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Phosphine-Catalyzed [4 + 1] Annulation between α,β-Unsaturated Imines and Allylic Carbonates: Synthesis of 2-Pyrrolines

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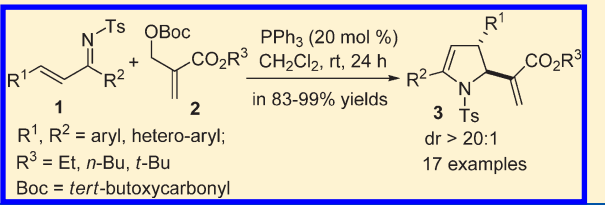
Supporting Information

ABSTRACT: In this report, a phosphine-catalyzed [4 + 1] annulation between α,β-unsaturated imines and allylic carbonates is described. This reaction represents the first realization of catalytic [4 + 1] cyclization of 1,3-azadienes with in situ formed phosphorus ylides, which provides highly efficient and diastereoselective synthesis of 2-pyrrolines.



Five-membered nitrogen heterocycles are important and ubiquitous substructures in a vast array of natural products and biologically interesting compounds.[1−3] Among this group of heterocycles, pyrrolines (dihydropyrroles) are not only versatile intermediates which allow ready access to pyrrolidines and pyrroles,[4,5] but also occur in numerous natural products and therapeutic agents.[6−8] A number of synthetic approaches toward pyrrolines therefore have been developed,[9−12] but the majority of the existing synthetic methods are centered upon 3-pyrrolines. The synthetic methodology on 2-pyrrolines featuring an enamine skeleton is pretty underdeveloped,[13−22] although 2-pyrrolines are very important with regard to their versatility in organic synthesis and interest in pharmaceuticals.[1−8] Developing new and efficient synthesis of 2-pyrrolines is thus highly desirable.

The formal [4 + 1] cycloaddition of 1-aza-1,3-dienes (α,β-unsaturated imines) with one-carbon units such as ylides provides a potential and straightforward protocol to construct 2-pyrroline ring system (Scheme 1).[23] The analogous syntheses of 2,3-dihydrofurans by the [4 + 1] cyclization between α,β-unsaturated carbonyl compounds and ylides have been well documented.[23,24] It is only recently that the syntheses of 2-pyrrolines via the [4 + 1] annulations of α,β-unsaturated imines have been realized with sulfur and nitrogen ylides independently by Xiao[13] and Tang.[14] It is recognized that phosphorus ylides have been rarely applied to ylide-based cyclizations, primarily due to their intrinsic reactivity preference for Wittig olefinations and the poorest leaving group ability of the phosphonium moiety compared with sulfur and nitrogen ylides.[25,26] Consequently, the formal [4 + 1] cycloaddition of 1-aza-1,3-dienes with phosphorus ylides has not yet been realized prior to this study.

In the past decade, the nucleophilic phosphine catalysis has effected many powerful annulations of electron-deficient alkenes or alkynes with various electrophiles to construct carbo- and heterocycles.[27,28] In principle, those phosphine-mediated annulations proceed via an addition−elimination mechanism, by which the intramolecularity of the ring-closure step can circumvent the problem arising from the poor leaving group ability of the phosphonium moiety. Even in some cases, in situ formed phosphorus ylide intermediates are presumably involved in such cyclizations.[28] To date, many important annulations like [3 + 2] and [4 + 2] annulations to generate five- and six-membered nitrogen heterocycles have been developed under nucleophilic phosphine catalysis.[29−32] Very recently, two examples of the phosphine-catalyzed [4 + 1] annulations to produce five-membered oxygen heterocycles were also reported.[33,34] Herein, we wish to report a PPh_3-catalyzed [4 + 1] annulation between α,β-unsaturated imines and allylic carbonates which represents the first synthesis of 2-pyrrolines through a phosphorus ylide-based [4 + 1] cyclization of 1,3-azadienes (vide infra).

As part of our continuous efforts on exploring phosphorus ylide-based carbon−carbon bond forming reactions, recently we disclosed a PBu_3-catalyzed cascade [3 + 2] cyclization−allylic alkylation reaction of conjugated enones with allylic carbonates (Scheme 2).[35] While we attempted to extend the reaction to α,β-unsaturated imines, to our surprise, a phosphine-catalyzed [4 + 1] annulation between α,β-unsaturated imines and allylic carbonates occurred, leading to a highly efficient and diastereoselective synthesis of polysubstituted 2-pyrrolines (Scheme 2).

Our investigation was initiated with the model reaction of the chalcone-derived imine **1a** and allylic carbonate **2a** (Table 1). In CH_2Cl_2 solvent and at rt, several tertiary phosphines were screened as catalysts (Table 1, entries 1−6). All tested phosphines could effectively catalyze the model reaction with PPh_3 and P(4-MeO-Ph)$_3$ giving almost quantitative yields of **3a** (entries 4 and 5). Lowering the catalyst loading of PPh_3 to 10 mol % resulted in considerable reduction of the yield (entry 7). Choosing PPh_3 as the catalyst, some common solvents were also investigated. It was found that the model reaction readily occurred in nonpolar or polar aprotic solvents, giving the product

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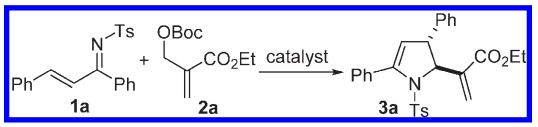
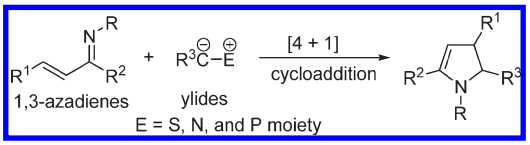
Table 1. Preliminary Survey on Model Reaction Conditions[a]



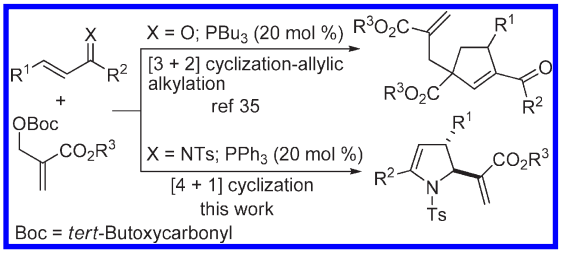
entry	catalyst	solvent	yield of **3a** (%)[b]
1	PBu_3	CH_2Cl_2	40
2	$PhPMe_2$	CH_2Cl_2	58
3	Ph_2PMe	CH_2Cl_2	66
4	PPh_3	CH_2Cl_2	99
5	$P(4\text{-MeO-Ph})_3$	CH_2Cl_2	99
6	$P(4\text{-F-Ph})_3$	CH_2Cl_2	50
7[c]	PPh_3	CH_2Cl_2	90
8	PPh_3	toluene	99
9	PPh_3	THF	70
10	PPh_3	ether	60
11	PPh_3	CH_3CN	88

[a] Typical conditions: under N_2 atmosphere, a mixture of **1a** (0.25 mmol), **2a** (0.3 mmol), and phosphine (0.05 mmol) in solvent (2.0 mL) was stirred at rt for 24 h. [b] Isolated yield based on **1a** and dr >20:1 by ^1H NMR of **3a**. [c] 10 mol % of PPh_3 was employed.

Scheme 1. Formal [4 + 1] Ylide Cycloaddition of 1,3-Azadienes To Generate 2-Pyrrolines



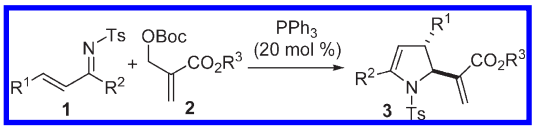
Scheme 2. Phosphine-Catalyzed Annulations of Enones or Azadienes with Allylic Carbonates



3a in good to excellent yields (entries 8−11). The results in Table 1 show that the annulation of **1a** and **2a** has good tolerance to reaction conditions.

Under the preferred conditions (PPh_3 used as the catalyst in CH_2Cl_2 at rt for 24 h), the substrate scope and limitations for the [4 + 1] annulation of unsaturated imines **1** and allylic carbonates **2** were studied (Table 2). For a wide range of aryl-substituted imines **1** (R^1, R^2 = aryl) with either relatively electron-poor or -rich aryl groups, their corresponding [4 + 1] annulations with the allylic carbonate **2a** readily proceeded, giving 2-pyrrolines **3** in good to excellent yields (entries 1−14). Bulky alkyl-substituted allylic carbonates **2b** (R^3 = *n*-Bu) and **2c** (R^3 = *t*-Bu) were also examined in the reactions with the imine **1a**, readily affording the corresponding 2-pyrrolines **3o** and **3p** in high yields (entries

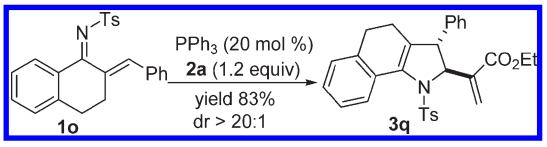
Table 2. Synthesis of 2-Pyrrolines 3[a]



entry	R^1 in **1**	R^2 in **1**	R^3 in **2**	yield of **3** (%),[b] dr[c]
1	Ph	Ph (**1a**)	Et (**2a**)	**3a**, 99, >20:1
2	4-MeO-Ph	Ph (**1b**)	Et (**2a**)	**3b**, 80, >20:1
3	4-Cl-Ph	Ph (**1c**)	Et (**2a**)	**3c**, 85, >20:1
4	4-F-Ph	Ph (**1d**)	Et (**2a**)	**3d**, 97, >20:1
5	4-CF_3-Ph	Ph (**1e**)	Et (**2a**)	**3e**, 99, >20:1
6	3-NO_2-Ph	Ph (**1f**)	Et (**2a**)	**3f**, 94, >20:1
7	2-furyl	Ph (**1g**)	Et (**2a**)	**3g**, 87, >20:1
8	4-Cl-Ph	4-Br-Ph (**1h**)	Et (**2a**)	**3h**, 88, >20:1
9	4-F-Ph	4-Br-Ph (**1i**)	Et (**2a**)	**3i**, 84, >20:1
10	Ph	4-Cl-Ph (**1j**)	Et (**2a**)	**3j**, 96, >20:1
11	4-CF_3−Ph	4-Cl-Ph (**1k**)	Et (**2a**)	**3k**, 89, >20:1
12	Ph	4-NO_2-Ph (**1l**)	Et (**2a**)	**3l**, 95, >20:1
13	4-Cl-Ph	4-NO_2-Ph (**1m**)	Et (**2a**)	**3m**, 91, >20:1
14	4-F-Ph	4-NO_2-Ph (**1n**)	Et (**2a**)	**3n**, 84, >20:1
15	Ph	Ph (**1a**)	*n*-Bu (**2b**)	**3o**, 94, >20:1
16	Ph	Ph (**1a**)	*t*-Bu (**2c**)	**3p**, 90, >20:1

[a] For details, see the Experimental Section. [b] Isolated yield based on **1**. [c] Determined by ^1H NMR.

Scheme 3. Synthesis of Fused Cyclic Product 3q



15 and 16). In all tested cases, the product 2-pyrroline **3** was isolated as a single diastereomer, as determined by ^1H and ^{13}C NMR.

Interestingly, cyclic unsaturated imine **1o** was also an effective substrate (Scheme 3). Under the optimized conditions, the corresponding fused cyclic product **3q** was obtained in 83% isolated yield. However, methyl- or phenyl-substituted analogues (**2d** and **2e**) of the allylic carbonate **2a** failed in giving the expected [4 + 1] annulation products with the imine **1a**, when subjected to similar conditions (Scheme 4). In the case of **2d**, the imine substrate **1a** was inert, but the carbonate **2d** gradually decomposed into a complex mixture under the influence of PPh_3; for the phenyl-substituted allylic carbonate **2e**, a [3 + 2] annulation product **4** was obtained in 65% yield under the catalysis of more nucleophilic phosphine $PhPMe_2$. Similar PBu_3-catalyzed [3 + 2] annulation of the carbonate **2e** with enones was also developed in our laboratory.[35]

The structures of compounds **3** and **4** were identified by ^1H, ^{13}C NMR, and HRMS-ESI measurements. X-ray crystallographic analysis for representative compound **3a** provided unequivocal evidence for structural assignments of **3** (for details, also see the Supporting Information).

Possible mechanisms to account for the formation of **3** are depicted in Scheme 5. Presumably, the catalytic cycle is initiated with the in situ formation of the allylic phosphorus ylide **5**

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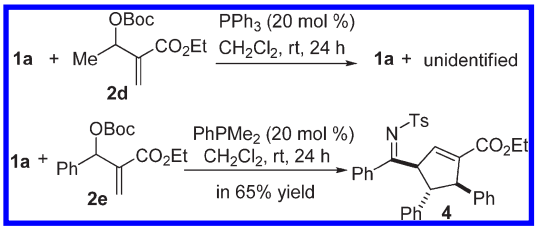
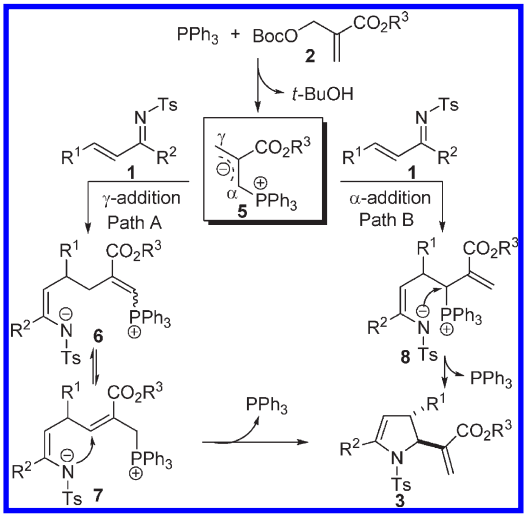
Scheme 4. Investigations on Methyl- or Phenyl-Substituted Allylic Carbonates 2d and 2e



Scheme 5. Possible Mechanisms for Formation of 3



through an addition−elimination−deprotonation process.[36] Ylide **5** most likely undergoes the sterically favored γ-carbanion addition to 1,3-azadiene **1** (path A) leading to intermediate **6**, which interconverts with intermediate **7** through a hydrogen transfer process.[37] Intermediate **7** furnishes 2-pyrroline **3** and regenerates the PPh_3 catalyst via an intramolecular Michael addition followed by elimination of PPh_3. The failure of methyl- and phenyl-substituted allylic carbonates **2d** and **2e** to undergo the [4 + 1] annulations and the formation of the [3 + 2] annulation product **4** (Scheme 4) are in favor of the path A mechanism. Another possibility that could not be completely ruled out is the formation of the 2-pyrroline **3** through α-carbanion addition of the allylic phosphorus ylide **5** to the imine **1** (path B). The resulting intermediate **8** subsequently undertakes an intramolecular S_N2 cyclization to afford **3** and release the PPh_3 catalyst (Scheme 5). Similar mechanisms were also proposed to rationalize the [4 + 1] annulations of 1,3-azadienes with sulfur and nitrogen ylides.[13,14] Recently, our group reported a PPh_3-catalyzed [2 + 2 + 2] annulation between two different alkenes, in which an intramolecular S_N2 cyclization step involving PPh_3 moiety as a leaving group was also proposed.[38]

In summary, the [4 + 1] annulation between α,β-unsaturated imines and allylic carbonates has been realized under the catalysis of PPh_3, which provides highly efficient and diastereoselective synthesis of polysubstituted 2-pyrrolines. This annulation represents the first example of the formal [4 + 1] cycloaddition of 1,3-azadienes and phosphorus ylides, although it is very likely that the annulation proceeds through a typical nucleophilic phosphine-catalyzed mechanism. Efforts to clarify the accurate mechanism and to exploit the use of this reaction in organic synthesis are ongoing.

EXPERIMENTAL SECTION

Unless otherwise noted, all reactions were carried out in a nitrogen atmosphere under anhydrous conditions. Column chromatography was performed on silica gel (200−300 mesh). The unsaturated imines **1** were readily prepared from the corresponding ketones according to the reported procedure.[39] Allylic carbonates **2** were prepared by the known method.[36]

Preparation of *N*-(2-benzylidene-3,4-dihydro-2*H*-naphthalen-1-ylidene)-4-methylbenzenesulfonamide (1o): To a solution of 4-methylbenzenesulfonamide (0.86 g, 5.0 mmol) and (*E*)-2-benzylidene-3,4-dihydronaphthalen-1(2*H*)-one (1.17 g, 5.0 mmol) in CH_2Cl_2 (15 mL) were successively added Et_3N (1.01 g, 10 mmol) and $TiCl_4$ (0.95 g, 5.0 mmol) at 0 °C with stirring. The resulting mixture was heated at reflux overnight. After being cooled to room temperature and quenched with water (100 mL), the organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (3 × 50 mL). The combined organic phase was washed with water (3 × 20 mL) and dried over Na_2SO_4. After filtration and evaporation of solvent, the crude product was further purified by recrystallization from petroleum ether/ethyl acetate (5:1) to afford pure imine **1o** (1.26 g) in 65% yield. Yellow solid; mp 132−133 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.16 (d, J = 7.7 Hz, 1H), 7.94 (d, J = 8.2 Hz, 2H), 7.84 (s, 1H), 7.47−7.37 (m, 5H), 7.36−7.29 (m, 3H), 7.25 (t, J = 3.8 Hz, 1H), 7.19 (d, J = 7.7 Hz, 1H), 2.97 (s, 4H), 2.44 (s, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 174.6, 142.8, 142.7, 139.7, 138.6, 135.4, 135.3, 133.4, 132.9, 129.4, 129.3, 128.6, 128.4, 128.2, 126.8, 126.7, 30.0, 27.2, 21.4; HRMS-ESI calcd for $C_{24}H_{21}NO_2S$ $[M + Na]^+$ 410.1185, found 410.1180.

General procedure for PPh_3-catalyzed [4 + 1] annulation of 1 and 2: A mixture consisting of the imine **1** (0.25 mmol), allylic carbonate **2** (0.3 mmol), and PPh_3 (13 mg, 0.05 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 24 h. The reaction mixture was then concentrated on a rotary evaporator under reduced pressure and the residue was subjected to purification by column chromatography (gradient elution with petroleum ether−ethyl acetate from 20:1 to 10:1) to afford the product **3**. Following the above procedure, 2-pyrrolines **3a**−**q** were readily prepared from corresponding 1,3-azadienes **1** and allylic carbonates **2** (Table 2 and Scheme 3).

Ethyl *trans*-2-(3,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3a): yield 99%; white solid; mp 153−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (dd, J = 6.6, 2.9 Hz, 2H), 7.42 (m, 3H), 7.30 (d, J = 8.2 Hz, 2H), 7.03 (m, 5H), 6.72 (d, J = 7.3 Hz, 2H), 6.50 (s, 1H), 6.26 (s, 1H), 5.27 (d, J = 3.4 Hz, 1H), 5.01 (d, J = 3.0 Hz, 1H), 4.28 (q, J = 7.2 Hz, 2H), 3.61 (t, J = 3.4 Hz, 1H), 2.40 (s, 3H), 1.30 (t, J = 7.2 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 144.8, 143.6, 142.2, 140.9, 133.6, 132.6, 129.5, 129.1, 128.4, 128.1, 128.0, 127.9, 127.4, 126.2, 125.5, 116.0, 69.7, 61.1, 53.4, 21.5, 14.1; HRMS-ESI calcd for $C_{28}H_{27}NO_4S$ $[M + Na]^+$ 496.1553, found 496.1550.

Ethyl *trans*-2-(3-(4-methoxyphenyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3b): yield 80%; white solid; mp 154−155 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (dd, J = 6.5, 2.9 Hz, 2H), 7.42 (m, 3H), 7.31 (d, J = 8.2 Hz, 2H), 7.09 (d, J = 8.2 Hz, 2H), 6.64 (d, J = 8.7 Hz, 2H), 6.56 (d, J = 8.7 Hz, 2H), 6.48 (s, 1H), 6.25 (s, 1H), 5.25 (d, J = 3.5 Hz, 1H), 4.97 (d, J = 2.7 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.77 (s, 3H), 3.57 (t, J = 3.2 Hz, 1H), 2.42 (s, 3H), 1.31 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 158.1, 144.6, 143.7, 140.9, 134.6, 133.9, 132.7, 129.5, 129.0, 128.4, 128.0, 127.9, 125.3, 116.3, 113.5, 70.0, 61.0, 55.2, 52.7, 21.5, 14.2; HRMS-ESI calcd for $C_{29}H_{29}NO_5S$ $[M + Na]^+$ 526.1659, found 526.1663.

Ethyl *trans*-2-(3-(4-chlorophenyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3c): yield 85%; white solid; mp

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195−197 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 6.3, 2.6 Hz, 2H), 7.45 (m, 3H), 7.26 (d, J = 3.4 Hz, 1H), 7.03 (d, J = 8.1 Hz, 2H), 6.98 (d, J = 8.3 Hz, 2H), 6.79 (d, J = 8.3 Hz, 2H), 6.51 (s, 1H), 6.30 (s, 1H), 5.29 (d, J = 3.5 Hz, 1H), 5.02 (s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.57 (t, J = 2.8 Hz, 1H), 2.42 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 145.4, 144.2, 141.0, 140.3, 133.7, 132.4, 132.1, 129.4, 129.3, 128.7, 128.4, 128.2, 128.0, 127.8, 125.6, 115.3, 69.6, 61.2, 52.1, 21.5, 14.2; HRMS-ESI calcd for $C_{28}H_{26}ClNO_4S$ $[M + Na]^+$ 530.1163, found 530.1157.

Ethyl *trans*-2-(3-(4-fluorophenyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3d): yield 97%; white solid; mp 183−185 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (dd, J = 6.1, 2.5 Hz, 2H), 7.44 (m, 3H), 7.29 (d, J = 8.1 Hz, 2H), 7.06 (d, J = 8.0 Hz, 2H), 6.79−6.68 (m, 4H), 6.50 (s, 1H), 6.29 (s, 1H), 5.28 (d, J = 3.5 Hz, 1H), 4.99 (br s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.59 (t, J = 2.9 Hz, 1H), 2.41 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 161.4 (d, J = 245.0 Hz), 145.1, 144.0, 140.6, 138.2 (d, J = 2.7 Hz), 133.8, 132.5, 129.5, 129.3, 129.0 (d, J = 7.9 Hz), 128.4, 127.93, 127.90, 125.5, 115.6, 114.8 (d, J = 21.1 Hz), 69.8, 61.1, 52.3, 21.5, 14.2; HRMS-ESI calcd for $C_{28}H_{26}FNO_4S$ $[M + Na]^+$ 514.1459, found 514.1450.

Ethyl *trans*-2-(5-phenyl-1-tosyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3e): yield 99%; white solid; mp 177−178 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71 (m, 2H), 7.45 (m, 3H), 7.28 (s, 1H), 7.23 (s, 1H), 6.99 (d, J = 8.1 Hz, 4H), 6.53 (s, 1H), 6.34 (s, 1H), 5.32 (d, J = 3.6 Hz, 1H), 5.06 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.65 (t, J = 2.8 Hz, 1H), 2.37 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 146.3, 145.8, 144.1, 140.3, 133.8, 132.3, 129.4, 128.40, 128.43 (q, J = 32.1 Hz), 128.3, 128.0, 127.8, 127.7, 125.7, 124.9 (q, J = 3.7 Hz), 124.2 (q, J = 272.0 Hz), 114.8, 69.4, 61.2, 52.4, 21.3, 14.2; HRMS-ESI calcd for $C_{29}H_{26}F_3NO_4S$ $[M + Na]^+$ 564.1427, found 564.1422.

Ethyl *trans*-2-(3-(3-nitrophenyl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3f): yield 94%; white solid; mp 197−199 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.99 (d, J = 6.6 Hz, 1H), 7.75 (dd, J = 6.6, 2.8 Hz, 2H), 7.65 (d, J = 7.8 Hz, 1H), 7.59 (s, 1H), 7.48 (m, 3H), 7.32 (t, J = 7.9 Hz, 1H), 7.21 (d, J = 8.1 Hz, 2H), 6.93 (d, J = 8.1 Hz, 2H), 6.56 (s, 1H), 6.38 (s, 1H), 5.38 (d, J = 3.6 Hz, 1H), 5.10 (s, 1H), 4.33 (m, 2H), 3.70 (t, J = 2.8 Hz, 1H), 2.26 (s, 3H), 1.37 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.9, 147.9, 146.6, 144.7, 144.1, 139.9, 134.3, 133.6, 132.1, 129.6, 129.4, 129.2, 128.5, 128.1, 127.6, 126.0, 122.1, 121.4, 113.8, 69.4, 61.4, 51.8, 21.3, 14.2; HRMS-ESI calcd for $C_{28}H_{26}N_2O_6S$ $[M + Na]^+$ 541.1404, found 541.1408.

Ethyl *trans*-2-(3-(furan-2-yl)-5-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3g): yield 87%; white solid; mp 122−124 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.64 (m, 2H), 7.42 (m, 3H), 7.35 (d, J = 8.2 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 7.09 (s, 1H), 6.51 (s, 1H), 6.29 (s, 1H), 6.03 (m, 1H), 5.39 (d, J = 3.0 Hz, 1H), 5.25 (d, J = 3.6 Hz, 1H), 5.14 (br s, 1H), 4.30 (m, 2H), 3.64 (t, J = 3.0 Hz, 1H), 2.40 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 154.2, 145.3, 143.6, 141.4, 140.1, 133.5, 132.3, 129.4, 129.2, 128.3, 128.0, 127.9, 125.7, 113.4, 109.9, 105.8, 67.2, 61.1, 47.2, 21.5, 14.1; HRMS-ESI calcd for $C_{26}H_{25}NO_5S$ $[M + Na]^+$ 486.1346, found 486.1345.

Ethyl *trans*-2-(5-(4-bromophenyl)-3-(4-chlorophenyl)-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3h): yield 88%; white solid; mp 231−232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 (m, 4H), 7.25 (d, J = 8.4 Hz, 2H), 7.04 (d, J = 8.0 Hz, 2H), 6.97 (d, J = 8.4 Hz, 2H), 6.74 (d, J = 8.4 Hz, 2H), 6.50 (s, 1H), 6.24 (s, 1H), 5.31 (d, J = 3.6 Hz, 1H), 4.99 (br s, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.57 (t, J = 2.9 Hz, 1H), 2.43 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 144.4, 144.6, 140.7, 140.2, 133.4, 132.2, 131.3, 131.2, 129.8, 129.5, 128.6, 128.2, 127.7, 125.6, 123.4, 115.9, 69.7, 61.2, 52.1, 21.5, 14.2; HRMS-ESI calcd for $C_{28}H_{25}BrClNO_4S$ $[M + Na]^+$ 608.0268, found 608.0261.

Ethyl *trans*-2-(5-(4-bromophenyl)-3-(4-fluorophenyl)-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3i): yield 84%; white solid; mp 233−234 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.56 (m, 4H), 7.28 (m, 2H), 7.07 (d, J = 8.0 Hz, 2H), 6.72 (m, 4H), 6.49 (s, 1H), 6.21 (s, 1H), 5.29 (d, J = 3.6 Hz, 1H), 4.96 (d, J = 2.7 Hz, 1H), 4.29 (q, J = 7.1 Hz, 2H), 3.59 (t, J = 3.2 Hz, 1H), 2.41 (s, 3H), 1.32 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 161.5 (d, J = 245.4 Hz), 144.2, 144.1, 140.5, 137.9 (d, J = 2.8 Hz), 133.6, 131.4, 131.2, 129.9, 129.7, 128.9 (d, J = 7.8 Hz), 127.9, 125.5, 123.3, 116.2, 114.9 (d, J = 21.2 Hz), 69.9, 61.2, 52.4, 21.5, 14.2; HRMS-ESI calcd for $C_{28}H_{25}BrFNO_4S$ $[M + Na]^+$ 592.0564, found 592.0560.

Ethyl *trans*-2-(5-(4-chlorophenyl)-3-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3j): yield 96%; white solid; mp 209−210 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.62 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8.4 Hz, 2H), 7.30 (d, J = 8.1 Hz, 2H), 7.14−7.00 (m, 5H), 6.68 (d, J = 7.4 Hz, 2H), 6.49 (s, 1H), 6.19 (s, 1H), 5.28 (d, J = 3.5 Hz, 1H), 4.98 (d, J = 3.0 Hz, 1H), 4.28 (m, 2H), 3.63 (t, J = 3.3 Hz, 1H), 2.41 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 144.0, 143.8, 142.0, 140.8, 134.9, 133.4, 131.1, 129.6, 129.4, 129.1, 128.2, 128.0, 127.3, 126.4, 125.6, 116.6, 69.9, 61.1, 53.4, 21.6, 14.2; HRMS-ESI calcd for $C_{28}H_{26}ClNO_4S$ $[M + Na]^+$ 530.1163, found 530.1159.

Ethyl *trans*-2-(5-(4-chlorophenyl)-1-tosyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3k): yield 89%; white solid; mp 211−212 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.65 (d, J = 8.4 Hz, 2H), 7.42 (d, J = 8.4 Hz, 2H), 7.30−7.20 (m, 4H), 7.00 (d, J = 8.1 Hz, 2H), 6.95 (d, J = 8.1 Hz, 2H), 6.52 (s, 1H), 6.27 (s, 1H), 5.33 (d, J = 3.5 Hz, 1H), 5.04 (s, 1H), 4.31 (q, J = 7.1 Hz, 2H), 3.66 (s, 1H), 2.37 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 146.1, 144.7, 144.3, 140.2, 135.3, 133.5, 130.7, 129.6, 129.5, 128.4 (q, J = 32.2 Hz), 128.3, 127.7, 127.6, 125.7, 125.0 (q, J = 3.6 Hz), 124.1 (q, J = 272.0 Hz), 115.3, 69.5, 61.2, 52.4, 21.3, 14.2; HRMS-ESI calcd for $C_{29}H_{25}ClF_3NO_4S$ $[M + Na]^+$ 598.1037, found 598.1036.

Ethyl *trans*-2-(5-(4-nitrophenyl)-3-phenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3*l*): yield 95%; white solid; mp 224−225 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.7 Hz, 2H), 7.85 (d, J = 8.7 Hz, 2H), 7.31 (d, J = 8.2 Hz, 2H), 7.13 (m, 3H), 7.03 (m, 2H), 6.64 (d, J = 7.4 Hz, 2H), 6.50 (s, 1H), 6.16 (s, 1H), 5.48 (d, J = 3.5 Hz, 1H), 4.93 (d, J = 3.4 Hz, 1H), 4.29 (m, 2H), 3.71 (t, J = 3.5 Hz, 1H), 2.43 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.5, 147.9, 144.4, 143.1, 141.5, 140.6, 139.2, 132.9, 129.8, 128.9, 128.3, 128.0, 127.3, 126.6, 125.9, 123.3, 119.7, 70.2, 61.2, 53.8, 21.6, 14.1; HRMS-ESI calcd for $C_{28}H_{26}N_2O_6S$ $[M + Na]^+$ 541.1404, found 541.1403.

Ethyl *trans*-2-(3-(4-chlorophenyl)-5-(4-nitrophenyl)-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3m): 91% yield; white solid; mp 231−232 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.30 (d, J = 8.7 Hz, 2H), 7.86 (d, J = 8.7 Hz, 2H), 7.27 (d, J = 7.0 Hz, 2H), 7.09 (d, J = 8.0 Hz, 2H), 7.00 (d, J = 8.4 Hz, 2H), 6.71 (d, J = 8.4 Hz, 2H), 6.51 (s, 1H), 6.21 (s, 1H), 5.50 (d, J = 3.5 Hz, 1H), 4.97 (d, J = 2.3 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.66 (t, J = 3.0 Hz, 1H), 2.44 (s, 3H), 1.34 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 148.1, 144.8, 143.6, 140.2, 140.1, 138.9, 133.0, 132.5, 129.7, 128.9, 128.6, 128.4, 127.8, 125.8, 123.4, 118.9, 69.9, 61.3, 52.6, 21.6, 14.2; HRMS-ESI calcd for $C_{28}H_{25}ClN_2O_6S$ $[M + Na]^+$ 575.1014, found 575.1012.

Ethyl *trans*-2-(3-(4-fluorophenyl)-5-(4-nitrophenyl)-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3n): yield 84%; white solid; mp 203−205 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.29 (d, J = 8.8 Hz, 2H), 7.85 (d, J = 8.8 Hz, 2H), 7.30 (d, J = 8.3 Hz, 2H), 7.12 (d, J = 8.0 Hz, 2H), 6.71 (m, 4H), 6.50 (s, 1H), 6.19 (s, 1H), 5.48 (d, J = 3.6 Hz, 1H), 4.93 (d, J = 3.0 Hz, 1H), 4.30 (q, J = 7.1 Hz, 2H), 3.68 (t, J = 3.3 Hz, 1H), 2.43 (s, 3H), 1.33 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.6, 161.6 (d, J = 245.7 Hz) 148.0, 144.6, 143.3, 140.3, 139.0, 137.4 (d, J = 3.3 Hz), 133.1, 129.7, 128.94, 128.86 (d, J = 7.8 Hz), 127.9, 125.8, 123.3, 119.3, 115.0 (d, J = 21.3 Hz), 70.1, 61.2, 52.7, 21.5, 14.2; HRMS-ESI calcd for $C_{28}H_{25}FN_2O_6S$ $[M + Na]^+$ 559.1310, found 559.1313.

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Butyl *trans*-2-(3,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3o): yield 94%; white solid; mp 131−132 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 (m, 2H), 7.43 (m, 3H), 7.31 (d, J = 7.9 Hz, 2H), 7.06 (m, 5H), 6.71 (d, J = 7.6 Hz, 2H), 6.49 (s, 1H), 6.26 (s, 1H), 5.27 (d, J = 3.4 Hz, 1H), 5.00 (s, 1H), 4.30−4.05 (m, 2H), 3.61 (s, 1H), 2.40 (s, 3H), 1.68−1.59 (m, 2H), 1.38 (m, 2H), 0.93 (t, J = 7.4 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.8, 144.8, 143.8, 142.3, 141.0, 133.6, 132.6, 129.5, 129.1, 128.4, 128.1, 128.0, 127.9, 127.4, 126.2, 125.4, 116.0, 69.7, 64.9, 53.5, 30.5, 21.6, 19.2; 13.7; HRMS-ESI calcd for $C_{30}H_{31}NO_4S$ $[M + Na]^+$ 524.1866, found 524.1860.

***tert*-Butyl *trans*-2-(3,5-diphenyl-1-tosyl-2,3-dihydro-1*H*-pyrrol-2-yl)acrylate (3p):** yield 90%; white solid; mp 93−95 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67 (m, 2H), 7.41 (m, 3H), 7.33 (m, 2H), 7.10 (m, 3H), 7.02 (m, 2H), 6.68 (d, J = 7.5 Hz, 2H), 6.38 (s, 1H), 6.16 (s, 1H), 5.24 (s, 1H), 4.98 (s, 1H), 3.60 (s, 1H), 2.41 (s, 3H), 1.49 (s, 9H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.9, 144.8, 143.7, 142.5, 142.4, 133.6, 132.7, 129.5, 129.0, 128.4, 128.1, 128.1, 127.8, 127.4, 126.3, 124.4, 116.2, 81.5, 69. 7, 53.8, 28.0, 21.6; HRMS-ESI calcd for $C_{30}H_{31}NO_4S$ $[M + Na]^+$ 524.1866, found 524.1869.

Ethyl *trans*-2-(3-phenyl-1-tosyl-2,3,4,5-tetrahydro-1*H*-benzo[*g*]indol-2-yl)acrylate (3q): yield 83%; white solid; mp 142−144 °C; ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03 (d, J = 7.7 Hz, 1H), 7.37 (m, 4H), 7.23 (m, 1H), 7.13−7.06 (m, 3H), 6.99 (m, 2H), 6.54 (d, J = 7.4 Hz, 2H), 6.39 (s, 1H), 6.07 (s, 1H), 4.90 (d, J = 3.3 Hz, 1H), 4.21 (m, 2H), 3.42 (s, 1H), 2.91−2.70 (m, 2H), 2.44 (s, 3H), 2.12−1.89 (m, 2H), 1.21 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.7, 143.8, 141.1, 141.0, 138.0, 135.8, 132.9, 131.1, 129.6, 129.4, 129.1, 128.4, 128.2, 127.7, 127.6, 127.2, 126.3, 126.0, 125.4, 70.2, 61.00, 56.6, 29.3, 23.2, 21.6, 14.0; HRMS-ESI calcd for $C_{30}H_{29}NO_4S$ $[M + Na]^+$ 522.1709, found 522.1706.

Ethyl 4,5-diphenyl-3-(phenyl(tosylimino)methyl)cyclopent-1-enecarboxylate (4): A mixture of imine **1a** (90 mg, 0.25 mmol), allylic carbonate **2e** (93 mg, 0.3 mmol), and $PhPMe_2$ (8 μL, 0.05 mmol) in CH_2Cl_2 (2 mL) was stirred at room temperature for 24 h. Then the reaction mixture was concentrated on a rotary evaporator under reduced pressure and the residue was purified by column chromatography (eluted with petroleum ether−ethyl acetate 10:1) to afford the product **4** (90 mg) in 65% yield: colorless oil; ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.82 (d, J = 8.1 Hz, 2H), 7.33 (d, J = 8.1 Hz, 2H), 7.27 (m, 1H), 7.19−7.09 (m, 7H), 7.08 (m, 3H), 6.92 (m, 2H), 6.85 (m, 2H), 6.79 (s, 1H), 4.46 (d, J = 8.0 Hz, 2H), 4.10−3.88 (m, 2H), 3.66 (m, 1H), 2.46 (s, 3H), 1.01 (t, J = 7.1 Hz, 3H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 184.6, 163.9, 143.9, 143.5, 142.9, 141.9, 138.2, 137.5, 136.9, 130.9, 129.4, 128.6, 128.3, 127.8, 127.5, 127.4, 127.3, 127.2, 127.0, 126.4, 70.0, 60.2, 54.8, 53.9, 21.5, 13.8; HRMS-ESI calcd for $C_{34}H_{31}NO_4S$ $[M + H]^+$ 550.2047, found 550.2050.

■ ASSOCIATED CONTENT

Supporting Information. Copies of ^{1}H and ^{13}C NMR spectra for **1o**, **3**, and **4**, X-ray crystallographic data (CIF file), and an ORTEP drawing for **3a**. This material is available free of charge via the Internet at http://pubs.acs.org.

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