Electronic Supplementary Information

Gold-Catalyzed Tandem Annulation towards 3,4-Fused Bi/tri-cyclic Furans
Involving a [3+2+2]-Cycloaddition

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1. General information
All the reactions were carried out under argon atmosphere in a flame-dried schlenk tube. Solvents were dried prior to use. For column chromatography, 200-300 mesh silica gel was used. NMR spectra were recorded on Bruker 300MHz, 400MHz or 500 MHz spectrometer in CDCl₃. High resolution mass spectra (HRMS) were performed on Agilent 6540 TOF mass spectrometer. Melting points were determined on a SGW X-4B melting point apparatus.
Compounds 1a-1c,[1] 1d-1k,[2] 1l-1n,[1] 1o,[2] 1p-1q[3] and 2[4] were prepared according to related literatures.

2. Preparation and characterization of compounds 3

\[
\begin{align*}
\text{Ph} & \quad \text{Me} \\
\text{1a} \quad \text{Ph} & \\
\text{Bn} & \quad \text{Bn} \\
\text{2a} \quad \text{Bn} & \\
\text{(p-Tolyl)}_3\text{PAuNTf}_2 & \quad \text{(p-Tolyl)}_3\text{PAuNTf}_2 \\
\text{DCM}, \text{rt}, \text{Ar} & \\
\begin{array}{c}
\text{Ph} \\
\text{Me} \\
\text{Bn} \\
\text{Bn} \\
\text{O} \\
\text{Ph}
\end{array} & \quad \text{3a}
\end{align*}
\]

1a (0.2 mmol), 2a (0.24 mmol), (p-Tolyl)₃PAuNTf₂ (5 mol%) were added into DCM (2.0 mL). The mixture was stirred at room temperature under Ar atmosphere for 12 h. Then solvent was removed under vacuum. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate =50:1) to afford the desired product 3a as white solid in 85% yield (82.1 mg). M.p.: 128–130 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.52–7.48 (m, 2H), 7.43–7.20 (m, 18H), 4.84 (s, 1H), 4.13 (d, \( J = 12.0 \) Hz, 1H), 4.05–3.88 (m, 4H), 3.63 (s, 2H), 3.40 (d, \( J = 16.0 \) Hz, 1H), 2.10 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.78, 147.59, 141.47, 140.36, 139.64, 131.41, 129.02, 129.00, 128.65, 128.43, 128.36, 128.25, 128.23, 127.08, 126.91, 126.88, 126.79, 126.21, 120.86, 120.68, 73.63, 58.97, 57.94, 57.27, 48.93, 11.59. HRMS (ESI+): calcd for C₃₄H₃₃N₂O [M+H⁺]: 485.2587, found : 485.2586.
According to the general procedure, **3b** was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 20:1) to afford 66.9 mg (65% yield) of the desired product as white solid. M.p.: 135-136 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.0$ Hz, 2H), 7.32 (m, 7H), 7.24–7.16 (m, 8H), 6.77 (d, $J = 8.0$ Hz, 2H), 4.79 (s, 1H), 4.07 (s, 1H), 3.95 (m, 2H), 3.87 (d, $J = 12.0$ Hz, 2H), 3.81 (s, 3H), 3.58 (s, 2H), 3.44 (d, $J = 12.0$ Hz, 1H), 2.05 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 158.58, 148.07, 147.54, 141.55, 140.39, 139.71, 128.99, 128.97, 128.38, 128.30, 128.19, 127.62, 127.01, 126.84, 126.71, 124.32, 120.62, 119.30, 113.85, 77.28, 77.03, 76.77, 73.59, 58.96, 58.00, 57.21, 55.31, 49.01, 11.51. HRMS (ESI+): calcd for C$_{35}$H$_{35}$N$_2$O$_2$ [M+H]$^+$ : 515.2693, found : 515.2692.

According to the general procedure, **3c** was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 54.0 mg (55% yield) of the desired product as white solid. M.p.: 103-105 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.46 (d, $J = 8.0$ Hz, 2H), 7.37–7.19 (m, 14H), 6.97 (m, 2H), 4.79 (s, 1H), 4.11 (d, $J = 16.0$ Hz, 1H), 4.03–3.83 (m, 4H), 3.66–3.58 (m, 2H), 3.33 (d, $J = 12.0$ Hz, 1H), 2.05 (s, 3H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 148.15, 144.41, 141.33, 140.27, 139.70, 132.25, 128.95, 128.88, 128.30, 128.26, 128.20, 127.03, 126.92, 126.75, 125.74, 125.42, 120.53, 119.86, 77.26, 77.00, 76.75, 73.57, 58.75, 58.89, 57.29, 48.45, 11.49. HRMS (ESI+): calcd for C$_{32}$H$_{31}$N$_2$O$_2$ [M+H]$^+$ : 491.2152, found : 491.2153.
According to the general procedure, **3d** was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 90.8 mg (83% yield) of the desired product as white solid. M.p.: 173-175 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 9.0$ Hz, 2H), 7.40–7.20 (m, 18H), 7.17 (m, 2H), 7.11–7.04 (m, 3H), 5.19 (s, 1H), 4.09 (d, $J = 12.0$ Hz, 1H), 4.01–3.92 (m, 2H), 3.84 (m, 2H), 3.61 (d, $J = 12.0$ Hz, 1H), 3.49 (d, $J = 12.0$ Hz, 1H), 3.37 (d, $J = 15.0$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 150.33, 148.83, 140.80, 139.60, 131.04, 130.76, 129.11, 129.08, 128.67, 128.49, 128.46, 128.30, 127.99, 127.44, 127.32, 127.07, 127.01, 126.71, 126.66, 126.16, 123.21, 121.75, 77.47, 77.04, 76.62, 73.54, 59.02, 57.09, 48.97. HRMS (ESI+): calcd for C$_{39}$H$_{35}$N$_2$O $[\text{M}+\text{H}]^+$: 547.2744, found: 547.2743.

According to the general procedure, **3e** was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 98.0 mg (85% yield) of the desired product as white solid. M.p.: 81-83 °C. $^1$H NMR (300 MHz, CDCl$_3$) $\delta$ 7.48 (d, $J = 6.0$ Hz, 2H), 7.38–7.16 (m, 17H), 7.10 (m, 3H), 6.80–6.75 (m, 2H), 5.14 (s, 1H), 4.09 (d, $J = 15.0$ Hz, 1H), 4.01–3.91 (m, 2H), 3.85 (d, $J = 15.0$ Hz, 2H), 3.78 (s, 3H), 3.61 (d, $J = 12.0$ Hz, 1H), 3.49 (d, $J = 12.0$ Hz, 1H), 3.36 (d, $J = 15.0$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) $\delta$ 159.11, 150.39, 148.83, 140.80, 139.60, 131.14, 129.13, 129.10, 128.67, 128.48, 128.31, 127.99, 127.60, 127.46, 127.05, 126.71, 126.57, 123.65, 121.82, 121.62, 113.99, 77.48, 77.06, 76.64, 73.49, 59.09, 59.01, 57.10, 55.35, 48.95. HRMS (ESI+): calcd for C$_{40}$H$_{37}$N$_2$O$_2$ [M+H]$^+$: 577.2850,
According to the general procedure, 3f was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 95.2 mg (82% yield) of the desired product as white solid. M.p.: 166-168 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.46 (d, $J = 6.0$ Hz, 2H), 7.39–7.06 (m, 22H), 5.12 (s, 1H), 4.09 (d, $J = 15.0$ Hz, 1H), 4.00–3.77 (m, 4H), 3.61 (d, $J = 15.0$ Hz, 1H), 3.50 (d, $J = 15.0$ Hz, 1H), 3.36 (d, $J = 12.0$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 149.15, 140.49, 139.54, 139.43, 133.19, 130.81, 129.21, 129.08, 129.01, 128.67, 128.58, 128.52, 128.30, 128.03, 127.49, 127.24, 127.18, 127.03, 126.85, 126.68, 123.76, 121.85, 77.45, 77.03, 76.61, 73.63, 59.05, 58.71, 57.09, 48.91. HRMS (ESI+): calcd. for C$_{39}$H$_{34}$ClN$_2$O $[M+H]^+$: 581.2354, found: 581.2355.

According to the general procedure, 3g was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 79.8 mg (80% yield) of the desired product as colorless oil. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.47 (d, $J = 6.0$ Hz, 2H), 7.40–7.19 (m, 18H), 4.84 (s, 1H), 4.10 (d, $J = 15.0$ Hz, 1H), 4.00–3.82 (m, 4H), 3.58 (s, 2H), 3.34 (d, $J = 15.0$ Hz, 1H), 2.52–2.23 (m, 2H), 1.12 (t, $J = 15.0$ Hz, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 153.93, 147.46, 141.63, 140.40, 139.61, 131.49, 129.00, 128.86, 128.39, 128.37, 128.32, 128.21, 127.03, 126.89, 126.82, 126.73, 126.21, 120.50, 119.92, 77.47, 77.04, 76.62, 73.56, 59.01, 57.98, 57.14, 49.04, 19.39, 13.34. HRMS (ESI+): calcd for C$_{35}$H$_{35}$N$_2$O $[M+H]^+$: 499.2744, found:
According to the general procedure, 3h was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 20:1) to afford 84.2 mg (73% yield) of the desired product as white solid. M.p.: 157-158 °C. $^1$H NMR (300 MHz, CDCl$_3$) δ 7.49 (d, $J = 9.0$ Hz, 2H), 7.35–7.15 (m, 17H), 7.09–7.06 (m, 3H), 6.80–6.75 (m, 2H), 5.18 (s, 1H), 4.09 (d, $J = 12.0$ Hz, 1H), 3.97–3.78 (m, 7H), 3.66–3.58 (m, 1H), 3.47 (d, $J = 15.0$ Hz, 1H), 3.34 (d, $J = 12.0$ Hz, 1H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 158.90, 149.77, 148.87, 140.87, 139.72, 139.65, 130.87, 129.13, 129.08, 128.70, 128.46, 128.43, 128.29, 128.09, 127.97, 127.26, 127.03, 126.95, 126.68, 126.06, 123.87, 123.09, 120.48, 113.92, 77.46, 77.04, 76.61, 73.53, 59.05, 57.05, 55.33, 49.02. HRMS (ESI+): calcd. for C$_{40}$H$_{37}$N$_2$O$_2$ [M+H]$^+$: 577.2850, found: 577.2852.

According to the general procedure, 3i was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 81.3 mg (70% yield) of the desired product as white solid. M.p.: 153-155 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.47 (d, $J = 4.0$ Hz, 2H), 7.36 (t, $J = 8.0$ Hz, 2H), 7.31–7.22 (m, 11H), 7.17 (d, $J = 4.0$ Hz, 6H), 7.11–7.05 (m, 3H), 5.19 (s, 1H), 4.10 (d, $J = 12.0$ Hz, 1H), 3.97 (d, $J = 12.0$ Hz, 1H), 3.88 (m, 2H), 3.79 (d, $J = 12.0$ Hz, 1H), 3.61 (d, $J = 12.0$ Hz, 1H), 3.45 (d, $J = 12.0$ Hz, 1H), 3.33 (d, $J = 16.0$ Hz, 1H). $^{13}$C NMR (125 MHz, CDCl$_3$) δ 150.60, 147.63, 140.64, 139.58, 139.51, 133.00, 130.55, 129.50, 129.11, 129.05, 128.63, 128.53, 128.49, 128.37, 128.01, 127.76, 127.61, 127.13, 126.75, 126.19,
According to the general procedure, 3j was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 70.6 mg (67% yield) of the desired product as colorless oil. \(^1\)H NMR (300 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 9.0\) Hz, 2H), 7.36–6.99 (m, 18H), 5.09 (s, 1H), 4.01 (d, \(J = 12.0\) Hz, 1H), 3.91 (d, \(J = 15.0\) Hz, 1H), 3.82–3.69 (m, 2H), 3.59 (s, 2H), 3.50 (m, 1H), 3.25 (d, \(J = 15.0\) Hz, 1H), 2.59–2.36 (m, 2H), 1.67–1.55 (m, 2H), 1.32 (m, 2H), 0.91 (t, \(J = 9.0\) Hz, 3H). \(^1\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 151.50, 149.05, 141.14, 139.99, 139.72, 131.24, 129.10, 128.68, 128.50, 128.41, 128.35, 128.25, 127.93, 126.92, 126.88, 126.64, 125.74, 121.51, 119.70, 77.48, 77.06, 76.64, 72.93, 58.78, 57.12, 48.85, 31.03, 25.87, 22.37, 13.92. HRMS (ESI\(^+\)) calcd for C\(_{37}\)H\(_{39}\)N\(_2\)O [M+H]\(^+\): 527.3057, found: 527.3056.

According to the general procedure, 3k was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 66.4 mg (65% yield) of the desired product as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.42 (d, \(J = 8.0\) Hz, 2H), 7.37–7.00 (m, 18H), 5.09 (s, 1H), 4.03 (d, \(J = 12.0\) Hz, 1H), 3.97 (d, \(J = 12.0\) Hz, 1H), 3.84 (d, \(J = 12.0\) Hz, 1H), 3.76 (d, \(J = 12.0\) Hz, 1H), 3.67–3.65 (m, 3H), 3.31 (d, \(J = 16.0\) Hz, 1H), 1.68–1.60 (m, 1H), 1.08–0.78 (m, 4H). \(^1\)C NMR (125 MHz, CDCl\(_3\)) \(\delta\) 151.08, 148.14, 140.95, 139.93, 139.72, 131.08, 129.02, 128.65, 128.61, 128.33, 128.30, 128.19, 127.89, 126.88, 126.79, 126.60, 125.60, 122.03, 119.82, 77.26, 77.00, 76.75, 72.94, 58.61, 58.55, 57.28, 48.16, 7.52, 6.89, 6.45.
HRMS (ESI+): calcd. for C_{36}H_{35}N_{2}O [M+H]^+: 511.2744, found: 511.2745.

According to the general procedure, 3l was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 79.9 mg (70% yield) of the desired product as white solid. M.p.: 177-179 °C. \(^1\)H NMR (300 MHz, CDCl \(_3\)) \(\delta\) 7.55–7.50 (m, 2H), 7.40–7.15 (m, 23H), 5.15 (s, 1H), 4.12 (m, 2H), 4.04–3.90 (m, 3H), 3.67–3.57 (m, 2H), 3.46 (d, \(J = 15.0\) Hz, 1H). \(^{13}\)C NMR (75 MHz, CDCl \(_3\)) \(\delta\) 150.80, 140.58, 139.99, 139.32, 135.04, 132.40, 131.37, 130.49, 129.29, 128.94, 128.53, 128.48, 128.35, 128.25, 128.19, 127.90, 126.99, 126.96, 126.76, 122.26, 121.27, 96.78, 78.67, 77.49, 77.07, 76.64, 73.43, 58.66, 58.29, 57.57, 48.30. HRMS (ESI+): calcd. for C\(_{41}\)H\(_{35}\)N\(_2\)O [M+H]^+: 571.2744, found: 571.2743.

According to the general procedure, 3m was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 53.9 mg (62% yield) of the desired product as colorless oil. \(^1\)H NMR (400 MHz, CDCl \(_3\)) \(\delta\) 7.35 (d, \(J = 8.0\) Hz, 2H), 7.32–7.13 (m, 13H), 4.05 (m, 4H), 3.71 (d, \(J = 12.0\) Hz, 1H), 3.62 (d, \(J = 12.0\) Hz, 2H), 3.51 (t, \(J = 12.0\) Hz, 2H), 2.61 (m, 2H), 2.23–1.98 (m, 2H), 1.75 (m, 2H). \(^{13}\)C NMR (75 MHz, CDCl \(_3\)) \(\delta\) 150.84, 146.27, 141.06, 139.61, 131.53, 129.02, 128.57, 128.39, 128.33, 128.20, 126.97, 126.60, 126.53, 125.68, 123.17, 119.49, 78.60, 77.46, 77.04, 76.62, 59.14, 58.12, 50.56, 50.27, 28.84, 23.04, 22.59. HRMS (ESI+): calcd. for C\(_{30}\)H\(_{31}\)N\(_2\)O [M+H]^+: 435.2431, found: 435.2433.
According to the general procedure, **3n** was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 43.8 mg (55% yield) of the desired product as colorless oil. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.36–7.14 (m, 10H), 4.09–3.91 (m, 3H), 3.60 (m, 5H), 3.35 (d, \(J = 16.0\) Hz, 1H), 2.44 (m, 2H), 2.14–1.93 (m, 2H), 1.73–1.59 (m, 2H), 1.56–1.48 (m, 1H), 0.69 (d, \(J = 4.0\) Hz, 4H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.21, 141.21, 139.83, 128.78, 128.53, 128.21, 128.14, 126.84, 126.44, 121.89, 117.69, 79.25, 77.47, 77.04, 76.62, 58.73, 58.46, 50.50, 49.26, 28.99, 22.80, 7.13, 5.98, 5.61. HRMS (ESI+): calcd for C\(_{27}\)H\(_{31}\)N\(_2\)O \([M+H]^+\): 399.2431, found: 399.2432.

According to the general procedure, **3o** was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 77.8 mg (78% yield) of the desired product as white solid. M.p.: 122-123 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 8.0\) Hz, 2H), 7.34 (t, \(J = 8.0\) Hz, 2H), 7.24 (m, 13H), 7.11 (d, \(J = 8.0\) Hz, 2H), 4.77 (s, 1H), 4.08 (d, \(J = 12.0\) Hz, 1H), 3.92 (m, 4H), 3.58 (s, 2H), 3.36 (d, \(J = 12.0\) Hz, 1H), 2.33 (s, 3H), 2.05 (s, 3H). \(^{13}\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.65, 147.47, 140.39, 139.67, 138.38, 136.38, 131.42, 128.99, 128.95, 128.41, 128.32, 128.27, 128.21, 127.01, 126.89, 126.83, 126.18, 121.06, 120.70, 77.48, 77.06, 76.64, 73.52, 58.98, 57.77, 57.18, 48.99, 21.10, 11.54. HRMS (ESI+): calcd for C\(_{35}\)H\(_{38}\)N\(_2\)O \([M+H]^+\): 499.2744, found: 499.2743.
According to the general procedure, 3p was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 77.7 mg (75% yield) of the desired product as white solid. M.p.: 175-177 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.44 (d, \(J = 8.0\) Hz, 2H), 7.35 (t, \(J = 8.0\) Hz, 2H), 7.30–7.18 (m, 15H), 4.73 (s, 1H), 4.07 (d, \(J = 12.0\) Hz, 1H), 3.91 (m, 4H), 3.59 (s, 2H), 3.31 (d, \(J = 16.0\) Hz, 1H), 2.06 (s, 3H). \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 148.84, 147.72, 140.13, 140.07, 139.47, 132.51, 131.23, 129.75, 128.97, 128.44, 128.39, 128.35, 128.24, 127.16, 126.97, 126.95, 126.20, 120.42, 120.40, 77.47, 77.05, 76.63, 73.62, 59.01, 57.44, 57.19, 48.98, 11.54. HRMS (ESI\(^+\)): calcd. for C\(_{41}\)H\(_{35}\)ClN\(_2\)O \([\text{M+H}]^+\): 519.2198, found: 519.2199.

According to the general procedure, 3q was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 60:1) to afford 47.2 mg (47% yield) of the desired product as white solid. M.p.: 159-161 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.45 (d, \(J = 4.0\) Hz, 2H), 7.40–7.17 (m, 15H), 6.98 (t, \(J = 8.0\) Hz, 2H), 4.74 (s, 1H), 4.08 (d, \(J = 16.0\) Hz, 1H), 3.96–3.83 (m, 4H), 3.59 (s, 2H), 3.33 (d, \(J = 16.0\) Hz, 1H), 2.07 (s, 3H). \(^1^3\)C NMR (75 MHz, CDCl\(_3\)) \(\delta\) 163.43, 160.18, 148.75, 147.70, 140.23, 139.51, 137.09, 137.05, 131.28, 129.92, 129.81, 128.96, 128.42, 128.37, 128.22, 127.12, 126.93, 126.20, 120.70, 120.46, 115.09, 114.81, 77.46, 77.04, 76.61, 73.50, 58.99, 57.38, 57.22, 48.95, 11.53. HRMS (ESI\(^+\)): calcd. for C\(_{34}\)H\(_{32}\)FN\(_2\)O \([\text{M+H}]^+\): 503.2493, found: 503.2498.
According to the general procedure, 3r was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 60:1) to afford 96.8 mg (76% yield) of the desired product as colorless oil. ¹H NMR (400 MHz, CDCl₃) δ 7.64 (d, J = 8.0 Hz, 2H), 7.56 (d, J = 8.0 Hz, 2H), 7.43 (d, J = 8.0 Hz, 2H), 7.35–7.00 (m, 22H), 6.95 (d, J = 8.0 Hz, 2H), 5.38 (s, 1H), 5.10 (s, 1H), 4.19 (d, J = 16.0 Hz, 1H), 4.09 (s, 1H), 4.03 (d, J = 12.0 Hz, 1H), 3.61 (d, J = 12.0 Hz, 1H), 3.18 (d, J = 16.0 Hz, 1H), 1.64 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 148.81, 146.10, 143.65, 143.34, 142.42, 142.04, 141.22, 131.43, 128.70, 128.66, 128.49, 128.34, 128.27, 128.25, 128.21, 128.09, 128.03, 127.83, 126.95, 126.87, 126.81, 126.65, 126.56, 126.20, 125.86, 121.42, 120.09, 77.47, 77.05, 76.63, 72.26, 70.49, 69.13, 57.62, 48.08, 11.18. HRMS (ESI+): calcd. for C₄₆H₄₁N₂O [M+H]+: 637.3213, found: 637.3215.

According to the general procedure, 3s was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 56.6 mg (62% yield) of the desired product as white solid. M.p.: 156-158 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.59 (d, J = 8.0 Hz, 2H), 7.46 (t, J = 8.0 Hz, 2H), 7.38–7.23 (m, 3H), 7.20–7.08 (m, 5H), 7.04–6.93 (m, 4H), 6.87 (t, J = 8.0 Hz, 1H), 6.61 (t, J = 8.0 Hz, 1H), 6.44 (d, J = 8.0 Hz, 2H), 5.90 (s, 1H), 5.09 (d, J = 12.0 Hz, 1H), 4.85 (d, J = 12.0 Hz, 1H), 4.47 (d, J = 16.0 Hz, 1H), 4.36 (d, J = 16.0 Hz, 1H), 2.28 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 149.87, 147.87, 147.52, 146.60, 140.26, 131.07, 129.41, 128.75, 128.09, 127.24, 126.80, 125.78, 120.75, 120.34, 118.85, 117.38, 115.52, 113.25, 77.48,
77.06, 76.64, 63.01, 59.42, 44.53, 12.09. HRMS (ESI+): calcd. for C_{32}H_{29}N_{2}O [M+H]^+: 457.2274, found: 457.2266.

According to the general procedure, 3t was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 71.3 mg (69% yield) of the desired product as white solid. M.p.: 136-137 °C. ¹H NMR (300 MHz, CDCl₃) δ 7.58–7.53 (m, 2H), 7.46–7.39 (m, 2H), 7.33–7.26 (m, 1H), 7.25–7.12 (m, 5H), 6.95–6.87 (m, 2H), 6.83–6.75 (m, 2H), 6.58–6.51 (m, 2H), 6.45–6.36 (m, 2H), 5.73 (s, 1H), 5.00 (d, J = 12.0 Hz, 1H), 4.61 (d, J = 15.0 Hz, 1H), 4.48 (d, J = 15.0 Hz, 1H), 4.27 (d, J = 15.0 Hz, 1H), 3.76 (s, 3H), 3.65 (s, 3H), 2.23 (s, 3H). ¹³C NMR (75 MHz, CDCl₃) δ 153.19, 152.16, 147.30, 146.73, 144.73, 142.81, 140.78, 131.18, 128.71, 128.19, 127.55, 127.20, 126.88, 125.94, 121.54, 121.00, 118.45, 115.90, 114.59, 114.22, 77.50, 77.08, 76.65, 66.02, 60.35, 55.65, 55.63, 46.13, 12.00. HRMS (ESI+): calcd. for C_{34}H_{33}N_{2}O_{3} [M+H]^+: 517.2486, found: 517.2487.

According to the general procedure, 3u was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 50:1) to afford 62.0 mg (64% yield) of the desired product as white solid. M.p.: 175-177 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.57 (d, J = 8.0 Hz, 2H), 7.44 (t, J = 8.0 Hz, 2H), 7.31 (t, J = 8.0 Hz, 1H), 7.22–7.04 (m, 7H), 6.87 (d, J = 8.0 Hz, 2H), 6.8 (d, J = 8.0 Hz, 2H), 6.37 (d, J = 8.0 Hz, 2H), 5.84 (s, 1H), 5.03 (d, J = 12.0 Hz, 1H), 4.74 (d, J = 12.0 Hz, 1H), 4.46 (d, J
According to the general procedure, 3v was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 30:1) to afford 68.2 mg (66% yield) of the desired product as white solid. M.p.: 150-151 °C. \(^{1}\text{H NMR (400 MHz, CDCl}_3\) δ 7.58 (d, \(J = 8.0\) Hz, 2H), 7.34 (t, \(J = 8.0\) Hz, 4H), 7.25 (m, 4H), 6.85 (t, \(J = 8.0\) Hz, 1H), 6.77–6.60 (m, 5H), 6.56 (d, \(J = 8.0\) Hz, 1H), 6.43 (d, \(J = 8.0\) Hz, 1H), 5.57 (d, \(J = 4.0\) Hz, 1H), 5.12 (d, \(J = 4.0\) Hz, 1H), 4.17 (s, 1H), 4.07 (s, 2H), 3.72 (s, 3H), 3.69 (s, 3H), 2.34 (s, 3H). \(^{13}\text{C NMR (75 MHz, CDCl}_3\) δ 149.58, 148.22, 147.11, 146.79, 141.92, 138.00, 137.30, 130.75, 128.73, 128.56, 127.40, 127.08, 127.03, 125.85, 122.75, 121.15, 117.64, 116.82, 116.58, 110.71, 110.28, 109.20, 109.11, 77.51, 77.08, 76.66, 55.23, 55.22, 53.61, 38.39, 12.59. HRMS (ESI+) calcd. for C\(_{34}\)H\(_{33}\)N\(_2\)O\(_3\) [M+H]\(^+\): 517.2486, found: 517.2485.

According to the general procedure, 3w was isolated by column chromatography on silica gel, eluted by (petroleum ether/ethyl acetate = 80:1) to afford 50.2 mg (51% yield) of the desired product as white solid. M.p.: 125-127 °C. \(^{1}\text{H NMR (300 MHz, CDCl}_3\) δ 7.59–7.52 (m, 2H), 7.45 (m, 2H), 7.37–7.27 (m, 1H), 7.15 (s, 5H),
6.98–6.83 (m, 4H), 6.63 (m, 2H), 6.35–6.26 (m, 2H), 5.72 (s, 1H), 5.04 (d, $J = 15.0$ Hz, 1H), 4.65 (d, $J = 15.0$ Hz, 1H), 4.45 (d, $J = 15.0$ Hz, 1H), 4.28 (d, $J = 15.0$ Hz, 1H), 2.24 (s, 3H). $^{13}$C NMR (75 MHz, CDCl$_3$) δ 158.38, 157.34, 155.22, 154.21, 147.55, 146.93, 146.87, 146.84, 144.46, 144.44, 140.13, 130.95, 128.79, 128.24, 127.40, 127.32, 127.05, 125.89, 120.94, 120.47, 118.00, 117.90, 115.90, 115.61, 115.22, 114.93, 114.86, 114.76, 77.48, 77.05, 76.63, 64.94, 60.21, 45.49, 11.99. HRMS (ESI+): calcd. for C$_{32}$H$_{27}$F$_{2}$N$_{2}$O [M+H]$^+$: 493.2086, found: 493.2088.

3. Scheme 2 Controlled experiment

$^{1a}$ (50 mg, 0.2 mmol), $^{2a}$ (43 mg, 0.12 mmol), $^{2b}$ (70 mg, 0.12 mmol), ($p$-Tolyl)$_3$PAuNTf$_2$ (7.8 mg, 0.01 mmol) were added into DCM (2.0 mL). The mixture was stirred at room temperature under Ar atmosphere for 12 h. Then solvent was removed under vacuum. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate =50:1) to afford product as a mixture of $^3a$, $^3r$, $^4a$ and/or $^4a'$ determined by mass spectrum analysis.
Table 1: Mass spectrum analysis of controlled experiment

4. Scheme 3 Deuterium labeling experiment

1a (55 mg, 0.22 mmol), 2d (30 mg, 0.074 mmol), D-2d (30.4 mg, 0.074 mmol), (p-Tolyl)$_3$PAuNTf$_2$ (6.0 mg, 0.0074 mmol) were added into DCM (2.0 mL). The mixture was stirred at room temperature under Ar atmosphere for 12 h. Then solvent was removed under vacuum. The crude residue was purified by column chromatography (petroleum ether/ethyl acetate =20:1) to afford product as a mixture of 3t, D-3t, 4b and/or 4b'determined by mass spectrum analysis.

Table 2: Mass spectrum analysis of deuterium labelling experiment

5. References


$3a(400Hz, CDCl_3)$
$3b(400\text{Hz, CDCl}_3)$
3b (500Hz, CDCl₃)
$3c(400\text{Hz, CDCl}_3)$
3e (300Hz, CDCl₃)
$3f(300\text{Hz,CDCl}_3)$
$^3$g (300 Hz, CDCl$_3$)
$^{1}H(300\text{Hz},\text{CDCl}_3)$
$3i(500\text{Hz, CDCl}_3)$

-10 0 10 20 30 40 50 60 70 80 90 100

f1 (ppm)

Bn N N Bn
\[\begin{array}{c}
\text{Bn} \\
\text{Ph} \\
\text{Ph}
\end{array}\]

Cl

48.66 57.08 58.99 59.09 73.68 76.78 77.03 77.28 100.00 122.24 123.34 126.19 126.75 127.13 127.61 127.76 128.01 128.37 128.49 128.53 128.63 129.05 129.11 129.50 130.55
$^{3}J(300\text{Hz},\text{CDCl}_3)$
$3\nu(300\text{Hz},\text{CDCl}_3)$
$^3$H(400 Hz, CDCl$_3$)
$3k(500\text{Hz, CDCl}_3)$
$^{1}H\,(300\text{Hz},\text{CDCl}_3)$
$3(300\,\text{Hz},\text{CDCl}_3)$
$3m(400Hz, CDCl_3)$
$3o \ (400\text{Hz}, \text{CDCl}_3)$
$^{3}$p (400Hz, CDCl$_3$)
$3q \ (400 \text{Hz}, \text{CDCl}_3)$
3q (300Hz, CDCl₃)
$3r$ (400 Hz, CDCl$_3$)
$3r \ (300\text{Hz}, \text{CDCl}_3)$
3a (400Hz, CDCl₃)
$3t$ (300Hz, CDCl$_3$)
$3t$ (300Hz, CDCl$_3$)
$[\text{Image}]$

$3u \ (400\text{Hz, CDCl}_3)$
$3u \ (300Hz, CDCl_3)$
$3\nu (300\text{Hz},\text{CDCl}_3)$
$3 \omega \ (300 \text{Hz, CDCl}_3)$