Tetrahedron xxx (xxxx) xxx

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Anti-Markovnikov stereoselective hydroamination and hydrothiolation of (hetero)aromatic alkynes using a metal-free cyclic trimeric phosphazene base

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ARTICLE INFO

Article history:
Received 24 February 2019
Received in revised form
3 April 2019
Accepted 28 April 2019
Available online xxx

Keywords:
Hydroamination
Hydrothiolation
Cyclic trimeric phosphazene base
Organocatalysis

ABSTRACT

Hydroamination and hydrothiolation are the most efficient and completely atom-economical process to construct important enamine and vinyl sulfide intermediates in pharmaceutical and organic chemistry. The cyclic trimeric phosphazene base (CTPB) showed great catalytic activity for the anti-Markovnikov stereoselective hydroamination and hydrothiolation of alkynes in good to excellent yields. A broad substrate scope of alkynes and nucleophiles was demonstrated, including aryl and heteroaryl alkynes, terminal and internal alkynes, different *N*-heterocycles, thiols and thiophenols. This versatile and cost-efficient approach with good stereoselectivity and excellent functional group tolerance provided new opportunity for the organocatalyzed hydrofunctionalization of alkynes.

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1. Introduction

Nucleophilic addition of amines or thiols onto alkynes, known as hydroamination [1] and hydrothiolation [2] processes, have gain considerable interest in recent years. As a completely atom economical process, this transformation provides an efficient approach for the formation of C(sp^2)-N and C(sp^2)-S bond, which are both important structural motifs in modern synthesis. Different synthetic strategies such as radical transfer hydroamination [3], photocatalyzed hydroamination [4], and cope-type hydroamination [5] have been developed to construct various nitrogen-containing molecules. The existing studies focus on the intermolecular hydroamination and hydrothiolation reactions of aromatic and heteroaromatic alkynes, for that the adduct enamine and vinyl thioether compounds are essential organic synthons of many bioactive molecules [6], pharmaceuticals and natural products [7].

Despite the fact that the addition of nucleophiles to the carbon-carbon multiple bond is slightly exothermic or nearly thermoneutral, there are kinetic limitations due to the electrostatic repulsion [8]. Therefore, the process of the reaction needs to overcome a high energy barrier, which means that the direct addition of nucleophiles to the C≡C triple bond is difficult and a catalyst is required accordingly. Various metal-based catalysts across the periodic table have been used successfully for catalytic addition to achieve efficiency and selectivity [1d,1e,9]. Great progress regarding the synthetic potential offered by different bases have been reported as well for anti-Markovnikov hydroamination and hydrothiolation [1e,10]. Apart from the catalytic performance, an ideal catalyst system should possess the advantages of availability and cheap raw material, as well as low toxicity and excellent functional group tolerance. Indeed, organocatalysis and asymmetric hydroamination are both summarised as “Key green chemistry research areas” in pharmaceutical industry [11], sparking ongoing interest in developing novel organocatalysts for these atom-economical transformations. However, the effectiveness of organic catalysts has not been studied comprehensively, and few studies have been reported on metal-free catalytic nucleophilic addition [12].

It was known that phosphazene compounds are extremely strong but non-nucleophilic Brønsted bases [13]. Though rather expensive, they have been employed as effective catalysts in both

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https://doi.org/10.1016/j.tet.2019.04.075
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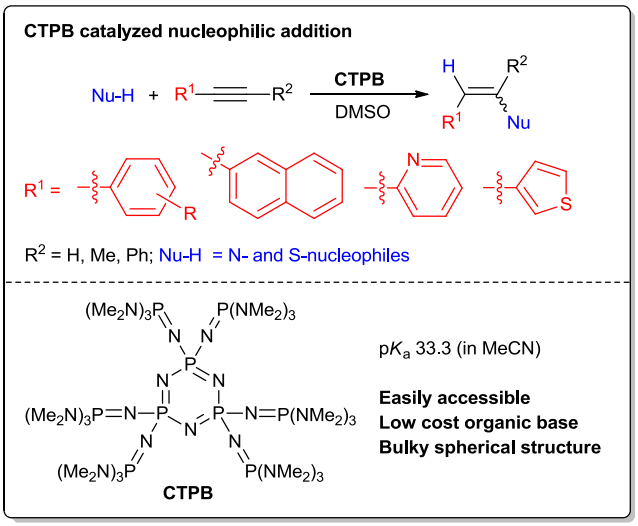


Scheme 1. Nucleophilic additions of alkynes catalyzed by **CTPB**.

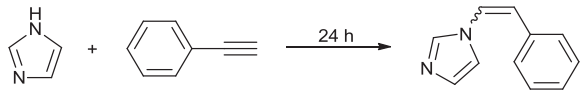
organic and polymer synthesis [13,14]. We recently reported the convenient one-step low cost preparation of a novel cyclic trimeric phosphazene base (**CTPB**) with moderate basicity (Scheme 1) from industrial product hexachlorocyclotriphosphazene (HCCP) [15]. According to our study results, **CTPB** exhibited high efficiency and controllability in the ring-opening polymerization (ROP) of different cyclic esters [15,16]. And now our interest shifted to the catalytic properties of **CTPB** in synthetic organic chemistry. It has been reported that a branched phosphazene superbase *t*-BuP_4 could accomplish the addition of *O*- and *N*-nucleophiles to alkynes but with poor stereoselectivity [17]. While a weaker phosphazene base BEMP could only catalyze hydroamination of terminal alkynes with *N*-heterocycles under solvent-free conditions [18]. To the best of our knowledge, these are the only two contributions of organic bases on the hydroamination of alkynes, and there's no report about the metal-free organic base catalyzed regio- and stereoselective hydrothiolation of alkynes with thiols. Herein we disclose the **CTPB** mediated anti-Markovnikov nucleophilic addition of (hetero)aromatic terminal and internal alkynes to form various enamines and vinyl thioethers with good efficiency and stereoselectivity.

2. Results and discussion

Our studies toward the **CTPB** catalyzed nucleophilic addition of alkynes began by using imidazole **1** and phenylacetylene **2** as a model reaction. To identify the optimal conditions for the reaction, different temperature, alkyne/imidazole ratio, and various organic solvents were investigated (Table 1). Initially, we tested the reaction in DMSO at different reaction temperatures with 10 mol% **CTPB** catalyst. The results showed that hydroamination of **2** proceeded with only 13% and 46% conversion at 80 °C and 100 °C respectively after 24 h, but with remarkable completely *Z*-stereoselectivity (Table 1, entries 1 and 2). As expected, the adducts follow the anti-Markovnikov's rule in the nucleophilic addition. Elevating the reaction temperature from 100 °C to 120 °C and 140 °C (Table 1, entries 3 and 4) resulted in the improvement of the yield, while the thermodynamically favored *E*-isomer increased at 140 °C accordingly (*E*/*Z* = 6/94 for entry 4). Based on the above results, 120 °C was proved to be the optimal reaction temperature in consideration of the balance between efficiency and stereoselectivity.

To further increase the product yield of the hydroamination,

Table 1
Optimization of the **CTPB**-catalyzed hydroamination reaction for **3a**.[a]



1 **2** **3a**

Entry	Cat.	2/1[b]	Solvent	Temp (°C)	Yield (%)[c]	*E*/*Z*[d]
1	CTPB	1	DMSO	80	13	0/100
2	CTPB	1	DMSO	100	46	0/100
3	CTPB	1	DMSO	120	72	0/100
4	CTPB	1	DMSO	140	77	6/94
5	CTPB	1.2	DMSO	120	89	0/100
6	CTPB	1.5	DMSO	120	99	0/100
7	CTPB	2/3	DMSO	120	74	0/100
8	CTPB	1.5	DMF	120	42	0/100
9	CTPB	1.5	Xylene	120	63	17/83
10	CTPB	1.5	None	120	9	18/82
11	*t*BuP_2	1.5	DMSO	120	79	0/100
12	TBD	1.5	DMSO	120	–	–
13	*t*BuOK	1.5	DMSO	120	10	10/90
14	–	1.5	DMSO	120	0	–

[a] Reactions were performed by using imidazole **1** (0.5–0.75 mmol), alkyne **2** (0.5–1.0 mmol) in solvent (1.0 mL); **CTPB**/imidazole = 10 mol%.
[b] Molar ratio of alkyne **2** and imidazole.
[c] All yields are ^{1}H NMR yields with Bn_2O standard.
[d] The *E*/*Z* ratio was determined by ^{1}H NMR without purification.

different alkyne/imidazole ratios were tested in DMSO at 120 °C (Table 1, entries 5–7). As shown in Table 1, a growth in the amount of phenylacetylene **2** from 1.0 to 1.2 and 1.5 equivalent raised the conversion significantly (89% yield for entry 5 and complete conversion for entry 6), whereas excess amount of imidazole **1** made no difference to the result (74% yield for entry 7). Fortunately, perfect stereoselectivity was maintained no matter what the alkyne/imidazole proportion was. We then examined the influence of different reaction media on the formation of **3a**. According to conventional metal-based hydroamination of alkynes, the transformation was tested in different solvent (Table 1, entries 8 and 9) and in solvent-free conditions (Table 1, entry 10). All the cases provided product, albeit in decreased yields from 9% (Table 1, entry 10) to 63% (Table 1, entry 9), which clearly indicated the critical role of DMSO in this process. It is worth noting that the lower conversion under solvent free condition compared with BEMP [18] is probably due to the solid feature of **CTPB**.

The activities of different bases in this transformation were then evaluated. 1-*tert*-Butyl-2,2,4,4,4-pentakis(dimethylamino)-2λ^5,4λ^5-catenadi(phosphazene) (*t*BuP_2) has almost identical basicity with **CTPB**. However, it provided the hydroaminated product **3a** in lower yields (Table 1, entry 11). Moreover, superbasic guanidine 1,4,7-triazabicyclodecene (TBD) failed to provide the desired product **3a** (Table 1, entry 12). When the reactants were treated with 10 mol% potassium *tert*-butoxide (*t*BuOK) in DMSO at 120 °C for 24 h, **3a** was obtained only in 10% yield (Table 1, entry 13, *E*/*Z* = 10/90). Besides, the hydroamination without catalyst was conducted as a reference and no target product **3a** was observed after 24 h (Table 1, entry 14). These results in turn verified the catalytic effect of **CTPB**. Finally, we tested the gram-scale hydroamination under the optimized reaction condition. The results showed that with 10 mol% catalyst loading, 2.35 g of **3a** could be obtained via column chromatography from the 15 mmol scale addition with 92% yield.

With the optimized conditions in hand, we then explored the substrate scope of the stereoselective hydroamination reaction by using a variety of aromatic/heteroaromatic alkynes and nitrogen

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heterocycles. Diverse functional groups on alkynes were well-tolerated, including both electron rich and electron deficient substituents. The results are summarised in Table 2 and only the anti-Markvnikov product was formed in all cases. Phenylacetylene and alkynes containing electron-donating substituents on the phenyl ring gave the corresponding hydroamination products in moderate to good yields (Table 2, **3b-d**, 92%, 78% and 90% yield). The *E*/*Z* ratio of the addition products with tertiary butyl and methoxyl group are 4/96 and 8/92 respectively, and methyl substituted product was obtained as *Z*-isomers. When alkynes with electron with-drawing groups were used, the reaction proceeded with moderate conversion values (70% for **3e** and 64% for **3f**) and complete *Z*-isomer stereoselectivity was obtained for **3e** with chlorine atom on the phenyl ring. Interestingly, the addition of alkyne with stronger electron-withdrawing fluorine atom afforded *E*-isomer dominated products with 81:19 stereoselectivity, presumably due to the decreased electron density at the distal end of the C≡C bond. Similarly, alkynes containing electron-withdrawing substituents −COOMe, −CN and $-CF_3$ on the phenyl ring gave *E*-selective hydroaminated products with high yields (Table 2, **3g-i**, 99%, 99% and 89% yield). However, hydroamination of alkyne with nitro group failed to afford the desired product. When the reaction of imidazole was conducted using bulkier 2-ethynyl-naphthalene, products were also obtained in 95% yield with 95% *E*-stereoselectivity (Table 2, **3j**).

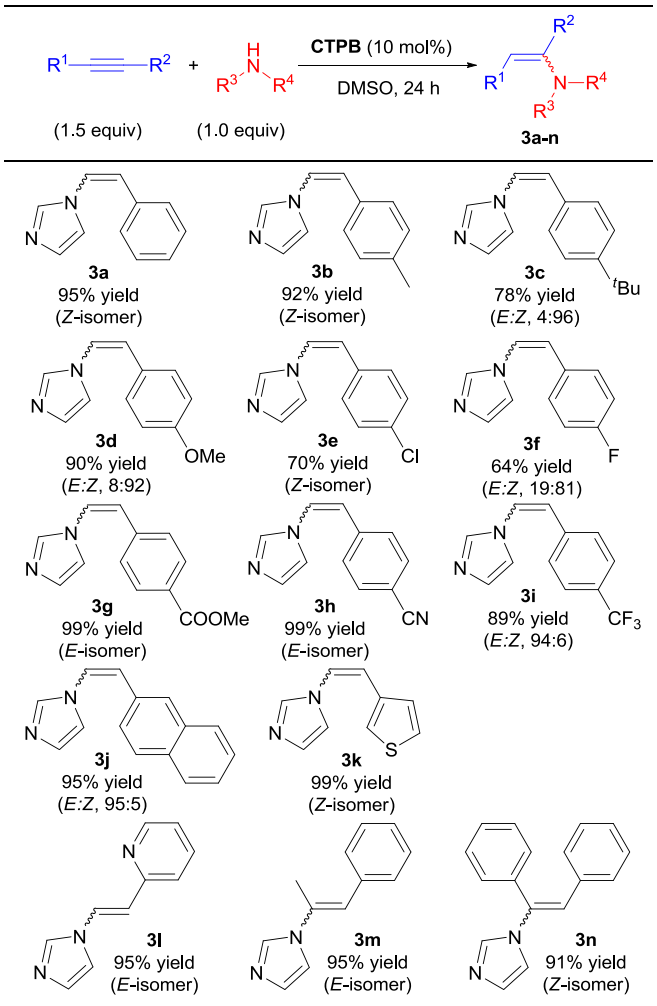
The addition of heteroaromatic alkynes was studied for their potential applications in bioactive molecules and synthetic drugs (Table 2, **3k** and **3l**). To our delight, the addition of both thiophene and pyridine based alkynes delivered the corresponding hydroamination products in high yields (99% for **3k** and 95% for **3l**). Consistent with above results, alkyne with electron-donating thiophene group gave completely *Z*-stereoselective adducts while electron-deficient 2-ethynylpyridine led to the *E*-isomers.

It has been reported that the kinetically favored thiophene substituted N-vinylimidazole (*Z*)-**3k** could isomerized to the thermodynamically stable *E*-isomers in the presence of potassium hydroxide at 120 °C [19]. We tried the isomerization for the same substrate at 120 °C using 10 mol% **CTPB** (Scheme 2), and the result showed that *Z*-structure remain unchanged even after 72 h. Similarly, we monitored the hydroamination of 2-ethynylpyridine with imidazole and no *Z*-isomer was found even at the very beginning of the reaction. These results highlight once again the good stereoselectivity of **CTPB** in the nucleophilic addition of alkynes.

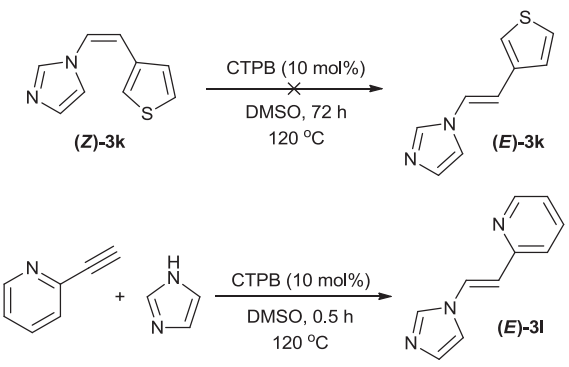
The efficacy of internal alkynes were also evaluated under the optimized reaction condition (Table 2, **3m** and **3n**). Compared with terminal alkynes, internal alkynes usually showed much lower reactivity and poor regioselectivity in hydroamination, even in the metal-based catalytic system [10b,10c,20]. The regioselective attack of the nucleophile on the internal triple bond mainly depended on the electronic bias of the substituents on both carbons of C≡C bond. Treated with 10 mol% **CTPB** at 120 °C for 24 h, both the symmetrical diphenylacetylene and the asymmetrical 1-phenylpropyne delivered the desired products in high yields (95% for **3m** and 91% for **3n**). The absolute structure of **3n** was further confirmed by the single-crystal X-ray diffraction as shown in supplementary information. The hydroamination of both internal alkynes exhibited completely stereocontrol of the double-bond geometry, which was superior to other methods for the synthesis of *N*-vinylimidazoles **3m** and **3n** [21].

N-heterocycle scope for the hydroamination reaction of alkynes was also explored as shown in Table 3. It has been proved that the electronic biases and pKa value of the *N*-heterocyclic moiety are crucial in the reactivity and stereoselectivity of the reaction [1e]. The *N*-heterocycle scope for the hydroamination process is exhibited in Table 3, using indole (for **3o**, pKa = 20.95), benzimidazole (for **3p**, pKa = 16.4), 1,2,3-1*H*-triazole (for **3q**, pKa = 13.9), and much bulkier carbazole (for **3r**, pKa = 19.9) as the *N*-nucleophiles

Table 2
Alkyne scope for the hydroamination reaction of alkynes.[a]



[a] Reaction conditions: *N*-nucleophile (0.5 mmol, 1.0 equiv.), alkyne (0.75 mmol, 1.5 equiv.), **CTPB** (0.05 mmol, 10 mol%), DMSO (1 mL), 120 °C, 24 h. Yields are total yields of two isomers. Isomer ratios were determined by ^{1}H NMR without purification.



Scheme 2. Isomerization study of adducts from heteroaromatic alkynes.

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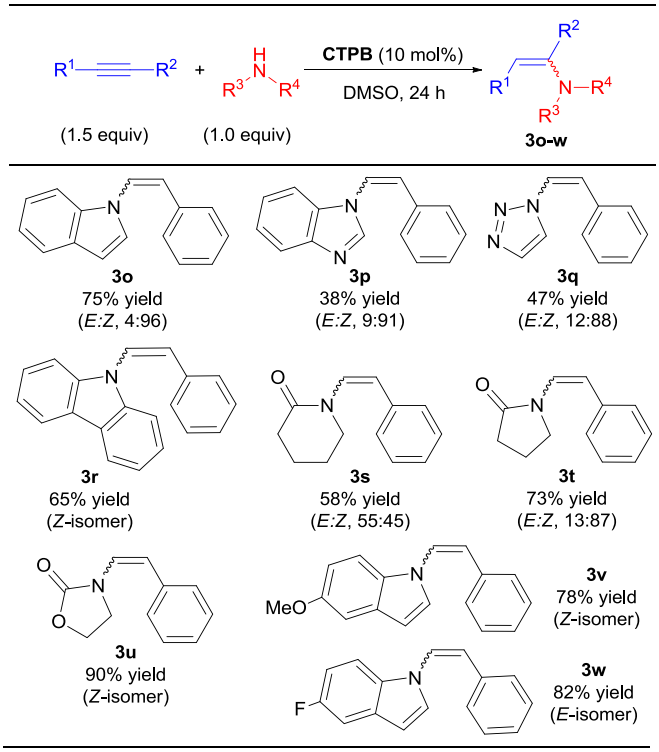
Table 3
N-heterocycle scope for the hydroamination reaction of alkynes.[a]



[a] Reaction conditions: *N*-nucleophile (0.5 mmol, 1.0 equiv.), alkyne (0.75 mmol, 1.5 equiv.), **CTPB** (0.05 mmol, 10 mol%), DMSO (1 mL), 120 °C, 24 h. Yields are total yields of two isomers. Isomer ratios were determined by ^{1}H NMR without purification.

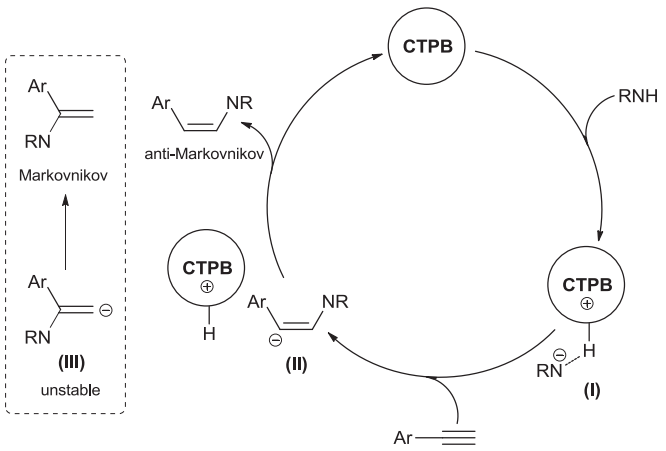
(pKa values were measured in DMSO from Bordwell pKa Table [22]). In the **CTPB** catalytic system, the acidities of the *N*-heterocycles have only limited effect on the yield of the transformation, while the electronic biases play a critical role in the reactivity. The yields lowered with the decrease of the electron density of the *N*-heterocycle. Compared with imidazole, the electron of benzimidazole delocalized in the fused rings, leading to the lower reactivity with lowest yield of 38% (Table 3, **3p**). Other *N*-heterocycles with modest electron density afforded moderate yields (75% for **3o**, 47% for **3q**, and 65% for **3r**). All of the hydroamination of phenylacetylene with *N*-heterocycles exhibited good stereoselectivity, giving *E*/*Z* from 12/88 to completely *Z*-selectivity, irrespective of the reactivity. Then, the electron withdrawing and electron donating effects of N-nucleophiles were examined using 5-position substituted indole (Table 3, **3v** and **3w**). Similar to indole, the hydroamination of substituted indoles afforded moderate product yields (78% for **3v** and 82% for **3w**). Because of the lowered electron density of the N-heterocycle, 5-fluorinated indole only lead to the *E*-product. Finally, we tried the nucleophilic addition of *O*-containing heterocycles 2-piperidone, 2-pyrrolidinone, and 2-oxazolidone (Table 3, **3s**-**u**). Five and six-membered ring lactams exhibited moderate reactivities but lower stereoselectivities (*E*:*Z*, 55/45 for **3s** and 13/87 for **3t**). Compared with aforementioned *N*-heterocycles, the special cycle 2-oxazolidone showed wonderful completely *Z*-selectivity and high product yield (90%), which has potential use in total synthesis and pharmaceutics.

We also checked the toleration of structurally more complicated N, C-protected L-Histidine and *L*-Tryptophan. The hydroamination of ethyl N-acetyl-L-Tryptophan with phenylacetylene only afforded *Z*-selective product in 5% yield (see supplementary information). While the hydroamination of Boc-L-Histidine-OMe was less active, lead to trace product which could not be separated via column chromatography. The proposed mechanism for **CTPB** catalyzed hydroamination of alkynes was shown in Scheme 3. **CTPB** could efficiently activate N-nucleophiles and form the ion pair [CTPBH$^+$ … NR$^-$] (I), which then went through nucleophilic addition to alkyne. The possible intermediate was the more stable alkenyl anion (II) rather than unstable anion (III), so the transformation proceeded in an anti-Markovnikov fashion.

We then tested the catalytic performance of **CTPB** system for the intermolecular hydrothiolation reaction of alkynes. Alkylthiols, benzyl mercaptane, and substituted thiophenols were utilized for the addition to terminal and internal alkynes, giving good to excellent yields (Table 4). The reaction of phenylacetylene with butanethiol, 4-methoxybenzenethiol, and *p*-toluenethiol provided the anti-Markovnikov *Z*-selective products **4a-c** in good yields (95%–99%) and stereosectivity (*E*:*Z*, 8/92 for **4a**, 6/94 for **4b**, and *Z*-isomer for **4c**). The thiophenol with *o*-bromine atom also delivered 96% high yield and fully *Z*-isomers **4d**. We then examined the selective functionalization of thiophenols containing multiple nucleophilic heteroatoms. We found that selective addition of mercapto group occurred over a primary amines in an aromatic ring (Table 4, **4e**, 92% yield). This selectivity is promising for developing selective reactions of more complex molecules and leaves unprotected heteroatoms available for further functionalization.

Besides, nucleophilic addition of benzyl mercaptan to phenylacetylene and heteroaromatic thiophene/pyridine alkynes afforded products **4f-h** in good yields (99% for **4f**, 91% for **4g** and 99% for **4h**). Interestingly, both electron-withdrawing pyridine group containing alkyne and electron-rich thiophene alkyne gave the *Z*-selective products, which was different from the case in hydroamination of heteroaryl alkynes. However, the stereosectivity was not that good in the hydrothiolation of benzyl mercaptan to internal alkyne and the *E*:*Z* value for **4i** was 70:30. The two isomers were not separable via column chromatography and analytical data for the mixture were given in experimental section.

As an organic base catalyzed hydrothiolation reaction, a plausible ion pair mechanism was proposed (Scheme 4). **CTPB** could efficiently activate thiols and form the ion pair [CTPBH$^+\cdots$SR$^-$] (**I**), which then went through nucleophilic addition to alkyne in an



Scheme 3. Proposed mechanism of **CTPB** catalyzed hydroamination reaction.

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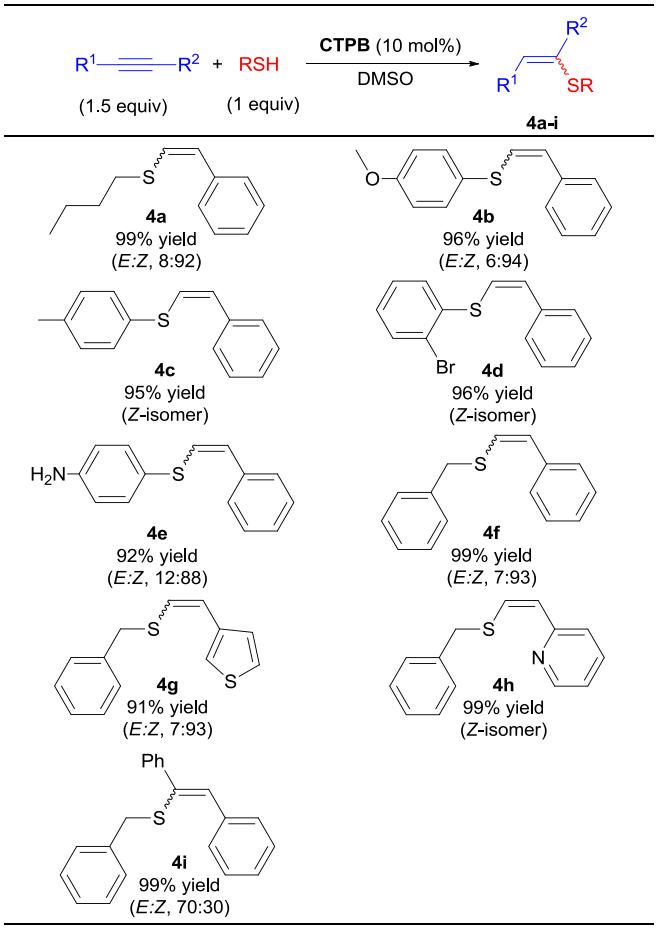
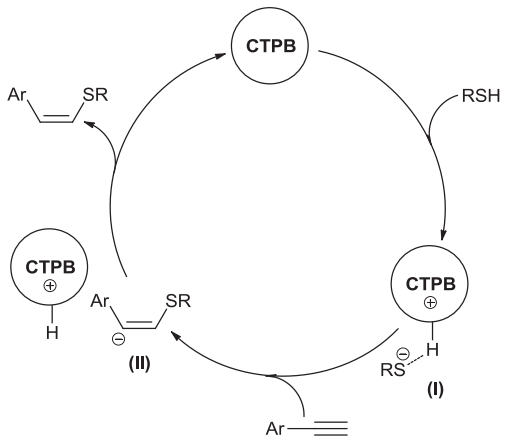
Table 4
Substrate scope for the hydroamination reaction of alkynes.[a]



[a] Reaction conditions: thiol (0.5 mmol, 1.0 equiv.), alkyne (0.75 mmol, 1.5 equiv.), **CTPB** (0.05 mmol, 10 mol%), DMSO (1 mL), 120 °C, 24 h. Yields are total yields of two isomers. Isomer ratios were determined by ^{1}H NMR without purification.



Scheme 4. Proposed mechanism of **CTPB** catalyzed hydrothiolation reaction.

anti-Markovnikov fashion to form alkenyl anion (**II**). Final hydrogen abstraction delivered the product and enabled regeneration of the catalyst **CTPB**.

3. Conclusions

In summary, a versatile metal-free protocol has been developed for the anti-Markovnikov hydroamination and hydrothiolation of various aromatic and heteroaromatic alkynes. Using low-cost metal-free cyclic trimeric phosphazene superbase **CTPB** as catalyst, these nucleophilic additions gave good to excellent yields and high stereoselectivity in DMSO with operationally simplicity. This process displays wonderful functional group tolerance and the hydroamination of low reactive internal alkynes were also realized in high yields. Ongoing efforts to develop other useful reactions enabled by organic superbase **CTPB** and the practical applications of this method are under way in our group.

4. Experimental

4.1. Materials

Toluene were purified by purging with dry nitrogen, followed by passing through columns of activated alumina. Dimethyl sulfoxide (DMSO) was purchased from Aladdin Co, and stirred with CaH_2 for 24 h, then distilled under reduced pressure and stored over activated 4 Å molecular sieves in a glovebox. **CTPB** was synthesized according to the procedure reported before [15]. All other chemicals were purchased from commercial suppliers and used without further purification unless otherwise noted. Thin-layer chromatography (TLC) was performed on silica gel 60 Å F254 plates purchased from Qingdao Haiyang Chemical Co. and visualized with UV light.

4.2. Instrumentation

Reaction temperatures were controlled using an IKA temperature modulator. All new compounds were characterized by nuclear magnetic resonance (NMR) spectroscopy and high resolution mass spectrum (HRMS). NMR spectra were recorded on a Bruker AVANCE NEO 400 MHz NMR spectrometer (400 MHz for ^{1}H NMR and 100 MHz for ^{13}C NMR). Chemical shifts were reported in δ (ppm) and the residual deuterated solvent peak was used as reference. HRMS were investigated on a Bruker APEX II type FT-ICR-MS. Melting points were measured on a RY-1 capillary melting point apparatus.

4.3. General procedures for hydroamination and hydrothiolation

In a nitrogen-filled glovebox, imidazole (34 mg, 0.5 mmol, 1.0 equiv), **CTPB** (60 mg, 0.05 mmol, 0.1 equiv) and solvent (molarity varied) were added to an oven-dried 25 mL Schlenk tube. Phenylacetylene (equivalents varied), was then added to the reaction solution. The reaction vial was capped, removed from the glovebox, and placed in a preheated oil-bath for certain reaction time. Then the reaction was allowed to cool to room temperature. An aliquot (approximately 50 μL) of the reaction solution was then directly transferred to an NMR tube and $CDCl_3$ (0.6 mL) was added. The final mixture was purified by column chromatography on silica gel (petroleum ether/ethyl acetate) to give the pure product.

4.4. Gram-scale protocol for the synthesis of ***3a***

In a nitrogen-filled glovebox, imidazole (1.02 g, 15 mmol, 1.0 equiv), **CTPB** (0.1 equiv) and DMSO (30 mL) were added to an oven-dried 100 mL Schlenk tube. Phenylacetylene (2.47 mL, 22.5 mmol, 1.5 equiv) was then added to the reaction solution. The reaction vial was capped, removed from the glovebox, and placed in a preheated oil-bath for 24 h. After naturally cooled to room temperature, the

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crude product was poured into water (100 mL) and extracted with dichloromethane for three times. The combined organic phase was dried with anhydrous sodium sulfate and condensed under reduced pressure. The final product was purified by column chromatography on silica gel using petroleum ether/ethyl acetate (50/1) as the eluent, yielding **3a** as yellow oil (2.35 g, 13.8 mmol, 92% yield).

4.5. (Z)-1-Styryl-1H-imidazole (**3a**)

Yellow oil (81.5 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.46$ (s, 1H), 7.28–7.25 (m, 3H), 7.09 (m, 2H), 7.02 (s, 1H), 6.85 (t, 1H), 6.72 (d, $J = 9.3$ Hz, 1H), 6.35 (d, $J = 9.3$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.92, 133.63, 129.52, 128.70, 128.48, 128.26, 123.31, 122.32, 118.45$; HRMS: calcd for $C_{11}H_{10}N_2$: 171.0922 $[M + H]^+$; found: 171.0924.

4.6. (Z)-1-(4-Methylstyryl)-1H-imidazole (**3b**)

Yellow oil (85.2 mg, 92% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.46$ (s, 1H), 7.07 (d, $J = 8.0$ Hz, 2H), 7.03 (s, 2H), 6.97 (d, $J = 8.0$ Hz, 2H), 6.86 (s, 1H), 6.67 (d, $J = 9.2$ Hz, 1H), 6.31 (d, $J = 9.2$ Hz, 1H), 2.31 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.07, 136.74, 130.50, 129.30, 129.20, 128.24, 123.56, 121.57, 118.33, 21.02$; HRMS: calcd for $C_{12}H_{12}N_2$: 185.1079 $[M + H]^+$; found: 185.1075.

4.7. (Z)-1-(4-(Tert-butyl)styryl)-1H-imidazole (**3c**)

Brown oil (85.2 mg, 75% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.48$ (s, 1H), 7.29–7.26 (m, 1H), 7.06 (s, 2H), 7.00 (d, $J = 8.4$ Hz, 2H), 6.90 (s, 1H), 6.67 (d, $J = 9.2$ Hz, 1H), 6.32 (d, $J = 9.2$ Hz, 1H), 1.28 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 151.61, 136.96, 130.61, 129.53, 128.33, 125.67, 124.06, 121.76, 118.58, 34.66, 31.20$; HRMS: calcd for $C_{15}H_{18}N_2$: 227.1548 $[M + H]^+$; found: 227.1547.

4.8. (Z)-1-(4-Methoxystyryl)-1H-imidazole (**3d**)

Brown oil (83.5 mg, 83% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.49$ (s, 1H), 7.06 (s, 1H), 6.97 (m, 2H), 6.88 (s, 1H), 6.78 (m, 2H), 6.63 (d, $J = 9.2$ Hz, 1H), 6.31 (d, $J = 9.2$ Hz, 1H), 3.76 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.58, 136.87, 129.97, 129.44, 125.83, 124.38, 120.88, 118.62, 114.16, 55.25$; HRMS: calcd for $C_{11}H_{10}N_2$: 201.1028 $[M + H]^+$; found: 201.1030.

4.9. (Z)-1-(4-Chlorostyryl)-1H-imidazole (**3e**)

Yellow solid (71.9 mg, 70% yield): mp 46–48 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.39$ (s, 1H), 7.20–7.18 (m, 2H), 6.98–6.94 (m, 2H), 6.77 (s, 1H), 6.69 (d, $J = 9.2$ Hz, 1H), 6.23 (d, $J = 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.87, 134.18, 132.03, 129.84, 128.99, 127.30, 122.91, 122.28, 118.36$; HRMS: calcd for $C_{11}H_9ClN_2$: 205.0533 $[M + H]^+$; found: 205.0533.

4.10. (Z)-1-(4-Fluorostyryl)-1H-imidazole (**3f**)

Yellow oil (49.5 mg, 52% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.47$ (s, 1H), 7.09–7.05 (m, 3H), 7.00–6.96 (m, 2H), 6.85 (t, 1H), 6.74 (d, $J = 9.2$ Hz, 1H), 6.33 (d, $J = 9.2$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 163.63, 161.16, 136.87, 130.40, 130.32, 129.79, 122.68, 122.37, 118.39, 115.94, 115.72$; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -112.31$; HRMS: calcd for $C_{11}H_9FN_2$: 190.0828 $[M + H]^+$; found: 190.0829.

4.11. (E)-Methyl 4-(2-(1H-imidazole-1-yl)vinyl)benzoate (**3g**)

White solid (113.3 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.01$ (d, $J = 8.0$ Hz, 2H), 7.76 (s, 1H), 7.45–7.42 (m, 3H), 7.28 (s, 1H), 7.15 (s, 1H), 6.74 (d, $J = 14.8$ Hz, 1H), 3.90 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 166.51, 138.97, 136.56, 130.74, 130.12, 129.28, 125.87, 124.50, 117.24, 116.04, 52.07$; HRMS: calcd for $C_{13}H_{12}N_2O_2$: 229.0977 $[M + H]^+$; found: 229.0975.

4.12. (E)-4-(2-(1H-Imidazole-1-yl)vinyl)benzonitrile (**3h**)

White solid (98.1 mg, 99% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.81–7.78$ (m, 2H), 7.65–7.63 (m, 2H), 7.50–7.44 (m, 3H), 7.30 (t, 1H), 7.17 (s, 1H), 6.73 (d, $J = 14.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.16, 136.70, 132.64, 131.01, 127.93, 126.48, 125.44, 118.60, 116.37, 116.02, 111.09$; HRMS: calcd for $C_{12}H_9N_3$: 196.0874 $[M + H]^+$; found: 196.0874.

4.13. (E)-1-(4-(Trifluoromethyl)styryl)-1H-imidazole (**3i**)

Brown semi-solid (100.6 mg, 84% yield). ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.78$ (s, 1H), 7.62 (d, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 8.0$ Hz, 2H), 7.43 (d, $J = 14.8$ Hz, 1H), 7.29 (t, 1H), 7.17 (s, 1H), 6.76 (d, $J = 14.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.05, 136.61, 130.90, 129.94, 129.62, 126.25, 125.89$ (q, 1C), $125.34, 124.60, 122.63, 116.95, 116.10$; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -62.59$; HRMS: calcd for $C_{12}H_9F_3N_2$: 239.0796 $[M + H]^+$; found: 239.0801.

4.14. (E)-1-(2-(Naphthalen-2-yl)vinyl)-1H-imidazole (**3j**)

Yellow solid (99.5 mg, 90% yield): mp 133–135 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.85–7.79$ (m, 5H), 7.58 (dd, $J_1 = 8.8$ Hz, $J_2 = 2.0$ Hz, 1H), 7.52–7.45 (m, 3H), 7.32 (m, 1H), 7.18 (s, 1H), 6.91 (d, $J = 14.4$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.43, 132.55, 132.01, 130.81, 129.56, 127.67, 126.86, 126.73, 125.64, 125.37, 125.25, 121.91, 121.84, 117.90, 115.23$; HRMS: calcd for $C_{15}H_{12}N_2$: 221.1079 $[M + H]^+$; found: 221.1082.

4.15. (Z)-1-(2-(Thiophen-3-yl)vinyl)-1H-imidazole (**3k**)

Yellow solid (88.1 mg, 99% yield): mp 67–69 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (s, 1H), 7.22–7.20 (m, 1H), 7.12 (s, 1H), 7.08 (d, $J = 2.8$ Hz, 1H), 6.93 (s, 1H), 6.66 (d, $J = 8.8$ Hz, 1H), 6.58 (dd, $J_1 = 4.8$ Hz, $J_2 = 0.8$ Hz, 1H), 6.43 (d, $J = 8.8$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 136.92, 134.13, 129.80, 127.05, 126.23, 125.77, 121.38, 120.78, 118.67$; HRMS: calcd for $C_9H_8N_2S$: 177.0486 $[M + H]^+$; found: 177.0481.

4.16. (E)-2-(2-(1H-Imidazole-1-yl)vinyl)pyridine (**3l**)

Yellow solid (81.8 mg, 95% yield): mp 60–62 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.57–8.55$ (m, 1H), 7.98 (d, $J = 14.0$ Hz, 1H), 7.79 (s, 1H), 7.68–7.64 (m, 1H), 7.31 (t, 1H), 7.22 (d, $J = 7.6$ Hz, 1H), 7.18–7.15 (m, 2H), 6.73 (d, $J = 14.0$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 153.33, 149.72, 137.00, 136.79, 130.83, 126.47, 122.42, 122.34, 116.73, 116.14$; HRMS: calcd for $C_{10}H_9N_3$: 172.0875 $[M + H]^+$; found: 172.0874.

4.17. (E)-1-(1-Phenylprop-1-en-2-yl)-1H-imidazole (**3m**)

Yellow solid (88.0 mg, 95% yield): mp 59–61 °C. ^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 7.80$ (s, 1H), 7.41–7.37 (m, 2H), 7.32–7.29 (m, 3H), 7.23 (t, 1H), 7.14 (t, 1H), 6.68 (s, 1H), 2.35 (d, $J = 0.8$ Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.21, 135.17, 132.96, 129.85, 128.99, 128.49, 127.32, 119.84, 117.09, 17.15$; HRMS: calcd for $C_{12}H_{12}N_2$:

Please cite this article as: N. Zhao et al., Anti-Markovnikov stereoselective hydroamination and hydrothiolation of (hetero)aromatic alkynes using a metal-free cyclic trimeric phosphazene base, Tetrahedron, https://doi.org/10.1016/j.tet.2019.04.075

185.1079 $[M + H]^+$; found: 185.1085.

4.18. (Z)-1-(1,2-Diphenylvinyl)-1H-imidazole (**3n**)

Yellow solid (112.4 mg, 91% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.45$ (s, 1H), 7.39–7.37 (m, 3H), 7.28–7.23 (m, 6H), 6.98 (s, 1H), 6.90 (t, 1H), 6.88–6.86 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.60$, 137.50, 134.47, 133.86, 130.18, 129.25, 128.82, 128.72, 128.61, 128.38, 125.91, 124.69, 119.64; HRMS: calcd for $C_{17}H_{14}N_2$: 247.1235 $[M + H]^+$; found: 247.1230.

4.19. (Z)-1-Styryl-1H-indole (**3o**)

Brown oil (79.3 mg, 72% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.53$ (d, 1H, $J = 8.0$ Hz), 7.29 (d, 1H, $J = 8.0$ Hz), 7.19–7.00 (m, 7H), 6.94 (d, 1H, $J = 3.2$ Hz), 6.88 (d, 1H, $J = 9.2$ Hz), 6.42 (d, 1H, $J = 3.2$ Hz), 6.21 (d, 1H, $J = 9.2$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.87$, 134.96, 128.69, 128.56, 128.42, 127.52, 127.09, 123.30, 122.43, 120.87, 120.69, 119.60, 110.11, 103.94; HRMS: calcd for $C_{16}H_{13}N$: 220.1126 $[M + H]^+$; found: 220.1121.

4.20. (Z)-1-Styryl-1H-benzo[d]imidazole (**3p**)

Yellow solid (38.8 mg, 35% yield): mp 115–117 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.84$–7.80 (m, 2H), 7.37–7.30 (m, 3H), 7.25–7.22 (m, 3H), 7.11–7.08 (m, 2H), 6.87 (d, 1H, $J = 8.8$ Hz), 6.58 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 143.29$, 141.99, 133.63, 133.00, 128.86, 128.46, 128.44, 125.36, 123.63, 122.86, 120.40, 120.31, 110.27; HRMS: calcd for $C_{15}H_{12}N_2$: 221.1079 $[M + H]^+$; found: 221.1083.

4.21. (Z)-1-Styryl-1H-1,2,3-triazole (**3q**)

Yellow solid (35.4 mg, 41% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.59$ (d, 1H, $J = 1.2$ Hz), 7.40 (d, 1H, $J = 1.2$ Hz), 7.34–7.32 (m, 3H), 7.28 (d, 1H, $J = 9.6$ Hz), 7.14–7.12 (m, 2H), 6.58 (d, 1H, $J = 9.6$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 133.47$, 133.11, 128.96, 128.76, 128.49, 123.98, 123.36; HRMS: calcd for $C_{10}H_9N_3$: 172.0875 $[M + H]^+$; found: 172.0879.

4.22. (Z)-9-Styryl-9H-carbazole (**3r**)

Yellow solid (87.9 mg, 65% yield): mp 90–92 °C. ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.09$ (d, 1H, $J = 8.0$ Hz), 7.36–7.32 (m, 2H), 7.27–7.23 (m, 2H), 7.19 (d, 1H, $J = 8.0$ Hz), 7.11–7.07 (m, 5H), 6.92 (d, 1H, $J = 8.8$ Hz), 6.67 (d, 1H, $J = 8.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 139.23$, 134.80, 128.75, 128.31, 127.83, 126.41, 125.89, 123.98, 122.01, 120.24, 120.11, 111.09; HRMS: calcd for $C_{20}H_{15}N$: 270.1283 $[M + H]^+$; found: 270.1287.

4.23. 1-Styrylpiperidin-2-one (**3s**)

Z-isomer: yellow oil (26.5 mg, 26% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$–7.29 (m, 2H), 7.27–7.21 (m, 3H), 6.79 (d, $J = 9.2$ Hz, 1H), 6.10 (d, $J = 9.2$ Hz, 1H), 3.20 (t, 2H), 2.51 (t, 2H), 1.84–1.78 (m, 2H), 1.72–1.66 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 170.83$, 135.77, 128.96, 128.56, 128.20, 127.25, 119.70, 48.79, 32.28, 23.09, 20.94; HRMS: calcd for $C_{13}H_{15}NO$: 202.1232 $[M + H]^+$; found: 202.1234.

E-isomer: white solid (32.4 mg, 32% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.17$ (d, $J = 15.2$ Hz, 1H), 7.38–7.36 (m, 2H), 7.29 (t, 2H), 7.17 (t, 1H), 5.96 (d, $J = 15.2$ Hz, 1H), 3.55–3.51 (m, 2H), 2.56–2.52 (m, 2H), 1.94–1.82 (m, 4H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 168.57$, 136.71, 128.51, 126.92, 126.32, 125.66, 110.68, 45.18, 32.92, 22.49, 20.36; HRMS: calcd for $C_{13}H_{15}NO$: 202.1232 $[M + H]^+$; found: 202.1235.

4.24. 1-Styrylpyrrolidin-2-one (**3t**)

Z-isomer: yellow oil (60.2 mg, 64% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.33$–7.29 (m, 2H), 7.25–7.22 (m, 1H), 7.20–7.18 (m, 2H), 6.79 (d, $J = 9.6$ Hz, 1H), 6.00 (d, $J = 9.6$ Hz, 1H), 3.20 (t, 2H), 2.41 (t, 2H), 1.94 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 175.54$, 136.25, 129.13, 127.77, 126.83, 123.82, 113.77, 48.04, 30.34, 18.82; HRMS: calcd for $C_{12}H_{13}NO$: 188.1075 $[M + H]^+$; found: 188.1078.

E-isomer: white solid (8.5 mg, 9% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.62$ (d, $J = 14.8$ Hz, 1H), 7.36–7.34 (m, 2H), 7.30–7.27 (m, 2H), 7.19–7.15 (m, 1H), 5.87 (d, $J = 14.8$ Hz, 1H), 3.63 (t, 2H), 2.53 (t, 2H), 2.14 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 173.30$, 136.28, 128.57, 126.46, 125.53, 123.48, 111.66, 45.13, 31.15, 17.33; HRMS: calcd for $C_{12}H_{13}NO$: 188.1075 $[M + H]^+$; found: 188.1074.

4.25. (Z)-3-Styryloxazolidin-2-one (**3u**)

Yellow oil (85.5 mg, 90% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.34$–7.30 (m, 2H), 7.27–7.25 (m, 1H), 7.23–7.20 (m, 2H), 6.67 (d, 1H, $J = 9.6$ Hz), 5.99 (d, 1H, $J = 9.6$ Hz), 4.26 (t, 2H), 3.37 (t, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 135.56$, 129.29, 127.94, 127.11, 124.24, 112.78, 62.63, 44.97; HRMS: calcd for $C_{11}H_{11}NO_2$: 190.0868 $[M + H]^+$; found: 190.0867.

4.26. (Z)-5-Methoxy-1-styryl-1H-indole (**3v**)

White solid (97.4 mg, 78% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.25$–7.17 (m, 6H), 7.07 (d, $J = 2.4$ Hz, 1H), 6.99 (d, $J = 2.8$ Hz, 1H), 6.92–6.86 (m, 2H), 6.42 (d, $J = 3.2$ Hz, 1H), 6.24 (d, $J = 9.2$ Hz, 1H), 3.85 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 154.89$, 135.01, 130.97, 129.02, 128.65, 128.40, 127.61, 127.45, 123.41, 119.18, 112.24, 110.82, 103.63, 102.87, 55.83; HRMS: calcd for $C_{17}H_{15}NO$: 250.1232 $[M + H]^+$; found: 250.1234.

4.27. (E)-5-Fluoro-1-styryl-1H-indole (**3w**)

Yellow solid (97.7 mg, 82% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.58$ (d, $J = 14.8$ Hz, 1H), 7.51 (d, $J = 3.6$ Hz, 1H), 7.45–7.42 (m, 3H), 7.36 (t, 2H), 7.28–7.22 (m, 2H), 7.04–6.99 (m, 1H), 6.66 (d, $J = 14.4$ Hz, 1H), 6.61 (d, $J = 3.6$ Hz, 1H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 159.65$, 157.30, 135.80, 132.20, 129.60, 129.50, 128.83, 127.01, 125.71, 125.34, 123.43, 114.69, 111.07, 110.82, 110.32, 110.22, 106.37, 106.14, 105.06, 105.02; ^{19}F NMR (376 MHz, $CDCl_3$): $\delta = -123.34$; HRMS: calcd for $C_{16}H_{12}FN$: 238.1032 $[M + H]^+$; found: 238.1035.

4.28. (Z)-Butyl(styryl)sulfane (**4a**)

Yellow oil (87.7 mg, 91% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.50$ (d, 2H, $J = 7.6$ Hz), 7.36 (t, 2H), 7.23–7.19 (m, 1H), 6.44 (d, 1H, $J = 10.8$ Hz), 6.26 (d, 1H, $J = 10.8$ Hz), 2.80 (t, 2H), 1.73–1.65 (m, 2H), 1.51–1.41 (m, 2H), 0.94 (t, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.05$, 128.58, 128.18, 127.68, 126.53, 125.24, 35.58, 32.28, 21.68, 13.62; HRMS: calcd for $C_{12}H_{16}S$: 193.1051 $[M + H]^+$; found: 193.1054.

4.29. (Z)-(4-Methoxyphenyl)(styryl)sulfane (**4b**)

Yellow oil (109.4 mg, 90% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.60$ (d, 2H, $J = 7.2$ Hz), 7.44–7.37 (m, 3H), 7.29–7.26 (m, 2H), 7.00–6.97 (m, 1H), 6.91 (dd, 1H, $J_1 = 8.0$ Hz, $J_2 = 1.2$ Hz), 6.64 (d, 1H, $J = 10.8$ Hz), 6.48 (d, 1H, $J = 10.8$ Hz), 3.91 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 157.24$, 130.93, 128.84, 128.46, 128.20, 127.65, 126.97, 125.29, 121.29, 110.91, 55.87; HRMS: calcd for $C_{15}H_{14}OS$:

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243.0844 $[M + H]^+$; found: 243.0839.

4.30. (Z)-Styryl(p-tolyl)sulfane (**4c**)

Yellow oil (107.7 mg, 95% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.52$ (d, 2H, $J = 7.6$ Hz), 7.40–7.35 (m, 4H), 7.26–7.23 (m, 1H), 7.15 (d, 2H, $J = 7.6$ Hz), 6.54 (d, 1H, $J = 10.8$ Hz), 6.46 (d, 1H, $J = 10.8$ Hz), 2.34 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.40$, 136.58, 132.69, 130.52, 129.92, 128.71, 128.28, 127.04, 126.99, 126.51, 21.05; HRMS: calcd for $C_{15}H_{14}S$: 227.0894 $[M + H]^+$; found: 227.0897.

4.31. (Z)-(2-Bromophenyl)(styryl)sulfane (**4d**)

Yellow oil (139.4 mg, 96% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.55$ (d, 3H, $J = 8.0$ Hz), 7.42–7.35 (m, 3H), 7.29–7.24 (m, 2H), 7.08–7.04 (m, 1H), 6.73 (d, 1H, $J = 10.8$ Hz), 6.38 (d, 1H, $J = 10.8$ Hz); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.50$, 136.00, 133.05, 130.31, 129.86, 128.89, 128.30, 127.99, 127.93, 127.45, 124.06, 123.56; HRMS: calcd for $C_{14}H_{11}BrS$: 290.9843 $[M + H]^+$; found: 290.9846.

4.32. (Z)-4-(Styrylthio)aniline (**4e**)

Yellow oil (92.3 mg, 81% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.56$ (d, 2H, $J = 7.6$ Hz), 7.44–7.39 (m, 3H), 7.29–7.25 (m, 1H), 7.20–7.16 (m, 1H), 6.77–6.72 (m, 2H), 6.53 (d, 1H, $J = 10.8$ Hz), 6.19 (d, 1H, $J = 10.8$ Hz), 4.25 (br, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 147.69$, 136.58, 135.23, 130.45, 128.78, 128.34, 127.72, 127.00, 126.73, 118.70, 117.85, 115.31; HRMS: calcd for $C_{14}H_{13}NS$: 228.0847 $[M + H]^+$; found: 228.0845.

4.33. (Z)-Benzyl(styryl)sulfane (**4f**)

Yellow oil (104.4 mg, 92% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.46–7.44$ (m, 2H), 7.38–7.31 (m, 6H), 7.28–7.27 (m, 1H), 7.22–7.18 (m, 1H), 6.42 (d, 1H, $J = 10.8$ Hz), 6.24 (d, 1H, $J = 10.8$ Hz), 3.99 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 137.36$, 136.84, 128.97, 128.68, 128.65, 128.21, 127.39, 126.71, 125.97, 125.87, 39.51; HRMS: calcd for $C_{15}H_{14}S$: 227.0894 $[M + H]^+$; found: 227.0895.

4.34. (Z)-3-(2-(Benzylthio)vinyl)thiophene (**4g**)

Yellow solid (99.1 mg, 85% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.40–7.33$ (m, 5H), 7.33–7.28 (m, 1H), 7.28–7.25 (m, 1H), 7.23–7.21 (m, 1H), 6.46 (d, 1H, $J = 10.8$ Hz), 6.17 (d, 1H, $J = 10.8$ Hz), 4.02 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 138.26$, 137.45, 128.97, 128.71, 128.62, 127.42, 124.86, 124.84, 123.36, 120.19, 39.13; HRMS: calcd for $C_{13}H_{12}S_2$: 233.0459 $[M + H]^+$; found: 233.0453.

4.35. (Z)-2-(2-(Benzylthio)vinyl)pyridine (**4h**)

Yellow oil (112.7 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 8.66–8.65$ (m, 1H), 7.61–7.57 (m, 1H), 7.40–7.38 (m, 2H), 7.35–7.31 (m, 2H), 7.28–7.26 (m, 1H), 7.20 (d, 1H, $J = 8.0$ Hz), 7.06–7.02 (m, 1H), 6.60 (d, 1H, $J = 10.8$ Hz), 6.45 (d, 1H, $J = 10.8$ Hz), 3.98 (s, 2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 155.90$, 148.72, 137.91, 135.93, 132.79, 129.12, 128.67, 127.23, 123.42, 123.04, 120.42, 40.28; HRMS: calcd for $C_{14}H_{13}NS$: 228.0847 $[M + H]^+$; found: 228.0849.

4.36. Benzyl(1,2-diphenylvinyl)sulfane, 7/3 mixture of E and Z isomer (**4i**)

Yellow solid (150.0 mg, 99% yield). ^1H NMR (400 MHz, $CDCl_3$): $\delta = 7.59–7.53$ (m, 3H, $Z + E$), 7.42–7.28 (m, 6H, $Z + E$), 7.23–7.17 (m, 3.44H, $Z + E$), 7.08–7.04 (m, 2.37H, $Z + E$), 6.91–6.89 (m, 0.65H, Z-2H), 6.80 (s, 0.70H, E-1H), 6.76 (s, 0.30H, Z-1H), 3.75 (s, 0.63H, Z-2H), 3.64 (s, 1.42H, E-2H); ^{13}C NMR (100 MHz, $CDCl_3$): $\delta = 141.09$, 137.93, 137.84, 137.60, 137.18, 137.00, 136.67, 132.84, 129.84, 129.50, 128.94, 128.90, 128.87, 128.64, 128.45, 128.42, 128.29, 128.14, 127.99, 127.20, 126.93, 126.62, 37.45, 36.92; HRMS: calcd for $C_{14}H_{13}NS$: 303.1207 $[M + H]^+$; found: 303.1206.

Acknowledgments

The authors appreciate financial support from NSFC (Nos. 21704048 and 21434008), Major Program of Shandong Province Natural Science Foundation (No. ZR2017ZB0105), and Shandong Province Natural Science Foundation (No. ZR2017PB008).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.04.075.

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Please cite this article as: N. Zhao et al., Anti-Markovnikov stereoselective hydroamination and hydrothiolation of (hetero)aromatic alkynes using a metal-free cyclic trimeric phosphazene base, Tetrahedron, https://doi.org/10.1016/j.tet.2019.04.075