

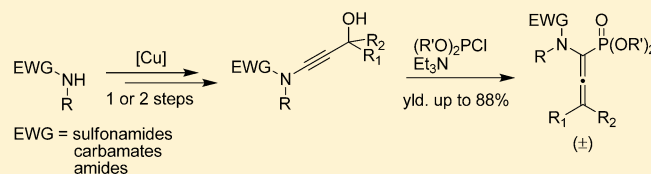
[2,3]-Sigmatropic Rearrangement of Ynamides: Preparation of α -Amino Allenephosphonates

Filipe Gomes, Antoine Fadel, and Nicolas Rabasso*

Laboratoire de Synthèse Organique et Méthodologie, ICMO, UMR CNRS 8182, Bât. 420, Université Paris-Sud, 15 rue Georges Clemenceau, 91405 Orsay Cedex, France

Supporting Information

ABSTRACT: α -Amino allenephosphonates were easily prepared in two steps from protected amines, propargyl alcohols, and chlorophosphites. First, ynamides were synthesized from unprotected 1-bromopropargyl alcohols using a copper(II) catalyzed coupling reaction. In the second step, the previously prepared ynamides were transformed directly to allenephosphonates through a [2,3]-sigmatropic rearrangement of propargyl phosphites. This efficient method led to the formation of a series of α -amino allenephosphonates with diverse substituents on the amine, the phosphonate, and the allene moieties.

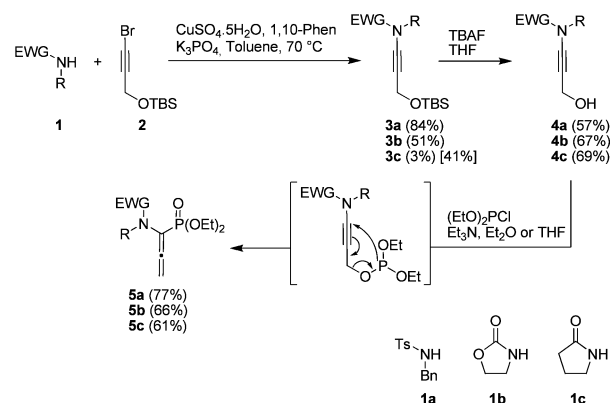


Over the past few years, ynamides have received considerable attention due to their ease of preparation by copper catalysis.^{1,2} Ynamides appeared to be useful synthons in natural product synthesis. Indeed, in 2005 Hsung and co-workers reported the synthesis of desbromoarborescines A and C based on an arene-ynamide cyclization step.³

Recently we reported the highly regio- and stereoselective synthesis of β -amino vinylphosphonates by hydrophosphonylation of ynamides.⁴ Continuing our efforts toward the preparation of amino vinylphosphonates, we became interested in amino allenephosphonates. Although the synthesis and transformation of allenephosphonates⁵ and alleneamides^{6,7} have been well described in the literature, to date the synthesis of amino allenephosphonates has not been reported. In addition to their obvious use as precursors of α -amino-phosphonates,⁸ α -amino allenephosphonates represent an interesting synthon due to the allene moiety that can be later functionalized to produce bioactive unsaturated aminophosphonates.^{9,10} Herein we report a straightforward synthesis of α -amino allenephosphonates by using ynamides as starting material.

The synthesis starts with the copper(II) coupling reaction between amines **1** and 1-bromoalkyne **2** to furnish ynamides **3**, following the protocol reported by Hsung and co-workers.¹¹ Deprotection of TBS ethers **3** led to the alcohols **4**, which were treated with diethyl chlorophosphite in the presence of triethylamine to give the corresponding α -amino allenephosphonates **5** in good yields (Scheme 1).^{12–16} Although efficient for the formation of α -amino allenephosphonates from tosylamine **1a** and oxazolidinone **1b**, this sequence failed with pyrrolidinone **1c**. Indeed, in that case, the yield for the preparation of ynamide **3c** was never higher than 3%. Improvements were made by using alkynylcopper reagents, as recently reported by Evano and co-workers,¹⁷ which led to ynamide **3c** in 41% yield. Moreover, because of the low solubility of ynamide **4c** in Et₂O, the synthesis of the allene **5c**

Scheme 1. Three-Step Sequence for the Preparation of Amino Allenephosphonates



was performed in THF. However, in that case the temperature was crucial; at 0 °C multiple products were obtained, whereas a clean amino allenephosphonate **5c** was obtained when the reaction was run at –78 °C and slowly warmed to rt.

Although efficient for the preparation of α -amino allenephosphonates as **5**, this three-step sequence suffers from the use of TBS protected propargyl alcohol **2**. In order to shorten this synthesis and avoid the protection of **2** as a silyl ether, *N*-tosyl ynamides **4a** and **7** were prepared directly from unprotected 1-bromopropargyl alcohols **6** and *N*-tosyl benzylamine **1a**. Thus, the resulting ynamides **4a** and **7**, prepared in moderate to excellent yields, were subjected to a [2,3]-sigmatropic rearrangement, by addition of diethyl chlorophosphite in the presence of triethylamine, to form the α -amino allenephosphonates **8** in good yields (Table 1). Although efficient for the

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Table 1. Scope and Limitations: Bromoalkyne Variation

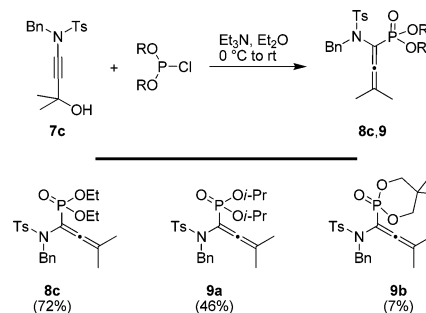
$\text{Bn-NH-Ts} + \text{Br-C}\equiv\text{C-CH}_2\text{OH} \xrightarrow[\text{Toluene, 70 } ^\circ\text{C}]{\text{CuSO}_4 \cdot 5\text{H}_2\text{O}, 1, 10\text{-Phen}, \text{K}_3\text{PO}_4} \text{Bn-N-Ts-C}\equiv\text{C-CH}_2\text{OH} \xrightarrow[\text{0 } ^\circ\text{C to rt}]{(\text{EtO})_2\text{P-Cl}, \text{Et}_3\text{N}, \text{Et}_2\text{O}} \text{Bn-N-Ts-C}\equiv\text{C-CH}_2\text{P(OEt)}_2$		
1a 6a-g	4a, 7	5a, 8
Bromoalkynes	Ynamides (yields [%])	Allenes (yields [%])
6a	4a (59%)	5a (77%)
6b	7b (60%)	8b (80%)
6c	7c (92%)	8c (72%)
6d	7d (90%)	8d (74%)
6e	7e (90%)	8e (77%)
6f	7f (50%)	8f (84%)
6g	7g (24%)	8g (88%)

preparation of α -amino allenephosphonates **8f** and **8g**, this strategy was challenging for the synthesis of precursor ynamides **7f** and **7g**. Indeed, for those the benzyl alcohol moiety is unstable, and decomposition occurred during the purification, which led to the ynamides **7f** and **7g** in moderate to low yields, 50 and 24%, respectively.

Next, we investigated the effect of the chlorophosphite reagent on the formation of the amino allenephosphonates (Scheme 2). Cyclic¹⁸ and acyclic¹⁹ chlorophosphite reagents were used to prepare allenephosphonates **9**.

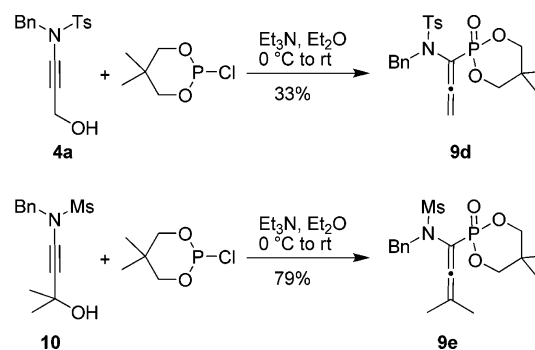
The low yields observed in the case of allenephosphonates **9** are explained by the steric hindrance of both the chlorophosphite reagent and the protecting group on the nitrogen atom. Indeed, further studies show that replacement of the tosyl group in ynamide **7c** by the mesyl group **10** increased the yield of allenephosphonate **9e** to 79%. Replacement of

Scheme 2. Scope and Limitations: Phosphite Variation

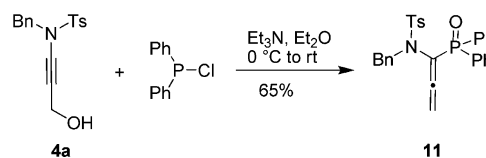


ynamide **7c** by **4a**, which does not bear the *gem*-dimethyl group, only moderately improves the yield of the [2,3]-sigmatropic rearrangement to 33% (Scheme 3).

Scheme 3. Effect of the Steric Hindrance on the Nitrogen Atom



To extend the scope of this [2,3]-sigmatropic rearrangement of ynamides, the same strategy was efficiently applied to the formation of α -amino allenephosphine oxide **11** with diphenyl chlorophosphine reagent (Scheme 4).

Scheme 4. Preparation of α -Amino Allenephosphine Oxide **11**

Finally, we investigated the influence of the electron-withdrawing groups on the nitrogen atom (Table 2). When the amine moiety is protected by a sulfonate and a benzyl group, the corresponding ynamides **10**, **12a** and α -amino allenephosphonates **13a,b** were obtained in good yields. However, with aniline derivatives, formation of ynamide **12c** required some adjustments. Indeed, our protocol without the use of protecting groups on the 1-bromopropargyl alcohol failed to provide the ynamide **12c** in the previous conditions. The use of the protocol developed by Stahl and co-workers provided the ynamide **12c** in moderate yield (40%).²⁰ Next, the latter was subjected to a [2,3]-rearrangement with diethyl chlorophosphite to furnish α -amino allenephosphonate **13c** in a moderate 53% yield. These conditions are difficult to adapt to all types of amines. Indeed, oxazolidinone **1b** was converted to ynamide **12d** in a low 21% yield. Moreover, the conversion to

Table 2. Scope and Limitations: α -Amino Allenephosphonates Formation with Representative Ynamides

Ynamides (yields [%])	Allenephosphonates (yields [%])
7c (92%)	8c (72%)
 12a (68%)	 13a (70%)
 10 (77%)	 13b (75%)
 12c (40%) ^a	 13c (53%)
 12d (21%)	 13d (26%) (40% BRSM) ^b

^aPreparation of ynamide **12c** was performed following the protocol reported by Stahl and co-workers.²⁰ ^bBRSM: Based on recovered starting material.

the corresponding allenephosphonate was also difficult (26% yield, 40% based on recovered starting material). This result can be explained by the steric hindrance induced by the oxazolidinone moiety and the presence of the *gem*-dimethyl group in the ynamide **12d**.

Extension of this methodology to other electron-withdrawing groups on the amine moiety such as Boc, acetyl, trifluoroacetyl, pyrrolidinyl, and phosphoryl failed to provide the respective ynamides by direct coupling with 1-bromopropargyl alcohol **6c**.

In conclusion, a variety of ynamides were easily transformed into α -amino allenephosphonates via a [2,3]-sigmatropic rearrangement of propargyl phosphites. This strategy yielded allenephosphonates in two steps from readily available amines and unprotected propargyl alcohols. Further developments are under way in our group to prepare these α -amino allenephosphonates in an enantiomerically pure form and investigate their reactivities.

EXPERIMENTAL SECTION

General Methods. All reactions were carried out under argon with magnetic stirring. All solvents and chemicals were purified on the basis

of standard procedures. Reagent grade solvents were used without purification for all extractions and workup procedures. *R_f* values refer to values obtained by TLC on 0.25 mm silica gel plates (60-F₂₅₄). Flash chromatography was performed on silica gel 60 (15–40 μ m) using a CombiFlash apparatus with various mixtures of ethyl acetate (EtOAc) and petroleum ether (PE). Yields refer to chromatographically and spectroscopically pure compounds. NMR measurements were performed at either 250, 300, or 360 MHz. HRMS spectra were recorded on a MicroTOFq spectrometer. 1-Bromopropargyl alcohols **2** and **6** were prepared following the protocol reported in the literature.²¹

General Method for the Preparation of Ynamides (Procedure A). Amines (2.19 mmol), CuSO₄·5H₂O (0.22 mmol), 1,10-phenanthroline (0.44 mmol), and K₃PO₄ (4.37 mmol) were heated to 70 °C in 5 mL of dry toluene under inert atmosphere. Bromoalkyne (3.28 mmol) in 5 mL of dry toluene was then slowly added. After 2–12 h at 70 °C, the mixture was cooled to room temperature, filtered through a pad of Celite, and concentrated in vacuo. Purification by flash chromatography on silica gel yielded the ynamides.

General Procedure for the Preparation of α -Amino Allenephosphonates (Procedure B). To a solution of ynamide (1.77 mmol) in 10 mL of anhydrous diethyl ether cooled at 0 °C were added triethylamine (1.94 mmol) and chlorophosphite (1.94 mmol). After 1–18 h of stirring at room temperature, the mixture was filtered through a pad of Celite, the solvent was removed in vacuo, and crude product was purified by flash chromatography on silica gel to yield the amino allenephosphonates.

N-Benzyl-N-[3-(*tert*-butyldimethylsilyloxy)prop-1-ynyl]-4-methylbenzenesulfonamide (3a). Prepared according to procedure A (3.3 g, 84% yield). Analytical data matched with that reported in the literature.²²

3-[3-(*tert*-Butyldimethylsilyloxy)prop-1-ynyl]oxazolidin-2-one (3b).²³ Prepared according to procedure A (428 mg, 51% yield). Analytical data matched with that reported in the literature.²³

1-[3-(*tert*-Butyldimethylsilyloxy)prop-1-ynyl]pyrrolidin-2-one (3c). Ynamide **3c** was prepared according to the procedure reported by Evano and co-workers.¹⁷ To a mixture of pyrrolidinone **1c** (24.6 mmol) and alkynylcopper (6.15 mmol), 12 mL of dry acetonitrile was added. Then, TMEDA (6.15 mmol) was added, and the mixture was stirred at room temperature under oxygen. After 3 days of stirring, the dark green solution was filtered through a pad of Celite, and the solvent was removed in vacuo, and then resulting crude product was purified by flash chromatography on silica gel (EtOAc/PE 20/80 to 80/20) to lead to ynamide **3c**, as a white solid (640 mg, 41% yield): mp 60–62 °C; *R_f* = 0.29 (EtOAc/PE = 20/80); ¹H NMR (250 MHz, CDCl₃) δ 4.46 (s, 2H), 3.67 (t, *J* = 7.3 Hz, 2H), 2.41 (dd, *J* = 7.3, 8.5 Hz, 2H), 2.10 (quint, *J* = 7.6 Hz, 2H), 0.88 (s, 9H), 0.10 (s, 6H); ¹³C NMR (90.56 MHz, CDCl₃) δ 176.2, 76.0, 71.5, 51.9, 49.9, 29.7, 25.9, 18.9, 18.9, –5.0; HRMS (ESI) *m/z* [MH⁺] calcd for C₁₃H₂₄NO₂Si 254.1571, found 254.1567.

N-Benzyl-N-(3-hydroxyprop-1-ynyl)-4-methylbenzenesulfonamide (4a).²⁴ Deprotection of ynamide **4a** followed the protocol reported by Zhang and co-workers (224 mg, 57% yield).²⁴ Direct synthesis of ynamide **4a** from amine **1a** followed procedure A (355 mg, 59% yield).

3-(3-Hydroxyprop-1-ynyl)oxazolidin-2-one (4b).²³ Deprotection of ynamide **3b** followed the protocol reported by Chemla and co-workers (150 mg, 67% yield).²³

1-(3-Hydroxyprop-1-ynyl)pyrrolidin-2-one (4c). Flash chromatography: EtOAc/PE 50/50 to 80/20; colorless oil, 255 mg, 69% yield; *R_f* = 0.24 (EtOAc/PE = 80/20); ¹H NMR (250 MHz, CDCl₃) δ 4.18 (s, 2H), 4.09 (br s, 1H), 3.49 (s, 2H), 2.28–2.20 (m, 2H), 1.90 (quint, *J* = 7.6 Hz, 2H); ¹³C NMR (62.9 MHz, CDCl₃) δ 176.7, 75.6, 71.3, 50.0, 49.5, 29.2, 18.3; HRMS (ESI) *m/z* [MH⁺] calcd for C₇H₁₀NO₂ 140.0706, found 140.0705.

Diethyl 1-(*N*-Benzyl-4-methylphenylsulfonamido)propa-1,2-dienylphosphonate (5a). Prepared according to procedure B. Flash chromatography: EtOAc/PE 20/80 to 60/40; colorless oil, 110 mg, 77% yield; *R_f* = 0.53 (EtOAc/PE = 90/10); IR (neat) 3084, 3062, 2929, 2908, 1868, 2239, 1955, 1927, 1597, 1492, 1455 cm^{–1}; ¹H NMR

(250 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.30 (d, J = 8.0 Hz, 2H), 7.26–7.20 (m, 5H), 5.04 (d, J = 10.4 Hz, 2H), 4.52 (s, 2H), 4.10–3.71 (m, 4H), 2.42 (s, 3H), 1.20 (td, J = 7.1, 0.7 Hz, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ 215.5 (d, J = 25.4 Hz), 143.8, 136.0, 135.6, 129.4, 129.1, 128.2, 128.1, 127.8, 99.6 (d, J = 232.8 Hz), 82.6 (d, J = 11.9 Hz), 62.9 (d, J = 6.0 Hz), 53.6, 21.5, 16.1 (d, J = 6.5 Hz); ³¹P NMR (101.25 MHz, CDCl₃) δ 10.9 HRMS (ESI) m/z [MH⁺] calcd for C₂₁H₂₇NO₃PS 436.1332, found 436.1342.

Diethyl 1-(2-Oxooxazolidin-3-yl)propa-1,2-dienylphosphonate (5b). Prepared according to procedure B. Flash chromatography: EtOAc(5% NH₃)/EP 60/40 to 100/0; colorless oil, 179 mg, 66% yield; R_f = 0.20 (EtOAc); ¹H NMR (360 MHz, CDCl₃) δ 5.37 (d, J = 10.7 Hz, 2H), 4.25 (dd, J = 8.9, 7.0 Hz, 2H), 4.13–3.88 (m, 4H), 3.74 (td, J = 7.8, 1.0 Hz, 2H), 1.20 (t, J = 7.1 Hz, 6H); ¹³C NMR (90.56 MHz, CDCl₃) δ 210.9 (d, J = 19.7 Hz), 155.7, 97.7 (d, J = 226.3 Hz), 84.1, 63.0 (d, J = 5.9 Hz), 62.1, 45.9, 15.9 (d, J = 6.6 Hz); ³¹P NMR (101.25 MHz, CDCl₃) δ 10.3; HRMS (ESI) m/z [MH⁺] calcd for C₁₀H₁₇NO₅P 262.0839, found 262.0837.

Diethyl 1-(2-Oxopyrrolidin-1-yl)propa-1,2-dienylphosphonate (5c). Prepared according to procedure B. The reaction was performed in THF at –78 °C. Flash chromatography: Et₂O/MeOH(5% NH₃) 98/2 to 92/8; colorless oil, 250 mg, 61% yield; R_f = 0.24 (Et₂O/MeOH(5% NH₃) 95/5); ¹H NMR (250 MHz, CDCl₃) δ 5.01 (d, J = 10.90 Hz, 2H), 3.77–3.65 (m, 4H), 3.22 (t, J = 7.27 Hz, 2H), 2.00–1.91 (m, 2H), 1.72–1.63 (m, 2H), 0.89 (t, J = 7.27 Hz, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ 210.4 (d, J = 18.5 Hz), 172.8 (d, J = 4.0 Hz), 97.2 (d, J = 222.0 Hz), 82.1 (d, J = 11.9 Hz), 62.1 (d, J = 5.3 Hz), 47.9, 29.7, 17.5, 15.3 (d, J = 6.6 Hz); ³¹P NMR (101.25 MHz, CDCl₃) δ 10.9; HRMS (ESI) m/z [MH⁺] calcd for C₁₁H₁₉NO₄P 260.1046, found 260.1045.

N-Benzyl-N-(3-hydroxybut-1-ynyl)-4-methylbenzenesulfonamide (7b).²⁵ Prepared according to procedure A (1.5 g, 60% yield).

N-Benzyl-N-(3-hydroxy-3-methylbut-1-ynyl)-4-methylbenzenesulfonamide (7c). Prepared according to procedure A. Flash chromatography: EtOAc/PE 10/90 to 50/50; yellow oil, 2.4 g, 92% yield; R_f = 0.75 (EtOAc/PE = 50/50); ¹H NMR (250 MHz, CDCl₃) δ 7.76 (d, J = 8.3 Hz, 2H), 7.45–7.13 (m, 7H), 4.46 (s, 2H), 2.45 (s, 3H), 2.42 (s, 1H), 1.40 (s, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ 144.7, 134.6, 134.5, 129.8, 129.1, 128.5, 128.4, 127.8, 76.2, 65.3, 55.5, 31.4, 21.7; HRMS (ESI) m/z [MH⁺] calcd for C₁₉H₂₂NO₃S 344.1315, found 344.1309.

N-Benzyl-N-[(1-hydroxycyclopentyl)ethynyl]-4-methylbenzenesulfonamide (7d). Prepared according to procedure A. Flash chromatography: EtOAc/PE 10/90 to 60/40; yellow oil, 1.2 g, 90% yield; R_f = 0.62 (EtOAc/PE = 40/60); ¹H NMR (250 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.38–7.27 (m, 7H), 4.51 (s, 2H), 2.49 (s, 3H), 2.35 (s, 1H), 1.91–1.57 (m, 8H); ¹³C NMR (62.9 MHz, CDCl₃) δ 144.7, 134.7, 134.5, 129.7, 129.0, 128.5, 128.4, 127.8, 77.1, 75.4, 74.6, 55.5, 42.4, 23.4, 21.7; HRMS (ESI) m/z [MH⁺] calcd for C₂₁H₂₄NO₃S 370.1471, found 370.1469.

N-Benzyl-N-(3-hydroxy-3-methylpent-1-ynyl)-4-methylbenzenesulfonamide (7e). Prepared according to procedure A. Flash chromatography: EtOAc/PE 20/80 to 80/20; colorless oil, 699 mg, 90% yield; R_f = 0.73 (EtOAc/PE = 40/60); ¹H NMR (250 MHz, CDCl₃) δ 7.77 (d, J = 8.2 Hz, 2H), 7.45–7.15 (m, 7H), 4.47 (s, 2H), 2.46 (s, 3H), 2.37 (s, 1H), 1.58 (qd, J = 7.3, 3.5 Hz, 2H), 1.36 (s, 3H), 0.86 (t, J = 7.4 Hz, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ 144.7, 134.7, 134.5, 129.8, 129.0, 128.5, 128.4, 127.8, 75.1, 68.9, 65.9, 55.5, 36.6, 29.4, 21.7, 9.0; HRMS (ESI) m/z [MH⁺] calcd for C₂₀H₂₄NO₃S 358.1471, found 358.1465.

N-Benzyl-N-(3-hydroxy-3-phenylbut-1-ynyl)-4-methylbenzenesulfonamide (7f). Prepared according to procedure A. Flash chromatography: EtOAc/PE 20/80 to 60/40; yellow oil, 379 mg, 50% yield; R_f = 0.53 (EtOAc/PE = 50/50); ¹H NMR (360 MHz, CDCl₃) δ 7.78 (dd, J = 8.4, 1.6 Hz, 2H), 7.44 (ddd, J = 6.8, 3.2, 1.6 Hz, 2H), 7.42–7.19 (m, 10H), 4.53 (AB syst, Δ_{AB} = 23.4 Hz, J_{AB} = 13.6 Hz, 2H), 2.98 (d, J = 1.4 Hz, 1H), 2.46 (s, 3H), 1.67 (d, J = 1.4 Hz, 3H); ¹³C NMR (90.56 MHz, CDCl₃) δ 145.5, 144.7, 134.4, 134.3, 129.8, 129.0, 128.5, 128.4, 128.1, 127.8, 127.4, 125.0, 78.6, 75.1, 70.0, 55.3,

33.1, 21.6; HRMS (ESI) m/z [MH⁺] calcd for C₂₄H₂₄NO₃S 406.1471, found 406.1465.

N-Benzyl-N-(3-hydroxy-3-phenylprop-1-ynyl)-4-methylbenzenesulfonamide (7g). Prepared according to procedure A. Flash chromatography: EtOAc/PE 10/90 to 50/50; orange oil, 372 mg, 24% yield; R_f = 0.61 (EtOAc/PE = 40/60); ¹H NMR (250 MHz, CDCl₃) δ 7.76 (d, J = 8.3 Hz, 2H), 7.32 (d, J = 4.4 Hz, 12H), 5.49 (d, J = 5.2 Hz, 1H), 4.52 (AB syst, Δ_{AB} = 21.5 Hz, J_{AB} = 14.0 Hz, 2H), 2.99 (d, J = 5.4 Hz, 1H), 2.44 (s, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ 144.7, 140.6, 134.4, 134.2, 129.8, 128.8, 128.5, 128.4, 128.0, 127.7, 126.6, 80.0, 71.7, 64.5, 55.3, 21.6; HRMS (ESI) m/z [MH⁺] calcd for C₂₃H₂₂NO₃S 392.1315, found 392.1310.

Diethyl 1-(N-Benzyl-4-methylphenylsulfonamido)buta-1,2-dienylphosphonate (8b). Prepared according to procedure B. Flash chromatography: EtOAc/PE 20/80 to 70/30; yellow oil, 185 mg, 80% yield; R_f = 0.24 (EtOAc/PE = 50/50); ¹H NMR (250 MHz, CDCl₃) δ 7.81 (d, J = 8.3 Hz, 2H), 7.34–7.15 (m, 7H), 5.45 (dq, J = 10.1, 7.4 Hz, 1H), 4.54 (s, 2H), 4.00–3.75 (m, 4H), 2.40 (s, 3H), 1.46 (dd, J = 7.4, 4.9 Hz, 3H), 1.19 (td, J = 7.1, 1.9 Hz, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ 212.7 (d, J = 25.4 Hz), 143.5, 136.3, 135.8, 129.3, 129.0, 128.2, 128.0, 127.6, 98.2 (d, J = 234.3 Hz), 94.2 (d, J = 12.0 Hz), 62.6 (d, J = 6.0 Hz), 53.2, 21.5, 16.1 (d, J = 6.3 Hz), 12.7 (d, J = 4.8 Hz); ³¹P NMR (101.25 MHz, CDCl₃) δ 11.4; HRMS (ESI) m/z [MH⁺] calcd for C₂₂H₂₉NO₅PS 450.1499, found 450.1498.

Diethyl 1-(N-Benzyl-4-methylphenylsulfonamido)-3-methylbuta-1,2-dienylphosphonate (8c). Prepared according to procedure B. Flash chromatography: EtOAc/PE 20/80 to 100/0; white solid, 242 mg, 72% yield; mp 86–88 °C; R_f = 0.24 (EtOAc/PE = 50/50); ¹H NMR (250 MHz, CDCl₃) δ 7.80 (d, J = 8.3 Hz, 2H), 7.42–7.06 (m, 7H), 4.56 (s, 2H), 4.03–3.63 (m, 4H), 2.38 (s, 3H), 1.50 (d, J = 4.5 Hz, 6H), 1.16 (td, J = 7.0, 0.7 Hz, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ 210.5 (d, J = 25.5 Hz), 143.3, 136.8, 136.0, 129.3, 128.8, 128.1, 127.9, 127.5, 104.7 (d, J = 12.1 Hz), 95.6 (d, J = 236.0 Hz), 62.4 (d, J = 6.0 Hz), 52.9, 21.4, 19.1 (d, J = 4.6 Hz), 16.1 (d, J = 6.5 Hz); ³¹P NMR (101.25 MHz, CDCl₃) δ 10.0; HRMS (ESI) m/z [MH⁺] calcd for C₂₃H₃₁NO₅PS 464.1655, found 464.1663.

Diethyl 1-(N-Benzyl-4-methylphenylsulfonamido)-2-cyclopentylidenevinylphosphonate (8d). Prepared according to procedure B. Flash chromatography: EtOAc/PE 20/80 to 80/20; white solid, 785 mg, 74% yield; mp 64–66 °C; R_f = 0.23 (EtOAc/PE = 40/60); ¹H NMR (250 MHz, CDCl₃) δ 7.78 (d, J = 8.3 Hz, 2H), 7.36–7.04 (m, 7H), 4.55 (s, 2H), 3.97–3.67 (m, 4H), 2.37 (s, 3H), 2.31–2.03 (m, 4H), 1.69–1.44 (m, 4H), 1.15 (t, J = 7.1 Hz, 6H); ¹³C NMR (62.9 MHz, CDCl₃) δ 205.7 (d, J = 25.4 Hz), 143.2, 136.6, 136.0, 129.2, 128.8, 128.0, 127.9, 127.4, 112.9 (d, J = 12.4 Hz), 97.6 (d, J = 236.9 Hz), 62.3 (d, J = 6.0 Hz), 53.1, 31.1 (d, J = 4.0 Hz), 26.7, 21.3, 16.0 (d, J = 6.6 Hz); ³¹P NMR (101.25 MHz, CDCl₃) δ 12.1; HRMS (ESI) m/z [MH⁺] calcd for C₂₅H₃₃NO₃PS 490.1812, found 490.1821.

Diethyl 1-(N-Benzyl-4-methylphenylsulfonamido)-3-methylpenta-1,2-dienylphosphonate (8e). Prepared according to procedure B. Flash chromatography: EtOAc/PE 20/80 to 80/20; white solid, 650 mg, 77% yield; mp 67–68 °C; R_f = 0.18 (EtOAc/PE = 40/60); ¹H NMR (250 MHz, CDCl₃) δ 7.93 (d, J = 8.3 Hz, 2H), 7.48–7.15 (m, 7H), 4.68 (AB syst, Δ_{AB} = 20.2 Hz, J_{AB} = 15.0 Hz, 2H), 4.14–3.77 (m, 4H), 2.49 (s, 3H), 1.96 (tq, J = 7.7, 4.2 Hz, 2H), 1.61 (d, J = 4.5 Hz, 3H), 1.28 (td, J = 7.0, 5.2 Hz, 6H), 0.92 (t, J = 7.4 Hz, 3H); ¹³C NMR (62.9 MHz, CDCl₃) δ 210.1 (d, J = 25.5 Hz), 143.4, 137.0, 136.2, 129.4, 128.9, 128.2, 128.1, 127.6, 110.7 (d, J = 11.9 Hz), 96.8 (d, J = 235.9 Hz), 62.4, 53.0, 27.0 (d, J = 4.2 Hz), 21.6, 17.4 (d, J = 4.8 Hz), 16.2 (d, J = 6.5 Hz), 11.5; ³¹P NMR (101.25 MHz, CDCl₃) δ 12.3; HRMS (ESI) m/z [MH⁺] calcd for C₂₄H₃₃NO₃PS 478.1812, found 478.1810.

Diethyl 1-(N-Benzyl-4-methylphenylsulfonamido)-3-phenylbuta-1,2-dienylphosphonate (8f). Prepared according to procedure B. Flash chromatography: EtOAc/PE 20/80 to 80/20; yellow oil, 404 mg, 84% yield; R_f = 0.29 (EtOAc/PE = 50/50); IR (neat) 3087, 3063, 3031, 2981, 2929, 2900, 2860, 2235, 1929, 1597, 1494, 1455 cm^{–1}; ¹H NMR (360 MHz, CDCl₃) δ 7.84 (d, J = 8.1 Hz, 2H), 7.33 (dd, J = 6.6, 3.0 Hz, 2H), 7.23 (td, J = 7.2, 6.8, 3.6 Hz, 8H), 7.10 (dd, J

= 6.3, 3.1 Hz, 2H), 4.89 (AB syst, $\Delta\nu_{AB}$ = 22.7 Hz, J_{AB} = 14.7 Hz, 2H), 4.06–3.85 (m, 4H), 2.38 (s, 3H), 1.93 (d, J = 4.6 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.15 (t, J = 7.0 Hz, 3H); ^{13}C NMR (90.56 MHz, CDCl_3) δ 213.0 (d, J = 23.6 Hz), 143.4, 136.7, 136.0, 133.3 (d, J = 5.6 Hz), 129.4, 128.9, 128.4, 128.3, 128.0, 127.7, 126.6, 109.3 (d, J = 12.2 Hz), 99.5 (d, J = 232.5 Hz), 62.8 (d, J = 7.0 Hz), 62.7 (d, J = 7.0 Hz), 52.8, 21.5, 16.2 (d, J = 7.2 Hz), 16.1 (d, J = 4.7 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 10.9; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{28}\text{H}_{33}\text{NO}_5\text{PS}$ 526.1812, found 526.1807.

Diethyl 1-(*N*-Benzyl-4-methylphenylsulfonamido)-3-phenylpropa-1,2-dienylphosphonate (8g). Prepared according to procedure B. Flash chromatography: EtOAc/PE 10/90 to 50/50; red solid, 401 mg, 88% yield; mp 39–41 °C; R_f = 0.24 (EtOAc/PE = 40/60); ^1H NMR (250 MHz, CDCl_3) δ 7.85 (d, J = 8.4 Hz, 2H), 7.49–7.14 (m, 10H), 6.95 (dd, J = 6.2, 2.4 Hz, 2H), 6.47 (d, J = 9.9 Hz, 1H), 4.68 (s, 2H), 4.17–3.82 (m, 4H), 2.38 (s, 3H), 1.21 (t, J = 7.0 Hz, 3H), 1.16 (t, J = 7.0 Hz, 3H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 213.5 (d, J = 23.5 Hz), 143.6, 136.3, 135.8, 130.3 (d, J = 6.0 Hz), 129.4, 128.8, 128.6, 128.3, 128.0, 127.6, 102.1 (d, J = 230.8 Hz), 101.7 (d, J = 12.1 Hz), 63.0 (d, J = 5.1 Hz), 62.9 (d, J = 5.1 Hz), 53.0, 21.4, 16.1 (d, J = 6.5 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 10.2; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{27}\text{H}_{31}\text{NO}_5\text{PS}$ 512.1653, found 512.1655.

Diisopropyl 1-(*N*-Benzyl-4-methylphenylsulfonamido)-3-methylbuta-1,2-dienylphosphonate (9a). Flash chromatography: EtOAc(5% NH_3)/PE 10/90 to 80/20; yellow oil, 134 mg, 46% yield; R_f = 0.26 (EtOAc/PE = 30/70); ^1H NMR (360 MHz, CDCl_3) δ 7.85 (d, J = 9.1 Hz, 2H), 7.15–7.40 (m, 7H), 4.63 (s, 2H), 4.38–4.56 (m, 2H), 2.40 (s, 3H), 1.54 (d, J = 4.5 Hz, 6H), 1.23 (d, J = 6.1 Hz, 6H), 1.14 (d, J = 6.4 Hz, 6H); ^{13}C NMR (90.56 MHz, CDCl_3) δ 210.6 (d, J = 26.4 Hz), 143.2, 137.2, 136.2, 129.3, 128.9, 128.2, 128.0, 127.4, 104.4 (d, J = 11.9 Hz), 97.0 (d, J = 237.8 Hz), 71.3 (d, J = 6.6 Hz), 52.8, 24.0 (d, J = 2.6 Hz), 23.7 (d, J = 5.3 Hz), 21.5, 19.1 (d, J = 5.3 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 10.1; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{25}\text{H}_{35}\text{NO}_5\text{PS}$ 492.1968, found 492.1973.

***N*-Benzyl-*N*-[1-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-3-methylbuta-1,2-dien-1-yl]-4-methylbenzenesulfonamide (9b).** Flash chromatography: EtOAc/PE 30/70 to 100/0; yellow oil, 21 mg, 7% yield; R_f = 0.65 (EtOAc/PE = 100/0); ^1H NMR (250 MHz, CDCl_3) δ 7.80 (d, J = 8.3 Hz, 2H), 7.39–7.22 (m, 7H), 4.63 (s, 2H), 4.15–3.61 (m, 4H), 2.42 (s, 3H), 1.56 (d, J = 4.6 Hz, 6H), 1.20 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (90.56 MHz, CDCl_3) δ 210.8 (d, J = 26.5 Hz), 143.7, 137.0, 135.9, 129.6, 129.6, 128.4, 128.1, 127.8, 105.2 (d, J = 12.4 Hz), 94.2 (d, J = 232.3 Hz), 77.2 (d, J = 6.7 Hz), 53.0, 32.4 (d, J = 7.1 Hz), 22.0, 21.7, 20.9, 19.5, 19.4; ^{31}P NMR (101.25 MHz, CDCl_3) δ 3.9; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{24}\text{H}_{31}\text{NO}_5\text{PS}$ 476.1655, found 476.1653.

***N*-Benzyl-*N*-[1-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)propa-1,2-dien-1-yl]-4-methylbenzenesulfonamide (9d).** Flash chromatography: EtOAc/PE 30/70 to 100/0; yellow oil, 93 mg, 33% yield; R_f = 0.24 (EtOAc/PE = 40/60); ^1H NMR (250 MHz, CDCl_3) δ 7.79 (d, J = 8.3 Hz, 2H), 7.41–6.82 (m, 7H), 5.10 (d, J = 10.7 Hz, 2H), 4.57 (s, 2H), 4.03–3.67 (m, 4H), 2.42 (s, 3H), 1.20 (s, 3H), 0.80 (s, 3H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 215.3 (d, J = 26.0 Hz), 143.9, 136.1, 135.4, 129.7, 129.5, 128.3, 128.1, 127.9, 98.3 (d, J = 227.9 Hz), 82.8 (d, J = 11.9 Hz), 77.4 (d, J = 6.8 Hz), 53.6, 32.4 (d, J = 7.2 Hz), 21.9, 21.6, 20.7; ^{31}P NMR (101.25 MHz, CDCl_3) δ 2.4; HRMS (ESI) m/z $[\text{MNa}^+]$ calcd for $\text{C}_{22}\text{H}_{26}\text{NO}_5\text{PSNa}$ 470.1162, found 470.1160.

***N*-Benzyl-*N*-[1-(5,5-dimethyl-2-oxido-1,3,2-dioxaphosphinan-2-yl)-3-methylbuta-1,2-dien-1-yl]-4-methylsulfonamide (9e).** Flash chromatography: EtOAc(5% NH_3)/PE 30/70 to 90/10; white solid, 293 mg, 79% yield; mp 99–100 °C; R_f = 0.54 (EtOAc(5% NH_3)/PE = 90/10); ^1H NMR (250 MHz, CDCl_3) δ 7.40 (dd, J = 7.9, 1.4 Hz, 2H), 7.33–7.16 (m, 3H), 4.72 (s, 2H), 3.99–3.74 (m, 4H), 2.93 (s, 3H), 1.57 (d, J = 4.6 Hz, 6H), 1.22 (s, 3H), 0.79 (s, 3H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 210.4 (d, J = 27.4 Hz), 135.7, 129.2, 128.3, 127.8, 104.6 (d, J = 12.2 Hz), 93.9 (d, J = 227.4 Hz), 77.3 (d, J = 6.8 Hz), 52.8, 40.5, 32.3 (d, J = 7.1 Hz), 21.8, 20.5, 19.2 (d, J = 4.6 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 3.9; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{18}\text{H}_{27}\text{NO}_5\text{PS}$ 400.1342, found 400.1328.

***N*-Benzyl-*N*-(3-hydroxy-3-methylbut-1-ynyl)-methanesulfonamide (10).** Prepared following procedure A. Flash chromatography: EtOAc(5% NH_3)/PE 20/80 to 80/20; yellow oil, 1.1 g, 77% yield; R_f = 0.31 (EtOAc/PE = 50/50); ^1H NMR (250 MHz, CDCl_3) δ 7.30–7.46 (m, 5H), 4.56 (s, 2H), 2.90 (s, 1H), 2.82–2.88 (m, 3H), 1.46 (s, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 134.5, 129.1, 128.8, 76.5, 65.3, 55.5, 38.7, 31.4; HRMS (ESI) m/z $[\text{MNa}^+]$ calcd for $\text{C}_{13}\text{H}_{17}\text{NO}_3\text{SNa}$ 290.0821, found 290.0825.

***N*-Benzyl-*N*-[1-(diphenylphosphoryl)propa-1,2-dienyl]-4-methylbenzenesulfonamide (11).** Prepared following procedure B. Flash chromatography: EtOAc/PE 50/50 to 100/0; colorless oil, 140 mg, 65% yield; R_f = 0.56 (EtOAc = 100); ^1H NMR (250 MHz, CDCl_3) δ 7.66 (d, J = 8.3 Hz, 2H), 7.59–7.44 (m, 6H), 7.43–7.31 (m, 4H), 7.30–7.11 (m, 7H), 4.88 (d, J = 8.7 Hz, 2H), 4.61 (s, 2H), 2.40 (s, 3H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 214.9 (d, J = 22.1 Hz), 143.6, 135.7, 135.5, 132.7, 131.9, 131.8, 129.4, 129.3, 128.2, 128.0, 127.7, 103.1 (d, J = 124.4 Hz), 83.3, 53.8, 21.5; ^{31}P NMR (101.25 MHz, CDCl_3) δ 24.0; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{29}\text{H}_{27}\text{NO}_3\text{PS}$ 500.1444, found 500.1446.

***N*-(3-Hydroxy-3-methylbut-1-ynyl)-*N*-(4-methoxybenzyl)-4-methylbenzenesulfonamide (12a).** Flash chromatography: EtOAc(5% NH_3)/PE 10/90 to 50/50; yellow solid, 1.7 g, 68% yield; mp = 56–58 °C; R_f = 0.59 (EtOAc/PE = 50/50); ^1H NMR (360 MHz, CDCl_3) δ 7.76 (d, J = 8.0 Hz, 2H), 7.33 (d, J = 8.0 Hz, 2H), 7.21 (d, J = 8.2 Hz, 2H), 6.83 (d, J = 8.1 Hz, 2H), 4.40 (s, 2H), 3.80 (s, 3H), 2.48 (s, 1H), 2.45 (s, 3H), 1.42 (s, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 166.5, 159.2, 155.2, 144.4, 137.3, 129.6, 129.4, 127.8, 118.0, 113.9, 55.3, 48.5, 27.2, 21.6, 20.7; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{20}\text{H}_{24}\text{NO}_4\text{S}$ 374.1421, found 374.1414.

***N*-(3-Hydroxy-3-methylbut-1-ynyl)-4-methyl-*N*-phenylbenzenesulfonamide (12c).** Flash chromatography: EtOAc(5% NH_3)/PE 10/90 to 100/0; white solid, 294 mg, 40% yield; mp 100–102 °C; R_f = 0.28 (EtOAc/PE = 20/80); ^1H NMR (300 MHz, CDCl_3) δ 7.58 (d, J = 8.3 Hz, 2H), 7.39–7.15 (m, 7H), 2.46 (br s, 3H), 1.96 (br s, 1H), 1.55 (s, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 145.2, 138.9, 132.9, 129.6, 129.2, 128.4, 128.3, 126.2, 76.4, 75.5, 65.4, 31.6, 21.8; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{18}\text{H}_{20}\text{NO}_3\text{S}$ 330.1158, found 330.1152.

3-(3-Hydroxy-3-methylbut-1-ynyl)oxazolidin-2-one (12d). Flash chromatography: EtOAc/PE 50/50 to 80/20; white solid, 77 mg, 21% yield; mp 84–86 °C; R_f = 0.21 (EtOAc/PE = 50/50); ^1H NMR (360 MHz, CDCl_3) δ 4.31–4.52 (m, 2H), 3.89 (dd, J = 8.63, 7.27 Hz, 2H), 2.35 (s, 1H), 1.55 (s, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 156.5, 75.8, 72.4, 65.1, 63.2, 46.8, 31.5; HRMS (ESI) m/z $[\text{MNa}^+]$ calcd for $\text{C}_8\text{H}_{11}\text{NO}_3\text{Na}$ 192.0631, found 192.0635.

Diethyl 1-[*N*-(4-Methoxybenzyl)-4-methylphenylsulfonamido]-3-methylbuta-1,2-dienylphosphonate (13a). Flash chromatography: EtOAc/PE 10/90 to 60/40; colorless oil, 201 mg, 70% yield; R_f = 0.44 (EtOAc/PE = 80/20); ^1H NMR (250 MHz, CDCl_3) δ 7.83 (d, J = 8.2 Hz, 2H), 7.29 (d, J = 8.2 Hz, 2H), 7.23 (d, J = 8.7 Hz, 2H), 6.80 (d, J = 8.6 Hz, 2H), 4.52 (s, 2H), 3.99–3.85 (m, 4H), 3.77 (s, 3H), 2.42 (s, 3H), 1.56 (d, J = 4.5 Hz, 6H), 1.22 (t, J = 7.1 Hz, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 210.6 (d, J = 25.8 Hz), 159.1, 143.2, 137.0, 130.3, 129.3, 128.1, 127.9, 113.6, 104.6 (d, J = 12.2 Hz), 95.5 (d, J = 236.6 Hz), 62.5, 55.2, 52.5, 21.5, 19.1 (d, J = 5.1 Hz), 16.2 (d, J = 6.7 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 12.1; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{24}\text{H}_{33}\text{NO}_6\text{PS}$ 494.1761, found 494.1754.

Diethyl 1-(*N*-Benzylmethylsulfonamido)-3-methylbuta-1,2-dienylphosphonate (13b). Flash chromatography: EtOAc/PE 20/80 to 80/20; yellow oil, 269 mg, 75% yield; R_f = 0.39 (EtOAc/PE = 90/10); ^1H NMR (250 MHz, CDCl_3) δ 7.30–7.06 (m, 5H), 4.57 (s, 2H), 3.96–3.78 (m, 4H), 2.90 (s, 3H), 1.42 (d, J = 4.4 Hz, 6H), 1.14 (t, J = 7.0 Hz, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 211.1 (d, J = 26.8 Hz), 135.8, 128.6, 128.1, 127.5, 103.7 (d, J = 11.9 Hz), 94.4 (d, J = 231.1 Hz), 62.3 (d, J = 6.1 Hz), 52.4, 40.0, 18.7 (d, J = 4.6 Hz), 15.9 (d, J = 6.6 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 12.1; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{17}\text{H}_{27}\text{NO}_3\text{PS}$ 388.1342, found 388.1335.

Diethyl 3-Methyl-1-(4-methyl-*N*-phenylphenylsulfonamido)buta-1,2-dienylphosphonate (13c). Flash chromatography: EtOAc/PE 30/70 to 100/0; white solid, 41 mg, 53% yield; mp

107–109 °C; R_f = 0.16 (EtOAc/PE = 50/50); ^1H NMR (250 MHz, CDCl_3) δ 7.46 (d, J = 8.2 Hz, 2H), 7.27–7.37 (m, 5H), 7.22 (d, J = 8.2 Hz, 2H), 3.86–4.13 (m, 4H), 2.43 (s, 3H), 1.88 (d, J = 4.7 Hz, 6H), 1.20 (t, J = 7.0 Hz, 6H); ^{13}C NMR (62.9 MHz, CDCl_3) δ 208.17 (d, J = 25.2 Hz), 143.5, 140.1, 136.5, 129.0, 128.9, 128.8, 128.1, 127.9, 106.2 (d, J = 12.5 Hz), 99.2 (d, J = 237.0 Hz), 62.5 (d, J = 5.0 Hz), 21.6, 19.8 (d, J = 5.0 Hz), 16.1 (d, J = 7.0 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 11.7; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{22}\text{H}_{29}\text{NO}_5\text{PS}$ 450.1499, found 450.1489.

Diethyl 3-Methyl-1-(2-oxooxazolidin-3-yl)buta-1,2-dienylphosphonate (13d). Flash chromatography: EtOAc(5% NH_3)/PE 30/70 to 100/0; colorless oil, 34 mg, 26% yield; R_f = 0.20 (EtOAc(5% NH_3)/PE = 90/10); ^1H NMR (400 MHz, CDCl_3) δ 4.36 (t, J = 7.9 Hz, 2H), 4.20–4.12 (m, 4H), 3.88 (t, J = 7.8 Hz, 2H), 1.89 (d, J = 4.9 Hz, 6H), 1.34 (t, J = 7.0 Hz, 6H); ^{13}C NMR (90.56 MHz, CDCl_3) δ 205.4 (d, J = 20.3 Hz), 156.4, 106.4 (d, J = 8.3 Hz), 94.8 (d, J = 232.5 Hz), 63.0 (d, J = 4.6 Hz), 62.1, 46.3, 20.0 (d, J = 5.3 Hz), 16.3 (d, J = 6.6 Hz); ^{31}P NMR (101.25 MHz, CDCl_3) δ 11.5; HRMS (ESI) m/z $[\text{MH}^+]$ calcd for $\text{C}_{12}\text{H}_{21}\text{NO}_5\text{P}$ 290.1152, found 290.1144.

■ ASSOCIATED CONTENT

■ Supporting Information

^1H and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at <http://pubs.acs.org/>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: nicolas.rabasso@u-psud.fr.

Notes

The authors declare no competing financial interest.

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■ REFERENCES

- (1) Evano, G.; Coste, A.; Jouvin, K. *Angew. Chem., Int. Ed.* **2010**, 49, 2840.
- (2) De Korver, K. A.; Li, H.; Lohse, A. G.; Hayashi, R.; Lu, Z.; Zhang, Y.; Hsung, R. P. *Chem. Rev.* **2010**, 110, 5064.
- (3) Zhang, Y. S.; Hsung, R. P.; Zhang, X. J.; Huang, J.; Slafer, B. W.; Davis, A. *Org. Lett.* **2005**, 7, 1047.
- (4) Fadel, A.; Legrand, F.; Evano, G.; Rabasso, N. *Adv. Synth. Catal.* **2011**, 353, 263.
- (5) Chakravarty, M.; Kumara Swamy, K. C. *J. Org. Chem.* **2006**, 71, 9128.
- (6) Anorbe, L.; Poblador, A.; Dominguez, G.; Perez-Castells, J. *Tetrahedron Lett.* **2004**, 45, 4441.
- (7) Li, X.-X.; Zhu, L.-L.; Zhou, W.; Chen, Z. *Org. Lett.* **2012**, 14, 1185.
- (8) Kukhar, V. P.; Hudson, H. R., Eds.; *Aminophosphonic and Aminophosphinic Acids: Chemistry and Biological Activity*; Wiley: Hoboken, NJ, 2000.
- (9) Krause, N.; Hashmi, A. S. K., Eds.; *Modern Allene Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, 2004.
- (10) Orsini, F.; Sello, G.; Sisti, M. *Curr. Med. Chem.* **2010**, 17, 264.
- (11) Zhang, Y. S.; Hsung, R. P.; Tracey, M. R.; Kurtz, K. C. M.; Vera, E. L. *Org. Lett.* **2004**, 6, 1151.
- (12) Mark, V. *Tetrahedron Lett.* **1962**, 3, 281.
- (13) Boisselle, A. P.; Meinhardt, N. A. *J. Org. Chem.* **1962**, 27, 1828.
- (14) Pudovik, A. N.; Aladzheva, I. M.; Yakovenko, L. N. *Zh. Obshch. Khim.* **1963**, 33, 3443.
- (15) Pudovik, A. N.; Aladzheva, I. M. *Dokl. Akad. Nauk SSSR* **1963**, 151, 1110.
- (16) Pudovik, A. N.; Aladzheva, I. M. *Dokl. Chem.* **1963**, 151, 634.
- (17) Jouvin, K.; Heimburger, J.; Evano, G. *Chem. Sci.* **2012**, 3, 756.

(18) Matos, R. M.; Gomes de Lima, L. C.; de Souza, E.; Barcelos de Souza, A. L. A.; Gomes de Lima, M. B.; Soares Raslan, D. *Phosphorus, Sulfur Silicon Relat. Elem.* **2002**, 177, 2859.

(19) Collins, D. J.; Drygala, P. F.; Swan, J. M. *Aust. J. Chem.* **1983**, 36, 2517.

(20) Hamada, T.; Ye, X.; Stahl, S. S. *J. Am. Chem. Soc.* **2008**, 130, 833.

(21) Basak, S.; Srivastava, S.; Le, N. W. *J. Org. Chem.* **1987**, 52, 5095.

(22) Dooleweerd, K.; Birkedal, H.; Ruhland, T.; Skrydstrup, T. *J. Org. Chem.* **2008**, 73, 9447.

(23) Chemla, F.; Dulong, F.; Ferreira, F.; Nullen, M. P.; Perez-Luna, A. *Synthesis* **2011**, 1347.

(24) Yao, B.; Liang, Z.; Niu, T.; Zhang, Y. *J. Org. Chem.* **2009**, 74, 4630.

(25) Barbazanges, M.; Meyer, C.; Cossy, J.; Turner, P. *Chem.—Eur. J.* **2011**, 17, 4480.