Supporting Information

Facile synthesis of 2-vinylindolines via a phosphine-mediated α-umpolung/Wittig olefinication/cyclization cascade process

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I. General Information

Unless otherwise specified, all reactions were carried out under a nitrogen atmosphere at room temperature. All solvents were purified according to the standard procedures. All chemicals which are commercially available were employed without further purification. Thin-layer chromatography (TLC) was performed on silica gel plates (GF254) using UV-light (254 and 365 nm). Flash chromatography was conducted on silica gel (200–300 mesh). $^1$H and $^{13}$C{$^1$H} NMR spectra were recorded on a Bruker 400 MHz spectrometer. Chemical shifts were reported in parts per million (ppm). The $^1$H NMR (400 MHz) chemical shifts were measured relative to residual non-deuterated solvent resonance (CDCl$_3$: $\delta = 7.260$ ppm, (CD$_3$)$_2$CO: $\delta = 2.050$ ppm). The $^{13}$C{$^1$H} NMR (100 MHz) chemical shifts were given using CDCl$_3$ or (CD$_3$)$_2$CO as the internal standard (CDCl$_3$: $\delta = 77.00$ ppm, (CD$_3$)$_2$CO: $\delta = 29.84$ ppm). All high-resolution mass spectra (HR-MS) were obtained on a Fourier Transform Ion Cyclotron Resonance (FT-ICR) mass spectrometer solariX (Bruker Daltonik GmbH, Bremen, Germany). Crystal measurement was performed by Bruker D8 Venture X-ray diffractionmeter.
II. Representative Procedure of the Reaction

To a stirred solution of o-aminobenzaldehyde 1 (0.1 mmol, 1.0 equiv) and allyl carbonate 2 (0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added \( \text{PPh}_2\text{Cy} \) (0.12 mmol, 1.2 equiv) and benzoic acid (20 mol %) at room temperature. After the reaction of the raw material, the reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) to afford compounds 3.
Table S1. Optimization of the reaction conditions.\(^a\)

<table>
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<th>Entry</th>
<th>Phosphine</th>
<th>Solvent</th>
<th>Additive</th>
<th>Yield [%](^b)</th>
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<tr>
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</table>

\(^a\)Unless otherwise stated, all reactions were performed with 1a (0.1 mmol), 2a (0.15 mmol), the phosphine reagent (0.12 mmol) and the additive (20 mol%) in the solvent specified (2.0 mL) at room temperature. \(^b\)Isolated yield. \(^c\)The additive (10 mol%) in the solvent specified (2.0 mL). \(^d\)The additive (30 mol%) in the solvent specified (2.0 mL).
III. Analytical Data

*Ethyl 2-(1-tosylindolin-2-yl)acrylate (3a)*

The 3a was prepared according to the general procedure described above using 1a (27.5 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (32.5 mg, 88% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6).

**¹H NMR (400 MHz, CDCl₃)** δ 7.73 (d, J = 8.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.34 (s, 1H), 6.04 (s, 1H), 5.16 – 5.11 (m, 1H), 4.30 – 4.16 (m, 1H), 3.10 (dd, J = 16.5, 10.2 Hz, 1H), 2.61 (dd, J = 16.5, 3.0 Hz, 1H), 2.36 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.8, 144.1, 141.6, 140.1, 134.7, 131.1, 129.7, 127.9, 127.1, 125.7, 125.2, 124.9, 117.0, 61.3, 61.0, 36.2, 21.5, 14.1. HRMS (ESI) m/z: calcd. for C₂₀H₂₁NO₄SNa⁺ [M+Na]⁺: 394.1083, found 394.1098.

*Isopropyl 2-(1-tosylindolin-2-yl)acrylate (3b)*

The 3b was prepared according to the general procedure described above using 1a (27.5 mg, 0.1 mmol), 2b (36.6 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (32.4 mg, 84% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). **¹H NMR (400 MHz, CDCl₃)** δ 7.72 (d, J = 8.1 Hz, 1H), 7.60 – 7.55 (m, 2H), 7.26 – 7.20 (m, 1H), 7.18 (d, J = 8.1 Hz, 2H), 7.05 – 6.98 (m, 2H), 6.31 (s, 1H), 6.01 (s, 1H), 5.16 – 5.11 (m, 1H), 5.11 – 5.03 (m, 1H), 3.09 (dd, J = 16.5, 10.2 Hz, 1H), 2.61 (dd, J = 16.5, 3.1 Hz, 1H), 2.36 (s, 3H), 1.26 (dd, J = 6.3, 2.9 Hz, 6H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.3, 144.0, 141.6, 140.4, 134.8, 131.2, 129.6, 127.8, 127.1, 125.4, 125.2, 124.9, 117.0, 68.5, 61.4, 36.2, 21.78, 21.75, 21.5. HRMS (ESI) m/z: calcd. for C₂₁H₂₃NO₄SNa⁺ [M+Na]⁺: 408.1240, found 408.1234.
Butyl 2-(1-tosylindolin-2-yl)acrylate (3c)

The 3c was prepared according to the general procedure described above using 1a (27.5 mg, 0.1 mmol), 2c (38.7 mg, 0.15 mmol), PPh2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (33.7 mg, 85% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). 1H NMR (400 MHz, CDCl3) δ 7.73 (d, J = 8.1 Hz, 1H), 7.60 – 7.54 (m, 2H), 7.26 – 7.21 (m, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.06 – 6.98 (m, 2H), 6.33 (s, 1H), 6.03 (s, 1H), 5.17 – 5.11 (m, 1H), 4.23 – 4.12 (m, 2H), 3.09 (dd, J = 16.6, 10.2 Hz, 1H), 2.61 (dd, J = 16.6, 3.1 Hz, 1H), 2.36 (s, 3H), 1.69 – 1.62 (m, 2H), 1.43 – 1.37 (m, 2H), 0.94 (t, J = 7.4 Hz, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 165.8, 144.1, 141.6, 140.1, 134.6, 131.1, 129.6, 127.8, 127.1, 125.6, 125.2, 124.9, 117.0, 64.8, 61.3, 36.2, 30.6, 21.5, 19.2, 13.7. HRMS (ESI) m/z: calcd. for C22H25NO4SNa+ [M+Na]+: 422.1397, found 422.1381.

Tert-Butyl 2-(1-tosylindolin-2-yl)acrylate (3d)

The 3d was prepared according to the general procedure described above using 1a (27.5 mg, 0.1 mmol), 2d (38.7 mg, 0.15 mmol), PPh2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (34.7 mg, 87% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). 1H NMR (400 MHz, CDCl3) δ 7.72 (d, J = 8.2 Hz, 1H), 7.60 – 7.53 (m, 2H), 7.25 – 7.20 (m, 1H), 7.17 (d, J = 8.0 Hz, 2H), 7.05 – 6.97 (m, 2H), 6.22 (s, 1H), 5.96 (s, 1H), 5.16 – 5.08 (m, 1H), 3.05 (dd, J = 16.6, 10.2 Hz, 1H), 2.59 (dd, J = 16.6, 3.0 Hz, 1H), 2.35 (s, 3H), 1.48 (s, 9H). 13C{1H} NMR (100 MHz, CDCl3) δ 165.0, 144.0, 141.6, 141.3, 134.7, 131.3, 129.6, 127.8, 127.1, 125.2, 124.9, 117.1, 81.4, 61.4, 36.2, 28.1, 21.5, 19.2, 13.7. HRMS (ESI) m/z: calcd. for C22H25NO4SNa+ [M+Na]+: 422.1397, found 422.1409.

Cyclohexyl 2-(1-tosylindolin-2-yl)acrylate (3e)

The 3e was prepared according to the general procedure described above using 1a (27.5 mg, 0.1 mmol), 2e (42.6 mg, 0.15 mmol), PPh2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (22.4 mg, 53% yield) after flash column
chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.73 (d, \(J = 8.1\) Hz, 1H), 7.62 – 7.53 (m, 2H), 7.25 – 7.20 (m, 1H), 7.18 (d, \(J = 8.1\) Hz, 2H), 7.07 – 6.96 (m, 2H), 6.32 (s, 1H), 6.01 (s, 1H), 5.20 – 5.08 (m, 1H), 4.93 – 4.81 (m, 1H), 3.08 (dd, \(J = 16.6, 10.2\) Hz, 1H), 2.62 (dd, \(J = 16.6, 3.1\) Hz, 1H), 2.36 (s, 3H), 1.89 – 1.68 (m, 4H), 1.56 – 1.36 (m, 6H). \(^{13}\)C\(^{\{1\}}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.1, 144.0, 141.6, 140.5, 134.7, 131.2, 129.6, 127.8, 127.1, 125.4, 125.2, 124.9, 117.0, 73.2, 61.4, 36.2, 31.5, 25.4, 23.6, 21.6. HRMS (ESI) m/z: calcd. for C\(_{24}\)H\(_{27}\)NO\(_4\)SNa\(^+\) [M+Na]\(^+\): 448.1553, found 448.1551.

**Benzyl 2-(1-tosylindolin-2-yl)acrylate (3f)**

The 3f was prepared according to the general procedure described above using 1a (27.5 mg, 0.1 mmol), 2f (43.9 mg, 0.15 mmol), PPh\(_2\)Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (20.2 mg, 46\% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.74 (d, \(J = 8.1\) Hz, 1H), 7.57 (d, \(J = 8.4\) Hz, 2H), 7.44 – 7.30 (m, 5H), 7.26 – 7.20 (m, 1H), 7.17 (d, \(J = 8.1\) Hz, 2H), 7.05 – 6.97 (m, 2H), 6.40 (s, 1H), 6.08 (s, 1H), 5.22 (d, \(J = 3.0\) Hz, 2H), 5.19 – 5.14 (m, 1H), 3.09 (dd, \(J = 16.6, 10.2\) Hz, 1H), 2.62 (dd, \(J = 16.6, 3.1\) Hz, 1H), 2.36 (s, 3H). \(^{13}\)C\(^{\{1\}}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.6, 144.1, 141.5, 139.9, 135.6, 134.6, 131.0, 129.6, 128.6, 128.3, 128.1, 127.8, 127.1, 126.2, 125.2, 124.9, 117.0, 66.7, 61.2, 36.2, 21.5. HRMS (ESI) m/z: calcd. for C\(_{25}\)H\(_{23}\)NO\(_4\)SNa\(^+\) [M+Na]\(^+\): 456.1240, found 456.1241.

**Ethyl 2-(1-((4-nitrophenyl)sulfonyl)indolin-2-yl)acrylate (3g)**

The 3g was prepared according to the general procedure described above using 1b (30.6 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh\(_2\)Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (25.2 mg, 63\% yield) after flash column chromatography on silica gel.
(PE:EtOAc:DCM = 19:1:6). \textit{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \(\delta\) 8.25 (d, \(J = 8.7\) Hz, 2H), 7.90 (d, \(J = 8.7\) Hz, 2H), 7.74 (d, \(J = 8.1\) Hz, 1H), 7.31 – 7.26 (m, 1H), 7.11 – 7.01 (m, 2H), 6.36 (s, 1H), 6.01 (s, 1H), 5.16 (d, \(J = 7.8\) Hz, 1H), 4.32 – 4.15 (m, 2H), 3.12 (dd, \(J = 16.7, 10.2\) Hz, 1H), 2.68 (dd, \(J = 16.7, 3.0\) Hz, 1H), 1.30 (t, \(J = 7.1\) Hz, 3H).

\textit{\textsuperscript{13}C{\textsuperscript{1}H}} NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 165.5, 150.4, 143.2, 140.6, 139.7, 130.9, 128.3, 128.2, 125.8, 125.67, 125.65, 124.3, 116.6, 61.6, 61.2, 36.2, 14.1.

HRMS (ESI) m/z: calcd. for C\textsubscript{19}H\textsubscript{18}N\textsubscript{2}O\textsubscript{6}SNa\textsuperscript{+} [M+Na]\textsuperscript{+}: 425.0778, found 425.0787.

**Ethyl 2-((1-((2-bromophenyl)sulfonyl)indolin-2-yl)acrylate (3h)**

The 3h was prepared according to the general procedure described above using 1c (33.9 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh\textsubscript{2}Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (23.9 mg, 55% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 121.0 – 122.5 °C. \textit{\textsuperscript{1}H NMR (400 MHz, CDCl\textsubscript{3})} \(\delta\) 8.22 (dd, \(J = 7.9, 1.7\) Hz, 1H), 7.66 (d, \(J = 7.7\) Hz, 1H), 7.47 – 7.41 (m, 1H), 7.39 – 7.33 (m, 1H), 7.28 (s, 1H), 7.12 – 7.04 (m, 2H), 6.97 – 6.91 (m, 1H), 6.32 (s, 1H), 6.02 (d, \(J = 1.4\) Hz, 1H), 5.75 (d, \(J = 10.0\) Hz, 1H), 4.32 – 4.17 (m, 2H), 3.62 (dd, \(J = 16.3, 10.0\) Hz, 1H), 2.81 (dd, \(J = 16.3, 2.0\) Hz, 1H), 1.30 (t, \(J = 7.1\) Hz, 3H). \textit{\textsuperscript{13}C{\textsuperscript{1}H}} NMR (100 MHz, CDCl\textsubscript{3}) \(\delta\) 165.6, 140.7, 139.8, 138.0, 135.7, 134.0, 133.3, 129.9, 127.5, 127.4, 125.6, 125.3, 123.9, 120.1, 114.2, 63.1, 61.0, 36.0, 14.1. HRMS (ESI) m/z: calcd. for C\textsubscript{19}H\textsubscript{18}BrNO\textsubscript{4}SNa\textsuperscript{+} [M+Na]\textsuperscript{+}: 458.0032, found 458.0038.

**Ethyl 2-((1-((3-bromophenyl)sulfonyl)indolin-2-yl)acrylate (3i)**

The 3i was prepared according to the general procedure described above using 1d (33.9 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh\textsubscript{2}Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (24.0 mg, 55% yield) after flash column chromatography on silica gel.
Ethyl 2-(1-(phenylsulfonyl)indolin-2-yl)acrylate (3j)

The 3j was prepared according to the general procedure described above using 1e (26.1 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (23.6 mg, 66% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 128.0 – 131.0 °C. 1H NMR (400 MHz, CDCl3) δ 7.75 (d, J = 8.1 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.57 – 7.50 (m, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.19 (m, 1H), 7.08 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.34 (s, 1H), 6.03 (s, 1H), 5.21 – 5.10 (m, 1H), 4.30 – 4.16 (m, 2H), 3.08 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 165.7, 141.4, 140.0, 137.6, 133.2, 131.1, 129.0, 127.9, 127.0, 125.7, 125.3, 125.0, 116.9, 61.3, 61.0, 36.2, 14.1. HRMS (ESI) m/z: calcd. for C19H18BrNO4SNa+ [M+Na]+: 458.0032, found 458.0031.

Ethyl 2-(1-((4-methoxyphenyl)sulfonyl)indolin-2-yl)acrylate (3k)

The 3k was prepared according to the general procedure described above using 1f (29.1 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh2Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (34.4 mg, 89% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 128.0 – 131.0 °C. 1H NMR (400 MHz, CDCl3) δ 7.75 (d, J = 8.1 Hz, 1H), 7.72 – 7.67 (m, 2H), 7.57 – 7.50 (m, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.19 (m, 1H), 7.08 – 7.01 (m, 1H), 7.01 – 6.96 (m, 1H), 6.34 (s, 1H), 6.03 (s, 1H), 5.21 – 5.10 (m, 1H), 4.30 – 4.16 (m, 2H), 3.08 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H). 13C{1H} NMR (100 MHz, CDCl3) δ 165.7, 141.4, 140.0, 137.6, 133.2, 131.1, 129.0, 127.9, 127.0, 125.7, 125.3, 125.0, 116.9, 61.3, 61.0, 36.2, 14.1. HRMS (ESI) m/z: calcd. for C19H19BrNO4SNa+ [M+Na]+: 380.0927, found 380.0935.
(PE:EtOAc:DCM = 19:1:6). ¹H NMR (400 MHz, CDCl₃) δ 7.73 (d, J = 8.1 Hz, 1H), 7.65 – 7.59 (m, 2H), 7.25 – 7.20 (m, 1H), 7.06 – 6.97 (m, 2H), 6.88 – 6.81 (m, 2H), 6.33 (s, 1H), 6.04 (s, 1H), 5.16 – 5.09 (m, 1H), 4.30 – 4.15 (m, 2H), 3.81 (s, 3H), 3.11 (dd, J = 16.6, 10.2 Hz, 1H), 2.62 (dd, J = 16.6, 3.0 Hz, 1H), 1.29 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.8, 163.2, 141.6, 140.2, 131.1, 129.24, 129.16, 127.8, 125.6, 125.2, 124.9, 117.0, 114.2, 61.2, 60.9, 55.5, 36.2, 14.1. HRMS (ESI) m/z: calcd. for C₂₀H₂₁NO₅SNa⁺ [M+Na]⁺ 410.1033, found 410.1025.

**Ethyl 2-(1-(1,1'-biphenyl-4-ylsulfonyl)indolin-2-y)acrylate (3l)**

The 3l was prepared according to the general procedure described above using 1g (33.7 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (22.3 mg, 51% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 122.0 – 123.8 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.82 – 7.74 (m, 3H), 7.60 (d, J = 8.4 Hz, 2H), 7.55 (d, J = 7.2 Hz, 2H), 7.45 (t, J = 7.3 Hz, 2H), 7.39 (t, J = 7.2 Hz, 1H), 7.29 – 7.26 (m, 1H), 7.04 (q, J = 7.6 Hz, 2H), 6.36 (s, 1H), 6.07 (s, 1H), 5.28 – 5.16 (m, 1H), 4.33 – 4.17 (m, 2H), 3.16 (dd, J = 16.6, 10.2 Hz, 1H), 2.66 (dd, J = 16.6, 2.9 Hz, 1H), 1.30 (t, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.7, 145.9, 141.4, 140.1, 138.9, 136.1, 131.1, 129.0, 128.5, 127.9, 127.6, 127.5, 127.2, 125.7, 125.3, 125.0, 116.9, 61.3, 61.0, 36.2, 14.1. HRMS (ESI) m/z: calcd. for C₂₅H₂₃NO₄SNa⁺ [M+Na]⁺ 456.1240, found 456.1240.

**Ethyl 2-(1-(mesitylsulfonyl)indolin-2-y)acrylate (3m)**

The 3m was prepared according to the general procedure described above using 1h (30.3 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (27.9 mg, 70% yield) after flash column chromatography on silica gel.
Ethyl 2-(1-(naphthalen-1-ylsulfonyl)indolin-2-yl)acrylate (3n)

The 3n was prepared according to the general procedure described above using 1i (31.1 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (24.9 mg, 62% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 80.5 – 82.1 °C. ¹H NMR (400 MHz, CDCl₃) δ 8.56 (d, J = 8.4 Hz, 1H), 8.26 – 8.19 (m 1H), 8.02 (d, J = 8.1 Hz, 1H), 7.88 – 7.83 (m 1H), 7.66 (d, J = 8.1 Hz, 1H), 7.53 – 7.45 (m, 3H), 7.24 – 7.16 (m 1H), 7.02 – 6.91 (m, 2H), 6.27 (s, 1H), 5.99 (d, J = 1.4 Hz, 1H), 5.36 – 5.29 (m 1H), 4.26 – 4.13 (m, 2H), 3.01 (dd, J = 16.4, 9.9 Hz, 1H), 2.60 (dd, J = 16.3, 2.2 Hz, 1H), 1.27 (t, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.6, 141.6, 139.5, 134.6, 134.6, 134.3, 133.8, 130.7, 130.4, 128.8, 128.7, 128.0, 127.6, 126.9, 125.7, 125.3, 124.7, 124.0, 116.6, 60.9, 36.1, 14.1. HRMS (ESI) m/z: calcd. for C₂₃H₂₁NO₄SNa⁺ [M+Na⁺]: 430.1083, found 430.1087.

Ethyl 2-(1-(methylsulfonyl)indolin-2-yl)acrylate (3o)

The 3o was prepared according to the general procedure described above using 1j (19.9 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (18.2 mg, 62% yield).
yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.52 (d, $J = 8.0$ Hz, 1H), 7.26 – 7.21 (m, 1H), 7.17 (d, $J = 7.4$ Hz, 1H), 7.11 – 7.04 (m, 1H), 6.34 (s, 1H), 5.98 (s, 1H), 5.29 – 5.17 (m, 1H), 4.33 – 4.17 (m, 2H), 3.69 (dd, $J = 16.7$, 10.4 Hz, 1H), 2.87 (s, 1H), 2.72 (dd, $J = 17.1$, 3.0 Hz, 1H), 2.37 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 165.5, 144.6, 142.3, 139.9, 135.0, 134.4, 130.5 (q, $J = 33$ Hz), 129.9, 127.1, 126.0, 125.5, 123.9 (d, $J = 270$ Hz), 121.7 (q, $J = 4$ Hz), 113.4 (q, $J = 33$ Hz), 61.7, 61.1, 36.2, 21.6, 14.1. HRMS (ESI) m/z: calcd. for C$_{14}$H$_{17}$NO$_4$SNa$^+$ [M+Na$^+$]: 318.0770, found 318.0770.

Ethyl 2-(1-tosyl-6-(trifluoromethyl)indolin-2-yl)acrylate (3p)

The 3p was prepared according to the general procedure described above using 1k (34.3 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh$_2$Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a reddish brown oily liquid (24.9 mg, 57% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6).

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.97 (s, 1H), 7.59 (d, $J = 8.3$ Hz, 2H), 7.28 (d, $J = 7.8$ Hz, 1H), 7.22 (d, $J = 8.0$ Hz, 2H), 7.10 (d, $J = 7.8$ Hz, 1H), 6.37 (s, 1H), 6.03 (s, 1H), 5.26 – 5.13 (m, 1H), 4.33 – 4.16 (m, 2H), 3.19 (dd, $J = 17.1$, 10.4 Hz, 1H), 2.72 (dd, $J = 17.1$, 3.0 Hz, 1H), 2.37 (s, 3H), 1.30 (d, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$165.5, 144.6, 142.3, 139.9, 135.0, 134.4, 130.5 (q, $J = 33$ Hz), 129.9, 127.1, 126.0, 125.5, 123.9 (d, $J = 270$ Hz), 121.7 (q, $J = 4$ Hz), 113.4 (q, $J = 33$ Hz), 61.7, 61.1, 36.2, 21.6, 14.1. $^{19}$F{$^1$H} NMR (376 MHz, CDCl$_3$) $\delta$ -62.2. HRMS (ESI) m/z: calcd. for C$_{21}$H$_{20}$F$_3$NO$_4$SNa$^+$ [M+Na$^+$]: 462.0957, found 462.0967.

Ethyl 2-(6-fluoro-1-tosylindolin-2-yl)acrylate (3q)

The 3q was prepared according to the general procedure described above using 1l (29.3 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh$_2$Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a white solid (19.7 mg, 51% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 79.2 – 80.2 °C. $^1$H
NMR (400 MHz, CDCl₃) δ 7.61 (d, J = 8.2 Hz, 2H), 7.50 – 7.44 (m, 1H), 7.22 (d, J = 8.0 Hz, 2H), 6.95 – 6.89 (m, 1H), 6.75 – 6.67 (m, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.20 – 5.14 (m, 1H), 4.30 – 4.16 (m, 2H), 3.09 (dd, J = 16.3, 10.4 Hz, 1H), 2.60 (dd, J = 16.3, 3.2 Hz, 1H), 2.38 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).

13C{¹H} NMR (100 MHz, CDCl₃) δ 165.6, 163.6 (d, J = 242 Hz), 144.4, 142.9 (d, J = 11 Hz), 140.0, 134.6, 129.8, 127.1, 126.2 (d, J = 3 Hz), 125.8, 125.8 (d, J = 3 Hz), 111.5 (d, J = 23 Hz), 104.7 (d, J = 28 Hz), 62.2, 61.0, 35.6, 21.6, 14.1. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -113.6. HRMS (ESI) m/z: calcd. for C₂₀H₂₀FNO₄SH⁺ [M+H]⁺: 406.0874, found 406.0863.

Ethyl 2-(6-chloro-1-tosylindolin-2-yl)acrylate (3r)

The 3r was prepared according to the general procedure described above using 1m (30.9 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (19.5 mg, 48% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 87.2 – 88.3 °C. ¹H NMR (400 MHz, CDCl₃) δ 7.74 (d, J = 1.9 Hz, 1H), 7.63 – 7.58 (m, 2H), 7.23 (d, J = 8.0 Hz, 2H), 6.99 (dd, J = 8.0, 1.9 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.18 – 5.11 (m, 1H), 4.30 – 4.15 (m, 2H), 3.08 (dd, J = 16.7, 10.4 Hz, 1H), 2.60 (dd, J = 16.7, 3.2 Hz, 1H), 2.38 (s, 3H), 1.29 (t, J = 7.1 Hz, 3H). ¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.6, 144.4, 142.8, 139.9, 134.5, 129.5, 127.1, 125.9, 125.8, 124.9, 117.0, 61.9, 61.1, 35.8, 21.6, 14.1. HRMS (ESI) m/z: calcd. for C₂₀H₂₀FNO₄SNa⁺ [M+Na]⁺: 412.0989, found 412.0989.

Ethyl 2-(6-bromo-1-tosylindolin-2-yl)acrylate (3s)

The 3s was prepared according to the general procedure described above using 1n (35.3 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (22.3 mg, 50% yield) after flash
column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 95.2 – 96.8 °C. ³¹H NMR (400 MHz, CDCl₃) δ 7.89 (d, J = 1.7 Hz, 1H), 7.62 – 7.58 (m, 2H), 7.23 (d, J = 8.1 Hz, 2H), 7.14 (dd, J = 7.9, 1.8 Hz, 1H), 6.86 (d, J = 7.9 Hz, 1H), 6.35 (s, 1H), 6.01 (s, 1H), 5.16 – 5.11 (m, 1H), 4.30 – 4.16 (m, 2H), 3.05 (dd, J = 8.1 Hz, 2H), 3.10 (s, 3H), 1.30 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.6, 144.7, 144.6, 139.8, 134.6, 131.5, 129.9, 127.0, 126.7 (q, J = 32 Hz), 126.0, 125.5 (q, J = 4 Hz), 122.7, 122.4 (q, J = 4 Hz), 116.0, 61.8, 61.1, 36.0, 21.5, 14.1. ¹⁹F{¹H} NMR (376 MHz, CDCl₃) δ -61.9. HRMS (ESI) m/z: calcd. for C₂₁H₂₀F₃NO₄SNa⁺ [M+Na]⁺: 462.0957, found 462.0962.

**Ethyl 2-(1-tosyl-5-(trifluoromethyl)indolin-2-yl)acrylate (3t)**

The 3t was prepared according to the general procedure described above using 1o (34.3 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (2.3 mg, 53% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). ³¹H NMR (400 MHz, CDCl₃) δ 7.79 (d, J = 8.5 Hz, 1H), 7.61 (d, J = 8.3 Hz, 2H), 7.49 (d, J = 8.4 Hz, 1H), 7.26 – 7.20 (m, 3H), 6.36 (s, 1H), 6.00 (s, 1H), 5.20 (dd, J = 10.4, 3.3 Hz, 1H), 4.30 – 4.16 (m, 2H), 3.22 (dd, J = 8.1 Hz, 2H), 3.22 (dd, J = 8.1 Hz, 2H), 2.38 (s, 3H), 1.28 (t, J = 7.1 Hz, 3H).

¹³C{¹H} NMR (100 MHz, CDCl₃) δ 165.6, 144.7, 144.6, 139.8, 134.6, 131.5, 129.9, 127.8, 127.1, 126.4, 125.8, 121.1, 119.8, 61.8, 61.0, 35.8, 21.6, 14.1. HRMS (ESI) m/z: calcd. for C₂₁H₂₀F₃NO₄SNa⁺ [M+Na]⁺: 462.0957, found 462.0962.

**Ethyl 2-(5-bromo-1-tosylindolin-2-yl)acrylate (3u)**

The 3u was prepared according to the general procedure described above using 1p (35.3 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh₂Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (21.2 mg, 47% yield)
after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 113.7 – 115.0 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J = 8.5\) Hz, 1H), 7.57 (d, \(J = 8.1\) Hz, 2H), 7.36 – 7.31 (m, 1H), 7.21 (d, \(J = 8.0\) Hz, 2H), 7.12 (s, 1H), 6.34 (s, 1H), 6.01 (s, 1H), 5.17 – 5.08 (m, 1H), 4.30-4.16 (m, 2H), 3.08 (dd, \(J = 16.8, 10.3\) Hz, 1H), 2.61 (dd, \(J = 16.9, 3.1\) Hz, 1H), 2.38 (s, 3H), 1.29 (t, \(J = 7.1\) Hz, 3H). \(^1\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.6, 144.4, 140.9, 139.8, 134.4, 133.5, 130.8, 129.8, 128.3, 125.9, 118.2, 117.7, 61.6, 61.1, 36.0, 21.6, 14.1. HRMS (ESI) m/z: calcd. for C\(_{20}\)H\(_{20}\)BrNO\(_4\)SNa\(^+\) [M+Na\(^+\): 472.0189, found 472.0193.

**Ethyl 2-(5-methyl-1-tosylindolin-2-yl)acrylate (3v)**

The 3v was prepared according to the general procedure described above using 1q (28.9 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh\(_2\)Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (23.6 mg, 61% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). m.p.: 165.0 – 165.9 °C. \(^1\)H NMR (400 MHz, CDCl\(_3\)) \(\delta\) 7.60 (d, \(J = 8.2\) Hz, 1H), 7.58 – 7.53 (m, 2H), 7.17 (d, \(J = 8.0\) Hz, 2H), 7.02 (dd, \(J = 8.2, 1.6\) Hz, 1H), 6.80 (s, 1H), 6.32 (s, 1H), 6.03 (s, 1H), 5.14 – 5.08 (m, 1H), 4.30 – 4.16 (m, 2H), 3.02 (dd, \(J = 16.5, 10.1\) Hz, 1H), 2.55 (dd, \(J = 16.5, 3.0\) Hz, 1H), 2.35 (s, 3H), 2.25 (s, 3H), 1.29 (t, \(J = 7.1\) Hz, 3H). \(^1\)C\(^{1}\)H NMR (100 MHz, CDCl\(_3\)) \(\delta\) 165.8, 144.0, 140.2, 139.2, 134.8, 134.7, 131.2, 129.6, 128.4, 127.1, 125.8, 125.5, 116.8, 61.4, 60.9, 36.1, 21.5, 20.9, 14.1. HRMS (ESI) m/z: calcd. for C\(_{21}\)H\(_{23}\)NO\(_4\)SNa\(^+\) [M+Na\(^+\): 408.1240, found 408.1243.

**Ethyl 2-(5-methoxy-1-tosylindolin-2-yl)acrylate (3w)**

The 3w was prepared according to the general procedure described above using 1r (30.5 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh\(_2\)Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow solid (25.6 mg, 64%
yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6).
m.p.: 148.0 – 149.9 °C. $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.8$ Hz, 1H), 7.58 – 7.50 (m, 2H), 7.17 (d, $J = 8.1$ Hz, 2H), 6.76 (dd, $J = 8.8$, 2.7 Hz, 1H), 6.53 (d, $J = 2.6$ Hz, 1H), 6.31 (s, 1H), 6.04 (s, 1H), 5.14 – 5.06 (m, 1H), 4.30 – 4.13 (m, 2H), 3.73 (s, 3H), 2.95 (dd, $J = 16.6$, 10.0 Hz, 1H), 2.52 (dd, $J = 16.7$, 2.8 Hz, 1H), 2.35 (s, 3H), 1.29 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 157.6, 143.9, 139.8, 134.8, 134.4, 133.1, 129.6, 127.1, 125.6, 118.3, 112.9, 110.8, 61.6, 60.9, 55.5, 36.3, 21.5, 14.1. HRMS (ESI) m/z: calcd. for C$_{21}$H$_{23}$NO$_5$Sn$^+$ [M+Na]$^+$: 424.1189, found 424.1182.

Ethyl 2-[(1-tosyl-2,3-dihydro-1H-benzof[f]indol-2-yl)acrylate (3x)

The 3x was prepared according to the general procedure described above using 1s (32.5 mg, 0.1 mmol), 2a (34.5 mg, 0.15 mmol), PPh$_2$Cy (32.2 mg, 1.2 equiv), PhCOOH (2.4 mg, 0.2 equiv) and isolated as a yellow oily liquid (30.3 mg, 72% yield) after flash column chromatography on silica gel (PE:EtOAc:DCM = 19:1:6). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.11 (s, 1H), 7.86 (d, $J = 8.2$ Hz, 1H), 7.68 – 7.62 (m, 3H), 7.48 – 7.42 (m, 2H), 7.37 (ddd, $J = 8.2$, 6.9, 1.3 Hz, 1H), 7.16 (d, $J = 8.0$ Hz, 2H), 6.33 (s, 1H), 6.09 – 6.01 (m, 1H), 5.32 – 5.23 (m, 1H), 4.31 – 4.17 (m, 2H), 3.26 (ddd, $J = 16.8$, 10.0, 1.8 Hz, 1H), 2.82 (dd, $J = 16.8$, 1.8 Hz, 1H), 2.33 (s, 3H), 1.30 (t, $J = 7.1$ Hz, 3H). $^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 165.7, 144.1, 140.1, 140.0, 135.1, 133.5, 131.40, 131.38, 129.7, 127.9, 127.3, 127.0, 126.0, 125.7, 125.0, 124.0, 113.1, 61.7, 61.0, 35.8, 21.5, 14.1. HRMS (ESI) m/z: calcd. for C$_{24}$H$_{23}$NO$_4$Sn$^+$ [M+Na]$^+$: 444.1240, found 444.1249.
IV. Gram-Scale and Synthetic Manipulations

(a) Synthesis of 3a on gram-scale.

To a stirred solution of o-aminobenzaldehyde 1a (4.0 mmol, 1.0 equiv.) and allyl carbonate 2a (6 mmol, 1.5 equiv) were added to toluene (80.0 mL) with PPh₂Cy (1.2 equiv) and PhCOOH (20 mol %), and stirred at room temperature. The reaction mixture was purified by flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) with a yield of 78%.

(b) Synthetic manipulations of 3a.

**Ethyl 3-(p-tolylthio)-2-(1-tosylindolin-2-yl)propanoate (4)**

According to the known procedure, p-Toluenethiol (18.6 mg, 0.15 mmol) and Pyrrolidine (16 μL, 0.2 mmol) were added to a solution of 3a (37.1 mg, 0.1 mmol) in CHCl₃ (4.0 mL) at room temperature. The resulting reaction mixture was stirred at rt for 12 hours. The reaction was quenched with saturated NH₄Cl and the mixture was extracted with CH₂Cl₂. The combined organic phases were dried over Na₂SO₄ and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:2:1) to afford a white solid 4 (46.6 mg, 94% yield, 3:1 d.r.).

m.p.: 99.5 – 101.0 °C. **¹H NMR (400 MHz, CDCl₃)** δ 7.66 (d, J = 8.0 Hz, 1H), 7.47 (d, J = 8.2 Hz, 2H), 7.27 (s, 1H), 7.25 (s, 1H), 7.24 – 7.18 (m, 1H), 7.16 – 7.08 (m, 4H), 7.03 (t, J = 7.3 Hz, 1H), 6.99 (d, J = 7.3 Hz, 1H), 4.55 (ddd, J = 9.7, 4.2, 2.4 Hz, 1H), 3.87 (q, J = 7.1 Hz, 2H), 3.17 (d, J = 6.9 Hz, 2H), 3.03 (ddd, J = 8.0, 6.3, 4.1 Hz, 1H).
1H), 2.81 (dd, \(J = 16.5, 9.7\) Hz, 1H), 2.34 (s, 3H), 2.31 (s, 3H), 1.10 (t, \(J = 7.1\) Hz, 3H). \(^{13}\text{C}\{\text{H}\} \text{NMR (100 MHz, CDCl}_3\) \(\delta 171.1, 144.1, 141.8, 136.5, 134.5, 132.4, 131.8, 130.5, 129.8, 129.6, 127.9, 127.1, 125.3, 124.7, 118.2, 62.4, 61.0, 51.3, 31.8, 31.6, 21.5, 21.0, 13.9.}

**Ethyl 2-(indolin-2-yl)acrylate (5)**

\[\text{3a} \xrightarrow{TfOH, \text{DCE, 90 \degree C}} \text{5, 66\% yield}\]

According to the known procedure.\(^2\) TfOH (30.0 mg, 0.2 mmol) was added to a solution of \textbf{3a} (37.1 mg, 0.1 mmol) in DCE (2.0 mL) at room temperature. The resulting reaction mixture was heated at 90 \degree C and stirred by reflux for 4 hours. The reaction was quenched with saturated NaHCO\(_3\) and the mixture was extracted with CH\(_2\)Cl\(_2\). The combined organic phases were dried over Na\(_2\)SO\(_4\) and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:1:1) to afford a brown oil \textbf{5} (14.3 mg, 66\% yield). \(^1\text{H NMR (400 MHz, CDCl}_3\) \(\delta 7.12 - 7.00\) (m, 2H), 6.73 – 6.68 (m, 1H), 6.65 (d, \(J = 7.7\) Hz, 1H), 6.29 (t, \(J = 1.2\) Hz, 1H), 5.95 (t, \(J = 1.4\) Hz, 1H), 4.78 (t, \(J = 9.0\) Hz, 1H), 4.31 – 4.19 (m, 2H), 4.07 (s, 1H), 3.40 (dd, \(J = 15.6, 9.1\) Hz, 1H), 2.84 (dd, \(J = 15.5, 8.9\) Hz, 1H), 1.33 (t, \(J = 7.1\) Hz, 3H). \(^{13}\text{C}\{\text{H}\} \text{NMR (100 MHz, CDCl}_3\) \(\delta 166.6, 150.4, 142.5, 127.8, 127.4, 124.6, 123.9, 118.9, 109.1, 60.8, 59.0, 36.5, 14.2. HRMS (ESI) m/z: calcd. for C\(_{13}\)H\(_{15}\)NO\(_2\)Na\(^+\) [M+Na\(^+\): 240.0995, found 240.0994.}

**Ethyl 2,3-dihydroxy-2-(1-tosylindolin-2-yl)propanoate (6)**

\[\text{3a} \xrightarrow{\text{K}_2\text{OsO}_4\cdot2\text{H}_2\text{O (0.2 equiv), NMO (5.2 equiv)}} \text{acetone:}\text{H}_2\text{O = 5:1}} \text{6, 71\% yield, 1:4.1 d.r.}\]

According to the known procedure.\(^3\) Potassium osmate dihydrate (7.3 mg, 0.02 mmol) and 4-methylmorpholine N-oxide (0.05 mL, 0.52 mmol) were added to a solution of \textbf{3a} (37.1 mg, 0.1 mmol) in acetone:H\(_2\)O = 5:1 (4.0 mL) at room temperature. The resulting reaction mixture was stirred at rt for 12 h. The reaction was
quenched with saturated Na$_2$SO$_3$ and the mixture was extracted with CH$_2$Cl$_2$. The combined organic phases were dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 5:2:1) to afford a white solid 6 (28.6 mg, 71% yield, 1.4:1 d.r.). m.p.: 109.2 – 110.9 °C. $^1$H NMR (400 MHz, CDCl$_3$) δ 7.64 (d, $J = 8.0$ Hz, 1H), 7.44 – 7.37 (m, 2H), 7.25 – 7.18 (m, 1H), 7.13 (d, $J = 8.0$ Hz, 2H), 7.08 – 7.02 (m, 1H), 7.00 – 6.95 (m, 1H), 4.61 (dd, $J = 8.9$, 2.5 Hz, 1H), 4.16 – 4.09 (m, 1H), 4.09 – 4.04 (m, 1H), 3.88 (dd, $J = 11.9$, 6.6 Hz, 1H), 3.50 (s, 1H), 2.70 (t, $J = 7.2$ Hz, 1H), 2.62 (dd, $J = 16.5$, 2.5 Hz, 1H), 2.54 (dd, $J = 16.4$, 8.9 Hz, 1H), 2.34 (s, 3H), 1.21 (t, $J = 7.1$ Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$) δ 172.7, 144.3, 141.9, 133.8, 133.7, 129.6, 127.6, 127.2, 125.8, 124.2, 118.9, 80.5, 64.8, 64.1, 62.5, 30.6, 21.5, 14.0. HRMS (ESI) m/z: calcd. for C$_{20}$H$_{23}$NO$_6$SNa$^+$ [M+Na]$^+$: 428.1138, found 428.1146.

**Ethyl 3-(benzylamino)-2-(1-tosylindolin-2-yl)propanoate (7)**

Benzylamine (53.6 mg, 0.5 mmol) was added to a solution of 3a (37.1 mg, 0.1 mmol) in Toluene (2.0 mL) at room temperature. The resulting reaction mixture was heated at 110 °C and stirred by reflux for 18 hours. The reaction was quenched with saturated NaHCO$_3$ and the mixture was extracted with CH$_2$Cl$_2$. The combined organic phases were dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc:DCM = 10:5:1) to afford a brown oil 7 (43.6 mg, 91% yield, 3:1 d.r.). $^1$H NMR (400 MHz, (CD$_3$)$_2$CO) δ 7.58 – 7.51 (m, 3H), 7.31 – 7.28 (m, 3H), 7.27 – 7.25 (m, 3H), 7.25 – 7.18 (m, 2H), 7.10 – 7.02 (m, 2H), 7.78 – 7.71 (m, 1H), 3.99 – 3.90 (m, 2H), 3.76 – 3.63 (m, 2H), 3.03 – 2.97 (m, 1H), 2.93 – 2.90 (m, 1H), 2.88 – 2.87 (m, 1H), 2.86 – 2.83 (m, 1H), 2.71 (dd, $J = 16.6$, 9.7 Hz, 1H), 2.34 (s, 3H), 1.13 (t, $J = 7.1$ Hz, 3H). $^{13}$C($^1$H) NMR (100 MHz, (CD$_3$)$_2$CO) δ 172.4, 145.1, 142.8, 141.7, 135.8, 134.1, 130.5, 128.9, 128.8, 128.3, 128.0, 127.4,
126.0, 125.8, 118.6, 62.8, 61.0, 54.3, 52.1, 46.9, 32.8, 21.4, 14.3. **HRMS (ESI) m/z:**
calcd. for C_{27}H_{30}N_{2}O_{4}SH^+ [M+H]^+: 479.1999, found 479.2005.

**Ethyl (Z)-2-ethyl-4-(2-((4-methylphenyl)sulfonamido)phenyl)but-2-enoate (8)**

![Chemical Structure](image)

The 3a (37.1 mg, 0.1 mmol) and CuBr$_2$ (11.2 mg, 0.05 mmol) was added to a reaction tube. Vacuum for 15 minutes and inject nitrogen. Then, THF (1 mL), Me$_3$SiCl (31.1 mg, 0.3 mmol) and HMPA (53.6 mg, 0.3 mmol) were added at -48 °C and MeMgBr (0.15 mL, 0.15 mmol) was added drop by drop for 1 hours. The reaction was quenched with saturated NH$_4$Cl and the mixture was extracted with EtOAc. The combined organic phases were dried over Na$_2$SO$_4$ and concentrated in vacuo. The residue was purified by flash column on silica gel (PE:EtOAc = 5:2) to afford a white solid 8 (29.1 mg, 75% yield) and 9 (2.9 mg, 8% yield). **Compound data of 8:**

**$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.59 (d, $J = 8.3$ Hz, 2H), 7.23 (d, $J = 8.0$ Hz, 2H), 7.20 – 7.13 (m, 3H), 7.12 – 7.05 (m, 1H), 6.57 (dd, $J = 15.4$, 8.0 Hz, 2H), 4.18 (q, $J = 7.1$ Hz, 2H), 3.29 (d, $J = 7.5$ Hz, 2H), 2.40 (s, 3H), 2.31 (q, $J = 7.5$ Hz, 2H), 1.28 (t, $J = 7.1$ Hz, 3H), 1.00 (t, $J = 7.5$ Hz, 3H).**

**$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 167.3, 143.9, 137.6, 136.5, 135.8, 134.4, 134.1, 129.8, 129.6, 127.5, 127.19, 127.15, 126.2, 60.6, 29.9, 21.5, 20.1, 14.2, 13.7.**

**HRMS (ESI) m/z:** calcd. for C$_{21}$H$_{25}$NO$_4$SNa$^+$ [M+Na]$^+$: 410.1397, found 410.1407.

Compound data of 9:

**$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.63 (d, $J = 8.0$ Hz, 1H), 7.45 (d, $J = 8.3$ Hz, 2H), 7.24 – 7.18 (m, 1H), 7.12 (d, $J = 8.1$ Hz, 2H), 7.07 – 6.98 (m, 2H), 4.41 (td, $J = 8.1$, 2.9 Hz, 1H), 4.11 – 3.98 (m, 2H), 2.59 – 2.49 (m, 3H), 2.33 (s, 3H), 1.97 – 1.76 (m, 2H), 1.15 (t, $J = 7.1$ Hz, 3H).**

**$^{13}$C{$^1$H} NMR (100 MHz, CDCl$_3$) $\delta$ 173.6, 143.9, 143.8, 141.4, 135.2, 133.1, 129.5, 127.6, 127.1, 125.4, 125.0, 118.9, 63.6, 60.5, 52.5, 32.8, 22.6, 21.5, 14.2, 11.6.**

**HRMS (ESI) m/z:** calcd. for C$_{21}$H$_{25}$NO$_4$SNa$^+$ [M+Na]$^+$: 410.1397, found 410.1402.
V. Mechanistic Studies

(a) Control Experiments of 1a and 2a.

To a stirred solution of o-aminobenzaldehyde 1a (27.5 mg, 0.1 mmol) and allyl carbonate 2a (34.5 mg, 0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh₂Cy (0.2-1.2 equiv) and benzoic acid (2.4 mg, 20 mol%) at room temperature for 12 h. The reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) to afford compounds 3a and 1a.

(b) Transformation Experiment of 3a'

To a stirred solution of o-aminobenzaldehyde 1a (27.5 mg, 0.1 mmol) and allyl carbonate 2a (34.5 mg, 0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh₂Cy (32.2 mg, 0.12 mmol, 1.2 equiv) and benzoic acid (2.4 mg, 20 mol%) at room temperature for 12 h. The reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 19:1:6) to afford compounds 3a' (1.9 mg, 5% yield). Compound data of 3a': ¹H NMR (400 MHz, (CD₃)₂CO) δ 7.73 (d, J = 8.3 Hz, 2H), 7.64 (d, J = 8.2 Hz, 1H), 7.38 – 7.25 (m, 4H), 7.10 – 7.04 (m, 1H), 6.26 (s, 1H), 5.86 (s, 1H), 4.99 (s, 1H), 4.85 – 4.79 (m, 2H), 4.21 (qd, J = 7.1, 4.6 Hz, 2H), 2.35 (s, 3H), 1.23 (t, J = 7.2 Hz, 3H). ¹³C{¹H} NMR (100 MHz, DMSO-d₆) δ 170.8, 159.0, 149.9, 147.4, 135.3, 129.6, 128.9, 128.8, 128.6, 128.3, 127.3, 126.8, 124.5, 122.8, 121.7, 79.4, 78.2, 68.2, 67.4, 65.3, 31.3, 30.1, 21.6.
(CD$_3$)$_2$CO) δ 166.0, 145.1, 142.9, 139.8, 135.9, 133.6, 130.5, 130.4, 128.4, 127.3, 126.2, 125.0, 115.9, 76.7, 72.8, 61.5, 21.4, 14.3. **HRMS (ESI)** m/z: calcd. for C$_{20}$H$_{21}$NO$_5$SNa$^+$ [M+Na]$^+$: 410.1033, found 410.1038.

(c) Control Experiment of 1a and 2g

To a stirred solution of o-aminobenzaldehyde 1a (27.5 mg, 0.1 mmol) and allyl carbonate 2g (46.0 mg, 0.15 mmol, 1.5 equiv) in toluene (2.0 mL) was added PPh$_2$Cy (32.2 mg, 0.12 mmol, 1.2 equiv) and benzoic acid (2.4 mg, 20 mol%) at room temperature for 12 h. The reaction mixture was purified without concentration via flash chromatography on silica gel (PE:EtOAc:DCM = 20:3:1) to afford compounds Int-2' (38.9 mg, 87% yield). Compound data of Int-2': H NMR (400 MHz, CDCl$_3$) δ 7.65 – 7.55 (m, 3H), 7.46 – 7.34 (m, 6H), 7.30 – 7.27 (m, 1H), 7.23 – 7.20 (m, 1H), 7.18 – 7.14 (m, 2H), 7.03 (d, $J$ = 16.2 Hz, 1H), 6.70 (d, $J$ = 16.3 Hz, 1H), 6.57 (s, 1H), 4.38 (q, $J$ = 7.1 Hz, 2H), 2.30 (s, 3H), 1.44 (t, $J$ = 7.1 Hz, 3H). C{H} NMR (100 MHz, CDCl$_3$) δ 167.0, 143.8, 139.9, 136.4, 135.3, 133.6, 132.4, 130.0, 129.51, 129.48, 129.0, 128.8, 128.7, 128.6, 127.3, 126.5, 126.3, 125.5, 125.3, 61.2, 21.5, 14.4. **HRMS (ESI)** m/z: calcd. for C$_{26}$H$_{25}$NO$_4$SNa$^+$ [M+Na]$^+$: 470.1397, found 470.1404.

(d) The Deuterium Labeling Experiment

To a stirred solution of o-aminobenzaldehyde 1a (27.5 mg, 0.1 mmol), allyl carbonate 2a (34.5 mg, 0.15 mmol, 1.5 equiv), D$_2$O (40.0 mg, 20.0 equiv), PPh$_2$Cy (32.2 mg,
0.12 mmol, 1.2 equiv), benzoic acid (2.4 mg, 20 mol%) and 2.0 mL of toluene. The resulting reaction mixture was stirred at room temperature for 12 h. The reaction mixture was concentrated and the residue was purified by silica gel flash column chromatography (PE:EtOAc:DCM = 19:1:6) to afford corresponding product d-3a'' as a yellow oily liquid (18.1 mg, 48% yield).
VI. References

1. (a) Patil, D. V.; Phun, L. H.; France, S. Indium-Catalyzed Homo-
**2010**, 12, 5684–5687. (b) Cabrera, S.; Alemán, J.; Bolze, P.;
Bertelsen, S.; Jørgensen, K. A. An Unexpected Organocatalytic
Asymmetric Tandem Michael/Morita–Baylis–Hillman Reaction.

2. Javorskis, T.; Orentas, E. Chemoselective Deprotection of
Sulfonamides Under Acidic Conditions: Scope, Sulfonyl Group
13423–13439.

3. Gao, J.; Li, Y.; Wang, N.; Li, Z.; Huang, N.; Yao, H. One-Pot
Stereoselective Synthesis of 2, 3, 4-Unprotected β-N-
**2023**, 365, 2350–2355.
VII. X-Ray Crystallographic Analysis

Crystal Growth Method: 20 mg of 3j was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

Figure S1. X-ray structure of 3j (ellipsoid contour at 50% probability CCDC 2287281)
Crystal Growth Method: 15 mg of 4 was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

Figure S2. X-ray structure of 4 (ellipsoid contour at 50% probability CCDC 2293949)
**Crystal Growth Method:** 5 mg of 3a' was added in a HPLC vial and dissolved by 1.0 mL DCM, closed the lid. Then put it in a large bottle, added PE to the same level of the liquid in the HPLC vial, tighten the lid, put it in a fumehood and waited for growth.

**Figure S3.** X-ray structure of 3a' (ellipsoid contour at 50% probability CCDC 2325027)
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<th>Crystal data for</th>
<th>Crystal data for</th>
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<td>4</td>
<td>3a'</td>
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<td><strong>Empirical formula</strong></td>
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VIII. Copies of $^1$H and $^{13}$C$^{[1]}$H NMR Spectra

$^1$H NMR (400 MHz, CDCl₃)

$^{13}$C$^{[1]}$H NMR (100 MHz, CDCl₃)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$($^1H$) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)

S32
$^1$H NMR (400 MHz, CDCl₃)

$^{13}$C($^1$H) NMR (100 MHz, CDCl₃)

S33
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^1H$ NMR (400 MHz, CDCl$_3$)

$^{13}C^1H$ NMR (100 MHz, CDCl$_3$)
$\text{H NMR (400 MHz, CDCl}_3\text{)}$

$\text{C}^{13}\text{H NMR (100 MHz, CDCl}_3\text{)}$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$($^1H$) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C($^{1}H$) NMR (100MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$\mathrm{^1}{\text{H}}\text{NMR (376 MHz, CDCl}_3\text{)}$
$^{19}$F($^1$H) NMR (376 MHz, CDCl₃)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}C$($^1H$) NMR (100MHz, CDCl$_3$)

S50
$^{19}\text{F} (^1\text{H})$ NMR (376 MHz, CDCl$_3$)
$\text{Br}$

$\text{NMR (400 MHz, CDCl}_3\text{)}$

$\text{Ts}$

$\text{OEt}$

$3u$

$\text{NMR (100 MHz, CDCl}_3\text{)}$

$\text{Ts}$

$\text{OEt}$

$3u$
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{15}$C$[^1]$H NMR (100 MHz, CDCl$_3$)
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$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C ($^1$H) NMR (100 MHz, CDCl$_3$)
\[^1H\text{NMR (400 MHz, CDCl}_3\text{)}\]

\[13C(^1H)\text{NMR (100 MHz, CDCl}_3\text{)}\]
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)
$^{1}H$ NMR (400 MHz, CDCl$_3$)

$^{13}$C($^{1}H$) NMR (100 MHz, CDCl$_3$)
$^1$H NMR (400 MHz, (CD$_3$)$_2$CO)

$^{13}$C($^1$H) NMR (100 MHz, (CD$_3$)$_2$CO)
$^1$H NMR (400 MHz, CDCl$_3$)

$^{13}$C($^1$H) NMR (100 MHz, CDCl$_3$)