various unsaturated systems like allenes (**9–10**), alkynes (**11–12**), and dibenzylideneacetone (**13**) lead to a diverse range of phosphonates (**14–18**). The

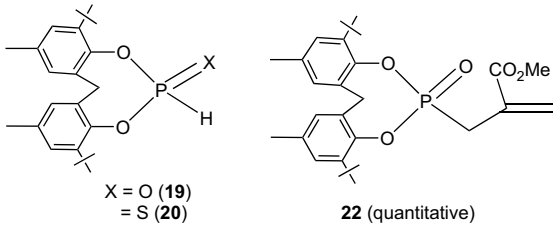
Table 4
Details on the reactions of cyclic phosphites **1a–b** with unsaturated systems **9–13** leading to the phosphonates **14–18**

Entry	Substrate	Product	Yield (%)
1	 **9**	 **14**	89
2	 **10**	 **15**	77
3	 **11**	 **16**	85 (Single isomer)
4	 **12**	 **17**	88 (Single isomer)
5	 **13**	 **18 (X-ray)**	88

yields are generally very good. Among the substrates listed here, only phosphonylation of phenylacetylene with other phosphites has been investigated by others before.[11] Also, synthesis of the diphosphonate such as **18** offers an opportunity for multiple phosphonylation in a single step.

Activation of the phosphites takes place via pentacoordinate phosphorus as evidenced by the following:

(a) Other salts like $(n\text{-Bu})_4N^+X^-$ [X=Cl, Br, I, and HPO_4] did not work, because the anions are not strong enough to lead to pentacoordination; CsF also did not work well. However, KF (or CsF)/18-crown-6 or $(n\text{-Bu})_4N^+Cl^-$/KF worked although not as efficiently as $(n\text{-Bu})_4N^+F^-$. (b) In place of more reactive **1a**–**b**, when we treated the less reactive (steric factors) **19** or **20** with an equimolar quantity of $(n\text{-Bu})_4N^+F^-$, the ^1H, ^{31}P, and ^{19}F NMR spectra clearly show P–F bonded intermediate [>95% by ^{31}P NMR; cf. Figure 1] with ^1J(P–F)=959.5 Hz, ^1J(P–H)=652.4 Hz, and ^2J(F–H)=129.4 Hz in the reaction using **19**. The resulting species (**21a** or **21b**) was obtained as a gummy material in >95% purity (based on ^{31}P NMR). The ^1H NMR and ^{13}C NMR spectra are consistent with the 8-membered phosphocin ring intact. This intermediate, on treatment with the allyl bromide $H_2C{=}C(CO_2Me)CH_2Br$, led to the phosphonate **22** as a single product.



Based on the above observations, we propose the pathway shown in Scheme 5 involving pentacoordinate phosphorus intermediate **21a** or **21b**. It is interesting to note that, in the oxidative Heck-type reaction involving cleavage of a carbon–phosphorus bond of arylphosphonic acids **23**, Inoue et al. have proposed the involvement the pentacoordinate species **24** (Scheme 6). Thus, our results are consistent with such a proposal.[5c] We could not detect any hexacoordinate species even at −40 °C when more than one equivalent of TBAF (solution in THF) was used. Solid TBAF (dried under vacuum at 100 °C for 2 h), also worked well. However, with added water, the reaction did not proceed. Under basic conditions (using Et_3N or NaH), the phosphites **1a**–**b** did not undergo hydrophosphonylation with **2a**, or **9**–**11** (^{31}P NMR evidence). The reaction of phosphite **1a** with **5a** using Et_3N as the base gave a lower yield of **6aa**.[12] For the subsequent step, it is possible that fluoride ion has simply increased the acidity of phosphorus or the reaction entails a free radical mechanism. Rico-Lattes and co-workers have earlier described an example wherein the stable *neutral* P–H pentacoordinate phosphorane **25** is utilized in the synthesis of aminophosphonic acid **27** via the P–C bonded phosphorane **26** (Scheme 7), but the details on the mode of P–H addition are not available, perhaps because the addition reaction was too fast.[13] Similar work done much earlier by Grechkin and Gubanova as well as Burgada and co-workers on the addition of the vinyl ether $CH_2{=}CH(OEt)$ to P–H phosphoranes had suggested a radical pathway.[14] We have conducted the reaction of **1a** with $(4\text{-MeO-}C_6H_4)CH(OH)C(CO_2Me){=}CH_2$ (**2b**) in the presence of 1,4-benzoquinone. At 10 and 20 mol % of the quinone, no significant reduction in the product **3ab** (yield 60–80%) was noticed; however, with 50 mol % of the quinone, there was a drastic reduction. Since we expect the

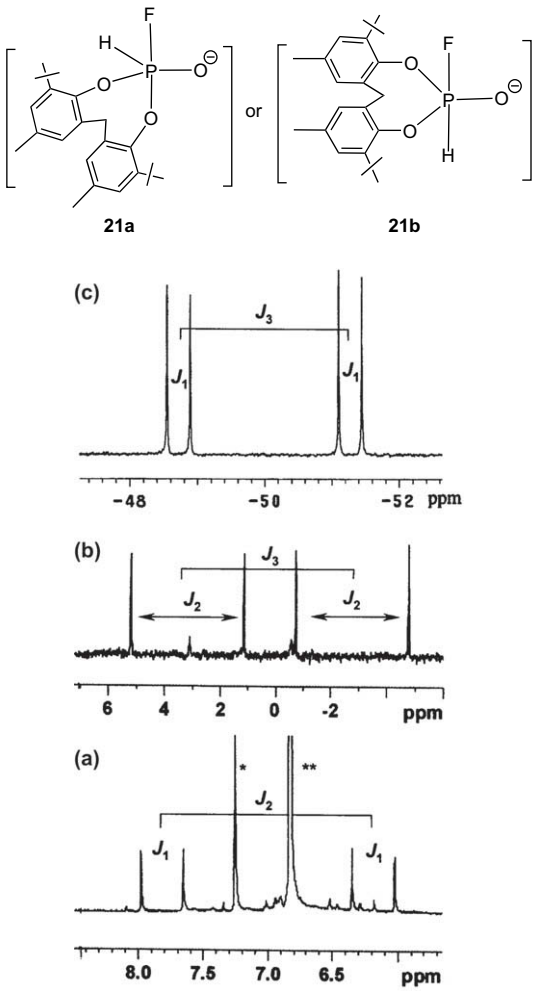
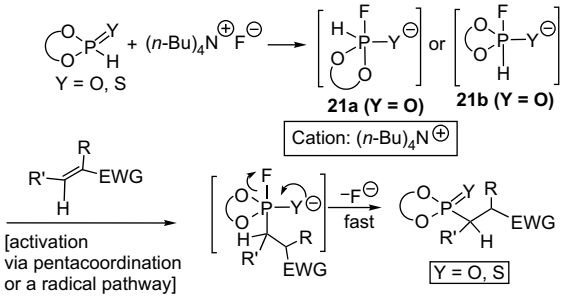
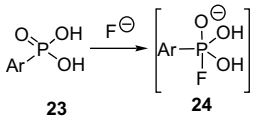


Figure 1. (a) ^1H [400 MHz], (b) ^{31}P [proton coupled, 160 MHz] and (c) ^{19}F [377 MHz] NMR spectra of 1:1 (molar) mixture of **19** and $[n\text{-Bu}]_4N^+F^-$ leading to **21a** or **21b** in the appropriate region in $CDCl_3$. $J_1={}^2J$(F–H)=129.4 Hz; $J_2={}^1J$(P–H)=652.4 Hz; $J_3={}^1J$(P–F) =959.5 Hz. Peaks marked by '*' and '**' in the ^1H NMR are due to $CHCl_3$ and *H*(Ar) protons, respectively.

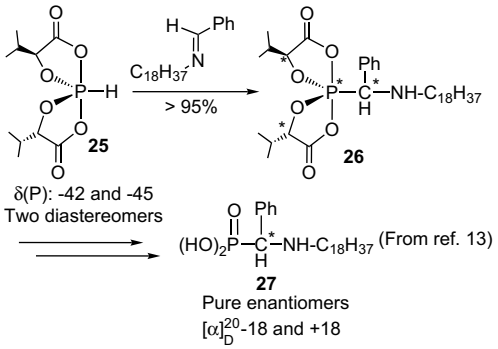


Scheme 5.



Scheme 6.

radical quencher to work at low concentrations also, in our opinion, the result is inconclusive as regards the involvement of a radical mechanism at the later stage of phosphonylation. However, since we are able to establish that **21a** or **21b** leads to



Scheme 7.

the phosphonate product **22**, it is very likely that pentacoordinate phosphorus is involved in these reactions. Finally, we note that species such as **21a**–**b** are still mechanistically very important,[4a] and hence efforts are underway to obtain them as crystalline solids.

3. Conclusion

A novel and convenient protocol for regio-/stereo-selective hydrophosphonylation in ionic liquid medium is presented. Many of these compounds cannot be prepared stereoselectively from the existing methods. Clear-cut evidence for the new P–F bonded intermediate is given for the first time. Efforts to make TBAF essentially catalytic at 2–3 mol % are in progress. As exemplified by the reactions using **1b** palladium-catalyzed and fluoride-mediated phosphonylation reactions to lead to different types of products. Although conjugate addition of P(X)–H (X=O, S) compounds is very well known, the present work adds on a new route with selectivity different from many of the existing methodologies.

4. Experimental

4.1. General

General experimental details are given in the Supplementary data. Compounds **1a** [δ(P) 2.3] and **19** [δ(P) 0.1] were prepared by using the methods previously reported from our laboratory.[15a,b] For compounds ($OCH_2CMe_2CH_2O$)P(S)H [**1b**: δ(P) 65.2] and [CH_2{6-*t*-Bu-4-Me-C_6H_4O}$_2$P(S)H] [**20**: δ(P) 64.9], a modified version of the literature procedure was followed.[15b,c] Dry H_2S gas [prepared from ~4.0 g of FeS with ~800 mL of 30% HCl] was bubbled for 0.5 h into a solution of respective chlorophosphite (1.84 mmol) in toluene (40 mL). Et_3N (1.88 mmol) was added drop-wise (15 min); H_2S gas was passed further for 1 h, and the mixture stirred overnight at room temperature. It was then filtered, the precipitate washed with toluene, and the washings added to the filtrate. Concentration of the filtrate afforded the desired product as a crystalline solid. This reaction was very clean and no side product (dithiaphosphoric salt) was observed.

Baylis–Hillman adducts **2a**–**e** and allyl bromides **5a**–**g** were synthesized according to the standard procedures.[16] Allenes **9**–**10** and the ionic liquid [bmim]$^+$[PF_6]$^-$ were prepared by known procedures.[17,18]

4.2. Synthesis of γ-hydroxy phosphonates 3aa–3be: representative procedure

To phosphite (**1a**) or thiophosphite (**1b**) (1.0 mmol) and Baylis–Hillman adduct (one of **2a**–**e**) (1.0 mmol) in 1 mL of [bmim]$^+PF_6^-$, 50 mol % of TBAF (1 M THF solution) was added via syringe over a period of 2 min at room temperature. The progress of the reaction was monitored by TLC (3–6 h). After the disappearance of the starting material (**1a** or **1b**), ethyl acetate (8 mL) was added and stirring continued for 15 min. The upper layer was separated and concentrated in vacuo to give the crude product, which was purified by column chromatography using 70–80% ethyl acetate–/hexanes as eluent. Only a single diastereomer was observed in the reaction mixture (^{31}P and ^{1}H NMR). The [bmim]$^+$[PF_6]$^-$ was collected and reused for the next reaction. When we used 30 mol % of the TBAF, it took ~2 h more for the completion of the reaction but the yields were essentially the same.

4.2.1. *3aa*

Isolated yield: 0.28 g (82%); R_f=0.3 (EtOAc/hexane 4:1); white solid; mp 112–114 °C; [Found: C, 56.04; H, 6.74. $C_{16}H_{23}O_6P$ requires C, 56.14; H, 6.77%]; ν_{max} (KBr) 3399, 2924, 1734, 1454, 1240, 1134, 1009, 868 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37–7.30 (5H, m, Ar-*H*), 4.91 (1H, br s, C*H*(Ar)), 4.33–4.30 (2H, m, OCH_2), 3.73–3.70 (2H, m, OCH_2), 3.64 (3H, s, OCH_3), 3.38–3.36 (1H, m, C*H*(CO_2Me)), 3.00 (1H, br s, O*H*), 2.56 (1H, dt, *J* 12.0, 16.0, 16.0 Hz, CH_2(B)), 2.22 (1H, ~dt, *J* 4.0, 16.0, 16.0 Hz, CH_2(A)), 1.14 and 0.91 (6H, 2 s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 173.8, 140.8, 128.8, 128.4, 126.3, 75.2, 74.1, 74.0, 52.2, 47.4, 33.4 (d, *J* 14.5 Hz), 32.2 (d, *J*(P–C) 104.2 Hz), 22.5, 21.5; δ_P (160 MHz, $CDCl_3$) 24.3.

4.2.2. *3ab*

Isolated yield: 0.27 g (72%); R_f=0.25 (EtOAc/hexane 4:1); white solid; mp 120–122 °C; [Found C, 54.95; H, 6.72. $C_{17}H_{25}O_7P$ requires C, 54.84; H, 6.77%]; ν_{max} (KBr) 3474, 2957, 1744, 1613, 1518, 1260, 1211, 1049, 997 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.26 and 6.89 (4H, 2d, *J* 8.8 Hz, Ar-*H*), 4.87 (1H, dd→t, *J* 5.6 Hz, C*H*(Anis)), 4.35–4.33 (2H, m, OCH_2), 3.80 (3H, s, OCH_3), 3.73–3.70 (2H, m, OCH_2), 3.68 (3H, s, OCH_3), 3.38–3.36 (1H, m, C*H*(CO_2Me)), 2.65 (1H, d, *J* 5.6 Hz, O*H* (The O*H* peak disappeared on D_2O exchange)), 2.56 (1H, ~dt, *J* 4.0, 16.0, 16.0 Hz, CH_2(B)), 2.19 (1H, ddd, *J* 4.0, 15.2, 16.0 Hz, CH_2(A)), 1.16 and 0.92 (6H, 2 s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 173.5, 159.7, 132.8, 127.7, 114.2, 75.1 (d, *J* 17.0 Hz), 74.0, 73.9, 55.4, 52.1, 47.5, 33.2, 32.3 (d, *J*(P–C) 104.3 Hz), 22.5, 21.5; δ_P (160 MHz, $CDCl_3$) 25.2; LC–MS *m*/*z* 371 [M−1]$^+$.

4.2.3. *3ac*

Isolated yield 0.29 g (76%); R_f=0.20 (EtOAc/hexane 4:1); pale yellow solid; mp 140–142 °C; [Found: C, 49.48; H, 5.75; N, 3.46. $C_{16}H_{22}NO_8P$ requires C, 49.62; H, 5.73; N, 3.62%]; ν_{max} (KBr) 3299, 2965, 1728, 1522, 1348, 1260, 1055, 1005, 837 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.23 and 7.54 (4H, 2d, *J* 8.6 Hz, Ar-*H*), 5.25 (1H, br s, O*H*), 4.19–4.16 (3H, m, OCH_2+C*H*(Ar)), 3.91–3.89 (2H, m, OCH_2), 3.64 (3H, s, OCH_3), 3.45–3.42 (1H, m, C*H*(CO_2Me)), 2.31–2.25 (2H, m, PCH_2), 1.09 and 1.08 (6H, 2 s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 172.6 (d, *J* 10.4 Hz), 148.2, 147.6, 127.0, 123.6, 75.7 and 75.6 (2d, *J* 6.3 Hz), 73.3 (d, *J* 10.2 Hz), 52.3, 46.4 (d, *J* 2.6 Hz), 33.2 (d, *J* 6.1 Hz), 22.7 (d, *J*(P–C) 137.5 Hz), 21.5, 21.4; δ_P (160 MHz, $CDCl_3$) 25.5.

4.2.4. *3ae*

Isolated yield 0.25 g (80%); R_f=0.30 (EtOAc/hexane 4:1); white solid; mp 138–140 °C; [Found: C, 58.50; H, 6.50; N, 4.35. $C_{15}H_{20}NO_4P$ requires C, 58.25; H, 6.52; N, 4.53%]; ν_{max} (KBr) 3447, 2973, 2259, 1456, 1221, 1044, 995 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.48–7.36 (5H, m, Ar-*H*), 5.12 (1H, dd~t, *J* 7.3 Hz, C*H*(Ar)), 4.43–4.40 (2H, m, OCH_2), 3.82–3.79 (2H, m, OCH_2), 3.54–3.51 (1H, m, C*H*(CN)), 2.68–2.63 and 2.56–2.51 (2H, 2m, PCH_AH_B), 2.46 (1H, d, *J* 7.3 Hz, O*H*), 1.22 and 0.95 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 139.6, 128.9, 126.0, 118.3 (d, *J* 14.6 Hz), 74.3 and 74.2 (2d, *J*~2.0 Hz), 72.8 (d, *J* 8.5 Hz), 36.1, 33.4 (d, *J* 6.1 Hz), 32.5 (d, *J*(P–C) 106.7 Hz), 22.5, 21.3; δ_P (160 MHz, $CDCl_3$) 24.9.

4.2.5. ***3ba***

Isolated yield 0.27 g (75%). R_f=0.30 (EtOAc/hexane 3:2); white solid; mp 132–134 °C; [Found: C, 53.65; H, 6.45; S, 9.09. $C_{16}H_{23}O_5PS$ requires C, 53.62; H, 6.47; S, 8.95%]; ν_{max} (KBr) 3522, 2953, 1742, 1456, 1364, 1269, 1208, 1046, 995 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39–7.31 (5H, m, Ar-*H*), 4.95 (1H, dd ~ t, *J* 7.6 Hz, C*H*(Ar)), 4.36–4.33 (2H, m, OCH_2), 3.76–3.73 (2H, m, OCH_2), 3.67 (3H, s, OCH_3), 3.42–3.39 (1H, m, C*H*(CO_2Me)), 2.81 (1H, d, *J* 7.6 Hz, O*H*, exchanges with D_2O), 2.58 (1H, dt, *J* 9.6, 17.2, 17.2 Hz, CH_2(B)) and 2.24 (1H, ddd → dt, *J* 4.0, 17.2, 17.2 Hz, CH_2(A)), 1.16 and 0.92 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 173.4 (d, *J* 3.0 Hz), 140.6, 128.7, 128.4, 126.3, 75.2 (d, *J* 15.6 Hz), 74.0 and 73.9 (2d, *J* 6.2 Hz), 52.1, 47.3 (d, *J* 1.6 Hz), 33.2 (d, *J* 5.7 Hz), 32.2 (d, *J*(P–C) 104.8 Hz), 22.4, 21.4; δ_P (160 MHz, $CDCl_3$) 96.3; This compound was crystallized from dichloromethane:hexane (1:1) mixture at room temperature over a period of 2 d (X-ray structure in Fig. S2; Supplementary data).

4.2.6. ***3bb***

Isolated yield 0.33 g (84%); R_f=0.42 (EtOAc/hexane 4:1); white solid; mp 144–146 °C; [Found: C, 52.32; H, 6.53; S, 8.21. $C_{17}H_{25}O_6PS$ requires C, 52.57; H, 6.49; S, 8.25%]; ν_{max} (KBr) 3522, 2958, 1758, 1454, 1368, 1268, 1200, 1041, 995 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.27 and 6.91 (4H, 2d, *J* 8.6 Hz, Ar-*H*), 4.95 (1H, dd → t, *J* 6.2 Hz, C*H*(Anis)), 4.36–4.34 (2H, m, OCH_2), 3.81 (3H, s, OCH_3), 3.74–3.66 (2H, m, OCH_2), 3.67 (3H, s, OCH_3), 3.41–3.38 (1H, m, C*H*(CO_2Me)), 2.73 (1H, d, *J* 6.2 Hz, O*H*), 2.57 (1H, dt, *J* 9.6, 17.2, 17.2 Hz, CH_2(B)) and 2.19 (1H, ddd → dt, *J* 4.0, 17.2, 17.2 Hz, CH_2(A)), 1.18 and 0.93 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 173.5 (d, *J* 5.5 Hz), 159.6, 132.6, 127.6, 114.1, 75.0 (d, *J* 16.7 Hz), 74.0 and 73.9 (2d, *J* 6.2 Hz), 55.3, 52.1, 47.4, 33.2 (d, *J* 5.7 Hz), 32.3 (d, *J*(P–C) 104.8 Hz), 22.4, 21.4; δ_P (160 MHz, $CDCl_3$) 96.7.

4.2.7. ***3bc***

Isolated yield 0.32 g (80%); R_f=0.32 (EtOAc/hexane 4:1); yellow solid; mp 156–158 °C; [Found: C, 47.48; H, 5.30; N, 3.41. $C_{16}H_{22}NO_7PS$ requires C, 47.64; H, 5.50; N, 3.47%]; ν_{max} (KBr) 3545, 2961, 1738, 1516, 1271, 1211, 1169, 1049, 995 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.20 and 7.51 (4H, 2d, *J* 8.6 Hz, Ar-*H*), 5.22 (1H, d, *J* 4.4 Hz, C*H*(Ar)), 4.15–4.12 (2H, m, OCH_2), 3.86–3.83 (2H, m, OCH_2), 3.62 (3H, s, OCH_3), 3.37–3.34 (1H, m, C*H*(CO_2Me)), 2.21–2.18 (3H, m, PCH_2+O*H*), 1.07 and 1.05 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 172.6 (d, *J* 10.4 Hz), 148.2, 147.6, 127.0, 123.6, 75.7 and 75.6 (2d, *J* 6.3 Hz), 73.3 (d, *J* 10.2 Hz), 52.3, 46.4 (d, *J* 2.6 Hz), 33.2 (d, *J* 6.1 Hz), 22.7 (d, *J*(P–C) 107.5 Hz), 21.5, 21.4; δ_P (160 MHz, $CDCl_3$) 94.6.

4.2.8. ***3bd***

Isolated yield 0.26 g (73%); R_f=0.33 (EtOAc/hexane 3:2); light brown solid; mp 126–128 °C; [Found: C, 47.68; H, 6.50. $C_{15}H_{23}O_6PS$ requires C, 49.72; H, 6.40%]; ν_{max} (KBr) 3526, 2959, 1742, 1613, 1518, 1260, 1211, 1175, 1053, 999 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38 and 7.26 (3H, 2br s, furfuryl-*H*), 5.25 (1H, br s, C*H*(CO_2Et)), 4.39–4.36 (2H, m, OCH_2), 4.20–4.17 (2H, m, OCH_2), 3.73 (2H, q, *J* 7.1 Hz, $CO_2CH_2CH_3$), 3.55–3.52 (1H, m, C*H*(Ar)), 2.95 (1H, d, *J* 8.0 Hz, O*H*, disappears on D_2O exchange), 2.70–2.60 and 2.41–2.33 (2H, 2m, PCH_AH_B), 1.22 (3H, t, *J* 7.1 Hz, $CO_2CH_2CH_3$), 1.18 and 0.93 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 172.6, 153.4, 142.6, 110.3, 107.6, 102.5, 73.9, 73.8, 69.1 (d, *J* 15.0 Hz), 61.4, 45.0, 33.2 (d, *J* 6.0 Hz), 32.1 (d, *J*(P–C) 105.0 Hz, PCH_2), 22.5, 21.4, 14.0; δ_P (160 MHz, $CDCl_3$) 96.3.

4.2.9. ***3be***

Isolated yield 0.26 g (79%); R_f=0.35 (EtOAc/hexane 3:2); white solid; mp 150–152 °C; [Found: C, 55.59; H, 6.19; N, 4.42; S, 9.88. $C_{15}H_{20}NO_3PS$ requires C, 55.37; H, 6.20; N, 4.30; S, 9.85%]; ν_{max} (KBr) 3445, 2973, 2254, 1467, 1402, 1228, 1044, 998 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.49–7.38 (5H, m, Ar-*H*), 5.12 (1H, d, *J* 7.6 Hz, C*H*(Ar)), 4.46–4.42 (2H, m, OCH_2), 3.85–3.81 (2H, m, OCH_2), 3.58–3.55 (1H, m, C*H*(CN)), 2.68–2.64 and 2.59–2.55 (2H, 2m, PCH_AH_B), 2.46 (1H, br s, O*H*), 1.23 and 0.97 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 139.5, 128.9, 128.8, 125.9, 118.2 (d, *J* 14.5 Hz), 74.2 and 74.1 (2d, *J* 6.1 Hz), 72.8 (d, *J* 8.8 Hz), 36.1, 33.4 (d, *J* 5.7 Hz), 32.4 (d, *J*(P–C) 105.8 Hz), 22.5, 21.3; δ_P (160 MHz, $CDCl_3$) 94.1.

4.3. Reaction using $Pd_2(dba)_3$ catalyst: synthesis of 4

To thiophosphite (**1b**) (1.0 mmol), Baylis–Hillman adduct (**2a**) (1.0 mmol) and $Pd_2(dba)_3$ (10 mol %) in 4 mL of dioxane was heated at 110 °C for about 24 h. The reaction mixture was quenched by adding 3 mL of distilled water and the compound extracted using (2×8 mL) ethyl acetate, dried over Na_2SO_4, and concentrated in vacuo to get the crude material. The reaction mixture showed many peaks in the expected phosphonate region in which compound **4** was present to an extent of 35–45% [^{31}P NMR]. From this, **4** was isolated using silica gel column chromatography (70% EtOAc/hexane). Under identical conditions, the phosphite (**1a**) did not give any appreciable amount of product/s (^{31}P NMR).

Isolated yield 0.12 g (35%); white solid; R_f=0.40 (EtOAc/hexane 3:2); mp 138–140 °C; [Found: C, 56.22; H, 6.24. $C_{16}H_{21}O_4PS$ requires C, 56.46; H, 6.22%]; ν_{max} (KBr) 2955, 1713, 1443, 1263, 1057, 1009 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.48–7.29 (5H, m, Ar-*H*), 6.59 and 6.48 (2H, 2d, *J* 2.9 Hz, C(C=CH_2)), 4.79 (1H, d, *J* 23.4 Hz, PC*H*(Ar)), 4.10–3.76 (4H, m, 2OCH_2), 3.73 (3H, s, OCH_3), 1.06 and 0.86 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 166.0, 135.2, 134.5, 130.0, 129.9, 129.6, 129.5, 128.7, 127.7, 76.1 (d, *J* 8.4 Hz), 52.4, 42.7 (d, *J* 136.0 Hz), 32.5 (d, *J* 5.0 Hz), 21.6, 21.1; δ_P (160 MHz, $CDCl_3$) 95.7.

4.4. Reaction of allyl bromides 5a–g with 1a–b: synthesis of α-aryl substituted allylphosphonates (6aa–6ag and 7–8), and other phosphonates (14–18)

To a stirred solution of **1a** or **1b** (1.0 mmol) and substituted allyl bromide **5a**–**g** (1.0 mmol) in 1 mL $[bmim]^+PF_6^-$, 30 mol % of 1.0 M THF solution of TBAF was added via syringe over a period of 2 min at room temperature. After disappearance of the starting material (TLC, **1a** or **1b**), ethyl acetate (10 mL) was added and stirring continued for 15 min. The upper layer was separated and the solvent removed in vacuo to get the crude product. This material showed only a single component in TLC (in the case of **1a**), but was passed through silica gel column (hexane/ethyl acetate) to remove traces of impurities, if any. The used ionic liquid was recovered in the reaction leading to **6aa** and reused without any significant loss in yield. In the case of **1b**, both the mono- and bis-phosphonylated products (**7** and **8**) were observed in the reaction mixture.

4.4.1. Reaction using solid TBAF

The above reaction using **1a** and **5a** was performed using solid TBAF in place of 1.0 M solution in THF; in this case also, we could isolate the product with essentially the same yield, although solid TBAF could contain traces of moisture.

4.4.2. ***6aa***

Isolated yield 0.27 g (84%); R_f=0.36 (EtOAc/hexane 3:2); white solid; mp 138–140 °C; [Found: C, 59.17; H, 6.52. $C_{16}H_{21}O_5P$ requires C, 59.26; H, 6.53%]; ν_{max} (KBr) 2957, 1719, 1626, 1491, 1263, 1246, 1057, 1009, 835 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.49–7.28 (5H, m, Ar-*H*), 6.60 and 6.50 (2H, 2d, *J* 2.7 Hz, C(C=CH_2)), 4.80 (1H, d, *J* 22.7 Hz, PC*H*(Ar)), 4.13–3.80 (4H, m, 2OCH_2), 3.75 (3H, s, OCH_3), 1.08 and 0.87 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 166.6 (d, *J* 13.0 Hz), 135.2, 134.5, 130.0, 129.9, 129.6, 129.5, 128.7, 127.7, 127.6, 76.0 (d, *J* 6.0 Hz), 52.4, 42.6 (d, *J* 135.0 Hz), 32.5 (d, *J* 7.0 Hz), 21.6, 21.1; δ_P (160 MHz, $CDCl_3$) 19.7.

4.4.3. **6ab**

Isolated yield 0.30 g (85%); R_f=0.34 (EtOAc/hexane 3:2); white solid; mp 150–152 °C; [Found: C, 60.41; H, 6.88. $C_{17}H_{23}O_5P$ requires C, 60.35; H, 6.85%]; ν_{max} (KBr) 2922, 1734, 1267, 1059, 1003, 835 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.39–7.15 (4H, m, Ar-*H*), 6.59 and 6.49 (2H, 2d, *J* 4.0 Hz, C(C=C*H*$_2$)), 4.78 (1H, d, *J* 22.7 Hz, PC*H*(Ar)), 4.12–3.81 (4H, m, 2OC*H*$_2$), 3.75 (3H, s, OC*H*$_3$), 2.34 (3H, s, C*H*$_3$), 1.09 and 0.91 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 166.0, 137.4, 135.3, 131.5, 131.3, 129.8, 129.7, 129.4, 129.3, 52.4, 42.1 (d, *J* 135.2 Hz), 32.6 (d, *J* 6.3 Hz), 21.6, 21.2, 21.1; δ_P (160 MHz, $CDCl_3$) 19.3; This compound was crystallized from dichloromethane/hexane mixture (2:1) at room temperature 1 d (X-ray structure in Fig. S2; Supplementary data).

4.4.4. **6ac**

Isolated yield 0.28 g (78%); R_f=0.33 (EtOAc/hexane 3:2); white solid; mp 172–174 °C; [Found: C, 53.50; H, 5.53. $C_{16}H_{20}ClO_5P$ requires C, 53.57; H, 5.62%]; ν_{max} (KBr) 2955, 1719, 1491, 1246, 1206, 1055, 1009 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) 7.42–7.26 (4H, m, Ar-*H*), 6.59 and 6.47 (2H, 2d, *J* 3.2 Hz, C(C=C*H*$_2$)), 4.74 (1H, d, *J* 22.7 Hz, PC*H*(Ar)), 4.10–3.76 (4H, m, 2OC*H*$_2$), 3.73 (3H, s, OC*H*$_3$), 1.05 and 0.90 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 166.5, 134.9, 130.9, 130.8, 130.1, 130.0, 128.9, 76.1, 76.0, 75.9, 52.5, 42.0 (d, *J*(P–C) 136.1 Hz), 32.6 (d, *J* 6.3 Hz), 21.6, 21.2; δ_p (160 MHz, $CDCl_3$) 18.8.

4.4.5. **6ad**

Isolated yield 0.32 g (88%); R_f=0.30 (EtOAc/hexane 4:1); yellow solid; mp 144–146 °C; [Found: C, 52.13; H, 5.42; N, 3.85. $C_{16}H_{20}NO_7P$ requires C, 52.04; H, 5.46; N, 3.79%]; ν_{max} (KBr) 2963, 1719, 1630, 1597, 1522, 1437, 1246, 1132, 1059 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 8.19 and 7.66 (4H, 2d, *J* 8.3 Hz, Ar-*H*), 6.68 and 6.57 (2H, 2d, *J* 2.8 Hz, C(C=C*H*$_2$)), 4.85 (1H, d, *J* 22.7 Hz, PC*H*(Ar)), 4.20–4.10 and 3.94–3.83 (4H, 2m, 2OC*H*$_2$), 3.76 (3H, s, OC*H*$_3$), 1.06 and 0.93 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 166.2 (d, *J* 13.1 Hz), 147.4, 142.3, 142.1, 134.2, 130.8, 130.7, 130.6, 130.4, 123.7, 76.2, 76.1, 76.0, 52.7, 42.6 (d, *J*(P–C) 135.3 Hz), 32.6 (d, *J* 6.3 Hz), 21.5, 21.2; δ_P (160 MHz, $CDCl_3$) 17.7.

4.4.6. **6ae**

Isolated yield 0.22 g (76%); R_f=0.34 (EtOAc/hexane 3:2); white solid; mp 180–182 °C; [Found: C, 61.80; H, 6.22; N, 4.72. $C_{15}H_{18}NO_3P$ requires C, 61.85; H, 6.23; N, 4.81%]; ν_{max} (KBr) 2971, 2224, 1478, 1267, 1055, 1001, 845 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.48–7.29 (5H, m, Ar-*H*), 6.38 and 6.23 (2H, 2d, *J* 2.8 Hz, C(C=C*H*$_2$)), 4.26–3.78 (5H, m, PC*H*(Ar)+2OC*H*$_2$), 1.06 and 0.95 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 138.3, 134.6, 129.8, 129.6, 129.5, 129.2, 128.5, 118.8, 118.7, 117.7, 117.6, 75.9 and 74.2 (d each, *J* 8.0 Hz), 47.4 (d, *J*(P–C) 138.0 Hz), 32.5 (d, *J* 6.0 Hz), 21.3, 21.2; δ_p (160 MHz, $CDCl_3$) 15.8 [lit. 14.6 (ref. 7)].

4.4.7. **6af**

Isolated yield 0.24 g (78%); R_f=0.32 (EtOAc/hexane 3:2); white solid; mp 194–196 °C; [Found: C, 62.85; H, 6.57; N, 4.62. $C_{16}H_{20}NO_3P$ requires C, 62.94; H, 6.60; N, 4.59%]; ν_{max} (KBr) 2971, 2226, 1498, 1267, 1059, 1003, 835 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.38–7.17 (4H, m, Ar-*H*), 6.32 and 6.17 (2H, 2d, *J*~3.1 Hz, C(C=C*H*$_2$)), 4.24–3.77 (5H, m, PC*H*(Ar)+2OC*H*$_2$), 2.37 (s, 3H, C*H*$_3$), 1.06 and 0.98 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 138.5, 134.8, 134.6, 129.8, 129.5, 129.3, 128.8, 128.7, 119.0, 76.5 and 76.1 (2d, each, *J* 8.0 Hz), 47.4 (d, *J* 137.1 Hz), 32.6 (d, *J* 6.2 Hz), 21.5, 21.4, 21.1; δ_P (160 MHz, $CDCl_3$) 16.0.

4.4.8. **6ag**

Isolated yield 0.25 g (78%); R_f=0.38 (EtOAc/hexane 4:1); white solid; mp 166–168 °C; [Found: C, 55.36; H, 5.32; N, 4.36. $C_{15}H_{17}NO_3PCl$ requires C, 55.31; H, 5.26; N, 4.30%]; ν_{max} (KBr) 2976, 2224, 1491, 1261, 1055, 1007, 833 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.43–7.28 (4H, m, Ar-*H*), 6.35 and 6.22 (2H, 2d, *J*~4.0 Hz, C(C=C*H*$_2$)), 4.28–3.78 (5H, m, PC*H*(Ar)+2OC*H*$_2$), 1.04 and 1.00 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 135.3, 130.9, 129.4, 118.5, 76.1, 47.2 (d, *J*(P–C) 137.9 Hz), 32.6 (d, *J* 6.3 Hz), 21.5, 21.4; δ_P (160 MHz, $CDCl_3$) 15.7.

4.4.9. **7**

Isolated yield 0.15 g (50%); R_f=0.36 (EtOAc/hexane 1:1); white solid; mp 188–190 °C; [Found: C, 58.55; H, 5.93; N, 4.65. $C_{15}H_{18}NO_2PS$ requires C, 58.62; H, 5.90; N, 4.56%]; ν_{max} (KBr) 2971, 2226, 1472, 1267, 1059, 1003, 835 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.47–7.26 (5H, m, Ar-*H*), 6.35 and 6.20 (2H, 2d, *J* 2.8 Hz, C(C=C*H*$_2$)), 4.18–3.75 (5H, m, PC*H*(Ar)+2OC*H*$_2$), 1.04 and 0.93 (6H, 2 s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 135.1, 135.0, 129.6, 129.5, 129.2, 128.7, 118.7, 76.3 (d, *J* 8.4 Hz), 47.4 (d, *J*(P–C) 138.0 Hz), 32.6 (d, *J* 6.2 Hz), 21.5, 21.4; δ_P (160 MHz, $CDCl_3$) 92.1.

4.4.10. **8**

Isolated yield 0.95 g (20%); R_f=0.42 (EtOAc/hexane 1:1); white solid; mp 224–226 °C; [Found: C, 50.82; H, 6.29; N, 2.97. $C_{20}H_{29}NO_4P_2S_2$ requires C, 50.73; H, 6.17; N, 2.96%]; ν_{max} (KBr) 2971, 2241, 1474, 1277, 1221, 1051, 1007 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.61–7.41 (5H, m, Ar-*H*), 4.48–4.41 (5H, m, PC*H*(Ar)+2OC*H*$_2$), 3.85–3.69 (5H, m, C*H*(CN)+2OC*H*$_2$), 2.48–2.37 (2H, m, PC*H*$_2$), 1.23, 0.94, 0.91 and 0.86 (12H, 4s, 4C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 130.7, 130.6, 128.9, 119.0, 74.2 and 74.1 (4d, *J* 5.8 Hz), 73.9, 73.8, 51.3 (dd, *J*(P–C) 102.5 Hz and *J* 7.5 Hz), 34.8 (dd, *J*(P–C) 105.5 Hz and *J* 11.9 Hz), 33.4, 33.3, 28.0, 22.6, 22.1, 21.3; δ_P (160 MHz, $CDCl_3$) 92.2 and 91.2; This compound was crystallized from dichloromethane/hexane mixture (1:1) at room temperature (2 d). X-ray structure was determined on this sample (Fig. S3; Supplementary data).

4.4.11. **14**

Isolated yield 0.37 g (89%); R_f=0.32 (EtOAc/hexane 9:1); white solid; mp 124–126 °C; [Found: C, 55.11; H, 6.80. $C_{19}H_{28}O_6P_2$ requires C, 55.07; H, 6.81%]; ν_{max} (KBr) 2971, 1634, 1476, 1273, 1059, 1009 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.37–7.13 (5H, m, Ar-*H*), 6.75 (1H, dd, *J* 48.2 Hz, *J*~3.0 Hz, PC=C*H*$_A$ (trans)), 6.28 (1H, dd, *J* 12.0 Hz, *J*~3.0 Hz, PC=C*H*$_A$ (*cis*)), 4.51 (dd, *J* 16.0, 20.0 Hz respectively, PC*H*(Ar)), 4.07–3.72 (8H, m, 4OC*H*$_2$), 1.02, 0.94, 0.79 and 0.76 (4s, 12H, 4C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 132.6, 129.5, 129.4, 128.6, 127.8, 76.1 and 75.5 (2d, *J*~8.0 Hz), 42.4 (dd, *J* 20.0, 140.0 Hz), 32.5 (d, *J* 6.0 Hz), 21.8, 21.7, 21.6, 21.0; δ_P (160 MHz, $CDCl_3$) 22.1 and 14.2 (2d, *J* 27.9 Hz each).

4.4.12. **15**

Isolated yield 0.28 g (77%); R_f=0.34 (EtOAc/hexane 9:1); white solid; mp 164–166 °C; [Found: C, 49.23; H, 7.78. $C_{15}H_{28}O_6P_2$ requires C, 49.18; H, 7.70%]; ν_{max} (KBr) 2961, 1624, 1474, 1217, 1051, 997 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 4.30–3.62 (8H, m, 4OC*H*$_2$), 2.98 (2H, dd~t, *J* 20.7 and 18.6 Hz, PC*H*$_2$), 2.12 (3H, dd, *J* 6.0 and 3.2 Hz, C*H*$_3$), 1.86 (3H, dd, *J* 4.4 and 2.4 Hz, C*H*$_3$), 1.02, 0.99, 0.95 and 0.92 (12H, 4s, 4C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 155.1 (dd~t, *J* 22.0 and 10.0 Hz), 118.1 (dd, *J*(P–C) 147.0 and 11.0 Hz), 75.1 and 74.0 (2d, *J* 7.0 Hz), 32.6 and 33.1 (2d, *J* 6.0 Hz), 26.4 (dd, *J*(P–C) 139.0 and 14.0 Hz), 24.7 and 24.6 (2dd, *J* 8.0 and 3.0 Hz), 24.2 and 24.1 (2dd, *J* 18.0 and 3.0 Hz), 22.5, 21.6, 21.5; δ_p (160 MHz, $CDCl_3$) 22.2 and 14.3 (2d, *J* 27.5 Hz each).

4.4.13. **16**

Only the trans isomer (~99%) was observed in the reaction mixture (^{31}P and ^{1}H NMR). Isolated yield 0.21 g (85%); R_f=0.32 (EtOAc/hexane 4:1); pale yellow solid; mp 112–114 °C; [Found: C, 61.84; H, 6.89. $C_{13}H_{17}O_3P$ requires C, 61.90; H, 6.79%]; ν_{max} (KBr) 2965, 1478, 1262, 1057, 1001 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.59–7.40 (6H, m, Ar-*H*+PCH=C*H*), 6.30 (1H, dd→t, *J* 36.0 Hz and J_{trans} 18.0 Hz, PC*H*), 3.92–3.86 and 4.29–4.22 (4H, 2m, 2OC*H*$_2$), 1.15 and 1.07 (6H, 2s, 2C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 150.3 (d, *J* 7.0 Hz), 134.5, 130.6, 128.9, 127.9, 111.8 (d, *J*(P–C) 192.0 Hz), 76.7, 75.5, 75.4, 32.5, 21.7, 21.4; δ_p (160 MHz, $CDCl_3$) 14.9.

4.4.14. ***17***

Only the trans isomer (~99%) was observed in the reaction mixture (^{31}P and ^{1}H NMR). Isolated yield 0.21 g (88%); R_f=0.36 (EtOAc/hexane 9:1); white solid; mp 134–136 °C; [Found: C, 46.22; H, 6.43. $C_9H_{15}O_5P$ requires C, 46.16; H, 6.46%]; ν_{max} 2976, 1721, 1277, 1055, 1007 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 6.83 and 6.78 (2H, dd, *J* 20.0 Hz and J_{trans} 17.4 Hz, PC*H*=C*H*(CO_2Me)), 4.01–3.75 (4H, m, 2OCH_2), 3.65 (3H, s, OCH_3), 0.99 and 0.87 (6H, 2s, 2CH_3); δ_C (100 MHz, $CDCl_3$) 162.1 (d, *J* 28.0 Hz), 135.1 (d, *J* 7.0 Hz), 127.6 (d, *J* 180.0 Hz), 74.0, 73.9, 49.9, 29.9 (d, *J* 6.0 Hz), 18.9, 18.6; δ_P (160 MHz, $CDCl_3$) 8.0.

4.4.15. ***18***

The reaction was performed by using 2.0 mmol of thiophosphite **1b**, 1.0 mmol of dba and 0.6 mmol of TBAF in 2 mL of [bmim]$^+PF_6^-$ at room temperature. Isolated yield 0.45 g (88%); R_f=0.33 (EtOAc/hexane 1:1); pale yellow solid; mp 190–192 °C; [Found: C, 57.31; H, 6.48. $C_{27}H_{36}O_5P_2S_2$ (after drying in vacuum for 2 h) requires C, 57.23; H, 6.40%]; ν_{max} (KBr) 2967, 1723, 1454, 1266, 1046, 993 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.30–7.28 (10H, m, Ar-*H*), 4.35–4.27 (4H, m, 2OCH_2), 4.02–3.96 (2H, m, PC*H*), 3.69–3.56 (4H, m, 2OCH_2), 3.38–3.32 (4H, m, 2C*H*C(O)), 0.85 and 0.84 (12H, 2s, 4CH_3); δ_C (100 MHz, $CDCl_3$) 202.2, 134.3, 134.2, 129.5, 129.3, 128.4, 128.2, 127.6, 127.5, 73.8, 44.9 and 44.7 (2d, *J*(P–C) 101.0 Hz), 43.0 (d, *J* 23.0 Hz), 33.2 (d, *J* 5.0 Hz), 22.0, 21.9, 21.3; δ_P (160 MHz, $CDCl_3$) 96.8 and 96.7; This compound was crystallized from ethyl acetate/hexane mixture (1:1) at room temperature (~3 days). X-ray structure was determined on this sample (Fig. S3; Supplementary data).

4.5. Synthesis of 22

To phosphite (**19**) (0.5 mmol) and allyl bromide (0.5 mmol) in 5 mL dry THF, 50 mol% of TBAF (1.0 M THF solution) was added via syringe over a period of 2 min at room temperature. After the disappearance of starting material (allyl bromide; by TLC), the solvent was removed in vacuo and distilled water (5 mL) was added. The compound was extracted with ethyl acetate (2×10 mL). The upper layer was separated and concentrated in vacuo to give the crude product. Pure compound **22** was obtained as white solid from toluene (5 mL) at room temperature after 12 h. Isolated yield 0.20 g (84%); R_f=0.34 (EtOAc/hexane 3:2); white solid; mp 124–126 °C; [Found: C, 69.46; H, 7.74. $C_{28}H_{37}O_5P$ requires C, 69.40; H, 7.70%]; ν_{max} (KBr) 2922, 1734, 1267, 1059, 1003, 835 cm^{-1}; δ_H (400 MHz, $CDCl_3$) 7.04 (4H, br s, Ar-*H*), 6.56 and 6.22 (2H, 2d, *J* 4.8 Hz, C(C=CH_2)), 4.20 (2H, d, *J* 11.4 Hz, ArCH_2), 3.82 (3H, s, OCH_3), 3.53 (2H, d, *J* 22.4 Hz, PCH_2), 2.28 (6H, s, 2CH_3), 1.41 (18H, s, 6×CH_3); δ_C (100 MHz, $CDCl_3$) 166.5 (d, *J* 7.0 Hz), 144.9, 141.0, 134.7, 132.9, 130.8, 130.2, 130.1, 129.0, 127.6, 52.5, 34.9, 34.4, 31.1, 29.7 (d, *J*(P–C) 149.0 Hz), 21.0; δ_P (160 MHz, $CDCl_3$) 18.5.

4.6. Identification of intermediate 21a (or 21b) (see Fig. 1 in the main text)

To phosphite (**19**) (1.0 mmol) in 5 mL of dry THF, 1.0 mmol of TBAF (1.0 M THF solution) was added via syringe over a period of 2 min at room temperature under nitrogen atmosphere. After 2 h, the solvent was removed under reduced pressure to get **21a** (or **21b**) as gummy material. The spectra are shown in the main text, Figure 1. The spectra related to the reaction using thiophosphite **20** [(a) ^{1}H NMR: δ=8.28 (dd, $^{1}J_{(P-H)}$=606 Hz and $^{2}J_{(F-H)}$=104 Hz); (b) ^{31}P NMR [proton decoupled, 160 MHz]: δ=59.0 and 52.8 (d, $^{1}J_{(P-F)}$=1006 Hz); (c) ^{31}P NMR [proton coupled, 160 MHz]: δ=59.1 and 52.9 ($^{1}J_{(P-F)}$=1006 Hz and $^{1}J_{(P-H)}$=606 Hz); (d) ^{19}F NMR [376.8 MHz]: δ=−32.9 and −33.1 (dd, $^{1}J_{(P-F)}$=1006 Hz and $^{2}J_{(F-H)}$=104 Hz)] are given as Figure S1 in Supplementary data.

4.7. X-ray crystallography

X-ray data were collected on a Bruker AXS SMART diffractometer using Mo-Kα (λ=0.71073 Å) radiation. The structures were solved and refined by standard methods.[19]

4.7.1. Crystal data

3ba: $C_{16}H_{23}O_5PS$, *M*=358.37, Orthorhombic, Space group *Pna2(1)*, *a*=17.675(4), *b*=17.125(4), *c*=6.0166(15) Å, *V*=1821.2(8) Å^3, *Z*=4, μ=0.286 mm^{-1}, data/restraints/parameters: 3102/1/215, Flack parameter: 0.06 (10), *R* indices ($I>2\sigma(I)$): *R*1=0.0415, *wR*2 (all data)=0.0989. CCDC no. 67227.

6ab: $C_{17}H_{23}O_5P$, *M*=338.32, Monoclinic, Space group *P2(1)/n*, *a*=9.7504(15), *b*=9.9681(15), *c*=18.162(3) Å, β=92.213(2)°, *V*=1763.9 (5) Å^3, *Z*=4, μ=0.177 mm^{-1}, data/restraints/parameters: 3107/0/212, *R* indices ($I>2\sigma(I)$): *R*1=0.0594, *wR*2 (all data)=0.1378. CCDC no. 67228.

8: $C_{20}H_{29}NO_4P_2S_2$, *M*=473.50, Monoclinic, Space group *P2(1)/c*, *a*=15.6676(17), *b*=15.1513(16), *c*=10.6775(11) Å, β=105.949(2)°, *V*=2437.1(4) Å^3, *Z*=4, μ=0.374 mm^{-1}, data/restraints/parameters: 4282/0/266, *R* indices ($I>2\sigma(I)$): *R*1=0.0508, *wR*2 (all data)=0.1257. CCDC no. 67229.

18: $C_{29}H_{36}O_6P_2S_2$, *M*=606.64, Triclinic, Space group *P-1*, *a*=6.285(2), *b*=13.461(4), *c*=19.169(5) Å, α=88.868(4)°, β=89.164(4)°, γ=87.965 (4)°, *V*=1620.2(8) Å^3, *Z*=2, μ=0.301 mm^{-1}, data/restraints/parameters: 5655/0/356, *R* indices ($I>2\sigma(I)$): *R*1=0.0607, *wR*2 (all data)=0.1729. There was disorder in the solvent molecule, and hence it could not be modelled properly. However, the main molecule is perfectly fine. CCDC no. 67230.

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Supplementary data

General experimental procedure, spectra related to the identification of pentacoordinate product from **20**+TBAF, PLATON and ORTEP drawings, CIF files and ^{1}H and ^{13}C NMR spectra. Supplementary data associated with this article can be found in the online version, at doi:10.1016/j.tet.2009.06.096.

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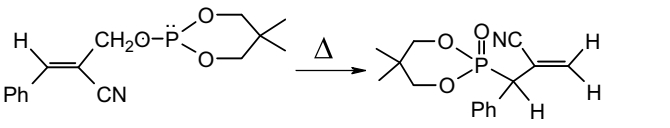

δ(P) 121.7 δ(P, 80 MHz) 14.6; yield 7%

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