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S-to-*O* phosphoryl migration in the rhodium-catalyzed reaction of phosphorothioates with α-diazocarbonyl compounds: An access to tetrasubstituted enol phosphates

Laurine Tual, Romain Pertschi, Gaëlle Blond, and Mihaela Gulea*

Université de Strasbourg, CNRS, Laboratoire d'Innovation Thérapeutique, LIT UMR 7200
F-67000 Strasbourg, France
Email: gulea@unistra.fr

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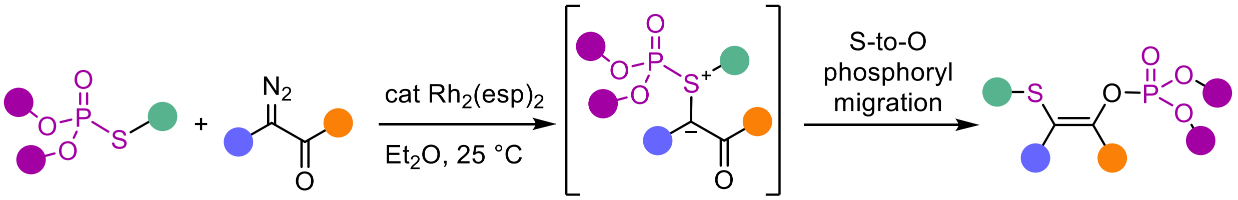
Abstract

The Rh(II)-catalyzed reaction of phosphorothioates with α-diazo carbonyl compounds proceeds predominantly via an *S*-to-*O* phosphoryl migration, affording tetrasubstituted enol phosphates with *Z*-geometry. *S*-aryl phosphorothioates react smoothly with several diazo partners, while *S*-alkyl substrates are unreactive. For allyl, propargyl, and benzyl derivatives, competing pathways lead to enol phosphates products incorporating two carbene units. DFT calculations on two model *S*-allyl ylides reveal that phosphoryl migration is energetically favored over the Doyle–Kirmse rearrangement for α-keto ylides, whereas the opposite trend is observed for α-ester ylides, which is consistent with the observed reactivities. These findings establish new advances in phosphorothioate chemistry.



Keywords: Sulfur ylide, phosphorothioate, sulfur rearrangement, phosphoryl migration, S-P bond cleavage, diazo compound.

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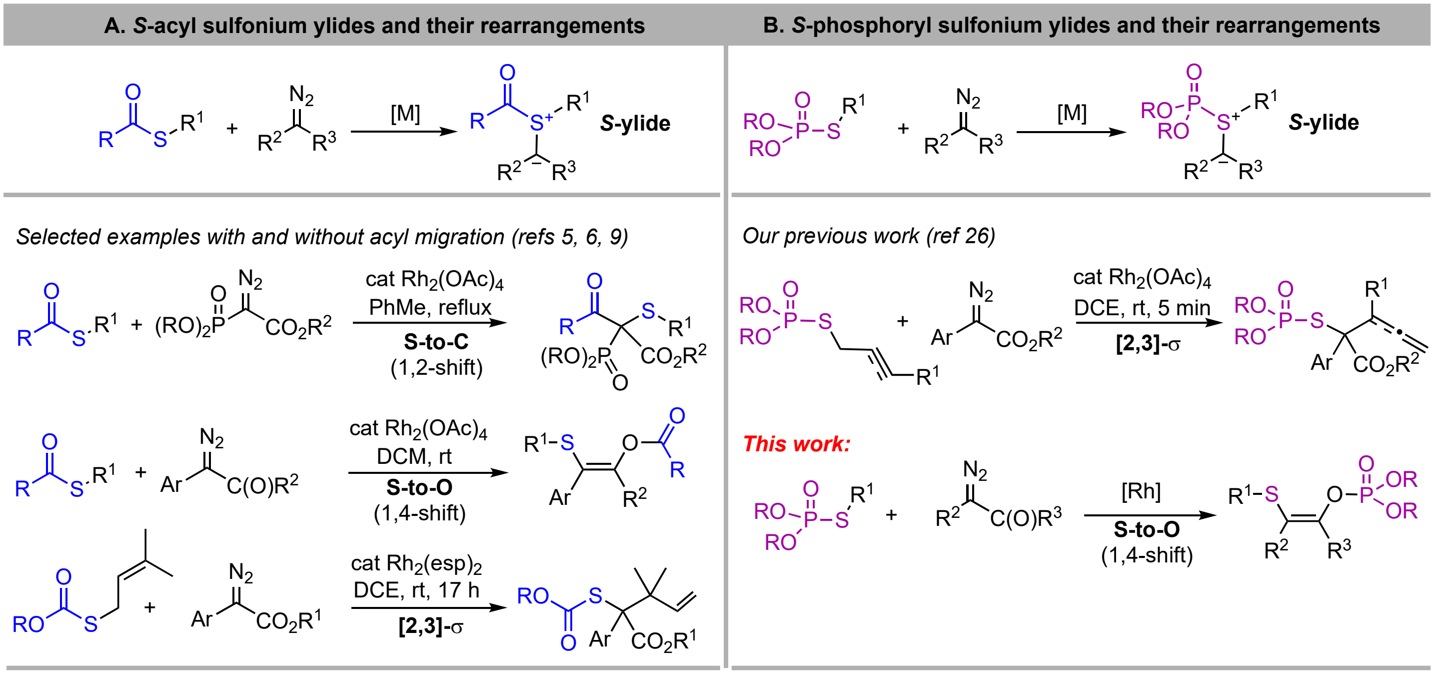
Introduction

Thioesters (thiocarboxylates) are well established as highly reactive acyl donors of importance in both biology and synthetic chemistry.[1-3] They enable native chemical ligation, a key method for protein synthesis that proceeds through transthioesterification followed by intramolecular *S*-to-*N* acyl migration.[4] Thioesters are also widely used in organic synthesis as acyl transfer reagents. Their reactions with metallocarbenes, generated by metal-catalyzed decomposition of diazo compounds, afford *S*-acyl sulfonium ylides (Scheme 1A), which can undergo diverse rearrangements, including *S*-to-*C*,[5] *S*-to-*O*,[6] or *S*-to-*N*[7] acyl migrations. Alternatively, thioesters may participate in transformations that proceed without sulfur-carbonyl cleavage, such as [2,3]-sigmatropic rearrangements.[8,9] Notably, Rh(II)-catalyzed reactions of α-diazo carbonyl compounds with *S*-allyl thioesters can proceed either through an *S*-to-*O* 1,4-acyl migration[6] or via a Doyle–Kirmse [2,3]-sigmatropic rearrangement.[9]

On the other hand, phosphorothioates, parent analogues of thioesters, have found broad applications as biologically active molecules in agrochemistry and pharmaceuticals, with the P(O)–S unit being a defining structural feature of modified oligonucleotides for therapeutic use.[10, 11] A distinctive aspect of phosphorothioate chemistry as synthetic intermediates is the anionic cleavage of the P–S bond, which frequently leads to molecular rearrangements via phosphoryl migration.[12, 13] Most studies have focused on *S*-to-*C* phosphoryl migration, in which the phosphoryl group transfers from sulfur to a carbanion at the 2-, 3-, or 4-position (i.e., 1,2-,[14, 15] 1,3-,[16-21] or 1,4-rearrangements[22]), thereby converting phosphorothioates into mercaptophosphonates. Other variants include *S*-to-*N* phosphoryl migration, known as the thiophosphate-to-phosphoroamidate rearrangement,[23] analogous to the *S*-to-*N* acyl migration, as well as *S*-to-*O* migration. The latter has been exploited in synthetic strategies toward *S*-heterocycles, typically involving intramolecular alkoxide addition on phosphorus in an acyclic phosphorothioate, followed by thiolate release and subsequent displacement of the phosphate group.[24, 25]



Scheme 1. Rearrangements involving *S*-acyl and *S*-phosphoryl sulfonium ylides.

Intrigued by the reactivity analogy between *S*-acyl and *S*-phosphoryl sulfonium ylides, we recently reported the Rh-catalyzed reactions of *S*-allyl and *S*-propargyl phosphorothioates with diazoesters, which proceeded exclusively via the Doyle–Kirmse [2,3]-rearrangement (Scheme 1B).[26]

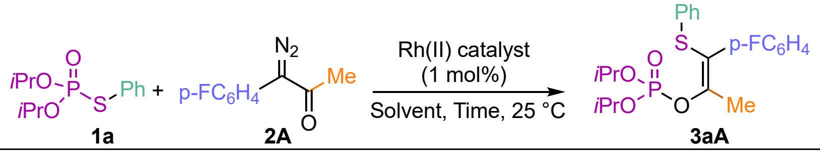
Building on this work, we have expanded our study to encompass other reactivities of *S*-phosphoryl sulfonium ylides, which may proceed through a variety of mechanistic pathways (i.e. *S*-to-*O* or *S*-to-*C* phosphoryl transfer, or a sigmatropic rearrangement). Here, we describe the Rh(II)-catalyzed reactions of phosphorothioates with α-diazo carbonyl compounds, which proceed predominantly through *S*-to-*O* phosphoryl transfer, with a competing *S*-to-*C* migration observed in specific cases. The method provides direct access to enol phosphates, a structural motif central to many agrochemicals and bioactive natural products,[27] and of considerable importance due to their broad synthetic utility.[28, 29]

Results and Discussion

To set up the reaction conditions, easily available phenylphosphorothioate **1a** and α-diazo phenyl ketone **2A** were selected as model substrates. Initial experiment was performed by mixing **1a** (1.0 equiv), **2A** (4.0 equiv), rhodium acetate (1 mol %) to ensure an efficient diazo decomposition in Et_2O (0.1 M) at room temperature. After 30 min, ^{1}H-NMR spectroscopic analysis of the crude mixture revealed a full conversion of diazo along with a partial conversion (53%) of the phosphorothioate partner **1a**, which was transformed in the expected phosphoenol ether **3aA** in 41% NMR yield (Table 1, entry 1).

With these preliminary results in hand, the reaction conditions were further optimized. First, the influence of the electronic properties of the catalyst were investigated by modifying the rhodium(II) ligand (entries 2-4). Switching from the electron-rich acetate ligand to the electron-poor trifluoroacetate ligand led to a longer reaction time, with only 54% conversion and a low yield of 10% (entry 1 vs entry 2). The slow reaction and poor yield observed may be due to the increased Lewis acidity of the rhodium(II) becoming too coordinative towards the reagents and product. Given that coordinating substrates and products might be problematic, we switched back to more electron-donating ligands and increased the steric hindrance to reduce the coordination of the sulfur derivatives towards Rh(II) further. Indeed, rhodium(II) pivalate and especially the $Rh_2(esp)_2$ (i.e. Du Bois catalyst) found to be slightly more efficient for the transformation (entries 3-4). Although $Rh_2(esp)_2$ showed a fast reaction with the best conversion and yield (60% and 54%, respectively), these conditions showed poor reproducibility. To solve this problem, the reaction conditions were optimized further using this catalyst. Thus, the influence of the number of diazo equivalents was evaluated, and both decreasing and increasing the amount proved detrimental (entries 5-6). Finally, the concentration was modified. While dilution (entry 7) was detrimental to the reaction, performing the reaction at a higher concentration led to the expected phosphoenol with a yield of 49%. Under these conditions, the reaction was found to be reproducible.

Table 1. Optimization of the reaction conditions



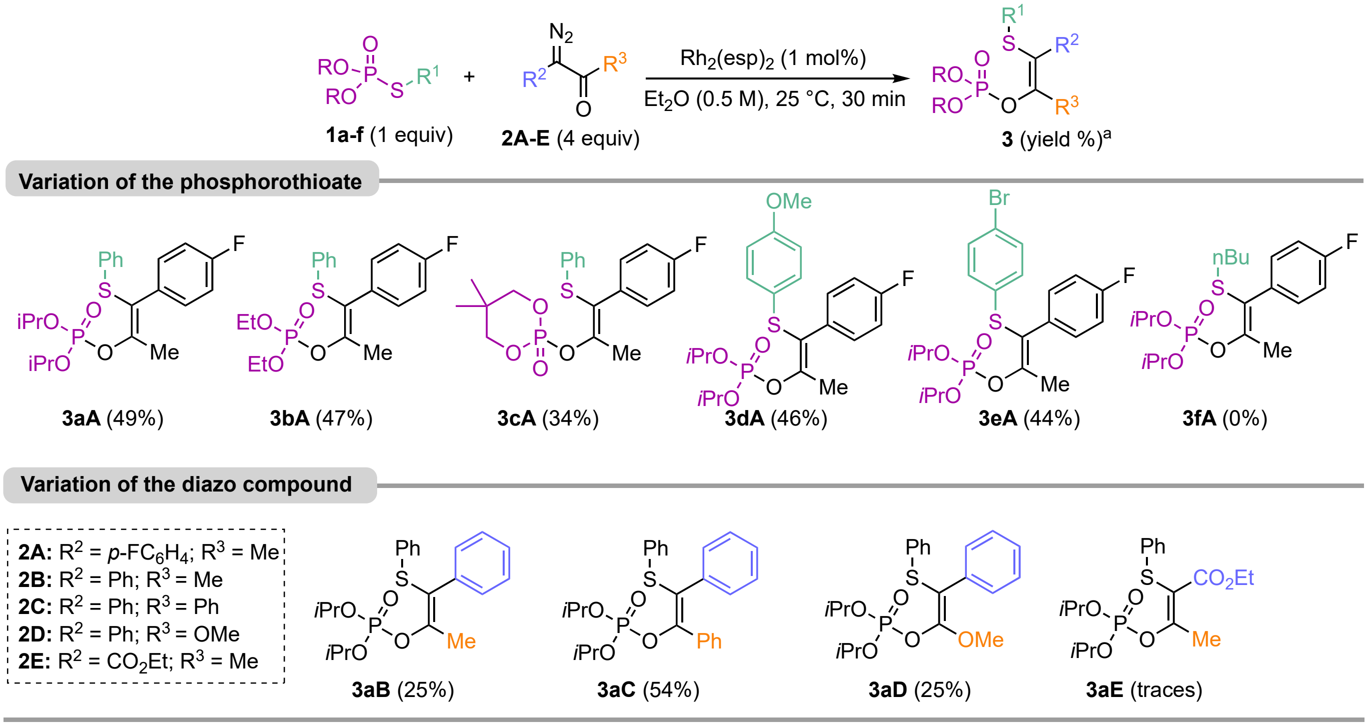
1a + **2A** → **3aA**

Entry	Catalyst	Equiv **2A**	Solvent (conc.)	Time (min)	Conversion (%)[a]	NMR yield (%)[b]
1	$Rh_2(OAc)_4$	4	Et_2O (0.1 M)	30	53	41
2	$Rh_2(TFA)_4$	4	Et_2O (0.1 M)	120	54	10
3	$Rh_2(OPiv)_4$	4	Et_2O (0.1 M)	60	52	48
4	$Rh_2(esp)_2$	4	Et_2O (0.1 M)	30	30 to 60[c]	27 to 54[c]
5	$Rh_2(esp)_2$	2	Et_2O (0.1 M)	30	28	21
6	$Rh_2(esp)_2$	6	Et_2O (0.1 M)	30	44	39
7	$Rh_2(esp)_2$	4	Et_2O (0.05 M)	30	55	34
8	$Rh_2(esp)_2$	4	Et_2O (0.5 M)	30	50	49 (49)

[a] Conversion based on **1a**. [b] Yield calculated by ^1H NMR with caffeine as internal standard. In parentheses, isolated yield. [c] Results were not reproducible.

Therefore, these conditions were selected to explore the scope and limitations of this transformation, examining variations in both the phosphorothioate and the diazo compound partners (Table 2).

Table 2. Scope and limitations of the reaction



1a-f (1 equiv) + **2A-E** (4 equiv) → **3** (yield %)[a]

3aA (49%) **3bA** (47%) **3cA** (34%) **3dA** (46%) **3eA** (44%) **3fA** (0%)

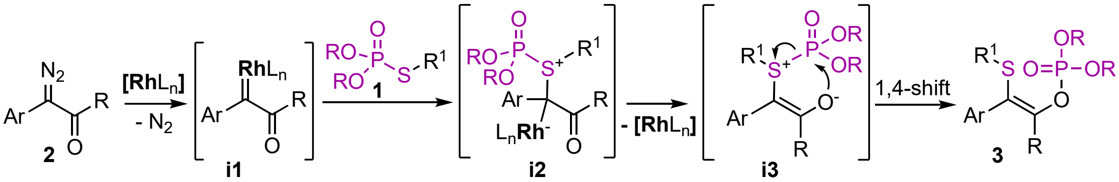
2A: R^2 = *p*-FC_6H_4; R^3 = Me
2B: R^2 = Ph; R^3 = Me
2C: R^2 = Ph; R^3 = Ph
2D: R^2 = Ph; R^3 = OMe
2E: R^2 = CO_2Et; R^3 = Me

3aB (25%) **3aC** (54%) **3aD** (25%) **3aE** (traces)

[a] Isolated yields are given.

Reaction of α-diazoketone **2A** with a range of *S*-aryl phosphorothioates (**1a-e**) gave the expected enol phosphates. In all cases, the conversion was incomplete, but the products could be separated from the recovered starting material. When the isopropyl groups on the phosphoryl unit of **1a** were replaced with ethyl groups, or when a cyclic phosphoryl group was used, the expected products **3bA** and **3cA** were isolated in good yields relative to converted material. Substrates bearing a *para*-methoxy (**1d**) or *para*-bromo substituent (**1e**) also reacted smoothly to give **3dA** and **3eA**, respectively. In contrast, no reaction occurred with the *S*-alkyl phosphorothioate **1f**. Variations in the diazo compound were then examined using *S*-phenyl phosphorothioate **1a**. Phenyl α-diazoketone **2C** gave higher conversion than the methyl analogue **2B**, but both furnished the corresponding enol phosphates **3aB** and **3aC**. Despite low conversion, phenyl diazoacetate **2D** provided the expected product **3aD**, whereas only traces of product were observed with the α-diazo ketoester compound **2E**.

Based on the thiocarboxylate/phosphorothioate analogy, we propose the mechanism outlined in Scheme 2, inspired by that reported for thioesters.[6] The reaction begins with the Rh(II)-catalyzed decomposition of diazo compound **2** to generate the rhodium carbene intermediate **i1**. This species reacts with phosphorothioate **1** to give the metal-bound ylide intermediate **i2**, which evolves into the free sulfur ylide enolate **i3**. A subsequent [1,4]-phosphoryl shift then affords the final product **3**.

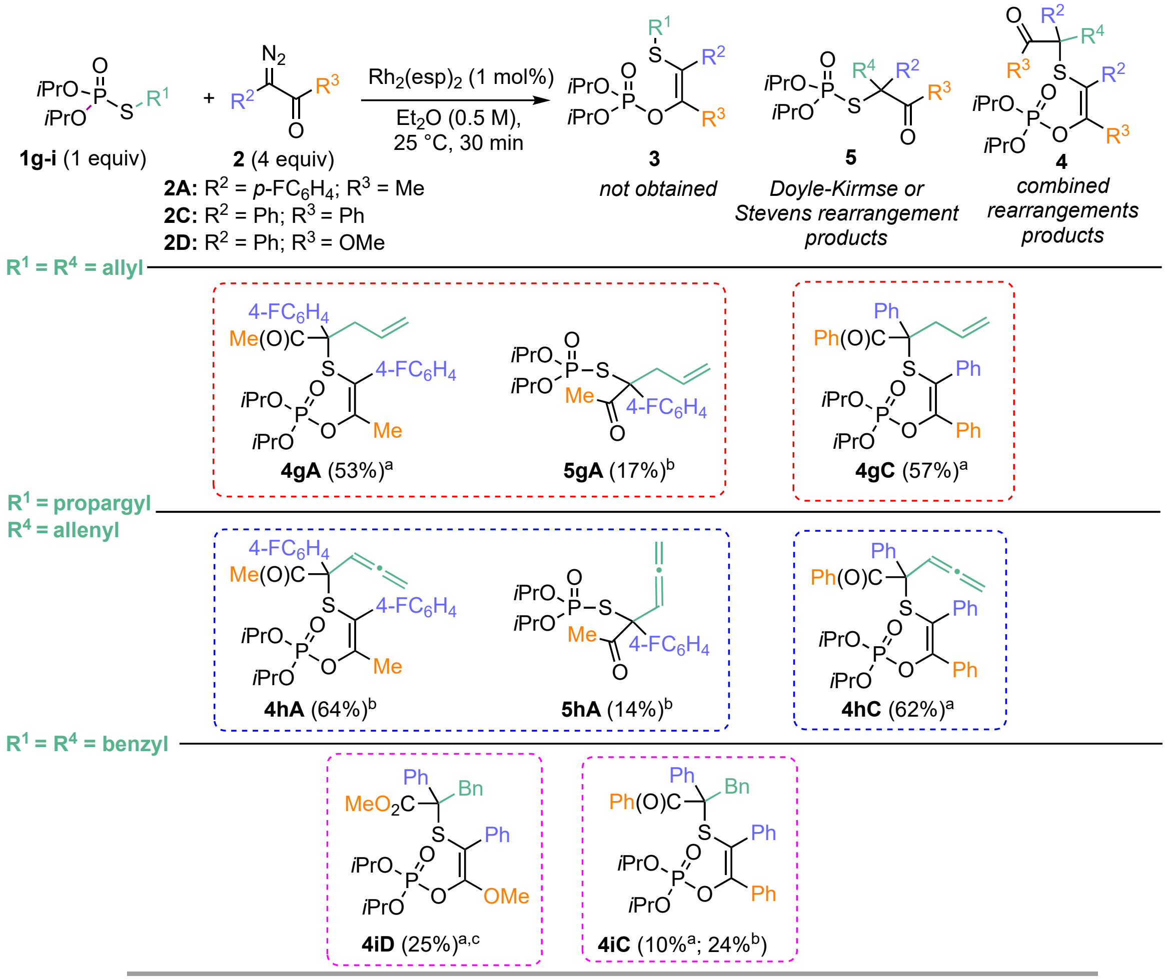


Scheme 2. Proposed mechanism of the reaction with *S*-to-*O* phosphoryl transfer.

We then examined the specific cases of *S*-allyl, *S*-propargyl, and *S*-benzyl phosphorothioates, where competitive rearrangements can arise from the initially formed *S*-ylide: a [2,3]-sigmatropic shift (Doyle–Kirmse reaction) for allyl and propargyl derivatives, or a [1,2]-benzyl migration (Stevens rearrangement) for the benzyl derivative. The reactivity of phosphonothioates **1g-i** with diazos **2** deviated from the expected rearrangement pathways (Table 3). Indeed, the reactions of *S*-allyl and *S*-propargyl phosphorothioates (**1g** and **1h**) with diazoesters **2A** or **2C** did not provide the expected enol phosphates **3**. With diazo ketone **2A**, the Doyle–Kirmse products **5gA** and **5hA** were obtained in low yield, while no products **5** were detected with **2C**. Unexpectedly, the major isolated products were enol phosphates **4** incorporating two carbene units, from a sequence combining a [2,3]-sigmatropic rearrangement with an *S*-to-*O* phosphoryl migration.

Similarly, the reactions of *S*-benzyl phosphorothioate **1i** with diazo compounds **2C** or **2D** did not afford the expected enol phosphates **3** or the Stevens rearrangement products **5**. Instead, enol phosphates **4iC** and **4iD**, each incorporating two carbene units, were obtained as the sole products, however, isolated in low yields. In this case, the transformation may involve the Stevens rearrangement followed by an *S*-to-*O* phosphoryl migration. In contrast, reaction of **1i** with **2A** produced a complex mixture from which no product could be identified. Notably, in all these cases, reducing the number of equivalents of diazo partner **2** from four to one or two did not improve the formation of products **3** or **5**, but instead further decreased the overall conversion.

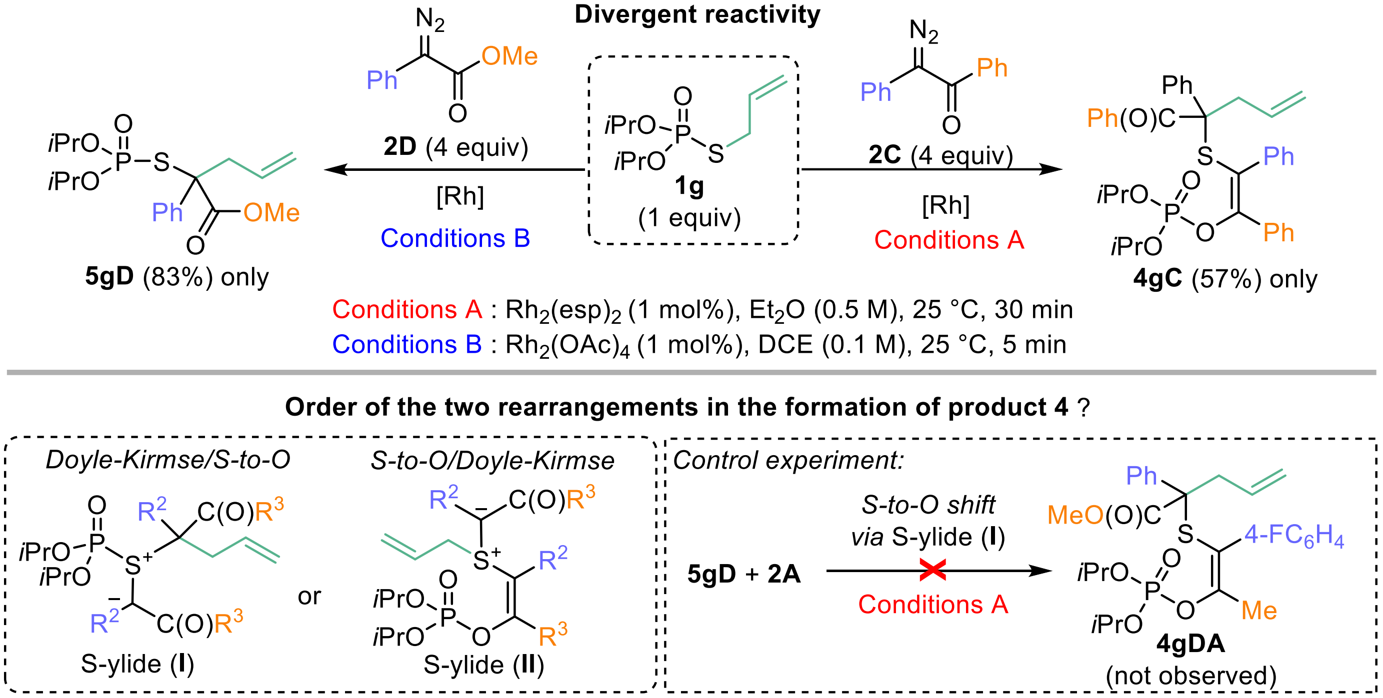
Table 3. Specific cases: *S*-allyl, *S*-propargyl, *S*-benzyl phosphorothioates



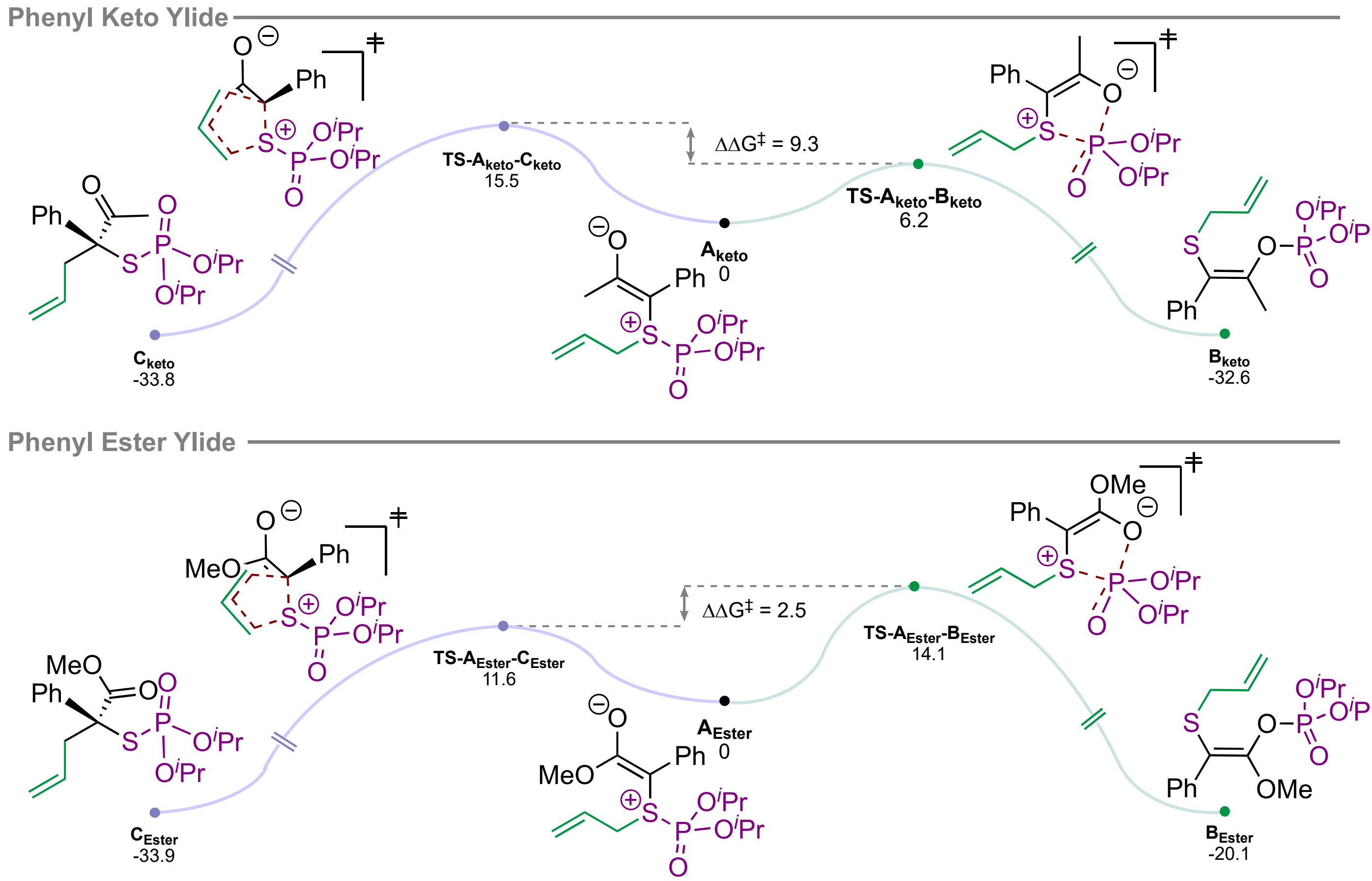
[a] Isolated yield. [b] NMR yields. [c] Conditions: $Rh_2(OAc)_4$, DCE (0.1 M), 1 h.

In view of these results, the reaction outcome and the nature of the products strongly depend on the substituents of the precursors. For *S*-allyl phosphorothioate **1g**, divergent reactivities were observed with diazo compounds **2C** and **2D** under Rh(II) catalysis (Scheme 3). As we previously described, with phenyl diazoester **2D** under conditions B, the reaction furnished the Doyle-Kirmse product **5gD** exclusively in 83% yield,[26] whereas, with diazo ketone **2C** under conditions A, only product **4gC** was obtained, in 57% yield. Mechanistically, the formation of product **4** could proceed either through a Doyle–Kirmse/*S*-to-*O* sequence (via *S*-ylide **I**) or through an *S*-to-*O*/Doyle–Kirmse sequence (via *S*-ylide **II**). A control experiment using **5gD** as the substrate with diazo ketone **2A** failed to produce **4gDA** (with two different carbene units), thus supporting a pathway in which the *S*-to-*O* shift precedes the Doyle-Kirmse rearrangement.

To confirm our hypothesis that the phosphoryl migration proceeds faster than the Doyle–Kirmse rearrangement when an α-diazo ketone is used in the presence of an *S*-allyl phosphorothioate, while the reverse trend is observed with an α-diazo ester, DFT calculations were performed (see Supplementary Material file for details). To set up our calculations, the free ylides $\mathbf{A}_{\mathbf{keto}}$ and $\mathbf{A}_{\mathbf{ester}}$ arising from the diazo decomposition/condensation were used as model substrates, and both pathways were computationally studied (Scheme 4). Calculations show that the phosphoryl migration is favored by 9.3 kcal·mol^{-1} over the [2,3]-sigmatropic shift in the case of the α-keto ylide formation, while for the α-ester ylide the Doyle–Kirmse rearrangement is favored by 2.5 kcal.mol^{-1}, thereby confirming our initial assumption.

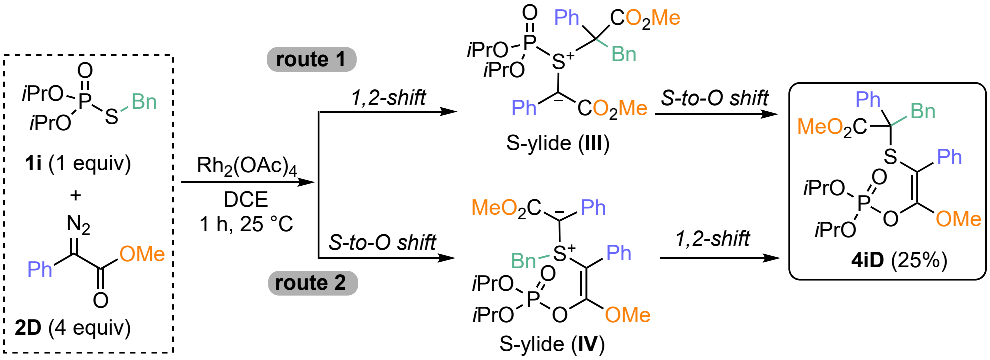


Scheme 3. *S*-to-*O* phosphoryl migration vs Doyle-Kirmse rearrangement.



Scheme 4. Free energy reaction profile (kcal/mol) for the *S*-to-*O* phosphoryl migration vs Doyle-Kirmse step using the free ylide $\mathbf{A}_{\mathbf{Keto}}$ and $\mathbf{A}_{\mathbf{Ester}}$ as model substrate at the M06-2X/6-311++G**, smd(CH_2Cl_2) level of theory.

In the Rh(II)-catalyzed reaction of phosphonyl *S*-benzyl phosphorothioate **1i** with diazoester **2D** (conditions B), compound **4iD** was obtained, whereas the alternative Stevens-rearrangement product **5iD** was not detected (Scheme 5). As in the previous case, two plausible mechanistic pathways can be proposed for the formation of **4**: either a 1,2-shift (Stevens rearrangement), followed by an *S*-to-*O* transfer (via *S*-ylide **III**), or an *S*-to-*O* transfer, followed by the 1,2-shift (via *S*-ylide **IV**).



Scheme 5. Possibles routes to **4iD**: *S*-to-*O* phosphoryl migration vs 1,2-shift (Stevens rearrangement).

Unfortunately, control experiments could not be carried out, since we were unable to prepare compounds **5iD** and **3iD** for this purpose.

Conclusions

In summary, we have demonstrated that phosphorothioates undergo Rh(II)-catalyzed reactions with α-diazo carbonyl compounds predominantly through an unprecedented *S*-to-*O* phosphoryl migration, leading to tetrasubstituted enol phosphates. This reactivity expands the chemistry of *S*-phosphoryl sulfonium ylides beyond the previously established Doyle–Kirmse rearrangement. The method tolerates variously substituted phosphorothioates and diazo partners, although *S*-alkyl derivatives remain unreactive. Notably, the reaction outcome is highly substrate-dependent. While simple *S*-aryl phosphorothioates cleanly afford enol phosphates, allyl, propargyl, and benzyl derivatives display divergent reactivity, often yielding products incorporating two carbene units through sequential rearrangements. These results reveal a subtle balance between competing [1,4]-phosphoryl shift, [2,3]-sigmatropic rearrangement, and [1,2]-phosphoryl shift, highlighting the mechanistic richness of this transformation. DFT studies on α-keto and α-ester ylides showed that phosphoryl migration is preferred for α-keto systems, while the Doyle–Kirmse rearrangement is favored for α-ester analogues, consistent with the observed switch in reactivity. The present study provides a new entry to enol phosphates and underscores the potential of phosphorothioates as versatile platforms for carbene transfer chemistry, opening perspectives for new synthetic applications.

Experimental Section

General. Chemicals: Unless otherwise stated, reagents and anhydrous solvents were used without any further purification and obtained from commercially available sources. TLC (Thin Layer Chromatography) were performed on Merck silica gel 60 F254 plates and visualized with UV light and/or chemical stain. Crude products were purified via column chromatography using VWR silica gel (40-63 µm).

NMR analysis: ^{1}H NMR, ^{13}C NMR, ^{31}P NMR and ^{19}F NMR spectra were recorded on 400 or 500 MHz instruments Bruker spectrometer. Chemical shifts are reported in parts per million (ppm) and the residual non deuterated solvent was used as c reference. Coupling constants values (*J*) are reported in Hertz (Hz). Signals are described as br (broad), s (singlet), d (doublet), t (triplet), hept (heptuplet) and m (multiplet). Spectra were processed with the software MestreNova (Version 14.2.3-29241). Assignments were determined either based on unambiguous chemical shifts or coupling patterns, and COSY, HSQC, HMBC, NOESY experiments were sometimes needed to fully interpret spectra for related compounds.

Mass analysis: High Resolution Mass Spectroscopy (HRMS) were performed by the "Plateforme d'analyse chimique de Strasbourg Illkirch" (PACSI) and were obtained on an Agilent Technologies 6520 Accurate-Mass Q-TOF LC/MS apparatus equipped with a Zorbax SB C18 column (1.8 µm, 2.1 × 50 mm) using electrospray ionization mode and a time-of-flight analyzer (ESI-TOF). The parent ions $[M + H]^+$, $[M + Na]^+$ are quoted.

Experimental procedures

General procedure A for *S*-to-*O* phosphoryl migration

The reaction did not require a controlled atmosphere. To a solution of **1** (1.0 equiv) in diethyl ether (c = 1 M) was added $Rh_2(esp)_2$ (1 mol%). Then, a solution of diazo compound **2** (4.0 equiv) in diethyl ether (c = 1 M) was added dropwise and the reaction mixture was stirred at 25 °C for 30 min. Solvent was removed under reduced pressure. Crude product was purified by reversed phase chromatography on C18 column (eluent: 30/70 to 100/0 MeCN/H_2O) and/or by column chromatography on silica gel (eluent: *n*-heptane/EtOAc) to afford the enol phosphates **3** and **4**.

General procedure B for *S*-to-*O* phosphoryl migration

The reaction did not require a controlled atmosphere. To a solution of **1** (1.0 equiv) in 1,2-dichloroethane (c = 0.2 M) was added $Rh_2(OAc)_4$ (1 mol%). Then, a solution of diazo compound **2** (4.0 equiv) in 1,2-dichloroethane (c = 0.2 M) was added dropwise and the reaction mixture was stirred at 25 °C for 30 min. The solvent was removed under reduced pressure. Crude product was purified by reversed phase chromatography on C18 column (eluent: 30/70 to 100/0 MeCN/H_2O) and/or by column chromatography on silica gel (eluent: *n*-heptane/EtOAc or *n*-pentane/Et_2O) to afford the enol phosphates **4**.

(*Z*)-1-(4-fluorophenyl)-1-(phenylthio)prop-1-en-2-yl diisopropyl phosphate (3aA)

3aA was obtained according to **General procedure A**, from **1a** (1.0 equiv, 50 mg, 0.18 mmol), diazo compound **2A** (4.0 equiv, 130 mg, 0.73 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) led to **3aA** (38 mg, 0.09 mmol, 49%, yellow oil) and recovered starting material **1a** (14 mg, 0.051 mmol, 28%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 2H), 7.19 – 7.14 (m, 2H), 7.14 – 7.08 (m, 2H), 7.08 – 7.03 (m, 1H), 6.88 – 6.82 (m, 2H), 4.88 – 4.78 (m, 2H), 2.13 (d, $^{4}J_{H\text{-}P}$ = 2.0 Hz, 3H), 1.38 (d, $^{4}J_{H\text{-}P}$ = 6.3 Hz, 12H). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$) δ -8.66. ^{19}F {^{1}H} NMR (471 MHz, $CDCl_3$) δ -114.28. ^{13}C NMR (126 MHz, $CDCl_3$) δ 161.8 (d, $^{1}J_{C\text{-}F}$ = 247.0 Hz), 147.1 (d, $^{2}J_{C\text{-}P}$ = 7.2 Hz), 134.1, 133.2 (d, $^{4}J_{C\text{-}F}$ = 3.4 Hz), 131.7 (d, $^{3}J_{C\text{-}F}$ = 8.3 Hz), 131.1 (2C), 128.5 (2C), 126.5, 119.3 (d, $^{3}J_{C\text{-}P}$ = 9.9 Hz), 114.9 (d, $^{2}J_{C\text{-}F}$ = 21.6 Hz), 73.5 (d, $^{2}J_{C\text{-}P}$ = 6.4 Hz), 23.7 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz), 23.7 (d, $^{3}J_{C\text{-}P}$ = 5.0 Hz), 19.0. HRMS (ESI-TOF): Calculated for $C_{21}H_{27}FO_4PS$ $[M+H]^+$: 425.1352, Found: 425.1363 (Δ_{HRMS} = -3.55 ppm). R_f = 0.42 (70/30 *n*-heptane/EtOAc).

(*Z*)-Diethyl (1-(4-fluorophenyl)-1-(phenylthio)prop-1-en-2-yl) phosphate (3bA). 3bA was obtained according to **General procedure A**, from **1b** (1.0 equiv, 44 mg, 0.18 mmol), diazo compound **2A** (4.0 equiv, 127 mg, 0.71 mmol. Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) and by column chromatography on silica gel (eluent: 90/10 to 70/30 *n*-heptane/EtOAc) led to **3bA** (33 mg, 0.083 mmol, 47%, yellow oil) and recovered starting material **1b** (7 mg, 0.028 mmol, 16%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24 – 7.16 (m, 4H), 7.13 – 7.03 (m, 3H), 6.88 – 6.82 (m, 2H), 4.30 – 4.23 (m, 4H), 2.12 (d, $^{4}J_{H-P}$ = 2.0 Hz, 3H), 1.37 (dt, J = 7.1 Hz, $^{4}J_{H-P}$ = 0.8 Hz, 6H), 1.37 (dt, J = 6.9 Hz, $^{4}J_{H-P}$ = 0.5 Hz, 6H). ^{31}P {^{1}H} NMR (202 MHz, CDCl$_3$) δ -7.14. ^{19}F {^{1}H} NMR (471 MHz, CDCl$_3$) δ -114.13. ^{13}C NMR (126 MHz, CDCl$_3$) δ 161.9 (d, $^{1}J_{C-F}$ = 247.3 Hz), 146.8 (d, $^{2}J_{C-P}$ = 7.3 Hz), 133.9, 133.0 (d, $^{4}J_{C-F}$ = 3.5 Hz), 131.7 (d, $^{3}J_{C-F}$ = 8.2 Hz), 131.2 (2C), 128.6 (2C), 126.7, 120.0 (d, $^{3}J_{C-P}$ = 9.5 Hz), 114.9 (d, $^{2}J_{C-F}$ = 21.6 Hz), 64.6 (d, $^{2}J_{C-P}$ = 6.3 Hz), 19.0, 16.1 (d, $^{3}J_{C-P}$ = 7.0 Hz).

HRMS (ESI-TOF): Calculated for $C_{19}H_{23}FO_4PS$ [M+H]$^+$: 397.1039, Found: 397.1046 (Δ_{HRMS} = -2.90 ppm). R$_f$ = 0.30 (70/30 *n*-heptane/EtOAc).

(*Z*)-2-((1-(4-Fluorophenyl)-1-(phenylthio)prop-1-en-2-yl)oxy)-5,5-dimethyl-1,3,2-dioxaphosphinane 2-oxide (3cA). 3cA was obtained according to **General procedure A**, from **1c** (1.0 equiv, 46 mg, 0.18 mmol), diazo compound **2A** (4.0 equiv, 127 mg, 0.71 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H$_2$O/MeCN) and by column chromatography on silica gel (eluent: 80/20 to 70/30 *n*-heptane/EtOAc) led to **3cA** (25 mg, 0.061 mmol, 34%, yellow oil) and recovered starting material **1c** (24 mg, 0.093 mmol, 52%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.24 – 7.17 (m, 4H), 7.16 – 7.11 (m, 2H), 7.11 – 7.05 (m, 1H), 6.92 – 6.85 (m, 2H), 4.42 (d, $^{3}J_{H-P}$ = 10.6 Hz, 2H), 3.93 (d, $^{3}J_{H-P}$ = 11.1 Hz, 1H), 3.88 (d, $^{3}J_{H-P}$ = 11.2 Hz, 1H), 2.21 (d, $^{4}J_{H-P}$ = 1.9 Hz, 3H), 1.31 (s, 3H), 0.82 (s, 3H). ^{31}P {^{1}H} NMR (202 MHz, CDCl$_3$) δ -14.71. ^{19}F {^{1}H} NMR (471 MHz, CDCl$_3$) δ -113.84.

^{13}C NMR (126 MHz, CDCl$_3$) δ 162.0 (d, $^{1}J_{C-F}$ = 247.5 Hz), 147.2 (d, $^{2}J_{C-P}$ = 6.8 Hz), 133.8, 132.8 (d, $^{4}J_{C-F}$ = 3.5 Hz), 131.8 (d, $^{3}J_{C-F}$ = 8.2 Hz), 130.6 (2C), 128.7 (2C), 126.7, 118.8 (d, $^{3}J_{C-P}$ = 9.9 Hz), 115.0 (d, $^{2}J_{C-F}$ = 21.7 Hz), 78.3 (d, $^{2}J_{C-P}$ = 6.9 Hz), 32.2 (d, J = 5.9 Hz), 21.9, 20.1, 19.2.

HRMS (ESI-TOF): Calculated for $C_{20}H_{23}FO_4PS$ [M+H]$^+$: 409.1039, Found: 409.1048 (Δ_{HRMS} = -3.29 ppm). R$_f$ = 0.22 (70/30 *n*-heptane/EtOAc).

(*Z*)-1-(4-Fluorophenyl)-1-((4-methoxyphenyl)thio)prop-1-en-2-yl diisopropyl phosphate (3dA). 3dA was obtained according to **General procedure A**, from **1d** (1.0 equiv, 55 mg, 0.18 mmol), diazo compound **2A** (4.0 equiv, 129 mg, 0.72 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H$_2$O/MeCN) led to **3dA** (38 mg, 0.084 mmol, 46%, yellow oil) and recovered starting material **1d** (10 mg, 0.033 mmol, 18%).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.17 – 7.12 (m, 2H), 7.11 – 7.04 (m, 2H), 6.85 – 6.79 (m, 2H), 6.65 – 6.60 (m, 2H), 4.92 – 4.82 (m, 2H), 3.70 (s, 3H), 1.40 (d, J = 6.2 Hz, 12H). ^{31}P {^{1}H} NMR (202 MHz, CDCl$_3$) δ -8.45. ^{19}F {^{1}H} NMR (471 MHz, CDCl$_3$) δ -114.51. ^{13}C NMR (126 MHz, CDCl$_3$) δ 161.8 (d, $^{1}J_{C-F}$ = 246.7 Hz), 159.1, 144.7 (d, $^{2}J_{C-P}$ = 7.6 Hz), 134.7 (2C), 133.0 (d, $^{4}J_{C-F}$ = 3.5 Hz), 131.7 (dd, $^{3}J_{C-F}$ = 8.1 Hz, J = 1.4 Hz, 2C), 123.9, 121.1 (d, $^{3}J_{C-P}$ = 9.8 Hz), 114.8 (d, $^{2}J_{C-F}$ = 21.5 Hz, 2C), 114.1 (2C), 73.4 (d, $^{2}J_{C-P}$ = 6.4 Hz), 55.2, 23.8 (d, $^{3}J_{C-P}$ = 2.8 Hz), 23.7 (d, $^{3}J_{C-P}$ = 3.6 Hz), 18.9.

HRMS (ESI-TOF): Calculated for $C_{22}H_{29}FO_5PS$ [M+H]$^+$: 455.1457, Found: 455.1456 (Δ_{HRMS} = -2.70 ppm). R$_f$ = 0.32 (70/30 *n*-heptane/EtOAc).

(*Z*)-1-((4-Bromophenyl)thio)-1-(4-fluorophenyl)prop-1-en-2-yl diisopropyl phosphate (3eA). 3eA was obtained according to **General procedure A**, from **1e** (1.0 equiv, 64 mg, 0.18 mmol), diazo compound **2A** (4.0 equiv, 129 mg, 0.72 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H$_2$O/MeCN) led to **3eA** (40 mg, 0.079 mmol, 44%, yellow oil).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.31 – 7.25 (m, 2H), 7.24 – 7.19 (m, 2H), 7.14 – 7.10 (m, 2H), 6.96 – 6.89 (m, 2H), 4.85 (dhept, $^{3}J_{H-P}$ = 7.3 Hz, J = 6.2 Hz, 2H), 2.17 (d, $^{4}J_{H-P}$ = 2.0 Hz, 3H), 1.41 (d, J = 6.2 Hz, 12H). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$) δ -8.61. ^{19}F {^{1}H} NMR (376 MHz, CDCl$_3$) δ -113.77. ^{13}C NMR (101 MHz, CDCl$_3$) δ 161.9 (d, $^{1}J_{C-F}$ =

247.6 Hz), 148.0 (d, ${}^{2}J_{C-P}$ = 7.4 Hz), 133.5 (d, J = 1.0 Hz), 133.0 (d, ${}^{4}J_{C-F}$ = 3.5 Hz), 132.4 (2C), 131.7 (dd, ${}^{3}J_{C-F}$ = 8.3 Hz, J = 1.4 Hz, 2C), 131.6 (d, J = 2.3 Hz, 2C), 120.6, 118.8 (d, ${}^{3}J_{C-P}$ = 9.7 Hz), 115.1 (d, ${}^{2}J_{C-F}$ = 21.6 Hz, 2C), 73.5 (d, ${}^{2}J_{C-P}$ = 6.4 Hz), 23.7 (d, ${}^{3}J_{C-P}$ = 2.5 Hz), 23.7 (d, ${}^{3}J_{C-P}$ = 3.3 Hz), 19.0 (d, J = 1.0 Hz).

HRMS (ESI-TOF): Calculated for $C_{21}H_{25}BrFNaO_4PS$ [M+Na]$^+$: 525.0271, Found: 525.0287 (Δ_{HRMS} = -2.68 ppm). R_f = 0.36 (70/30 *n*-heptane/EtOAc).

(*Z*)-Diisopropyl (1-phenyl-1-(phenylthio)prop-1-en-2-yl) phosphate (3aB). 3aB was obtained according to **General procedure A**, from **1a** (1.0 equiv, 49 mg, 0.18 mmol), diazo compound **2B** (4.0 equiv, 115 mg, 0.71 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) led to **3aB** (18 mg, 0.044 mmol, 25%, yellow oil) and recovered starting material **1a** (24 mg, 0.087 mmol, 49%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 4H), 7.20 – 7.15 (m, 2H), 7.14 – 7.08 (m, 3H), 7.06 – 7.02 (m, 1H), 4.83 (dp, ${}^{3}J_{H-P}$ = 7.3 Hz, J = 6.3 Hz, 2H), 2.16 (d, ${}^{4}J_{H-P}$ = 2.0 Hz, 3H), 1.37 (dd, J = 6.3 Hz, ${}^{4}J_{H-P}$ = 1.6 Hz, 12H). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$) δ -8.72. ^{13}C NMR (126 MHz, $CDCl_3$) δ 147.3 (d, ${}^{2}J_{C-P}$ = 7.3 Hz), 137.4, 134.5, 130.8 (2C), 130.1 (2C), 128.4 (2C), 127.9 (2C), 127.3, 126.3, 119.9 (d, ${}^{3}J_{C-P}$ = 9.9 Hz), 73.4 (d, ${}^{2}J_{C-P}$ = 6.4 Hz), 23.7 (d, ${}^{3}J_{C-P}$ = 4.7 Hz), 23.67 (d, ${}^{3}J_{C-P}$ = 5.9 Hz), 19.1.

HRMS (ESI-TOF): Calculated for $C_{21}H_{28}O_4PS$ [M+H]$^+$: 407.1446, Found: 407.1454 (Δ_{HRMS} = -3.15 ppm).

R_f = 0.44 (70/30 *n*-heptane/EtOAc).

(*Z*)-1,2-Diphenyl-2-(phenylthio)vinyl diisopropyl phosphate (3aC). 3aC was obtained according to **General procedure A**, from **1a** (1.0 equiv, 49 mg, 0.18 mmol), diazo compound **2C** (4.0 equiv, 159 mg, 0.71 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) and by column chromatography on silica gel (eluent: 95/5 to 70/30 *n*-heptane/EtOAc) led to **3aC** (45 mg, 0.096 mmol, 54%, yellow oil) and recovered starting material **1a** (11 mg, 0.038 mmol, 21%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.25 (ddd, J = 6.8, 3.0, 1.5 Hz, 5H), 7.16 – 7.00 (m, 7H), 6.95 (dd, J = 5.2, 2.0 Hz, 3H), 4.77 – 4.64 (m, J = 6.3 Hz, 2H), 1.28 (d, J = 6.3 Hz, 6H), 1.16 (d, J = 6.3 Hz, 6H). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$) δ -7.63. ^{13}C NMR (126 MHz, $CDCl_3$) δ 146.1 (d, ${}^{2}J_{C-P}$ = 9.3 Hz), 136.3, 134.9, 133.6, 131.9 (2C), 131.0 (2C), 130.0 (2C), 128.4 (2C), 128.3, 127.6 (2C), 127.6 (2C), 127.0, 126.6, 125.1 (d, ${}^{3}J_{C-P}$ = 8.6 Hz), 73.2 (d, ${}^{2}J_{C-P}$ = 6.0 Hz), 23.7 (d, ${}^{3}J_{C-P}$ = 4.2 Hz), 23.4 (d, ${}^{3}J_{C-P}$ = 6.0 Hz).

HRMS (ESI-TOF): Calculated for $C_{26}H_{30}O_4PS$ [M+H]$^+$: 469.1602, Found: 469.1609 (Δ_{HRMS} = -2.12 ppm). R_f = 0.31 (70/30 *n*-heptane/EtOAc).

(*Z*)-Diisopropyl (1-methoxy-2-phenyl-2-(phenylthio)vinyl) phosphate (3aD). 3aD was obtained according to **General procedure A**, from **1a** (1.0 equiv, 49 mg, 0.18 mmol), diazo compound **2D** (4.0 equiv, 126 mg, 0.71 mmol). Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) and by column chromatography on silica gel (eluent: 80/20 to 70/30 *n*-heptane/EtOAc) led to **3aD** (19 mg, 0.045 mmol, 25%, yellow oil) and recovered starting material **1a** (29 mg, 0.106 mmol, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.55 – 7.50 (m, 2H), 7.28 – 7.20 (m, 4H), 7.18 – 7.11 (m, 3H), 7.06 – 7.01 (m, 1H), 4.89 – 4.77 (m, 2H), 3.73 (s, 3H), 1.35 (d, J = 5.6 Hz, 6H), 1.33 (d, J = 5.6 Hz, 6H). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$) δ -9.01. ^{13}C NMR (126 MHz, $CDCl_3$) δ 155.1 (d, ${}^{2}J_{C-P}$ = 9.5 Hz), 136.3, 136.2, 129.4 (2C), 128.6 (2C), 127.9 (2C), 127.7 (2C), 126.9, 125.4, 99.4 (d, ${}^{3}J_{C-P}$ = 8.3 Hz), 74.1 (d, ${}^{2}J_{C-P}$ = 6.3 Hz), 59.7, 23.7 (d, ${}^{3}J_{C-P}$ = 4.6 Hz), 23.5 (d, ${}^{3}J_{C-P}$ = 5.7 Hz).

HRMS (ESI-TOF): Calculated for $C_{21}H_{28}O_5PS$ [M+H]$^+$: 423.1395, Found: 423.1399 (Δ_{HRMS} = -1.82 ppm). R_f = 0.43 (70/30 *n*-heptane/EtOAc).

(*Z*)-1-(4-Fluorophenyl)-1-((3-(4-fluorophenyl)-2-oxohex-5-en-3-yl)thio)prop-1-en-2-yl diisopropyl phosphate (4gA). 4gA was obtained according to **General procedure A**, from **1g** (1.0 equiv, 44 mg, 0.18 mmol), diazo compound **2A** (4.0 equiv, 132 mg, 0.72 mmol). 75% conversion was observed. Purification by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) and by column chromatography on silica gel (eluent: 95/5 to 70/30 *n*-heptane/EtOAc) led to **4gA** (53 mg, 0.098 mmol, 53%, yellow oil) and **5gA** (16 mg, 0.041 mmol, 17% NMR yield).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.18 – 7.07 (m, 4H), 6.93 (td, J = 8.6, 2.0 Hz, 4H), 5.65 (ddt, J = 17.1, 10.3, 6.9 Hz, 1H), 4.90 – 4.78 (m, 3H), 4.65 (dq, J = 17.1, 1.5 Hz, 1H), 2.05 (d, $^{4}J_{H-P}$ = 1.8 Hz, 3H), 1.87 (s, 3H), 1.42 – 1.35 (m, 12H). ^{31}P {^{1}H} NMR (202 MHz, CDCl$_3$) δ -9.07. ^{19}F {^{1}H} NMR (376 MHz, CDCl$_3$) δ -113.82, -114.44. ^{13}C NMR (101 MHz, CDCl$_3$) δ 203.7, 162.0 (d, $^{1}J_{C-F}$ = 247.8 Hz), 160.6 (d, $^{1}J_{C-F}$ = 248.2 Hz), 153.1 (d, $^{2}J_{C-P}$ = 7.1 Hz), 134.4 (d, J = 3.4 Hz), 134.0 (d, J = 3.4 Hz), 133.4, 132.0 (dd, J = 8.2, 1.3 Hz, 2C), 129.1 (d, J = 8.0 Hz, 2C), 118.1, 115.3 (d, J = 10.2 Hz) , 115.2 (d, $^{2}J_{C-F}$ = 21.6 Hz, 2C), 114.9 (d, $^{2}J_{C-F}$ = 21.6 Hz, 2C), 73.6 (d, $^{2}J_{C-P}$ = 6.3 Hz), 73.6 (d, $^{2}J_{C-P}$ = 6.3 Hz), 68.4, 40.6, 25.9, 23.8 – 23.7 (m, 4C), 18.8 (d, $^{3}J_{C-P}$ = 1.0 Hz).

HRMS (ESI-TOF): Calculated for $C_{27}H_{34}F_2O_5PS$ [M+H]$^+$: 539.1833, Found: 539.1847 (Δ_{HRMS} = -3.31 ppm).

R$_f$ = 0.38 (70/30 *n*-heptane/EtOAc).

(*Z*)-Diisopropyl (2-((1-oxo-1,2-diphenylpent-4-en-2-yl)thio)-1,2-diphenylvinyl) phosphate (4gC). 4gC was obtained according to **General procedure A**, from **4g** (1.0 equiv, 40 mg, 0.17 mmol), diazo compound **2C** (4.0 equiv, 149 mg, 0.67 mmol). 85% conversion was observed. Purification by column chromatography on silica gel (eluent: 90/10 to 70/30 *n*-heptane/EtOAc) and by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H$_2$O/MeCN) led to **4gC** (60 mg, 0.096 mmol, 57%, yellow oil).

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.51 – 7.47 (m, 2H), 7.35 – 7.29 (m, 3H), 7.30 – 7.18 (m, 3H), 7.17 – 6.98 (m, 7H), 6.94 – 6.86 (m, 4H), 5.92 (ddt, J = 17.2, 10.2, 7.0 Hz, 1H), 4.91 – 4.78 (m, 2H), 4.62 (ddt, J = 17.2, 2.5, 1.3 Hz, 1H), 4.53 (dq, $^{3}J_{H-P}$ = 12.5, 6.2 Hz, 1H), 2.84 – 2.72 (m, 2H), 1.36 (d, J = 6.2 Hz, 3H), 1.30 (dd, J = 6.2 Hz, $^{4}J_{H-P}$ = 1.0 Hz, 3H), 1.23 (d, J = 6.2 Hz, 3H), 1.01 (dd, J = 6.2 Hz, $^{4}J_{H-P}$ = 1.0 Hz, 3H). ^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$) δ -8.14. ^{13}C NMR (101 MHz, CDCl$_3$) δ 195.8, 151.4 (d, $^{2}J_{C-P}$ = 9.0 Hz), 140.1, 137.1, 134.9, 134.8, 133.7, 131.6, 131.2 (d, J = 1.7 Hz), 130.8, 129.9, 128.4, 128.3, 127.5, 127.4, 127.4, 127.3, 127.1, 121.3 (d, $^{3}J_{C-P}$ = 9.0 Hz), 118.1, 73.1 (d, $^{2}J_{C-P}$ = 5.8 Hz), 73.1 (d, $^{2}J_{C-P}$ = 5.8 Hz), 67.0, 43.7, 23.8 (d, $^{3}J_{C-P}$ = 4.0 Hz), 23.7 (d, $^{3}J_{C-P}$ = 5.9 Hz), 23.6 (d, $^{3}J_{C-P}$ = 4.0 Hz), 23.2 (d, $^{3}J_{C-P}$ = 6.5 Hz).

HRMS (ESI-TOF): Calculated for $C_{37}H_{40}O_5PS$ [M+H]$^+$: 627.2334, Found: 627.2344 (Δ_{HRMS} = -2.14 ppm). R$_f$ = 0.42 (70/30 *n*-heptane/EtOAc).

(Z)-1-(4-fluorophenyl)-1-((3-(4-fluorophenyl)-2-oxohexa-4,5-dien-3-yl)thio)prop-1-en-2-yl diisopropyl phosphate (4hA). 4hA was obtained according to **General procedure A**, from **4h** (1.0 equiv, 40 mg, 0.17 mmol), diazo compound **2A** (4.0 equiv, 121 mg, 0.68 mmol). Full conversion was observed. Compound **4hA** was obtained in 64% NMR yield, along with **5hA** (14% NMR yield), but was difficult to purify because it degraded rapidly. Only a small amount of **4hA** was isolated, enabling its characterization by ^{1}H and ^{31}P NMR.

^{1}H NMR (400 MHz, CDCl$_3$) δ 7.26 – 7.22 (m, 2H), 7.09 – 7.03 (m, 2H), 6.95 – 6.88 (m, 4H), 5.57 (t, J = 6.7 Hz, 1H), 4.84 (ddp, J = 9.9, 7.2, 6.2 Hz, 2H), 4.62 (d, J = 6.7 Hz, 2H), 2.06 (d, $^{4}J_{H-P}$ = 1.8 Hz, 3H), 1.92 (s, 3H), 1.42 – 1.37 (m, 12H).

^{31}P {^{1}H} NMR (162 MHz, CDCl$_3$) δ -9.13.

(*Z*)-Diisopropyl (2-((1-oxo-1,2-diphenylpenta-3,4-dien-2-yl)thio)-1,2-diphenylvinyl) phosphate (4hC). 4hC was obtained according to **General procedure A**, from **4h** (1.0 equiv, 28 mg, 0.12 mmol), diazo compound **2C** (4.0 equiv, 105 mg, 0.47 mmol). 90% conversion was observed. Purification by column chromatography on silica gel (eluent: 80/20 to 70/30 *n*-heptane/EtOAc) and by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H$_2$O/MeCN) led to **4hC** (46 mg, 0.074 mmol, 62%, yellow oil).

^{1}H NMR (500 MHz, CDCl$_3$) δ 7.61 – 7.57 (m, 2H), 7.36 – 7.30 (m, 3H), 7.24 – 7.14 (m, 5H), 7.12 – 6.99 (m, 6H), 6.97 – 6.90 (m, 4H), 5.86 (t, J = 6.6 Hz, 1H), 4.79 – 4.68 (m, J = 6.2 Hz, 1H), 4.57 – 4.44 (m, 3H), 1.29 (d, J = 6.2 Hz, 3H), 1.19 (d, J = 6.2 Hz, 3H), 1.17 (d, J = 6.2 Hz, 3H), 1.01 (d, J = 6.2 Hz, 3H). ^{31}P {^{1}H} NMR (202 MHz, CDCl$_3$) δ -8.30. ^{13}C NMR (126 MHz, CDCl$_3$) δ 208.1, 194.5, 152.0 (d, $^{2}J_{C-P}$ = 8.7 Hz), 139.4, 137.8, 134.9, 134.8, 131.9, 131.3 (d, *J* = 1.7 Hz), 130.7, 129.9, 128.4, 128.2, 128.0, 127.5 – 127.4 (m), 127.0, 95.8, 78.4, 73.1 (d, $^2J_{C\text{-}P}$ = 6.3 Hz), 73.1 (d, $^2J_{C\text{-}P}$ = 6.3 Hz), 67.8 (d, *J* = 1.7 Hz), 23.7 (d, $^3J_{C\text{-}P}$ = 4.1 Hz), 23.6 (d, $^3J_{C\text{-}P}$ = 4.1 Hz), 23.5 (d, $^3J_{C\text{-}P}$ = 6.3 Hz), 23.2 (d, $^3J_{C\text{-}P}$ = 6.3 Hz).

HRMS (ESI-TOF): Calculated for $C_{37}H_{38}O_5PS$ $[M+H]^+$: 625.2178, Found: 625.2166 (Δ_{HRMS} = 1.20 ppm). R_f = 0.14 (80/20 *n*-heptane/EtOAc).

(*Z*)-Diisopropyl (2-((1-oxo-1,2,3-triphenylpropan-2-yl)thio)-1,2-diphenylvinyl) phosphate (4iC). 4iC was obtained according to **General procedure A**, from **4i** (1.0 equiv, 49 mg, 0.17 mmol), diazo compound **2C** (4.0 equiv, 151 mg, 0.68 mmol). Purification by column chromatography on silica gel (eluent: 90/10 to 70/30 *n*-heptane/EtOAc) and by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) led to **4iC** (11 mg, 0.016 mmol, 24% NMR yield, 10% isolated yield, yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.66 – 7.59 (m, 2H), 7.32 (td, *J* = 7.3, 1.3 Hz, 1H), 7.20 – 6.93 (m, 20H), 6.74 – 6.70 (m, 2H), 4.67 (dp, *J* = 12.4, 6.2 Hz, 1H), 4.49 (dq, *J* = 12.4, 6.2 Hz, 1H), 3.65 (d, *J* = 13.7 Hz, 1H), 3.18 (d, *J* = 13.7 Hz, 1H), 1.30 (d, *J* = 6.2 Hz, 3H), 1.21 (d, *J* = 6.2 Hz, 3H), 1.20 (d, *J* = 6.2 Hz, 3H), 1.00 (d, *J* = 6.2 Hz, 3H). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$) δ -8.24. ^{13}C NMR (126 MHz, $CDCl_3$) δ 194.5, 151.3 (d, $^2J_{C\text{-}P}$ = 9.0 Hz), 139.8, 136.9, 136.8, 135.0, 134.6, 131.5, 131.4 (d, *J* = 1.8 Hz), 131.3, 129.9, 128.4, 128.1, 127.9, 127.5, 127.5, 127.4, 127.3, 127.1, 127.1, 125.9, 121.6 (d, $^3J_{C\text{-}P}$ = 9.0 Hz), 73.1 (d, $^2J_{C\text{-}P}$ = 6.3 Hz, 2C), 67.3 (d, *J* = 1.4 Hz), 46.2, 23.7 (d, $^3J_{C\text{-}P}$ = 4.1 Hz), 23.6 (d, $^3J_{C\text{-}P}$ = 2.3 Hz), 23.6 (d, $^3J_{C\text{-}P}$ = 4.1 Hz), 23.2 (d, $^3J_{C\text{-}P}$ = 6.3 Hz).

HRMS (ESI-TOF): Calculated for $C_{41}H_{42}O_5PS$ $[M+H]^+$: 677.2491, Found: 677.2469 (Δ_{HRMS} = 2.06 ppm). R_f = 0.31 (70/30 *n*-heptane/EtOAc).

Methyl (*Z*)-2-((2-((diisopropoxyphosphoryl)oxy)-2-methoxy-1-phenylvinyl)thio)-2,3-diphenylpropanoate (4iD)

4iD was obtained according to **General procedure B**, from **4i** (1.0 equiv, 51 mg, 0.18 mmol), diazo compound **2D** (4.0 equiv, 137 mg, 0.71 mmol). Purification by column chromatography on silica gel (eluent: 70/30 to 60/40 *n*-pentane/Et_2O) and by reversed phase chromatography on C18 column (eluent: 70/30 to 0/100 H_2O/MeCN) led to **4iD** (26 mg, 0.044 mmol, 25%, yellow oil).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.37 – 7.33 (m, 2H), 7.27 – 7.21 (m, 2H), 7.19 – 7.07 (m, 6H), 7.06 – 6.96 (m, 3H), 6.70 – 6.65 (m, 2H), 4.89 (dtd, *J* = 13.3, 12.3, 6.2 Hz, 2H), 3.62 (s, 3H), 3.56 (d, *J* = 13.7 Hz, 1H), 3.41 (s, 3H), 3.12 (d, *J* = 13.7 Hz, 1H), 1.39 (d, *J* = 6.2 Hz, 6H), 1.38 (d, *J* = 6.2 Hz, 3H), 1.34 (d, *J* = 6.2 Hz, 3H). ^{31}P {^{1}H} NMR (202 MHz, $CDCl_3$) δ -9.05. ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.4, 157.4 (d, $^2J_{C\text{-}P}$ = 9.7 Hz), 138.2, 137.3, 136.5, 130.9 (2C), 129.9 (d, *J* = 1.4 Hz, 2C), 128.6 (2C), 127.8 (2C), 127.3 (4C), 127.1, 126.8, 126.2, 98.7 (d, $^3J_{C\text{-}P}$ = 8.3 Hz), 74.1 (d, $^2J_{C\text{-}P}$ = 6.4 Hz), 74.1 (d, $^2J_{C\text{-}P}$ = 6.4 Hz), 64.4 (d, *J* = 1.7 Hz), 60.0, 51.9, 45.6, 23.8 (d, $^3J_{C\text{-}P}$ = 4.4 Hz, 2C), 23.6 (d, $^3J_{C\text{-}P}$ = 5.9 Hz), 23.5 (d, $^3J_{C\text{-}P}$ = 5.8 Hz).

HRMS (ESI-TOF): Calculated for $C_{31}H_{38}O_7PS$ $[M+H]^+$: 585.2076, Found: 585.2063 (Δ_{HRMS} = 1.36 ppm). R_f = 0.29 (70/30 *n*-heptane/EtOAc).

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Supplementary Material

The procedures for the synthesis of starting materials (i.e., phosphorothioates **1** and α-diazocarbonyl compounds **2**), as well as the copies of ^{1}H, ^{13}C, ^{19}F, and ^{31}P NMR spectra of products **3** and **4** are available in the Supplementary Material file associated with this paper.

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