Tetrahedron 67 (2011) 7728–7737

Contents lists available at ScienceDirect

Tetrahedron

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

Orthogonal synthesis of pyrroles and 1,2,3-triazoles from vinyl azides and 1,3-dicarbonyl compounds

Eileen Pei Jian Ng [a], Yi-Feng Wang [a], Benjamin Wei-Qiang Hui [a], Guillaume Lapointe [b], Shunsuke Chiba [a,*]

[a] Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore
[b] Department fur Chemie und Biochemie, Universitat Bern, Freiestrasse 3, CH-3012, Switzerland

ARTICLE INFO

Article history:
Received 2 May 2011
Received in revised form 13 July 2011
Accepted 2 August 2011
Available online 6 August 2011

Keywords:
Vinyl azides
Pyrroles
1,2,3-Triazoles
1,3-Dicarbonyl compounds

ABSTRACT

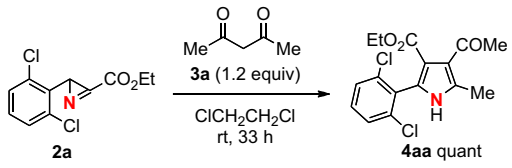
Tri- and tetrasubstituted *N*–H pyrroles were prepared by the simple treatment of vinyl azides with 1,3-dicarbonyl compounds in toluene at 100 °C via 2*H*-azirine intermediates generated in situ. When the reactions of vinyl azides and 1,3-dicarbonyl compounds were performed in DMF in the presence of a catalytic amount of K_2CO_3, 1-vinyl-1,2,3-triazoles were obtained via 1,3-dipolar cycloaddition. These methodologies exploited orthogonal modes of chemical reactivity of vinyl azides, which could be achieved by slight modification of the reaction conditions.

1. Introduction

Nitrogen-containing heterocyclic compounds (azaheterocycles) are one of the most abundant components in numerous natural products, potent pharmaceutical drugs, and various kinds of functional materials. Although diverse synthetic approaches toward azaheterocycles have been developed,[1] versatile and flexible methodologies to construct azaheterocycles with selective control of substitution patterns using readily available building blocks are still needed.

We have recently been interested in the application of vinyl azides as a three atom unit including one nitrogen to synthesize azaheterocycles. One of the intriguing chemical features of vinyl azides **1** is their thermal denitrogenative decomposition to highly strained three-membered cyclic imines, 2*H*-azirines **2** via vinyl nitrene intermediates (Scheme 1).[2] During the course of our study on the chemistry of the 2*H*-azirine derivatives,[3,4] we found that the reaction of 2*H*-azirine **2a** with acetylacetone (**3a**) in 1,2-dichloroethane at room temperature was slow, but gave tetrasubstituted pyrrole **4aa** in quantitative yield after 33 h (Scheme 2).

Scheme 1.



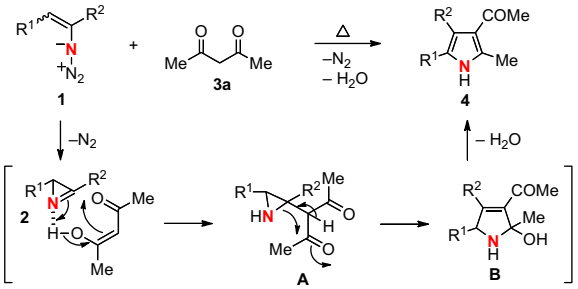
Scheme 2.

Although the reaction of 2*H*-azirine **2a** with acetylacetone (**3a**) in THF has been reported, the yield of pyrrole **4aa** was low.[5] The high yield of **4aa** in the above reaction (Scheme 2) prompted us to study the pyrrole formation in detail. The reaction may proceed through the addition of acetylacetone (**3a**) to the imino carbon of **2a**,[6] followed by the intramolecular nucleophilic attack of the nitrogen of the resulting aziridine to a carbonyl group with the ring opening of the strained three-membered ring as reported in the reactions with ketone enolates or enamines.[7] While this reaction seemed to be useful to synthesize pyrroles, most of 2*H*-azirines were difficult to prepare and to handle due to their instability. Accordingly, we planned to use vinyl azides as precursors of

* Corresponding author. Tel.: +65 6513 8013; fax: +65 6791 1961; e-mail address: shunsuke@ntu.edu.sg (S. Chiba).

0040-4020/$ – see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2011.08.006

2*H*-azirines, which can be easily synthesized[8] and handled (Scheme 3). This is a full account of the thermal reactions of vinyl azides with 1,3-dicarbonyl compounds for synthesis of pyrroles with broad evaluation of scope and limitation.[9,10] In addition, a methodology to prepare 1,2,3-triazoles was exploited from the same combination of the starting materials by slight modification of the reaction conditions.



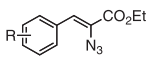
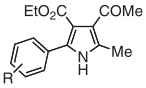
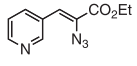
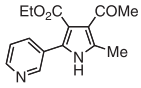
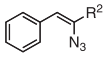
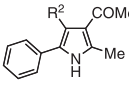
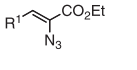
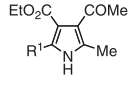
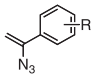
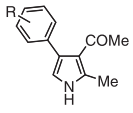
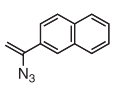
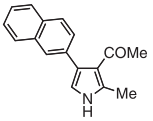
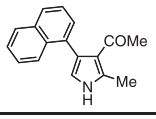
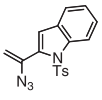
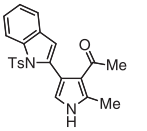
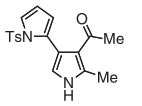
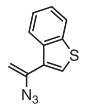
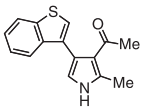
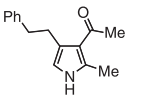
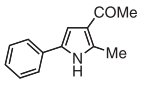
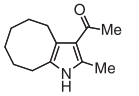
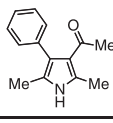
Scheme 3.

2. Results and discussion

As proposed in Scheme 3, when a mixture of ethyl 2-azido-3-(2,6-dichlorophenyl)acrylate (**1a**) and acetylacetone (**3a**) was heated in toluene at 100 °C, pyrrole **4aa** was obtained in 86% yield (Table 1, entry 1). Various α-aryl pyrroles (R^1=aryl) were prepared from 2-azido cinnamates **1** possessing not only both electron-donating and withdrawing groups (entries 2–8) on the phenyl group but also with a pyridyl moiety (entry 9). Instead of α-ethoxycarbonyl vinyl azides, α-acetyl and *N*,*N*-dimethylamino-carbonyl vinyl azides **1j** and **1k** could be employed to give the corresponding pyrroles **4ja** and **4ka**, respectively (entries 10 and 11). It is known that the thermolysis of 2-azido cinnamates and their derivatives result in the formation of indoles via intramolecular C–H amination,[11,12] whereas it is noteworthy that the intermolecular reactions with acetylacetone (**3a**) gave pyrroles exclusively without any indole formation. For the β-substituents (R^1) of azido acrylates **1**, ethoxycarbonyl, alkyl, and hydrogen could be introduced, giving the corresponding pyrroles in good yields (entries 12–14). The reactions of α-aryl vinyl azides **1o**–**z** with acetylacetone (**3a**) gave trisubstituted pyrroles **4**, where not only phenyl groups but also naphthyl, indolyl, pyrrolyl, and benzothiofuranyl moieties could be installed on C2 of the pyrrole ring (entries 15–26). α-Alkyl vinyl azides (**1aa**) resulted in a smooth reaction with **3a** to give corresponding pyrrole (**4aaa**) in 82% yield (entry 27). 2-Azidostyrene (**1bb**) could also be applied for this thermal pyrrole formation, giving trisubstituted pyrrole **4bba** in 85% yield (entry 28). Even trisubstituted vinyl azides **1cc** and **1dd** reacted smoothly with acetylacetone (**3a**) to afford tetrasubstituted pyrroles **4cca** and **4dda** (entries 29 and 30).

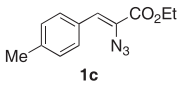
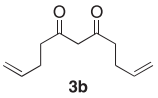
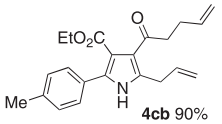
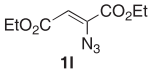
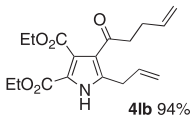
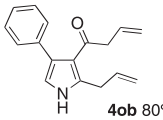
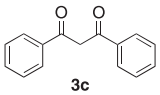
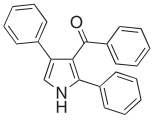
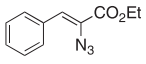
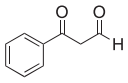
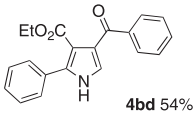
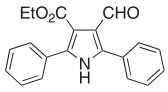
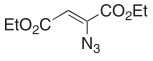
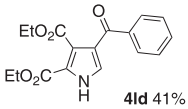
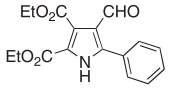
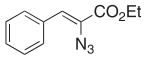
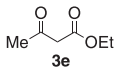
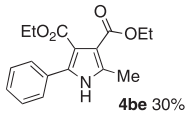
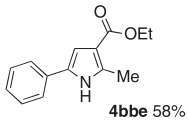
We next examined the scope of 1,3-dicarbonyl compounds for this pyrrole formation with vinyl azides (Table 2). The reactions of

Table 1
Synthesis of pyrroles **4** by reactions of vinyl azides **1** and acetylacetone (**3**)[a]

entry	vinyl azides 1		pyrroles 4[b]	
1		**1a**: R = 2,6-Cl_2		**4aa**: 86%
2		**1b**: R = H		**4ba**: 93%
3		**1c**: R = 4-Me		**4ca**: 90%
4		**1d**: R = 2-Me		**4da**: 89%
5		**1e**: R = 3-NO_2		**4ea**: 96%
6		**1f**: R = 4-Br		**4fa**: 90%
7		**1g**: R = 4-CN		**4ga**: 90%
8[c]		**1h**: R = 4-MeO		**4ha**: 81%
9		**1i**		**4ia** 94%
10[d]		**1j**: R^2 = COMe		**4ja** 74%
11		**1k**: R^2 = $CONMe_2$		**4ka** quant
12		**1l**: R^1 = CO_2Et		**4la** 82%
13[e]		**1m**: R^1 = CH_2Ph		**4ma** 96%
14		**1n**: R^1 = H		**4na** 85%
15		**1o**: R = H		**4oa** 75%
16		**1p**: R = 4-Me		**4pa** 98%
17		**1q**: R = 4-OMe		**4qa** 95%
18		**1r**: R = 2-OMe		**4ra** 86%
19		**1s**: R = 4-Br		**4sa** 92%
20		**1t**: R = 3-Br		**4ta** 91%
21		**1u**: R = 4-CO_2Me		**4ua** 86%
22		**1v**		**4va** 94%
23		**1w**		**4wa** 65%
24		**1x**		**4xa** 92%
25		**1y**		**4ya** 92%
26		**1z**		**4za** 96%
27		**1aa**		**4aaa** 82%
28		**1bb** (*E*:*Z* = 1:1)		**4bba** 85%
29		**1cc**		**4cca** 66%
30		**1dd**		**4dda** 91%

[a] Unless otherwise noted, the reactions were carried out by heating a mixture of vinyl azides **1** (0.3–0.5 mmol) and acetylacetone (**3a**) (1.2 equiv) in toluene at 100 °C for 2–24 h.
[b] Isolated yields were noted.
[c] The reaction was performed at 85 °C for 16 h.
[d] The reaction was performed at 85 °C for 20 h in the presence of 2 equiv of acetylacetone (**3a**).
[e] The reaction was performed at reflux for 5 h.

Table 2
Scope on 1,3-dicarbonyl compounds[a]

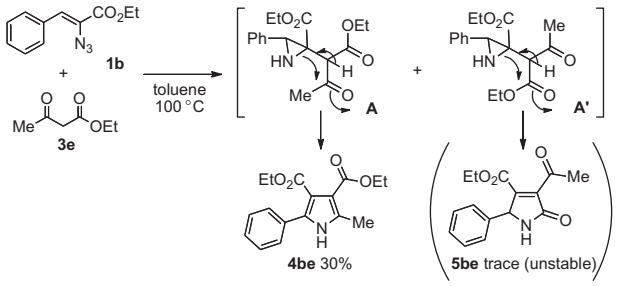
Entry	Vinyl azides **1**	1,3-Dicarbonyl compounds **3**	Pyrroles **4**[b]
1	 **1c**	 **3b**	 **4cb** 90%
2	 **1l**	**3b**	 **4lb** 94%
3	 **1o**	**3b**	 **4ob** 80%
4	**1o**	 **3c**	 **4oc** 95%
5	 **1b**	 **3d**	 **4bd** 54%  **4bd'** 43%
6	 **1l**	**3d**	 **4ld** 41%  **4ld'** 39%
7	 **1b**	 **3e**	 **4be** 30%
8	 **1bb**	**3e**	 **4bbe** 58%

[a] The reactions were carried out by heating a mixture of vinyl azides **1** (0.3–0.5 mmol) and 1,3-dicarbonyl compounds **3** (1.2 equiv) in toluene at 100 °C for 2–24 h.
[b] Isolated yields were noted.

1,3-diketones bearing alkenyl (for **3b**) as well as phenyl (for **3c**) moiety with several vinyl azides **1** resulted in the corresponding pyrroles **4** in good yields (entries 1–4). β-Oxo aldehyde **3d** reacted smoothly with vinyl azides **1b** and **1l** (entries 5 and 6), whereas tri- and tetrasubstituted pyrroles **4** and **4′** were obtained in almost 1:1 ratio via the nucleophilic attack of the nitrogen atom to both carbonyl groups (Scheme 3, A→B).

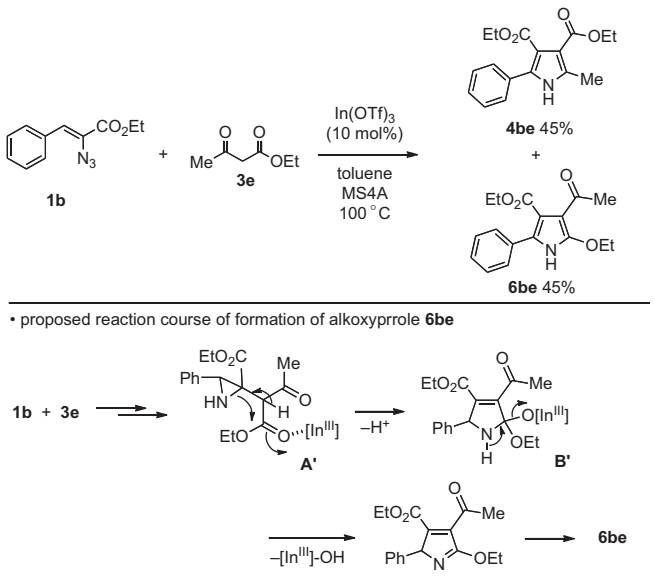
Although 1,3-diketones and β-oxo aldehyde could result in smooth pyrrole formation, treatment of vinyl azides **1b** and **1bb** with β-keto ester, ethyl acetoacetate (**3e**), gave desired pyrroles **4be** and **4bbe** in only 30% and 58% yields, respectively, along with complex mixtures (entries 7 and 8). From the reaction of **1b** (entry 7) was detected a trace amount of very unstable lactam **5be**, which might be formed via the nucleophilic attack of the nitrogen atom to

the ethoxycarbonyl group on aziridine intermediate **A**′ and resulted in complex mixtures (Scheme 4).



Scheme 4.

To improve the reaction of vinyl azides with β-keto esters, acid and base additives were extensively screened.[13] It was interestingly found that the reaction of vinyl azides **1b** with ethyl acetoacetate (**3e**) in the presence of a catalytic amount of $In(OTf)_3$ and molecular sieve 4 Å afforded pyrrole **4be** in 45% yield along with 2-ethoxypyrrole **6be** in 45% (Scheme 5). The formation of 2-ethoxypyrrole **6be** might commence with nucleophilic attack of the nitrogen atom of aziridine intermediate **A**′ to the ethoxycarbonyl group to give indium(III) alcoholate **B**′, followed by elimination of indium(III) hydroxide[14] and subsequent isomerization.



Scheme 5.

During the course of study on this thermal pyrrole formation, it was also found that 1-vinyl-1,2,3-triazoles **7** were exclusively formed from vinyl azides **1** and 1,3-dicarbonyl compounds **3** via intermolecular 1,3-dipolar cycloaddition when the reactions were run in DMF in the presence of a catalytic amount of K_2CO_3, at 40 °C. The reaction has much tolerance for a wide range of functional groups on vinyl azides **1**, where not only aryl and heteroaryl groups but also alkyl groups could be incorporated into 1-vinyl-1,2,3-triazoles **7** by the reactions with 1,3-diketones (entries 1–13). Instead of 1,3-diketones, β-keto esters **3e**–**g** could also be employed for this transformation (entries 14–16). Although there have been reported 1,3-dipolar cycloaddition reactions of organic azides with enamines or enol ethers derived from the corresponding 1,3-dicarbonyl compounds,[15] the direct addition with 1,3-dicarbonyl compounds under ambient reaction conditions are particularly rare.[16]

3. Conclusion

In conclusion, tri- and tetrasubstituted *N*–H pyrroles were prepared by the simple treatment of vinyl azides **1** with 1,3-dicarbonyl compounds **3** in toluene at 100 °C via 2*H*-azirine intermediates generated in situ. When the reactions of vinyl azides and 1,3-dicarbonyl compounds were performed in DMF in the presence of a catalytic amount of K_2CO_3, 1-vinyl-1,2,3-triazoles **7** were obtained via 1,3-dipolar cycloaddition. These methodologies exploited orthogonal modes of chemical reactivity of vinyl azides **1**, which could be achieved by slight modification of the reaction conditions.

4. Experimental section

4.1. General

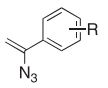
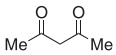
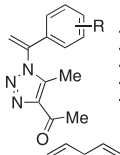
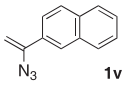
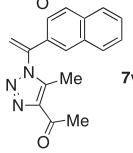
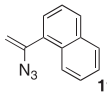
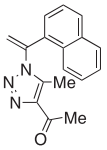
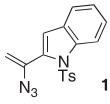
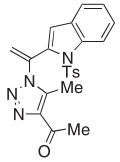
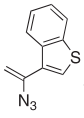
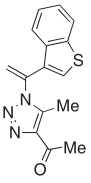
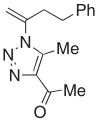
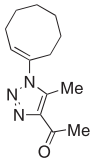
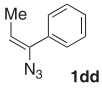
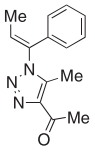
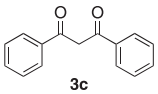
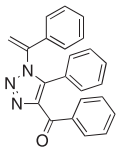
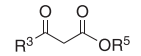
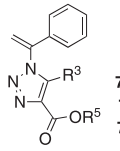
^{1}H NMR (300 MHz) spectra were recorded on a Bruker Avance 300 spectrometers, ^{1}H NMR (400 MHz) spectra were recorded on an ECA JEOL 400 spectrometers, and ^{1}H NMR (500 MHz) spectra on a Bruker Avance 500 spectrometers in $CDCl_3$ [using $CHCl_3$ (for ^{1}H, δ=7.26) as internal standard]. ^{13}C NMR (75 MHz) spectra on a Bruker Avance 300 spectrometers, ^{13}C NMR (100 MHz) spectra on a Bruker Avance 400 spectrometers, and ^{13}C NMR (125 MHz) spectra on a Bruker Avance 500 spectrometers in $CDCl_3$ [using $CHCl_3$ (for ^{13}C, δ=77.0) as internal standard]. The following abbreviations were used to explain the multiplicities: s=singlet, d=doublet, t=triplet, m=multiplet, br=broad. IR spectra were recorded on a Horiba FT 300-S by ATR method and on a Shimadzu IR Prestige-21 FT-IR Spectrometer. High-resolution mass spectra were obtained with a Q-Tof Premier LC HR mass spectrometer. Melting points (uncorrected) were recorded on a Buchi B-54 melting point apparatus. Flash column chromatographs were performed using Silicycle 60 silica gel with distilled eluting solvents. Toluene was dried by passing over a column of activated alumina (A-2, Purify) followed by a column of Q-5 scavenger (Engelhard). *N*,*N*-Dimethylmethanamide (DMF) was purchased from Sigma–Aldrich Co., Inc. Vinyl azides (**1a**–**o** and **1cc**),[13c] (**1p**, **1r**, **1s**, **1u**, **1v**, **1y**, **1aa**, **1cc**, and **1dd**),[13b] (**1q** and **1x**),[17] and (**1t**, **1w**, and **1z**)[18] were prepared by the following literature procedures. 1,3-Dicarbonyl compounds **3a**, **3c**, **3e**–**g** were purchased from Sigma–Aldrich Co., Inc. and used without further purification. 1,10-Undecadiene-5,7-dione **3b**[19] and 3-oxo-3-phenylpropanal **3d**[20] were prepared by following the literature procedures.

4.2. Thermal formation of pyrroles 4 from vinyl azides 1 and 1,3-dicarbonyl compounds 3 (Tables 1 and 2)

A typical procedure. To a solution of ethyl 2-azido-3-phenylacrylate (**1b**) (108 mg, 0.497 mmol) in toluene (5 mL) was added acetylacetone (**3a**) (76 μL, 0.60 mmol), and the reaction mixture was stirred at 100 °C for 3 h. The volatile materials were removed in vacuo, and the resulting crude residue was purified by flash column chromatography (silica gel; hexane/ethyl acetate/Et_3N=60:40:1), affording pyrrole **4ba** (125 mg, 0.461 mmol) in 93% yield.

*4.2.1. Ethyl 4-acetyl-2-(2,6-dichlorophenyl)-5-methyl-1H-pyrrole-3-carboxylate (**4aa**).* Colorless crystal; mp 162–163 °C; IR (ZnSe) 3263 (br), 2981, 1705, 1682, 1639, 1417, 1381, 1290, 1192, 1151, 1076, 1020 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.96 (3H, t, *J*=7.1 Hz), 2.42 (3H, s), 2.51 (3H, s), 4.06 (2H, q, *J*=7.1 Hz), 7.28 (1H, t, *J*=7.8 Hz), 7.37 (2H, d, *J*=7.8 Hz), 8.55 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.1, 13.7, 31.2, 60.1, 114.8, 122.7, 127.6, 129.0, 130.4, 130.9, 134.0, 136.5, 163.8, 198.1. Anal. Found: C, 56.31; H, 4.44; N, 4.10%. Calcd for $C_{16}H_{15}Cl_2NO_3$: C, 56.49; H, 4.44; N, 4.12%.

Table 3
Formation of 1-vinyl-1,2,3-triazoles[a]

Entry	Vinyl azides **1**	1,3-Dicarbonyl compounds **3**	Triazoles **7**[b]
1 2 3 4 5	 **1o:** R = H **1p**: R = 4-Me **1r :** R = 2-OMe **1s:** R = 4-Br **1t :** R = 3-Br	 **3a**	 **7oa:** 89% **7pa**: 83% **7ra :** 82% **7sa:** 83% **7ta :** 85%
6	 **1v**	**3a**	 **7va**: 91%
7	 **1w**	**3a**	 **7wa**: 94%
8	 **1x**	**3a**	 **7xa**: 95%
9	 **1z**	**3a**	 **7za**: 96%
10	 **1aa**	**3a**	 **7aaa**: 93%
11	 **1cc**	**3a**	 **7cca**: 83%
12	 **1dd**	**3a**	 **7dda**: 86%
13	 **1o**	 **3c**	 **7ob**: 93%
14 15 16	 **1o**	 **3e:** R^3 = Me, R^5 = Et **3f**: R^3 = Me, R^5 = *t*-Bu **3g**: R^3 = Ph, R^5 = Et	 **7oe**: 91% **7of**: 88% **7og**: 95%

[a] The reactions were carried out by treatment of a mixture of vinyl azides **1** (0.3–0.5 mmol) and 1,3-dicarbonyl compounds **3** (1.2 equiv) with K_2CO_3 (20 mol %) in DMF at 40 °C for 3–5 h.
[b] Isolated yields were noted.

*4.2.2. Ethyl 4-acetyl-5-methyl-2-phenyl-1H-pyrrole-3-carboxylate (**4ba**).* Colorless crystal; mp 89–91 °C; IR (ZnSe) 3276 (br), 2981, 1699, 1647, 1489, 1419, 1288, 1201, 1128, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.20 (3H, t, J=7.1 Hz), 2.38 (6H, s, overlapped), 4.20 (2H, q, J=7.1 Hz), 7.29–7.35 (3H, m), 7.43 (2H, dd, J=8.0, 1.5 Hz), 9.09 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 13.9, 30.3, 60.9, 113.2, 122.7, 127.8, 128.1, 128.3, 131.0, 132.7, 133.7, 166.3, 196.3. Anal. Found: C, 70.71; H, 6.46; N, 5.01%. Calcd for $C_{16}H_{17}NO_3$: C, 70.83; H, 6.32; N, 5.16%.

*4.2.3. Ethyl 4-acetyl-5-methyl-2-p-tolyl-1H-pyrrole-3-carboxylate (**4ca**).* Colorless crystal; mp 162–164 °C; IR (ZnSe) 3273 (br), 2981, 1695, 1635, 1498, 1417, 1284, 1198, 1113, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, J=7.1 Hz), 2.35 (3H, s), 2.40 (6H, s), 4.21 (2H, q, J=7.1 Hz), 7.15 (2H, d, J=7.8 Hz), 7.34 (2H, d, J=7.8 Hz), 8.79 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.0, 21.3, 30.4, 60.8, 112.8, 122.8, 127.8, 128.1, 129.0, 133.0, 133.3, 138.1, 166.2, 196.4. Anal. Found: C, 71.29; H, 6.71; N, 4.82%. Calcd for $C_{17}H_{19}NO_3$: C, 71.56; H, 6.71; N, 4.91%.

*4.2.4. Ethyl 4-acetyl-2-(2-methylphenyl)-5-methyl-1H-pyrrole-3-carboxylate (**4da**).* Colorless crystal; mp 111–113 °C; IR (KBr) 3277 (br), 3019, 1700, 1647, 1481, 1425, 1292, 1215, 1109, 1034 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (3H, t, J=7.2 Hz), 2.20 (3H, s), 2.37 (3H, s), 2.43 (H, s), 4.02 (2H, d, J=7.2 Hz), 7.16–7.23 (m, 3H), 7.26–7.30 (m, 1H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 13.6, 19.9, 30.8, 60.1 113.6, 122.5, 125.3, 128.8, 129.8, 130.3, 131.6, 132.8, 134.5, 137.7, 164.9, 198.1; EIHRMS: found: m/z 285.1365. Calcd for $C_{17}H_{19}NO_3$: M^+ 285.1359.

*4.2.5. Ethyl 4-acetyl-5-methyl-2-(3-nitrophenyl)-1H-pyrrole-3-carboxylate (**4ea**).* Pale yellow solid; mp 169–170 °C; IR (ZnSe) 3259 (br), 2985, 1705, 1651, 1533, 1446, 1417, 1348, 1292, 1207 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J=7.2 Hz), 2.44 (3H, s), 2.48 (3H, s), 4.26 (2H, q, J=7.2 Hz), 7.57 (1H, dd, J=7.8, 8.0 Hz), 7.86 (1H, d, J=7.8 Hz), 8.19 (1H, d, J=8.0 Hz), 8.35 (1H, s), 8.67 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.3, 14.0, 30.6, 61.2, 114.5, 122.68, 122.74, 123.5, 129.4, 130.0, 132.6, 134.0, 134.1, 148.0, 165.5, 196.4. Anal. Found: C, 60.61; H, 5.23; N, 8.61%. Calcd for $C_{16}H_{16}N_2O_5$: C, 60.75; H, 5.10; N, 8.86%.

*4.2.6. Ethyl 4-acetyl-2-(4-bromophenyl)-5-methyl-1H-pyrrole-3-carboxylate (**4fa**).* White needle; mp 142–143 °C; IR (KBr) 3274 (br), 3054, 1707, 1650, 1484, 1421, 1264, 1204, 896, 748 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J=7.2 Hz), 2.42 (3H, s), 2.43 (3H, s), 4.24 (2H, q, J=7.2 Hz), 7.34 (2H, d, J=8.4 Hz), 7.50 (2H, d, J=8.4 Hz), 8.59 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 13.9, 30.4, 61.0, 113.6, 122.3, 123.1, 129.5, 129.9, 131.5, 131.6, 133.8, 166.2, 196.4; EIHRMS: found: m/z 349.0308. Calcd for $C_{16}H_{16}^{79}BrNO_3$: M^+ 349.0314.

*4.2.7. Ethyl 4-acetyl-2-(4-cyanophenyl)-5-methyl-1H-pyrrole-3-carboxylate (**4ga**).* White solid; mp 197–198 °C; IR (KBr) 3206 (br), 3054, 1728, 1609, 1471, 1435, 1265, 1202, 896, 748 cm^{-1}; ^1H NMR (400 MHz, DMSO-d_6) δ 1.17 (3H, t, J=7.2 Hz), 2.33 (3H, s), 2.45 (3H, s), 4.19 (2H, q, J=7.2 Hz), 7.65 (2H, d, J=8.4 Hz), 7.90 (2H, d, J=8.4 Hz), 12.00 (1H, br s); ^{13}C NMR (100 MHz, DMSO-d_6) δ 13.1, 13.7, 29.9, 60.6, 109.7, 115.2, 118.8, 122.6, 127.4, 128.1, 132.5, 135.3, 135.5, 166.2, 193.6; EIHRMS: found: m/z 296.1156. Calcd for $C_{17}H_{16}N_2O_3$: M^+ 296.1161.

*4.2.8. Ethyl 4-acetyl-2-(4-methoxyphenyl)-5-methyl-1H-pyrrole-3-carboxylate (**4ha**).* Pale yellow crystal; mp 127–129 °C; IR (KBr) 3270 (br), 2965, 1696, 1648, 1500, 1431, 1265, 1204, 1181, 1124, 1041 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.23 (3H, t, J=7.2 Hz), 2.41 (6H, s, overlapped), 3.82 (3H, s), 4.22 (2H, q, J=7.2 Hz), 6.90 (2H, d, J=8.6 Hz), 7.41 (2H, d, J=8.6 Hz), 8.56 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.2, 14.0, 30.4, 55.3, 60.7, 112.5, 113.8, 123.0, 123.5, 129.6, 132.9, 133.3, 159.7, 166.1, 196.7; EIHRMS: found: m/z 301.1308. Calcd for $C_{17}H_{19}NO_4$: M^+ 301.1314.

*4.2.9. Ethyl 4-acetyl-5-methyl-2-(pyridin-3-yl)-1H-pyrrole-3-carboxylate (**4ia**).* White solid; mp 156–157 °C; IR (KBr) 3193 (br), 2988, 1704, 1665, 1488, 1433, 1265, 1204, 1196, 1160, 1035 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.22 (3H, t, J=7.2 Hz), 2.44 (3H, s), 2.45 (3H, s), 4.23 (2H, q, J=7.2 Hz), 7.32 (1H, dd, J=8.0, 4.8 Hz), 7.90 (1H, d, J=8.0 Hz), 8.50 (1H, d, J=4.8 Hz), 8.64 (1H, s), 10.5 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.0, 13.9, 30.6, 60.9, 114.2, 123.3, 123.5, 127.9, 129.7, 134.5, 136.5, 148.3 (overlapped), 165.6, 196.9; EIHRMS: found: m/z 272.1155. Calcd for $C_{15}H_{16}N_2O_3$: M^+ 272.1161.

*4.2.10. 3,4-Diacetyl-5-methyl-2-phenyl-1H-pyrrole (**4ja**).* White solid; mp 142–144 °C; IR (KBr) 3222 (br), 3005, 1645, 1622, 1487, 1448, 1412, 1354, 1188 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.16 (3H, s), 2.25 (3H, s), 2.31 (3H, s), 7.23–7.24 (5H, m), 9.41 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 30.2, 31.6, 122.7, 123.9, 127.8, 128.1, 128.6, 131.0, 131.1, 133.8, 195.9, 201.0; FABHRMS Found: m/z 242.1155. Calcd for $C_{15}H_{16}NO_2$: $(M+H)^+$, 242.1182.

*4.2.11. 4-Acetyl-N,N,5-trimethyl-2-phenyl-1H-pyrrole-3-carboxamide (**4ka**).* White solid; mp 224–226 °C; IR (KBr) 3229 (br), 2988, 1644, 1602, 1532, 1444, 1266, 1180, 1113, 1160, 1036 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.28 (3H, s), 2.32 (3H, s), 2.75 (3H, s), 3.09 (3H, s), 7.19–7.30 (5H, m), 10.0 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 29.3, 34.9, 38.2, 116.7, 120.5, 125.4, 126.8, 127.1, 128.8, 131.1, 136.5, 169.8, 193.7. EIHRMS: found: m/z 270.1361. Calcd for $C_{16}H_{18}N_2O_2$: M^+ 270.1368.

*4.2.12. Diethyl 4-acetyl-5-methyl-1H-pyrrole-2,3-dicarboxylate (**4la**).* White solid; mp 113–115 °C; IR (ZnSe) 3270 (br), 2983, 1704, 1689, 1652, 1419, 1272, 1182, 1056, 1018 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (3H, t, J=7.2 Hz), 1.42 (3H, t, J=7.2 Hz), 2.39 (3H, s), 2.57 (3H, s), 4.32 (2H, q, J=7.2 Hz), 4.41 (2H, q, J=7.2 Hz), 10.1 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 14.2, 14.4, 29.3, 61.3, 61.9, 118.1, 121.2, 123.7, 138.3, 160.1, 166.4, 193.1. Anal. Found: C, 58.36; H, 6.52; N, 5.10%. Calcd for $C_{13}H_{17}NO_5$: C, 58.42; H, 6.41; N, 5.24%.

*4.2.13. Ethyl 4-acetyl-2-benzyl-5-methyl-1H-pyrrole-3-carboxylate (**4ma**).* Pale yellow oil; IR (KBr) 3165 (br), 2982, 1697, 1645 (br), 1526, 1495, 1427, 1298, 1200, 1085, 1020 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, J=7.2 Hz), 2.20 (3H, s), 2.41 (3H, s), 4.18 (2H, s), 4.27 (2H, q, J=7.2 Hz), 7.19–7.25 (3H, m), 7.30 (2H, dd, J=7.6, 7.8 Hz), 8.61 (1H, br). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.4, 14.2, 31.1, 32.8, 60.2, 111.6, 122.9, 126.7, 128.66, 128.73, 131.8, 135.7, 137.9, 165.2, 198.9. ESIHRMS: found: m/z 286.1443. Calcd for $C_{17}H_{20}NO_3$: $(M+H)^+$ 286.1443.

*4.2.14. Ethyl 4-acetyl-5-methyl-1H-pyrrole-3-carboxylate (**4na**).* Yellow oil; IR (NaCl) 3280, 3109, 2983, 1709, 1694, 1645, 1520, 1179 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.34 (3H, t, J=7.1 Hz), 2.33 (3H, s), 2.55 (3H, s), 4.28 (2H, q, J=7.1 Hz), 7.20 (1H, d, J=2.8 Hz), 9.74 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.9, 14.2, 31.3, 60.2, 115.3, 121.9, 123.6, 134.8, 164.6, 199.4; ESIHRMS: found: m/z 196.0983. Calcd for $C_{10}H_{14}NO_3$: $(M+H)^+$ 196.0974.

*4.2.15. 1-(2-Methyl-4-phenyl-1H-pyrrol-3-yl)ethanone (**4oa**)*[21]. White needle; ^1H NMR (400 MHz, $CDCl_3$) δ 1.97 (3H, s), 2.46 (3H, s), 6.48 (1H, d, J=2.4 Hz), 7.25–7.30 (5H, m), 8.47 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 30.8, 115.2, 120.9, 126.7, 126.8, 128.1, 129.5, 135.1, 136.4, 197.3.

*4.2.16. 1-(2-Methyl-4-p-tolyl-1H-pyrrol-3-yl)ethanone (**4pa**).* White solid; mp 129–130 °C IR (NaCl) 3418, 3013, 1635, 1435 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.05 (3H, s), 2.37 (3H, s), 2.51 (3H, s), 6.51 (1H, d, J=2.3 Hz), 7.17 (2H, d, J=8.0 Hz), 7.22 (2H, d, J=8.0 Hz), 8.68 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 21.1, 30.8, 115.1, 120.9, 126.7, 128.9, 129.3, 133.4, 135.1, 136.4, 197.4; ESIHRMS: found: m/z 214.1229. Calcd for $C_{14}H_{16}NO$: $(M+H)^+$ 214.1232.

*4.2.17. 1-(4-(4-Methoxyphenyl)-2-methyl-1H-pyrrol-3-yl)ethanone (**4qa**).* White crystal; mp 179–180 °C; IR (NaCl) 3422, 3021, 2340, 1647, 1442 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.06 (3H, s), 2.52 (3H, s), 3.84 (3H, s), 6.52 (1H, d, J=2.3 Hz), 6.91 (2H, d, J=8.6 Hz), 7.25 (2H, d, J=8.6 Hz), 8.22 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.2, 30.8, 55.3, 113.6, 114.9, 121.0, 126.4, 128.7, 130.5, 134.9, 158.6, 197.1; ESIHRMS: found: m/z 230.1174. Calcd for $C_{14}H_{16}NO_2$: $(M+H)^+$ 230.1181.

*4.2.18. 1-(4-(2-Methoxyphenyl)-2-methyl-1H-pyrrol-3-yl)ethanone (**4ra**).* Orange solid; mp 105.5–106 °C; IR (NaCl) 3455, 3291, 3017, 2835, 1637, 1436 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.99 (3H, s), 2.48 (3H, s), 3.75 (3H, s), 6.50 (1H, d, J=2.3 Hz), 6.91 (1H, d, J=8.2 Hz), 6.07 (1H, ddd, J=7.4, 7.4, 1.0 Hz), 7.25 (1H, d, J=7.4, 1.8 Hz), 7.30 (1H, ddd, J=7.4, 7.4, 1.8 Hz), 8.92 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 29.2, 55.1, 110.4, 115.6, 120.6, 121.3, 122.0, 125.5, 128.5, 131.0, 134.8, 156.9, 197.5; ESIHRMS: found: m/z 230.1188. Calcd for $C_{14}H_{16}NO_2$: $(M+H)^+$ 230.1181.

*4.2.19. 1-(4-(4-Bromophenyl)-2-methyl-1H-pyrrol-3-yl)ethanone (**4sa**).* White crystal; mp 180–181 °C; IR (NaCl) 3422, 3237, 2924, 1624, 1439 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.06 (3H, s), 2.52 (3H, s), 6.54 (1H, s), 7.20 (2H, d, J=8.2 Hz), 7.48 (2H, d, J=8.2 Hz), 8.39 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 30.9, 115.4, 120.7, 120.8, 125.5, 131.0, 131.2, 135.32, 131.34, 196.8; ESIHRMS: found: m/z 278.0183. Calcd for $C_{13}H_{13}NOBr$: $(M+H)^+$ 278.0181.

*4.2.20. 1-(4-(3-Bromophenyl)-2-methyl-1H-pyrrol-3-yl)ethanone (**4ta**).* Pale red crystal; mp 109–110 °C; IR (NaCl) 3261, 3250, 1633, 1595, 1440, 964 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (3H, s), 2.52 (3H, s), 6.56 (1H, d, J=2.2 Hz), 7.21–7.27 (2H, m), 7.43 (1H, ddd, J=7.3, 1.9, 1.8 Hz), 7.49–7.50 (1H, m), 8.22 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 30.9, 115.7, 120.7, 122.1, 125.2, 128.1, 129.55, 129.62, 132.1, 135.5, 138.6, 196.8; ESIHRMS: found: m/z 278.0176. Calcd for $C_{13}H_{13}NOBr$: $(M+H)^+$ 278.0181.

*4.2.21. Methyl 4-(4-acetyl-5-methyl-1H-pyrrol-3-yl)benzoate (**4ua**).* White crystal; mp 162–163 °C; IR (NaCl) 3422, 3021, 1636, 1608, 1435 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.07 (3H, s), 2.52 (3H, s), 3.93 (3H, s), 6.61 (1H, d, J=2.4 Hz), 7.40 (2H, d, J=8.4 Hz), 8.03 (2H, d, J=8.4 Hz), 8.48 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.3, 31.1, 52.3, 116.1, 121.1, 126.0, 128.4, 129.4, 129.7, 135.7, 141.6 167.3, 197.1; ESIHRMS: found: m/z 258.1138. Calcd for $C_{15}H_{16}NO_3$: $(M+H)^+$ 258.1130.

*4.2.22. 1-(2-Methyl-4-(naphthalen-2-yl)-1H-pyrrol-3-yl)ethanone (**4va**).* Pale yellow crystal; mp 132–133 °C; IR (NaCl) 3285, 3017, 1620, 1520, 1427 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.11 (3H, s), 2.55 (3H, s), 6.59 (1H, d, J=2.3 Hz), 7.46–7.52 (3H, m), 7.79–7.87 (4H, m), 9.12 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 30.9, 115.8, 120.8, 125.6, 126.1, 126.6, 127.3, 127.5, 127.6, 127.7, 128.2, 132.2, 133.3, 133.9, 135.6, 197.5; ESIHRMS: found: m/z 250.1239. Calcd for $C_{17}H_{16}NO$: $(M+H)^+$ 250.1232.

*4.2.23. 1-(2-Methyl-4-(naphthalen-1-yl)-1H-pyrrol-3-yl)ethanone (**4wa**).* Brown crystal; mp 192–193 °C; IR (NaCl) 3267, 3019, 2361, 1624, 1442, 1396 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.67 (3H, s), 2.63 (3H, s), 6.59 (1H, d, J=2.4 Hz), 7.38–7.51 (4H, m), 7.81–7.88 (3H, m), 8.67 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.8, 39.9, 116.1, 121.8, 124.0, 125.3, 125.8, 126.1, 126.2, 127.6, 127.8, 128.1, 133.5, 133.6, 134.5, 135.6, 196.8; ESIHRMS: found: m/z 250.1234. Calcd for $C_{17}H_{16}NO$: $(M+H)^+$ 250.1232.

*4.2.24. 1-(2-Methyl-4-(1-tosyl-1H-indol-2-yl)-1H-pyrrol-3-yl)ethanone (**4xa**).* Pale yellow crystal; mp 220–221 °C; IR (NaCl) 3422, 3105, 1632, 1593, 1369 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 2.02 (3H, s), 2.32 (3H, s), 2.59 (3H, s), 6.40 (1H, d, J=2.4 Hz), 6.54 (1H, s), 7.10 (2H, d, J=8.2 Hz), 7.25–7.51 (6H, m), 8.33 (1H, d, J=8.2 Hz), 8.27 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.6, 21.6, 29.7, 112.8, 115.2, 115.4, 118.4, 120.5, 122.6, 123.7, 124.6, 126.8, 129.4, 129.6, 134.8, 135.4, 136.1, 137.4, 144.7, 195.8; ESIHRMS: found: m/z 393.1276. Calcd for $C_{22}H_{21}N_2O_3S$: $(M+H)^+$ 393.1273.

*4.2.25. 1-(5′-Methyl-1-tosyl-1H,1′H-2,3′-bipyrrol-4′-yl)ethanone (**4ya**).* Yellow crystal; mp 220–221 °C; IR (NaCl) 3453, 3264, 3019, 1638, 1433, 1364 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76 (3H, s), 2.36 (3H, s), 2.53 (3H, s), 6.15–6.17 (1H, m), 6.22 (1H, d, J=2.3 Hz), 6.30 (1H, t, J=3.3 Hz), 7.14 (2H, d, J=8.2 Hz), 7.36 (2H, d, J=8.2 Hz), 7.48–7.49 (1H, m), 8.60 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 21.6, 29.1, 111.2, 113.6, 116.6, 118.9, 122.2, 122.9, 127.4, 128.1, 129.4, 135.2, 135.7, 144.9, 196.1; ESIHRMS: found: m/z 343.1120. Calcd for $C_{18}H_{19}N_2O_3S$: $(M+H)^+$ 343.1116.

*4.2.26. 1-(4-(Benzo[b]thiophen-3-yl)-2-methyl-1H-pyrrol-3-yl)ethanone (**4za**).* Brown solid; mp 152.6–153 °C; IR (NaCl) 3266, 3019, 1628, 1427, 1360, 1078 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.87 (3H, s), 2.60 (3H, s), 7.28 (1H, s), 7.30 (1H, s), 7.33–7.38 (3H, m), 7.52–7.61 (1H, m), 7.86–7.90 (1H, m), 8.43 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.5, 29.7, 116.5, 118.9, 121.2, 122.7, 123.1, 123.8, 124.3, 124.4, 132.2, 136.0, 139.7, 139.9, 196.9; ESIHRMS: found: m/z 256.0803. Calcd for $C_{15}H_{14}NOS$: $(M+H)^+$ 256.0796.

*4.2.27. 1-(2-Methyl-4-phenethyl-1H-pyrrol-3-yl)ethanone (**4aaa**).* Pale red crystal; mp 133–134 °C; IR (NaCl) 3418, 3017, 1632, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.45 (3H, s), 2.51 (3H, s), 2.88 (2H, t, J=7.8 Hz), 3.00 (2H, t, J=7.8 Hz), 6.35 (1H, d, J=1.0 Hz), 7.18 (1H, t, J=6.8 Hz), 7.23–7.30 (4H, m), 8.18 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.5, 29.6, 31.0, 36.7, 114.3, 120.6, 125.7, 125.8, 128.2, 128.5, 135.0, 142.5, 195.1; ESIHRMS: found: m/z 228.1390. Calcd for $C_{15}H_{18}NO$: $(M+H)^+$ 228.1388.

*4.2.28. 1-(2-Methyl-5-phenyl-1H-pyrrol-3-yl)ethanone (**4bba**).* Pale yellow crystal; mp 178–180 °C; IR (ZnSe) 3263 (br), 3018, 1635, 1604, 1477, 1448, 1240 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.46 (3H, s), 2.62 (3H, s), 6.78 (1H, d, J=2.8 Hz), 7.23–7.25 (1H, m), 7.38 (2H, dd, J=7.6, 7.6 Hz), 7.47 (2H, d, J=7.6 Hz), 8.59 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 28.5, 107.4, 122.1, 123.7, 126.6, 128.9, 129.8, 131.6, 135.9, 195.1. Anal. Found: C, 78.24; H, 6.81; N, 6.88%. Calcd for $C_{13}H_{13}NO$: C, 78.36; H, 6.58; N, 7.03%.

*4.2.29. 1-(2-Methyl-4,5,6,7,8,9-hexahydro-1H-cycloocta[b]pyrrol-3-yl)ethanone (**4cca**).* Colorless crystal; mp 214–215 °C; IR (NaCl) 3418, 2920, 1647, 1612, 1453 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.32–1.36 (2H, m), 1.46–1.57 (2H, m), 1.62–1.71 (4H, m), 2.48 (3H, s), 2.42 (3H, s), 2.81 (2H, t, J=6.2 Hz), 2.59 (2H, t, J=6.2 Hz), 7.76 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 15.2, 23.2, 25.6, 25.7, 26.0, 29.9, 30.71, 30.74, 119.6, 120.6, 128.0, 132.6, 195.5; ESIHRMS: found: m/z 206.1540. Calcd for $C_{13}H_{20}NO$: $(M+H)^+$ 206.1545.

*4.2.30. 1-(2,5-Dimethyl-4-phenyl-1H-pyrrol-3-yl)ethanone (**4dda**)*[22]. Colorless crystal; ^1H NMR (400 MHz, $CDCl_3$) δ 1.94 (3H, s), 1.95 (3H, s), 2.50 (3H, s), 7.24 (2H, d, J=7.6 Hz), 7.29 (1H, t, J=7.2 Hz), 7.31 (2H, dd, J=7.2 Hz, 7.6 Hz), 9.33 (1H, br s); ^{13}C NMR (100 MHz,

$CDCl_3$) δ 10.9, 14.1, 30.6, 121.1, 122.0, 123.8, 126.4, 128.0, 130.4, 133.9, 136.8, 197.3.

*4.2.31. Ethyl 5-(but-3-enyl)-4-pent-4-enoyl-2-p-tolyl-1H-pyrrole-3-carboxylate (**4cb**).* Colorless oil; FTIR (NaCl) 3294, 2978, 2920, 1694, 1643, 1497, 1447 cm^{-1}; ^1H NMR (300 MHz, $CDCl_3$) δ 1.19 (3H, t, J=7.1 Hz), 2.36 (3H, s), 2.39–2.45 (4H, m), 2.80–2.87 (4H, m), 4.19 (2H, q, J=7.1 Hz), 4.94–5.10 (4H, m), 5.77–5.91 (2H, m), 7.18 (2H, d, J=8.0 Hz), 7.36 (2H, d, J=8.0 Hz), 8.67 (1H, br s); ^{13}C NMR (75 MHz, $CDCl_3$) δ 14.0, 21.2, 26.0, 28.6, 33.4, 42.0, 60.6, 112.0, 114.8, 116.2, 123.0, 128.3, 128.4, 129.0, 134.1, 135.9, 137.5, 137.6, 138.4, 165.7, 199.5; ESIHRMS: found: m/z 366.2061. Calcd for $C_{23}H_{28}NO_3$: M^+ 366.2069.

*4.2.32. Diethyl 5-allyl-4-pent-4-enoyl-1H-pyrrole-2,3-dicarboxylate (**4lb**).* Colorless oil; IR (NaCl) 3273, 2980, 2936, 1732, 1713, 1667, 1464, 1195 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.30 (3H, t, J=7.1 Hz), 1.78 (3H, t, J=7.1 Hz), 2.38–2.41 (4H, m), 2.75 (2H, t, J=7.6 Hz), 3.03 (2H, t, J=7.6 Hz), 4.29 (2H, q, J=7.1 Hz), 4.38 (2H, q, J=7.1 Hz), 4.96–5.05 (4H, m), 5.74–5.86 (2H, m), 10.3 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.2, 14.3, 27.4, 27.9, 30.1, 40.2, 61.6, 62.1, 115.1, 116.1, 118.5, 120.7, 123.4, 137.0, 137.5, 142.5, 160.6, 166.9, 195.3; ESIHRMS: found: m/z 348.1803. Calcd for $C_{19}H_{26}NO_5$: M^+ 348.1811.

*4.2.33. 1-(2-Allyl-4-phenyl-1H-pyrrol-3-yl)pent-4-en-1-one (**4ob**).* Colorless oil; IR (NaCl) 3452, 3300, 3017, 2920, 1719, 1639, 1602, 1454, 1121 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.22–2.26 (2H, m), 2.37–2.47 (4H, m), 3.00 (2H, t, J=7.4 Hz), 4.76–4.82 (2H, m), 5.02–5.13 (2H, m), 5.57–5.67 (1H, m), 5.84–5.95 (1H, m), 6.56 (1H, d, J=2.4 Hz), 7.27–7.38 (5H, m), 8.47 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 27.0, 28.7, 33.2, 41.6, 114.4, 115.4, 115.7, 120.4, 126.2, 126.7, 128.2, 129.3, 136.4, 137.6, 137.9, 138.5, 199.6; ESIHRMS: found: m/z 280.1712. Calcd for $C_{19}H_{22}NO$: M^+ 280.1701.

*4.2.34. (2,4-Diphenyl-1H-pyrrol-3-yl)(phenyl)methanone (**4oc**)*[23]. Yellow crystal; ^1H NMR (400 MHz, $CDCl_3$) δ 6.86 (1H, s), 7.10–7.34 (13H, m), 7.78 (2H, d, J=7.2 Hz), 8.98 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 116.9, 119.2, 126.0, 127.5, 127.6, 127.7, 127.8, 128.09, 128.10, 128.5, 130.0, 131.8, 132.4, 134.7, 135.1, 138.6, 195.3.

*4.2.35. Ethyl 4-benzoyl-2-phenyl-1H-pyrrole-3-carboxylate (**4bd**).* Pale yellow crystal; mp 154–155 °C; IR (ZnSe) 3255, 1689, 1627, 1513, 1488, 1450, 1405, 1349, 1270, 1211, 1083, 890, 752, 692 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.02 (3H, t, J=7.1 Hz), 4.02 (2H, q, J=7.1 Hz), 6.88 (1H, d, J=2.9 Hz), 7.19 (1H, t, J=7.5 Hz), 7.26 (2H, dd, J=7.5, 7.5 Hz), 7.39–7.43 (4H, m), 7.53 (1H, t, J=7.4 Hz), 7.78 (2H, d, J=7.8 Hz), 9.66 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 13.6, 60.9, 113.4, 124.3, 125.2, 127.9, 128.3, 128.4, 128.5, 129.2, 130.5, 132.2, 135.7, 139.0, 166.3, 191.0; FABHRMS Found: m/z 320.1293. Calcd for $C_{20}H_{18}NO_3$: $(M+H)^+$, 320.1287.

*4.2.36. Ethyl 4-formyl-2,5-diphenyl-1H-pyrrole-3-carboxylate (**4bd′**).* White solid; mp 170–172 °C; IR (ZnSe) 3226, 1698, 1639, 1482, 1430, 1380, 1253, 1085, 765, 696 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.23 (3H, t, J=7.1 Hz), 4.27 (2H, q, J=7.1 Hz), 7.37–7.44 (6H, m), 7.51–7.54 (2H, m), 7.56–7.58 (2H, m), 8.95 (1H, br s), 10.15 (1H, s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 60.9, 114.0, 120.9, 128.3, 128.5, 128.7, 128.8, 129.0, 129.4, 130.0, 130.7, 135.8, 139.1, 165.2, 187.2; FABHRMS Found: m/z 320.1293. Calcd for $C_{20}H_{18}NO_3$: $(M+H)^+$, 320.1287.

*4.2.37. Diethyl 4-benzoyl-1H-pyrrole-2,3-dicarboxylate (**4ld**).* Pale yellow oil; IR(ZnSe) 3262, 1706, 1635, 1508, 1403, 1263, 1180, 1083, 892, 752, 727, 698 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.33 (3H, t, J=7.1 Hz), 1.35 (3H, t, J=7.1 Hz), 4.32 (2H, q, J=7.1 Hz), 4.34 (2H, q, J=7.1 Hz), 7.30 (1H, d, J=3.1 Hz), 7.46 (2H, dd, J=7.5, 7.2 Hz), 7.56 (1H, t, J=7.5 Hz), 7.79 (2H, d, J=7.2 Hz), 9.93 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 61.6, 61.7, 122.1, 123.3, 124.3, 127.0, 128.4, 128.9, 132.3, 138.5, 159.9, 165.3, 189.2; FABHRMS Found: m/z 316.1186. Calcd for $C_{17}H_{18}NO_5$: $(M+H)^+$, 316.1185.

*4.2.38. Diethyl 4-formyl-5-phenyl-1H-pyrrole-2,3-dicarboxylate (**4ld′**).* White solid; mp 136–138 °C; IR (ZnSe) 3255, 1714, 1668, 1463, 1434, 1259, 1180, 1083, 1012, 896, 752 cm^{-1}; ^1H NMR (500 MHz, $CDCl_3$) δ 1.32 (3H, t, J=7.1 Hz), 1.42 (3H, t, J=7.1 Hz), 4.24 (2H, q, J=7.1 Hz), 4.46 (2H, q, J=7.1 Hz), 7.50–7.53 (3H, m), 7.55–7.57 (2H, m), 9.87 (1H, s), 10.07 (1H, br s); ^{13}C NMR (125 MHz, $CDCl_3$) δ 14.0, 14.1, 61.7, 61.9, 120.9, 121.0, 122.6, 128.6, 129.12, 129.14, 130.2, 142.6, 160.1, 165.0, 184.9; FABHRMS Found: m/z 316.1201. Calcd for $C_{17}H_{18}NO_5$: $(M+H)^+$, 316.1185.

*4.2.39. Diethyl 2-methyl-5-phenyl-1H-pyrrole-3,4-dicarboxylate (**4be**).* Pale yellow oil; IR (ZnSe) 3296 (br), 2981, 1697 (br), 1429, 1286, 1209, 1093, 1024 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.25 (3H, t, J=7.2 Hz), 1.29 (3H, t, J=7.2 Hz), 2.40 (3H, s), 4.22 (2H, q, J=7.2 Hz), 4.24 (2H, q, J=7.2 Hz), 7.23–7.40 (3H, m), 7.40 (2H, d, J=7.3 Hz), 8.52 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 14.0, 14.2, 59.9, 61.0, 112.0, 114.5, 126.9, 127.7, 128.5, 130.6, 130.9, 135.4, 164.7, 167.1; FABHRMS Found: m/z 302.1407. Calcd for $C_{17}H_{20}NO_4$: $(M+H)^+$ 302.1393.

*4.2.40. Ethyl 2-methyl-5-phenyl-1H-pyrrole-3-carboxylate (**4bbe**).* White solid; mp 115–116 °C; IR (ZnSe) 3309 (br), 2979, 2925, 1668, 1608, 1481, 1448, 1277, 1234, 1097, 1061 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.36 (3H, t, J=7.2 Hz), 2.59 (3H, s), 4.30 (2H, q, J=7.2 Hz), 6.84 (1H, d, J=3.2 Hz), 7.22 (1H, t, J=7.6 Hz), 7.36 (2H, dd, J=8.0, 7.6 Hz), 7.45 (2H, d, J=7.6 Hz), 8.61 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 14.6, 59.5, 107.3, 113.3, 123.6, 126.5, 128.8, 129.9, 131.7, 136.1, 165.5; FABHRMS Found: m/z 230.1158. Calcd for $C_{14}H_{15}O_2N$: $(M+H)^+$, 230.1182.

4.3. In(OTf)$_3$-catalyzed reaction of vinyl azide 1b and ethyl acetoacetate (3e) (Scheme 5)

A procedure. To a solution of ethyl 2-azido-3-phenylacrylate (**1b**) (40.0 mg, 0.184 mmol) and ethyl acetoacetate (**3e**) (57 μL, 0.450 mmol) in toluene (2.5 mL) were added MS 4 Å (80 mg) and $In(OTf)_3$ (10.5 mg, 0.0186 mmol, 10 mol %), and the reaction mixture was stirred at 100 °C for 1.5 h. After the reaction mixture was cooled to room temperature, MS 4 Å was removed by Celite filtration. The organic materials were extracted three times with ethyl acetate, and the combined extracts were washed with brine and dried over $MgSO_4$. The volatile materials were removed in vacuo, and the resulting crude residue was purified by flash column chromatography (silica gel; hexane/ethyl acetate/Et_3N=60:40:1), affording pyrrole **4be** (24.9 mg, 0.0826 mmol) in 45% yield and 2-ethoxypyrrole **6be** (25.2 mg, 0.0836 mmol) in 45% yield.

*4.3.1. Ethyl 4-acetyl-5-ethoxy-2-phenyl-1H-pyrrole-3-carboxylate (**6be**)*[24]. Pale brown crystal; mp 149–150 °C; IR (NaCl) 3240, 3016, 2987, 1713, 1694, 1549 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.24 (3H, t, J=7.1 Hz), 1.41 (3H, t, J=7.0 Hz), 2.34 (3H, s), 4.23 (2H, q, J=7.1 Hz), 4.24 (2H, q, J=7.0 Hz), 7.23–7.29 (3H, m), 7.38 (2H, d, J=6.8 Hz), 9.33 (1H, br s); ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.9, 15.0, 29.0, 61.3, 69.2, 76.7, 108.0, 121.3, 124.6, 126.8, 127.7, 128.6, 130.5, 149.8, 167.4, 192.0; ESIHRMS: found: m/z 302.1381. Calcd for $C_{17}H_{20}NO_4$: $(M+H)^+$ 302.1392.

4.4. Formation of 1-vinyl-1,2,3-triazoles 7 by K_2CO_3-catalyzed reactions of vinyl azide 1 and 1,3-dicarbonyl compounds 3 (Table 3)

A procedure. To a solution of (1-azidovinyl)benzene (**1o**) (45.8 mg, 0.315 mmol) and acetylacetone (39 μL, 0.38 mmol) in DMF (3 mL) was added K_2CO_3 (10.8 mg, 0.078 mmol), and the reaction mixture was stirred at 40 °C for 3 h. The reaction mixture was quenched with water, and then extracted twice with ethyl acetate. The combined organic extracts were washed with water and brine, dried over $MgSO_4$, and concentrated. Purification of the crude material by flash column chromatography (silica gel; hexane/ethyl acetate=60:40), affording triazole **4oa** (63.5 mg, 0.275 mmol) in 89% yield.

*4.4.1. 1-(5-Methyl-1-(1-phenylvinyl)-1H-1,2,3-triazol-4-yl)ethanone (**7op**).* Colorless oil; IR (NaCl) 3015, 1682, 1557, 1217 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (3H, s), 2.75 (3H, s), 5.59 (1H, d, J=1.1 Hz), 6.04 (1H, d, J=1.1 Hz), 7.12–7.15 (2H, m), 7.34–7.39 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 28.0, 115.3, 125.7, 129.2, 130.1, 134.2, 138.2, 141.8, 143.6, 162.5, 194.5; ESIHRMS: found: m/z 228.1139. Calcd for $C_{13}H_{14}N_3O$: $(M+H)^+$ 228.1137.

*4.4.2. 1-(5-Methyl-1-(1-p-tolylvinyl)-1H-1,2,3-triazol-4-yl)ethanone (**7pa**).* White crystal; mp 75.4–76.6 °C; IR (NaCl) 3009, 1684, 1555, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.35 (3H, s), 2.37 (3H, s), 2.75 (3H, s), 5.52 (1H, d, J=1.1 Hz), 5.98 (1H, d, J=1.1 Hz), 7.03 (2H, d, J=8.1 Hz), 7.17 (2H, d, J=8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.98, 21.5, 28.1, 114.4, 125.7, 129.9, 131.4, 138.2, 140.4, 141.8, 143.6, 194.6; ESIHRMS: found: m/z 242.1291. Calcd for $C_{14}H_{16}N_3O$: $(M+H)^+$ 242.1293.

*4.4.3. 1-(1-(1-(2-Methoxyphenyl)vinyl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (**7ra**).* White crystal; mp 76.3–77.9 °C; IR (NaCl) 3009, 1680, 1555, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 2.73 (3H, s), 3.69 (3H, s), 5.68 (1H, s), 5.97 (1H, s), 6.90 (1H, d, J=8.3 Hz), 6.97 (1H, dd, J=7.5, 8.3 Hz), 7.09 (2H, d, J=7.5 Hz), 7.37 (1H, dd, J=7.5, 8.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 27.8, 55.5, 111.3, 117.6, 120.9, 123.4, 129.6, 131.2, 137.6, 139.3, 143.0, 157.0 194.6; ESIHRMS: found: m/z 258.1247. Calcd for $C_{14}H_{16}N_3O$: $(M+H)^+$ 258.1243.

*4.4.4. 1-(1-(1-(4-Bromophenyl)vinyl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (**7sa**).* Pale yellow crystal; mp 74.4–75.6 °C; IR (NaCl) 3011, 1682, 1557, 1418 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.36 (3H, s), 2.73 (3H, s), 5.60 (1H, d, J=1.2 Hz), 6.04 (1H, d, J=1.2 Hz), 7.01 (2H, d, J=8.6 Hz), 7.49 (2H, d, J=8.6 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.0, 28.0, 115.9, 124.6, 127.3, 132.5, 133.2, 138.1, 140.9, 143.6, 194.4; ESIHRMS: found: m/z 306.0249. Calcd for $C_{13}H_{13}N_3O_{Br}$: $(M+H)^+$ 306.0242.

*4.4.5. 1-(1-(1-(3-Bromophenyl)vinyl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (**7ta**).* Yellow crystal; mp 77.9–78.4 °C; IR (NaCl) 3005, 1684, 1558, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 2.76 (3H, s), 5.64 (1H, d, J=1.4 Hz), 6.06 (1H, d, J=1.4 Hz), 7.03 (1H, ddd, J=8.0, 1.8, 1.0 Hz), 7.25 (1H, dd, J=8.0, 7.9 Hz), 7.37 (1H, dd, J=1.82, 1.8 Hz), 7.54 (1H, ddd, J=8.0, 1.8, 1.0 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 27.8, 116.5, 123.3, 124.2, 128.6, 130.6, 133.0, 136.1, 137.9, 140.3, 143.4, 194.3; ESIHRMS: found: m/z 306.0238. Calcd for $C_{13}H_{13}N_3OBr$: $(M+H)^+$ 306.0242.

*4.4.6. 1-(5-Methyl-1-(1-(naphthalen-2-yl)vinyl)-1H-1,2,3-triazol-4-yl)ethanone (**7va**).* Yellow oil; IR (NaCl) 3055, 3009, 1682, 1557, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 2.79 (3H, s), 5.67 (1H, d, J=1.2 Hz), 6.17 (1H, d, J=1.2 Hz), 7.39–7.41 (2H, m), 7.49–7.55 (2H, m), 7.75–7.77 (1H, m), 7.84–7.87 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.7, 28.0, 115.5, 122.4, 125.2, 126.9, 127.2, 127.9, 128.4, 129.0, 131.2, 132.9, 133.6, 138.0, 141.5, 143.3, 194.3; ESIHRMS: found: m/z 278.1297. Calcd for $C_{17}H_{16}N_3O$: $(M+H)^+$ 278.1293.

*4.4.7. 1-(5-Methyl-1-(1-(naphthalen-1-yl)vinyl)-1H-1,2,3-triazol-4-yl)ethanone (**7wa**).* Yellow oil; IR (NaCl) 3011, 1682, 1644, 1557, 1510, 1418, 1080 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.07 (3H, s), 2.71 (3H, s), 5.84 (1H, s), 6.12 (1H, s), 7.42–7.53 (4H, m), 7.74 (1H, d, J=8.5 Hz), 7.89 (1H, d, J=7.5 Hz), 7.93 (1H, dd, J=7.5, 1.7 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.8, 27.8, 117.9, 123.9, 125.1, 126.4, 127.3, 127.6, 128.8, 130.47, 130.5, 131.9, 133.7, 137.4, 141.1, 143.7, 194.3; ESIHRMS: found: m/z 278.1298. Calcd for $C_{17}H_{16}N_3O$: $(M+H)^+$ 278.1293.

*4.4.8. 1-(5-Methyl-1-(1-(1-tosyl-1H-indol-2-yl)vinyl)-1H-1,2,3-triazol-4-yl)ethanone (**7xa**).* White crystal; mp 174–175 °C; IR (NaCl) 3019, 2399, 1682, 1557, 1175 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.32 (3H, s), 2.61 (3H, s), 2.70 (3H, s), 5.73 (1H, d, J=0.8 Hz), 5.80 (1H, d, J=0.8 Hz), 6.98 (1H, d, J=0.4 Hz), 7.13 (2H, d, J=8.1 Hz), 7.12–7.31 (1H, m), 7.37–7.41 (1H, m), 7.49 (2H, d, J=8.1 Hz), 7.53 (1H, d, J=7.6 Hz) 8.09 (1H, d, J=8.1 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.6, 21.8, 28.1, 115.7, 116.0, 118.2, 121.9, 124.8, 126.68, 126.7, 129.4, 129.8, 134.4, 134.6, 135.1, 138.3, 143.9, 145.3, 194.6; ESIHRMS: found: m/z 421.1327. Calcd for $C_{22}H_{21}N_4O_3S$: $(M+H)^+$ 421.1334.

*4.4.9. 1-(1-(1-(Benzo[b]thiophen-3-yl)vinyl)-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (**7za**).* Brown oil; IR (NaCl) 3015, 2924, 1682, 1557, 1418, 1231 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.29 (3H, s), 2.74 (3H, s), 5.83 (1H, d, J=0.8 Hz), 6.02 (1H, d, J=0.8 Hz), 7.37–7.45 (4H, m), 7.89 (1H, dd, J=6.8, 1.3 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.5, 27.8, 116.1, 121.9, 123.1, 125.1, 125.2, 127.5, 130.5, 135.7, 136.5, 137.6, 140.4, 143.3, 194.2; ESIHRMS: found: m/z 284.0854. Calcd for $C_{15}H_{14}N_3OS$: $(M+H)^+$ 284.0858.

*4.4.10. 1-(5-Methyl-1-(4-phenylbut-1-en-2-yl)-1H-1,2,3-triazol-4-yl)ethanone (**7aaa**)[25].* White crystal; mp 71.7–73.3 °C; IR (NaCl) 3017, 1684, 1555, 1420 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.47 (3H, s), 2.72 (3H, s), 2.74 (2H, t, J=7.8 Hz), 3.01 (2H, t, J=7.8 Hz), 5.10 (1H, s), 5.38 (1H, s), 7.12–7.15 (2H, m), 7.34–7.39 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1, 27.8, 32.6, 36.2, 113.4, 126.2, 128.2, 128.4 137.0, 139.5, 141.9, 143.2, 194.1; ESIHRMS: found: m/z 256.1452. Calcd for $C_{15}H_{18}N_3O$: $(M+H)^+$ 256.1450.

*4.4.11. (E)-1-(1-Cyclooctenyl-5-methyl-1H-1,2,3-triazol-4-yl)ethanone (**7cca**).* White solid; mp 57.8–58.5 °C; IR (NaCl) 3005, 2927, 1682, 1557, 1422 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32–1.36 (8H, m), 2.32–2.37 (2H, m), 2.55 (3H, s), 2.59–2.61 (2H, m), 2.68 (3H, s), 5.83 (1H, t, J=8.5 Hz); ^{13}C NMR (100 MHz, $CDCl_3$) δ 10.1, 26.0, 26.1, 27.7, 28.0, 29.2, 29.8, 130.2, 136.0, 136.5, 143.1, 194.5; ESIHRMS: found: m/z 234.1604. Calcd for $C_{13}H_{20}N_3O$: $(M+H)^+$ 234.1606.

*4.4.12. (E)-1-(5-Methyl-1-(1-phenylprop-1-enyl)-1H-1,2,3-triazol-4-yl)ethanone (**7dda**).* Colorless oil; IR (NaCl) 3003, 1682, 1557, 1418 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 2.03 (3H, d, J=7.4 Hz), 2.21 (3H, s), 2.68 (3H, s), 6.19 (1H, q, J=7.4 Hz), 7.13–7.16 (2H, m), 7.30–7.38 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.59, 14.2, 27.7, 128.2, 128.3, 128.7, 129.0, 133.2, 134.7, 137.4, 143.2, 194.3; ESIHRMS: found: m/z 242.1302. Calcd for $C_{14}H_{16}N_3O$: $(M+H)^+$ 242.1293.

*4.4.13. Phenyl(5-phenyl-1-(1-phenylvinyl)-1H-1,2,3-triazol-4-yl) methanone (**7ob**).* Yellow oil; IR (NaCl) 3059, 3011, 1651, 1449, 1258 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 5.58 (1H, d, J=1.2 Hz), 5.88 (1H, d, J=1.2 Hz), 7.07–7.10 (2H, m), 7.21–7.33 (8H, m), 7.47–7.51 (2H, m), 7.56–7.60 (1H, m), 8.28–8.30 (2H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 115.5, 125.7, 125.8, 128.0, 128.2, 128.5, 129.4, 129.55, 129.62, 130.6, 133.0, 134.5, 137.0, 141.9, 142.2, 143.0, 186.5.

ESIHRMS: found: m/z 352.1456. Calcd for $C_{23}H_{18}N_3O$: $(M+H)^+$ 352.1450.

*4.4.14. Ethyl 5-methyl-1-(1-phenylvinyl)-1H-1,2,3-triazole-4-carboxylate (**7oe**).* Colorless oil; IR (NaCl) 2982, 2935, 1715, 1643, 1571 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.43 (3H, t, J=7.1 Hz), 2.34 (3H, s), 4.45 (2H, q, J=7.1 Hz), 5.59 (1H, d, J=1.1 Hz), 6.04 (1H, d, J=1.1 Hz), 7.12–7.15 (2H, m), 7.34–7.39 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 28.0, 115.3, 125.7, 129.2, 130.1, 134.2, 138.2, 141.8, 143.6, 162.5, 194.5; ESIHRMS: found: m/z 258.1240. Calcd for $C_{14}H_{16}N_3O_2$: $(M+H)^+$ 258.1243.

*4.4.15. 2,2-Dimethyl-1-(5-methyl-1-(1-phenylvinyl)-1H-1,2,3-triazol-4-yl)propan-1-one (**7of**).* Colorless oil; IR (NaCl) 3003, 2932, 1728, 1713, 1566, 1447 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.64 (9H, s), 2.32 (3H, s), 5.58 (1H, d, J=1.0 Hz), 6.03 (1H, d, J=1.0 Hz), 7.14–7.16 (2H, m), 7.35–7.39 (3H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 9.9, 28.0, 115.3, 125.7, 129.2, 130.1, 134.2, 138.2, 141.8, 143.6, 162.5, 194.5; ESIHRMS: found: m/z 286.1559. Calcd for $C_{16}H_{20}N_3O_2$: $(M+H)^+$ 286.1556.

*4.4.16. Ethyl 5-phenyl-1-(1-phenylvinyl)-1H-1,2,3-triazole-4-carboxylate (**7og**).* Yellow crystal; mp 131.0–131.8 °C; IR (NaCl) 3015, 1724, 1641, 1560, 1491 cm^{-1}; ^1H NMR (400 MHz, $CDCl_3$) δ 1.32 (3H, t, J=7.1 Hz), 4.36 (2H, q, J=7.1 Hz), 5.54 (1H, d, J=1.2 Hz), 5.85 (1H, d, J=1.2 Hz), 7.03–7.05 (2H, m), 7.20–7.33 (8H, m); ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 61.0, 115.5, 125.4, 125.6, 127.9, 128.5, 129.4, 129.5, 125.6, 134.4, 136.3, 141.5, 142.0, 160.7; ESIHRMS: found: m/z 320.1401. Calcd for $C_{19}H_{18}N_3O_2$: $(M+H)^+$ 320.1399.

Acknowledgements

This work was supported by funding from Nanyang Technological University and Singapore Ministry of Education, Singapore Ministry of Education, and Science & Engineering Research Council (A*STAR Grant No. 082 101 0019). We thank Dr. Yongxin Li (Division of Chemistry and Biological Chemistry, School of Physical and Mathematical Sciences, Nanyang Technological University) for assistance in X-ray crystallographic analysis.

References and notes

1. For recent reviews, see: (a) *Progress in Heterocyclic Chemistry*; Gribble, G. W., Joule, J. A., Eds.; Elsevier: Oxford, 2008; Vol. 20; and others in this series; (b) *Comprehensive Heterocyclic Chemistry III*; Katritzky, A. R., Ramsden, C. A., Scriven, E. F. V., Taylor, R. J. K., Eds.; Pergamon: Oxford, 2008; (c) *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. A., Scriven, E. F. V., Taylor, R. J. K., Eds.; Pergamon: Oxford, 2008; (d) *Comprehensive Heterocyclic Chemistry II*; Katritzky, A. R., Rees, C. W., Scriven, E. F. V., McKillop, A., Eds.; Pergamon: Oxford, 1996; and references therein; (e) Eicher, T.; Hauptmann, S. *The Chemistry of Heterocycles*; Wiley-VCH: Weinheim, 2003.
2. Timén, ÅS.; Risberg, E.; Somfai, P. *Tetrahedron Lett.* **2003**, *44*, 5339; (b) Söderberg, B. C. G. *Curr. Org. Chem.* **2000**, *4*, 727; (c) Knittel, D. *Synthesis* **1985**, 186.
3. For our previous report on Rh(II)-catalyzed indole formation from 2-aryl-2*H*-azirines, see: Chiba, S.; Hattori, G.; Narasaka, K. *Chem. Lett.* **2007**, *36*, 52.
4. Recently, Fe(II)-catalyzed similar transformation was reported, see: Jana, S.; Clements, M. D.; Sharp, B. K.; Zheng, N. *Org. Lett.* **2010**, *12*, 3736.
5. Alves, M. J.; Gilchrist, T. L.; Sousa, J. H. *J. Chem. Soc., Perkin Trans. 1* **1999**, 1305.
6. (a) Alves, M. J.; Ferreira, P. M. T.; Maia, H. L. S.; Monteiro, L. S.; Gilchrist, T. L. *Tetrahedron Lett.* **2000**, *41*, 4991; (b) Carlson, R. M.; Lee, S. Y. *Tetrahedron Lett.* **1969**, *10*, 4001; (c) Leonard, N. J.; Zwanenburg, B. *J. Am. Chem. Soc.* **1967**, *89*, 4456.
7. (a) Law, K. W.; Lai, T. F.; Sammes, M. P.; Katritzky, A. R.; Mak, T. C. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 111; (b) Laurent, A.; Mison, P.; Nafti, A.; Pellissier, N. *Tetrahedron* **1979**, *35*, 2285; (c) Padwa, A.; Kulkarni, Y. *Tetrahedron Lett.* **1979**, *20*, 107; (d) Faria dos Santos Filho, P.; Schuchardt, U. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 647.
8. (a) Nair, V.; George, T. G. *Tetrahedron Lett.* **2000**, *41*, 3199; (b) Gilchrist, T. L.; Mendonça, R. *Synlett* **2000**, 1843; (c) Palacios, F.; Aparicio, D.; de los Santos, J. M.; Perez de Heredia, I.; Rubiales, G. *Org. Prep. Proced. Int.* **1995**, *27*, 171.
9. For recent reviews on the synthesis of pyrroles, see: (a) Estévez, V.; Villacampa, M.; Menéndez, J. C. *Chem. Soc. Rev.* **2010**, *39*, 4402; (b) Ferreira, V. F.; de Souza, M.; Cunha, A. C.; Pereira, L. O. R.; Ferreira, M. L. G. *Org. Prep. Proced. Int.* **2001**, *33*, 411; (c) Geneviève, B. *Angew. Chem., Int. Ed.* **2004**, *43*, 6238; (d) Joshi, U.; Pipelier, M.; Naud, S.; Dubreuil, D. *Curr. Org. Chem.* **2005**, *9*, 261; (e) Patil, N. T.; Yamamoto, Y. *Arkivoc* **2007**, *10*, 121; (f) Schmuck, C.; Rupprecht, D. *Synthesis* **2007**, 3095.
10. For recent selected reports on the synthesis of polysubstituted pyrroles, see: (a) Rakshit, S.; Patureau, F. W.; Glorius, F. *J. Am. Chem. Soc.* **2010**, *132*, 9585; (b) Morin, M. A. T.; St-Cyr, D. J.; Arndtsen, B. A. *Org. Lett.* **2010**, *12*, 4916; (c) Wang, H.-Y.; Mueller, D. S.; Sachwani, R. M.; Londino, H. N.; Anderson, L. L. *Org. Lett.* **2010**, *12*, 2290; (d) Saito, A.; Konishi, T.; Hanzawa, Y. *Org. Lett.* **2010**, *12*, 372; (e) Zhao, X.; Zhang, E.; Tu, Y.-Q.; Zhang, Y.-Q.; Yuan, D.-Y.; Cao, K.; Fan, C.-A.; Zhang, F.-M. *Org. Lett.* **2009**, *11*, 4002; (f) Fu, X.; Chen, J.; Li, G.; Liu, Y. *Angew. Chem., Int. Ed.* **2009**, *48*, 5500; (g) Lu, Y.; Arndtsen, B. A. *Org. Lett.* **2009**, *11*, 1369; (h) Liu, W.; Jiang, H.; Huang, L. *Org. Lett.* **2009**, *12*, 312; (i) Kiren, S.; Hong, X.; Leverett, C. A.; Padwa, A. *Org. Lett.* **2009**, *11*, 1233; (j) Fontaine, P.; Masson, G.; Zhu, J. *Org. Lett.* **2009**, *11*, 1555; (k) Davies, P. W.; Martin, N. *Org. Lett.* **2009**, *11*, 2293; (l) Aponick, A.; Li, C.-Y.; Malinge, J.; Marques, E. F. *Org. Lett.* **2009**, *11*, 4624; (m) Mizuno, A.; Kusama, H.; Iwasawa, N. *Angew. Chem., Int. Ed.* **2009**, *48*, 8318; (n) Ackermann, L.; Sandmann, R.; Kaspar, L. T. *Org. Lett.* **2009**, *11*, 2031; (o) Lu, Y.; Arndtsen, B. A. *Angew. Chem., Int. Ed.* **2008**, *47*, 5430; (p) Cacchi, S.; Fabrizi, G.; Filisti, E. *Org. Lett.* **2008**, *10*, 2629; (q) Attanasi, O. A.; Favi, G.; Filippone, P.; Giorgi, G.; Mantellini, F.; Moscatelli, G.; Spinelli, D. *Org. Lett.* **2008**, *10*, 1983; (r) St. Cyr, D. J.; Arndtsen, B. A. *J. Am. Chem. Soc.* **2007**, *129*, 12366; (s) Cadierno, V.; Gimeno, J.; Nebra, N. *Chem.—Eur. J.* **2007**, *13*, 9973; (t) Su, S.; Porco, J. A., Jr. *J. Am. Chem. Soc.* **2007**, *129*, 7744; (u) Martín, R.; Rodríguez Rivero, M.; Buchwald, S. L. *Angew. Chem., Int. Ed.* **2006**, *45*, 7079; (v) Crawley, M. L.; Goljer, I.; Jenkins, D. J.; Mehlmann, J. F.; Nogle, L.; Dooley, R.; Mahaney, P. E. *Org. Lett.* **2006**, *8*, 5837; (w) Hiroya, K.; Matsumoto, S.; Ashikawa, M.; Ogiwara, K.; Sakamoto, T. *Org. Lett.* **2006**, *8*, 5349; (x) Binder, J. T.; Kirsch, S. F. *Org. Lett.* **2006**, *8*, 2151; (y) Gorin, D. J.; Davis, N. R.; Toste, F. D. *J. Am. Chem. Soc.* **2005**, *127*, 11260.
11. (a) Moody, C. J. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Ley, S., Eds.; Pergamon: Oxford, 1991; Vol. 7, p 21; (b) Smolinsky, G.; Pryde, C. A. *J. Org. Chem.* **1968**, *33*, 2411; (c) L'abbé, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 775; (d) Hemetsberger, H.; Knittle, D.; Weidmann, H. *Monatsh. Chem.* **1970**, *101*, 161; (e) MacKenzie, A. R.; Moody, C. J.; Rees, C. W. *J. Chem. Soc., Chem. Commun.* **1983**, 1372; (f) Bolton, R. E.; Moody, C. J.; Pass, M.; Rees, C. W.; Tojo, G. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2491.
12. Fe(II)- and Rh(II)-catalyzed indole formation from azidocinnamates was reported, see: (a) Bonnamour, J.; Bolm, C. *Org. Lett.* **2011**, *13*, 2012; (b) Stokes, B. J.; Dong, H.; Lesile, B. E.; Pumphrey, A. L.; Driver, T. G. *J. Am. Chem. Soc.* **2007**, *129*, 7500.
13. It was also found that the reaction of vinyl azides with 1,3-dicarbonyl compounds in the presence of Cu(II) or Mn(III) catalysts provided pyrroles bearing the different substitution pattern via totally distinct reaction mechanisms, see: (a) Ng, E. P. J.; Wang, Y.-F.; Chiba, S. *Synlett* **2011**, 783; (b) Wang, Y.-F.; Toh, K. K.; Chiba, S.; Narasaka, K. *Org. Lett.* **2008**, *10*, 5019; (c) Chiba, S.; Wang, Y.-F.; Lapointe, G.; Narasaka, K. *Org. Lett.* **2008**, *10*, 313.
14. For reports on In(III)-catalyzed reduction of esters and amides to the corresponding ethers and amines with hydrosilanes, see: (a) Sakai, N.; Moriya, T.; Fujii, T.; Konakahara, T. *Synthesis* **2008**, 3533; (b) Sakai, N.; Fujii, T.; Konakahara, T. *Tetrahedron Lett.* **2008**, *49*, 6873; (c) Sakai, N.; Moriya, T.; Konakahara, T. *J. Org. Chem.* **2007**, *72*, 5920.
15. (a) Roque, D. R.; Neill, J. L.; Antoon, J. W.; Stevens, E. P. *Synthesis* **2005**, 2497; (b) Peng, W.; Zhu, S. *Synlett* **2003**, 187; (c) Peng, W.; Zhu, S. *Tetrahedron Lett.* **2003**, *59*, 4395.
16. For a report on amine-catalyzed [3+2]cycloaddition of azides and 1,3-dicarbonyl compounds, see: Danence, L. J. T.; Gao, Y.; Li, M.; Huang, Y.; Wang, J. *Chem.—Eur. J.* **2011**, *17*, 3584.
17. Wang, Y.-F. *J. Am. Chem. Soc.* **2009**, *131*, 12570.
18. Wang, Y.-F.; Toh, K. K.; Lee, J.-Y.; Chiba, S. *Angew. Chem., Int. Ed.* **2011**, *50*, 5927.
19. Drouin, J.; Leyendecker, F.; Conia, J. M. *Tetrahedron* **1980**, *36*, 1195.
20. Sezer, ö; Anaç, O. *Helv. Chim. Acta* **1994**, *77*, 2323.
21. Alberola, A.; Andrés, J. M.; González, A.; Pedrosa, R.; Vicente, M. *Heterocycles* **1989**, *29*, 1973.
22. Angel, A.; Gonzalez, O. A.; Luisa, A. M.; Carmen, S. *Tetrahedron* **1999**, *55*, 6555.
23. Houwing, H. A.; van Leusen, A. M. *J. Heterocycl. Chem.* **1981**, *18*, 1127.
24. The structure of **6be** was secured by X-ray crystallographic analysis. CCDC 823703 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/conts/retrieving.html.
25. The structure of **7aaa** was secured by X-ray crystallographic analysis. CCDC 823704 contains the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/conts/retrieving.html.