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Nickel-catalyzed regio- and stereoselective hydrophosphinylation of internal ynamides with *H*-phosphinates

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ABSTRACT

A method for the catalytic hydrophosphinylation of internal ynamides with *H*-phosphinates has been developed for the first time. The protocol employing the catalyst generated from $NiBr_2$ and PPh_3 could be applied to several types of ynamides and *H*-phosphinates, affording (*E*)-β-aminovinylphosphinates in a highly regio- and stereoselective manner.

1. Introduction

Phosphinic acid derivatives are an important class of compounds because of their usefulness in medicinal chemistry [1] and organocatalysis [2]. Some β-aminophosphinic acid derivatives function as potent inhibitors for protease enzymes [3–5] and integrin antagonists [6]. Several synthetic methods for these compounds have been developed, involving nucleophilic addition of (1,1-diethoxyethyl)methylphosphinate to imines [7], the Michael addition of amines to vinylphosphinates [8], addition of hypophosphorus acid to *N*-vinylphthalimide [9], and ring opening of *N*-tosyl aziridines with phosphinic nucleophiles [10,11]. The transition metal-catalyzed addition of *H*-phosphinates to alkenes and alkynes is a powerful and efficient method for preparing phosphinic acid derivatives [12,13]. Various alkynes are applicable to this hydrophosphinylation for the preparation of alkenylphosphinates; however, examples of similar reactions employing ynamides [14], which are amino alkynes containing an electron-withdrawing substituent at the nitrogen atom and are useful synthons for organic synthesis, had not been reported. In 2017, we succeeded in the first development of Cu-catalyzed hydrophosphinylation of ynamides, followed by conversion of the products to β-aminophosphinates (Scheme 1) [15]. The reactions of terminal ynamides proceeded efficiently in the presence of $Cu(OAc)_2$ catalyst, giving (*E*)-β-aminovinylphosphinates in high regio- and stereoselectivities. However, the method was limited to terminal ynamides because the reaction of internal ynamides resulted in complicated mixtures. Therefore, alternative protocols of hydrophosphinylation to improve the substrate limitation are desirable. A related report by Rabasso and co-workers revealed that hydrophosphonylation of internal ynamides with dialkyl phosphites proceeded by using $NiBr_2$ as a catalyst [16], while Kang and co-workers disclosed a hydrophosphorylation of internal ynamides with diaryl phosphine oxides under metal-free conditions [17]. In this paper, we report a hydrophosphinylation of internal ynamides catalyzed by $NiBr_2$-PPh_3, affording (*E*)-β-aminovinylphosphinates in a highly regio- and stereoselective manner (Scheme 1).

2. Results and discussion

The requisite ynamides **2b** and **2d** were prepared by alkynylation of carbamates **1b** and **1d** according to Danheiser's method [18] and Hsung's method [19], respectively (Scheme 2). Other compounds **2a** [15], **2c** [20], **2e**, **g**, **h**, **j** [21], **2f** [22], **2i** [23], and **2k** [24] were prepared according to literature procedures.

In order to achieve the desired transformation, internal ynamide **2a** and *H*-phosphinate **3a** were employed as model substrates to optimize the reaction parameters, in particular the transition metal catalysts (Table 1). When **2a** was treated with **3a** in the presence of $NiBr_2$ (10 mol %) in toluene at reflux for 2 h, the adduct **4** was

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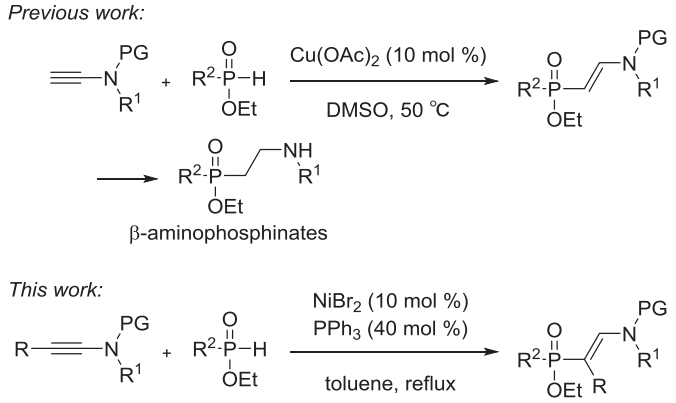
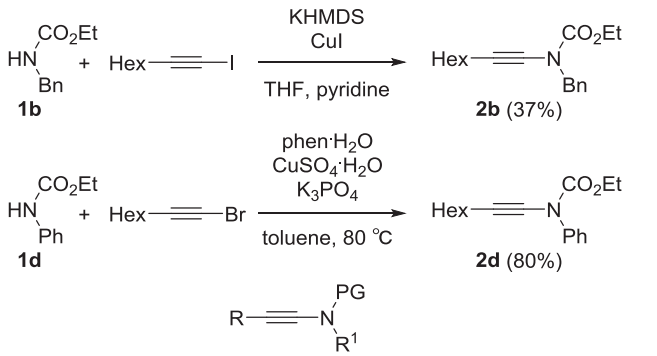


Scheme 1. Catalytic hydrophosphinylation of terminal and internal ynamides.



2a: R=Hex, R^1=Bn, PG=Cbz
2c: R=Hex, R^1=Bn, PG=Ts
2e: R=Ph, R^1=Bn, PG=Ts
2f: R=4-$MeO_2CC_6H_4$, R^1=Bn, PG=Ts
2g: R=4-$MeOC_6H_4$, R^1=Bn, PG=Ts
2h: R=4-ClC_6H_4, R^1=Bn, PG=Ts
2i: R=CO_2Et, R^1=Bn, PG=Ts
2j: R=TIPS, R^1=Bn, PG=Ts
2k: R=H, R^1=Bn, PG=Ts

Scheme 2. Preparation of ynamides.

Table 1
Optimization of reaction conditions.

Entry	Catalyst	Ligand (mol %)	Time (h)	Yield (%)[a]
1	$NiBr_2$	None	2	55
2	$NiCl_2$	None	2	0
3	NiI_2	None	2	46
4	$Ni(acac)_2$	None	6	15
5	$PdCl_2$	None	2	0
6	$FeCl_2$	None	18	Trace
7	AgCl	None	2	0
8	AuCl	None	2	0
9	$NiBr_2$	PPh_3 (20)	2	76
10	$NiBr_2$	PPh_3 (40)	2	99
11	$NiBr_2$	PPh_2Me (40)	2	37
12	$NiBr_2$	P(*o*-Tol)$_3$ (40)	2	50
13	$NiBr_2$	P(*n*-Bu)$_3$ (40)	2	41
14[b]	$NiBr_2$	PPh_3 (40)	24	19
15	$Ni(cod)_2$	PPh_3 (40)	3	80

[a] Isolated yield.
[b] Carried out at room temperature.

obtained in 55% yield (entry 1). The formation of other isomers could not be detected by ^1H and ^{31}P NMR analysis of the crude products, indicating the reaction proceeded in a highly regio- and stereoselective manner. The stereochemistry of **4** was confirmed to be the *E* configuration by NOE experiments (Fig. 1). The reagent $NiCl_2$ could not catalyze the reaction, with 61% of **2a** recovered

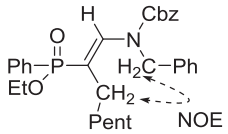
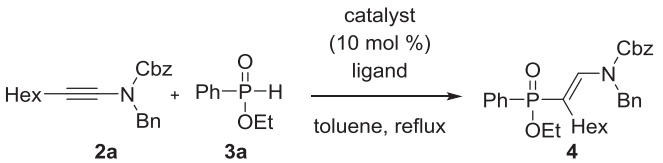


Fig. 1. NOE correlation of **4**.

(entry 2). The use of NiI_2 and $Ni(acac)_2$ decreased the chemical yields in comparison with that of $NiBr_2$ (entries 3 and 4). Other metal complexes with affinities for π-electrons such as $PdCl_2$, $FeCl_2$, AgCl, and AuCl failed to catalyze the reaction (entries 5–8). It is clear that the reactivity depended upon the ligands, since employing PPh_3 (20 mol %) in combination with $NiBr_2$ led to an increase in the chemical yield (76%, entry 9). The yield was significantly improved up to 99% by loading 40 mol % of PPh_3 (entry 10). When the reaction was carried out using less bulky PPh_2Me in place of PPh_3, which has been shown to be effective ligand for the related Ni-catalyzed hydrophosphonylation of alkynes [25], the yield was decreased to 37% (entry 11). The use of P(*o*-Tol)$_3$ and more basic P(*n*-Bu)$_3$ resulted in similar decreased chemical yields (entries 12 and 13). The reactions using bidentate ligands (dppe, dppp, bipy, phen) were examined, however, no product or only a trace amount of **4** was observed. The results demonstrate PPh_3 is a good ligand for the present hydrophosphinylation among those examined. The reaction at room temperature proceeded quite sluggishly, providing **4** in a low yield after 24 h (entry 14), thus indicating that toluene at reflux was necessary for the reaction to proceed. $Ni(cod)_2$ and PPh_3 were also found to catalyze the reaction efficiently, which suggested that zerovalent nickel species might be associated with the catalysis (entry 15).



With the reaction conditions optimized, the scope of ynamide substrates **2b-k** was examined (Table 2). The hydrophosphinylation of **2b**, which contained an ethoxycarbonyl group in place of Cbz, with **3a** proceeded regio- and stereoselectively to give **5** in 99% yield (entry 1). The *E* stereochemistry of **5** was verified by NOE. Ynamides **2c** having a tosyl group and **2d** having a phenyl group on the nitrogen atom also furnished the target products **6** and **7** in 78% and 97% yields, respectively (entries 2 and 3). Aryl-substituted ynamides **2e-h** proved to be applicable substrates (entries 4–7), although the reaction of **2h** bearing a 4-chlorophenyl group only gave a moderate chemical yield, which might be ascribed to insertion of the catalyst into the aromatic C–Cl bond [26]. On the other hand, the reactions of ethoxycarbonyl- and TIPS-substituted ynamides **2i** and **2j** did not afford the desired products resulting in complicated mixtures, wherein each ynamide was not recovered (Table 2, entries 8 and 9). When the terminal ynamide **2k** was employed, only a trace amount of the product was formed (entry 10). Our previous work demonstrated that $Cu(OAc)_2$-catalyzed hydrophosphinylation of **2k** with **3a** gave the product in good yield (90%) [15], therefore, the catalytic system utilizing $NiBr_2$-PPh_3 for internal ynamides was complementary to our previous methodology for terminal ynamides.

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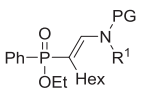
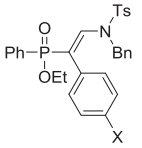
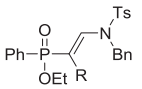
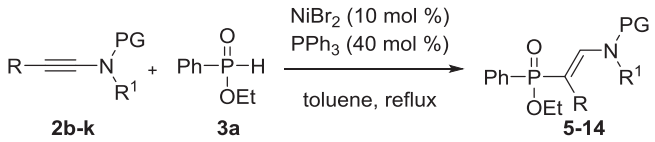
Table 2
Substrate scope for ynamides.

Entry	2	Product		Time (h)	Yield (%)[a]
					
1	**2b**	PG = CO_2Et, R^1 = Bn	**5**	2	99
2	**2c**	PG = Ts, R^1 = Bn	**6**	4	78
3	**2d**	PG = CO_2Et, R^1 = Ph	**7**	2	97
					
4	**2e**	X = H	**8**	4	97
5	**2f**	X = CO_2Me	**9**	4	77
6	**2g**	X = MeO	**10**	6	83
7	**2h**	X = Cl	**11**	6	55
					
8	**2i**	R = CO_2Et	**12**	6	0
9	**2j**	R = TIPS	**13**	2	0
10	**2k**	R = H	**14**	2	trace

[a] Isolated yield.

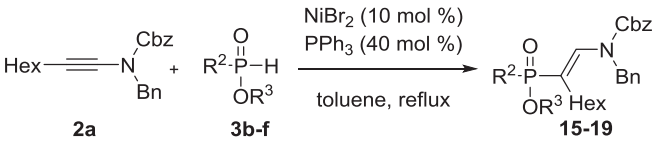


The substrate scope for *H*-phosphinates **3b-f** was subsequently investigated (Table 3). The reaction of **2a** with **3b** having an isopropyl phosphinate moiety instead of ethyl phosphinate **3a** gave the product **15** in 90% yield (entry 1). The use of *tert*-butyl phosphinate **3c** brought about a deterioration in chemical yield, probably due to steric hindrance (entry 2). Compounds **3d** possessing a decyl phosphinate moiety and **3e** with a benzyl group on the phosphorus atom worked well under the present conditions (entries 3 and 4). However, the reaction with **3f** containing a 1,1-diethoxyethyl group resulted in a complicated mixture, which might be due to decomposition of the acetal moiety by Lewis acidic $NiBr_2$ (entry 5).

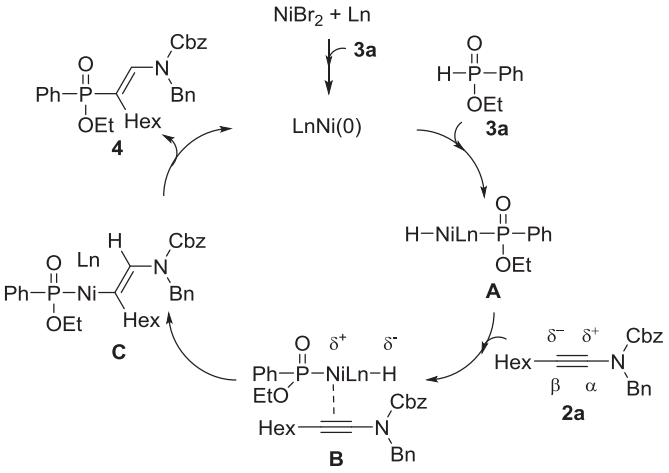
Table 3
Substrate scope for *H*-phosphinates.

Entry	3	Product		Time (h)	Yield (%)[a]
1	**3b**	R^2 = Ph, R^3 = *i*-Pr	**15**	2	90
2	**3c**	R^2 = Ph, R^3 = *t*-Bu	**16**	5	48
3	**3d**	R^2 = Ph, R^3 = Dec	**17**	3	86
4	**3e**	R^2 = Bn, R^3 = Et	**18**	4	75
5	**3f**	R^2 = $C(OEt)_2Me$, R^3 = Et	**19**	2	0

[a] Isolated yield.



On the basis of these experimental results and related reports, the catalytic cycle for the present hydrophosphinylation is proposed as illustrated in Scheme 3. The zerovalent $Ni(cod)_2$ as well as $NiBr_2$ was found to catalyze the reaction efficiently (Table 1), thus, we consider Ni(II)/Ni(0) catalytic cycle would proceed. Montchamp and co-workers elucidated that reduction of $NiCl_2$ with an alkyl phosphinate occurred to form a Ni(0) species [13a], therefore, we also propose that a Ni(0) species might be generated from $NiBr_2$ and ligand (Ln) through reduction with *H*-phosphinate **3a**. The subsequent reaction of this nickel species with **3a** would afford complex **A** via oxidative addition [12a,13d] or complexation of Ni(0) to the P(III) phosphinate tautomer [13a]. **A** then undergoes π-complexation with ynamide **2a** to provide **B**. Next, H—Ni addition to the C—C triple bond occurs to form *syn* adduct **C**, and subsequent reductive elimination affords the product **4** with regeneration of the Ni(0) species. Insertion of C—C triple bond into the H—Ni bond, rather than into the P(O)—Ni, would take place, because theoretical study on Ni-catalyzed hydrophosphorylation of alkynes by Ananikov and co-workers reported alkyne insertion into the M-H bond should be much easier compared to alkyne insertion into the M-P bond [27]. Although exact reason for high regioselectivity remained unclear, it might be associated with interaction between partially negative charged hydrogen of H—Ni and partially positive charged α carbon of ynamides because of their polarization of triple bond by nitrogen atom in the complex **B** [14]. We proposed that the role of ligand PPh_3 would be to stabilize the unstable Ni(0) species, and contribute to promoting reductive elimination from the complex **C**. A theoretical study on Ni- and Pd-catalyzed Heck reactions suggested that conversion of Ni(II) into Ni(0) by reductive elimination of hydrogen halide after β-hydride elimination would be relatively difficult to proceed due to the unstable Ni(0) species [28]. However, the detailed role of PPh_3, such as steric and electronic effect, is not clear at present. The proposed catalytic cycle is different from that of the related hydrophosphonylation [16], wherein Ni(II) is an active catalyst simply acting as a strong Lewis acid to activate electron-rich triple bond of ynamides.



Scheme 3. Possible reaction mechanism.

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3. Conclusion

In conclusion, a highly regio- and stereoselective hydrophosphinylation of internal ynamides catalyzed by $NiBr_2$-PPh_3 was achieved. The present method was applicable to alkyl- and aryl-substituted internal ynamides containing *N*-Ts and *N*-Cbz groups, and *H*-phosphinates with less bulky alkyl groups. Both internal and terminal ynamides could be applied to the synthesis of β-aminophosphinic acid derivatives by using this and our previously developed method. Investigations into a detailed reaction mechanism and the preparation of biologically active compounds are now underway.

4. Experimental

All melting points were obtained on a Yanagimoto micromelting point apparatus and are uncorrected. IR spectra were recorded on a JASCO FTIR-4100 instrument. Mass spectra were measured on a JEOL JMS-MS700V instrument by FAB^+. NMR spectra were obtained on a JEOL JNM-ECA500 instrument. The chemical shift data for each signal on ^1H NMR are given in units of δ relative to $CHCl_3$ (δ = 7.26) for $CDCl_3$ solution. For ^{13}C NMR spectra, the chemical shifts in $CDCl_3$ are recorded relative to the $CDCl_3$ resonance (δ = 77.0). The chemical shifts of ^{31}P are recorded relative to external 85% H_3PO_4 (δ = 0) with broad-band ^1H decoupling. Commercial reagents were used as received. Starting materials **3a** [29], **3b** [30], **3c** [31], **3d** [32], **3e** [33], and **3f** [34] were prepared according to literature procedures.

4.1. Ethyl benzyl(oct-1-yn-1-yl)carbamate *2b*

To a solution of **1b** (1.57 g, 6.67 mmol) in pyridine (39.0 mL) was added THF (6.0 mL) and KHMDS (0.5 M toluene solution, 13.5 mL, 6.74 mmol) at 0 °C under an Ar atmosphere, and the mixture was stirred at the same temperature for 10 min. To the mixture was added CuI (1.27 g, 6.67 mmol) at 0 °C, and the mixture was stirred at room temperature for 2 h. Then, to the mixture was added a solution of 1-iodooct-1-yne (2.36 g, 10.0 mmol) in THF (7.0 mL) at room temperature, and the mixture was stirred at same temperature for 15 h. The reaction mixture was diluted with brine and extracted with Et_2O. The organic layer was washed with brine, dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by a silica gel column chromatography (hexane/AcOEt = 20: 1) to give **2b** (710 mg, 37% yield) as a colorless oil: IR (neat) cm^{-1}: 2929, 2262, 1718, 1496, 1455; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.35–7.29 (5H, m), 4.59 (2H, s), 4.23 (2H, q, *J* = 6.9 Hz), 2.24 (2H, t, *J* = 6.9 Hz), 1.44 (2H, t, *J* = 7.5 Hz), 1.35–1.22 (9H, m), 0.88 (3H, t, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 155.7, 136.4, 128.4 (2C), 128.3, 127.7 (2C), 63.0, 53.6, 31.3, 28.9, 28.3, 22.5, 18.4, 14.4, 14,0, (two signal was missing); HRMS (FAB^+) calcd for $C_{18}H_{26}NO_2$ ($[M+H]^+$) 288.1964, found 288.1983.

4.2. Ethyl oct-1-yn-1-yl(phenyl)carbamate *2d*

A mixture of 1-bromooct-1-yne (330 mg, 2.00 mmol), **1d** (416 mg, 2.20 mmol), K_3PO_4 (849 mg, 4.00 mmol), $CuSO_4{\cdot}5H_2O$ (50.0 mg, 0.200 mmol) and 1,10-phenanthroline·H_2O (72.0 mg, 0.400 mmol) in toluene (10.0 mL) was stirred at the 80 °C for 48 h. After the mixture was cooled to room temperature, it filtered through a short path silica gel column. The filtrate was concentrated under reduced pressure to give the residue, which was purified by a silica gel column chromatography (hexane/AcOEt = 30: 1) to give **2d** (435 mg, 80% yield) as a pale yellow oil: IR (neat) cm^{-1}: 2929, 2268, 1732, 1596, 1492, 1458; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.48 (2H, d, *J* = 7.5 Hz), 7.35 (2H, t, *J* = 7.5 Hz), 7.24 (1H, t, *J* = 7.5 Hz), 4.29 (2H, q, *J* = 6.9 Hz), 2.33 (2H, t, *J* = 6.9 Hz), 1.55–1.51 (2H, m), 1.43–1.26 (9H, m), 0.88 (3H, t, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.8, 140.0, 128.7 (2C), 126.4, 124.4 (2C), 73.8, 69.7, 63.3, 31.3, 28.8, 28.5, 22.5, 18.4, 14.3, 14.0; HRMS (FAB^+) calcd for $C_{17}H_{24}NO_2$ ($[M+H]^+$) 274.1807, found 274.1827.

4.3. Typical procedure for the catalytic hydrophosphinylation of internal ynamides

To a solution of *H*-phosphinate **3a** (24.5 mg, 0.144 mmol) and ynamide **2a** (54.6 mg, 0.156 mmol) in toluene (2.0 mL) was added $NiBr_2$ (3.0 mg, 13.6 μmol) and PPh_3 (14.3 mg, 54.4 μmol) at room temperature under an Ar atmosphere and the mixture was refluxed for 2 h. After the mixture was cooled to room temperature, it was added H_2O and was extracted AcOEt. The organic layer was washed with H_2O and brine, and dried over $MgSO_4$, filtered and concentrated under reduced pressure. The residue was purified by a preparative TLC (AcOEt) to give alkenylphosphinate **4** (74.0 mg, 99% yield) as a colorless oil.

4.4. Benzyl (E)-benzyl(2-(ethoxy(phenyl)phosphoryl)oct-1-en-1-yl) carbamate *4*

Colorless oil; IR (neat) cm^{-1}: 2956, 2928, 1715, 1622, 1496, 1455, 1438; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 35.3; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.65 (2H, dd, *J* = 11.5, 8.0 Hz), 7.48 (1H, t, *J* = 7.5 Hz), 7.39–7.24 (11H, m), 7.17 (2H, d, *J* = 6.9 Hz), 5.20 (2H, s), 4.79 (2H, q, *J* = 16.0 Hz), 3.98–3.90 (2H, m), 2.04–1.95 (2H, m), 1.25 (3H, t, *J* = 6.9 Hz), 1.21–0.97 (8H, m), 0.79 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.7, 138.4 (d, J_{PC} = 22.8 Hz), 137.0, 135.6, 131.8 (d, J_{PC} = 2.4 Hz), 131.7, 131.5 (2C, d, J_{PC} = 9.6 Hz), 128.6 (2C), 128.5 (2C), 128.4, 128.3, 128.3, 128.2, 128.1 (2C), 127.4 (2C), 126.9, 68.4, 60.7 (d, J_{PC} = 4.8 Hz), 50.9, 31.2, 29.3, 28.7, 27.0 (d, J_{PC} = 8.4 Hz), 22.4, 16.3 (d, J_{PC} = 7.2 Hz), 14.0; HRMS (FAB^+) calcd for $C_{31}H_{39}NO_4P$ ($[M+H]^+$) 520.2617, found 520.2665.

4.5. Ethyl (E)-benzyl(2-(ethoxy(phenyl)phosphoryl)oct-1-en-1-yl) carbamate *5*

This compound (61.7 mg, 99%) was prepared from **3a** (23.2 mg, 0.136 mmol) with **2b** (43.1 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2956, 2928, 2855, 1715, 1620, 1496, 1437; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 35.6; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.68 (2H, dd, *J* = 12.0, 7.5 Hz), 7.42 (1H, m), 7.42–7.23 (6H, m), 7.18 (2H, d, *J* = 6.9 Hz), 4.80 (2H, dd, *J* = 34.4, 16.0 Hz), 4.24 (2H, q, *J* = 6.9 Hz), 4.02–3.93 (2H, m), 2.04–1.96 (2H, m), 1.31–1.00 (14H, m), 0.85 (3H, t, *J* = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.9, 138.6 (d, J_{PC} = 22.8 Hz), 137.2, 132.0, 131.8, 131.8, 131.5, 131.5, 130.9, 128.6 (2C), 128.3, 128.2, 127.3, 126.7, 62.8, 60.5 (d, J_{PC} = 6.0 Hz), 50.4, 31.2, 29.3, 28.8 (d, J_{PC} = 2.4 Hz), 26.9 (d, J_{PC} = 9.6 Hz), 22.4, 16.4 (d, J_{PC} = 7.2 Hz), 14.4, 13.9; HRMS (FAB^+) calcd for $C_{26}H_{37}NO_4P$ ($[M+H]^+$) 458.2460, found 458.2517.

4.6. Ethyl (E)-(1-(N-benzyl-4-methylphenylsulfonamido)oct-1-en-2-yl)(phenyl)phosphinate *6*

This compound (57.3 mg, 78%) was prepared from **3a** (23.3 mg, 0.136 mmol) with **2c** (63.0 mg, 0.170 mmol). Colorless oil; IR (neat) cm^{-1}: 2925, 2854, 1618, 1496, 1455, 1439; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 33.6; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.65 (2H, d, *J* = 8.6 Hz), 7.58–7.48 (3H, m), 7.40 (2H, dt, *J* = 7.5, 3.4 Hz), 7.32 (2H, d, *J* = 8.0 Hz), 7.25–7.20 (5H, m), 6.64 (1H, d, *J* = 14.9 Hz), 4.41 (2H, s), 3.99–3.83 (2H, m), 2.45 (3H, s), 2.12–1.95 (2H, m), 1.29–1.25 (4H, m), 1.10 (2H, quin, *J* = 6.9 Hz), 1.00–0.91 (5H, m), 0.80 (3H, t, *J* = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.2, 137.4 (d, J_{PC} = 21.6 Hz), 135.4, 134.9, 132.0, 132.0, 131.6 (d, J_{PC} = 122.4 Hz),

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131.4, 131.3, 129.9 (2C), 128.5 (2C), 128.4, 128.3, 128.2 (2C), 127.8, 127.4 (2C), 60.5 (d, J_{PC} = 6.0 Hz), 53.4, 31.3, 29.4, 28.3, 27.5 (d, J_{PC} = 8.4 Hz), 22.4, 21.6, 16.3 (d, J_{PC} = 7.2 Hz), 14.0; HRMS (FAB^+) calcd for $C_{30}H_{39}NO_4PS$ ($[M+H]^+$) 540.2337, found 540.2388.

4.7. Ethyl (E)-(2-(ethoxy(phenyl)phosphoryl)oct-1-en-1-yl)(phenyl)carbamate **7**

This compound (58.8 mg, 97%) was prepared from **3a** (23.2 mg, 0.136 mmol) with **2d** (41.5 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2962, 2927, 2857, 1723, 1620, 1593, 1496, 1463, 1439; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 35.8; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.79 (2H, dd, J = 12.0, 6.9 Hz), 7.68 (1H, d, J = 17.2 Hz), 7.52 (1H, t, J = 6.9 Hz), 7.47–7.44 (2H, m), 7.35 (2H, t, J = 7.5 Hz), 7.29 (1H, t, J = 6.9 Hz), 7.22 (2H, d, J = 7.5 Hz), 4.23 (2H, q, J = 6.9 Hz), 4.12–4.02 (2H, m), 1.47–1.39 (2H, m), 1.36 (3H, t, J = 6.9 Hz), 1.25 (3H, t, J = 6.9 Hz), 1.06 (2H, quin, J = 7.5 Hz), 0.95–0.80 (4H, m), 0.76 (3H, t, J = 7.5 Hz), 0.67 (2H, quin, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.3, 139.6, 138.5 (d, J_{PC} = 24.0 Hz), 131.8, 131.8, 131.7, 131.7, 131.5 (d, J_{PC} = 135.6 Hz), 128.9 (2C), 128.4, 128.3, 127.6 (2C), 127.4, 63.0, 60.6 (d, J_{PC} = 6.0 Hz), 31.2, 29.1, 28.6, 25.8 (d, J_{PC} = 7.2 Hz), 22.3, 16.4 (d, J_{PC} = 7.2 Hz), 14.3, 13.9; HRMS (FAB^+) calcd for $C_{25}H_{35}NO_4P$ ($[M+H]^+$) 444.2304, found 444.2356.

4.8. Ethyl (E)-(2-(N-benzyl-4-methylphenylsulfonamido)-1-phenylvinyl)(phenyl)phosphinate **8**

This compound (70.0 mg, 97%) was prepared from **3a** (23.2 mg, 0.136 mmol) with **2e** (61.5 mg, 0.170 mmol). Colorless oil; IR (neat) cm^{-1}: 1615, 1594, 1492, 1469; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 31.3; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.84 (1H, d, J = 16.0 Hz), 7.68 (2H, d, J = 8.0 Hz), 7.43–7.38 (3H, m), 7.32–7.27 (4H, m), 7.15–7.08 (4H, m), 6.96 (2H, t, J = 8.0 Hz), 6.65 (2H, d, J = 7.5 Hz), 6.47 (2H, d, J = 8.0 Hz), 4.28 (2H, dd, J = 76.8, 16.6 Hz), 3.98–3.87 (2H, m), 2.45 (3H, s), 1.23 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.4, 136.7 (d, J_{PC} = 21.6 Hz), 135.8, 135.3, 132.5 (d, J_{PC} = 7.2 Hz), 131.7, 131.7, 131.6, 130.7 (d, J_{PC} = 140.4 Hz), 130.4, 130.3, 129.9 (2C), 128.0, 128.0 (2C), 127.9, 127.7, 127.6, 127.6, 127.2 (2C), 127.0, 126.5 (2C), 116.3 (d, J_{PC} = 132.0 Hz), 60.7 (d, J_{PC} = 4.8 Hz), 49.8, 21.6, 16.3 (d, J_{PC} = 7.2 Hz); HRMS (FAB^+) calcd for $C_{30}H_{31}NO_4PS$ ($[M+H]^+$) 532.1711, found 532.1779.

4.9. Methyl (E)-4-(2-(N-benzyl-4-methylphenylsulfonamido)-1-(ethoxy(phenyl)phosphoryl)vinyl)benzoate **9**

This compound (62.1 mg, 77%) was prepared from **3a** (23.2 mg, 0.136 mmol) with **2f** (62.9 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2980, 1720, 1605, 1496, 1438; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 30.9; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.89 (1H, d, J = 16.0 Hz), 7.69 (2H, d, J = 8.6 Hz), 7.61 (2H, d, J = 8.0 Hz), 7.45–7.27 (7H, m), 7.14 (1H, t, J = 7.5 Hz), 7.08 (2H, t, J = 7.5 Hz), 6.60 (2H, d, J = 7.5 Hz), 6.54 (2H, dd, J = 8.6, 1.7 Hz), 4.27 (2H, dd, J = 83.1, 16.6 Hz), 3.98–3.90 (2H, m), 3.88 (3H, s), 2.47 (3H, s), 1.24 (3H, t, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 166.6, 144.6, 137.8 (d, J_{PC} = 7.2 Hz), 137.2 (d, J_{PC} = 20.4 Hz), 135.6, 134.8, 131.9 (d, J_{PC} = 2.4 Hz), 131.7, 131.6, 130.5 (2C, d, J_{PC} = 4.8 Hz), 130.4 (d, J_{PC} = 141.6 Hz), 130.1 (2C), 129.2 (d, J_{PC} = 2.4 Hz), 128.6 (2C), 128.2, 128.1 (2C), 128.1, 127.2 (2C), 127.2, 126.3 (2C), 115.3 (d, J_{PC} = 130.8 Hz), 60.9 (d, J_{PC} = 6.0 Hz), 52.1, 50.1, 21.6, 16.3 (d, J_{PC} = 7.2 Hz); HRMS (FAB^+) calcd for $C_{32}H_{33}NO_6PS$ ($[M+H]^+$) 590.1766, found 590.1741.

4.10. Ethyl (E)-(2-(N-benzyl-4-methylphenylsulfonamido)-1-(4-methoxyphenyl)vinyl)(phenyl)phosphinate **10**

This compound (60.1 mg, 83%) was prepared from **3a** (22.0 mg, 0.129 mmol) with **2g** (58.7 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2980, 1600, 1508, 1454, 1439; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 31.6; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.78 (1H, d, J = 16.0 Hz), 7.68 (2H, d, J = 8.6 Hz), 7.43–7.39 (3H, m), 7.31–7.27 (4H, m), 7.14–7.09 (3H, m), 6.70 (2H, d, J = 6.9 Hz), 6.50 (2H, d, J = 8.6 Hz), 6.41 (2H, d, J = 7.5 Hz), 4.31 (2H, dd, J = 67.0, 16.6 Hz), 3.95–3.88 (2H, m), 3.71 (3H, s), 2.45 (3H, s), 1.23 (3H, t, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 156.1 (d, J_{PC} = 2.4 Hz), 144.3, 136.8 (d, J_{PC} = 22.8 Hz), 135.9, 135.4, 131.7, 131.7 (2C, d, J_{PC} = 9.6 Hz), 131.5 (2C, d, J_{PC} = 4.8 Hz), 130.8 (d, J_{PC} = 139.2 Hz), 129.9 (2C), 128.7 (d, J_{PC} = 13.2 Hz), 128.0, 128.0 (2C), 127.9, 127.2 (2C), 127.0, 126.7 (2C), 124.3 (d, J_{PC} = 7.2 Hz), 116.3 (d, J_{PC} = 133.2 Hz), 113.2, 60.7 (d, J_{PC} = 6.0 Hz), 55.1, 49.9, 21.6, 16.3 (d, J_{PC} = 6.0 Hz); HRMS (FAB^+) calcd for $C_{31}H_{33}NO_5PS$ ($[M+H]^+$) 562.1817, found 562.1773.

4.11. Ethyl (E)-(2-(N-benzyl-4-methylphenylsulfonamido)-1-(4-chlorophenyl)vinyl)(phenyl)phosphinate **11**

This compound (42.0 mg, 55%) was prepared from **3a** (23.2 mg, 0.136 mmol) with **2h** (59.4 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2979, 1602, 1488, 1439; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 31.1; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.84 (1H, d, J = 16.6 Hz), 7.69 (2H, d, J = 8.0 Hz), 7.46–7.39 (3H, m), 7.33–7.30 (4H, m), 7.15–7.09 (3H, m), 6.89 (2H, d, J = 8.6 Hz), 6.65 (2H, d, J = 7.5 Hz), 6.39 (2H, d, J = 6.9 Hz), 4.30 (2H, dd, J = 69.3, 16.6 Hz), 3.94 (2H, dt, J = 7.5, 2.3 Hz), 2.46 (3H, s), 1.25 (3H, t, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 144.6, 137.1 (d, J_{PC} = 21.6 Hz), 135.6, 135.0, 133.8 (d, J_{PC} = 3.6 Hz), 133.0, 131.9 (d, J_{PC} = 2.4 Hz), 131.8, 131.7, 131.7, 130.9, 130.8, 130.4 (d, J_{PC} = 140.4 Hz), 130.0 (2C), 128.6 (d, J_{PC} = 13.2 Hz), 128.2, 128.1 (2C), 127.7, 127.3 (2C), 127.1, 126.3 (2C), 114.9 (d, J_{PC} = 134.4 Hz), 60.9 (d, J_{PC} = 6.0 Hz), 50.1, 21.6, 16.3 (d, J_{PC} = 7.2 Hz); HRMS (FAB^+) calcd for $C_{30}H_{30}ClNO_4PS$ ($[M+H]^+$) 566.1322, found 566.1272.

4.12. Benzyl (E)-benzyl(2-(isopropoxy(phenyl)phosphoryl)oct-1-en-1-yl)carbamate **15**

This compound (65.3 mg, 90%) was prepared from **3b** (25.0 mg, 0.136 mmol) with **2a** (52.4 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2956, 2927, 1715, 1622, 1496, 1454, 1438; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 33.5; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.67–7.63 (2H, m), 7.47 (1H, t, J = 6.9 Hz), 7.38–7.24 (11H, m), 7.17 (2H, d, J = 6.9 Hz), 5.20 (2H, d, J = 4.0 Hz), 4.79 (2H, dd, J = 60.2, 16.0 Hz), 4.52 (1H, m), 2.05–1.92 (2H, m), 1.27–0.94 (14H, m), 0.78 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.8, 138.0 (d, J_{PC} = 21.6 Hz), 137.1, 135.7, 132.6, 131.7, 131.7, 131.6, 131.5, 128.6 (2C), 128.5 (2C), 128.3 (2C), 128.2, 128.1 (2C), 127.4 (2C), 126.9, 69.8 (d, J_{PC} = 6.0 Hz), 68.3, 50.9, 31.2, 29.3, 28.7, 27.1 (d, J_{PC} = 8.4 Hz), 24.2 (d, J_{PC} = 3.6 Hz), 24.1 (d, J_{PC} = 4.8 Hz), 22.4, 14.0; HRMS (FAB^+) calcd for $C_{32}H_{41}NO_4P$ ($[M+H]^+$) 534.2773, found 534.2810.

4.13. Benzyl (E)-benzyl(2-(tert-butoxy(phenyl)phosphoryl)oct-1-en-1-yl)carbamate **16**

This compound (35.9 mg, 48%) was prepared from **3c** (27.0 mg, 0.136 mmol) with **2a** (52.5 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2956, 2929, 1715, 1624, 1496, 1455, 1438; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 29.5; ^1H NMR (500 MHz, $CDCl_3$) δ: 7.64–7.60 (2H, m), 7.44 (1H, t, J = 6.9 Hz), 7.33–7.21 (11H, m), 7.18 (2H, d, J = 6.9 Hz), 5.19 (2H, d, J = 1.7 Hz), 4.76 (2H, dd, J = 44.7, 16.0 Hz), 2.04–1.91 (2H, m), 1.40 (9H, s), 1.19–0.93 (8H, m), 0.79 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 137.1, 135.7, 134.6, 133.5, 131.3, 131.3, 131.3, 131.2, 128.6 (2C), 128.5 (2C), 128.3, 128.1 (2C), 128.0 (2C), 127.4 (2C), 127.1, 83.2 (d, J_{PC} = 8.4 Hz), 68.2, 51.1, 31.3, 30.7, 30.7 (2C), 29.4, 28.5, 27.2 (d, J_{PC} = 8.4 Hz), 22.4, 14.0; HRMS (FAB^+) calcd for $C_{33}H_{43}NO_4P$

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([M+H]$^+$) 548.2930, found 548.2823.

4.14. Benzyl (E)-benzyl(2-((decyloxy)(phenyl)phosphoryl)oct-1-en-1-yl)carbamate **17**

This compound (73.9 mg, 86%) was prepared from **3d** (38.9 mg, 0.136 mmol) with **2a** (52.4 mg, 0.150 mmol). Colorless oil; IR (neat) cm^{-1}: 2924, 2854, 1717, 1623, 1496, 1455, 1438; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 35.1; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.64 (2H, dd, J = 11.5, 8.0 Hz), 7.48 (1H, t, J = 6.9 Hz), 7.38–7.27 (11H, m), 7.17 (2H, d, J = 6.9 Hz), 5.20 (2H, d, J = 1.7 Hz), 4.79 (2H, dd, J = 26.4, 16.0 Hz), 3.88–3.81 (2H, m), 2.05–1.94 (2H, m), 1.63–1.60 (2H, m), 1.29–0.96 (22H, m), 0.88 (3H, t, J = 6.9 Hz), 0.79 (3H, t, J = 7.5 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.7, 138.4 (d, J_{PC} = 22.8 Hz), 137.0, 135.7, 131.8, 131.8, 131.6, 131.5, 130.7, 128.6 (2C), 128.5 (2C), 128.4, 128.3 (2C), 128.1 (2C), 127.4 (2C), 126.9, 68.3, 64.6 (d, J_{PC} = 6.0 Hz), 50.9, 31.9, 31.3, 30.5, 30.4, 29.5, 29.3 (d, J_{PC} = 4.8 Hz), 29.2, 28.7, 27.1, 27.0, 25.6, 22.7, 22.4, 14.1, 14.0; HRMS (FAB$^+$) calcd for $C_{39}H_{55}NO_4P$ ([M+H]$^+$) 632.3869, found 632.3877.

4.15. Benzyl (E)-benzyl(2-(benzyl(ethoxy)phosphoryl)oct-1-en-1-yl)carbamate **18**

This compound (54.3 mg, 75%) was prepared from **3e** (25.0 mg, 0.136 mmol) with **2a** (58.9 mg, 0.169 mmol). Colorless oil; IR (neat) cm^{-1}: 2956, 2922, 2855, 1715, 1622, 1496, 1454; ^{31}P NMR (202 MHz, $CDCl_3$) δ: 43.8; ^{1}H NMR (500 MHz, $CDCl_3$) δ: 7.34–7.15 (13H, m), 7.07–7.04 (3H, m), 5.17 (2H, d, J = 4.6 Hz), 4.70 (2H, d, J = 2.9 Hz), 3.92 (1H, m), 3.72 (1H, m), 3.09 (2H, m), 1.99–1.92 (2H, m), 1.25–1.07 (11H, m), 0.85 (3H, t, J = 6.9 Hz); ^{13}C NMR (125 MHz, $CDCl_3$) δ: 154.5, 139.0 (d, J_{PC} = 21.6 Hz), 137.0, 135.6, 131.7, 131.6, 129.9, 129.9, 128.6 (2C), 128.5 (2C), 128.4, 128.3, 128.3, 128.1 (2C), 127.4 (2C), 126.8, 126.6 (d, J_{PC} = 2.4 Hz), 68.3, 60.3 (d, J_{PC} = 6.0 Hz), 50.9, 36.8 (d, J_{PC} = 96.0 Hz), 31.4, 29.5, 28.7, 27.3 (d, J_{PC} = 8.4 Hz), 22.5, 16.3 (d, J_{PC} = 6.0 Hz), 14.0; HRMS (FAB$^+$) calcd for $C_{32}H_{41}NO_4P$ ([M+H]$^+$) 534.2773, found 534.2810.

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References

[1] For reviews, see: (a) M. Collinsová, J. Jirácek, Curr. Med. Chem. 7 (2000) 629; (b) A. Yiotakis, D. Geogiadis, M. Matziari, A. Makaritis, V. Dive, Curr. Org. Chem. 8 (2004) 1135; (c) A. Mucha, P. Kafarski, Ł. Berlicki, J. Med. Chem. 54 (2011) 5955.
[2] For selected examples, see: (a) A. Chelouan, R. Recio, L.G. Borrego, E. Alvarez, N. Khiar, I. Fernandez, Org. Lett. 18 (2016) 3258; (b) D. Liu, S. Zhou, J. Gao, Synth. Commun. 44 (2014) 1286; (c) L. Xia, S. Li, R. Chen, K. Liu, X. Chen, J. Org. Chem. 78 (2013) 3120; (d) B. Alcalde, P. Almendros, C. Aragoncillo, R. Callejo, M.P. Ruiz, J. Org. Chem. 78 (2013) 10154; (e) C.S. Pan, B. List, Angew. Chem. Int. Ed. 47 (2008) 3622.
[3] D.V. Patel, K. Rielly-Gauvin, D.E. Ryono, C.A. Free, W.L. Rogers, S.A. Smith, J.M. DeForrest, R.S. Oehl, E.W. Petrillo Jr., J. Med. Chem. 38 (1995) 4557.
[4] B. Stowasser, K.-H. Budt, L. Jian-Qi, A. Peyman, D. Ruppert, Tetrahedron Lett. 33 (1992) 6625.
[5] E. Weglarz-Tomczak, L. Berlicki, M. Pawelczak, B. Nocek, Eur. J. Med. Chem. 117 (2016) 187.
[6] M. Bollinger, F. Manzenrieder, R. Kolb, A. Bochen, S. Neubauer, L. Marinelli, V. Limongelli, E. Novellino, G. Moessmer, R. Pell, W. Lindner, J. Fanous, A. Hoffman, H. Kessler, J. Med. Chem. 55 (2012) 871.
[7] D. Zhang, C. Yuan, Chem. Eur. J. 15 (2009) 4088.
[8] (a) G. Märkl, B. Merkl, Tetrahedron Lett. 22 (1981) 4459; (b) H. Krawczyk, Phosphorus, sulfur silicon 118 (1996) 195; (c) J. Mortier, A.-D. Fortineau, M. Vaultier, Phosphorus, sulfur silicon 149 (1999) 221.
[9] C. Queffelec, P. Ribière, J.-L. Montchamp, J. Org. Chem. 73 (2008) 8987.
[10] M.E. Duggan, D.S. Karanewsky, Tetrahedron Lett. 24 (1983) 2935.
[11] For reviews of synthesis of β-aminophosphinates, see: (a) F. Palacios, C. Alonso, J.M. de los Santos, Chem. Rev. 105 (2005) 899; (b) F. Palacios, C. Alonso, J.M. de los Santos, Curr. Org. Chem. 8 (2004) 1481.
[12] For reviews, see: (a) Q. Xu, Y.-B. Zhou, C.-Q. Zhao, S.-F. Yin, L.-B. Han, Mini Rev. Med. Chem. 13 (2013) 824; (b) J.-L. Montchamp, J. Organomet. Chem. 690 (2005) 2388.
[13] For selected examples, see: (a) S. Ortial, H.C. Fisher, J.-L. Montchamp, J. Org. Chem. 78 (2013) 6599; (b) P. Ribière, K. Bravo-Altamirano, M.I. Antczak, J.D. Hawkins, J.-L. Montchamp, J. Org. Chem. 70 (2005) 4064; (c) S. Deprèle, J.-L. Montchamp, J. Am. Chem. Soc. 124 (2002) 9386; (d) L.-B. Han, C.-Q. Zhao, S. Onozawa, M. Goto, M. Tanaka, J. Am. Chem. Soc. 124 (2002) 3842; (e) M. Niu, H. Fu, Y. Zhao, Chem. Commun. (2007) 272.
[14] For reviews of ynamides, see: (a) X.-N. Wang, H.-S. Yeom, L.-C. Fang, S. He, Z.-X. Ma, B.L. Kedrowski, R.P. Hsung, Acc. Chem. Res. 47 (2014) 560; (b) K.A. DeKorver, H. Li, A.G. Lohse, R. Hayashi, Z. Lu, Y. Zhang, R.P. Hsung, Chem. Rev. 110 (2010) 5064; (c) G. Evano, A. Coste, K. Jouvin, Angew. Chem. Int. Ed. 49 (2010) 2840; (d) A.R. Katritzky, R. Jiang, S.K. Singh, Heterocycles 63 (2004) 1455; (e) J.A. Mulder, K.C.M. Kurtz, R.P. Hsung, Synlett (2003) 1379; (f) C.A. Zificsak, J.A. Mulder, R.P. Hsung, C. Rameshkumar, L.-L. Wei, Tetrahedron 57 (2001) 7575.
[15] A. Kinbara, M. Sato, K. Yumita, T. Yamagishi, Tetrahedron 73 (2017) 1705.
[16] A. Fadel, F. Legrand, G. Evano, N. Rabasso, Adv. Synth. Catal. 353 (2011) 263.
[17] H. Huang, H. Zhu, J.Y. Kang, Org. Lett. 20 (2018) 2778.
[18] J.R. Dunetz, R.L. Danheiser, Org. Lett. 5 (2003) 4011.
[19] Y. Zhang, R.P. Hsung, M.R. Tracey, K.C.M. Kurtz, E.L. Vera, Org. Lett. 6 (2004) 1151.
[20] H. Liu, Y. Yang, S. Wang, J. Wu, X.-N. Wang, J. Chang, Org. Lett. 17 (2015) 4472.
[21] B. Yao, Z. Liang, T. Niu, Y. Zhang, J. Org. Chem. 74 (2009) 4630.
[22] H. Wakamatsu, M. Takeshita, Synlett (2010) 2322.
[23] S.J. Mansfield, C.D. Campbell, M.W. Jones, E.A. Anderson, Chem. Commun. 51 (2015) 3316.
[24] Y.-P. Wang, R.L. Danheiser, Tetrahedron Lett. 52 (2011) 2111.
[25] L.-B. Han, C. Zhang, H. Yazawa, S. Shimada, J. Am. Chem. Soc. 126 (2004) 5080.
[26] J. Heinicke, N. Gupta, A. Surana, N. Peulecke, B. Witt, K. Steinhauser, R.K. Bansal, P.G. Jones, Tetrahedron 57 (2001) 9963.
[27] V.P. Ananikov, I.P. Beletskaya, Chem. Asian J. 6 (2011) 1423.
[28] B.-L. Lin, L. Liu, Y. Fu, S.-W. Luo, Q. Chen, Q.-X. Guo, Organometallics 23 (2004) 2114.
[29] Y.R. Dumond, R.L. Baker, J.L. Montchamp, Org. Lett. 2 (2000) 3341.
[30] L.Y. Kuo, D.C. Baker, A.K. Dortignacq, K.M. Dill, Organometallics 32 (2013) 4759.
[31] E. Jablonkaia, R. Henyecza, M. Milena, J. Kotib, G. Keglevicha, Tetrahedron 70 (2014) 8280.
[32] K. Afarinkia, H. Yu, Tetrahedron Lett. 44 (2003) 781.
[33] L. Gavara, C. Petit, J.L. Montchamp, Tetrahedron Lett. 53 (2012) 5000.
[34] (a) E.K. Baylis, Tetrahedron Lett. 36 (1995) 9385; (b) W. Froestl, S.J. Mickel, R.G. Hall, G. von Sprecher, D. Strub, P.A. Baumann, F. Brugger, C. Gentsch, J. Jaekel, H.-R. Olpe, G. Rihs, A. Vassout, P.C. Waldmeier, H. Bittiger, J. Med. Chem. 38 (1995) 3297.

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