Supporting Information


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General information

The $^1$H NMR, $^{13}$C NMR and $^{19}$F NMR spectra were tested by the Bruker AVANCE III-400 spectrometer. Tetramethylsilane (TMS) was selected as the internal reference and chemical shifts (δ) were reported in ppm. The abbreviations of the signal couplings were used in s (singlet); d (doublet); t (triplet) and m (multiplet). The high resolution mass spectra (HRMS) were tested by the ESI mode of the Micromass Q-Tof instrument. IR spectra were detected with the ATR mode of the Nicolet iS50 FT-IR of Thermo Scientific. Chemicals were purchased from chemical suppliers without purification. The 5-W blue LEDs was afforded by the supermarket. All of experiments were carried out under Argon atmosphere unless otherwise explanation. All starting compounds were synthesized according to the literature.[1]

Characterization of unknown starting materials

2-(4-bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1c): The compound 1c was synthesized according the previous literature,[1] as light red oil. IR (neat, cm$^{-1}$): 2983, 2934, 1736, 1394, 1233, 1043, 937, 812. $^1$H NMR (400 MHz, CDCl$_3$) δ = 7.61 (d, $J$ = 2.4 Hz, 1H), 7.36 – 7.26 (m, 1H), 7.21 – 7.12 (m, 3H), 7.08 – 7.02 (m, 1H), 7.01 – 6.89 (m, 2H), 5.69 (dd, $J$ = 17.6, 1.2 Hz, 1H), 5.26 (dd, $J$ = 11.2, 1.2 Hz, 1H), 4.09 (s, 2H), 3.21 (t, $J$ = 6.0 Hz, 2H), 2.96 (t, $J$ = 6.0 Hz, 2H). $^{13}$C NMR (101 MHz, CDCl$_3$) δ = 149.6 , 134.8 , 134.5, 134.4, 133.3, 131.2, 129.6, 129.0, 126.4, 126.4, 125.9, 120.7, 116.1, 114.9, 54.3, 50.6, 29.4. HRMS (ESI) Calcd for C$_{17}$H$_{17}$BrN [M+H]$^+$: 314.0539, 316.0518; found: 314.0533, 316.0517.
2-(3-fluoro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1d): The compound 1d was synthesized according the previous literature,\textsuperscript{[1]} as light red oil. IR (neat, cm\textsuperscript{-1}): 2984, 2941, 1736, 1372, 1233, 1043, 937, 847. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.61 (d, \(J = 2.4\) Hz, 1H), 7.33 (dd, \(J = 8.4, 2.4\) Hz, 1H), 7.25 – 7.11 (m, 3H), 7.10 – 7.03 (m, 1H), 7.03 – 6.90 (m, 2H), 5.70 (dd, \(J = 17.6, 1.2\) Hz, 1H), 5.27 (dd, \(J = 11.2, 1.2\) Hz, 1H), 4.11 (s, 2H), 3.24 (t, \(J = 6.0\) Hz, 2H), 2.98 (t, \(J = 6.0\) Hz, 2H). \textsuperscript{19}F NMR (376 MHz, CDCl\textsubscript{3}) δ = -119.67. \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ = 149.52, 134.73, 134.46, 134.36, 133.22, 131.11, 129.58, 128.96, 126.40, 126.37, 125.87, 120.66, 116.04, 114.88, 54.26, 50.57, 29.31. HRMS (ESI) Calcd for C\textsubscript{17}H\textsubscript{15}FN [M+H]\textsuperscript{+}: 254.1340, found: 254.1349.

2-(3-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1e): The compound 1e was synthesized according the previous literature,\textsuperscript{[1]} as light red oil. IR (neat, cm\textsuperscript{-1}): 2983, 2941, 1736, 1393, 1233, 1043, 938, 847. \textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3}) δ = 7.20 – 7.12 (m, 3H), 7.12 – 7.08 (m, 2H), 7.08 – 7.03 (m, 1H), 7.01 – 6.93 (m, 1H), 6.80 (dd, \(J = 18.0, 12.0\) Hz, 1H), 5.96 (dd, \(J = 18.0, 2.0\) Hz, 1H), 5.57 (dd, \(J = 12.0, 2.0\) Hz, 1H), 4.14 (s, 2H), 3.28 (t, \(J = 6.0\) Hz, 2H), 2.94 (t, \(J = 6.0\) Hz, 2H). \textsuperscript{13}C NMR (101 MHz, CDCl\textsubscript{3}) δ = 152.8, 134.9, 134.5, 133.8, 131.6, 130.5, 129.0, 128.2, 126.4, 126.4, 125.8, 124.5, 120.5, 117.4, 53.8, 50.3, 29.4. HRMS (ESI) Calcd for C\textsubscript{17}H\textsubscript{17}ClN [M+H]\textsuperscript{+}: 270.1044, 272.1015; found: 270.1040, 272.1015.
8-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1j): The compound 1j was synthesized according the previous literature,[1] as light yellow oil. IR (neat, cm\(^{-1}\)): 2984, 2941, 1736, 1393, 1233, 1043, 938, 847. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.51\) (dd, \(J = 7.6, 1.6\) Hz, 1H), 7.37 (dd, \(J = 7.6, 2\) Hz, 1H), 7.32 – 7.19 (m, 1H), 7.13 – 6.94 (m, 5H), 5.70 (dd, \(J = 17.6, 1.6\) Hz, 1H), 5.23 (dd, \(J = 11.2, 1.6\) Hz, 1H), 4.11 (s, 2H), 3.20 (t, \(J = 5.6\) Hz, 2H), 2.94 (t, \(J = 5.6\) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 150.2, 137.6, 134.7, 134.3, 132.6, 130.0, 128.7, 128.2, 127.5, 127.0, 123.4, 122.8, 119.3, 114.0, 55.2, 50.1, 29.9. HRMS (ESI) Calcd for C\(_{17}\)H\(_{17}\)BrN [M+H]\(^+\): 314.0539, 316.0518, found: 314.0538, 316.0520.

5-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline (1k): The compound 1k was synthesized according the previous literature,[1] as light red oil. IR (neat, cm\(^{-1}\)): 2984, 2941, 1736, 1372, 1233, 1043, 937, 847. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.52\) (dd, \(J = 8.0, 1.2\) Hz, 1H), 7.44 (dd, \(J = 6.0, 3.2\) Hz, 1H), 7.34 – 7.19 (m, 1H), 7.11 – 6.96 (m, 5H), 5.71 (dd, \(J = 18.0, 1.6\) Hz, 1H), 5.24 (dd, \(J = 11.2, 1.6\) Hz, 1H), 4.12 (s, 2H), 3.26 (t, \(J = 6.0\) Hz, 2H), 2.95 (t, \(J = 6.0\) Hz, 2H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 150.0, 137.8, 134.5, 134.2, 132.5, 130.4, 128.6, 127.1, 126.9, 125.6, 125.5, 123.3, 118.8, 114.0, 54.5, 50.8, 30.7. HRMS (ESI) Calcd for C\(_{17}\)H\(_{17}\)BrN [M+H]\(^+\): 314.0539, 316.0518, found: 314.0536, 316.0517.
General procedure for the desired compounds

4 Å molecular sieve (100 mg), fac-Ir(ppy)$_3$ (1 mg, 0.0015 mmol, 0.5 mol %) and anhydrous K$_2$HPO$_4$ (157 mg, 0.9 mmol, 3 equiv) were charged into 10 ml Schlenk tube. The mixture solution of 2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline derivative 1 (0.3 mmol) and dibromide 2 (0.75 mmol, 2.5 equiv) dissolved in the anhydrous DMF (2 mL) was syringed into the Schlenk tube under argon atmosphere. The reaction solution was stirred and irradiated by the 5-W blue LEDs at 25°C. When the starting material 1 was completely consumed by the TLC analysis, reaction solution was quenched by water (25 mL), extracted by ethyl acetate (3 × 20 mL), dried, filtered and collected organic solvent. The organic solvent was removed under reduced pressure. The desired product 3 was afforded by column chromatography on silica gel (PE: EtOAc = 1:35 ~ 1:4).

diethyl 2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)malonate (3a):
According to the general procedure using 2-(2-vinylphenyl)-1,2,3,4-tetrahydro isoquinoline 1a (71 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3a (81 mg, 70%) was obtained as yellow

¹H NMR (400 MHz, CDCl₃) δ = 8.31 (s, 1H), 7.67 (d, J = 7.6 Hz, 1H), 7.59 (dt, J = 8.0, 1.2 Hz, 1H), 7.41 (dd, J = 7.6, 5.2, 3.6 Hz, 1H), 7.38 – 7.32 (m, 3H), 7.31 – 7.23 (m, 1H), 7.16 (dd, J = 8.0, 7.0, 1.2 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.27 (t, J = 6.4 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H), 4.10 (q, J = 7.2 Hz, 2H), 3.17 (t, J = 6.4 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.05 (t, J = 7.2 Hz, 3H).

¹³C NMR (101 MHz, CDCl₃) δ = 167.0, 165.6, 140.1, 136.9, 136.0, 134.2, 128.6, 128.5, 128.2 (2C), 127.7, 126.4, 123.2, 123.0, 121.1, 120.5, 109.3, 107.4, 61.2 (2C), 40.0, 29.5, 14.3, 13.8. HRMS (ESI) Calcd for C₂₄H₂₄NO₄ [M+H]⁺: 390.1700, found: 390.1699.

Diethyl 2-((9-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3b): According to the general procedure using 2-(5-bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1b (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3b (112 mg, 80%) was obtained as light yellow solid (mp: 132.0 -132.5 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847. ¹H NMR (400 MHz, CDCl₃) δ = 8.22 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.50 (d, J = 1.6 Hz, 1H), 7.47 – 7.30 (m, 4H), 7.26 – 7.21 (m, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.20 (t, J = 6.4 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 3.14 (t, J = 6.4 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H).

diethyl 2-((10-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (1c): According to the general procedure using 2-(4-bromo-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1c (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3c (84 mg, 60%) was obtained as light yellow solid (mp: 134.0 -134.6 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 917, 847. ¹H NMR (400 MHz, CDCl₃) δ = 8.20 (s, 1H), 7.71 (d, J = 1.6 Hz, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.43 – 7.30 (m, 4H), 7.20 (d, J = 8.8 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.23 (p, J = 7.2 Hz, 4H), 3.16 (t, J = 6.4 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.24 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 166.8, 165.3, 139.0, 137.6, 134.7, 134.1, 128.9, 128.5, 128.3, 127.8, 127.7, 125.7, 124.3, 122.9, 114.4, 110.8, 106.5, 61.7, 61.3, 40.2, 29.4, 14.3, 13.9. HRMS (ESI) Calcd for C₂₄H₂₃BrNO₄ [M+H]⁺: 468.0805, 470.0785, found: 468.0805, 470.0789.

diethyl 2-((11-fluoro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3d): According to the general procedure using 2-(3-fluoro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1d (76 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3d (85 mg, 70%) was obtained as light yellow solid (mp: 175.0 -175.4 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ¹H NMR (400 MHz, CDCl₃) δ =
8.36 (s, 1H), 7.69 (d, J = 6.8 Hz, 1H), 7.34 (ddd, J = 12.8, 5.6, 3.2 Hz, 3H), 7.18 – 7.11 (m, 2H), 6.84 – 6.77 (m, 1H), 4.35 (q, J = 7.2 Hz, 2H), 4.22 (t, J = 6.4 Hz, 2H), 3.93 (q, J = 7.2 Hz, 2H), 3.16 (t, J = 6.4 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 0.99 (t, J = 7.2 Hz, 3H). $^{19}$F NMR (376 MHz, CDCl$_3$) $\delta = -118.15$. $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 165.8, 165.3$ (d, J = 1.4 Hz), 156.9 (d, J = 248.8 Hz), 140.9 (d, J = 1.7 Hz), 138.3 (d, J = 10.6 Hz), 135.7, 134.0, 128.7, 128.1, 128.0, 127.8, 127.6, 125.0 (d, J = 1.1 Hz), 123.3 (d, J = 8.2 Hz), 115.8, 106.6 (d, J = 20.4 Hz), 105.4 (d, J = 3.5 Hz), 61.3, 60.6, 40.6, 29.6, 14.3, 13.7. HRMS (ESI) Calcd for C$_{24}$H$_{23}$FNO$_4$ [M+H]$^+$: 408.1606, found: 408.1603.

diethyl 2-((11-chloro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3e): According to the general procedure using 2-(3-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1e (81 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3e (82 mg, 65%) was obtained as light yellow solid (mp: 115.0 - 115.5 ºC). IR (neat, cm$^{-1}$): 2984, 1736, 1372, 1233, 1043, 938, 847. $^1$H NMR (400 MHz, CDCl$_3$) $\delta = 8.75$ (s, 1H), 7.83 (dd, J = 6.8, 1.6 Hz, 1H), 7.30 – 7.25 (m, 3H), 7.21 (dt, J = 7.6, 3.6 Hz, 1H), 7.15 – 7.10 (m, 2H), 4.34 (q, J = 7.2 Hz, 2H), 4.23 – 4.11 (m, 2H), 3.62 (q, J = 6.8 Hz, 2H), 3.13 (t, J = 6.4 Hz, 2H), 1.35 (t, J = 7.2 Hz, 3H), 0.82 (t, J = 7.2 Hz, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta = 165.2, 165.0, 141.2, 137.0, 134.5, 133.6, 128.5, 128.0, 127.5, 127.3, 127.0, 126.5, 125.1, 123.0, 121.9, 107.8, 106.0, 61.3, 60.4, 40.6, 29.6, 14.2, 13.5. HRMS (ESI) Calcd for C$_{24}$H$_{23}$ClNO$_4$ [M+H]$^+$: 424.1310, 426.1281; found: 424.1309, 426.1283.
diethyl 2-((9-chloro-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3f): According to the general procedure using 2-(5-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1f (81 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3f (99 mg, 80%) was obtained as light yellow solid (mp: 138.0 -138.4 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ¹H NMR (400 MHz, CDCl₃) δ = 8.23 (s, 1H), 7.63 (d, J = 7.6 Hz, 1H), 7.48 (d, J = 8.8 Hz, 1H), 7.43 - 7.30 (m, 4H), 7.10 (dd, J = 8.8, 1.6 Hz, 1H), 4.36 (q, J = 7.2 Hz, 2H), 4.20 (t, J = 6.4 Hz, 2H), 4.13 (q, J = 7.2 Hz, 2H), 3.15 (t, J = 6.4 Hz, 2H), 1.08 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 166.8, 165.3, 139.3, 137.2, 136.5, 134.0, 128.8, 128.4, 128.3, 127.8, 127.7, 124.9, 124.2, 121.5, 121.3, 109.4, 107.2, 61.4, 61.3, 40.2, 29.4, 14.3, 13.8. HRMS (ESI) Calcd for C₂₄H₂₃ClN₂O₄ [M+H]⁺: 424.1310, 426.1281; found: 424.1309, 426.1283.

diethyl 2-((9-(trifluoromethyl)-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)malonate (3g): According to the general procedure using 2-(5-(trifluoromethyl)-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1g (91 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3g (96 mg, 70%) was obtained as light yellow solid (mp: 120.0 -120.5 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847. ¹H NMR (400 MHz,
CDCl₃ δ = 8.24 (s, 1H), 7.66 (dd, J = 14.8, 6.8 Hz, 3H), 7.46 – 7.34 (m, 4H), 4.37 (q, J = 7.2 Hz, 2H), 4.32 (t, J = 6.4 Hz, 2H), 4.12 (q, J = 7.2 Hz, 2H), 3.21 (t, J = 6.4 Hz, 2H), 1.38 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H). ¹³F NMR (376 MHz, CDCl₃) δ = -60.83. ¹³C NMR (101 MHz, CDCl₃) δ = 166.6, 165.2, 139.1, 138.6, 135.0, 134.2, 129.2, 128.7, 128.6, 128.4, 127.9, 127.6, 125.0, 124.9 (q, J = 272.6 Hz), 124.8 (q, J = 32.3 Hz), 120.6, 117.5 (q, J = 3.5 Hz), 107.1, 107.0 (q, J = 4.3 Hz), 61.5, 61.4, 40.3, 29.4, 14.3, 13.8. HRMS (ESI) Calcd for C$_{25}$H$_{23}$F$_3$NO$_4$ [M+H]$^+$: 458.1574, found: 458.1572.

diethyl 2-((9-methyl-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3h): According to the general procedure using 2-(5-methyl-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1h (75 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3h (72 mg, 60%) was obtained as light yellow solid (mp: 149.0 -149.3 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ¹H NMR (400 MHz, CDCl₃) δ = 8.29 (s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.45 (d, J = 8.4 Hz, 1H), 7.39 (dt, J = 7.6, 4.4 Hz, 1H), 7.32 (d, J = 4.0 Hz, 2H), 7.14 (s, 1H), 7.02 – 6.93 (m, 1H), 4.35 (q, J = 7.2 Hz, 2H), 4.22 (t, J = 6.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.14 (t, J = 6.4 Hz, 2H), 2.48 (s, 3H), 1.37 (t, J = 7.2 Hz, 3H), 1.09 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 167.1, 165.7, 140.2, 136.7, 136.4, 134.1, 133.0, 128.4, 128.4, 128.3, 128.2, 127.6, 124.3, 122.9, 122.6, 120.2, 109.3, 107.4, 61.2, 39.9, 29.6, 21.8, 14.3, 13.8. HRMS (ESI) Calcd for C$_{25}$H$_{26}$NO$_4$ [M+H]$^+$: 404.1856, found: 404.1855.
diethyl 2-((9-methoxy-5,6-dihydropyrido[2,1-a]isoquinol-12-yl)methylene) malonate (3i): According to the general procedure using 2-(5-methoxy-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1i (70 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3i (57 mg, 45%) was obtained as light yellow solid (mp: 131.0 -131.4 °C). IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 847, 786. ¹H NMR (400 MHz, CDCl₃) δ = 8.27 (s, 1H), 7.61 (d, J = 7.6 Hz, 1H), 7.48 – 7.44 (m, 1H), 7.39 (dt, J = 8.0, 4.4 Hz, 1H), 7.34 – 7.29 (m, 2H), 6.83 – 6.76 (m, 2H), 4.35 (q, J = 7.2 Hz, 2H), 4.21 (t, J = 6.4 Hz, 2H), 4.15 (q, J = 7.2 Hz, 2H), 3.89 (s, 3H), 3.15 (t, J = 6.4 Hz, 2H), 1.37 (t, J = 7.2 Hz, 3H), 1.08 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 167.1, 165.6, 157.0, 140.0, 137.0, 136.4, 133.8, 128.3, 128.2, 128.2, 127.6, 122.9, 121.3, 120.6, 110.7, 110.4, 107.5, 92.9, 61.2, 55.7, 40.1, 29.6, 14.3, 13.8. HRMS (ESI) Calcd for C₂₅H₂₆NO₅ [M+H]^+: 420.1805, found: 420.1804.

diethyl 2-((1-bromo-5,6-dihydropyrido[2,1-a]isoquinol-12-yl)methylene) malonate (3j): According to the general procedure using 8-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1j (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3j (116 mg, 83%) was obtained as light yellow solid (mp: 145.0 -145.3 °C). IR (neat, cm⁻¹): 2984, 1736, 1373, 1233, 1043, 938, 847. ¹H NMR (400 MHz, CDCl₃) δ = 8.09
(s, 1H), 7.70 – 7.59 (m, 2H), 7.35 (d, \( J = 8.4 \) Hz, 1H), 7.28 (t, \( J = 8.8 \) Hz, 2H), 7.17 (q, \( J = 8.0 \) Hz, 2H), 4.31 (q, \( J = 7.2 \) Hz, 2H), 4.17 - 4.11 (m, 2H), 3.96 (q, \( J = 7.2 \) Hz, 2H), 2.97 (t, \( J = 6.4 \) Hz, 2H), 1.33 (t, \( J = 7.2 \) Hz, 3H), 1.06 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 166.9, 165.6, 141.9, 139.2, 136.4, 135.8, 133.8, 129.9, 129.7, 126.7, 123.3, 122.0, 121.1, 120.5, 109.5, 108.9, 61.2, 60.9, 40.4, 31.8, 14.3, 13.8. HRMS (ESI) Calcd for C\(_{24}\)H\(_{23}\)BrNO\(_4\) [M+H]\(^{+}\): 468.0805, 470.0785, found: 468.0802, 470.0782.

diethyl 2-((4-bromo-5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3k): According to the general procedure using 5-bromo-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1k (94 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3k (91 mg, 65%) was obtained as light yellow solid (mp: 177.0 -177.6 °C). IR (neat, cm\(^{-1}\))): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \( \delta = 8.21 \) (s, 1H), 7.64 – 7.56 (m, 3H), 7.36 (d, \( J = 8.4 \) Hz, 1H), 7.30 – 7.25 (m, 2H), 7.20 – 7.12 (m, 1H), 4.36 (q, \( J = 7.2 \) Hz, 2H), 4.27 (t, \( J = 6.4 \) Hz, 2H), 4.12 (q, \( J = 7.2 \) Hz, 2H), 3.31 (t, \( J = 6.4 \) Hz, 2H), 1.37 (t, \( J = 7.2 \) Hz, 3H), 1.06 (t, \( J = 7.2 \) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \( \delta = 166.7, 165.4, 139.6, 135.8, 135.3, 133.6, 132.4, 130.2, 128.7, 127.4, 126.5, 124.3, 124.2, 123.4, 121.3, 120.5, 109.4, 107.9, 61.4, 61.3, 39.6, 29.3, 14.3, 13.8. HRMS (ESI) Calcd for C\(_{24}\)H\(_{23}\)BrNO\(_4\) [M+H]\(^{+}\): 468.0805, 470.0785, found: 468.0804, 470.0783.
diethyl 2-((2,3-dimethoxy-5,6-dihygroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3I): According to the general procedure using 6,7-dimethoxy-2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1I (88 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2a (237 mg, 0.75 mmol, 2.5 equiv), the desired product 3I (87 mg, 65%) was obtained as light yellow solid (mp: 140.0 -140.5 °C). IR (neat, cm\(^{-1}\)): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.41\) (s, 1H), 7.55 (d, \(J = 8.0\) Hz, 1H), 7.33 (d, \(J = 8.0\) Hz, 1H), 7.27 –7.22 (m, 2H), 7.15 (ddd, \(J = 8.0, 7.2, 1.2\) Hz, 1H), 6.85 (s, 1H), 4.33 (q, \(J = 7.2\) Hz, 2H), 4.24 (t, \(J = 6.4\) Hz, 2H), 4.17 (q, \(J = 7.2\) Hz, 2H), 3.96 (s, 6H), 3.10 (t, \(J = 6.4\) Hz, 2H), 1.35 (t, \(J = 7.2\) Hz, 3H), 1.10 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta =\) 167.1, 165.6, 149.4, 148.2, 140.0, 137.7, 136.1, 127.3, 126.5, 122.7, 121.8, 121.1, 120.6, 120.3, 111.5, 111.3, 109.2, 106.2, 61.2, 56.0, 40.1, 29.1, 14.4, 13.8. HRMS (ESI) Calcd for C\(_{26}\)H\(_{28}\)NO\(_6\) [M+H]\(^+\): 450.1911, found: 450.1911.

diisopropyl 2-((9-chloro-5,6-dihygroindolo[2,1-a]isoquinolin-12-yl)methylene) malonate (3m): According to the general procedure using 2-(5-chloro-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1f (81 mg, 0.3 mmol) and diethyl 2,2-dibromomalonate 2b (258 mg, 0.75 mmol, 2.5 equiv), the desired product 3m (108 mg, 80%) was obtained as light yellow solid (mp: 166.0 -166.5 °C). IR (neat, cm\(^{-1}\)): 2984, 1736, 1372, 1232, 1043, 938, 847. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 8.16\)
(s, 1H), 7.64 (d, J = 7.6 Hz, 1H), 7.52 (d, J = 8.8 Hz, 1H), 7.42 – 7.29 (m, 4H), 7.09 (dd, J = 8.8, 1.6 Hz, 1H), 5.23 (q, J = 6.4 Hz, 1H), 5.05 (p, J = 6.4 Hz, 1H), 4.20 (t, J = 6.4 Hz, 2H), 3.13 (d, J = 6.4 Hz, 2H), 1.36 (d, J = 6.4 Hz, 6H), 1.17 (d, J = 6.4 Hz, 6H). 13C NMR (101 MHz, CDCl3) δ = 166.4, 164.9, 138.5, 136.9, 136.4, 134.0, 128.8, 128.7, 128.3, 127.9, 127.7, 125.5, 124.9, 121.5, 121.3, 109.4, 107.2, 68.9, 68.9, 40.2, 29.4, 22.0, 21.6. HRMS (ESI) Caled for C26H27ClNO4 [M+H]+: 452.1623, 454.1594; found: 452.1620, 454.1593.

ethyl (E)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)butanoate (3n: E): According to the general procedure using 2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1a (71 mg, 0.3 mmol) and ethyl 2,2-dibromobutanoate 2e (204 mg, 0.75 mmol, 2.5 equiv), the desired product 3n: E (28 mg, 27.5%) was obtained as light yellow oil. IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847. 1H NMR (400 MHz, CDCl3) δ = 7.90 (s, 1H), 7.74 (d, J = 7.6 Hz, 1H), 7.49 (d, J = 8.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.17 – 7.13 (m, 1H), 4.34 (q, J = 7.2 Hz, 2H), 4.28 (t, J = 6.4 Hz, 2H), 3.19 (t, J = 6.4 Hz, 2H), 2.49 (q, J = 7.2 Hz, 2H), 1.39 (t, J = 7.2 Hz, 3H), 0.98 (t, J = 7.2 Hz, 3H). 13C NMR (101 MHz, CDCl3) δ = 168.4, 135.8, 135.8, 133.3, 132.8, 132.7, 129.2, 128.2, 127.6, 127.4, 126.9, 126.8, 122.3, 120.4, 120.1, 109.1, 107.8, 60.5, 40.1, 29.6, 22.3, 14.4, 13.7. HRMS (ESI) Caled for C23H24NO2 [M+H]+: 346.1802, found: 346.1798.
ethyl (Z)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)butanoate (3n: Z):
the desired product 3n: Z (28 mg, 27.5%) was obtained as light yellow oil. IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847. ¹H NMR (400 MHz, CDCl₃) δ = 7.80 (d, J = 7.6 Hz, 1H), 7.41 (d, J = 8.0 Hz, 1H), 7.38 – 7.23 (m, 4H), 7.20 (ddd, J = 8.4, 7.2, 1.2 Hz, 1H), 7.10 – 7.02 (m, 2H), 4.26 (t, J = 6.4 Hz, 2H), 3.89 (q, J = 7.2 Hz, 2H), 3.15 (t, J = 6.4 Hz, 2H), 2.64 (qd, J = 7.2, 1.2 Hz, 2H), 1.29 (t, J = 7.2 Hz, 3H), 0.75 (t, J = 7.2 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 169.3, 135.6, 135.5, 133.5, 132.0, 129.5, 129.0, 128.2, 127.5, 127.3, 127.2, 126.9, 122.1, 120.1, 119.9, 109.6, 108.8, 60.2, 40.0, 29.8, 28.2, 14.0, 13.5. HRMS (ESI) Calcd for C₂₃H₂₄NO₂ [M+H]⁺: 346.1802, found: 346.1801.

ethyl (E)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)octanoate (3o: E):
According to the general procedure using 2-(2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1a (71 mg, 0.3 mmol) and ethyl 2,2-dibromo-octanoate 2f (246 mg, 0.75 mmol, 2.5 equiv), the desired product 3o: E (25 mg, 21%) was obtained as light yellow oil. IR (neat, cm⁻¹): 2984, 1736, 1372, 1233, 1043, 938, 847, 786. ¹H NMR (400 MHz, CDCl₃) δ = 7.93 (s, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.47 (d, J = 8.0 Hz, 1H), 7.38 – 7.31 (m, 2H), 7.30 – 7.24 (m, 3H), 7.18 – 7.12 (m, 1H), 4.33 (q, J = 7.2 Hz, 2H), 4.28 (t, J = 6.4 Hz, 2H), 3.19 (t, J = 6.4 Hz, 2H), 2.53 – 2.42 (m, 2H), 1.38 (t, J = 7.2 Hz, 5H), 1.28 (dd, J = 13.2, 5.6 Hz, 3H), 1.09 – 1.04 (m, 4H), 0.70 (t, J = 6.8 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ = 168.5,
ethyl (Z)-2-((5,6-dihydroindolo[2,1-a]isoquinolin-12-yl)methylene)octanoate (3o: Z): the desired product 3o: Z (35 mg, 29%) was obtained as light yellow oil. IR (neat, cm\(^{-1}\)): 2984, 1736, 1372, 1233, 1043, 938, 847. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta = 7.82\) (d, \(J = 7.6\) Hz, 1H), 7.41 (d, \(J = 8.0\) Hz, 1H), 7.35 – 7.25 (m, 4H), 7.22 – 7.17 (m, 1H), 7.08 (dd, \(J = 8.0\), 1.2 Hz, 1H), 7.01 (s, 1H), 4.25 (t, \(J = 6.4\) Hz, 2H), 3.88 (q, \(J = 7.2\) Hz, 2H), 3.15 (t, \(J = 6.4\) Hz, 2H), 2.60 (t, \(J = 8.0\) Hz, 2H), 1.66 (p, \(J = 7.2\) Hz, 2H), 1.46 (dd, \(J = 8.4\), 5.6 Hz, 2H), 1.40 – 1.34 (m, 4H), 0.95 – 0.89 (m, 3H), 0.75 (t, \(J = 7.2\) Hz, 3H). \(^{13}\)C NMR (101 MHz, CDCl\(_3\)) \(\delta = 169.3, 135.6, 134.2, 133.5, 132.0, 129.8, 129.5, 128.2, 127.5, 127.3, 127.1, 127.0, 122.1, 120.1, 119.9, 109.7, 108.8, 60.2, 40.0, 35.2, 31.8, 29.8, 29.3, 29.0, 22.7, 14.2, 13.5. HRMS (ESI) Calcd for C\(_{27}\)H\(_{32}\)NO\(_2\) [M+H]\(^+\): 402.2428, found: 402.2433.

The 2.6 mmol scale reaction and Stern-Volmer quenching studies

(a) The 2.6 mmol reaction

4 Å molecular sieve (400 mg), \(\text{fac-Ir(ppy)}_3\) (10 mg, 0.5 mol %) and anhydrous K\(_2\)HPO\(_4\) (1300 mg, 7.7 mmol, 3 equiv) were charged into 35 ml Schlenk tube. The mixture solution of ortho-tetrahydroisoquinoline-substituted styrene 1a (600 mg, 2.6 mmol) and diethyl 2,2-dibromomalonate 2a (2000 mg, 6.4 mmol, 2.5 equiv) dissolved
in the anhydrous DMF (10 mL) was syringed into the Schlenk tube under argon atmosphere. The reaction solution was stirred and irradiated by the 40-W blue LEDs at 25°C. When the starting material 1a was completely consumed by the TLC analysis, reaction solution was quenched by water (35 mL), extracted by ethyl acetate (3 × 30 mL), dried, filtered and collected organic solvent. The organic solvent was removed under reduced pressure. The desired product 3 (620 mg, 63%) was afforded by column chromatography on silica gel.

(b) Stern-Volmer quenching studies

The Stern-Volmer quenching dates were measured by Cary Eclipse fluorescent spectrophotometer (F-7000, HITACHI). Experiments were conducted in 0.05mmol/L of fac-Ir(ppy)₃/DMF at 25 °C and the excitation wavelength was 375 nm. The quenching’s concentration in DMF were 0, 0.17 mmol/L, 0.85 mmol/L, 1.7 mmol/L, 3.3 mmol/L, 5.0 mmol/L, 6.6 mmol/L.

[Graphs showing Stern-Volmer quenching of fac-Ir(ppy)₃]

Stern-Volmer quenching of fac-Ir(ppy)₃ by diethyl 2,2-dibromomalonate 2a

Stern-Volmer quenching of fac-Ir(ppy)₃ by 2-(5-methoxy-2-vinylphenyl)-1,2,3,4-tetrahydroisoquinoline 1i
X-ray crystal diffraction data

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Reference

NMR spectra of the unknown compounds

(a) The NMR spectra of the unknown starting materials
(b) The NMR spectra of the desired compounds
3n: E
containing a little Z

3n: Z
NOESY spectrum for 3o (E)
NOESY spectrum for 3o (Z)
3o. Z
containing a little Z