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# Copper-catalyzed transformation of carbonyl-ene-nitrile compounds: Vinylation, imino ene reaction, and alkynylation of 2-aza-2,4-cyclopentadienone intermediates generated via Ritter-type hydration and dehydrative cyclization reactions

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**Abstract**

1*H*-pyrrolin-2(5*H*)-one derivatives are easily obtained from carbonyl-ene-nitrile compounds and alkenes or alkynes by copper(II)-catalyzed tandem sequence involving vinylation or allylation as well as Ritter-type hydration and dehydrative cyclization.


*Keywords:* Copper(II)-catalysis; Carbonyl-ene-nitrile; Azacyclopentadienone; Pyrrolinone; Vinylation; Allylation

## 1. Introduction

The development of the in situ generation of transient electrophilic carbenoids from α-diazocarbonyl compounds with various transition metal complexes have been well investigated to apply for various inter- or intramolecular carbene transfer reactions [1,2]. We have continuously investigated several catalytic carbene transfer reactions via (2-furyl)carbene complexes in situ generated from carbonyl-ene-yne compounds leading to formation of functionalized furan derivatives (Scheme 1a) [3]. The transition metal-triggered intramolecular 5-exo-dig cyclization of carbonyl-ene-yne compounds is proposed as the key step to form (2-furyl)carbene intermediates **A** [4]. Generally, 2-furfurylidenes generated from diazoalkanes by thermolysis or photolysis are well known to be converted to give carbonyl-ene-yne compounds via rapid rearrangement (Scheme 1b) [5–8]. Transition metal compounds as catalysts for (2-furyl)carbene transfer reactions are considered to act as a soft Lewis acid for activation of the alkyne moiety leading to stabilized (2-furyl)carbene complexes.

Recent studies have focused on the reactivity of nitrene derivatives in situ generated from azido compounds by flash vacuum thermolysis or photolysis (Scheme 2a) [9]. These in situ generated nitrene intermediates are found to convert to more stable isomeric nitriles even though under the mild conditions [9e]. Based on the similar protocol for in situ generation of (2-furyl)carbene complexes, we envisioned the nitrene transfer reactions using carbonyl-ene-nitrile compounds **1** as a precursor of (2-furyl)nitrene intermediate **B** stabilized with transition metals (Scheme 2b). Although the intermediary of the nitrene species have not yet been observed, we found the unique copper-catalyzed transformation of carbonyl-ene-nitrile compounds **1** to 1*H*-pyrrolin-2(5*H*)-ones via reactive 2-aza-2,4-cyclopentadienone intermediates [10,11].

## 2. Results and discussion

When we carried out the reaction of carbonyl-ene-nitrile compound **1** with 5 equiv. of styrene as a nitrene acceptor

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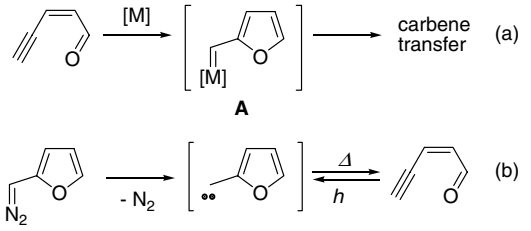
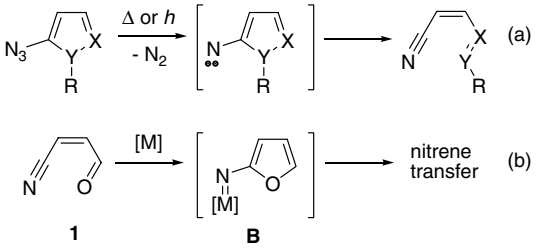
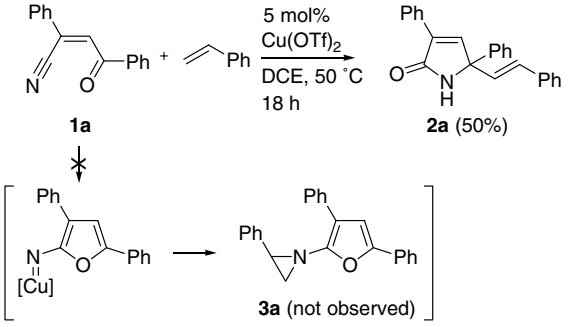



Scheme 1. Generation of (2-furyl)carbene (a) complexes and 2-furfurylidenes (b).



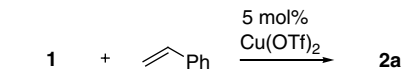

Scheme 2. Generation of 2-furfurylnitrenes (a) and (2-furyl)nitrene complexes (b).

in the presence of a catalytic amount of $Cu(OTf)_2$ (5 mol%) in DCE (1,2-dichloroethane) at 50 °C, we obtained the unexpected 1*H*-pyrrolin-2(5*H*)-one derivative **2a** in 50% yield (59% conversion) instead of the expected aziridinated product **3a** (Scheme 3). When carbonyl-ene-nitrile compound **1** was treated with a catalytic amount of $[Rh(OAc)_2]_2$, which is one of the most efficient catalysts for carbene transfer reactions, no reaction took place, the starting material being recovered intact. The reactions of **1** with other several transition metal complexes, such as $[RuCl_2(CO)_3]_2$, $PtCl_2$, $AuCl_3$, $PdCl_2$, Cu(OTf) · benzene, CuCl, and $CuCl_2$, did not afford the pyrrolinone **2a** at all. The structure of pyrrolinone **2a** suggests the reaction mechanism involving dehydrative lactam formation as well as hydration of nitrile moiety of **1**. As expected, the copper-catalyzed reaction of **1** with styrene in hydrous DCE slightly improved the yield of **2a** as well as the conversion of **1**. Effects of temperature, amounts of water, and solvents on formation of **2a** are summarized in Table 1. The addition of 2 equiv. of water increased the yield of **2a**, although decreasing the selectivity. Lesser amount of water used was




Scheme 3. Copper-catalyzed transformation of carbonyl-ene-nitrile compound **1**.

Table 1
Cu-catalyzed vinylation of **1** with styrene




| Entry | Temperature (°C) | Solvent | Additive (equiv.) | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 50 | DCE | – | 50 (59) |
| 2 | 50 | DCE | $H_2O$ (2) | 58 (76) |
| 3 | 50 | DCE | $H_2O$ (1) | 50 (72) |
| 4[b] | 50 | DCE | $H_2O$ (2) | 28 (100) |
| 5 | 60 | DCE | $H_2O$ (2) | 59 (81) |
| 6 | 70 | DCE | $H_2O$ (2) | 58 (100) |
| 7 | 50 | Toluene | $H_2O$ (2) | 52 (81) |
| 8 | 70 | Toluene | $H_2O$ (2) | 54 (100) |

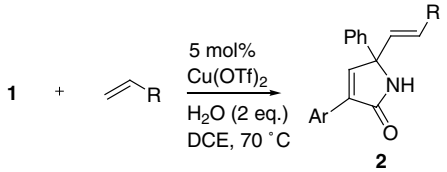
*Reaction conditions*: **1** (0.40 mmol), styrene (2.0 mmol), $Cu(OTf)_2$ (0.020 mmol), additive (if necessary) in a solvent (1.6 mL) for 18 h.
[a] Isolated yields. The conversions of **1** were shown in parentheses.
[b] For 79 h.

not effective for the reaction (entries 2–4). Toluene is a comparable solvent to DCE in the reaction (entries 7 and 8).

By using the reaction conditions of entry 6 (Table 1), we examined the vinylation reaction with various styrene derivatives. Selected results are summarized in Table 2. The reaction of **1** with 4-methylstyrene gave the corresponding pyrrolinone **2b** in 50% yield, while the reactions of **1** with 4-chlorostyrene or 4-bromostyrene gave the corresponding products **2c** and **2d** in slightly lower yields, respectively (entries 2 and 3). On the contrary, no vinylated product was observed from the reaction of **1** with 4-methoxystyrene, because polymerization of 4-methoxystyrene occurred quickly under the identical conditions (entry 4) [12]. The reaction of **1** with 2-vinylnaphthalene also gave the corresponding product **2e** in 53% yield (entry 5).

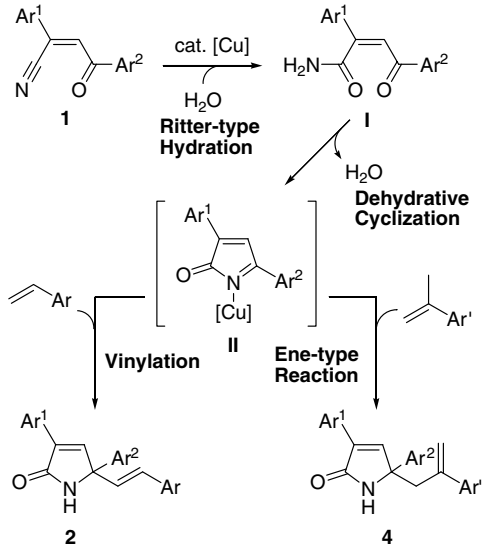
Most plausible mechanism of the pyrrolinone formation from carbonyl-ene-nitrile compounds is shown in Scheme 4 [10]. Ritter-type hydration of a nitrile moiety activated by a

Table 2
Cu-catalyzed vinylation of **1** with alkenes




| Entry | R | Time (h) | Product | Yield (%)[a] |
|---|---|---|---|---|
| 1 | 4-$MeC_6H_4$ | 9 | **2b** | 50 |
| 2 | 4-$ClC_6H_4$ | 9 | **2c** | 41 |
| 3[b] | 4-$BrC_5H_4$ | 24 | **2d** | 40 |
| 4 | 4-$MeOC_6H_4$ | 24 | –[c] | –[c] |
| 5 | 2-Naphthyl | 15 | **2e** | 53 |

*Reaction conditions*: **1** (0.40 mmol), alkene (2.0 mmol), $Cu(OTf)_2$ (0.020 mmol), $H_2O$ (0.80 mmol) in DCE (1.6 mL) at 70 °C.
[a] Isolated yields.
[b] 80 °C.
[c] Complex mixture.




Scheme 4. Plausible mechanism for the Cu-catalyzed transformation of carbonyl-ene-nitrile compound **1**.

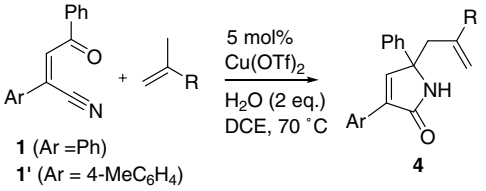
copper catalyst affords carbonyl-ene-amide intermediate **I**. The following dehydrative cyclization between carbonyl and amide moieties in the intermediate **I** takes place to afford the more reactive intermediate, 2-aza-2,4-cyclopentadienone **II**. Although Gaviña et al. have already reported that non-substituted 2-aza-2,4-cyclopentadienone smoothly reacts with both of an enophile and a dienophile to give the corresponding Diels–Alder adducts, the imino moiety in 2-aza-2,4-cyclopentadienone **II** selectively reacts at a β-carbon atom of styrenes to form vinylated product **2** [13,14]. To the best of our knowledge, this is the first example of transition metal-catalyzed direct vinylation of imino moieties with alkenes [15–18].

Next, we investigated the imino ene reaction of intermediary 2-aza-2,4-cyclopentadienone **II** leading to allylated pyrrolinones (Eq. 1) [19]. Typical results are summarized in Table 3. When the reaction of **1** with α-methylstyrene was carried out under the identical reaction conditions, the imino ene reaction-type adduct **4a** was obtained in 67% yield (entry 1). 4-Methyl, 4-chloro-, and 4-bromo-α-methylstyrene also reacted with **1** to afford the corresponding allylated products **4b**, **4c**, and **4d** in modest yields, respectively (entries 2–4). The structure of **4b** containing a pyrrolinone structure was unambiguously determined by X-ray crystallographic analysis [20]. 2-(2-Propenyl)naphthalene could be used for this reaction to give the corresponding product **4e** in 57% yield (entry 5). Carbonyl-ene-nitrile compound **1′** (Ar = 4-$MeC_6H_4$) was also reacted with both of α-methylstyrene and 2-(2-propenyl)naphthalene to give the corresponding products **4f** and **4g** in 70% and 57% yields, respectively (entries 6 and 7)

Table 3
Cu-catalyzed allylation of **1** with α-methylstyrenes

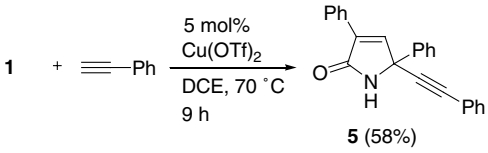
| Entry | Ar | R | Time (h) | Product | Yield(%)[a] |
|---|---|---|---|---|---|
| 1 | Ph | Ph | 4 | **4a** | 67 |
| 2 | Ph | 4-$MeC_6H_4$ | 3 | **4b** | 44 |
| 3 | Ph | 4-$ClC_6H_4$ | 4 | **4c** | 39 |
| 4 | Ph | 4-$BrC_6H_4$ | 4 | **4d** | 47 |
| 5 | Ph | 2-Naphthyl | 10 | **4e** | 57 |
| 6 | *p*-Tol | Ph | 24 | **4f** | 70 |
| 7 | *p*-Tol | 2-Naphthyl | 40 | **4g** | 57 |

*Reaction conditions*: **1** or **1′** (0.40 mmol), alkene (2.0 mmol), $Cu(OTf)_2$ (0.020 mmol), $H_2O$ (0.80 mmol) in DCE (1.6 mL) at 70 °C.
[a] Isolated yields.




(1)

Finally, we examined the alkynylation reaction of 2-aza-2,4-cyclopentadienone intermediate **II** generated from **1** [21]. When the reaction of **1** with phenylacetylene was carried out in the presence of copper catalyst, 5-alkynyl substituted pyrrolinone **5** was obtained in 58% yield (Eq. 2)




(2)

## 3. Conclusion

We have demonstrated the copper-catalyzed transformation of carbonyl-ene-nitrile compounds with various alkenes and an acetylene. The reactive intermediate **II** might be generated from carbonyl-ene-nitrile compounds via Ritter-type hydration of nitrile moiety activated by copper catalyst followed by dehydrative cyclization between the resulting amide and carbonyl moieties. Furthermore, we found the unique vinylation as well as imino ene reaction and alkynylation reactions of imino moieties in 2-aza-2,4-cyclopentadienone intermediate **II** leading to pyrrolinone derivatives containing a tertiary carbon. The present method might provide an efficient tool for the synthesis of various natural products containing γ-lactam skeleton, such as salinosporamide A-C, omuralide, lactacystin, PI-091, and lucilactaene [22]. Further studies on more efficient transformation of intermediary 2-aza-2,4-cyclopentadienones as well as in situ generation of nitrene complexes are currently investigated in our laboratory.

## 4. Experimental

### 4.1. General

All reactions and manipulations of oxygen- and moisture-sensitive materials were conducted with a standard Schlenk technique under nitrogen. All other chemicals were obtained commercially and without further purification.

Carbonyl-ene-nitrile compounds **1** and **1′** were prepared according to the reported procedure [11]. Solvents were dried by the usual methods and distilled before use. The progresses of reactions were monitored by analytical thin-layer chromatography (TLC, silica gel 60 Merck F-254 plates). Column chromatographies were performed with SILICYCLE (Ultra Pure Silica Gel (230–400 mesh)). NMR spectra were recorded for solutions in $CDCl_3$. Chemical shifts for $^1H$ and $^{13}C$ are referenced to internal solvent resonances and reported relative $SiMe_4$. IR spectra were recorded with an FT-IR spectrometer. Melting points (m.p.) are uncorrected. High-resolution mass spectra (HRMS) and low-resolution mass spectra (LRMS) were measured with JEOL JMX-SX 102A spectrometer. Element analyses were performed at Microanalytical Center of Kyoto University. All pyrrolinone compounds were fully characterized by NMR spectra.

### 4.2. Typical procedure for copper-catalyzed transformation of carbonyl-ene-nitrile compounds

A flame dried Schlemk flask was charged with $Cu(OTf)_2$ (7.2 mg, 0.020 mmol) in an inert atmosphere ($N_2$) glove box. Upon removal from the glove box, to the Schlenk flask was added a solution of substrate (0.40 mmol) and alkene (2.0 mmol) in DCE (2.0 mL). The solution was stirred at room temperature for 5 min. Then, water (14.4 mg, 0.80 mmol) was added dropwise. After stirring at the temperature specified in Scheme 3, Tables 1–3 and Eqs. 1,2, the mixture was diluted with ethyl acetate and was filtered through a short silica gel pad. Filterate was evaporated under reduced pressure and the residue was purified by flash column chromatography over silica gel (hexane/AcOEt = 7/1–4/1).

#### 4.2.1. 3,5-Diphenyl-5-[(1E)-2-phenylethenyl]-3-pyrrolin-2-one (**2a**)

A white solid, m.p. 78.8–79.8 °C. IR (KBr), $\nu/cm^{-1}$: 693, 746, 794, 966, 1447, 1491, 1690 (C=O), 3027, 3060, 3203 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.51 (d, $J = 16.0$ Hz, 1H), 6.66 (d, $J = 16.0$ Hz, 1H), 7.23–7.48 (m, 14H), 7.55 (br, 1H), 7.90 (d, $J = 6.8$ Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 67.22, 126.3, 126.6, 127.2, 128.0, 128.1, 128.4, 128.6, 128.7, 128.8, 128.9, 130.7, 130.9, 133.6, 135.9, 139.5, 145.3, 172.0. Anal. Calc. for $C_{24}H_{19}NO$: C, 85.43; H, 5.68; N, 4.15. Found: C, 85.44; H, 5.89; N, 3.85%.

#### 4.2.2. 3,5-Diphenyl-5-[(1E)-2-(4-methylphenyl)ethenyl]-3-pyrrolin-2-one (**2b**)

A white solid, m.p. 75.1–76.8 °C. IR (KBr), $\nu/cm^{-1}$: 695, 746, 795, 968, 1447, 1490, 1691 (C=O), 2920, 3024, 3057, 3211 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$2.33 (s, 3H), 6.46 (d, $J = 16.0$ Hz, 1H), 6.62 (d, $J = 16.0$ Hz, 1H), 6.95 (br, 1H), 7.12 (d, $J = 7.6$ Hz, 2H), 7.34–7.48 (m, 9H), 7.46 (d, $J = 7.6$ Hz, 2H), 7.90 (d, $J = 6.8$ Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.28, 67.09, 126.3, 126.5, 127.2, 127.7, 128.1, 128.4, 128.6, 128.7, 128.8, 129.3, 130.7, 130.9, 133.1, 138.1, 139.6, 145.5, 171.8. HRMS (FAB); $m/z$: 352.1707 ($[M^+ + H]$, calc. for $C_{25}H_{22}NO$: 352.1701).

#### 4.2.3. 3,5-Diphenyl-5-[(1E)-2-(4-chlorophenyl)ethenyl]-3-pyrrolin-2-one (**2c**)

A white solid, m.p. 180.3–181.9 °C. IR (KBr), $\nu/cm^{-1}$: 693, 745, 972, 1490, 1687 (C=O), 3031, 3060, 3214 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.49 (d, $J = 16.0$ Hz, 1H), 6.62 (d, $J = 16.0$ Hz, 1H), 6.84 (s, 1H), 7.26–7.46 (m, 13H), 7.91 (d, $J = 8.0$ Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 67.99, 126.2, 127.2, 127.8, 128.2, 128.4, 128.8, 128.9, 129.0, 129.5, 129.6, 130.8, 133.7, 133.8, 134.4, 139.2, 145.1, 171.7. HRMS (FAB); $m/z$: 372.1151 ($[M^+ + H]$, calc. for $C_{24}H_{19}ClNO$: 372.1155).

#### 4.2.4. 3,5-Diphenyl-5-[(1E)-2-(4-bromophenyl)ethenyl]-3-pyrrolin-2-one (**2d**)

A white solid, m.p. 186.2–187.6 °C. IR (KBr), $\nu/cm^{-1}$: 695, 793, 1008, 1446, 1490, 1690 (C=O), 2926, 3027, 3060, 3209 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.50 (d, $J = 16.0$ Hz, 1H), 6.60 (d, $J = 16.0$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.35–7.46 (m, 12H), 7.91 (d, $J = 8.0$ Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 67.11, 122.0, 126.3, 127.2, 128.1, 128.2, 128.4, 128.8, 128.9, 129.6, 129.7, 130.8, 131.7, 133.7, 134.8, 139.2, 145.0, 171.9. HRMS (FAB); $m/z$: 418.0639 ($[M^+ + H]$, calc. for $C_{24}H_{19}BrNO$: 418.0633).

#### 4.2.5. 3,5-Diphenyl-5-[(1E)-2-naphthalenylethenyl]-3-pyrrolin-2-one (**2e**)

A white solid, m.p. 88.9–90.3 °C. IR (KBr), $\nu/cm^{-1}$: 695, 745, 965, 1447, 1490, 1688 (C=O), 2872, 3055, 3211 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.64 (d, $J = 16.0$ Hz, 1H), 6.72 (br, 1H), 6.82 (d, $J = 16.0$ Hz, 1H), 7.36–7.51 (m, 11H), 7.59 (m, 1H), 7.73 (s, 1H), 7.79 (m, 3H), 7.93 (d, $J = 6.8$ Hz, 2H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 67.13, 123.4, 126.2, 126.4, 126.5, 127.0, 127.3, 127.7, 128.1, 128.3, 128.4, 128.5, 128.6, 128.9, 129.0, 129.1, 130.9, 131.1, 133.2, 133.4, 133.5, 139.5, 145.6, 171.8. HRMS(FAB); $m/z$: 388.1708 ($[M^+ + H]$, calc. for $C_{28}H_{22}NO$: 388.1701).

#### 4.2.6. 3,5-Diphenyl-5-(2-phenyl-2-propenyl)-3-pyrrolin-2-one (**4a**)

A white solid, m.p. 182.2–184.1 °C. IR (KBr), $\nu/cm^{-1}$: 699, 754, 793, 977, 1447, 1492, 1599, 1635, 1691 (C=O), 2872, 3028, 3061, 3142, 3181 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.29 (d, $J = 13.6$ Hz, 1H) 3.40 (d, $J = 13.6$ Hz, 1H), 5.05 (s, 1H), 5.26 (s, 1H), 7.00 (br, 1H), 7.21–7.35 (m, 12H), 7.39 (d, $J = 7.2$ Hz, 2H), 7.53 (d, $J = 7.2$ Hz, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 45.85, 66.31, 118.9, 125.5, 126.4, 127.1, 127.4, 127.5, 128.1, 128.3, 128.5, 128.6, 131.0, 133.5, 140.4, 141.7, 143.1, 146.6, 171.8. HRMS (FAB); $m/z$: 352.1710 ($[M^+ + H]$, calc. for $C_{25}H_{22}NO$: 352.1701).

#### 4.2.7. 3,5-Diphenyl-5-[2-(4-methylphenyl)-2-propenyl]-3-pyrrolin-2-one (**4b**)

A colorless crystal, m.p. 146.5–147.9 °C. IR (KBr), $\nu/cm^{-1}$: 697, 749, 794, 915, 1447, 1492, 1514, 1623, 1692 (C=O), 2863, 2920, 3027, 3061, 3147, 3197 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.30 (s, 3H), 3.25 (d, $J = 13.6$ Hz, 1H), 3.38 (d, $J = 13.6$ Hz, 1H), 4.99 (s, 1H), 5.21 (s, 1H), 7.00 (s, 1H), 7.05 (d, $J = 7.2$ Hz, 2H), 7.13 (d, $J = 7.2$ Hz, 2H), 7.23–7.34 (m, 6H), 7.40 (d, $J = 7.6$ Hz, 2H), 7.53–7.60 (m, 3H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.08, 46.00, 66.42, 118.1, 125.6, 126.2, 127.1, 127.4, 128.0, 128.3, 128.6, 128.8, 129.1, 131.0, 137.2, 138.8, 140.5, 142.8, 146.7, 172.0. HRMS (FAB); *m/z*: 366.1846 ([$M^+ + H$], calc. for $C_{26}H_{24}NO$: 366.1858).

#### 4.2.8. 3,5-Diphenyl-5-[2-(4-chlorophenyl)-2-propenyl]-3-pyrrolin-2-one (**4c**)

A white solid, m.p. 127.3–128.8 °C. IR (KBr), $\nu/cm^{-1}$: 694, 748, 794, 919, 1447, 1491, 1597, 1625, 1689 (C=O), 2857, 2920, 3027, 3062, 3147, 3179 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 3.26 (d, $J = 14.0$ Hz, 1H), 3.35 (d, $J = 14.0$ Hz, 1H), 5.09 (s, 1H), 5.24 (s, 1H), 7.00 (s, 1H), 7.14 (d, $J = 8.0$ Hz, 2H), 7.18 (d, $J = 8.0$ Hz, 2H), 7.23–7.27 (m, 2H), 7.30–7.34 (m, 4H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.54–7.57 (m, 2H), 7.89 (br, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 45.86, 66.34, 119.5, 125.5, 127.0, 127.5, 127.7, 128.2, 128.5, 128.7, 129.7, 130.9, 133.2, 133.7, 134.9, 140.3, 142.1, 146.2, 172.0. HRMS (FAB); m/z: 386.1313 ([$M^+ + H$], calcd. for $C_{25}H_{21}ClNO$: 386.1312).

#### 4.2.9. 3,5-Diphenyl-5-[2-(4-bromophenyl)-2-propenyl]-3-pyrrolin-2-one (**4d**)

A white solid, m.p. 66.3–67.2 °C. IR (KBr), $\nu/cm^{-1}$: 695, 794, 909, 1489, 1625, 1691 (C=O), 2919, 3062, 3185 (N–H). $^1H$ NMR (300 MHz, $CDCl_3$): $\delta$ 3.25 (d, $J = 13.8$ Hz, 1H), 3.35 (d, $J = 13.8$ Hz, 1H), 5.09 (s, 1H), 5.24 (s, 1H), 6.98 (s, 1H), 7.07 (d, $J = 8.1$ Hz, 2H), 7.23–7.42 (m, 10H), 7.52–7.56 (m, 2H), 8.04 (br, 1H). $^{13}C$ NMR (75 MHz, $CDCl_3$): $\delta$ 45.82, 66.39, 119.6, 121.4, 125.6, 127.1, 127.6, 128.0 128.2, 128.5, 128.7, 130.9, 131.5, 133.8, 140.4, 140.9, 142.2, 146.3, 172.2. HRMS (FAB); *m/z*: 432.0786 ([$M^+ + H$], calc. for $C_{25}H_{21}BrNO$: 432.0790).

#### 4.2.10. 3,5-Diphenyl-5-[2-naphthalenyl-2-propenyl]-3-pyrrolin-2-one (**4e**)

A white solid, m.p. 51.2–52.9 °C. IR (KBr), $\nu/cm^{-1}$: 695, 748, 794, 1220, 1446, 1491, 1597, 1626, 1691 (C=O), 2856, 3026, 3057, 3210 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$):$\delta$ 3.37 (d, $J = 13.6$ Hz, 1H), 3.51 (d, $J = 13.6$ Hz, 1H), 5.16 (s, 1H), 5.37 (s, 1H), 6.95 (s, 1H), 7.15–7.25 (m, 4H), 7.28–7.34 (m, 2H), 7.36–7.47 (m, 7H), 7.66 (br, 1H), 7.68–7.95 (m, 4H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 46.02, 66.47, 119.41, 124.80, 125.12, 125.58, 125.86, 126.15, 127.07, 127.42, 127.46, 127.99, 128.02, 128.10, 128.26, 128.60, 130.89, 132.61, 133.19, 133.61, 139.21, 140.49, 142.98, 146.40, 172.01. HRMS (FAB); *m/z*: 402.1852 ([$M^+ + H$], calc. for $C_{29}H_{24}NO$: 402.1858).

#### 4.2.11. 3-(4-Methylphenyl)-5-phenyl-5-(2-phenyl-2-propenyl)-3- pyrrolin-2-one (**4f**)

A white solid, m.p. 146.0–147.8 °C. IR (KBr), $\nu/cm^{-1}$: 698, 779, 911, 1446, 1495, 1509, 1625, 1687 (C=O), 2864, 2920, 3025, 3060, 3179 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.32 (s, 3H), 3.26 (d, $J = 13.6$ Hz, 1H), 3.38 (d, $J = 13.6$ Hz, 1H), 5.04 (s, 1H), 5.23 (s, 1H), 6.93 (s, 1H), 7.15 (d, $J = 7.6$ Hz, 2H), 7.21–7.25 (m, 5H), 7.31 (t, $J = 7.6$ Hz, 3H), 7.39 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.74 (br, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.35, 45.97, 66.34, 118.8, 125.6, 126.4, 127.0, 127.3, 128.2, 128.4, 128.5, 128.8, 133.4, 138.2, 140.5, 140.6, 141.8, 143.1, 145.5, 172.1. HRMS (FAB); *m/z*: 366.1857 ([$M^+ + H$], calc. for $C_{26}H_{24}NO$: 366.1858).

#### 4.2.12. 3-(4-Methylphenyl)-5-phenyl-5-(2-naphthalenyl-2-propenyl)-3-pyrrolin-2-one (**4g**)

A white solid, m.p. 164.2–165.8 °C. IR (KBr), $\nu/cm^{-1}$: 697, 751, 822, 1507, 1689 (C=O), 2860, 2924, 3049, 3056, 3193 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$2.29 (s, 3H), 3.36 (d, $J = 13.6$ Hz, 1H), 3.42 (d, $J = 13.6$ Hz, 1H), 5.14 (s, 1H), 5.36 (s, 1H), 6.91 (s, 1H), 7.00 (d, $J = 8.0$ Hz, 2H), 7.20–7.46 (m, 10H), 7.64 (d, $J = 9.6$ Hz, 2H), 7.71 (d, $J = 8.0$ Hz, 2H), 7.76–7.79 (m, 1H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 21.32, 46.02, 66.36, 119.3, 124.8, 125.1, 125.6, 125.8, 126.1, 126.9, 127.4, 128.0, 128.1, 128.6, 128.7, 132.6, 133.2, 133.5, 138.1, 139.2, 140.6, 143.0, 145.5, 172.1. HRMS (FAB); *m/z*: 416.2017 ([$M^+ + H$], calc. for $C_{30}H_{26}NO$: 416.2014).

#### 4.2.13. 3,5-Diphenyl-5-(phenylethynyl)-3-pyrrolin-2-one (**5**)

A yellow solid, m.p. 98.4–99.9 °C. IR (KBr), $\nu/cm^{-1}$: 691, 761, 793, 957, 1063, 1223, 1254, 1354, 1446, 1490, 1596, 1696 (C=O), 2842, 3061, 3168 (N–H). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 6.96 (s, 1H), 7.20 (d, $J = 1.6$ Hz, 1H), 7.32–7.42 (m, 9H), 7.49–7.52 (m, 2H), 7.65–7.68 (m, 2H), 7.88–7.91 (m, 2H). $^{13}C$ NMR (100 MHz, $CDCl_3$): $\delta$ 60.62, 84.81, 86.22, 121.8, 125.8, 127.3, 128.3, 128.4, 128.6, 128.8, 128.9, 129.0, 130.4, 131.7, 132.9, 137.7, 144.7, 171.8. HRMS (FAB); *m/z*: 336.1381 ([$M^+ + H$], calc. for $C_{24}H_{18}NO$: 336.1388).

## 5. Supplementary data

Crystallographic information of compound **4b** has been deposited with the Cambridge Crystallographic Data Centre (CCDC) No. 604095. The data can be obtained free of charge via Internet http://www.ccdc.cam.ac.uk. Copies of this information may be obtained free of charge from the Director, CCDC, 12 Union Road Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk.

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