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Asymmetric Addition of Terminal Alkynes to *N*-(Diphenylphosphinoyl)imines Promoted by Stoichiometric Amounts of a Proline-Derived β-Amino Alcohol

Wenjin Yan,[a,b] Bin Mao,[a] Shaoqun Zhu,[a] Xianxing Jiang,[a,b] Zhongli Liu,[a] and Rui Wang*[a,b]

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A new synthetic methodology for the preparation of optically active propargylamines is described. The alkynylation of aromatic, heteroaromatic, aliphatic and α,β-unsaturated *N*-(diphenylphosphinoyl)imines was investigated by using diethylzinc and a proline-derived β-amino alcohol. *N*-(Diphenylphosphinoyl)-protected propargylic amines can be synthesized in high yields and with good to excellent enantioselectivities.

Introduction

Optically active propargylamines are valuable chiral intermediates for the synthesis of various drugs and biologically active compounds.[1] Therefore, it is not surprising that many excellent catalytic systems have been developed for the construction of α-chiral propargylamines.[2] Most of the examples focused on the use of Cu^{I} salts in combination with nitrogen-containing ligands to catalyze the enantioselective alkynylation of *N*-arylimines.[3] Chan et al. developed the addition processes by using *N*-tosylated amino-imine ligands/Cu^{I}/$Zn(Me)_2$[4] and *N*-tosylated amino-imine ligands/Cu^{II}/$Zn(Me)_2$ systems.[5] Some other methods include Hoveyda's peptide-Zr-(O*i*Pr)$_4$·HO*i*Pr system,[6] Bolm's amino alcohol catalysis system[7] and Rueping's dual catalysis system.[8] Jiang et al.[9] used stoichiometric amounts of a chiral amino alcohol ligand to mediate the addition of alkynes to trifluoromethyl-activated cyclic imine. Chonget al.[10] and Soderquist et al.[11] carried out the alkynylation of *N*-acylimines by using chiral alkynylboronates or alkynylboranes as nucleophilic reagents, respectively. Recently, Pedro et al.[12] accomplished the alkynylation of *N*-sulfonylaldimines by using a zinc/Binol catalysis system. Hou et al.[13] provided *N*-(*tert*-butylsulfinyl)-propargylamines by the addition of alkynes to optically pure *tert*-butylsulfinimines. Unfortunately, the further application of these α-chiral propargylamines in organic synthesis and in the pharmaceutical industry remains a challenging task due to the harsh conditions of protecting group removal.

By contrast, *N*-phosphinoylimines have drawn considerable attention because the resulting phosphonamide products can be easily deprotected under mild conditions (e.g. HCl/MeOH).[14] For this reason, they were widely used in catalytic asymmetric nitro-Mannich,[15] Mannich[16] and Strecker[17] processes besides the addition of organometallics.[18] Nevertheless, the enantioselective alkynylation of *N*-phosphinoylimines has not yet been reported. Herein, we report the first asymmetric addition of terminal alkynes to *N*-(diphenylphosphinoyl)imines promoted by a proline-derived β-amino alcohol.

Results and Discussion

In the past few years, a great effort in our group has been devoted to the investigation of the enantioselective catalytic alkynylation of aldehydes and ketones[19] by using the ligands derived from natural amino acids. Gratifyingly, β-amino alcohols have proved to be efficient in the alkylation of ketones.

Thus, we initially decided to employ **L1** (Figure 1) as a promoter in the addition of phenylacetylene to *N*-(diphenylphosphinoyl)benzaldimine. In view of the solubility of the substrate imine, we chose CH_2Cl_2 as the solvent. The substrate was consumed after 24 h, but we found no enantioselectivity (Table 1). We supposed that the steric bulk at the α-position of the chiral amino alcohol was crucial for the coordination of the ligand-zinc complex with the imine. Hence, we prepared ligand **L2** (Figure 1) to optimize the reaction. Unfortunately, we obtained only racemic product. We examined ligands **L3**–**L5** next. We note that our hypothesis, as described above, was further supported by the inves-

[a] State Key Laboratory of Applied Organic Chemistry, Lanzhou University,
Lanzhou 730000, P. R. China
Fax: +86-931-8912567
E-mail: wangrui@lzu.edu.cn
[b] State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences,
Lanzhou 730000, P. R. China
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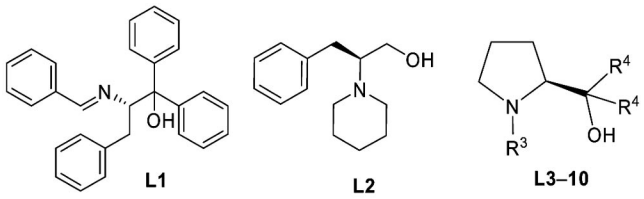
tigation of **L3**–**L5**. These results revealed that the enantioselectivity increased in the order of **L5** < **L4** < **L3**, which corresponds to the α-position of the chiral amino alcohols bearing a dihydrogen, diehthyl and two phenyl substituents, respectively. Encouraged by these results, we designed ligands **L6**–**L10** (Figure 1) to test the effect of nitrogen substituent. We found that the size of the substituents bonded to the nitrogen had a significant effect on achieving high enantioselectivity and yield in the reaction.



L3: $R^3 = CH_2C_6H_5$, $R^4 = H$ **L7**: $R^3 = 2\text{-}CH_2C_{10}H_7$, $R^4 = H$

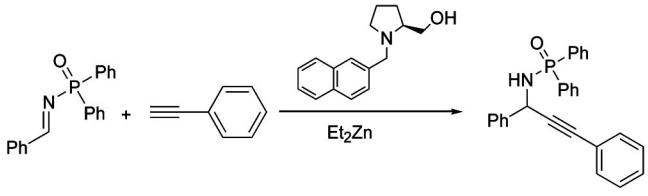
L4: $R^3 = CH_2C_6H_5$, $R^4 = C_2H_5$ **L8**: R^3 = 2,4,6-trimethylbenzyl, $R^4 = H$

L5: $R^3 = CH_2C_6H_5$, $R^4 = C_6H_5$ **L9**: $R^3 = C_6H_{11}$, $R^4 = H$

L6: $R^3 = 1\text{-}CH_2C_{10}H_7$, $R^4 = H$ **L10**: $R^3 = CH_3$, $R^4 = H$

Figure 1. The various catalysts in the alkynylation of *N*-phosphinoylimines.

Table 1. Alkynylation of *N*-phosphinoylimines using **L1**–**L10** as catalysts.[a]



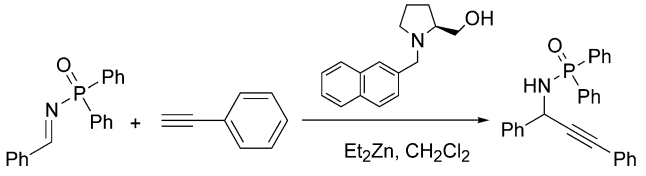
Entry	Ligand	Cat. [mol-%]	*t* [h]	Yield [%][b]	*ee* [%][c]
1	**L1**	20	24	37	0
2	**L2**	20	24	42	0
3	**L3**	20	24	55	47
4	**L4**	20	24	52	4
5	**L5**	20	24	45	0
6	**L6**	20	24	57	53
7	**L7**	20	24	63	57
8	**L8**	20	24	54	20
9	**L9**	20	24	50	40
10	**L10**	20	24	53	11

[a] Reaction conditions: reactions were carried out in CH_2Cl_2 at room temperature on a 0.2 mmol scale with aldimine/Et_2Zn/phenylacetylene = 1:3:3; all reactions were processed under argon. [b] Isolated yields. [c] The *ee* was determined by HPLC analysis on a Chiralcel AD column.

Ligand **L10**, with the smallest substituent, gave the lowest enantioselectivity and a moderate yield, while [1-(naphthalene-2-ylmethyl)pyrrolidin-2-yl]methanol (**L7**) gave the best result of 57% enantiomeric excess (*ee*) and 63% yield. Further increases to the steric hindrance of the substituents on nitrogen led to a decrease in enantioselectivities (Table 1, Entries 8 and 9), perhaps due to the rigidity of the pyrrolidine ring in these ligands.

Further reaction optimization focused on the solvent, catalyst loading and temperature. After screening the solvent, we found that satisfactory yield and enantioselectivity were achieved when we employed CH_2Cl_2 (Table 1, Entries 1–3). When we employed 0.4 equiv. of **L7**, the standard addition of phenylacetylene to the *N*-(diphenylphosphinoyl)-imine derived from benzaldehyde required 24 h at room temperature, and the *ee* of the resulting phosphinamide (isolated in 69% yield) increased to 68%. Therefore, we used stoichiometric amounts of ligand to further enhance the *ee* of the product, which we obtained in 85% *ee* and 73% yield (Table 2, Entry 5). In the above experiments, we added 3 equiv. of diethylzinc and alkyne. To our delight, the enantioselectivity slightly improved to 87% (79% yield) in the presence of 4 equiv. of diethylzinc and alkyne (Table 2, Entry 6). Further increasing the amount of diethylzinc and alkyne did not improve enantioselectivity, although the yield improved slightly (Table 2, Entry 7). We next probed the effect of temperature on the reaction. As expected, we obtained the addition product in 79% yield and 91% *ee* after 36 h at 10 °C and in 78% yield and 95% *ee* after 48 h at 0 °C (Table 2, Entries 8 and 9, respectively). When we lowered the temperature to –10 °C, the substrate could not be converted completely even after 72 h (Table 2, Entry 10).

Table 2. Alkynylation of *N*-phosphinoylimines using L7.[a]



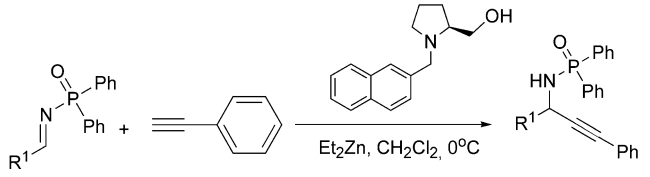
Entry	Solvent	Cat. [mol-%]	*T* [°C]	*t* [h]	Yield [%][e]	*ee* [%][f]
1[b]	Et_2O	20	Rt	24	63	42
2[b]	Tol	20	Rt	24	59	46
3[b]	THF	20	Rt	12	83	0
4[b]	DCM	40	Rt	24	69	68
5[b]	DCM	100	Rt	24	73	85
6[c]	DCM	100	Rt	24	79	87
7[d]	DCM	100	Rt	24	81	84
8[c]	DCM	100	10	36	79	91
9[c]	DCM	100	0	48	78	95
10[c]	DCM	100	–10	72	23	97

[a] Reaction conditions: reactions were carried out on a 0.2 mmol scale; all reactions were processed under argon. [b] Aldimine/Et_2Zn/phenylacetylene = 1:3:3. [c] Aldimine/Et_2Zn/phenylacetylene = 1:4:4. [d] Aldimine/Et_2Zn/phenylacetylene = 1:5:5. [e] Isolated yields. [f] The *ee* was determined by HPLC analysis on a Chiralcel AD column.

Under the above-optimized conditions, we examined various substituted imines (Table 3). All imines derived from aromatic aldehydes could be readily converted into the corresponding products in moderate to high yields. The presence of an electron-donating group on the *para* position of the aromatic ring gave excellent enantioselectivity (up to

96% *ee*), but in moderate yields (Table 3, Entries 2 and 3). The reaction proceeded not only with an electron-drawing group on the *para* position but also on the *meta* position to give high enantioselectivities and yields (Table 3, Entries 4–6 and 10). When we used *N*-(diphenylphosphinoyl)-2-methylbenzaldimine, we obtained low enantioselectivity (Table 3, Entry 11). We observed a large difference in enantioselectivity between the 1-naphthyl and 2-naphthyl cases (16% *ee* for 1-naphthyl and 90% *ee* for 2-naphthyl). As expected, both α,β-unsaturated imine (Table 3, Entry 8) and heteroarylimines (Table 3, Entries 12–15) also exhibited high reactivities, providing good to excellent enantioselectivities (78–96% *ee*) and moderate to good yields. We employed the aliphatic imines as substrates for the process next. We also obtained the desirable products in satisfactory yields (72% and 60%, Table 3, Entries 16 and 17) despite the low enantioselectivity for the product from *t*Bu-imine (Table 3, Entry 17).

Table 3. Addition of phenylacetylene to various *N*-phosphinoylimines.[a]

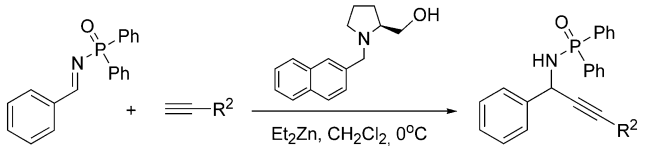


Entry	R^1	*t* [h]	Yield [%][b]	*ee* [%][c]
1	Ph	48	78	95 (s)
2	4-MeC_6H_4	36	70	95
3	4-$MeOC_6H_4$	48	74	96
4	4-FC_6H_4	48	83	93
5	4-ClC_6H_4	48	87	92
6	4-BrC_6H_4	48	86	87
7	2-naphthyl	48	72	90
8	cinnamyl	48	75	78
9	1-naphthyl	48	84	16
10	3-ClC_6H_4	48	77	84
11	2-MeC_6H_4	48	72	33
12	2-furyl	48	72	78
13	3-furyl	36	62	96
14	2-thienyl	48	70	95
15	3-thienyl	36	79	90
16	*i*Pr	24	72	88
17	*t*Bu	24	60	21

[a] Reaction conditions: reactions were carried out in CH_2Cl_2 and 0 °C on a 0.2 mmol scale with aldimine/ligand/Et_2Zn/phenylacetylene = 1:1:4:4; all reactions were processed under argon. [b] Isolated yields. [c] The *ee* was determined by HPLC analysis on a Chiralcel AD column.

Furthermore, the optimized conditions were also applicable to some quite challenging alkynes, and the results are summarized in Table 4. Gratifyingly, the reactions of 2-ethynylthiophene, 3-ethynylthiophene, 2-methylbut-1-en-3-yne, prop-2-yn-1-ol protected by TBS and (trimethylsilyl)acetylene with *N*-(diphenylphosphinoyl)benzaldimine afforded the corresponding products in high to excellent enantioselectivities (83–94% *ee*).

Table 4. Addition of various alkynes to *N*-(diphenylphosphinoyl)-benzaldimine.[a]



Entry	R^2	*t* [h]	Yield [%][b]	*ee* [%][c]
1	2-thienyl	12	74	94
2	3-thienyl	36	85	91
3	2-propenyl	48	75	85
4	$TBSOCH_2$	72	70	90
5	TMS	72	53	84

[a] Reaction conditions: reactions were carried out in CH_2Cl_2 at 0 °C on a 0.2 mmol scale with aldimine/ligand/Et_2Zn/alkyne = 1:1:4:4; all reactions were processed under argon. [b] Isolated yields. [c] The *ee* was determined by HPLC analysis on a Chiralcel AD column.

Importantly, this reaction could be carried out on gram scale (2 mmol) to demonstrate the synthetic utility of the present system. We found no obvious reduction of enantioselectivity and yield on a 0.2 mmol scale. The catalyst was conveniently recovered over 90% through flash column chromatography. The enantioselectivity of the product could be upgraded to 99% by a simple recrystallization in 57% yield from hexane/ethyl acetate. Importantly, our results indicated that the free amine may easily be accessed. *N*-(Diphenylphosphinoyl)propargylamine underwent a deprotection with HCl/MeOH to the free amine in 94% yield. We determined the absolute configuration of *N*-(1,3-diphenylprop-2-ynyl)-*P*,*P*-diphenylphosphinic amide to be (*S*)-configured by chemical correlation with (*S*)-*N*-(1,3-diphenylprop-2-ynyl)-4-methylbenzenesulfonamide (Figure 2).[12]

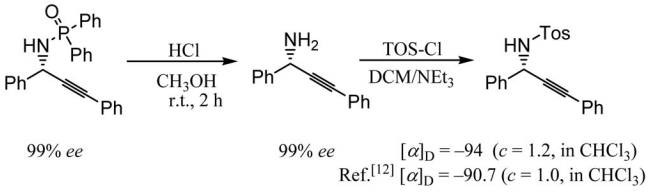


Figure 2. Determination of the absolute stereochemistry of *N*-(1,3-diphenylprop-2-ynyl)-*P*,*P*-diphenylphosphinic amide. The literature value is from ref.[12]

Conclusions

We have developed a procedure for the enantioselective alkynylation of *N*-(diphenylphosphinoyl)benzaldimine to give *N*-(diphenylphosphinoyl)-protected propargylic amines by using diethylzinc and stoichiometric amounts of a proline-derived β-amine alcohol. A variety of *N*-phosphinoylimines derived from aromatic, heteroaromatic, aliphatic and α,β-unsaturated aldehydes were tested with different alkynes, providing the expected products in generally good

yields and high to excellent enantioselectivities. The products could be conveniently converted into the corresponding propargylic amines by treatment with HCl/MeOH. Although the reaction required stoichiometric amounts of the amino alcohols, the ligands could be recovered in 90% yield by column chromatography, and the reaction conditions were quite mild.

Experimental Section

***N*-(1,3-Diphenylprop-2-ynyl)-*P*,*P*-diphenylphosphinic Amide:** In an oven-dried Schlenk flask, under an inert atmosphere of argon, were placed **L7** (48.2 mg, 0.2 mmol), followed by anhydrous CH_2Cl_2 (2 mL). A solution of diethylzinc in CH_2Cl_2 (0.8 mL, 0.8 mmol, 4.0 equiv.) was then added. The reaction mixture was stirred for 30 min, and phenylacetylene (88 μL, 0.8 mmol, 4 equiv.) was added. The resulting solution was stirred for an additional 7 h, and *N*-benzylidene-*P*,*P*-diphenylphosphinic amide was then added. The reaction mixture was stirred at 0 °C for 48 h. Subsequently, saturated aqueous NH_4Cl (2 mL) was added slowly at 0 °C, and the resulting mixture was extracted with CH_2Cl_2 (3 × 10 mL). The combined organic layers were dried with Na_2SO_4. After filtration and evaporation of the solvents, the crude residue was purified by flash chromatography (silica gel, hexane/ethyl acetate) to give the product as a white solid; m.p. 178–180 °C, 78% yield, 95% *ee*, as determined by HPLC analysis (Daicel Chiralcel AD column, hexane/2-propanol, 85:15, 1.0 mL/min, 254 nm). Retention times: t_{major} = 11.86 and t_{minor} = 10.70 min. $[\alpha]_D^{20}$ = –92 (*c* = 1.0, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 8.13–8.06 (m, 2 H), 7.90–7.83 (m, 2 H), 7.71–7.69 (m, 2 H), 7.54–7.46 (m, 4 H), 7.44–7.37 (m, 5 H), 7.35–7.30 (m, 5 H), 5.40 (t, *J* = 9.6 Hz, 1 H), 3.55 (t, *J* = 9.3 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, CDCl3): δ = 140.4 [d, $J_{C,P}$ = 4.5 Hz], 133.4, 132.8 [d, $J_{C,P}$ = 9.8 Hz], 132.1 [d, $J_{C,P}$ = 6.8 Hz], 132.8 [d, $J_{C,P}$ = 9.8 Hz], 131.7, 131.5, 129.0, 128.7 [d, $J_{C,P}$ = 6 Hz], 128.4 [d, $J_{C,P}$ = 12 Hz], 128.0, 127.4, 122.8, 89.0 [d, $J_{C,P}$ = 6 Hz], 85.6, 47.2 ppm. IR (neat): $\tilde{\nu}$ = 3160, 1489, 1437, 1186, 1125, 1060, 695, 544 cm^{-1}. HRMS for $C_{27}H_{22}NOP$ [M + H$^+$]: calculated 408.1512; found 408.1524.

(1,3-Diphenylprop-2-ynyl)amine: *N*-(1,3-Diphenylprop-2-ynyl)-*P*,*P*-diphenylphosphinic amide (40.7 mg, 99% *ee*, 0.1 mmol) was added to a 50 mL round-bottomed flask. A mixture of MeOH (10 mL) and concentrated aqueous HCl (1 mL) was added. The resulting mixture was capped and stirred at room temperature for 2 h. The reaction mixture was then concentrated by rotary evaporation, the residue was dissolved in aqueous HCl (1 M, 5 mL), and the precipitate was removed by filtration. The filtrate was basified (pH > 12) by the addition of NaOH (2 M), and the resulting mixture was extracted with CH_2Cl_2 (4 × 20 mL). The combined organic layers were dried with Na_2SO_4. After filtration and evaporation of the solvents, the crude residue was purified by flash chromatography (silica gel, hexane/ethyl acetate), giving the product as a colorless oil, 94.2% yield, 99% *ee*, as determined by HPLC analysis (Daicel Chiralcel AD column, hexane/2-propanol, 85:15, 1.0 mL/min, 254 nm). Retention times: t_{major} = 8.30 and t_{minor} = 9.08 min. $[\alpha]_D^{20}$ = –27 (*c* = 0.6, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.10 (d, *J* = 7.2 Hz, 2 H), 7.48–7.45 (m, 2 H), 7.39 (t, *J* = 7.2 Hz, 2 H), 7.33–7.30 (m, 4 H), 5.03 (s, 1 H), 2.31 (t, *J* = 7.5 Hz, 1 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 142.2, 131.6, 128.7, 128.3, 128.2, 127.9, 127.7, 126.8, 123.0, 91.3, 84.2, 48.1 ppm. IR (neat): $\tilde{\nu}$ = 3384, 2924, 2855, 2517, 1737, 1654, 1456, 1441, 1381, 1071, 1025, 727, 696, 527 cm^{-1}. HRMS for $C_{15}H_{13}N$ [M + H$^+$]: calculated 208.1121; found 208.1129.

(*S*)-*N*-(1,3-Diphenylprop-2-ynyl)-4-methylbenzenesulfonamide: Compound **3a** (20.7 mg, 99% *ee*, 0.1 mmol) was dissolved in CH_2Cl_2 (15 mL) in a 50 mL round-bottomed flask, and Et_3N (21 μL, 0.15 mmol) was added. The mixture was then cooled to 0 °C, and Tos-Cl (19 mg, 0.1 mmol) was added in one portion. The resulting mixture was stirred overnight and then washed successively with aqueous HCl (1 M, 5 mL) and H_2O (5 mL). The organic layer was separated and dried with Na_2SO_4. After filtration and evaporation of the solvents, the crude residue was purified by flash chromatography (silica gel, hexane/CH_2Cl_2), giving the product as a white solid, m.p. 213–216 °C, 85% yield. $[\alpha]_D^{20}$ = –94 (*c* = 1.2, $CHCl_3$). ^{1}H NMR (300 MHz, $CDCl_3$): δ = 7.82 (dd, *J* = 5.1, 1.5 Hz, 2 H), 7.56 (dd, *J* = 5.7, 1.8 Hz, 2 H), 7.36–7.23 (m, 8 H), 7.12 (dd, *J* = 6.6, 1.8 Hz, 2 H), 5.57 (d, *J* = 9 Hz, 1 H), 4.89 (d, *J* = 9.3 Hz, 2 H), 2.32 (s, 3 H) ppm. ^{13}C NMR (75 MHz, $CDCl_3$): δ = 143.6, 137.3, 131.5, 129.6, 128.7, 128.6, 128.5, 128.1, 127.5, 127.3, 121.9, 86.7, 85.4, 49.8, 21.4 ppm. IR (KBr): $\tilde{\nu}$ = 3265, 2920, 2221, 1595, 1488, 1326, 1153, 1088, 1047, 814, 752, 673, 556 cm^{-1}. HRMS for $C_{22}H_{19}NO_2S$ [M + Na$^+$]: calculated 384.1029; found 384.1034.

Supporting Information (see also the footnote on the first page of this article): Preparative details and NMR spectra.

Acknowledgments

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