Supporting Information

Electrochemical-mediated fixation of CO\textsubscript{2}: three-component synthesis of carbamate compounds from CO\textsubscript{2}, amines and N-alkenylsulfonamides

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1. General Methods

Unless otherwise noted, all reagents and solvents were obtained commercially and used without further purification. Column chromatography on silica gel (300-400 mesh) was carried out using technical grade 60-90 °C petroleum ether and analytical grade EtOAc (without further purification). $^1$H and $^{13}$C spectra were recorded on a 400 MHz, 500 MHz or 600MHz spectrometer. Chemical shifts were reported in ppm. $^1$H NMR spectra were referenced to CDCl$_3$ (7.26 ppm) or DMSO (2.5 ppm), and $^{13}$C-NMR spectra were referenced to CDCl$_3$ (77.0 ppm) or DMSO (39.5 ppm). Peak multiplicities were designated by the following abbreviations: s, singlet; d, doublet; t, triplet; m, multiplet; brs, broad singlet and J, coupling constant in Hz. The HRMS spectrum was measured by micromass QTOF2 Quadrupole/Time of Flight Tandem mass spectrometer with electron spray ionization. Cyclic voltammograms were recorded on a CHI 660E potentiostat.
2. Supplementary experiments

Table S1 Screening of Reaction electrode

<table>
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<tr>
<th>Entry</th>
<th>Electrode</th>
<th>Yield (%)a</th>
</tr>
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<tr>
<td>1</td>
<td>Pt (+) / Pt (-)</td>
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</tr>
<tr>
<td>2</td>
<td>C (+) / Pt (-)</td>
<td>42</td>
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<tr>
<td>3</td>
<td>Pt (+) / C (-)</td>
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<td>Pt (+) / Cu (-)</td>
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<td>trace</td>
</tr>
<tr>
<td>7</td>
<td>Pt (+) / Ag (-)</td>
<td>trace</td>
</tr>
</tbody>
</table>

aReactions conditions: 1a (0.3 mmol), 2a (1.2 mmol), CO₂ (atmospheric pressure), NH₄I as electrolyte (0.3 mmol), CH₃CN as solvent (3 mL), electrolysis at a constant current of 25 mA for 3 h in an undivided cell at -10 °C.

Fig. S1 Cyclic voltammograms. a) background, b) NH₄I (3 mmol/L), c) 1a (8 mmol/L), and d) NH₄I (3 mmol/L) and 1a (8 mmol/L).
**Fig. S2** GC spectrum of pure hydrogen

**Fig. S3** Gas spectrum of reaction bottle (Reaction time: 60 minutes)
3. Synthesis of Substrates and Characterization

(1) N-(2-vinylphenyl)-sulfonamides (1a-1d)

A dry round bottom flask charged with 2-(2-aminophenyl)ethan-1-ol (4.571 g, 20 mmol) and KOH (1.122 g, 20 mmol) was stirred at 180 °C for 4 h, the mixture was then cooled to room temperature, and H₂O (20 mL) was added. The organic layer was separated and the aqueous layer was extracted with ethyl acetate, then the combined organic phase was washed with brine, dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product 2-vinylaniline B as a yellow oil (1.380 g, 58 %).
To a solution of 2-vinylaniline (B) (1.119 g, 10 mmol) in CH$_2$Cl$_2$ (40 mL) were added pyridine (1.105 g, 14 mmol) and RCl (12 mmol) at 0 ºC. After being stirred at 25 ºC for 12h, the reaction mixture was poured into water and the product was extracted with CH$_2$Cl$_2$ (30 mL x 3), dried over Na$_2$SO$_4$, filtered, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product 1a-1d as a white solid.
(2) N-(2-vinylphenyl)-sulfonamides (1e-1j)

Scheme S2 Synthesis of N-(2-vinylphenyl)-sulfonamides (1e-1j)

To a suspension of potassium vinyltrifluoroborate (0.736 g, 5.5 mmol), Cs₂CO₃ (4.875 g, 15 mmol), PdCl₂(dppf) (0.363 g, 0.45 mmol) and the corresponding 2-bromoaniline (5 mmol) in THF (50 mL) was added water (5.0 mL). The reaction mixture was heated to 130 °C under reflux for 16 h, then cooled to room temperature and diluted with water (30 mL) followed by extraction with ether (30 mL x 3). The ethereal solution was washed with brine (50 mL), and then dried over Na₂SO₄. The solvent was removed under reduced pressure and the crude product was purified by flash chromatography on silica gel (PE/EA = 10/1) to give the desired products D as a yellow oil.

To a solution of products D (2 mmol) in CH₂Cl₂ (20 mL) were added pyridine (0.221 g, 2.8 mmol) and TsCl (0.457 g, 2.4 mmol) at 0 °C. After being stirred at 25 °C for 12 h, the reaction mixture was poured into water and the product was extracted with CH₂Cl₂ (20 mL x 3), dried over Na₂SO₄, filtered, and concentrated by rotary evaporation. The crude mixture was purified by column chromatography on silica gel (PE/EA = 10/1) to afford the corresponding product 1e-1j as a white solid.
4. General procedure for the preparation of products 3

A 10 mL three-necked round-bottomed flask was charged with the 1 derivatives (0.3 mmol) and NH$_4$I (0.3 mmol). The cell was equipped with platinum electrodes (1.0×1.0 cm$^{-2}$) as both the anode and cathode. The three-necked flask is pumped and ventilated three times so that the inside is filled with CO$_2$. Then inject amine 2 (1.2 mmol), CH$_3$CN (3 mL) into the three-necked flask. Continuously inject CO$_2$ into the bottle at room temperature. After half an hour, place the reaction flask in cold hydrazine at -10°C and electrolyzed at a constant current of 25 mA for corresponding time. When the reaction was finished, the solvent was removed with a rotary evaporator. The residue was purified by column chromatography on silica gel to afford the desired product 3.
5. Characterization Data for the Substrates Products

5.1 Characterization data for the products

4-methyl-N-(4-methyl-2-vinylphenyl)benzenesulfonamide (1e). White solid (0.487 g, 85%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.59 (d, $J = 8.0$ Hz, 2H), 7.22-7.18 (m, 3H), 7.14 (d, $J = 8.1$ Hz, 1H), 7.00 (d, $J = 7.9$ Hz, 1H), 6.58-6.51 (m, 2H), 5.49 (d, $J = 17.4$ Hz, 1H), 5.20 (d, $J = 11.1$ Hz, 1H), 2.34 (d, $J = 35.3$ Hz, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 143.68, 136.50, 136.37, 133.11, 131.56, 130.39, 129.52, 129.25, 127.20, 127.10, 125.69, 117.45, 21.50, 20.96.

N-(4-chloro-2-vinylphenyl)-4-methylbenzenesulfonamide (1f). White solid (0.503 g, 82%). $^1$H NMR (400 MHz, Chloroform-d) $\delta$ 7.60 (d, $J = 8.3$ Hz, 2H), 7.33 (d, $J = 2.4$ Hz, 1H), 7.24-7.21 (m, 3H), 7.16-7.13 (m, 1H), 6.92 (s, 1H), 6.57-6.50 (m, 1H), 5.52 – 5.48 (m, 1H), 5.27-5.24 (m, 1H), 2.38 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 144.05, 135.93, 134.69, 132.21, 131.57, 130.36, 129.65, 128.35, 127.13, 126.74, 126.51, 118.97, 21.49.

N-(4-bromo-2-vinylphenyl)-4-methylbenzenesulfonamide (1g). White solid (0.504 g, 72%). $^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.60 (d, $J = 8.2$ Hz, 2H), 7.47 (d, $J = 2.2$ Hz, 1H), 7.31-7.29 (m, 1H), 7.22 (d, $J = 8.1$ Hz, 1H), 7.19 (d, $J = 8.6$ Hz, 0H), 6.76 (s, 1H), 6.51-6.46 (m, 1H), 5.50 (d, $J = 17.3$ Hz, 1H), 5.28 (d, $J = 11.1$ Hz, 1H), 2.39 (s, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 144.12, 135.94, 134.72, 132.15, 131.37, 130.25, 129.71, 129.62, 127.14, 126.63, 120.03, 119.33, 21.54.
N-(4-methoxy-2-vinylphenyl)-4-methylbenzenesulfonamide (1h). White solid (0.460 g, 76%). \( ^1\text{H NMR} \) (600 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.56 (d, \( J = 8.2 \) Hz, 2H), 7.19 (d, \( J = 8.1 \) Hz, 2H), 7.06 (d, \( J = 8.8 \) Hz, 1H), 6.92 (d, \( J = 2.9 \) Hz, 1H), 6.72-6.69 (m, 2H), 6.63-6.58 (m, 1H), 5.49 (d, \( J = 17.4 \) Hz, 1H), 5.16 (d, \( J = 11.2 \) Hz, 1H), 3.77 (s, 3H), 2.37 (s, 3H).

13\text{C NMR} \) (151 MHz, CDCl\( _3 \)) \( \delta \) 158.39, 143.57, 136.19, 135.91, 131.57, 129.43, 128.74, 127.20, 125.67, 116.99, 113.91, 110.88, 21.44.

N-(4-cyano-2-vinylphenyl)-4-methylbenzenesulfonamide (1i). Red solid (0.482 g, 81%). \( ^1\text{H NMR} \) (600 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.67 (d, \( J = 8.2 \) Hz, 1H), 7.54-7.51 (m, 2H), 7.46 (d, \( J = 10.1 \) Hz, 1H), 7.25 (d, \( J = 7.9 \) Hz, 2H), 7.05 (s, 1H), 6.53-6.48 (m, 1H), 5.56 (d, \( J = 17.3 \) Hz, 1H), 5.46 (d, \( J = 11.0 \) Hz, 1H), 2.38 (s, 3H).

13\text{C NMR} \) (151 MHz, CDCl\( _3 \)) \( \delta \) 144.72, 137.59, 135.75, 132.14, 131.46, 131.15, 129.96, 129.63, 127.11, 121.68, 121.63, 118.29, 108.66, 21.58.

4-methyl-N-(5-methyl-2-vinylphenyl)benzenesulfonamide (1j). White solid (0.464 g, 81%). \( ^1\text{H NMR} \) (600 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.59 (d, \( J = 8.3 \) Hz, 2H), 7.26-7.16 (m, 4H), 6.97 (d, \( J = 7.8 \) Hz, 1H), 6.45-6.40 (m, 2H), 5.44 (d, \( J = 18.3 \) Hz, 1H), 5.18 (d, \( J = 12.0 \) Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H).

13\text{C NMR} \) (151 MHz, CDCl\( _3 \)) \( \delta \) 143.81, 138.77, 136.35, 132.85, 131.19, 129.69, 129.56, 127.33, 127.16, 126.61, 125.44, 117.40, 21.54, 21.16.

4-methyl-N-(2-vinylphenyl)benzenesulfonamide (1a). White solid (2.211 g, 81%). \( ^1\text{H NMR} \) (600 MHz, Chloroform-\( \text{d} \)) \( \delta \) 7.66 (d, \( J = 8.3 \) Hz, 2H), 7.53 (d, \( J = 8.0 \) Hz, 2H), 7.16 (d, \( J = 10.0 \) Hz, 2H), 6.96 (d, \( J = 7.8 \) Hz, 1H), 6.45-6.40 (m, 2H), 5.44 (d, \( J = 18.3 \) Hz, 1H), 5.18 (d, \( J = 12.0 \) Hz, 1H), 2.38 (s, 3H), 2.29 (s, 3H).
NMR (400 MHz, Chloroform-d) δ 7.62 (d, J = 8.3 Hz, 2H), 7.37-7.35 (m, 1H), 7.32 - 7.28 (m, 1H), 7.21-7.13 (m, 4H), 6.81 (s, 1H), 6.64 - 6.56 (m, 1H), 5.51 (d, J = 17.4 Hz, 1H), 5.24 (d, J = 11.0 Hz, 1H), 2.37 (s, 3H). 13C NMR (101 MHz, CDCl₃) δ 143.90, 136.37, 133.16, 132.94, 131.53, 129.66, 128.58, 127.26, 126.85, 126.55, 125.11, 118.07, 21.59.

N-(2-vinylphenyl)benzenesulfonamide (1b). White solid (2.150 g, 83%). ¹H NMR (400 MHz, Chloroform-d) δ 7.75-7.72 (m, 2H), 7.55-7.51 (m, 1H), 7.43-7.39 (m, 2H), 7.38-7.36 (m, 1H), 7.31-7.29 (m, 1H), 7.22-7.14 (m, 2H), 6.89 (s, 1H), 6.61-6.54 (m, 1H), 5.51-5.47 (m, 1H), 5.23-5.20 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.12, 133.07, 132.93, 132.83, 131.25, 128.94, 128.48, 127.09, 126.67, 125.39, 111.92.

4-methoxy-N-(2-vinylphenyl)benzenesulfonamide (1c). White solid (2.349 g, 83%). ¹H NMR (600 MHz, Chloroform-d) δ 7.65 (d, J = 8.9 Hz, 1H), 7.37-7.36 (m, 1H), 7.28 (d, J = 7.9 Hz, 1H), 7.20-7.17 (m, 1H), 7.16-7.13 (m, 1H), 6.89-6.85 (m, 3H), 6.66-6.61 (m, 1H), 5.51 (d, J = 17.4 Hz, 1H), 5.23 (d, J = 11.0 Hz, 1H), 3.80 (s, 3H). ¹³C NMR (151 MHz, CDCl₃) δ 163.02, 133.08, 132.93, 131.40, 130.70, 129.27, 128.41, 126.63, 126.44, 125.18, 117.74, 114.03, 55.49.

4-chloro-N-(2-vinylphenyl)benzenesulfonamide (1d). White solid (2.473 g, 84%). ¹H NMR (400 MHz, Chloroform-d) δ 7.65 (d, J = 8.7 Hz, 2H), 7.39 (d, J = 8.6 Hz, 3H), 7.30-7.28 (m, 1H), 7.24-7.17 (m, 2H), 6.83 (s, 1H), 6.61-6.54 (m, 1H), 5.54-5.49 (m, 1H), 5.26-5.23 (m, 1H). ¹³C NMR (101 MHz, CDCl₃) δ 139.50, 137.64, 133.20, 132.48, 131.14, 129.25, 128.62, 127.00, 126.85, 125.53, 118.20.
5.2 Characterization data for the products

1-tosylindolin-3-yl pyrrolidine-1-carboxylate (3aa). White solid (0.089 g, 77%). mp: 107-109°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.74 (d, $J = 8.2$ Hz, 1H), 7.68 (d, $J = 8.3$ Hz, 2H), 7.40 – 7.34 (m, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.07-7.03 (m, 1H), 5.93-5.90 (m, 1H), 4.01 (d, $J = 5.2$ Hz, 2H), 3.37-3.33 (m, 2H), 2.97-2.94 (m, 2H), 2.35 (s, 3H), 1.82-1.76 (m, 4H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 154.04, 144.07, 142.76, 133.88, 130.62, 129.69, 129.62, 127.33, 126.90, 123.93, 115.00, 71.59, 56.13, 46.12, 45.62, 25.57, 24.85, 21.47. HRMS (m/z) [ESI]: calculated for C$_{20}$H$_{22}$N$_2$O$_4$SNa$^+$ [M+Na]$^+$: 409.1300, found 409.1195.

1-tosylindolin-3-yl diisobutylcarbamate (3ab). White solid (0.092 g, 69%). mp: 135-137°C. Petroleum ether/ethyl acetate = 20/1 (v/v) as eluent for column chromatography. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.74 (d, $J = 8.2$ Hz, 1H), 7.67 (d, $J = 8.4$ Hz, 2H), 7.37-7.31 (m, 2H), 7.21 (d, $J = 8.1$ Hz, 2H), 7.06-7.02 (m, 1H), 5.94-5.92 (m, 1H), 4.06-4.01 (m, 1H), 3.94-3.90 (m, 1H), 3.16-3.10 (m, 1H), 2.98-2.93 (m, 1H), 2.80-2.69 (m, 2H), 2.35 (s, 3H), 1.96-1.89 (m, 1H), 1.74-1.67 (m, 1H), 0.87 (d, $J = 6.6$ Hz, 6H), 0.73-0.65 (m, 6H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.94, 144.12, 142.70, 133.75, 130.56, 129.68, 129.38, 127.25, 126.66, 123.87, 114.87,
71.77, 56.01, 54.75, 54.04, 27.18, 26.81, 21.50, 19.96, 19.78. **HRMS (m/z)** [ESI]: calculated for C_{24}H_{32}N_{2}O_{4}SNa^{+} [M+Na]^{+}: 467.2083, found 467.1984.

1-tosylindolin-3-yl dibutylcarbamate (3ac). White solid (0.061 g, 47%). mp: 129-131°C. Petroleum ether/ethyl acetate = 20/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (600 MHz, Chloroform-d) δ 7.74 (d, J = 8.2 Hz, 1H), 7.68 (d, J = 8.2 Hz, 2H), 7.37-7.33 (m, 2H), 7.22 (d, J = 8.1 Hz, 2H), 7.06-7.03 (m, 1H), 5.93-5.91 (m, 1H), 4.03-3.95 (m, 2H), 3.26-3.21 (m, 1H), 3.15-3.11 (m, 1H), 2.91-2.88 (m, 1H), 2.36 (s, 3H), 1.50-1.47 (m, 2H), 1.10-1.06 (m, 2H), 0.94-0.92 (m, 3H), 0.77-0.75 (m, 1H). **^{13}C NMR** (151 MHz, CDCl_{3}) δ 155.43, 144.15, 142.70, 133.74, 130.59, 129.67, 129.47, 127.30, 126.68, 123.86, 114.85, 77.21, 77.00, 76.79, 71.80, 56.04, 47.10, 46.17, 30.53, 30.10, 21.54, 20.01, 19.68, 13.87, 13.72. **HRMS (m/z)** [ESI]: calculated for C_{24}H_{32}N_{2}O_{4}SNa^{+} [M+Na]^{+}: 467.2083, found 467.1982.

1-tosylindolin-3-yl diethylcarbamate (3ad). Yellow oil (0.084 g, 72%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. **^{1}H NMR** (400 MHz, DMSO-d_{6}) δ 7.67 (d, J = 8.3 Hz, 2H), 7.60 (d, J = 8.2 Hz, 1H), 7.43-7.34 (m, 4H), 7.12-7.08 (m, 1H), 5.86-5.84 (m, 1H), 4.16-4.11 (m, 1H), 3.89-3.85 (m, 1H), 3.33-3.13 (m, 2H), 2.78 (d, J = 6.7 Hz, 2H), 2.32 (s, 3H), 1.03-1.00 (m, 3H), 0.79-
0.76 (m, 3H). ¹³C NMR (101 MHz, DMSO) δ 154.15, 144.46, 142.11, 133.10, 130.73, 129.96, 129.90, 127.06, 126.94, 124.20, 114.56, 71.24, 55.76, 41.26, 40.47, 20.97, 13.80, 13.35. HRMS (m/z) [ESI]: calculated for C₂₀H₂₄N₂O₄SNa⁺ [M+Na]⁺: 411.1457, found 411.1352.

1-tosylindolin-3-yl propylcarbamate (3ae). White solid (0.084 g, 75%). mp: 109-111°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ¹H NMR (400 MHz, Chloroform-d) δ 7.73 (d, J = 8.2 Hz, 1H), 7.66 (d, J = 8.2 Hz, 2H), 7.39-7.34 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.08-7.04 (m, 1H), 5.88-5.86 (m, 1H), 4.39 (s, 1H), 4.01-3.92 (m, 2H), 3.12-3.06 (m, 2H), 2.36 (s, 3H), 1.52-1.43 (m, 2H), 0.91-0.87 (m, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 155.42, 144.04, 142.83, 133.78, 130.76, 129.58, 129.46, 127.48, 126.69, 124.12, 115.35, 71.51, 56.05, 42.68, 23.08, 21.50, 11.15. HRMS (m/z) [ESI]: calculated for C₁₉H₂₂N₂O₄SNa⁺ [M+Na]⁺: 397.1300, found 397.1188.

1-tosylindolin-3-yl isopropylcarbamate (3af). White solid (0.058 g, 52%). mp: 113-115°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. ¹H NMR (600 MHz, Chloroform-d) δ 7.73 (d, J = 8.1 Hz, 1H), 7.65 (d, J = 7.9 Hz, 2H), 7.38-7.35 (m, 2H), 7.22 (d, J = 8.0 Hz, 2H), 7.07-7.05 (m, 1H), 5.85 (d, J = 5.7 Hz, 1H), 4.21 (d, J = 6.9 Hz, 1H), 3.99-3.94 (m, 2H), 3.78-3.73 (m, 1H), 2.36 (s, 3H), 1.14-1.09 (m, 6H). ¹³C NMR (151 MHz, CDCl₃) δ 154.47, 143.97,
142.82, 133.72, 130.74, 129.59, 129.51, 127.47, 126.67, 124.16, 115.43, 71.33, 56.08, 43.04, 22.86, 21.53. HRMS (m/z) [ESI]: calculated for C_{19}H_{22}N_{2}O_{4}SNa^+ [M+Na]^+: 397.1300, found 397.1184.

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\text{HRMS (m/z) [ESI]: calculated for C}_{19}\text{H}_{22}\text{N}_{2}\text{O}_{4}\text{SNa}^+ [M+Na]^+: 397.1300, found 397.1184.}
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1-tosylindolin-3-yl butylcarbamate (3ag). White solid (0.078 g, 67%). mp: 121-123°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography.  

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\text{1H NMR (400 MHz, Chloroform-d)} \delta 7.73 (d, J = 8.2 \text{ Hz}, 1\text{H}), 7.65 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.38-7.34 (m, 2\text{H}), 7.08-7.04 (m, 1\text{H}), 5.87-5.85 (m, 1\text{H}), 4.38 (s, 1\text{H}), 4.00-3.91 (m, 2\text{H}), 3.15-3.09 (m, 2\text{H}), 2.36 (s, 3\text{H}), 1.45-1.41 (m, 2\text{H}), 1.33-1.28 (m, 2\text{H}), 0.93-0.89 (m, 3\text{H}). \text{13C NMR (101 MHz, CDCl}_3) \delta 155.39, 144.04, 142.80, 133.73, 130.75, 129.57, 129.44, 127.46, 126.68, 124.11, 115.32, 71.48, 56.04, 40.66, 31.87, 21.49, 19.80, 13.66. \text{HRMS (m/z) [ESI]: calculated for C}_{20}\text{H}_{24}\text{N}_{2}\text{O}_{4}\text{SNa}^+ [M+Na]^+: 411.1457, found 411.1347.}
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1-tosylindolin-3-yl isobutylcarbamate (3ah). White solid (0.055 g, 47%). mp: 135-137°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography.  

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\text{1H NMR (400 MHz, Chloroform-d)} \delta 7.74 (d, J = 8.1 \text{ Hz}, 1\text{H}), 7.66 (d, J = 8.2 \text{ Hz}, 2\text{H}), 7.39-7.34 (m, 2\text{H}), 7.22 (d, J = 8.0 \text{ Hz}, 2\text{H}), 7.08-7.04 (m, 1\text{H}), 5.88-5.86 (m, 1\text{H}), 4.45-4.43 (m, 1\text{H}), 4.01-3.92 (m, 2\text{H}), 2.97-2.93 (m, 2\text{H}), 2.36 (s,
3H), 1.73-1.66 (m, 1H), 0.88–0.86 (m, 6H). \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 155.53, 144.05, 142.81, 133.75, 130.76, 129.45, 127.47, 126.68, 124.12, 115.33, 71.51, 56.04, 48.36, 28.69, 21.50, 19.83. \( ^{1}\text{H NMR} \) (400 MHz, Chloroform-\(d\)) \( \delta \) 7.73 (d, \( J = 7.8 \) Hz, 1H), 7.63 (d, \( J = 6.7 \) Hz, 2H), 7.37-7.33 (m, 2H), 7.21 (d, \( J = 6.7 \) Hz, 2H), 7.07-7.03 (m, 1H), 5.85-5.84 (m, 1H), 4.75 (s, 1H), 4.00-3.93 (m, 2H), 3.40-3.30 (m, 7H), 2.36-2.35 (m, 3H). HRMS (m/z) [ESI]: calculated for C\(_{20}\)H\(_{24}\)N\(_2\)O\(_4\)SNa\(^+\) [M+Na\(^+\)]: 411.1457, found 411.13473.

1-tosylindolin-3-yl (2-methoxyethyl)carbamate (3ai). Yellow oil (0.070 g, 65%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. \( ^{1}\text{H NMR} \) (400 MHz, Chloroform-\(d\)) \( \delta \) 7.74 (d, \( J = 8.1 \) Hz, 1H), 7.66 (d, \( J = 8.1 \) Hz, 2H), 7.38-7.35 (m, 2H), 7.22 (d, \( J = 8.1 \) Hz, 2H), 7.08-7.05 (m, 1H), 5.86 (d, \( J = 5.5 \) Hz, 1H), 4.31 (d, \( J = 6.8 \) Hz, 1H), 4.00-3.93 (m, 2H), 2.37 (s, 3H), 1.98-1.96 (m, 1H), 2.00-1.95 (m, 1H). \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 155.38, 144.15, 142.82, 133.64, 130.75, 129.53, 129.42, 127.42, 126.68, 124.16, 115.52, 71.62, 71.11, 58.70, 56.04, 40.69, 21.42. HRMS (m/z) [ESI]: calculated for C\(_{19}\)H\(_{22}\)N\(_2\)O\(_5\)SNa\(^+\) [M+Na\(^+\)]: 413.1249, found 413.1138.

1-tosylindolin-3-yl cyclopentylcarbamate (3aj). White solid (0.068 g, 57%). mp: 157-159°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. \( ^{1}\text{H NMR} \) (600 MHz, Chloroform-\(d\)) \( \delta \) 7.74 (d, \( J = 8.1 \) Hz, 1H), 7.66 (d, \( J = 8.1 \) Hz, 2H), 7.38-7.35 (m, 2H), 7.22 (d, \( J = 8.1 \) Hz, 2H), 7.08-7.05 (m, 1H), 5.86 (d, \( J = 5.5 \) Hz, 1H), 4.31 (d, \( J = 6.8 \) Hz, 1H), 4.00-3.93 (m, 2H), 2.37 (s, 3H), 1.98-1.96 (m, 1H), 2.00-1.95 (m, 1H). \( ^{13}\text{C NMR} \) (101 MHz, CDCl\(_3\)) \( \delta \) 155.38, 144.15, 142.82, 133.64, 130.75, 129.53, 129.42, 127.42, 126.68, 124.16, 115.52, 71.62, 71.11, 58.70, 56.04, 40.69, 21.42. HRMS (m/z) [ESI]: calculated for C\(_{19}\)H\(_{22}\)N\(_2\)O\(_5\)SNa\(^+\) [M+Na\(^+\)]: 413.1249, found 413.1138.
1.95-1.91 (m, 2H), 1.63-1.59 (m, 6H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 154.83, 144.01, 142.84, 133.74, 130.77, 129.59, 129.47, 127.49, 126.68, 124.15, 115.41, 71.40, 56.11, 52.66, 33.11, 23.43, 21.55. HRMS (m/z) [ESI]: calculated for C$_{21}$H$_{24}$N$_2$O$_4$SNa$^+$ [M+Na]$^+$: 423.1457, found 423.1341.

![Chemical structure of 3ak](image)

1-tosylindolin-3-yl benzylcarbamate (3ak). White solid (0.061 g, 49%). mp: 161-163°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. $^1$H NMR (400 MHz, Chloroform-$d$) $\delta$ 7.75 (d, $J$ = 8.3 Hz, 1H), 7.62 (d, $J$ = 8.2 Hz, 2H), 7.40-7.29 (m, 5H), 7.23 (d, $J$ = 7.0 Hz, 2H), 7.14-7.06 (m, 3H), 5.90-5.88 (m, 1H), 4.60 (s, 1H), 4.36-4.24 (m, 2H), 4.02-3.98 (m, 2H), 2.23 (s, 3H). $^{13}$C NMR (101 MHz, CDCl$_3$) $\delta$ 155.32, 144.02, 142.88, 137.92, 133.76, 130.85, 129.53, 129.46, 128.73, 127.70, 127.53, 127.45, 126.73, 124.26, 115.66, 71.85, 56.06, 45.05, 21.33. HRMS (m/z) [ESI]: calculated for C$_{23}$H$_{22}$N$_2$O$_4$SNa$^+$ [M+Na]$^+$: 445.1300, found 445.1188.

![Chemical structure of 3al](image)
methyl 2-(((1-tosylindolin-3-yl)oxy)carbonyl)amino)pentanoate (3al). Yellow oil (0.044 g, 33%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. $^1$H NMR (600 MHz, Chloroform-$d$) $\delta$ 7.75 (d, $J$ = 8.2 Hz, 1H), 7.66-7.64 (m, 2H), 7.39-7.34 (m, 2H), 7.24-7.22 (m, 2H), 7.08-7.06 (m, 1H), 5.86 (d,
\[ J = 4.3 \text{ Hz, 1H}, \ 4.88-4.80 \text{ (m, 1H)}, \ 4.30 \text{ (d, } J = 7.9 \text{ Hz, 1H)}, \ 4.01-3.98 \text{ (m, 2H)}, \ 3.74 \text{ (d, } J = 25.8 \text{ Hz, 2H)}, \ 2.37 \text{ (d, } J = 2.2 \text{ Hz, 3H)}, \ 1.78-1.74 \text{ (m, 2H)}, \ 1.36-1.33 \text{ (m, 2H)}, \ 0.91-0.86 \text{ (m, 3H)}. \]

\[^{13}\text{C NMR} \ (151 \text{ MHz, CDCl}_3) \ \delta 172.76, 154.86, 144.18, 142.90, 133.70, 130.89, 129.58, 127.52, 126.71, 124.26, 115.75, 115.56, 71.96, 56.05, 53.51, 52.36, 34.78, 21.52, 18.45, 13.63. \]

HRMS (m/z) [ESI]: calculated for \( \text{C}_{22}\text{H}_{26}\text{N}_2\text{O}_6\text{SNa}^+ [M+Na]^+ \): 469.1512, found 469.1405.

\[
\begin{align*}
\text{tert-butyl } & \text{(((1-tosylindolin-3-yl)oxy)carbonyl)alaninate (3ak). Yellow oil (0.042 g,} \\
& \text{31%). Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column} \\
& \text{chromatography.} \\
\text{\[^{1}\text{H NMR} \ (600 \text{ MHz, Chloroform-d}) \ \delta 7.74 \text{ (d, } J = 8.1 \text{ Hz, 1H)}, \\
& 7.64-7.62 \text{ (m, 2H)}, 7.38-7.34 \text{ (m, 2H)}, 7.23-7.21 \text{ (m, 2H)}, 7.08-7.05 \text{ (m, 1H)}, 5.86- \\
& 5.82 \text{ (m, 1H)}, 4.95-4.91 \text{ (m, 1H)}, 4.17-4.14 \text{ (m, 1H)}, 3.99-3.98 \text{ (m, 2H), 2.37 (s, 3H),} \\
& 1.44 \text{ (d, } J = 4.6 \text{ Hz, 9H}, 1.36-1.34 \text{ (m, 3H)}. \]^{13}\text{C NMR} \ (151 \text{ MHz, CDCl}_3) \ \delta 171.79, \\
& 154.49, 144.24, 142.87, 133.65, 130.81, 129.59, 129.37, 127.43, 126.73, 124.27, \\
& 115.70, 82.09, 71.73, 56.04, 49.97, 49.30, 27.92, 21.48, 19.28. \] \text{HRMS (m/z) [ESI]: calculated for } \\
& \text{C}_{23}\text{H}_{28}\text{N}_2\text{O}_6\text{SNa}^+ [M+Na]^+: 483.1668, \text{found 483.1559.}
\end{align*}
\]

\[
\begin{align*}
\text{1-(phenylsulfonyl)indolin-3-yl pyrrolidine-1-carboxylate (3ba). White solid (0.084 g,} \\
& \text{75%). mp:117-119^\circ \text{C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for} \\
& \text{column chromatography.} \]^{1}\text{H NMR} \ (400 \text{ MHz, Chloroform-d}) \ \delta 7.81 \text{ (d, } J = 7.3 \text{ Hz,}
\end{align*}
\]
1H, 7.75 (d, J = 8.2 Hz, 1H), 7.56-7.52 (m, 1H), 7.45-7.35 (m, 4H), 7.08-7.04 (m, 1H), 5.93-5.90 (m, 1H), 4.04-4.03 (m, 2H), 3.36-3.33 (m, 2H), 2.97-2.94 (m, 2H), 1.82-1.77 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 154.03, 142.65, 136.90, 133.16, 130.68, 129.66, 129.03, 127.29, 126.96, 124.04, 114.95, 71.58, 56.19, 46.16, 45.66, 25.52, 24.85. HRMS (m/z) [ESI]: calculated for C19H20N2O4SNa [M+Na]+: 395.1144, found 395.1035.

1-(4-methoxyphenyl)sulfonylindolin-3-yl pyrrolidine-1-carboxylate (3ca). White solid (0.081 g, 67%). mp:137-139°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. 1H NMR (400 MHz, Chloroform-d) δ 7.75-7.72 (m, 3H), 7.40-7.34 (m, 2H), 7.07-7.03 (m, 1H), 6.88 (d, J = 8.8 Hz, 2H), 5.92-5.90 (m, 1H), 4.00 (d, J = 4.6 Hz, 2H), 3.80 (s, 3H), 3.36-3.33 (m, 2H), 2.99-2.96 (m, 2H), 1.82-1.76 (m, 4H). 13C NMR (101 MHz, CDCl3) δ 163.35, 154.05, 142.86, 130.61, 129.71, 129.45, 128.43, 126.90, 123.90, 115.03, 114.15, 71.65, 56.10, 55.51, 46.14, 45.67, 25.52, 24.85. HRMS (m/z) [ESI]: calculated for C20H22N2O5SNa+ [M+Na]+: 425.1249, found 425.1140.

1-((4-chlorophenyl)sulfonyl)indolin-3-yl pyrrolidine-1-carboxylate (3da). White solid (0.090 g, 73%). mp:131-133°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. 1H NMR (400 MHz, Chloroform-d) δ 7.73 (t, J =
8.1 Hz, 2H), 7.45-7.34 (m, 3H), 7.09 (td, J = 7.5, 0.8 Hz, 1H), 5.89 (dd, J = 6.8, 2.1 Hz, 1H), 3.34 (t, J = 6.1 Hz, 2H), 2.89 (dt, J = 9.1, 5.0 Hz, 2H), 1.86-1.75 (m, 5H).

\(^{13}\text{C NMR}\) (101 MHz, CDCl\(_3\)) \(\delta\) 153.90, 142.39, 139.82, 135.33, 130.77, 129.87, 129.30, 128.66, 127.05, 124.46, 115.28, 71.53, 56.22, 46.17, 45.66, 25.58, 24.84.

\(\text{HRMS (m/z) [ESI]}:\) calculated for C\(_{19}\)H\(_{19}\)ClN\(_2\)O\(_4\)SNa\(^+\) [M+Na\(^+\)]: 429.0754, found 429.0634.

5-methyl-1-tosylidinolin-3-yl pyrrolidine-1-carboxylate (3ea). White solid (0.090 g, 75%). mp:152-153°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. \(^1\text{H NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) 7.67-7.61 (m, 3H), 7.21-7.15 (m, 4H), 5.88-5.86 (m, 1H), 3.39-3.38 (m, 2H), 3.36-3.33 (m, 2H), 2.96-2.93 (m, 2H), 2.32 (d, J = 32.7 Hz, 6H), 1.82-1.77 (m, 4H).

\(^{13}\text{C NMR}\) (151 MHz, CDCl\(_3\)) \(\delta\) 154.08, 143.94, 140.43, 133.81, 133.75, 131.33, 129.83, 129.59, 127.23, 114.93, 71.69, 56.26, 46.12, 45.63, 25.58, 24.86, 21.49, 20.85. \(\text{HRMS (m/z) [ESI]}:\) calculated for C\(_{21}\)H\(_{24}\)N\(_2\)O\(_4\)SNa\(^+\) [M+Na\(^+\)]: 423.1457, found 423.1368.

5-chloro-1-tosylidinolin-3-yl pyrrolidine-1-carboxylate (3fa). White solid (0.066 g, 53%). mp:126-128°C. Petroleum ether/ethyl acetate = 20/1-10/1 (v/v) as eluent for column chromatography. \(^1\text{H NMR}\) (600 MHz, Chloroform-\(d\)) \(\delta\) 7.68-7.65 (m, 3H), 7.37 (d, J = 1.8 Hz, 1H), 7.32-7.31 (m, 1H), 7.23 (d, J = 8.1 Hz, 2H), 5.87-5.86 (m, 1H), 4.02-4.00 (m, 2H), 3.36-3.34 (m, 2H), 2.96-2.94 (m, 2H), 2.37 (s, 3H), 1.83-1.78
(m, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 153.74, 144.37, 141.39, 133.51, 131.53, 130.68, 129.75, 129.11, 127.32, 127.04, 116.13, 70.98, 56.26, 46.18, 45.67, 25.58, 24.84, 21.51. HRMS (m/z) [ESI]: calculated for C$_{20}$H$_{21}$ClN$_2$O$_4$Na$^+$ [M+Na]$^+$: 443.0911, found 443.0798.

5-bromo-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (3ga). White solid (0.050 g, 36%). mp:133-135°C. Petroleum ether/ethyl acetate = 20/1-5/1 (v/v) as eluent for column chromatography. $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.66 (d, $J = 8.3$ Hz, 2H), 7.62 (d, $J = 8.7$ Hz, 1H), 7.52 (d, $J = 1.8$ Hz, 1H), 7.47-7.45 (m, 1H), 7.24 (d, $J = 8.1$ Hz, 2H), 5.88-5.87 (m, 1H), 4.01-3.99 (m, 2H), 3.36-3.34 (m, 2H), 2.97-2.95 (m, 2H), 2.37 (s, 3H), 1.83-1.78 (m, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 153.73, 144.40, 141.91, 133.55, 133.50, 131.89, 129.96, 129.77, 127.31, 116.53, 116.48, 70.90, 56.20, 46.19, 45.68, 25.58, 24.84, 21.52. HRMS (m/z) [ESI]: calculated for C$_{20}$H$_{21}$BrN$_2$O$_4$Na$^+$ [M+Na]$^+$: 487.0405, found 489.0274.

5-methoxy-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (3ha). White solid (0.028 g, 23%). mp:116-118°C. Petroleum ether/ethyl acetate = 20/1-5/1 (v/v) as eluent for column chromatography. $^1$H NMR (600 MHz, Chloroform-$d$) δ 7.67 (d, $J = 9.6$ Hz, 1H), 7.63 (d, $J = 8.3$ Hz, 2H), 7.20 (d, $J = 8.1$ Hz, 2H), 6.92-6.91 (m, 2H), 5.85-5.84 (m, 1H), 4.05-4.01 (m, 1H), 3.97-3.95 (m, 1H), 3.76 (s, 3H), 3.36-3.32 (m, 2H), 2.91-2.89 (m, 2H), 2.35 (s, 4H), 1.82-1.77 (m, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) δ 156.72,
5-cyano-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (3ia). White solid (0.039 g, 32%). mp: 119-120°C. Petroleum ether/ethyl acetate = 10/1-8/1 (v/v) as eluent for column chromatography. $^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.77 (d, $J = 8.5$ Hz, 1H), 7.69-7.67 (m, 3H), 7.62-7.61 (m, 1H), 7.24 (d, $J = 4.1$ Hz, 2H), 5.93-5.91 (m, 1H), 4.04-4.03 (m, 2H), 3.35-3.33 (m, 2H), 3.02-2.97 (m, 2H), 2.36 (s, 3H), 1.82-1.78 (m, 4H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$ 153.55, 146.28, 144.96, 135.06, 133.50, 131.29, 130.65, 129.97, 127.15, 118.54, 114.79, 106.87, 70.31, 56.14, 46.25, 45.73, 25.56, 24.81, 21.55. HRMS (m/z) [ESI]: calculated for C$_{21}$H$_{21}$N$_3$O$_4$Sn$^+$/[M+Na]$^+$: 434.1100, found 434.1105.

6-methyl-1-tosylindolin-3-yl pyrrolidine-1-carboxylate (3ja). White solid (0.080 g, 67%). mp: 123-125°C. Petroleum ether/ethyl acetate = 10/1-8/1 (v/v) as eluent for column chromatography. $^1$H NMR (600 MHz, Chloroform-d) $\delta$ 7.67 (d, $J = 8.2$ Hz, 2H), 7.56 (s, 1H), 7.25 (d, $J = 6.6$ Hz, 2H), 7.21 (d, $J = 8.1$ Hz, 1H), 6.86 (d, $J = 7.7$ Hz, 1H), 5.86-5.85 (m, 1H), 3.98 (d, $J = 4.6$ Hz, 2H), 3.34-3.31 (m, 2H), 2.93-2.91 (m, 2H), 2.39 (s, 3H), 2.34 (s, 3H), 1.80-1.74 (m, 3H). $^{13}$C NMR (151 MHz, CDCl$_3$) $\delta$
154.11, 144.00, 142.95, 141.12, 133.96, 129.62, 127.29, 126.89, 126.53, 124.89, 115.46, 71.47, 56.44, 46.08, 45.59, 25.57, 24.85, 21.91, 21.49. **HRMS (m/z) [ESI]:** calculated for C$_{21}$H$_{24}$N$_2$O$_4$SNa$^+$ [M+Na]$^+$: 423.1457, found 423.1364.
6. NMR Data

NMR Spectra of Substrates

[Images of NMR spectra and chemical structures]
NMR spectra for the products