Silver Triflate-Catalyzed Three-Component Reaction of 2-Alkynylbenzaldehyde, Sulfonohydrazide, and α,β-Unsaturated Carbonyl Compound

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Supporting Information

1. General experimental methods (S2)
2. Condition screening, general experimental procedure and characterization data. (S2-S16).
3. ¹H and ¹³C NMR spectra of compound 3 (S17-S68).
4. The crystal structure and crystallographic data of compound 3a (S69).
General experimental methods:

All reactions were performed in reaction tubes under air atmosphere. Flash column chromatography was performed using silica gel (60-Å pore size, 32–63 µm, standard grade). Analytical thin–layer chromatography was performed using glass plates pre-coated with 0.25 mm 230–400 mesh silica gel impregnated with a fluorescent indicator (254 nm). Thin layer chromatography plates were visualized by exposure to ultraviolet light. Organic solutions were concentrated on rotary evaporators at ~20 Torr (house vacuum) at 25–35°C. Commercial reagents and solvents were used as received. Nuclear magnetic resonance (NMR) spectra are recorded in parts per million from internal tetramethylsilane on the δ scale.

Initial Studies for the reaction of (3-phenylisoquinolinium-2-yl)(tosyl)amide B with ethyl acrylate 2a.

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Isolated yield based on 2-alkynylbenzaldehyde 1a.

Initial Studies for the Three-Component Reaction of 2-Alkynylbenzaldehyde 1a, Sulfonohydrazide, and Acrylate 2a.

**General procedure for three-component reaction of 2-alkynylbenzaldehyde, sulfonohydrazide, and α,β-unsaturated carbonyl compound.**
2-alkynylbenzaldehyde 1 (0.2 mmol) was added to a solution of sulfonohydrazide (0.2 mmol) in DCE (0.5 mL). After stirred at room temperature for 30 minutes, AgOTf (0.01 mmol) was added and the solution was stirred at 60 °C for 1 hours. Subsequently, DMAc (2 mL) and α,β-unsaturated carbonyl compound 2 (0.4 mmol, 2 equiv) was added and the mixture was stirred at 60 °C. After completion of reaction as indicated by TLC, the reaction was quenched with aqueous NH₄Cl (10 mL, 1.0 M), extracted with EtOAc (2 x 10 mL), dried by anhydrous Na₂SO₄. Evaporation of the solvent followed by purification on silica gel provided the product 3.

![Image](attachment:image.jpg)

Ethyl 5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3a)

¹H NMR (400 MHz, CDCl₃) δ 1.45 (t, J = 7.3 Hz, 3H), 4.43 (q, J = 7.3 Hz, 2H), 7.19 (s, 1H), 7.49–7.55 (m, 3H), 7.62–7.68 (m, 2H), 7.75 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 8.47 (s, 1H), 9.87 (d, J = 7.8 Hz, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 14.4, 60.3, 108.0, 115.2, 123.8, 126.9, 127.6, 127.7, 128.4, 129.4, 129.6, 130.7, 133.5, 138.3, 139.5, 145.0, 163.9; HRMS (ESI) calcd for C₂₀H₁₆N₂O₂: 339.1109 (M + Na⁺), found: 339.1084.

![Image](attachment:image.jpg)

Methyl 5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3b)

¹H NMR (400 MHz, CDCl₃) δ 3.95 (s, 3H), 7.19 (s, 1H), 7.49–7.55 (m, 3H), 7.62–7.66 (m, 2H), 7.74 (d, J = 8.3 Hz, 1H), 7.80 (d, J = 8.3 Hz, 2H), 8.46 (s, 1H),...
9.85 (d, J = 7.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 51.6, 107.6, 115.3, 123.7, 126.9, 127.6, 128.4, 129.4, 129.5, 129.6, 130.7, 133.4, 138.3, 139.5, 145.0, 164.2; HRMS (ESI) calcd for C\(_{19}\)H\(_{14}\)N\(_2\)O\(_2\): 325.0953 (M + Na\(^+\)), found: 325.0924.

\[
\text{Butyl 5-phenyl}H\text{-pyrazolo}\[5,1-a\]\text{-isoquinoline-1-carboxylate (3c)}
\]
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 1.00 (t, J = 7.3 Hz, 3H), 1.50-1.52 (m, 2H), 1.81-1.82 (m, 2H), 4.38 (t, J = 6.8 Hz, 2H), 7.19 (s, 1H), 7.50–7.54 (m, 3H), 7.63–7.67 (m, 2H), 7.75–7.81 (m, 3H), 8.47 (s, 1H), 9.87 (d, J = 7.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.8, 19.3, 30.8, 64.3, 108.0, 115.2, 123.8, 126.9, 127.6, 127.7, 128.4, 129.4, 129.6, 130.7, 133.5, 138.3, 139.5, 145.0, 163.9; HRMS (ESI) calcd for C\(_{22}\)H\(_{20}\)N\(_2\)O\(_2\): 367.1422 (M + Na\(^+\)), found: 367.1417.

\[
\text{1-(5-Phenyl}H\text{-pyrazolo}\[5,1-a\]\text{-isoquinolin-1-yl)ethanone (3d)}
\]
\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 2.72 (s, 3H), 7.27 (s, 1H), 7.52–7.56 (m, 3H), 7.68–7.70 (m, 2H), 7.78–7.81 (m, 3H), 8.44 (s, 1H), 9.96 (d, J = 7.8 Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 29.7, 116.1, 117.2, 124.1, 126.1, 127.7, 128.0, 128.4, 129.5, 129.6, 129.9, 131.0, 133.4, 138.1, 138.8, 145.5, 192.1; HRMS (ESI) calcd for C\(_{19}\)H\(_{14}\)N\(_2\)O: 309.1004 (M + Na\(^+\)), found: 309.0992.
6-Phenyl-10,11-dihydroindazolo[3,2-a]isoquinolin-12(9H)-one (3e)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.20-2.22 (m, 2H), 2.73 (t, $J = 6.8$ Hz, 2H), 3.05 (t, $J = 6.8$ Hz, 2H), 7.25 (s, 1H), 7.50–7.56 (m, 3H), 7.67–7.71 (m, 2H), 7.77 (d, $J = 8.3$ Hz, 1H), 7.83 (d, $J = 8.3$ Hz, 2H), 10.11 (d, $J = 7.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 23.4, 24.3, 40.3, 112.7, 115.8, 123.9, 126.6, 127.6, 128.3, 128.4, 129.5, 129.7, 129.9, 131.0, 133.5, 138.0, 139.3, 159.6, 193.4; HRMS (ESI) calcd for C$_{21}$H$_{16}$N$_2$O: 335.1160 (M + Na$^+$), found: 335.1151.

Butyl 5-cyclopropyl$H$-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3f)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89–0.93 (m, 2H), 1.01 (t, $J = 7.3$ Hz, 3H), 1.18–1.22 (m, 2H), 1.51-1.52 (m, 2H), 1.80-1.82 (m, 2H ), 2.66–2.73 (m, 1H), 4.38 (t, $J = 6.8$ Hz, 2H), 6.82 (s, 1H), 7.58–7.61 (m, 2H), 7.64–7.68 (m, 1H), 8.53 (s, 1H), 9.81 (d, $J = 7.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.1, 11.6, 13.8, 19.3, 30.8, 64.2, 107.9, 109.6, 123.1, 126.2, 126.8, 127.6, 129.1, 130.7, 139.0, 140.6, 144.8, 163.9; HRMS (ESI) calcd for C$_{19}$H$_{20}$N$_2$O$_2$: 331.1422 (M + Na$^+$), found: 331.1404.
1-(5-Cyclopropylpyrazolo[5,1-a]isoquinolin-1-yl)ethanone (3g)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.91–0.95 (m, 2H), 1.20–1.24 (m, 2H), 2.69–2.72 (m, 1H), 2.73 (s, 3H), 6.90 (s, 1H), 7.61–7.68 (m, 3H), 8.51 (s, 1H), 9.90 (d, $J$ = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.1, 11.7, 29.6, 53.4, 110.5, 117.2, 123.4, 126.2, 126.9, 127.9, 129.6, 130.9, 138.4, 140.4, 145.4, 192.0; HRMS (ESI) calcd for C$_{16}$H$_{14}$N$_2$O: 273.1004 (M + Na$^+$), found: 273.0999.

6-Cyclopropyl-10,11-dihydroindazolo[3,2-a]isoquinolin-12(9H)-one (3h)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.92–0.94 (m, 2H), 1.22–1.25 (m, 2H), 2.25 (m, $J$ = 6.4 Hz, 2H), 2.72–2.76 (m, 3H), 3.14 (t, $J$ = 6.4 Hz, 2H), 6.86 (s, 1H), 7.61–7.69 (m, 3H), 1.04 (d, $J$ = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.6, 11.6, 23.5, 24.2, 40.1, 109.8, 112.7, 123.1, 125.9, 126.8, 128.2, 129.7, 131.0, 138.9, 140.4, 159.5, 193.4; HRMS (ESI) calcd for C$_{18}$H$_{16}$N$_2$O: 299.1160 (M + Na$^+$), found: 299.1168.

Butyl 5-butylpyrazolo[5,1-a]isoquinoline-1-carboxylate (3i)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.98–1.03 (m, 6H), 1.48–1.55 (m, 4H), 1.77–1.87 (m,
4H), 3.18 (t, J = 7.3 Hz, 2H), 4.38 (t, J = 6.4 Hz, 2H), 6.99 (s, 1H), 7.59–7.62 (m, 2H), 7.68–7.70 (m, 1H), 8.48 (s, 1H), 9.81 (d, J = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.8, 13.9, 19.3, 22.5, 29.0, 30.8, 30.9, 64.2, 107.8, 112.2, 123.3, 126.2, 126.8, 127.6, 129.2, 130.7, 139.0, 139.3, 144.7, 164.0; HRMS (ESI) calcd for C$_{20}$H$_{24}$N$_2$O$_2$: 347.1735 (M + Na$^+$), found: 347.1706.

![1-(5-ButylH-pyrazolo[5,1-a]isoquinolin-1-yl)ethanone (3j)]

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.00 (t, J = 7.3 Hz, 3H), 1.50-1.52 (m, 2H), 1.85-1.87 (m, 2H), 2.72 (s, 3H), 3.19 (t, J = 7.8 Hz, 2H), 7.06 (s, 1H ), 7.62–7.72 (m, 3H), 8.46 (s, 1H), 9.90 (d, J = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.9, 22.5, 29.1, 29.6, 30.9, 113.1, 117.0, 123.5, 126.1, 126.8, 127.9, 129.6, 130.9, 138.4, 139.1, 145.3, 192.0; HRMS (ESI) calcd for C$_{17}$H$_{18}$N$_2$O: 289.1317 (M + Na$^+$), found: 289.1319.

![6-Butyl-10,11-dihydroindazolo[3,2-a]isoquinolin-12(9H)-one (3k)]

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.01 (t, J = 7.3 Hz, 3H), 1.50-1.52 (m, 2H), 1.86-1.88 (m, 2H), 2.23-2.25 (m, 2H), 2.73 (t, J = 6.4 Hz, 2H), 3.10 (t, J = 6.4 Hz, 2H), 3.20 (t, J = 7.3 Hz, 2H), 7.06 (s, 1H), 7.64–7.73 (m, 3H), 10.05 (d, J = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.9, 22.4, 23.5, 24.2, 29.0, 30.8, 40.1, 112.5, 112.6, 123.3, 125.9, 126.8, 128.2, 129.6, 131.0, 138.8, 139.1, 159.4, 193.3; HRMS (ESI) calcd for C$_{19}$H$_{20}$N$_2$O: 315.1473 (M + Na$^+$), found: 315.1450.
Butyl 8-fluoro-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3I)

$^1$H NMR (400 MHz, CDCl$_3$) δ 1.01 (t, $J$ = 7.3 Hz, 3H), 1.50-1.52 (m, 2H), 1.80-1.82 (m, 2H), 4.37 (t, $J$ = 6.8 Hz, 2H), 7.12 (s, 1H), 7.37 (d, $J$ = 8.7 Hz, 2H), 7.52-7.55 (m, 3H), 7.78 (d, $J$ = 7.3 Hz, 2H), 8.45 (s, 1H), 9.95 (d, $J$ = 7.3 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.7, 19.3, 30.8, 64.4, 107.7, 111.4 (d, $^2$J$_{CF}$ = 21.9 Hz), 114.3 (d, $^4$J$_{CF}$ = 2.8 Hz), 116.2 (d, $^2$J$_{CF}$ = 22.9 Hz), 120.5, 128.4, 129.5, 129.6, 130.7 (d, $^3$J$_{CF}$ = 8.6 Hz), 132.7 (d, $^3$J$_{CF}$ = 9.5 Hz), 133.0, 139.2, 139.3, 145.1, 162.6 (d, $^1$J$_{CF}$ = 249.8 Hz), 163.8; HRMS (ESI) calcd for C$_{22}$H$_{19}$FN$_2$O$_2$: 385.1328 (M + Na$^+$), found: 385.1346.

1-(8-Fluoro-5-phenylH-pyrazolo[5,1-a]isoquinolin-1-yl)ethanone (3m)

$^1$H NMR (400 MHz, CDCl$_3$) δ 2.70 (s, 3H), 7.19 (s, 1H), 7.35–7.40 (m, 2H), 7.52–7.56 (m, 3H), 7.77–7.79 (m, 2H), 8.43 (s, 1H), 10.03–10.07 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 29.6, 111.3 (d, $^2$J$_{CF}$ = 20.9 Hz), 115.1 (d, $^4$J$_{CF}$ = 3.8 Hz), 116.2 (d, $^2$J$_{CF}$ = 22.9 Hz), 116.7, 120.8, 128.4, 129.6, 129.7, 131.2 (d, $^3$J$_{CF}$ = 8.6 Hz), 132.9, 133.0 (d, $^3$J$_{CF}$ = 9.6 Hz), 138.5, 139.1, 145.6, 162.9 (d, $^1$J$_{CF}$ = 249.8 Hz), 191.9; HRMS (ESI) calcd for C$_{19}$H$_{13}$FN$_2$O: 327.0910 (M + Na$^+$), found: 327.0919.
3-Fluoro-6-phenyl-10,11-dihydroindazolo[3,2-a]isoquinolin-12(9H)-one (3n)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.20-2.22 (m, 2H), 2.73 (t, $J = 6.4$ Hz, 2H), 3.04 (t, $J = 6.4$ Hz, 2H), 7.19 (s, 1H), 7.38–7.43 (m, 2H), 7.51–7.55 (m, 3H), 7.82–7.84 (m, 2H), 10.17–10.21 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 23.4, 24.2, 40.1, 111.0 (d, $^2J_{CF} = 21.9$ Hz), 112.4, 114.9 (d, $^4J_{CF} = 2.8$ Hz), 116.3 (d, $^2J_{CF} = 22.9$ Hz), 120.6, 128.4, 129.7, 131.4 (d, $^3J_{CF} = 8.6$ Hz), 133.0, 133.1, 138.9, 139.0, 159.7, 163.1 (d, $^1J_{CF} = 249.8$ Hz), 193.4; HRMS (ESI) calcd for C$_{21}$H$_{15}$FN$_2$O: 353.1066 (M + Na$^+$), found: 353.1069.

Butyl 5-cyclopropyl-8-fluoroH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3o)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.90–0.94 (m, 2H), 1.02 (t, $J = 7.3$ Hz, 3H), 1.20–1.24 (m, 2H), 1.51-1.53 (m, 2H), 1.80-1.82 (m, 2H), 2.67–2.74 (m, 1H), 4.37 (t, $J = 6.8$ Hz, 2H), 6.74 (s, 1H), 7.26–7.30 (m, 2H), 8.51 (s, 1H), 9.86 – 9.90 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.3, 10.6, 13.8, 19.3, 30.8, 64.3, 107.6, 108.6 (d, $^4J_{CF} = 3.8$ Hz), 110.8 (d, $^2J_{CF} = 21.0$ Hz), 115.5 (d, $^2J_{CF} = 22.9$ Hz), 119.8, 130.6 (d, $^3J_{CF} = 9.5$ Hz), 132.8 (d, $^3J_{CF} = 9.5$ Hz), 138.8, 141.8, 144.9, 162.5 (d, $^1J_{CF} = 248.9$ Hz), 163.9; HRMS (ESI) calcd for C$_{19}$H$_{19}$FN$_2$O$_2$: 349.1328 (M + Na$^+$), found: 349.1320.
Butyl 5-butyl-8-fluoroH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3p)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.98–1.03 (m, 6H), 1.47–1.55 (m, 4H), 1.79–1.86 (m, 4H), 3.17 (t, $J = 7.8$ Hz, 2H), 4.37 (t, $J = 6.4$ Hz, 2H), 6.91 (s, 1H), 7.29–7.32 (m, 2H), 8.46 (s, 1H), 9.86–9.89 (m, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.8, 13.9, 19.3, 22.5, 28.9, 30.8, 30.9, 64.3, 107.5, 110.7 (d, $^2J_{CF} = 20.1$ Hz), 111.4 (d, $^4J_{CF} = 3.8$ Hz), 115.4 (d, $^2J_{CF} = 22.9$ Hz), 120.0, 130.6 (d, $^3J_{CF} = 8.6$ Hz), 132.8 (d, $^3J_{CF} = 9.5$ Hz), 138.8, 140.5, 144.8, 162.6 (d, $^1J_{CF} = 249.8$ Hz), 163.9; HRMS (ESI) calcd for C$_{20}$H$_{23}$FN$_2$O$_2$: 365.1641 (M + Na$^+$), found: 365.1630.

Butyl 9-chloro-5-phenylH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3q)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 1.01 (t, $J = 7.3$ Hz, 3H), 1.50-1.52 (m, 2H), 1.80-1.82 (m, 2H), 4.38 (t, $J = 7.3$ Hz, 2H), 7.14 (s, 1H), 7.51–7.57 (m, 4H), 7.66 (d, $J = 8.7$ Hz, 1H), 7.78 (d, $J = 7.8$ Hz, 2H), 8.46 (s, 1H), 9.93 (d, $J = 1.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 13.8, 19.3, 30.7, 64.5, 108.4, 114.4, 124.6, 127.0, 128.1, 128.4, 128.9, 129.5, 129.6, 129.9, 133.1, 133.4, 138.3, 138.5, 145.1, 163.6; HRMS (ESI) calcd for C$_{22}$H$_{19}$ClN$_2$O$_2$: 401.1033 (M + Na$^+$), found: 401.1029.
1-(9-Chloro-5-phenyl-1H-pyrazolo[5,1-a]isoquinolin-1-yl)ethanone (3r)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.71 (s, 3H), 7.23 (s, 1H), 7.53–7.56 (m, 3H), 7.62 (d, $J = 8.3$ Hz, 1H), 7.70 (d, $J = 8.3$ Hz, 1H), 7.79 (d, $J = 7.8$ Hz, 2H), 8.44 (s, 1H), 10.07 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 29.6, 115.3, 117.4, 124.9, 127.4, 128.1, 128.4, 129.2, 129.6, 129.7, 130.4, 133.1, 133.5, 137.9, 138.4, 145.6, 192.0; HRMS (ESI) calcd for C$_{19}$H$_{13}$ClN$_2$O: 343.0614 (M + Na$^+$), found: 343.0603.

Butyl 9-chloro-5-cyclopropyl-1H-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3s)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.89–0.93 (m, 2H), 1.02 (t, $J = 7.3$ Hz, 3H), 1.19–1.24 (m, 2H), 1.51–1.53 (m, 2H), 1.82–1.84 (m, 2H), 2.66–2.71 (m, 1H), 4.39 (t, $J = 7.3$ Hz, 2H), 6.76 (s, 1H), 7.51–7.58 (m, 2H), 8.52 (s, 1H), 9.87 (d, $J = 1.8$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.2, 11.6, 13.8, 19.3, 30.8, 64.5, 108.4, 108.8, 123.9, 126.9, 127.6, 129.0, 129.6, 132.5, 137.9, 141.1, 145.0, 163.7; HRMS (ESI) calcd for C$_{19}$H$_{19}$ClN$_2$O$_2$: 365.1033 (M + Na$^+$), found: 365.1020.
Butyl 5-butyl-9-chloroH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3f)

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.98–1.04 (m, 6H), 1.47–1.54 (m, 4H), 1.79–1.86 (m, 4H), 3.14 (t, $J = 7.3$ Hz, 2H), 4.39 (t, $J = 6.4$ Hz, 2H), 6.91 (s, 1H), 7.51–7.59 (m, 2H), 8.46 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 13.8, 13.9, 19.3, 22.5, 28.9, 30.8, 30.9, 64.5, 108.2, 111.4, 124.1, 126.8, 127.5, 128.9, 129.6, 132.5, 137.8, 139.7, 144.8, 163.7; HRMS (ESI) calcd for C$_{20}$H$_{23}$ClN$_2$O$_2$: 381.1346 (M + Na$^+$), found: 381.1347.

Butyl 5-cyclopropyl-8,9-dimethoxyH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3u)

$^1$H NMR (400 MHz, CDCl$_3$) δ 0.86–0.91 (m, 2H), 1.01 (t, $J = 7.3$ Hz, 3H), 1.17–1.20 (m, 2H), 1.51–1.53 (m, 2H), 1.80–1.82 (m, 2H), 2.64–2.70 (m, 1H), 4.01 (s, 3H), 4.12 (s, 3H), 4.35 (t, $J = 7.3$ Hz, 2H), 6.75 (s, 1H), 7.02 (s, 1H), 8.50 (s, 1H), 9.54 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) δ 6.9, 11.6, 13.8, 19.3, 30.9, 55.8, 56.3, 64.1, 106.1, 106.3, 108.6, 109.0, 117.8, 126.2, 138.89, 138.91, 145.0, 148.8, 150.7, 164.2; HRMS (ESI) calcd for C$_{21}$H$_{24}$N$_2$O$_4$: 391.1634 (M + Na$^+$), found: 391.1629.
Butyl 5-butyl-8,9-dimethoxyH-pyrazolo[5,1-α]isoquinoline-1-carboxylate (3v)

$^1$H NMR (400 MHz, CDCl₃) $\delta$ 0.98–1.03 (m, 6H), 1.47–1.55 (m, 4H), 1.76–1.86 (m, 4H), 3.16 (t, $J = 7.8$ Hz, 2H), 4.02 (s, 3H), 4.12 (s, 3H), 4.35 (t, $J = 6.4$ Hz, 2H), 6.91 (s, 1H), 7.05 (s, 1H), 8.45 (s, 1H), 9.54 (s, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 13.8, 13.9, 19.3, 22.5, 29.1, 30.8, 30.9, 55.8, 56.3, 64.1, 106.0, 106.1, 108.5, 111.4, 117.9, 126.3, 137.7, 138.9, 144.8, 148.8, 150.8, 164.3; HRMS (ESI) calcd for C$_{22}$H$_{28}$N$_2$O$_4$: 407.1947 (M + Na$^+$), found: 407.1942.

Butyl 8-methyl-5-phenylH-pyrazolo[5,1-α]isoquinoline-1-carboxylate (3w)

$^1$H NMR (400 MHz, CDCl₃) $\delta$ 1.00 (t, $J = 7.3$ Hz, 3H), 1.50-1.52 (m, 2H), 1.80-1.82 (m, 2H), 2.51 (s, 3H), 4.37 (t, $J = 6.4$ Hz, 2H), 7.10 (s, 1H), 7.45–7.53 (m, 5H), 7.78 (d, $J = 7.8$ Hz, 2H), 8.43 (s, 1H), 9.74 (d, $J = 8.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl₃) $\delta$ 13.7, 19.3, 21.6, 30.8, 64.2, 107.4, 114.9, 121.6, 126.5, 127.6, 128.3, 129.2, 129.3, 129.5, 130.9, 133.5, 138.2, 139.5, 139.6, 144.9, 163.9; HRMS (ESI) calcd for C$_{23}$H$_{22}$N$_2$O$_2$: 381.1579 (M + Na$^+$), found: 381.1579.
1-(8-Methyl-5-phenylH-pyrazolo[5,1-a]isoquinolin-1-yl)ethanone (3x)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 2.54 (s, 3H), 2.70 (s, 3H), 7.19 (s, 1H), 7.49–7.55 (m, 5H), 7.78 (d, $J = 7.8$ Hz, 2H), 8.41 (s, 1H), 9.85 (d, $J = 8.7$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 21.7, 29.6, 115.8, 116.7, 121.9, 126.5, 127.9, 128.4, 129.3, 129.4, 129.6, 131.2, 133.5, 138.0, 138.9, 140.2, 145.5, 191.9; HRMS (ESI) calcd for C$_{20}$H$_{16}$N$_2$O: 323.1160 (M + Na$^+$), found: 323.1157.

Butyl 5-cyclopropyl-8-methylH-pyrazolo[5,1-a]isoquinoline-1-carboxylate (3y)

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 0.87–0.91 (m, 2H), 1.01 (t, $J = 7.3$ Hz, 3H), 1.17–1.22 (m, 2H), 1.51–1.53 (m, 2H), 1.80-1.82 (m, 2H), 2.50 (s, 3H), 2.64–2.71 (m, 1H), 4.37 (t, $J = 6.4$ Hz, 2H), 6.74 (s, 1H), 7.40 (d, $J = 7.8$ Hz, 1H), 7.43 (s, 1H), 8.50 (s, 1H), 9.67 (d, $J = 8.3$ Hz, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 7.1, 11.6, 13.8, 19.3, 21.6, 30.8, 64.1, 107.4, 109.3, 120.9, 125.9, 127.4, 128.5, 130.9, 139.1, 139.3, 140.5, 144.8, 164.0; HRMS (ESI) calcd for C$_{20}$H$_{22}$N$_2$O$_2$: 345.1579 (M + Na$^+$), found: 345.1573.
Butyl 5-butyl-8-methylH-pyrazolo[5,1-\(a\)]isoquinoline-1-carboxylate (3z)

\(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 0.97–1.03 (m, 6H), 1.46–1.55 (m, 4H), 1.78–1.85 (m, 4H), 2.51 (s, 3H), 3.15 (t, \(J = 7.8\) Hz, 2H), 4.36 (t, \(J = 6.4\) Hz, 2H), 6.89 (s, 1H), 7.41 (d, \(J = 8.3\) Hz, 1H), 7.45 (s, 1H), 8.45 (s, 1H), 9.67 (d, \(J = 8.7\) Hz, 1H); \(^{13}\)C NMR (100 MHz, CDCl\(_3\)) \(\delta\) 13.8, 13.9, 19.3, 21.6, 22.5, 29.0, 30.88, 30.90, 64.1, 107.3, 111.9, 121.1, 125.8, 127.4, 128.4, 131.0, 139.1, 139.2, 139.3, 144.6, 164.0; HRMS (ESI) calcd for C\(_{21}\)H\(_{26}\)N\(_2\)O\(_2\): 361.1892 (M + Na\(^+\)), found: 361.1885.