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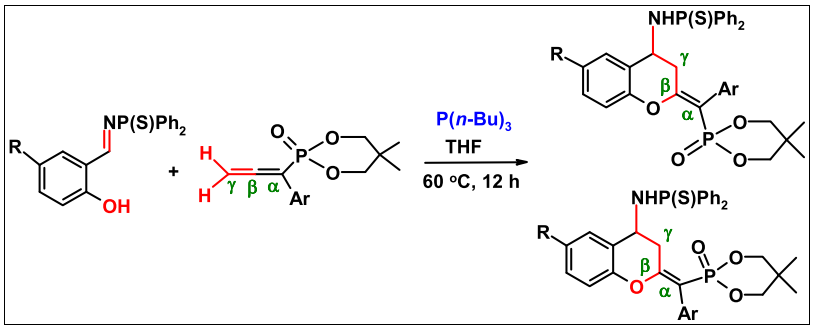

A phosphine [P(*n*-Bu)$_3$]-catalyzed reaction for the synthesis of phosphono-chromans from allenylphosphonates and salicyl *N*-thiophosphinyl imines has been described and compared with reactions for phosphorus-free allenes. The products are (β,γ)-cyclized and are obtained in good yields (57–83%). A key product is characterized by X-ray crystallography.

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INTRODUCTION

Lewis base catalysis exploiting phosphines and amines has emerged as a prominent area in organic synthesis [1]. In particular, phosphine catalysis in the reactions using allenes has been demonstrated for the development of new annulation providing various carbo- and hetero-cycles [1,2]. Addition of a Lewis base to allenoates results in the generation of a zwitterionic species (1,3-dipole), which can react with aldehydes, α,β-unsaturated ketones, imines, activated alkenes, salicylaldehydes, and so on to give diverse products depending on the nature of nucleophile and the substituent on the allenoate [2]. Chromenes and chromans are widespread in natural products and have attracted much attention in diverse areas including physical chemistry (photochromism) and medicinal chemistry (anti HIV, anticancer, antimicrobial, inhibitory effect on histamine release, antihypertensive, and antiviral activity [3]). Thus, a number of research groups have developed different methodologies to synthesize these compounds [4]. Recently, Huang reported the phosphine catalyzed domino reactions of salicyl-*N*-thiophosphinyl imines with allenoate to afford *cis*-2,3-dihydrobenzofurans or functionalized chroman derivatives in good yields under mild conditions [5]. Our research group has recently reported that allenylphosphonates react with substituted salicylaldehydes in the presence of DBU to afford phosphono-chromenes in good yields [6]. We envisioned that allenylphosphonates on reaction with salicyl-*N*-thiophosphinyl imines could lead to functionalized phosphono-chromans [7]. In our earlier papers on allene chemistry [8], on several occasions, we had found that the allenylphosphonates differ in terms of reactivity compared with phosphorus-free allenes. Whether this is so in phosphine catalyzed reactions also or not was one of the things that we were interested in. Herein, we report phosphine catalyzed reaction of allenylphosphonates with salicyl-*N*-thiophosphinyl imines in the presence of phosphine also gives chromans.

RESULTS AND DISCUSSION

We first treated the allenylphosphonate **2a** with *N*-thiophosphinyl imine **1a** (cf. Scheme 1) in the presence of various bases and in different solvents to optimize the reaction conditions. The results are summarized in Table 1. It was found that the reaction of allenylphosphonate **2a** with *N*-thiophosphinyl imine **1a** led to the expected product **3a** in poor yield by using PPh_3 (20 mol %) as the base and DMSO as the solvent (Table 1 entry 1). The reaction was not complete, and the ^{31}P NMR of the reaction mixture showed approximately 50% of the allene **1a** remaining. When the reaction was performed under the conditions previously reported from our laboratory [6], instead of the expected product **3a**, phosphono-chromenes **4** (*E* and *Z*) were obtained (entry 2). Use of K_2CO_3 or P(*n*-Bu)$_3$ as the base also afforded the chromene **4** [^{31}P NMR evidence] (Table 1, entries 3 and 4). No desired product was observed by using the base PPh_3, and dichloromethane or dimethylformamide as the solvent (entries 5 and 6); also the product formation was negligible in toluene or THF (entries 7 and 8). Interestingly, the reaction proceeded well in CH_3CN to lead to the expected product

Scheme 1. Reaction of **1a** and **2a** to form phosphono-chroman **3a**.

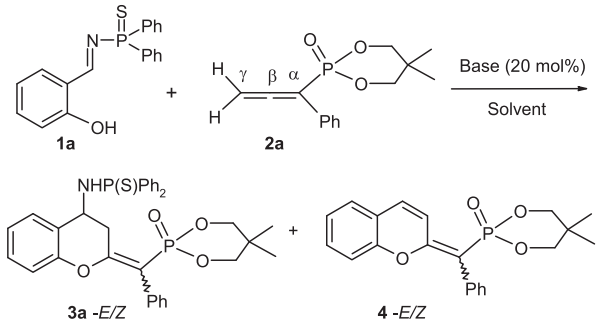


Table 1

Screening of reaction conditions for the optimization of product **3a**.

Entry	Catalyst	Solvent	Temperature (°C)/time (h)	Yield %[a]
1	PPh_3	DMSO	80/16	50
2	DBU	DMSO	80/12	[b]
3	K_2CO_3	DMSO	80/8	[b]
4	P(*n*-Bu)$_3$	DMSO	80/10	[b]
5	PPh_3	DCM	40/18	n.r.
6	PPh_3	DMF	80/18	n.r.
7	PPh_3	Toluene	80/18	8
8	PPh_3	THF	50/12	6
9	PPh_3	CH_3CN	80/12	56
10	P(*n*-Bu)$_3$	THF	60/12	78
11	P(*n*-Bu)$_3$	Toluene	60/12	36

[a]Yield of **3a** (*E* + *Z*) based on ^{31}P NMR spectra of the reaction mixtures.
[b]In these cases, chromene **4** (quantitative yield) was obtained.

3a (*E* + *Z*) in moderate yields (entry 9). It is noteworthy that use of P(*n*-Bu)$_3$ as the base in *toluene* medium also led to the product **3a** [^{31}P NMR] with lower yield (entry 11); however, there were some side products also. Hence, we continued with P(*n*-Bu)$_3$ in THF as the medium. Thus, these phosphine-catalyzed reactions of allenylphosphonates follow the same pathway as the phosphorus-free allenes. The chroman product **3a** shows two sets of dominant signals corresponding to the *E* and *Z* isomers, the first one at 58.8/ 10.1 (*Z*-isomer) and the second set at 58.9/ 14.1 (*E*-isomer). There are also additional signals at the thiophosphinate region [δ ~48, 57], but these do not correspond to the products from the allene; an unassigned minor signal at δ 16.5 is also seen.

By using the previous conditions, we then conducted the reaction of *N*-thiophosphinyl imines **1a** and **1b** with allenylphosphonates **2a–e** and allenylphosphine oxide **5** for the synthesis of different phosphono-chromans **3a–j** and phosphinoyl-chromans **6a–b**, respectively, and also for checking the scope and limitations of the reaction (Scheme 2 (a and b)). The yields and *E*/*Z* ratio of the compounds based on the ^{31}P NMR spectra of the reaction mixtures were presented in Table 2. We separated the *individual isomers in all the cases* except for **6a** and **b**. The major isomer had the *Z*-configuration (*vide infra*). In the case of **6a–b**, the *Z*-isomer was isolated in pure state. For the identification of *E*- and *Z*-isomers, ^{1}H and ^{13}C NMR spectra were quite useful. In the ^{1}H NMR, signals for the CH_2(CHNP(S)Ph$_2$) protons appear as a multiplet in the region δ 3.02–3.14 for the *E*-isomer, whereas for the *Z*-isomer, the signals appear up-field at δ ~2.78–2.88 (cf. Figure 1). In the ^{13}C NMR spectra, the ^1J(P–C) value for the *E*-isomer [~195.6 Hz] was higher than that for the *Z*-isomer [~173.4 Hz]. The structure of *Z*-isomer of **3a** was determined by X-ray crystallography (Figure 2) [9]. The double bond between C6 and C7 was confirmed by the distance [C(6)–C(7) 1.346(8) Å], whereas the *Z*-stereochemistry at this double bond was clearly shown by the attached substituents. On the basis of these data, we could assign the ^{31}P NMR chemical shifts for all the other compounds. Thus, the signal for the *E*-isomer [δ(P) = 14.5] appeared downfield compared with that for the *Z*-isomer [δ(P) = 10.4].

In continuation of the previous work, we also treated the allenylphosphonate **2a** with 2-hydroxybenzaldehyde phenylhydrazone **7** (cf. Scheme 3) in the presence of P(*n*-Bu)$_3$ as the base and THF as the solvent. No desired product was observed in this reaction; instead, we obtained the phosphono-chromenes **4** (*E*/*Z*), which were previously reported in our laboratory [6].

CONCLUSIONS

In conclusion, we have demonstrated the synthesis of various phosphono-chromans catalyzed by P(*n*-Bu)$_3$ from the corresponding allenylphosphonates and salicyl-*N*-thiophosphinyl imines in moderate to good yields.

EXPERIMENTAL

General. Solvents were dried according to known methods as appropriate [10]. ^{1}H, ^{13}C, and ^{31}P NMR spectra (^{1}H-400 or 500 MHz, ^{13}C-100 or 125 MHz, and ^{31}P-162 MHz) were recorded using a 400 or 500-MHz spectrometer in $CDCl_3$ (unless stated otherwise) with shifts referenced to $SiMe_4$ (δ = 0) or 85% H_3PO_4 (δ = 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 GCMS or LCMS instruments. High resolution mass spectra (HR-MS) were performed using a Bruker MaXis mass spectrometer (Bruker Daltonik GmbH, Bremen, Germany) with ESI-QTOF-II method. Single crystal X-ray diffraction was collected on OXFORD diffractometer by using Mo–Ka (l = 0.71073 Å) radiation. The structure was solved and refined by standard methods [9b–d]. The allenylphosphonates and allenylphosphine oxide were prepared by literature procedures [11]. Salicyl N-thiophosphinyl imines **1a–b** were synthesized by the reported method [6a].

General procedure for the formation of chromans. To a 25-mL round–bottom flask containing allene **2a–e/5** (0.2–0.5 mmol)

Scheme 2. Synthesis of various phosphono/phosphinoyl-chromans (cf. Table 2).

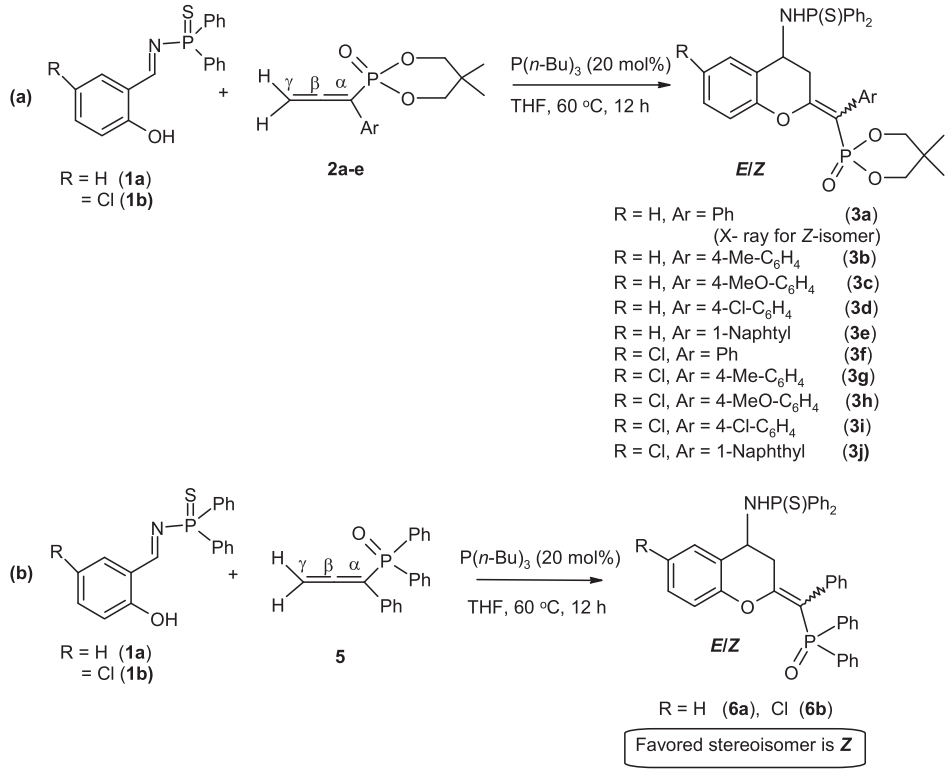


Table 2

^{31}P NMR data and isolated yields of the compounds **3a–j** and **6a–b**.

			δ(P)		
Entry	Reactant	Product	*E*	*Z*	Yield %[a] (*E:Z*)
1	**1a + 2a**	**3a**	14.5; 59.1	10.4; 59.3	70 (17:53)
2	**1a + 2b**	**3b**	14.7; 59.1	10.7; 59.3	75 (26:49)
3	**1a + 2c**	**3c**	14.8; 59.1	10.8; 59.3	67 (23:44)
4	**1a + 2d**	**3d**	14.4; 59.1	10.8; 59.2	76 (21:55)
5	**1a + 2e**	**3e**	11.0, 59.0	10.1, 59.9	83[b]
6	**1b + 2a**	**3f**	14.1; 59.0	10.0; 59.5	61 (26:35)
7	**1b + 2b**	**3g**	14.3; 59.0	10.3; 59.5	62 (17:45)
8	**1b + 2c**	**3h**	14.3; 59.0	10.3; 59.4	57 (24:33)
9	**1b + 2d**	**3i**	14.0; 59.2	9.5; 59.5	62 (17:45)
10	**1b + 2e**	**3j**	9.3, 10.2	59.3, 60.2	78[b]
11	**1a + 5**	**6a**	28.6; 58.1	24.0; 58.9	41[c]

[a]Isolated yields of the pure compounds.
[b]Isomers were not separated.
[c]*Z*-isomer was only separated.

and salicyl *N*-thiophosphinyl imine (**1a**) or (**1b**) (0.22–0.55 mmol) was added THF (0.1 M with respect to allene, 2.5–5.0 mL). The contents were stirred at RT for 5 min. To this solution, P(*n*-Bu)$_3$ (0.04–0.1 mmol) was added, and the round-bottom flask was sealed after flushing three times with N_2. The reaction mixture was stirred at 60°C for 12 h. After that, the solvent was removed by rotary evaporator and the residue subjected to column chromatography (hexane/EtOAc; 1.5:1) to obtain the pure product. Compounds **3a–j** and **6a–b** were prepared by this procedure. Both *Z* and *E* isomers were formed in most cases. Details on the combined yield of *Z* and *E* isomers are given in Table 2 and in the succeeding discussion.

Compound (E)-3a (higher R_f). Yield: 0.210 g (70%, *E* + *Z*); 0.051 g (*E*, isolated, 17%) (using 0.50 mmol of allene **2a**). Mp:

226–232°C. IR (KBr): 3189, 1630, 1482, 1258, 1231, 1057, 835 cm^{-1}. ^1H NMR: δ 0.65 (s, 3H, CH_3), 0.98 (s, 3H, CH_3), 3.02–3.14 (m, 2H, $=CCH_2$), 3.48 (dd → t, ^3J(P-H) = ^2J(H-H) = 12.2 Hz, 1H, OCH_AH_B), 3.62 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 12.0 Hz, 1H, OCH_AH_B), 3.95–4.06 (m, 3H, NH + OCH_2), 4.73–4.80 (m, 1H, CHNH), 6.63 (d, ^3J(H–H) = 8.0 Hz, 1H, Ar-H), 6.84 (dd → t, ^3J(H-H) ~ 7.4 Hz, 1H, Ar-H), 7.05 (dd → t, ^3J(H-H) ~ 7.8 Hz, 1H, Ar-H), 7.27–7.41 (m, 8H, Ar-H), 7.51–7.55 (m, 4H, Ar-H), 7.92–7.97 (m, 2H, Ar-H), 8.14–8.19 (m, 2H, Ar-H). ^{13}C NMR (125 MHz, $CDCl_3$): δ 21.2, 21.7, 32.4 (d, J(P-C) = 6.3 Hz, $C(CH_3)_2$), 33.5 (dd, J(P-C) ~ 7.3 Hz, 1.6 Hz, CH_2), 45.4 (NHCH), 75.4 (d, J(P-C) = 5.9 Hz, OCH_2(A)), 75.5 (d, J(P-C) = 6.3 Hz, OCH_2(B)), 109.3 (d, ^1J(P-C) = 195.6 Hz, PC = C), 116.4, 122.9, 124.5, 127.4 (d, J(P-C) = 1.6 Hz), 128.1, 128.3 (d, J(P-C) = 13.0 Hz), 128.7 (d, J(P-C) = 13.0 Hz), 129.5 (d, J(P-C) = 28.3 Hz), 130.7 (d, J(P-C) = 4.6 Hz), 131.5 (d, J(P-C) = 2.9 Hz), 131.7 (d, J(P-C) = 11.1 Hz), 131.8 (d, J(P-C) = 2.8 Hz), 132.0 (d, J(P-C) = 11.5 Hz), 133.9 (d, J(P-C) = 4.8 Hz), 134.0 (d, J(P-C) = 22.9 Hz), 134.8 (d, J(P-C) = 25.0 Hz), 151.3, 161.0, 161.1. ^{31}P NMR: δ 14.5 and 59.1. LC-MS: *m/z* 602 $[M+1]^+$. Anal. Calcd. for $C_{33}H_{33}NO_4P_2S$: C, 65.88; H, 5.53; N, 2.33. Found: C, 65.76; H, 5.61; N, 2.30.

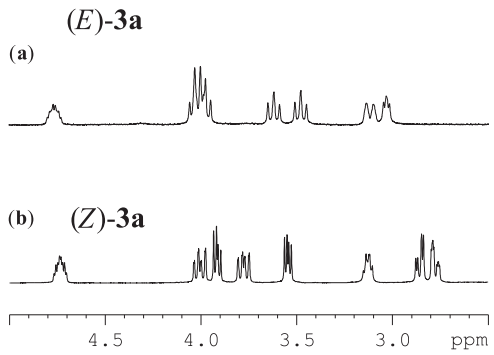


Figure 1. ^1H NMR spectra in the region δ 2.0–5.0 for phosphono-chromans: (a) (*E*)-**3a** and (b) (*Z*)-**3a**.

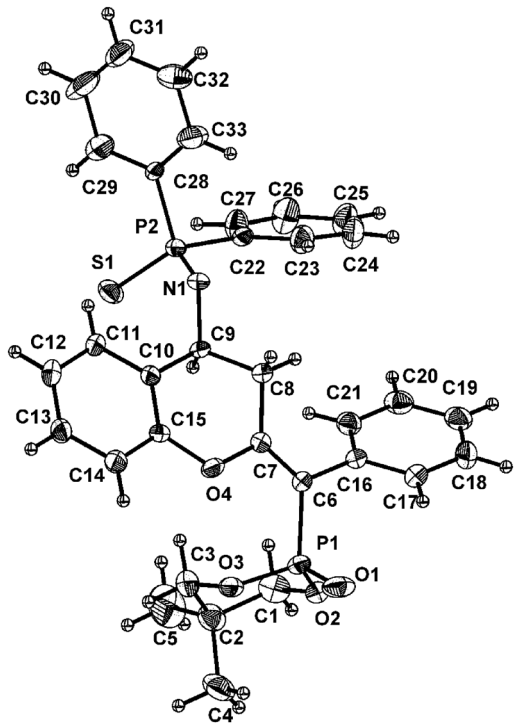
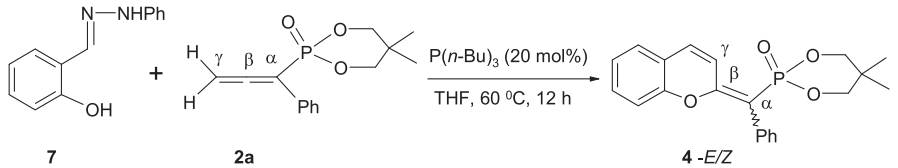


Figure 2. Molecular structure of compound (*Z*)-**3a**. Selected bond lengths [Å] with esds in parentheses. O(4)–C(7) 1.365(6), C(8)–C(9) 1.516(8), N(1)–C(9) 1.472(7), C(7)–C(8) 1.488(8), C(6)–C(7) 1.346(8), P(1)–C(6) 1.800(6) and C(6)–C(16) 1.504(7).

Compound (Z)-3a (lower R_f). Yield: 0.210 g (70%, *E* + *Z*); 0.051 g (*Z*, isolated, 53%). Mp: 188–190°C. IR (KBr): 3069, 2926, 1645, 1460, 1226, 1055, 826 cm^{-1}. ^1H NMR (500 MHz): δ 0.82 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.78–2.88 (m, 2H, CCH_2), 3.11–3.15 (m, 1H, N*H*), 3.53–3.56 (m, 1H, OCH_AH_B), 3.75–4.01 (m, 3H, OCH_AH_B + OCH_2), 4.70–4.77 (m, 1H, C*H*NH), 6.97–7.00 (m, 1H, Ar-*H*), 7.08 (d, ^3J(H-H) = 8.0 Hz, 1H, Ar-*H*), 7.24–7.48 (m, 13H, Ar *H*), 7.71–7.75 (m, 2H, Ar *H*), 7.82–7.86 (m, 2H, Ar *H*). ^{13}C NMR (125 MHz): δ 21.1, 22.0, 32.4 (d, *J*(P-C) = 6.0 Hz, *C*$(CH_3)_2$), 33.4 (dd, *J* (P-C) ~ 10.2 Hz, *J*(P-C) ~ 4.2 Hz, *C*H_2), 44.9 (NH*C*H), 76.0 (d, *J* (P-C) = 6.5 Hz, O*C*H_2(A)), 76.1 (d, ^2J(P-C) = 6.1 Hz, O*C*H_2(B)), 109.1 (d, ^1J(P-C) = 173.4 Hz, P*C* = C), 117.0, 123.2, 124.3 (d, *J* (P-C) = 4.5 Hz), 127.9, 128.4 (d, *J*(P-C) = 2.5 Hz), 128.5 (d, *J* (P-C) = 2.4 Hz), 128.7, 128.9, 129.7, 130.8 (d, *J*(P-C) = 4.8 Hz), 131.5 (d, *J*(P-C) = 4.3 Hz), 131.6 (d, *J*(P-C) = 4.4 Hz), 131.7 (d, *J*(P-C) = 2.8 Hz), 131.8 (d, *J*(P-C) = 2.8 Hz), 133.9, 134.0 (d, *J* (P-C) = 22.5 Hz), 134.8 (d, *J*(P-C) = 28.0 Hz), 151.4, 160.2. ^{31}P NMR: δ 10.4 and 59.3. LC-MS: *m/z* 602 $[M+1]^+$. Anal. Calcd. for $C_{33}H_{33}NO_4P_2S$: C, 65.88; H, 5.53; N, 2.33. Found: C, 65.78; H, 5.49; N, 2.26.

Compound (E)-3b (higher R_f). Yield: 0.231 g (75%, *E* + *Z*); 0.080 g (*E*, isolated, 26%) (using 0.5 mmol of allene **2b**). Mp: 196–198°C. IR (KBr): 3239, 1626, 1572, 1437, 1240, 1107, 810 cm^{-1}. ^1H NMR: δ 0.68 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 2.39 (s, 3H, $C_6H_4CH_3$), 3.04–3.13 (m, 2H, CCH_2), 3.47 (dd → t, ^3J(P-H) = ^2J(H-H) = 11.6 Hz, 1H, OCH_AH_B), 3.62 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 11.6 Hz, 1H, OCH_AH_B), 3.90–4.02 (m, 3H, OCH_2 + N*H*), 4.73–4.80 (m, 1H, C*H*NH), 6.66 (d, ^3J (H-H) = 8.4 Hz, 1H, Ar-*H*), 6.83 (dd → t, ^3J(H-H) = 7.6 Hz, 1H, Ar-*H*), 7.05 (dd → t, ^3J(H-H) ~ 7.0 Hz, 1H, Ar-*H*), 7.20–7.40 (m, 7H, Ar-*H*), 7.50–7.54 (m, 4H, Ar-*H*), 7.91–7.97 (m, 2H, Ar-*H*), 8.13–8.18 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz): δ 21.3, 21.4 (s, $C_6H_4CH_3$), 21.8, 32.4 (d, *J*(P-C) = 5.8 Hz, *C*$(CH_3)_2$),

Scheme 3. Formation of chromene **4** via hydrazone **7**.



33.6 (d, J(P-C) ~ 7.4 Hz, CH$_2$), 45.4 (s, NHCH), 75.5 (d, J(P-C) = 6.3 Hz, OCH$_2$(A)), 75.6 (d, J(P-C) = 6.3 Hz, OCH$_2$(B)), 109.2 (d, ^1J(P-C) = 192.9 Hz, PC = C), 116.5, 122.8, 124.5, 128.3 (d, J(P-C) = 13.0 Hz), 128.7 (d, J(P-C) = 13.3 Hz), 128.9, 129.5 (d, J(P-C) = 29.4 Hz), 130.5 (d, J(P-C) = 5.0 Hz), 130.6 (d, J(P-C) = 5.1 Hz), 131.5 (d, J(P-C) = 2.9 Hz), 131.7 (d, J(P-C) = 11.0 Hz), 131.8 (d, J(P-C) = 2.8 Hz), 132.0 (d, J(P-C) = 11.1 Hz), 134.1 (d, J(P-C) = 19.8 Hz), 134.9 (d, J(P-C) = 21.0 Hz), 137.0 (d, J(P-C) = 1.9 Hz), 151.4, 160.5, 160.7. ^{31}P NMR: δ 14.7 and 59.1. LC-MS: *m/z* 616 $[M+1]^+$. Anal. Calcd. for $C_{34}H_{35}NO_4P_2S$: C, 66.33; H, 5.73; N, 2.28. Found: C, 66.15; H, 5.81; N, 2.32.

Compound (Z)-3b (lower R_f). Yield: 0.231 g (75%, $E+Z$); 0.151 g (Z, isolated, 49%). Mp: 204–210°C. IR (KBr):3214, 2920, 1626, 1597, 1455, 1238, 1059, 831 cm^{-1}. ^{1}H NMR: δ 0.81 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.44 (s, 3H, C$_6$H$_4$CH_3), 2.74–2.88 (m, 2H, CHCH_2), 3.11–3.14 (m, 1H, NH), 3.53–3.56 (m, 1H, OCH_AH$_B$), 3.73–4.03 (m, 3H, OCH_2 + OCH$_A$$H_B$), 4.72–4.77 (m, 1H, C$H$NH), 6.96–7.44 (m, 14H, Ar-H), 7.70–7.71 (m, 2H, Ar-H), 7.80–7.83 (m, 2H, Ar-H). ^{13}C NMR (125 MHz): δ 21.0, 21.3 (s, C$_6$H$_4$$CH_3$), 22.0, 32.3 (d, J(P-C) = 6.1 Hz, C(CH$_3$)$_2$), 33.5 (dd, ^3J(P-C) = 4.3 Hz, 10.3 Hz, CH$_2$), 44.9 (s, NHCH), 76.0 (d, J(P-C) = 7.5 Hz, OCH$_2$(A)), 76.1 (d, J(P-C) = 6.6 Hz, OCH$_2$(B)), 108.8 (d, ^1J(P-C) = 172.3 Hz, PC = C), 116.9, 123.0, 124.3, 128.3 (d, J(P-C) = 2.6 Hz), 128.4 (d, J(P-C) = 2.9 Hz), 128.7, 129.4, 129.6, 130.5 (d, J(P-C) = 4.8 Hz), 130.7 (d, J(P-C) = 6.4 Hz), 131.4$_6$, 131.4$_9$, 131.6 (d, J(P-C) = 3.3 Hz), 131.7, 133.9 (d, J(P-C) = 32.3 Hz), 134.7 (d, J(P-C) = 35.5 Hz), 137.4, 151.4, 159.7. ^{31}P NMR: δ 10.7 and 59.3. LC-MS: *m/z* 616 $[M+1]^+$. Anal. Calcd. for $C_{34}H_{35}NO_4P_2S$: C, 66.33; H, 5.73; N, 2.28. Found: C, 66.48; H, 5.70; N, 2.21.

Compound (E)-3c (higher R_f). Yield: 0.212 g (67%, $E+Z$); 0.049 g (E, isolated, 23%) (using 0.5 mmol of allene **2c**). Mp: 180–184°C. IR (KBr): 3478, 3198, 1628, 1510, 1233, 1058, 833 cm^{-1}. ^{1}H NMR: δ 0.69 (s, 3H, CH_3), 1.00 (s, 3H, CH_3), 3.04–3.13 (m, 2H, CCH_2), 3.49 (dd → t, ^3J(P-H) = ^2J(H-H) = 11.6 Hz, 1H, OCH_AH$_B$), 3.63 (dd → t, ^3J(P-H) ~ ^2J(H-H) ~ 12.0 Hz, 1H, OCH$_A$$H_B$), 3.86 (s, 3H, C$_6H_4OCH_3$), 3.93–4.04 (m, 3H, OC$H_2$ + NH), 4.75–4.76 (m, 1H, CHNH), 6.66 (d, ^3J(H-H) = 8.0 Hz, 1H, Ar-H), 6.82–6.94 (m, 3H, Ar-H), 7.04–7.07 (m, 1H, Ar-H), 7.27–7.56 (m, 9H, Ar-H), 7.92–7.97 (m, 2H, Ar-H), 8.15–8.17 (m, 2H, Ar-H). ^{13}C NMR: δ 21.3, 21.7, 32.4 (d, J(P-C) = 5.8 Hz, C(CH$_3$)$_2$), 33.5 (d, J(P-C) ~ 6.0 Hz, CH$_2$), 45.4 (NHCH), 55.3 (OCH$_3$), 75.4 (d, J(P-C) = 6.3 Hz, OCH$_2$(A)), 75.5 (d, J(P-C) = 6.3 Hz, OCH$_2$(B)), 108.8 (d, ^1J(P-C) = 195.4 Hz, PC = C), 113.6, 116.4, 122.8, 124.5, (d, J(P-C) = 2.1 Hz), 125.8 (d, J(P-C) = 4.9 Hz), 128.3 (d, J(P-C) = 13.3 Hz), 128.5 (d, J(P-C) = 13.3 Hz), 128.7 (d, J(P-C) = 13.1 Hz), 129.5 (d, J(P-C) = 28.8 Hz), 131.3 (d, J(P-C) = 11.5 Hz), 131.5 (d, J(P-C) = 2.5 Hz), 131.7, 131.8, 132.0 (d, J(P-C) = 11.4 Hz), 134.1 (d, J(P-C) = 22.4 Hz), 134.9 (d, J(P-C) = 23.4 Hz), 151.4, 159.0, 160.7. ^{31}P NMR: δ 14.8 and 59.1. LC-MS: *m/z* 632 $[M+1]^+$. Anal. Calcd. for $C_{34}H_{35}NO_5P_2S$: C, 64.65; H, 5.58; N, 2.22. Found: C, 64.53; H, 5.61; N, 2.27.

Compound (Z)-3c (lower R_f). Yield: 0.212 g (67%, $E+Z$); 0.093 g (Z, isolated, 44%). Mp: 184–188°C. IR (KBr): 3191, 2963, 1628, 1510, 1244, 1061, 772 cm^{-1}. ^{1}H NMR: δ 0.81 (s, 3H, CH_3), 1.20 (s, 3H, CH_3), 2.72–2.89 (m, 2H, CHCH_2), 3.13–3.17 (m, 1H, NH), 3.52–3.56 (m, 1H, OCH_AH$_B$), 3.77–4.04 (m, 6H, OCH$_A$$H_B$ + OCH_2 + OCH_3), 4.72–4.78 (m, 1H, CHNH), 6.91–7.08 (m, 4H, Ar-H), 7.21–7.44 (m, 10H, Ar-H), 7.70–7.85 (m, 4H, Ar H). ^{13}C NMR: δ 21.0, 22.0, 32.3 (d, J(P–C) = 5.6 Hz, C(CH$_3$)$_2$), 33.3 (~d, J(P-C) ~ 7.4 Hz, CH$_2$), 44.9 (NHCH), 55.3 (OCH$_3$), 76.0 (OCH$_2$), 108.5 (d, ^1J(P-C) = 173.1 Hz, PC = C), 114.1, 116.9, 123.0, 124.3, 125.8, 128.4, 128.5, 128.7, 129.6, 131.5, 131.6, 131.7, 131.8, 133.9 (d, J(P-C) = 32.1 Hz), 134.7 (d, J(P-C) = 32.1 Hz), 151.4, 159.2, 159.8. ^{31}P NMR: δ 10.8 and 59.3. LC-MS: *m/z* 632 $[M+1]^+$. Anal. Calcd. for $C_{34}H_{35}NO_5P_2S$: C, 64.65; H, 5.58; N, 2.22. Found: C, 64.58; H, 5.51; N, 2.26.

Compound (E)-3d (higher R_f). Yield: 0.097 g (76%, $E+Z$); 0.027 g (E, isolated, 21%) (using 0.2 mmol of allene **2d**). Mp: 188–192°C. IR (KBr): 3181, 3058, 1630, 1597, 1485, 1088, 1006 cm^{-1}. ^{1}H NMR: δ 0.70 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 2.98–3.00 (m, 1H, CHCH_AH$_B$), 3.13–3.16 (m, 1H, CHCH$_A$$H_B$), 3.51 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 12.2 Hz, 1H, OCH_AH$_B$), 3.63 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 12.6 Hz, 1H, OCH$_A$$H_B$), 3.95–4.11 (m, 3H, OC$H_2$ + NH), 4.75–4.76 (m, 1H, CHNH), 6.64 (d, ^3J(H–H) = 8.0 Hz, 1H, Ar-H), 6.84–6.88 (m, 1H, Ar-H), 7.05–7.09 (m, 1H, Ar-H), 7.26–7.55 (m, 11H, Ar-H), 7.91–7.96 (m, 2H, Ar-H), 8.13–8.16 (m, 2H, Ar-H). ^{13}C NMR (125 MHz): δ 21.4, 21.6, 32.4 (d, ^3J(P-C) = 5.9 Hz, C(CH$_3$)$_2$), 33.4 (d, J(P-C) = 7.3 Hz, CH$_2$), 45.3 (NHCH), 75.3 (d, J(P-C) = 6.1 Hz, OCH$_2$(A)), 75.4 (d, J(P-C) = 5.9 Hz, OCH$_2$(B)), 107.8 (d, ^1J(P-C) = 197.0 Hz, PC = C), 116.4, 123.1, 124.5 (d, J(P-C) = 2.8 Hz), 128.3, 128.4, 128.8 (d, J(P-C) = 13.1 Hz), 129.5 (d, J(P-C) = 4.3 Hz), 131.6 (d, J(P-C) = 2.6 Hz), 131.7 (d, J(P-C) = 17.5 Hz), 131.9 (d, J(P-C) = 2.3 Hz), 132.0 (d, J(P-C) = 11.4 Hz), 132.1 (d, J(P-C) = 4.6 Hz), 132.4 (d, J(P-C) = 5.1 Hz), 133.4 (d, J(P-C) = 2.1 Hz), 133.9 (d, J(P-C) = 24.0 Hz), 134.8 (d, J(P-C) = 24.8 Hz), 151.2, 161.6, 161.8. ^{31}P NMR: δ 14.4 and 59.2. LC-MS: *m/z* 635 $[M-1]^+$ and 637 $[M+1]^+$. Anal. Calcd. for $C_{33}H_{32}ClNO_4P_2S$: C, 62.31; H, 5.07; N, 2.20. Found: C, 62.21; H, 5.15; N, 2.26.

Compound (Z)-3d (lower R_f). Yield: 0.097 g (76%, $E+Z$); 0.070 g (Z, isolated, 55%). Mp: 176–180°C. IR (KBr): 3202, 3058, 1630, 1483, 1242, 1059, 1009, 791 cm^{-1}. ^{1}H NMR: δ 0.83 (s, 3H, CH_3), 1.18 (s, 3H, CH_3), 2.76–2.77 (m, 2H, CHCH_2), 3.05–3.09 (m, 1H, NH), 3.53–3.58 (m, 1H, OCH_AH$_B$), 3.79–4.06 (m, 3H, OCH$_A$$H_B$ + OCH_2), 4.71–4.76 (m, 1H, CHNH), 7.00–7.08 (m, 2H, Ar-H), 7.23–7.48 (m, 12H, Ar-H), 7.72–7.77 (m, 2H, Ar-H), 7.81–7.86 (m, 2H, Ar-H). ^{13}C NMR: δ 21.2, 22.0, 32.4 (d, J(P-C) = 6.5 Hz, C(CH$_3$)$_2$), 33.5 (dd, J(P-C) ~ 10.4 Hz, J(P-C) ~ 3.4 Hz, CH$_2$), 45.0 (NHCH), 76.0 (d, J(P-C) = 6.3 Hz, OCH$_2$(A)), 76.1 (d, J(P-C) = .6.1 Hz, OCH$_2$(B)), 107.9 (d, ^1J(P-C) = 174.9 Hz, PC = C), 117.1, 123.4, 124.4 (d, J(P-C) = 5.4 Hz), 128.5, 128.5$_1$, 128.5$_7$, 128.6, 129.0, 129.8, 131.5 (d, J(P-C) = 2.3 Hz), 131.6 (d, J(P-C) = 1.6 Hz), 131.9, 132.1 (d, J(P-C) = 4.8 Hz), 132.5 (d, J(P-C) = 6.6 Hz), 133.9 (d, J(P-C) = 16.0 Hz), 134.0, 134.7 (d, J(P-C) = 18.4 Hz), 151.4, 160.5. ^{31}P NMR: δ 10.1 and 59.3. LC-MS: *m/z* 634 $[M-2]^+$ and 636 $[M]^+$. Anal. Calcd. for $C_{33}H_{32}ClNO_4P_2S$: C, 62.31; H, 5.07; N, 2.20. Found: C, 62.21; H, 5.15; N, 2.28.

Compound (E + Z)-3e. Yield: 0.16 g (83%, $E+Z$) (using 0.3 mmol of allene **2e**). Mp: 210–214°C. IR (KBr): 3212, 3058, 1628, 1601, 1453, 1289, 1244, 1060 cm^{-1}. ^{1}H NMR: (E/Z ~ 1:1) δ 0.70, 0.79 and 1.10 (3 s, 12H, CH_3), 2.51–2.66 (m, 4H), 3.30–3.50 (m, 4H), 3.68–3.76 (m, 2H), 3.93–4.14 (m, 4H), 4.61–4.68 (m, 2H, CHNH), 6.95–7.00 (m, 4H, Ar-H), 7.16–7.82 (m, 37H, Ar-H), 8.34 (d, ^3J(H-H) = 8.4 Hz, 1H, Ar-H). ^{13}C NMR: ($E+Z$) δ 21.2, 21.3, 21.9, 32.4 (d, J(P-C) = 6.0 Hz, C(CH$_3$)$_2$), 32.5 (d, J(P-C) = 6.2 Hz, C(CH$_3$)$_2$), 33.5 (dd, J(P-

C) ~ 10.2 Hz, *J*(P-C) ~ 5.4 Hz, *C*H_2), 33.8 (dd, *J*(P-C) ~ 10.7 Hz, *J* (P-C) ~ 4.2 Hz,*C*H_2), 44.3 (d, *J*(P-C) = 4.5 Hz, -NH*C*H), 44.7 (d, *J* (P-C) = 4.9 Hz, -NH*C*H), 75.8 (d, *J*(P-C) = 3.6 Hz, O*C*H_2(A)), 76.0 (d, *J*(P-C) = .6.0 Hz, O*C*H_2(B)), 76.3, 76.4, 106.4 (d, ^1J(P-C) = 176.0 Hz, P*C* = C), 107.5 (d, ^1J(P-C) = 177.0 Hz, P*C* = C), 117.0, 117.1, 123.9 (d, *J*(P-C) = 28.0 Hz), 125.0, 125.5 (d, *J*(P-C) = 13.0 Hz), 126.2, 126.4, 126.6, 126.9, 128.1, 128.3$_0$, 128.3$_2$, 128.4$_0$, 128.4$_4$, 128.7, 128.9, 129.0, 129.1, 129.2$_0$, 129.2$_4$, 129.3, 129.6, 129.7, 130.7, 130.8, 131.4, 131.5, 131.7, 131.9, 132.8, 133.3, 133.6, 133.8, 134.0, 134.3, 134.9 (d, *J*(P-C) = 19.0 Hz), 151.3, 151.4, 161.2, 161.3 (the spectrum was complicated because of the peaks for both the isomers). ^{31}P NMR: δ 10.1, 11.0 and 59.0, 59.9. LC-MS: *m/z* 650 $[M-1]^+$. Anal. Calcd. for $C_{37}H_{35}NO_4P_2S$: C, 68.19; H, 5.41; N, 2.15. Found: C, 68.32; H, 5.38; N, 2.21.

Compound (E)-3f (higher R_f). Yield: 0.194 g (61%, *E* + *Z*); 0.083 g (*E*, isolated, 26%) (using 0.5 mmol of allene **2a**). Mp: 260–264°C. IR (KBr): 3229, 1624, 1595, 1472, 1250, 1057, 837, 787 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.66 (s, 3H, C*H*$_3$), 0.99 (s, 3H, C*H*$_3$), 3.08–3.12 (m, 2H, CHC*H*$_2$), 3.46–3.51 (m, 1H, OC*H*$_A$H$_B$), 3.62–3.67 (m, 1H, OCH$_A$*H*$_B$), 3.97–4.05 (m, 3H, N*H* + OC*H*$_2$), 4.73–4.75 (m, 1H, C*H*NH), 6.57 (d, ^3J(H-H) = 9.0 Hz, 1H, Ar-*H*), 6.97–7.00 (m, 1H, Ar-*H*), 7.32–7.54 (m, 12H, Ar-*H*), 7.93–7.97 (m, 2H, Ar-*H*), 8.12–8.17 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz): δ 21.2, 21.7, 32.3 (d, *J*(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 33.0 (d, *J*(P-C) = 8.0 Hz, *C*H_2), 45.1 (NH*C*H), 75.5 (d, *J*(P-C) = 6.1 Hz, O*C*H_2 (A)), 75.6 (d, *J*(P-C) = 6.1 Hz, O*C*H_2(B)), 110.0 (d, ^1J(P-C) = 194.6 Hz, P*C* = C), 117.8, 125.8, 127.6 (d, *J*(P-C) = 27.8 Hz), 128.2, 128.3 (d, *J*(P-C) = 13.3 Hz), 129.4 (d, *J*(P-C) = 17.5 Hz), 130.6 (d, *J*(P-C) = 4.6 Hz), 131.6, 131.7$_0$, 131.7$_2$, 131.8, 131.9, 133.6 (d, *J*(P-C) = 4.8 Hz), 133.8 (d, *J*(P-C) = 12.5 Hz), 134.6 (d, *J* (P-C) = 10.6 Hz), 149.9, 160.2, 160.4. ^{31}P NMR: δ 14.1 and 59.0. LC-MS: *m/z* 636 $[M]^+$ and 638 $[M+2]^+$. Anal. Calcd. for $C_{33}H_{32}ClNO_4P_2S$: C, 62.31; H, 5.07; N, 2.20. Found: C, 62.21; H, 5.13; N, 2.27.

Compound (Z)-3f (lower R_f). Yield: 0.194 g (61%, *E* + *Z*) 0.111 g (*Z*, isolated, 35%). Mp: 236–238°C. IR (KBr): 3223, 1628, 1476, 1248, 1105, 1060, 828 cm^{-1}. ^{1}H NMR: δ 0.80 (s, 3H, C*H*$_3$), 1.18 (s, 3H, C*H*$_3$), 2.74–2.85 (m, 2H, CHC*H*$_2$), 3.17–4.04 (m, 5H, OC*H*$_2$ + N*H*), 4.68–4.73 (m, 1H, C*H*NH), 7.00–7.01 (m, 1H, Ar-*H*), 7.16–7.18 (m, 1H, Ar-*H*), 7.27–7.46 (m, 12H, Ar-*H*), 7.68–7.74 (m, 2H, Ar-*H*), 7.81–7.86 (m, 2H, Ar-*H*). ^{13}C NMR: δ 21.1, 22.0, 32.4 (d, *J*(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 33.1 (dd, *J*(P-C) ~ 10.1 Hz, *J*(P-C) ~ 4.2 Hz, *C*H_2), 44.7 (NH*C*H), 76.0$_5$ (d, *J* = 7.0 Hz, O*C*H_2(A)), 76.1$_0$ (d, *J* = 6.6 Hz, O*C*H_2(B)), 110.0 (d, ^1J(P-C) = 172.6 Hz, P*C* = C), 118.4, 125.8 (d, *J*(P-C) = 4.8 Hz), 128.0, 128.5 (d, *J*(P-C) = 1.5 Hz), 128.6 (d, *J*(P-C) = 1.8 Hz), 128.8, 129.6, 130.7 (d, *J*(P-C) = 4.8 Hz), 131.4, 131.5, 131.6, 131.7, 131.8 (d, *J*(P-C) = 2.9 Hz), 132.0 (d, *J* (P-C) = 3.0 Hz), 133.6$_8$ (d, *J*(P-C) = 6.1 Hz), 133.6$_9$ (d, *J* (P-C) = 57.8 Hz), 134.5 (d, *J*(P-C) = 54.1 Hz), 150.0, 159.4. ^{31}P NMR: δ 10.0 and 59.5. LC-MS: *m/z* 635 $[M-1]^+$and 637 $[M+1]^+$. Anal. Calcd. for $C_{33}H_{32}ClNO_4P_2S$: C, 62.31; H, 5.07; N, 2.20. Found: C, 62.28; H, 5.11; N, 2.15.

Compound (E)-3 g (higher R_f). Yield: 0.201 g (62%, *E* + *Z*); 0.055 g (*E*, isolated, 17%) (using 0.5 mmol of allene **2b**). Mp: 216–220°C. IR (KBr): 3169, 1624, 1597, 1474, 1250, 1101, 716 cm^{-1}. ^{1}H NMR: δ 0.68 (s, 3H, C*H*$_3$), 0.99 (s, 3H, C*H*$_3$), 2.39 (s, 3H, C$_6$H$_4$C*H*$_3$), 3.05–3.12 (m, 2H, CHC*H*$_2$), 3.46 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 11.4 Hz, 1H, OC*H*$_A$H$_B$), 3.63 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 11.4 Hz, 1H, OCH$_A$*H*$_B$), 3.90–4.04 (m, 3H, OC*H*$_2$ + N*H*), 4.74–4.75 (m, 1H, C*H*NH), 6.57 (d, 1H, ^3J(H-H) = 8.8 Hz, Ar-*H*), 6.95–6.98 (m, 1H, Ar-*H*), 7.18–7.51 (m, 11H, Ar-*H*), 7.90–7.96 (m, 2H, Ar-*H*), 8.10–8.14 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz): δ 21.2, 21.3 (s, C$_6$H$_4$*C*H$_3$), 21.7, 32.3 (d, *J*(P-C) = 6.0 Hz, *C*(CH$_3$)$_2$), 33.1 (d, *J*(P-C) ~ 6.1 Hz, *C*H_2), 45.1 (NH*C*H), 75.5 (d, *J*(P-C) = 6.0 Hz, O*C*H_2(A)), 75.6 (d, ^3J(P-C) = 6.1 Hz, O*C*H_2(B)), 109.8 (d, ^1J(P-C) = 193.1 Hz, P*C* = C), 117.7, 125.9, 127.6, 128.2 (d, *J*(P-C) = 13.1 Hz), 128.7 (d, *J*(P-C) = 13.1 Hz), 128.9, 129.3 (d, *J*(P-C) = 17.3 Hz), 130.2$_6$ (d, *J*(P-C) = 4.6 Hz), 130.3$_2$, 131.6 (d, *J*(P-C) = 2.1 Hz), 131.7$_0$, 131.7$_4$, 131.8, 133.8 (d, *J*(P-C) = 17.5 Hz), 134.6 (d, *J* (P-C) = 15.9 Hz), 137.1, 149.9, 159.7. ^{31}P NMR: δ 14.3 and 59.0. LC-MS: *m/z* 650 $[M]^+$ and 652 $[M+2]^+$. Anal. Calcd. for $C_{34}H_{34}ClNO_4P_2S$: C, 62.82; H, 5.27; N, 2.15. Found: C, 62.75; H, 5.15; N, 2.21.

Compound (Z)-3 g (lower R_f). Yield: 0.201 g (62%, *E* + *Z*); 0.146 g (*Z*, isolated, 45%). Mp: 230–234°C. IR (KBr): 3208, 2963, 1630, 1597, 1474, 1254, 1061, 720 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.80 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$), 2.44 (s, 3H, C$_6$H$_4$C*H*$_3$), 2.72–2.87 (m, 2H, CHC*H*$_2$), 3.26–3.30 (m, 5H, OC*H*$_2$ + N*H*), 4.69–4.75 (m, 1H, C*H*NH), 6.98–7.00 (m, 1H, Ar-*H*), 7.14–7.53 (m, 12H, Ar-*H*), 7.67–7.73 (m, 2H, Ar-*H*), 7.80–7.85 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz): δ 21.0, 21.4, 22.0, 32.4 (d, *J*(P-C) = 6.1 Hz, *C*(CH$_3$)$_2$), 33.0 (d, *J* (P-C) = 14.4 Hz, *C*H_2), 44.7 (NH*C*H), 76.1 (O*C*H_2(A)), 76.2 (O*C*H_2(B)), 109.9 (d, ^1J(P-C) = 171.1 Hz, P*C* = C), 118.4, 125.7 (d, *J*(P-C) = 4.4 Hz), 128.0, 128.5 (d, *J*(P-C) = 1.3 Hz), 128.6, 128.7, 129.5, 129.6, 130.5 (d, *J*(P-C) = 4.9 Hz), 130.6, 131.5 (d, *J*(P-C) = 11.5 Hz), 131.7 (d, *J*(P-C) = 11.1 Hz), 131.8 (d, *J* (P-C) = 2.9 Hz), 132.0 (d, *J*(P-C) = 2.9 Hz), 133.8 (d, *J* (P-C) = 67.5 Hz), 134.6 (d, *J*(P-C) = 68.5 Hz), 137.9, 150.1, 159.2. ^{31}P NMR: δ 10.3 and 59.5. LC-MS: *m/z* 650 $[M]^+$ and 652 $[M+2]^+$. Anal. Calcd. for $C_{34}H_{34}ClNO_4P_2S$: C, 62.82; H, 5.27; N, 2.15. Found: C, 62.71; H, 5.35; N, 2.19.

Compound (E)-3 h (higher R_f). Yield: 0.190 g (57%, *E* + *Z*); 0.080 g (*E*, isolated, 24%) (using 0.5 mmol of allene **2c**). Mp: 208–210°C. IR (KBr): 3229, 2481, 1624, 1596, 1474, 1246, 1057, 839 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.69 (s, 3H, C*H*$_3$), 1.00 (s, 3H, C*H*$_3$), 3.08–3.23 (m, 2H, CHC*H*$_2$), 3.47 (dd → t, ^3J(P–H) ~ ^2J(H-H) ~ 12.5 Hz, 1H, OC*H*$_A$H$_B$), 3.64 (dd → t, ^3J(P-H) ~ ^2J(H-H) ~ 12.5 Hz, 1H, OCH$_A$*H*$_B$), 3.85 (s, 3H, OC*H*$_3$), 3.91–4.03 (m, 3H, OC*H*$_2$ + N*H*), 4.73–4.76 (m, 1H, C*H*NH), 6.59 (d, ^3J(H-H) = 5.0 Hz, 1H, Ar-*H*), 6.92–6.99 (m, 3H, Ar-*H*), 7.25–7.52 (m, 9H, Ar *H*), 7.92–7.96 (m, 2H, Ar *H*), 8.10–8.15 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz): δ 21.1, 22.0, 32.4 (d, *J*(P-C) = 6.3 Hz, *C*(CH$_3$)$_2$), 33.0 (d, *J*(P-C) ~ 10.0 Hz, *C*H_2), 44.7 (NH*C*H), 55.4 (C$_6$H$_4$O*C*H$_3$), 76.1$_0$ (O*C*H_2(A)), 76.1$_3$ (O*C*H_2(B)), 109.3 (d, ^1J(P-C) = 172.5 Hz, P*C* = C), 114.2, 118.3, 125.6 (d, *J*(P-C) = 6.3 Hz), 125.8 (d, *J*(P-C) = 5.0 Hz), 127.9, 128.5, 128.6, 129.6, 131.4, 131.5, 131.6, 131.7$_0$, 131.7$_4$, 131.8, 131.9, 133.8 (d, *J*(P-C) = 13.7 Hz), 134.6 (d, *J* (P-C) = 12.5 Hz), 150.0, 159.3. ^{31}P NMR: δ 14.3 and 59.0. Anal. Calcd. for $C_{34}H_{34}ClNO_5P_2S$: C, 61.31; H, 5.14; N, 2.10. Found: C, 61.25; H, 5.19; N, 2.18.

Compound (Z)-3 h (lower R_f). Yield: 0.190 g (57%, *E* + *Z*); 0.110 g (*Z*, isolated, 33%). Mp: 228–232°C. IR (KBr): 3235, 1632, 1601, 1439, 1057, 1009, 756 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.81 (s, 3H, C*H*$_3$), 1.19 (s, 3H, C*H*$_3$), 2.74–2.86 (m, 2H, CHC*H*$_2$), 3.22–3.26 (m, 1H, N*H*), 3.53 (dd, ^3J(P-H) = 12.5 Hz, ^2J(H-H) = 7.5 Hz, 1H, OC*H*$_A$H$_B$), 3.74–4.02 (m, 6H, OCH$_A$*H*$_B$ + OC*H*$_2$ + C$_6$H$_4$OC*H*$_3$), 4.70–4.75 (m, 1H, C*H*NH), 6.92–7.00 (m, 3H, Ar-*H*), 7.15–7.49 (m, 10H, Ar-*H*), 7.71–7.76 (m, 2H, Ar-*H*), 7.82–7.86 (m, 2H, Ar-*H*). ^{13}C NMR (125 MHz):

δ 21.2, 21.7, 32.3 (d, *J*(P-C) = 5.9 Hz, *C*(CH_3)$_2$), 33.1 (d, *J*(P-C) ~ 6.9 Hz, *C*H_2), 45.2 (NH*C*H), 55.3 (O*C*H_3), 75.5 (d, *J*(P-C) = 6.1 Hz, O*C*H_2(A)), 75.6 (d, *J*(P-C) = 6.3 Hz, O*C*H_2(B)), 109.4 (d, ^1J(P-C) = 193.9 Hz, P*C* = C), 113.6, 117.7, 125.5 (d, *J*(P-C) = 5.1 Hz), 125.9 (d, *J*(P-C) = 1.9 Hz), 127.6, 128.2 (d, *J*(P-C) = 12.9 Hz), 128.7 (d, *J*(P-C) = 12.9 Hz), 129.3 (d, *J*(P-C) = 16.6 Hz), 131.6$_0$, 131.6$_3$, 131.6$_7$, 131.8, 131.9, 133.8 (d, *J*(P-C) = 14.1 Hz), 134.6 (d, *J*(P-C) = 12.5 Hz), 149.9, 158.9, 159.9, 160.2. ^{31}P NMR: δ 10.3 and 59.4. LC-MS: *m/z* 666 $[M]^+$ and 668 $[M+2]^+$. Anal. Calcd. for $C_{34}H_{34}ClNO_5P_2S$: C, 61.31; H, 5.14; N, 2.10. Found: C, 61.35; H, 5.09; N, 2.18.

Compound (E)-3i (higher R_f). Yield: 0.208 g (62%, *E* + *Z*); 0.057 g (*E*, isolated, 17%) (using 0.5 mmol of allene **2d**). Mp: 186–190°C. IR (KBr): 3200, 1628, 1474, 1250, 1059, 789 cm^{-1}. ^{1}H NMR: δ 0.70 (s, 3H, CH_3), 0.96 (s, 3H, CH_3), 3.06–3.14 (m, 2H, CHCH_2), 3.50 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 12.7 Hz, 1H, OCH_AH$_B$), 3.64 (dd → t, ^3J(P-H) = ^2J(H-H) ~ 12.7 Hz, 1H, OCH$_A$$H_B$), 3.95–4.12 (m, 3H, OC$H_2$ + N*H*), 4.70–4.77 (m, 1H, C*H*NH), 6.56 (d, ^3J(H-H) = 8.8 Hz, 1H, Ar-*H*), 6.98–7.00 (m, 1H, Ar-*H*), 7.26–7.52 (m, 11H, Ar-*H*), 7.90–7.96 (m, 2H, Ar-*H*), 8.08–8.14 (m, 2H, Ar-*H*). ^{13}C NMR: δ 21.4, 21.6, 32.4 (d, *J*(P-C) = 5.6 Hz, *C*(CH_3)$_2$), 33.0 (dd → ~d, *J*(P-C) ~ 7.2 Hz, *C*H_2), 45.0 (NH*C*H), 75.3 (d, *J*(P-C) = 5.9 Hz, O*C*H_2(A)), 75.5 (d, *J*(P-C) = 6.1 Hz, O*C*H_2(B)), 108.4 (d, ^1J(P-C) = 196.3 Hz, P*C* = C), 117.7, 125.9, 128.0, 128.3, 128.4, 128.8 (d, *J*(P-C) = 13.0 Hz), 129.4 (d, *J*(P-C) = 3.8 Hz), 131.7, 131.8, 131.9$_0$, 131.9$_4$, 132.0, 132.1, 133.5 (d, *J*(P-C) = 9.7 Hz), 134.6 (d, *J*(P-C) = 7.4 Hz), 149.7, 155.9, 160.9, 161.2. ^{31}P NMR: δ 14.0 and 59.2. LC-MS: *m/z* 670 $[M]^+$, 672 $[M+2]^+$ and 674 $[M+4]^+$. Anal. Calcd. for $C_{33}H_{31}Cl_2NO_4P_2S$: C, 59.11; H, 4.66; N, 2.09. Found: C, 59.23; H, 4.61; N, 2.15.

Compound (Z)-3i (lower R_f). Yield: 0.208 g (62%, *E* + *Z*); 0.151 g (*Z*, isolated, 45%). Mp: 232–236°C. IR (KBr): 3187, 3058, 1628, 1474, 1248, 1059, 791 cm^{-1}. ^{1}H NMR (500 MHz): δ 0.84 (s, 3H, CH_3), 1.17 (s, 3H, CH_3), 2.75–2.81 (m, 2H, CHCH_2), 3.12–3.16 (m, 1H, N*H*), 3.53–3.56 (m, 1H, OCH_AH$_B$), 3.82–4.06 (m, 3H, OCH$_A$$H_B$ + O*C*H_2), 4.69–4.76 (m, 1H, C*H*NH), 7.01 (d, ^3J(H-H) = 9.0 Hz, 1H, Ar-*H*), 7.19–7.22 (m, 3H, Ar-*H*), 7.35–7.52 (m, 9H, Ar *H*), 7.74–7.78 (m, 2H, Ar *H*), 7.84–7.88 (m, 2H, Ar *H*). ^{13}C NMR (125 MHz): δ 21.2, 21.9, 32.4 (d, *J*(P-C) = 6.3 Hz, *C*(CH_3)$_2$), 33.1 (dd, *J*(P-C) ~ 10.4 Hz, *J*(P-C) ~ 3.8 Hz,*C*H_2), 44.8 (s, NH*C*H), 76.0 (d, *J*(P-C) = 6.4 Hz, O*C*H_2(A)), 76.1 (d, *J*(P-C) = .6.0 Hz, O*C*H_2(B)), 108.7 (d, ^1J(P-C) = 174.6 Hz, P*C* = C), 118.4, 126.0 (d, *J*(P-C) = 5.4 Hz), 128.3, 128.6 (d, *J*(P-C) = 6.1 Hz), 128.7 (d, *J*(P-C) = 5.6 Hz), 129.0, 129.7, 131.5 (d, *J*(P-C) = 11.1 Hz), 131.6 (d, *J*(P-C) = 11.4 Hz), 132.0 (d, *J*(P-C) = 3.5 Hz), 132.1 (d, *J*(P-C) = 2.9 Hz), 132.2 (d, *J*(P-C) = 6.3 Hz), 133.5, 133.9, 134.1 (d, *J*(P-C) = 2.0 Hz), 134.3, 134.7, 150.0, 159.9. ^{31}P NMR: δ 9.8 and 59.5. LC-MS: *m/z* 670 $[M]^+$, 672 $[M+2]^+$ and 674 $[M+4]^+$. Anal. Calcd. for $C_{33}H_{31}Cl_2NO_4P_2S$: C, 59.11; H, 4.66; N, 2.09. Found: C, 59.25; H, 4.56; N, 2.15.

Compound (E + Z)-3j. Yield: 0.27 g (78%, *E* + *Z*; using 0.5 mmol of allene **2e**). Mp: 240–244°C. IR (KBr): 3198, 2963, 1628, 1472, 1258, 1057, 806 cm^{-1}. ^{1}H NMR (500 MHz): (*E*/*Z* = ~1:1). Major isomer: δ 0.67 (s, 3H, CH_3), 0.76 (s, 3H, CH_3), 2.23–2.60 (m, 2H, CHCH_2), 3.06–4.06 (m, 5H, OCH_2 (A) + O*C*H_2(B) + N*H*), 4.59 (br m, 1H, C*H*NH), 7.03–7.95 (m, 19H, Ar-*H*), 8.24–8.26 (m, 1H, Ar-*H*). Minor isomer: δ 1.07 (s, 6H, 2 CH_3); remaining peaks were merged with peaks due to the major isomer. ^{13}C NMR (125 MHz): δ 21.1, 21.2, 21.8$_7$, 21.8$_8$, 32.4 (d, *J*(P-C) = 6.3 Hz, *C*(CH_3)$_2$) and 32.5 (d, *J*(P-C) = 6.3 Hz, *C*(CH_3)$_2$), 33.2 (dd, *J*(P-C) ~ 10.1 Hz, *J*(P-C) ~ 5.6 Hz, *C*H_2) and 33.4 (dd, *J*(P-C) ~ 10.7 Hz, *J*(P-C) ~ 4.7 Hz, *C*H_2), 44.2 (NH*C*H) and 44.5 (NH*C*H), 75.8$_1$ (d, *J*(P-C) = 5.9 Hz, O*C*H_2(A)), 75.8$_3$ (d, *J*(P-C) = .6.0 Hz, O*C*H_2(B)), 76.0 (d, *J*(P-C) = 6.1 Hz, O*C*H_2(A)), 76.4 (d, *J*(P-C) = 6.5 Hz, O*C*H_2(B)), 107.3 (d, ^1J(P-C) = 176.3 Hz, P*C* = C) and 108.3 (d, ^1J(P-C) = 176.8 Hz, P*C* = C), 118.4$_1$, 118.4$_3$, 124.5, 125.3, 125.4, 125.5, 125.6, 126.2 (d, *J*(P-C) = 16.6 Hz), 126.6, 126.9, 127.0, 128.1, 128.2, 128.3, 128.4$_0$ 128.4$_1$, 128.4, 128.5, 128.9, 129.0, 129.1$_0$, 129.1$_1$, 129.2$_0$, 129.2$_3$, 129.6$_5$, 129.6$_7$, 130.5 (d, *J*(P-C) = 5.6 Hz), 131.4 (d, *J*(P-C) = 11.1 Hz), 131.5$_5$, 131.5$_7$, 131.6$_2$, 131.6$_4$, 131.7$_1$, 131.7$_3$, 131.9, 132.6 (d, *J*(P-C) = 4.8 Hz), 133.1, 133.3, 133.4 (d, *J*(P-C) = 2.5 Hz), 133.5, 133.9, 134.0 (d, *J*(P-C) = 5.5 Hz), 134.1, 134.3, 134.8, 149.9, 150.0, 160.5, 160.6 (the spectrum was complicated because of the peaks for both the isomers). ^{31}P NMR: δ 9.3, 10.2 and 59.3, 60.2. LC-MS: *m/z* 686 $[M]^+$ and 688 $[M+2]^+$. Anal. Calcd. for $C_{37}H_{34}ClNO_4P_2S$: C, 64.77; H, 4.99; N, 2.04. Found: C, 64.85; H, 4.91; N, 2.12.

Compound (Z)-6a (higher R_f). Yield: 0.134 g (41%; using 0.5 mmol of allene **5**). Mp: 248–250°C. IR (KBr): 3187, 3058, 1628, 1474, 1248, 1059, 791 cm^{-1}. ^{1}H NMR: δ 2.65–2.70 (br d, ^3J(H–H) ~ 12.0 Hz, 1H, CHCH_A), 2.85–2.90 (dd, ^3J(H-H) ~ 14.8 Hz, ^4J(P-H) = 4.1 Hz, 1H, CHCH_B), 3.35–3.39 (dd, ^3J(H-H) ~ 6.4 Hz, ^4J(P-H) ~ 6.8 Hz, 1H, N*H*), 4.66–4.72 (m, 1H, C*H*NH), 6.14 (d, ^3J(H-H) = 7.6 Hz, 1H, Ar-*H*), 6.83–6.85 (m, 1H, Ar-*H*), 7.01–7.18 (m, 1H, Ar *H*), 7.23–7.46 (m, 18H, Ar-*H*), 7.68–7.85 (m, 8H, Ar *H*). ^{13}C NMR: δ 33.5 (dd → t, *J*(P-C) ~ *J*(P-C) ~ 5.5 Hz, *C*H_2), 44.8 (s, NH*C*H), 115.1 (d, ^1J(P-C) = 95.6 Hz, P*C* = C), 116.1, 122.9, 124.3 (d, *J*(P-C) = 4.1 Hz), 127.4, 128.0, 128.1, 128.2, 128.3$_0$, 128.3$_1$, 128.3$_4$, 128.4, 128.5, 128.8, 129.3, 130.9, 131.0$_2$, 131.0$_6$, 131.0$_9$, 131.1$_1$, 131.1$_4$, 131.1$_8$, 131.2$_2$, 131.4$_3$, 131.4$_4$, 131.4$_5$, 131.5, 131.6, 131.7, 132.6, 133.7, 133.8, 133.9, 134.2, 134.3, 134.6, 134.8, 134.9, 135.6, 150.6, 158.1 (the spectrum was complicated). ^{31}P NMR: δ 24.7 and 59.2. LC-MS: *m/z* 654 $[M+1]^+$. Anal. Calcd. for $C_{40}H_{33}NO_2P_2S$: C, 73.49; H, 5.09; N, 2.14. Found: C, 73.38; H, 5.15; N, 2.19.

Compound (Z)-6b (higher R_f). Yield: 0.107 g (31%; using 0.5 mmol of allene **5**). Mp: 190–194°C. IR (KBr): 3113, 3058, 1630, 1474, 1265, 1165, 926 cm^{-1}. ^{1}H NMR: (500 MHz): δ 2.65–2.70 (m, 1H, CHCH_A), 2.87–2.91 (m, 1H, CHCH_B), 3.66–3.71 (m, 1H, N*H*), 4.66–4.73 (m, 1H, C*H*NH), 6.08 (d, ^3J(H-H) = 8.8 Hz, 1H, Ar-*H*), 7.16–7.48 (m, 19H, Ar-*H*), 7.64–7.86 (m, 8H, Ar-*H*). ^{13}C NMR (125 MHz): δ 33.3 (dd → t, *J*(P-C) ~ *J*(P-C) ~ 6.1 Hz, *C*H_2), 44.5 (NH*C*H), 115.8 (d, ^1J(P-C) = 95.1 Hz, P*C* = C), 117.5, 125.7$_5$, 125.7$_9$, 127.5, 127.7, 128.0, 128.1, 128.2$_6$, 128.3$_0$, 128.3$_8$, 128.4$_3$, 128.5, 128.6, 129.2, 130.8, 130.9, 131.0, 131.1, 131.2, 131.4, 131.4$_7$, 131.5$_1$, 131.6, 131.8, 132.3, 133.4, 133.9, 134.0, 134.1, 134.4, 134.5, 134.9, 135.4, 149.2, 157.8 (the spectrum was complicated). ^{31}P NMR: δ 24.7 and 59.3. LC-MS: *m/z* 688 $[M]^+$and 690 $[M+2]^+$. Anal. Calcd. for $C_{40}H_{32}ClNO_2P_2S$: C, 69.81; H, 4.69; N, 2.04. Found: C, 69.73; H, 4.61; N, 2.08.

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