Supporting Information

Gold-catalyzed cascade C–H/C–H cross-coupling/cyclization/alkynylation: An efficient access to 3-alkynylpyrroles

Shuai Zhang, Yuanhong Ma, Jingbo Lan, Feijie Song* and Jingsong You*

Key Laboratory of Green Chemistry and Technology of Ministry of Education, College of Chemistry, and State Key Laboratory of Biotherapy, West China Medical School, Sichuan University, 29 Wangjiang Road, Chengdu 610064, PR China
Fax: 86-28-85412203; E-mail: jsyou@scu.edu.cn; fsong@scu.edu.cn
# Table of contents

I. General remarks........................................................................................................S3

II. Optimization of the reaction of β-enamino esters with terminal alkynes...........S3

III. General procedure for the synthesis of fully substituted 3-alkynylpyrroles........S5

IV. General procedure for the synthesis of C5-unsubstituted 3-alkynylpyrroles......S5

V. ORTEP diagrams of compounds 3a and 11a......................................................S6

VI. Characterization of new β-enamino esters.......................................................S6

VII. Characterization of products 3-5.......................................................................S9

VIII. Mechanism study.............................................................................................S23

IX. The derivation of 3-alkynylpyrroles.................................................................S25

X. References..........................................................................................................S28

XI. Copies of ¹H, ¹³C and ¹⁹F NMR spectra.........................................................S29
I. General remarks

NMR spectra were obtained on a Bruker AV II-400 MHz (1H NMR at 400 MHz, 13C NMR at 100 MHz, and 19F NMR at 376 MHz). The 1H NMR chemical shifts were measured relative to CDCl3 (δ = 7.26 ppm) or DMSO-d6 (δ = 2.50 ppm) as the internal reference. The 13C NMR chemical shifts were given using CDCl3 (δ = 77.16 ppm) or DMSO-d6 (δ = 39.52 ppm) as the internal standard. High-resolution mass spectra (HRMS) were obtained with a Waters-Q-TOF-Premier (ESI). X-Ray single-crystal diffraction data were collected on an Oxford Xcalibur E or Agilent Technologies Gemini single crystal diffractometers. Melting points were determined with XRC-1 and are uncorrected.

Unless otherwise noted, all reactions were carried out under N2. All reagents were obtained from commercial suppliers and used without further purification. HAuCl4·xH2O (≥ 50% Au) were purchased from Shanxi Kaida Chemical Engineering (China) Co., Ltd. AuCl3 and AuBr3 were purchased from Acros and Alfa Aesar, respectively. [(bpy)AuCl2]Cl,1 1-ethyl-2-(methoxymethoxy)benzene,2 4-ethynylbenzonitrile,3 1-ethynlnaphthalene,4 2-ethylthiophene,5 β-aryl enamines 1h-1l,6a β-alkyl enamines 1a-1g and 1m-1p,6b and α,β-disubstituted enamines 1q-1r6c were prepared according to the literature procedure. Solvents were dried by refluxing over CaH2 (for CH2Cl2, DMF, CH3CN, and PhCl) or sodium (for toluene, THF, and MeOH) and freshly distilled prior to use.

II. Optimization of the reaction of β-enamino esters with terminal alkynes

A flame-dried sealable tube with a magnetic stir bar was charged with gold species, base, oxidant, (Z)-ethyl 3-(phenylamino)but-2-enoate 1a (232.4 μL, 1.2 mmol), phenylacetylene 2a (65.9 μL, 0.6 mmol), and solvent (3.0 mL) under an N2 atmosphere. The tube was sealed and the reaction mixture was stirred at 50 °C for 4 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH2Cl2, filtered through a celite pad, and washed with 30 mL of CH2Cl2. The filtrate was concentrated and the residue was purified by column chromatography on
silica gel (petroleum ether/ethyl acetate = 20/1, v/v) to provide the desired product 3a.

**Table S1.** Optimization of the gold-catalyzed reaction of (Z)-ethyl 3-(phenylamino)but-2-enoate 1a with phenylacetylene 2a

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst (mol%)</th>
<th>oxidant</th>
<th>base (equiv)</th>
<th>solvent</th>
<th>yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>none</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Ph$_3$PAuCl (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>45</td>
</tr>
<tr>
<td>3</td>
<td>AuCl$_3$ (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>34</td>
</tr>
<tr>
<td>4</td>
<td>AuBr$_3$ (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>30</td>
</tr>
<tr>
<td>5</td>
<td>HAuCl$_4$·xH$_2$O (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>42</td>
</tr>
<tr>
<td>6</td>
<td>AuCl$_3$ (4) + bpy (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>26</td>
</tr>
<tr>
<td>7</td>
<td>AuCl$_3$ (4) + phen (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>57</td>
</tr>
<tr>
<td>8</td>
<td>[(bpy)AuCl$_2$]Cl (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>61</td>
</tr>
<tr>
<td>9</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>54</td>
</tr>
<tr>
<td>10</td>
<td>[(bpy)AuCl$_2$]Cl (10)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>38</td>
</tr>
<tr>
<td>11</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OPiv)$_2$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>12</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PIFA</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>13</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>K$_2$S$_2$O$_8$</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>14</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>NFSI</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>15</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>Selectfluor</td>
<td>KOAc (2.0)</td>
<td>toluene</td>
<td>0</td>
</tr>
<tr>
<td>16</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>DCM</td>
<td>43</td>
</tr>
<tr>
<td>17</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>PhCl</td>
<td>44</td>
</tr>
<tr>
<td>18</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>THF</td>
<td>21</td>
</tr>
<tr>
<td>19</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>CH$_3$CN</td>
<td>trace</td>
</tr>
<tr>
<td>20</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>DMF</td>
<td>0</td>
</tr>
<tr>
<td>21</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>MeOH</td>
<td>0</td>
</tr>
<tr>
<td>22</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (2.0)</td>
<td>none</td>
<td>39</td>
</tr>
<tr>
<td>23</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>NaOAc (2.0)</td>
<td>toluene</td>
<td>40</td>
</tr>
<tr>
<td>24</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>CsOAc (2.0)</td>
<td>toluene</td>
<td>52</td>
</tr>
<tr>
<td>25</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>K$_3$PO$_4$ (2.0)</td>
<td>toluene</td>
<td>44</td>
</tr>
<tr>
<td>26</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>Cs$_2$CO$_3$ (2.0)</td>
<td>toluene</td>
<td>50</td>
</tr>
<tr>
<td>27</td>
<td>[(bpy)AuCl$_2$]Cl (5)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (3.0)</td>
<td>toluene</td>
<td>66</td>
</tr>
<tr>
<td>28</td>
<td>[(bpy)AuCl$_2$]Cl (4)</td>
<td>PhI(OAc)$_2$</td>
<td>KOAc (3.0)</td>
<td>toluene</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>[(bpy)AuCl₂]Cl</td>
<td>PhI(OAc)₂</td>
<td>KOAc (3.0 equiv)</td>
<td>toluene</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>29°</td>
<td>[(bpy)AuCl₂]Cl (4)</td>
<td>PhI(OAc)₂</td>
<td>KOAc (3.0)</td>
<td>toluene</td>
<td>35</td>
</tr>
<tr>
<td>30°</td>
<td>[(bpy)AuCl₂]Cl (4)</td>
<td>PhI(OAc)₂</td>
<td>KOAc (3.0)</td>
<td>toluene</td>
<td>66</td>
</tr>
</tbody>
</table>

Reaction conditions: 1a (1.2 mmol), 2a (0.6 mmol), gold species, base (2.0-3.0 equiv), oxidant (2.0 equiv), and solvent (3.0 mL) at 50 °C for 4 h. Isolated yields based on 2a are given.  

The ratio of 1a/2a was 1/1. The ratio of 1a/2a was 2.5/1. bpy = 1,2-bipyridine; PIFA = phenyliodine bis(trifluoroacetate); NFSI = N-fluorobenzenesulfonimide; Selectfluor = 1-chloromethyl-4-fluoro-1,4-diaziobicyclo[2.2.2]octane bis(tetrafluoroborate).

### III. General procedure for the synthesis of fully substituted 3-alkynylpyrroles

A flame-dried sealable tube with a magnetic stir bar was charged with [(bpy)AuCl₂]Cl (11.1 mg, 0.024 mmol), KOAc (176.7 mg, 1.8 mmol), PhI(OAc)₂ (386.5 mg, 1.2 mmol), β-enamino ester 1 (1.5 mmol), terminal alkyne 2 (0.6 mmol), and toluene (3.0 mL) under an N₂ atmosphere. The tube was sealed and the reaction mixture was stirred at 50 °C for 4 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH₂Cl₂, filtered through a celite pad, and washed with 30 mL of CH₂Cl₂. The filtrate was evaporated and the residue was purified by column chromatography on silica gel to provide the desired product 3 and 4.

### IV. General procedure for the synthesis of C5-unsubstituted 3-alkynylpyrroles

A flame-dried sealable tube with a magnetic stir bar was charged with [(bpy)AuCl₂]Cl (9.2 mg, 0.02 mmol), KOAc (117.8 mg, 1.2 mmol), PhI(OAc)₂ (257.7 mg, 0.8 mmol), 2,3-disubstituted β-enamino ester 1 (1.2 mmol), terminal alkyne 2 (0.4 mmol), and chlorobenzene (2.0 mL) under an N₂ atmosphere. The tube was sealed and the reaction mixture was stirred at 50 °C for 4 h. After being cooled to ambient temperature, chlorobenzene was evaporated and the residue was diluted with 10 mL of CH₂Cl₂, filtered through a celite pad, and washed with 30 mL of CH₂Cl₂. The filtrate was concentrated and the residue was purified by column chromatography on silica gel to provide the desired product 5.
V. ORTEP diagrams of compounds 3a and 11a

![Figure S1. ORTEP diagram of 3a (CCDC 1031864). Thermal ellipsoids are set at 50% probability.](image)

![Figure S2. ORTEP diagram of 11a (CCDC 1031865). Thermal ellipsoids are set at 50% probability.](image)

VI. Characterization of new β-enamino esters

(Z)-Ethyl 3-(phenylamino)-3-(o-tolyl)acrylate (1i)<sup>a</sup>

Purification by column chromatography on basic Al<sub>2</sub>O<sub>3</sub> (petroleum ether/ethyl acetate = 20/1, v/v) afforded 1i as a pale yellow solid in 49% yield. M.p.: 84-86 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz): δ = 1.32 (t, J = 7.2 Hz, 3H), 2.12 (s, 3H), 4.22 (q, J = 7.2 Hz, 2H), 4.76 (s, 1H), 6.58 (d, J = 7.6 Hz, 2H), 6.88 (t, J = 7.6 Hz, 1H), 7.03 (t, J = 7.6 Hz, 2H), 7.08 (d, J = 7.6 Hz, 1H), 7.21 (t, J = 7.6 Hz, 1H), 7.27 (td, J = 7.6 Hz, 1.6 Hz, 1H), 7.32 (dd, J = 7.6 Hz, 1.6 Hz, 1H), 10.62 (s, 1H) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz): δ
\[
\delta = 14.7, 19.6, 59.3, 89.6, 120.8, 123.1, 126.1, 128.8, 129.0, 129.3, 130.4, 135.7, 136.0, \\
140.0, 159.5, 170.4 \text{ ppm. HRMS (ESI\textsuperscript{+}): calcd for C}_{18}\text{H}_{19}\text{NNaO}_2 [M+Na\textsuperscript{+}] 304.1313, \\
\text{found 304.1318.}
\]

**\textbf{(Z)-Ethyl 3-(naphthalen-1-yl)-3-(phenylamino)acrylate (1j)}\textsuperscript{6a}**

Purification by column chromatography on basic Al\textsubscript{2}O\textsubscript{3} (petroleum ether/ethyl acetate = 20/1, v/v) afforded 1j as a white solid in 30\% yield. M.p.: 108-110 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 1.34 (t, J = 7.2 \text{ Hz}, 3\text{H}), 4.25 (q, J = 6.8 \text{ Hz}, 2\text{H}), 4.95 (s, 1\text{H}),
\)
6.55 (d, \(J = 8.0 \text{ Hz}, 2\text{H}), 6.76 (t, J = 7.6 \text{ Hz}, 1\text{H}), 6.89 (t, J = 8.0 \text{ Hz}, 2\text{H}), 7.41-7.47 
\text{(m, 4\text{H}), 7.80-7.86 (m, 2\text{H}), 8.09-8.12 (m, 1\text{H}), 10.81 (s, 1\text{H}) ppm. \textsuperscript{13}C NMR}
(CDCl\textsubscript{3}, 100 MHz): \(\delta = 14.7, 59.4, 91.2, 121.2, 123.2, 125.2, 125.4, 126.3, 126.9, 127.0, 128.4,
\)
128.7, 129.6, 130.7, 133.5, 133.9, 140.0, 158.3, 170.4 ppm. HRMS (ESI\textsuperscript{+}): calcd for 
C\textsubscript{21}H\textsubscript{19}NNaO\textsubscript{2} [M+Na\textsuperscript{+}] 340.1315, found 340.1315.

\[\text{(Z)-Methyl 3-(4-bromophenyl)-3-(phenylamino)acrylate (1l)}\textsuperscript{6a}\]

Purification by column chromatography on basic Al\textsubscript{2}O\textsubscript{3} (petroleum ether/ethyl acetate = 20/1, v/v) afforded 1l as a white solid in 48\% yield. M.p.: 88-90 °C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 3.74 (s, 3\text{H}), 4.98 (s, 1\text{H}), 6.67 (d, J = 7.6 \text{ Hz}, 2\text{H}), 6.94 (t, J = 7.2 \text{ Hz}, 1\text{H}), 7.11 (t, J = 8.0 \text{ Hz}, 2\text{H}), 7.21 (dt, J = 8.8 \text{ Hz}, 2.0 \text{ Hz}, 2\text{H}), 7.42 (dt, J = 8.8 \text{ Hz}, 2.0 \text{ Hz}, 2\text{H}), 10.22 (s, 1\text{H}) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta = 50.9, 91.1, 
\)
122.6, 123.5, 123.9, 128.9, 129.9, 131.8, 135.0, 140.2, 158.0, 170.4 ppm. HRMS (ESI\textsuperscript{+}): calcd for 
C\textsubscript{16}H\textsubscript{14}BrNNaO\textsubscript{2} [M+Na\textsuperscript{+}] 354.0106, found 354.0109.
(Z)-Benzyl 3-((o-tolylamino)but-2-enoate (1m)\textsuperscript{6b}

Purification by column chromatography on basic Al\textsubscript{2}O\textsubscript{3} (petroleum ether/ethyl acetate = 20/1, v/v) afforded 1m as colorless oil in 89% yield. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 1.86 \) (s, 3H), 2.30 (s, 3H), 4.78 (s, 1H), 5.17 (s, 2H), 7.08 (dd, \( J = 7.2 \) Hz, 1.2 Hz, 1H), 7.12-7.20 (m, 2H), 7.22-7.24 (m, 1H), 7.29-7.33 (m, 1H), 7.35-7.42 (m, 4H), 10.12 (s, 1H) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta = 18.2, 20.3, 64.8, 85.0, 126.3, 126.6, 126.7, 128.0, 128.1, 128.6, 130.9, 134.1, 137.4, 138.0, 160.5, 170.4 \) ppm. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{18}H\textsubscript{19}NNaO\textsubscript{2} [M+Na]\textsuperscript{+} 304.1313, found 304.1316.

(Z)-Benzyl 3-((m-tolylamino)but-2-enoate (1n)\textsuperscript{6b}

Purification by column chromatography on basic Al\textsubscript{2}O\textsubscript{3} (petroleum ether/ethyl acetate = 20/1, v/v) afforded 1n as a pale brown solid in 58% yield. M.p.: 50-52 \textdegree C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 2.01 \) (s, 3H), 2.35 (s, 3H), 4.77 (s, 1H), 5.17 (s, 2H), 6.90-6.92 (m, 2H), 6.99 (d, \( J = 6.8 \) Hz, 1H), 7.20-7.23 (m, 1H), 7.29-7.40 (m, 5H), 10.35 (s, 1H) ppm. \textsuperscript{13}C NMR (CDCl\textsubscript{3}, 100 MHz): \(\delta = 20.5, 21.5, 64.7, 85.5, 121.7, 125.4, 126.0, 127.9, 128.0, 128.6, 128.9, 137.3, 139.1, 139.2, 159.7, 170.2 \) ppm. HRMS (ESI\textsuperscript{+}): calcd for C\textsubscript{18}H\textsubscript{19}NNaO\textsubscript{2} [M+Na]\textsuperscript{+} 304.1313, found 304.1311.

(Z)-Benzyl 3-((4-bromophenyl)amino)but-2-enoate (1o)\textsuperscript{6b}

Purification by column chromatography on basic Al\textsubscript{2}O\textsubscript{3} (petroleum ether/ethyl acetate = 20/1, v/v) afforded 1o as a white solid in 55% yield. M.p.: 58-60 \textdegree C. \textsuperscript{1}H NMR (CDCl\textsubscript{3}, 400 MHz): \(\delta = 1.99 \) (s, 3H), 4.80 (s, 1H), 5.16 (s, 2H), 6.96 (d, \( J = 8.8 \) Hz,
2H), 7.31-7.40 (m, 5H), 7.43-7.45 (m, 2H), 10.33 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 20.4, 64.9, 86.8, 118.3, 126.0, 128.0, 128.6, 132.3, 137.1, 138.5, 158.9, 170.1 ppm. HRMS (ESI$^+$): calcd for C$_{17}$H$_{16}$BrNNaO$_2$ [M+Na]$^+$ 368.0262, found 368.0261.

VII. Characterization of products 3-5

**Ethyl 2-methyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3a)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3a as a pale yellow solid (80.2 mg, 66% yield). M.p.: 140-142 ºC. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 1.45 (t, $J$ = 7.2 Hz, 3H), 2.41 (s, 3H), 4.41 (q, $J$ = 7.2 Hz, 2H), 7.10-7.12 (m, 2H), 7.18-7.22 (m, 3H), 7.26-7.30 (m, 5H), 7.36-7.40 (m, 5H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 12.9, 14.7, 60.0, 85.2, 91.5, 104.4, 113.5, 124.7, 127.41, 127.44, 127.8, 128.2, 128.55, 128.63, 129.3, 130.1, 130.8, 131.2, 137.6, 137.9, 138.1, 165.2 ppm. HRMS (ESI$^+$): calcd for C$_{28}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 428.1626, found 428.1627.

**Methyl 2-methyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3b)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3b as a pale yellow solid (80.8 mg, 69% yield). M.p.: 158-160 ºC. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 2.40 (s, 3H), 3.94 (s, 3H), 7.09-7.11 (m, 2H), 7.16-7.22 (m, 3H), 7.23-7.30 (m, 5H), 7.33-7.37 (m, 3H), 7.39 (dd, $J$ = 7.6 Hz, 1.2 Hz , 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 12.9, 51.2, 85.1, 91.7, 104.5, 113.5, 124.6, 127.4, 127.5, 127.8, 128.2, 128.59, 128.63, 129.3, 130.1, 130.8, 131.3, 137.6, 138.01,
138.05, 165.6 ppm. HRMS (ESI\(^+\)): calcd for C\(_{27}\)H\(_{21}\)NNaO\(_2\) [M+Na]\(^+\) 414.1470, found 414.1478.

**tert-Butyl 2-methyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3c)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3c as a pale yellow solid (85.3 mg, 66% yield). M.p.: 182-184 °C. 

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 1.64\) (s, 9H), 2.39 (s, 3H), 7.08-7.11 (m, 2H), 7.16-7.21 (m, 3H), 7.23-7.30 (m, 5H), 7.34-7.39 (m, 5H) ppm. \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 12.8, 28.8, 80.4, 85.6, 91.2, 104.3, 114.7, 124.8, 127.3, 127.4, 127.7, 128.2, 128.5, 128.6, 129.3, 130.1, 130.9, 131.3, 137.4, 137.7, 138.1, 164.5\) ppm. HRMS (ESI\(^+\)): calcd for C\(_{30}\)H\(_{27}\)NNaO\(_2\) [M+Na]\(^+\) 456.1939, found 456.1937.

**Allyl 2-methyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3d)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3d as a pale yellow solid (74.0 mg, 59% yield). M.p.: 108-110 °C. 

\(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 2.42\) (s, 3H), 4.88 (dt, \(J = 5.6\) Hz, 1.2 Hz, 2H), 5.26 (dq, \(J = 10.4\) Hz, 1.6 Hz, 1H), 5.52 (dq, \(J = 17.2\) Hz, 1.6 Hz, 1H), 6.06-6.14 (m, 1H), 7.10-7.13 (m, 2H), 7.18-7.23 (m, 3H), 7.25-7.31 (m, 5H), 7.36-7.39 (m, 5H) ppm. \(^13\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 13.0, 64.8, 85.3, 91.6, 104.5, 113.3, 117.8, 124.6, 127.5, 127.8, 128.2, 128.6, 129.4, 130.1, 130.8, 131.3, 133.1, 137.6, 138.2, 138.3, 164.8 ppm. HRMS (ESI\(^+\)): calcd for C\(_{29}\)H\(_{23}\)NNaO\(_2\) [M+Na]\(^+\) 440.1626, found 440.1630.
**Benzyl 2-methyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3e)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3e as a pale yellow solid (103.4 mg, 74% yield). M.p.: 149-151 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.45$ (s, 3H), 5.44 (s, 2H), 7.11-7.16 (m, 4H), 7.18-7.24 (m, 6H), 7.31-7.32 (m, 5H), 7.35-7.39 (m, 3H), 7.55-7.57 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 13.0, 65.9, 85.2, 91.6, 104.4, 113.0, 124.4, 127.37, 127.45, 127.8, 127.9, 128.1, 128.3, 128.6, 129.3, 130.1, 130.7, 131.3, 136.8, 137.6, 138.2, 138.5, 165.0$ ppm. HRMS (ESI$^+$): calcd for C$_{33}$H$_{25}$NNaO$_2$ [M+Na]$^+$ 490.1783, found 490.1788.

**N,N,2-Trimethyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxamide (3f)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1–2/1, v/v) afforded 3f as a pale yellow solid (42.3 mg, 35% yield). M.p.: 206-208 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.17$ (s, 3H), 3.19 (s, 3H), 3.25 (s, 3H), 7.13-7.22 (m, 5H), 7.24-7.30 (m, 5H), 7.33-7.37 (m, 5H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 12.1, 35.2, 39.3, 84.9, 91.3, 103.0, 119.4, 124.4, 127.1, 127.5, 127.9, 128.2, 128.4, 128.6, 129.3, 129.7, 131.06, 131.13, 136.6, 138.2, 167.8$ ppm. HRMS (ESI$^+$): calcd for C$_{28}$H$_{24}$N$_2$NaO [M+Na]$^+$ 427.1786, found 427.1789.

**Ethyl 2-isopropyl-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3g)**
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded \(3g\) as a pale yellow solid (50.7 mg, 39% yield). M.p.: 202-204 °C. 
\[ ^1H \text{ NMR (CDCl}_3\text{, 400 MHz): } \delta = 1.32 \text{ (d, } J = 7.2 \text{ Hz, 6H), 1.45 \text{ (t, } J = 7.2 \text{ Hz, 3H), 3.05-3.16 \text{ (m, 1H), 4.42 \text{ (q, } J = 7.2 \text{ Hz, 2H), 7.12-7.18 \text{ (m, 5H), 7.23-7.28 \text{ (m, 5H), 7.35-7.36 \text{ (m, 5H) ppm.} } ^{13}\text{C NMR (CDCl}_3\text{, 100 MHz): } \delta = 14.7, 20.8, 27.0, 60.3, 85.1, 91.4, 105.0, 113.2, 124.7, 127.41, 127.43, 127.7, 128.3, 128.8, 129.15, 129.19, 130.4, 131.0, 131.2, 138.0, 138.1, 146.0, 165.1 \text{ ppm. HRMS (ESI\textsuperscript+): calcd for C}_{30}\text{H}_{27}\text{NNaO}_2\text{ [M+Na}^+]\text{ 456.1939, found 456.1945.} \]

**Ethyl 1,2,5-triphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3h)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded \(3h\) as a pale yellow solid (66.3 mg, 47% yield). M.p.: 187-189 °C. 
\[ ^1H \text{ NMR (CDCl}_3\text{, 400 MHz): } \delta = 1.20 \text{ (t, } J = 7.2 \text{ Hz, 3H), 4.23 \text{ (q, } J = 7.2 \text{ Hz, 2H), 6.88-6.90 \text{ (m, 2H), 7.09-7.15 \text{ (m, 3H), 7.19-7.31 \text{ (m, 11H), 7.32-7.34 \text{ (m, 2H), 7.42 \text{ (dd, } J = 7.2 \text{ Hz, 1.2 Hz, 2H) ppm.} } ^{13}\text{C NMR (CDCl}_3\text{, 100 MHz): } \delta = 14.3, 60.1, 84.6, 92.0, 105.2, 115.3, 124.6, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.3, 128.7, 129.0, 130.4, 130.7, 131.4, 131.5, 137.6, 138.7, 139.6, 164.3 \text{ ppm. HRMS (ESI\textsuperscript+): calcd for C}_{33}\text{H}_{26}\text{NO}_2\text{ [M+H}^+]\text{ 468.1964, found 468.1960.} \]

**Ethyl 1,5-diphenyl-4-(phenylethynyl)-2-(o-tolyl)-1H-pyrrole-3-carboxylate (3i)**

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded \(3i\) as a pale yellow solid (80.3 mg, 56% yield). M.p.: 162-164 °C. 
\[ ^1H \text{ NMR (CDCl}_3\text{, 400 MHz): } \delta = 1.12 \text{ (t, } J = 7.2 \text{ Hz, 3H), 2.11 \text{ (s, 3H), 4.14-4.22 \text{ (m,} \text{ ppm. HRMS (ESI\textsuperscript+): calcd for C}_{33}\text{H}_{26}\text{NO}_2\text{ [M+H}^+]\text{ 468.1964, found 468.1960.} \]
2H), 6.88 (d, J = 6.0 Hz, 2H), 7.03-7.10 (m, 6H), 7.16 (td, J = 7.2 Hz, 1.6 Hz, 1H),
7.21-7.32 (m, 6H), 7.35-7.37 (m, 2H), 7.44 (dd, J = 8.0 Hz, 1.6 Hz, 2H) ppm. 13C NMR (CDCl3, 100 MHz): δ = 14.2, 20.3, 59.9, 84.7, 92.1, 105.0, 115.3, 124.5, 125.0,
127.6, 127.8, 127.9, 128.3, 128.4, 128.6, 128.7, 129.4, 130.2, 130.7, 131.4, 131.5,
131.7, 137.6, 138.4, 138.5, 139.6, 164.0 ppm. HRMS (ESI+): calcd for C34H27NNaO2 [M+Na]+ 504.1939, found 504.1945.

Ethyl 2-(naphthalen-1-yl)-1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-
carboxylate (3j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =
20/1, v/v) afforded 3j as a pale yellow solid (103.0 mg, 66% yield). M.p.: 192-194 ºC.
1H NMR (CDCl3, 400 MHz): δ = 0.74 (t, J = 6.8 Hz, 3H), 3.97 (q, J = 6.8 Hz, 2H),
6.85-7.03 (m, 5H), 7.21-7.33 (m, 8H), 7.40-7.49 (m, 6H), 7.75-7.80 (m, 3H) ppm. 13C NMR (CDCl3, 100 MHz): δ = 13.7, 59.7, 84.5, 92.3, 105.2, 116.7, 124.5, 124.7, 125.8,
126.0, 126.4, 127.6, 127.7, 127.86, 127.89, 128.2, 128.3, 128.5, 128.9, 129.5, 129.9,
130.3, 130.6, 131.4, 133.1, 133.8, 137.6, 137.8, 138.9, 163.8 ppm. HRMS (ESI+):

Ethyl 1,5-diphenyl-4-(phenylethynyl)-2-(thiophen-2-yl)-1H-pyrrole-3-
carboxylate (3k)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =
20/1, v/v) afforded 3k as a pale yellow solid (72.7 mg, 51% yield). M.p.: 166-168 ºC.
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 1.27$ (t, $J = 7.2$ Hz, 3H), 4.29 (q, $J = 7.2$ Hz, 2H), 6.88-6.90 (m, 1H), 6.92 (dd, $J = 3.6$ Hz, 1.2 Hz, 1H), 6.98-7.00 (m, 2H), 7.16-7.306 (m, 10H), 7.314-7.35 (m, 2H), 7.41 (dd, $J = 7.6$ Hz, 1.6 Hz, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 14.4$, 60.3, 84.2, 92.1, 105.4, 117.3, 124.4, 126.3, 127.7, 127.9, 128.3, 128.8, 128.9, 130.36, 130.40, 131.0, 131.2, 131.4, 131.5, 137.5, 139.5, 164.0 ppm. HRMS (ESI$^+$): calcd for C$_{31}$H$_{23}$NNaO$_2$S [M+Na]$^+$ 496.1347, found 496.1342.

Methyl 2-(4-bromophenyl)-1,5-diphenyl-4-(phenylethynyl)-1$^H$-pyrrole-3-carboxylate (3l)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3l as a pale yellow solid (69.0 mg, 43% yield). M.p.: 189-191 ºC. $^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 3.80$ (s, 3H), 6.88 (d, $J = 7.2$ Hz, 2H), 7.06 (d, $J = 8.0$ Hz, 2H), 7.13-7.20 (m, 3H), 7.23-7.25 (m, 3H), 7.28-7.32 (m, 5H), 7.35 (d, $J = 8.4$ Hz, 2H), 7.41-7.43 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 51.4$, 84.3, 92.3, 105.3, 115.2, 122.7, 124.3, 127.7, 127.9, 128.2, 128.3, 128.8, 129.0, 130.2, 130.4, 130.8, 131.4, 133.0, 137.2, 138.2, 138.9, 164.6 ppm. HRMS (ESI$^-$): calcd for C$_{32}$H$_{23}$BrNO$_2$ [M+H]$^-$ 532.0912, found 532.0917.

Benzyl 2-methyl-5-phenyl-4-(phenylethynyl)-1-(o-tolyl)-1$^H$-pyrrole-3-carboxylate (3m)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate =
20/1, v/v) afforded 3m as pale yellow oil (98.2 mg, 68% yield). M.p.: 153-155 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 1.88\) (s, 3H), 2.32 (s, 3H), 5.39-5.46 (m, 2H), 7.11-7.14 (m, 2H), 7.18-7.23 (m, 8H), 7.25-7.27 (m, 1H), 7.28-7.34 (m, 6H), 7.54-7.56 (m, 2H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 12.6, 17.5, 66.0, 85.3, 91.6, 104.1, 112.9, 124.4, 126.9, 127.4, 127.6, 127.8, 127.9, 128.1, 128.4, 128.6, 129.3, 129.4, 129.8, 130.7, 131.2, 131.3, 136.4, 136.6, 136.8, 138.2, 138.3, 165.1 \) ppm. HRMS (ESI\(^+\)): calcd for C\(_{34}\)H\(_{28}\)NO\(_2\) [M+H\(^+\)] \(\text{calcd for C}_{34}\text{H}_{28}\text{NO}_{2}\) \([\text{M+H}^+]^+ 482.2120, \text{found 482.2114.}

Benzyl 2-methyl-5-phenyl-4-(phenylethynyl)-1-(m-tolyl)-1H-pyrrole-3-carboxylate (3n)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3n as a pale yellow solid (107.6 mg, 74% yield). M.p.: 131-133 °C. \(^1\)H NMR (CDCl\(_3\), 400 MHz): \(\delta = 2.32\) (s, 3H), 2.42 (s, 3H), 5.41 (s, 2H), 6.89 (d, \(J = 8.0\) Hz, 1H), 6.93 (s, 1H), 7.10-7.12 (m, 2H), 7.15-7.24 (m, 8H), 7.29-7.31 (m, 5H), 7.53-7.55 (m, 2H) ppm. \(^{13}\)C NMR (CDCl\(_3\), 100 MHz): \(\delta = 13.1, 21.4, 65.9, 85.3, 91.6, 104.3, 112.9, 124.5, 125.7, 127.37, 127.44, 127.8, 127.9, 128.1, 128.3, 128.6, 129.1, 129.4, 130.1, 130.8, 131.3, 136.8, 137.5, 138.2, 138.3, 138.6, 139.4, 165.1 \) ppm. HRMS (ESI\(^+\)): calcd for C\(_{34}\)H\(_{28}\)NO\(_2\) [M+H\(^+\)] \(\text{calcd for C}_{34}\text{H}_{28}\text{NO}_{2}\) \([\text{M+H}^+]^+ 482.2120, \text{found 482.2120.}

Benzyl 1-(4-bromophenyl)-2-methyl-5-phenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3o)
Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3o as a pale yellow solid (117.1 mg, 71% yield). M.p.: 159-161 °C. 

$^1$H NMR (CDCl₃, 400 MHz): $\delta = 2.43$ (s, 3H), 5.42 (s, 2H), 6.97-7.01 (m, 2H), 7.10-7.12 (m, 2H), 7.17-7.31 (m, 11H), 7.50 (d, $J = 8.8$ Hz, 2H), 7.53-7.54 (m, 2H) ppm. 

$^{13}$C NMR (CDCl₃, 100 MHz): $\delta = 13.0$, 66.0, 84.9, 91.8, 104.8, 113.4, 122.6, 124.3, 127.5, 127.7, 127.96, 128.01, 128.1, 128.3, 128.6, 130.1, 130.2, 130.4, 131.3, 132.6, 136.6, 136.7, 138.1, 138.3, 164.9 ppm. HRMS (ESI⁺): calcd for C₃₃H₂₄BrNaO₂ [M+Na]⁺ 568.0888, found 568.0890.

Benzyl 1-benzyl-2-methyl-5-phenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (3p)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 3p as a pale yellow solid (72.1 mg, 50% yield). M.p.: 128-130 °C. 

$^1$H NMR (CDCl₃, 400 MHz): $\delta = 2.49$ (s, 3H), 5.14 (s, 2H), 5.40 (s, 2H), 6.92 (d, $J = 6.8$ Hz, 2H), 7.05-7.06 (m, 2H), 7.15-7.19 (m, 3H), 7.24-7.33 (m, 6H), 7.35-7.39 (m, 3H), 7.43-7.45 (m, 2H), 7.52-7.55 (m, 2H) ppm. $^{13}$C NMR (CDCl₃, 100 MHz): $\delta = 12.0$, 48.4, 65.9, 85.2, 91.2, 104.3, 112.8, 124.4, 125.7, 127.3, 127.6, 127.9, 128.1, 128.36, 128.39, 128.44, 128.6, 129.1, 130.4, 130.8, 131.3, 136.8, 137.1, 137.7, 139.0, 165.0 ppm. HRMS (ESI⁺): calcd for C₃₄H₂₇NaO₂ [M+Na]⁺ 504.1939, found 504.1935.

Benzyl 5-(2-(methoxymethoxy)phenyl)-4-((2-(methoxymethoxy)phenyl)ethynyl)-
2-methyl-1-phenyl-1H-pyrrole-3-carboxylate (4a)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1, v/v) afforded 4a as a pale yellow solid (86.3 mg, 49% yield). M.p.: 119-121 °C. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 2.45 (s, 3H), 3.26 (s, 3H), 3.28 (s, 3H), 4.77 (d, $J$ = 6.8 Hz, 1H), 4.86 (d, $J$ = 1.6 Hz, 2H), 4.89 (d, $J$ = 6.8 Hz, 1H), 5.41 (s, 2H), 6.80 (td, $J$ = 7.6 Hz, 1.2 Hz, 1H), 6.92-6.97 (m, 3H), 6.99-7.04 (m, 2H), 7.10-7.15 (m, 1H), 7.18-7.22 (m, 2H), 7.35 (dd, $J$ = 7.6 Hz, 2.0 Hz, 1H), 7.52-7.54 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta$ = 13.2, 56.0, 56.1, 65.8, 87.8, 88.7, 95.1, 95.4, 105.5, 112.7, 115.1, 115.5, 116.0, 121.4, 121.5, 122.0, 127.8, 128.16, 128.19, 128.5, 128.7, 130.0, 133.3, 133.4, 135.5, 137.0, 137.6, 137.7, 156.0, 157.4, 165.1 ppm. HRMS (ESI$^+$): calcd for C$_{37}$H$_{33}$NNaO$_6$ [M+Na]$^+$ 610.2206, found 610.2207.

Benzyl 5-(2-fluorophenyl)-4-((2-fluorophenyl)ethynyl)-2-methyl-1-phenyl-1H-pyrrole-3-carboxylate (4b)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4b as a pale yellow solid (110.1 mg, 73% yield). M.p.: 128-130 °C. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta$ = 2.44 (s, 3H), 5.42 (s, 2H), 6.89 (t, $J$ = 9.2 Hz, 1H), 6.92-7.01 (m, 3H), 7.08 (t, $J$ = 7.6 Hz, 2H), 7.15-7.24 (m, 3H), 7.27-7.32 (m, 6H), 7.44 (t, $J$ = 7.6 Hz, 1H), 7.52-7.54 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): 13.0, 65.9, 85.4, 89.3 (d, $J$ = 3.0 Hz), 105.8, 112.9 (d, $J$ = 16.0 Hz), 113.0, 115.3 (d, $J$ = 20.0 Hz), 115.5 (d, $J$ = 22.0 Hz), 118.9 (d, $J$ = 15.0 Hz), 123.7 (d, $J$ = 4.0 Hz), 123.8 (d, $J$ = 4.0 Hz), 127.8, 128.2, 128.3, 128.5, 128.6, 129.0, 129.1, 130.4, 130.5, 133.12 (d, $J$ = 3.0 Hz), 133.3 (d, $J$ = 1.0 Hz), 136.8, 137.1, 138.8, 160.0 (d, $J$ = 247.0 Hz), 162.5 (d, $J$ = 250.0 Hz), 164.8 ppm. $^{19}$F NMR (CDCl$_3$, 376 MHz): $\delta$ = -110.6, -109.9 ppm. HRMS (ESI$^+$): calcd for C$_{33}$H$_{23}$F$_2$NNaO$_2$ [M+Na]$^+$ 526.1595, found 526.1594.
Benzyl 2-methyl-1-phenyl-5-(4-propylphenyl)-4-((4-propylphenyl)ethynyl)-1H-pyrrole-3-carboxylate (4c)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4c as a pale yellow solid (102.1 mg, 62% yield). M.p.: 121-123 °C. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 0.90$ (t, $J = 7.6$ Hz, 3H), 0.93 (t, $J = 7.6$ Hz, 3H), 1.57-1.65 (m, 4H), 2.42 (s, 3H), 2.51 (t, $J = 8.0$ Hz, 2H), 2.55 (t, $J = 8.0$ Hz, 2H), 5.42 (s, 2H), 6.99-7.02 (m, 4H), 7.06 (d, $J = 8.4$ Hz, 2H), 7.10-7.12 (m, 2H), 7.20 (d, $J = 8.0$ Hz, 2H), 7.29-7.32 (m, 3H), 7.34-7.38 (m, 3H), 7.54-7.56 (m, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 13.1, 13.91, 13.93, 24.4, 24.6, 37.9, 38.1, 65.9, 84.7, 91.8, 104.3, 112.9, 121.8, 127.8, 128.1, 128.27, 128.29, 128.5, 128.6, 128.7, 129.3, 129.9, 131.2, 136.9, 137.8, 138.2, 141.9, 142.1, 165.1 ppm. HRMS (ESI$^+$): calcd for C$_{39}$H$_{37}$NNaO$_2$ [M+Na]$^+$ 574.2722, found 574.2725.

Benzyl 5-(4-methoxyphenyl)-4-((4-methoxyphenyl)ethynyl)-2-methyl-1-phenyl-1H-pyrrole-3-carboxylate (4d)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 10/1, v/v) afforded 4d as a pale yellow solid (84.0 mg, 53% yield). M.p.: 141-143 °C. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.40$ (s, 3H), 3.75 (s, 3H), 3.79 (s, 3H), 5.40 (s, 2H), 6.73 (dd, $J = 8.8$ Hz, 2.0 Hz, 4H), 7.06 (d, $J = 8.8$ Hz, 2H), 7.09-7.11 (m, 2H), 7.20 (d, $J = 8.8$ Hz, 2H), 7.28-7.31 (m, 3H), 7.36-7.38 (m, 3H), 7.53-7.54 (m, 2H) ppm. $^{13}$C
NMR (CDCl₃, 100 MHz): δ = 13.1, 55.3, 55.4, 65.9, 83.8, 91.4, 104.1, 112.8, 113.3, 113.8, 116.8, 123.3, 127.9, 128.3, 128.55, 128.63, 128.7, 129.4, 131.4, 132.7, 136.9, 137.75, 137.82, 138.1, 158.8, 159.0, 165.2 ppm. HRMS (ESI⁺): calcd for C₃₅H₂₉NNaO₄ [M+Na]+ 550.1994, found 550.1994.

Benzyl 5-(4-chlorophenyl)-4-((4-chlorophenyl)ethynyl)-2-methyl-1-phenyl-1H-pyrrole-3-carboxylate (4e)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4e as a pale yellow solid (91.4 mg, 57% yield). M.p.: 190-192 °C. 

¹H NMR (CDCl₃, 400 MHz): δ = 2.42 (s, 3H), 5.40 (s, 2H), 6.96 (dt, J = 8.8 Hz, 2.0 Hz, 2H), 7.08-7.11 (m, 2H), 7.14-7.21 (m, 6H), 7.31-7.32 (m, 3H), 7.38-7.40 (m, 3H), 7.50-7.52 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100 MHz): δ = 13.0, 66.1, 85.8, 90.9, 104.5, 113.2, 122.7, 128.1, 128.2, 128.4, 128.5, 128.6, 128.7, 128.9, 129.2, 129.6, 131.3, 132.5, 133.4, 133.5, 136.6, 137.0, 137.3, 138.9, 164.8 ppm. HRMS (ESI⁺): calcd for C₃₃H₂₃Cl₂NNaO₂ [M+Na]+ 558.1004, found 558.1001.

Benzyl 5-(4-cyanophenyl)-4-((4-cyanophenyl)ethynyl)-2-methyl-1-phenyl-1H-pyrrole-3-carboxylate (4f)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4f as a pale yellow solid (63.1 mg, 41% yield). M.p.: 204-206 °C.
1H NMR (CDCl₃, 400 MHz): δ = 2.44 (s, 3H), 5.39 (s, 2H), 7.01 (d, J = 8.4 Hz, 2H), 7.10-7.12 (m, 2H), 7.32-7.37 (m, 5H), 7.42-7.44 (m, 9H) ppm. 13C NMR (CDCl₃, 100 MHz): δ = 13.0, 66.3, 89.1, 91.1, 105.3, 110.8, 111.1, 113.9, 118.7, 118.8, 128.2, 128.4, 128.6, 128.7, 128.8, 129.4, 129.8, 130.3, 131.6, 131.7, 131.9, 135.0, 136.4, 136.5, 136.8, 140.2, 164.4 ppm. HRMS (ESI⁺): calcd for C₃₅H₂₃N₃NaO₂ [M+Na]⁺ 540.1688, found 540.1690.

Benzy1 2-methyl-1-phenyl-5-(m-tolyl)-4-(m-tolylethynyl)-1H-pyrrole-3-carboxylate (4g)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4g as a pale yellow solid (108.8 mg, 73% yield). M.p.: 117-119 ℃. 1H NMR (CDCl₃, 400 MHz): δ = 2.23 (s, 3H), 2.25 (s, 3H), 2.42 (s, 3H), 5.42 (s, 2H), 6.93-7.13 (m, 9H), 7.21 (s, 1H), 7.29-7.31 (m, 3H), 7.36-7.39 (m, 3H), 7.54 (dd, J = 7.2 Hz, 1.6 Hz, 2H) ppm. 13C NMR (CDCl₃, 100 MHz): δ = 13.1, 21.4, 21.5, 65.9, 85.0, 92.0, 104.4, 113.0, 124.4, 127.1, 127.6, 127.9, 128.0, 128.2, 128.3, 128.5, 128.57, 128.60, 128.7, 129.3, 130.6, 131.0, 131.9, 136.9, 137.2, 137.67, 137.73, 138.4, 165.1 ppm. HRMS (ESI⁺): calcd for C₃₅H₂₉NNaO₂ [M+Na]⁺ 518.2096, found 518.2098.

Benzy1 5-(3-bromophenyl)-4-((3-bromophenyl)ethynyl)-2-methyl-1-phenyl-1H-
pyrrole-3-carboxylate (4h)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4h as a pale yellow solid (104.0 mg, 55% yield). M.p.: 122-124 °C. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.43$ (s, 3H), 5.41 (s, 2H), 6.99-7.08 (m, 4H), 7.11-7.13 (m, 2H), 7.31-7.36 (m, 6H), 7.39-7.43 (m, 3H), 7.51-7.54 (m, 2H), 7.64-7.65 (m, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 13.0$, 66.1, 86.2, 90.9, 104.8, 113.3, 121.9, 122.0, 126.1, 128.19, 128.24, 128.3, 128.5, 128.7, 129.0, 129.3, 129.6, 130.0, 130.6, 130.7, 132.5, 133.0, 133.9, 136.5, 136.7, 137.2, 139.1, 164.7 ppm. HRMS (ESI$^+$): calcd for C$_{33}$H$_{23}$Br$_2$NaN$_2$O$_2$ [M+Na]$^+$ 647.9973, found 647.9980.

Benzyl 2-methyl-5-(naphthalen-1-yl)-4-(naphthalen-1-ylethynyl)-1-phenyl-1H-pyrrole-3-carboxylate (4i)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4i as a pale yellow solid (89.3 mg, 52% yield). M.p.: 137-139 °C. 

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.54$ (s, 3H), 5.46 (d, $J = 12.4$ Hz, 1H), 5.56 (d, $J = 12.4$ Hz, 1H), 6.87-6.98 (m, 4H), 7.14 (t, $J = 8.0$ Hz, 2H), 7.19 (t, $J = 6.8$ Hz, 2H), 7.28-7.37 (m, 7H), 7.45-7.48 (m, 2H), 7.57-7.60 (m, 3H), 7.64 (d, $J = 8.4$ Hz, 1H), 7.83 (d, $J = 7.6$ Hz, 1H), 7.86-7.89 (m, 1H), 8.00-8.02 (m, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 13.2$, 66.0, 89.4, 90.7, 106.8, 112.6, 121.8, 125.1, 125.9, 126.06, 126.13, 126.3, 126.5, 126.7, 127.5, 127.9, 128.2, 128.4, 128.5, 128.7, 128.98, 129.01, 129.1, 129.5, 130.1, 132.9, 133.0, 133.1, 133.6, 136.87, 136.93, 137.2, 138.3, 165.1 ppm. HRMS (ESI$^+$): calcd for C$_{41}$H$_{29}$NN$_2$O$_2$ [M+Na]$^+$ 590.2096, found 590.2095.
Benzyl 2-methyl-1-phenyl-5-(thiophen-2-yl)-4-(thiophen-2-ylethynyl)-1H-pyrrole-3-carboxylate (4j)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 4j as a pale yellow solid (55.7 mg, 39% yield). M.p.: 148-149 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.36$ (s, 3H), 5.41 (s, 2H), 6.86 (t, $J = 4.4$ Hz, 1H), 6.94-6.97 (m, 2H), 7.00-7.01 (m, 1H), 7.15 (d, $J = 5.2$ Hz, 1H), 7.20-7.23 (m, 3H), 7.27-7.32 (m, 3H), 7.44-7.48 (m, 3H), 7.53 (d, $J = 7.2$ Hz, 2H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 12.9$, 65.9, 87.1, 89.1, 104.2, 113.1, 124.6, 125.9, 126.5, 126.7, 127.0, 127.6, 127.9, 128.2, 128.6, 129.1, 129.5, 129.7, 131.1, 132.0, 132.1, 136.7, 137.3, 139.0, 164.6 ppm. HRMS (ESI$^+$): calcd for C$_{29}$H$_{22}$NO$_2$S$_2$ [M+H]$^+$ 480.1092, found 480.1095.

Methyl 1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (5a)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 5a as a pale yellow solid (42.8 mg, 57% yield). M.p.: 184-186 °C.

$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 3.92$ (s, 3H), 7.13-7.16 (m, 2H), 7.26-7.31 (m, 6H), 7.32-7.36 (m, 5H), 7.45 (dd, $J = 7.2$ Hz, 1.2 Hz, 2H), 7.55 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 51.5$, 84.0, 92.4, 105.8, 117.3, 124.3, 125.8, 127.7, 127.9, 128.0, 128.1, 128.3, 128.8, 129.4, 130.1, 130.3, 131.5, 138.2, 139.2, 164.4 ppm. HRMS (ESI$^+$): calcd for C$_{26}$H$_{19}$NNaO$_2$ [M+Na]$^+$ 400.1313, found 400.1317.
Benzyl 1,5-diphenyl-4-(phenylethynyl)-1H-pyrrole-3-carboxylate (5b)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 5b as a pale yellow solid (41.2 mg, 45% yield). M.p.: 136-138 °C.  
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 5.40$ (s, 2H), 7.13-7.15 (m, 2H), 7.24-7.30 (m, 8H), 7.32-7.35 (m, 8H), 7.49-7.51 (m, 2H), 7.60 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 66.1, 84.1, 92.4, 105.8, 117.2, 124.2, 125.8, 127.7, 127.9, 127.98, 128.05, 128.1, 128.2, 128.3, 128.7, 129.1, 129.4, 130.1, 130.3, 131.5, 136.6, 138.4, 139.2, 163.9 ppm. HRMS (ESI$^+$): calcd for C$_{32}$H$_{23}$NNaO$_2$ [M+Na]$^+$ 476.1626, found 476.1632.

Methyl 1-phenyl-5-((m-tolyl)-4-((m-tolylethynyl)-1H-pyrrole-3-carboxylate (5c)

Purification by column chromatography on silica gel (petroleum ether/ethyl acetate = 20/1, v/v) afforded 5c as a pale yellow solid (37.8 mg, 47% yield). M.p.: 116-118 °C.  
$^1$H NMR (CDCl$_3$, 400 MHz): $\delta = 2.29$ (s, 3H), 2.32 (s, 3H), 3.92 (s, 3H), 7.03 (d, $J = 7.6$ Hz, 1H), 7.08 (d, $J = 7.6$ Hz, 2H), 7.12-7.16 (m, 3H), 7.19 (d, $J = 7.2$ Hz, 1H), 7.24 (s, 1H), 7.28 (s, 2H), 7.31-7.37 (m, 3H), 7.54 (s, 1H) ppm. $^{13}$C NMR (CDCl$_3$, 100 MHz): $\delta = 21.4, 21.6, 51.5, 83.8, 92.7, 105.7, 117.2, 124.1, 125.7, 127.1, 127.86, 127.90, 128.2, 128.5, 128.6, 128.7, 129.4, 130.1, 130.8, 132.0, 137.6, 137.9, 138.3, 139.3, 164.4 ppm. HRMS (ESI$^+$): calcd for C$_{28}$H$_{24}$NO$_2$ [M+H]$^+$ 406.1807, found 406.1807.

VIII. Mechanism study

1. The reaction of enamino ester 1a with gold(I)-acetylide 6
A flame-dried sealable tube with a magnetic stir bar was charged with (Z)-ethyl 3-(phenylamino)but-2-enoate 1a (97.7 μL, 0.5 mmol), gold(I)-acetylide 6\(^7\) (59.6 mg, 0.2 mmol), bpy (156.2 mg, 1.0 mmol), PhI(OAc)\(_2\) (128.8 mg, 0.4 mmol), KOAc (58.9 mg, 0.6 mmol), and toluene (1.0 mL) under an N\(_2\) atmosphere. The tube was sealed and the resulting mixture was stirred at 50 °C for 4 h. After being cooled to ambient temperature, the reaction solution was diluted with 20 mL of CH\(_2\)Cl\(_2\), filtered through a celite pad and washed with 10 mL of CH\(_2\)Cl\(_2\). The filtrate was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/ether = 20/1, v/v) to afford 12.1 mg of 3a (30% yield).

When the reaction was carried out in the absence of PhI(OAc)\(_2\), no desired 3a was observed.

2. The reaction of enamino ester 1a with internal alkynes

A flame-dried sealable tube with a magnetic stir bar was charged with (Z)-ethyl 3-(phenylamino)but-2-enoate 1a (1.5 mmol), 1,4-diphenylbuta-1,3-diyne 7 (121.4 mg, 0.6 mmol) or 1,2-diphenylacetylene 8 (121.4 mg, 0.6 mmol), [(bpy)AuCl\(_2\)]Cl (11.1 mg, 0.024 mmol), KOAc (176.7 mg, 1.8 mmol), PhI(OAc)\(_2\) (386.5 mg, 1.2 mmol), and toluene (3.0 mL) under an N\(_2\) atmosphere. The tube was sealed and the reaction mixture was stirred at 50 °C for 4 h. No 3a or 9 was formed.
3. The reaction of C3-unsubstituted pyrrole 10 with phenylacetylene 2a

A flame-dried sealable tube with a magnetic stir bar was charged with pyrrole 10 (182.3 mg, 0.6 mmol), phenylacetylene 2a (65.9 μL, 0.6 mmol), [(bpy)AuCl2]Cl (11.1 mg, 0.024 mmol), KOAc (176.7 mg, 1.8 mmol), PhI(OAc) 2 (386.5 mg, 1.2 mmol), and toluene (3.0 mL) under an N 2 atmosphere. The tube was sealed and the reaction mixture was stirred at 50 °C for 4 h. No desired 3a was formed.

IX. The derivation of 3-alkynylypyrroles

7-Iodo-3-methyl-1,2,6-triphenylpyrano[3,4-c]pyrrol-4(2H)-one (11a)

A solution of I2 (76.2 mg, 0.3 mmol) in DCM (1.5 mL) was added to a solution of 3b (39.1 mg, 0.1 mmol) in DCM (1.5 mL) and the resulting mixture was stirred at room temperature for 12 h. The reaction mixture was diluted with DCM (10 mL), washed with NaHSO3, and dried over anhydrous Na2SO4. The solvent was evaporated and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1, v/v) to afford 11a as a pale yellow solid (36.3 mg, 72% yield). M.p.: >250 ºC. 1H NMR (CDCl3, 400 MHz): δ = 2.54 (s, 3H), 7.06-7.07 (m, 2H), 7.17-7.25 (m, 5H), 7.31-7.32 (m, 3H), 7.39-7.42 (m, 3H), 7.61 (d, J = 7.2 Hz, 2H) ppm. 13C NMR (CDCl3, 100 MHz): δ = 12.2, 64.9, 105.6, 120.7, 127.3, 128.0, 128.5, 128.6, 129.0, 129.2, 129.4, 129.9, 130.3, 133.8, 135.4, 136.1, 136.7, 151.7, 160.6 ppm. HRMS (ESI+): calcd for C26H18INaO2 [M+Na]+ 526.0280, found 526.0277.
3-Methyl-1,2,6-triphenylpyrano[3,4-c]pyrrol-4(2H)-one (11b)

A flame-dried sealable tube with a magnetic stir bar was charged with 11a (50.3 mg, 0.1 mmol), Pd(OAc)_2 (0.5 mg, 0.002 mmol), PPh_3 (1.1 mg, 0.004 mmol), formic acid (7.5 μL, 0.2 mmol), Et_3N (41.7 μL, 0.3 mmol), and DMF (1.5 mL) under an N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 60 °C for 4 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH_2Cl_2, filtered through a celite pad, and washed with 30 mL of CH_2Cl_2. The filtrate was evaporated, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1, v/v) to afford 11b as a pale yellow solid (36.0 mg, 95% yield). M.p.: 227-229 ºC. ^1H NMR (CDCl_3, 400 MHz): δ = 2.59 (s, 3H), 6.89 (s, 1H), 7.10-7.12 (m, 2H), 7.16-7.18 (m, 2H), 7.21-7.28 (m, 3H), 7.31-7.35 (m, 1H), 7.38-7.42 (m, 5H), 7.81-7.83 (m, 2H) ppm. ^13C NMR (CDCl_3, 100 MHz): δ = 12.4, 96.5, 106.4, 120.6, 124.9, 126.9, 127.2, 128.3, 128.5, 128.6, 128.7, 128.8, 129.5, 129.6, 130.8, 133.5, 136.3, 137.3, 151.4, 160.9 ppm. HRMS (ESI^+): calcd for C_{26}H_{19}NNaO_2 [M+Na]^+ 400.1313, found 400.1315.

7-((4-Methoxyphenyl)ethynyl)-3-methyl-1,2,6-triphenylpyrano[3,4-c]pyrrol-4(2H)-one (11c)

A flame-dried sealable tube with a magnetic stir bar was charged with 11a (25.2 mg, 0.05 mmol), (PPh_3)_2PdCl_2 (2.0 mg, 5 mol%), CuI (0.5 mg, 5 mol%), 1-ethynyl-4-methoxybenzene (25.9 μL, 0.2 mmol), Pr_2NH (0.5 mL), and DMF (1.0 mL) under an N_2 atmosphere. The tube was sealed and the reaction mixture was stirred at 85 °C for
2 h. After being cooled to ambient temperature, the reaction solution was diluted with 10 mL of CH₂Cl₂, filtered through a celite pad, and washed with 30 mL of CH₂Cl₂. The filtrate was collected and evaporated, and the residue was purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 8/1, v/v) to provide 11c as a pale yellow solid (19.2 mg, 76% yield). M.p.: 223-225 °C. ¹H NMR (CDCl₃, 400 MHz): \( \delta = 2.56 \) (s, 3H), 3.75 (s, 3H), 6.61-6.67 (m, 4H), 7.06-7.09 (m, 2H), 7.13-7.20 (m, 3H), 7.22-7.24 (m, 2H), 7.32-7.34 (m, 3H), 7.38-7.45 (m, 3H), 8.12-8.14 (m, 2H) ppm. ¹³C NMR (CDCl₃, 100 MHz): \( \delta = 12.4, 55.3, 83.3, 96.2, 96.4, 105.2, 113.6, 115.4, 118.5, 127.4, 127.75, 127.85, 128.5, 128.6, 128.8, 128.9, 129.2, 130.7, 132.4, 132.6, 133.6, 135.8, 137.0, 154.5, 159.4, 160.0 \) ppm. HRMS (ESI⁺): calcd for C₃₅H₂₆NO₃ [M+H]+ 508.1913, found 508.1909.
X. References

XI. Copies of $^1$H, $^{13}$C and $^{19}$F NMR spectra