Supporting Information
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A Simple and Efficient Protocol to 1, 2, 4-Substituted Pyrroles via Sonogashira Coupling or Lewis Acid Promotion.

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**General procedure for the synthesis of 3a:**

To a solution of 1a (0.5 mmol) and 2a (0.6 mmol) in 5 mL of THF was charged CuI (2 mg. 0.01 mmol) and PdCl$_2$(PPh$_3$)$_2$ (7 mg, 0.01 mmol), then charged 1 mL of Et$_3$N under a N$_2$ atmosphere at room temperature. The reaction was monitored by TLC until going to completion (4h). The reaction mixture was quenched with water, extracted with Et$_2$O (30 mL), and dried over anhydrous Na$_2$SO$_4$. After evaporation of the Et$_2$O, chromatography on silica gel (petrol ether) of the crude product afforded 3a.

**General procedure for the synthesis of 4a:**

To a solution of N-(2-bromoallyl)acetamide (0.5 mmol) and oct-1-yn (0.6 mmol) in 5 mL of THF was charged CuI (2 mg. 0.01 mmol) and PdCl$_2$(PPh$_3$)$_2$ (7 mg, 0.01 mmol), then charged 1 mL of Et$_3$N under a N$_2$ atmosphere at 30 °C. The reaction was monitored by TLC until going to completion. The reaction mixture was quenched with water, extracted with Et$_2$O (30 mL), and dried over anhydrous Na$_2$SO$_4$. After evaporation of the Et$_2$O, chromatography on silica gel (petrol ether/EtOAc = 5:1) of the crude product afforded 4a.

**General procedure for the synthesis of 5a:**

To a solution of 4a (0.5 mmol) in 3 mL of toluene was charged gallium (III) triflate (13 mg, 0.025 mmol) under a N$_2$ atmosphere at 90 °C. The reaction was monitored by TLC until going to completion (8h). After evaporation of the toluene, chromatography on silica gel (petrol ether/EtOAc = 15:1) of the crude product afforded 5a.
 Compound 3a

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.35–7.32$ (m, 4 H), 7.27–7.23 (m, 1 H), 6.52–6.52 (d, $J = 0.8$ Hz, 1 H), 6.01–6.00 (d, $J = 2.0$ Hz, 1 H), 3.84–3.81 (t, $J = 7.4$ Hz, 2 H), 2.12 (s, 3 H), 1.64–1.56 (m, 2 H), 1.23–1.17 (q, $J = 7.5$ Hz, 2 H), 0.83–0.79 (t, $J = 7.4$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 134.6$, 134.2, 129.1, 128.6, 126.9, 120.4, 118.7, 110.3, 47.0, 34.0, 20.2, 14.0, 12.2. IR (neat, cm$^{-1}$). 1491, 1342. HRMS calcd for C$_{15}$H$_{19}$N: 213.1517. Found: 213.1518.

 Compound 3b

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.69–7.67$ (d, $J = 6.8$ Hz, 1 H), 7.52–7.38 (m, 7 H), 7.20–7.18 (d, $J = 8.0$ Hz, 2 H), 6.67 (s, 1 H), 6.33 (s, 1 H), 5.21 (s, 2 H), 2.33 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 139.2$, 132.7, 128.8, 128.8, 128.6, 128.5, 127.4, 126.9, 126.6, 121.2, 119.2, 110.5, 50.6, 12.2. IR (neat, cm$^{-1}$) 1490, 1342. HRMS calcd for C$_{18}$H$_{17}$N: 247.1361. Found: 247.1366.

 Compound 3c

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.25–7.23$ (d, $J = 7.6$ Hz, 2 H), 6.90–6.88 (d, $J = 7.6$ Hz, 2 H), 6.32 (s, 1 H), 5.79 (s, 1 H), 4.88 (s, 2 H), 2.38–2.34 (t, $J = 7.8$ Hz, 2 H), 2.07 (s, 3 H), 1.54–1.48 (q, $J = 7.6$ Hz, 2 H), 1.33–1.21 (m, 6 H), 0.87–0.84 (t, $J = 6.8$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 137.4$, 133.6, 133.0, 128.8, 127.7, 118.4, 117.9, 107.6, 49.3, 31.6, 29.2, 28.9, 26.2, 22.6, 14.1, 11.9. IR (neat, cm$^{-1}$) 1492, 1343. HRMS calcd for C$_{18}$H$_{24}$ClN: 289.1597. Found: 289.1592.

 Compound 3d
\[ \text{Compound 3e} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.26–7.23 (m, 2 H), 6.91–6.89 (m, 2 H), 6.38 (s, 1 H), 5.85 (s, 1 H), 4.93 (s, 2 H), 5.69–3.65 (m, 2 H), 2.08–2.07 (d, J = 3.6 Hz, 3 H), 1.98 (br, 1 H). \]

\[ \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 137.1, 133.1, 129.1, 128.8, 127.6, 119.4, 118.2, 108.9, 61.6, 49.4, 29.5, 11.8. \]

\[ \text{IR (neat, cm}^{-1}\text{) 1491, 1344. HRMS calcd for C}_{14}\text{H}_{16}\text{ClNO: 249.0920. Found: 249.0925.} \]

\[ \text{Compound 3f}^2 \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 8.16 (br, 1 H), 7.45–7.43 (m, 2 H), 7.37–7.33 (m, 2 H), 7.21–7.17 (m, 1 H), 6.92 (s, 1 H), 6.38 (s, 1 H), 2.16 (s, 3 H). \]

\[ \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 132.8, 132.0, 128.8, 126.0, 123.6, 120.6, 116.7, 107.4, 11.9. \]

\[ \text{IR (neat, cm}^{-1}\text{) 1512, 1450. HRMS calcd for C}_{11}\text{H}_{11}\text{N: 157.0891. Found: 157.0896.} \]

\[ \text{Compound 3g} \]

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 7.17–7.08 (m, 5 H), 7.04–7.02 (d, J = 8.8 Hz, 2 H), 6.78–6.76 (d, J = 8.8 Hz, 2 H), 6.64 (s, 1 H), 6.27 (s, 1 H), 3.71 (s, 3 H), 2.17 (s, 3 H). \]

\[ \text{^13C NMR (100 MHz, CDCl}_3\text{): } \delta = 158.1, 134.0, 133.7, 133.3, 128.2, 128.1, 126.9, 126.1, 122.8, 119.5, 114.2, 111.9, 55.4, 11.9. \]

\[ \text{IR (neat, cm}^{-1}\text{) 1512, 1246. HRMS calcd for C}_{18}\text{H}_{17}\text{NO: 263.1310. Found: 263.1316.} \]
Compound 3h

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.32–7.28 (m, 2 H), 6.92–6.89 (m, 2 H), 6.48 (s, 1 H), 5.70–5.69 (d, $J$ = 1.6 Hz, 1 H), 3.79 (s, 3 H), 2.08 (s, 3 H), 1.59–1.55 (m, 1 H), 0.74–0.70 (m, 2 H), 0.62–0.58 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 158.1, 136.0, 133.8, 126.8, 119.5, 118.1, 114.0, 106.1, 55.4, 11.9, 8.1, 7.8. IR (neat, cm$^{-1}$) 1512, 1244. HRMS calcd for C$_{13}$H$_{15}$NO: 227.1310. Found: 227.1318.

Compound 3i

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.28–7.26 (d, $J$ = 8.4 Hz, 2 H), 7.01–6.99 (d, $J$ = 8.4 Hz, 2 H), 6.55 (s, 1 H), 5.98 (s, 1 H), 3.90 (s, 3 H), 2.55–2.52 (t, $J$ = 7.6 Hz, 2 H), 2.22 (s, 3 H), 1.60–1.57 (t, $J$ = 7.2 Hz, 2 H), 1.35–1.32 (d, $J$ = 12 Hz, 6 H), 0.96–0.92 (t, $J$ = 6.4 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 158.4, 134.4, 133.7, 127.3, 119.4, 118.1, 114.1, 108.0, 55.4, 31.6, 29.2, 29.1, 26.7, 22.6, 14.1, 11.8. IR (neat, cm$^{-1}$) 1512, 1245. HRMS calcd for C$_{18}$H$_{25}$NO: 271.1936. Found: 271.1933.

Compound 3j

$^1$H NMR (400 MHz, CDCl$_3$): δ = 7.39–7.37 (d, $J$ = 8.8 Hz, 2 H), 6.98–6.95 (m, 2 H), 6.62 (s, 1 H), 6.17–6.17 (d, $J$ = 1.6 Hz, 1 H), 4.45 (s, 2 H), 3.86 (s, 3 H), 2.16 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): δ = 158.4, 133.0, 132.6, 126.7, 121.4, 118.5, 114.2, 111.5, 56.2, 55.4, 11.6. IR (neat, cm$^{-1}$) 1511, 1243. HRMS calcd for C$_{13}$H$_{15}$NO$_2$: 217.1103. Found: 217.1110.
Compound 3k

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.94 (s, 1 H), 7.18–7.16 (d, $J$ = 8.0 Hz, 2 H), 6.95–6.93 (d, $J$ = 8.4 Hz, 2 H), 6.50 (s, 1 H), 5.72 (s, 1 H), 4.60 (s, 2 H), 2.37 (s, 3 H), 2.06 (s, 3 H), 1.84 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 171.6, 140.8, 137.8, 130.1, 128.7, 127.3, 117.6, 115.8, 109.1, 47.1, 22.5, 21.0, 11.7. HRMS calcd for C$_{15}$H$_{18}$N$_2$O: 242.1419. Found: 242.1418.

Compound 3l

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.14 (s, 1 H), 7.36–7.26 (m, 4 H), 6.62 (s, 1 H), 6.35 (s, 1 H), 2.15 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 131.4, 131.3, 128.9, 128.8, 124.7, 120.8, 117.1, 107.8, 11.8. HRMS calcd for C$_{11}$H$_{10}$NCl: 191.0502. Found: 191.0509.

Compound 3m

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 7.61 (s, 1 H), 6.38 (s, 1 H), 5.75 (s, 1 H), 2.54–2.50 (t, $J$ = 7.6 Hz, 2 H), 2.08 (s, 3 H), 1.61–1.53 (m, 2 H), 1.34–1.32 (m, 4 H), 0.93–0.88 (m, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 132.9, 118.7, 113.5, 106.5, 31.5, 29.3, 27.7, 22.4, 13.9, 11.8. HRMS calcd for C$_{10}$H$_{17}$N: 151.1361. Found: 151.1366.

Compound 3n

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.12 (s, 1 H), 7.39–7.37 (d, $J$ = 8.0 Hz, 2 H), 7.21–7.18 (d, $J$ = 8.4 Hz, 2 H), 6.60 (s, 1 H), 6.38 (s, 1 H), 2.65–2.61 (t, $J$ = 7.8 Hz, 2 H), 2.21 (s, 3 H), 1.73–1.68 (q, $J$ = 7.5 Hz, 2 H), 1.03–1.00 (t, $J$ = 7.4 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 140.5, 132.1, 130.4, 128.9, 123.6, 120.4, 116.4, 106.9, 37.6, 24.5, 13.8, 11.9. HRMS calcd for C$_{14}$H$_{17}$N: 199.1361. Found: 199.1368.

Compound 4a

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 6.46 (s, 1 H), 5.26 (s, 1 H), 5.23 (s, 1 H), 3.81–3.80 (d, $J$ = 5.6 Hz, 2 H), 2.24–2.21 (t, $J$ = 7.0 Hz, 2 H), 2.00–1.95 (d, $J$ = 16.8 Hz, 3 H), 1.48–1.42 (q, $J$ = 7.3 Hz, 2 H), 1.34–1.19 (m, 6 H), 0.84–0.81 (m, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta$ = 170.4, 128.7, 120.0, 92.0, 79.1, 44.6, 31.5, 28.8, 28.7, 23.2, 22.7, 19.4,
**Compound 4b**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.73–7.68$ (m, 2 H), 7.42–7.40 (t, $J = 3.4$ Hz, 2 H), 7.30–7.28 (m, 3 H), 7.22–7.20 (d, $J = 7.6$ Hz, 2 H), 6.64 (s, 1 H), 5.56 (s, 1 H), 5.52 (s, 1 H), 4.22–4.20 (d, $J = 6.0$ Hz, 2 H), 2.36 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 167.3, 141.9, 131.6, 131.4, 129.2, 128.4, 128.2, 128.1, 127.0, 122.6, 121.8, 90.8, 87.5, 44.5, 21.3.

**Compound 4c**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.69–7.67$ (d, $J = 8.0$ Hz, 2 H), 7.21–7.19 (m, 2 H), 5.20–5.20 (d, $J = 0.8$ Hz, 1 H), 5.16 (s, 1 H), 5.14–5.11 (t, $J = 6.4$ Hz, 1 H), 3.53–3.51 (d, $J = 6.4$ Hz, 2 H), 2.32 (s, 3 H), 2.16–2.12 (t, $J = 7.2$ Hz, 2 H), 1.42–1.35 (m, 2 H), 1.30–1.16 (m, 6 H), 0.82–0.78 (t, $J = 7.0$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 143.2, 137.1, 129.5, 127.2, 127.1, 120.9, 92.6, 78.2, 47.9, 31.2, 28.5, 28.4, 22.4, 21.4, 19.1, 13.9.

**Compound 4d**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.80–7.78$ (d, $J = 7.2$ Hz, 2 H), 7.40–7.36 (t, $J = 7.4$ Hz, 1 H), 7.32–7.28 (t, $J = 7.6$ Hz, 2 H), 6.92 (s, 1 H), 5.24–5.23 (d, $J = 3.2$ Hz, 2 H), 3.96–3.95 (d, $J = 5.6$ Hz, 2 H), 1.24–1.17 (m, 1 H), 0.71–0.60 (m, 2 H), 0.59–0.56 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 167.4, 134.4, 131.4, 128.4, 128.3, 127.0, 120.0, 95.1, 74.1, 44.7, 8.6, -0.03.

**Compound 4e**
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.82–7.80$ (m, 2 H), 7.53–7.49 (m, 1 H), 7.46–7.41 (m, 4 H), 7.33–7.29 (m, 3 H), 6.46 (s, 1 H), 5.59 (s, 1 H), 5.56–5.56 (d, $J = 1.2$ Hz, 1 H), 4.26–4.24 (d, $J = 6.0$ Hz, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 167.6$, 134.7, 131.9, 131.8, 128.9, 128.8, 128.6, 128.3, 127.2, 122.9, 122.4, 91.2, 87.7, 44.9.

Compound 4f
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.30–5.29$ (d, $J = 1.2$ Hz, 1 H), 5.24 (s, 1 H), 5.21–5.18 (t, $J = 6.4$ Hz, 1 H), 3.62–3.61 (d, $J = 6.4$ Hz, 2 H), 2.87–2.85 (d, $J = 9.2$ Hz, 3 H), 1.25–1.21 (m, 1 H), 0.74–0.69 (m, 2 H), 0.62–0.58 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 128.2$, 121.6, 96.2, 73.8, 48.2, 41.4, 8.8, 0.2.

Compound 4g
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 5.44–5.44$ (d, $J = 1.2$ Hz, 1 H), 5.40 (s, 1 H), 5.34–5.31 (t, $J = 6.2$ Hz, 1 H), 3.78–3.76 (d, $J = 6.0$ Hz, 2 H), 2.98 (s, 3 H), 2.33–2.29 (t, $J = 7.2$ Hz, 2 H), 1.55–1.50 (m, 2 H), 1.41–1.26 (m, 6 H), 0.91–0.88 (t, $J = 7.0$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 128.4$, 121.4, 93.1, 78.5, 48.3, 41.4, 31.4, 28.7, 28.7, 22.7, 19.4, 14.2.

Compound 5a
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 6.76$ (s, 1 H), 5.87 (s, 1 H), 2.88–2.84 (t, $J = 7.6$ Hz, 2 H), 2.49 (s, 3 H), 2.04 (s, 3 H), 1.63–1.56 (m, 2 H), 1.40–1.28 (m, 6 H), 0.92–0.89 (t, $J = 6.4$ Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta = 169.1$, 138.2, 122.2, 117.5, 114.2, 31.9, 29.7, 29.4, 28.9, 24.6, 22.8, 14.3, 12.0. HRMS calcd for C$_{13}$H$_{21}$NO: 207.1623. Found: 207.1626.

Compound 5b
$^1$H NMR (400 MHz, CDCl$_3$): $\delta = 7.71–7.69$ (d, $J = 8.0$ Hz, 2 H), 7.30–7.20 (m, 7 H),
6.82 (s, 1 H), 6.31 (s, 1 H), 2.41 (s, 3 H), 2.10 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 168.4, 143.5, 136.4, 133.3, 130.8, 130.4, 129.0, 127.9, 127.8, 126.7, 122.1, 121.4, 117.2, 21.6, 11.7. HRMS calcd for C$_{19}$H$_{17}$NO: 275.1310. Found: 275.1319.

**Compound 5c**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.63–7.61 (d, $J =$ 8.8 Hz, 2 H), 7.27–7.25 (d, $J =$ 7.2 Hz, 2 H), 7.00 (s, 1 H), 5.83 (s, 1 H), 2.63–2.59 (t, $J =$ 7.6 Hz, 2 H), 2.39 (s, 3 H), 2.00–2.00 (d, $J =$ 0.8 Hz, 3 H), 1.53–1.47 (q, $J =$ 7.7 Hz, 2 H), 1.31–1.21 (m, 6 H), 0.88–0.84 (t, $J =$ 7.0 Hz, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 144.3, 136.8, 136.1, 129.8, 126.6, 121.8, 119.0, 114.2, 31.5, 28.9, 28.6, 27.1, 22.5, 21.5, 14.0, 11.7. HRMS calcd for C$_{18}$H$_{15}$NO$_2$S: 319.1606. Found: 319.1612.

**Compound 5d**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.75–7.74 (d, $J =$ 7.2 Hz, 2 H), 7.60–7.56 (t, $J =$ 7.6 Hz, 1 H), 7.50–7.47 (t, $J =$ 7.6 Hz, 2 H), 6.56 (s, 1 H), 5.86 (s, 1 H), 2.33–2.29 (m, 1 H), 1.99 (s, 3 H), 0.88–0.84 (m, 2 H), 0.65–0.61 (m, 2 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 168.8, 139.5, 134.9, 131.9, 129.5, 128.2, 120.8, 120.1, 112.6, 11.7, 9.5, 7.4. HRMS calcd for C$_{15}$H$_{15}$NO: 225.1154. Found: 225.1159.

**Compound 5e**

$^1$H NMR (400 MHz, CDCl$_3$): $\delta =$ 7.78–7.76 (d, $J =$ 7.2 Hz, 2 H), 7.52–7.50 (m, 1 H), 7.42–7.38 (m, 2 H), 7.30–7.19 (m, 5 H), 6.84 (s, 1 H), 6.32–6.31 (d, $J =$ 0.8 Hz, 1 H), 2.11 (s, 3 H). $^{13}$C NMR (100 MHz, CDCl$_3$): $\delta =$ 168.7, 136.8, 134.0, 133.6, 132.9, 130.5, 128.5, 128.3, 128.2, 127.1, 122.3, 121.9, 117.7, 12.0. HRMS calcd for C$_{18}$H$_{18}$NO: 261.1154. Found: 261.1155.
**Compound 5f**

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 6.83 \text{ (s, 1 H), 5.74 (s, 1 H), 3.17 (s, 3 H), 2.20–2.14 (m, 1 H), 1.98 (s, 3 H), 0.95–0.88 (m, 2 H), 0.65–0.61 (m, 2 H).} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta = 137.4, 121.6, 118.9, 112.3, 42.3, 11.9, 7.9, 7.6.} \]

HRMS calcd for C\textsubscript{9}H\textsubscript{13}NO\textsubscript{2}S: 199.0667. Found: 199.0662.

**Compound 5g**

\[ \text{H NMR (400 MHz, CDCl}_3\text{): } \delta = 6.79 \text{ (s, 1 H), 5.91 (s, 1 H), 3.01 (s, 3 H), 2.73–2.69 (t, } J = 7.6 \text{ Hz, 2 H), 2.00–2.00 (d, } J = 0.8 \text{ Hz, 3 H), 1.65–1.59 (m, 2 H), 1.39–1.25 (m, 6 H), 0.90–0.86 (m, 3 H).} \]

\[ \text{\textsuperscript{13}C NMR (100 MHz, CDCl}_3\text{): } \delta = 136.2, 122.5, 118.8, 114.7, 42.4, 31.9, 29.3, 29.1, 27.6, 22.8, 14.3, 11.9.} \]

HRMS calcd for C\textsubscript{12}H\textsubscript{21}NO\textsubscript{2}S: 243.1293. Found: 243.1298.

**References:**

