Supplementary material

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General considerations

Organic transformations were carried out at ambient temperature, unless indicated otherwise. Organic solvents used in this study were of reagent grade and were used without purification. All other commercially available reagents were of the highest purity (from Sigma Aldrich, Alfa Aesar, Fluorochem, TCI). Metathesis catalysts used were either purchased from Sigma Aldrich, Apeiron-Synthesis (NO_2-Grela) or given by Umicore AG & Co. KG and Materia Inc. All workup and purification procedures were carried out with reagent-grade solvents under ambient atmosphere. Substrates 1a-g were prepared according to literature. Continuous flow experiments were performed using a Uniqsis Flowsyn Multi-X equipment connected to an automated fraction collector (Fig. 1). A 5 mL high temperature PTFE coil reactor was set-up. Flow rates were adapted to ensure an appropriate residence time in the reaction coil.

HPLC analyses were performed with an Agilent model 1220 instrument at 214 nm using: column Phenomenex® Onyx Monolithic HD-C18, 2m, (50 x 4.6 mm), flow 3 ml/min, H_2O (0.1 % TFA)/CH_3CN (0.1 % TFA), gradient 0-0 % (30 s), 0-100 % (3 min) and 100 % (1 min).

^1^H NMR and ^13^C NMR spectra were recorded at 400 MHz and 101 MHz (Bruker Avance III) or at 600 MHz and 150 MHz (Bruker Avance III) using CDCl_3, as solvent. Chemical shifts are given in ppm. The J values are reported in Hertz (Hz), and the splitting patterns are designated as follows: s (singlet), d (doublet), dd (doublet of doublet), t (triplet), m (multiplet), bs (broad singlet).

General procedure

**Flow Procedure using one pump.** The mixture of substrate (1 mmol), catalyst (0.03 mmol, 3 mol%) and dimethylcarbonate (8 mL, 0.125 mmol) was prepared in a vial. After setting the temperature to 120°C, the valve position was switched to place the mixture inline. The reaction mixture was then flowed into the 5mL PTFE residence coil and then through a back-pressure-regulator (BPR) rated to 6.9 bars (100 psi). The collected sample was quenched with ethylvinyl ether to stop the reaction before drying under reduced pressure. Then the residue was diluted with dichloromethane and filtrated through a layer of silica gel (about 1g). The filtrate was evaporated and the obtained residue was treated with diethyl ether giving a grey-white precipitate, which was filtrated off and dried under reduced pressure.

**Flow Procedure using two pumps.** A solution of substrate 1a (430.5 mg, 1 mmol) in dimethylcarbonate (4 mL) was prepared and connected to pump A. Similarly, a solution of M2 (28.5 mg, 0.03 mmol) in dimethyl carbonate (4 mL) was prepared and connected to pump B. After setting the temperature to 120°C, both valve positions were switched to place the mixture inline. Solution A and B, pumped using pump A and pump B, respectively, were flowed in a T-shaped mixer, then into the 5mL PTFE residence coil and then through a back-pressure-regulator (BPR) rated to 6.9 bars (100 psi) at a flow rate ensuring a 1 min residence time (5 mL.min^{-1}). The collected sample was quenched with ethylvinyl ether to stop the reaction before drying under reduced pressure. Then the residue was
diluted with dichloromethane and filtrated through a layer of silica gel (about 1g). The filtrate was evaporated and the obtained residue was treated with diethyl ether giving a grey-white precipitate, which was filtrated off and dried under reduced pressure. Pure compound (334.0 mg, 83% yield) was obtained as a grey-white solid.
Optimization of the reaction conditions

**Table S1.** Optimization of the reaction conditions

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<th>Residence Time (min)</th>
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a Reaction conditions: 1a (0.125 mmol), catalyst (3 mol%), solvent (1 mL), T, residence time. HPLC conversion of 1a into 2a is given. Ratio of isomer iso-1a is given in brackets.

Isomer iso-1a was isolated after 2.0 mmol scale RCM using HG-II (conditions from Table 1, entry 4 (DMC, 110°C, 5 min)) and fully characterized (see below).
**Description of compounds**

**Methyl (Z)-2-(((4-methyl-N-(prop-1-en-1-yl)phenyl)sulfonamido)(2-nitrophenyl)methyl)acrylate (iso-1a)**

\[ ^1H \text{NMR (600 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 7.94 (d, \(J = 8.1\), 1.3 Hz, 1H), 7.77 (d, \(J = 7.6\) Hz, 1H), 7.64 (td, \(J = 7.7, 1.2\) Hz, 1H), 7.59 (d, \(J = 8.4\) Hz, 2H), 7.47 (td, \(J = 7.2, 1.2\) Hz, 1H), 7.23 (d, \(J = 7.8\) Hz 2H), 6.97 (s, 1H), 6.47 (s, 1H), 6.02 (dd, \(J = 13.8, 1.6\) Hz, 1H), 5.53 (d, \(J = 1.2\) Hz, 1H), 5.45 (dq, \(J = 13.5, 6.7\) Hz, 1H), 3.56 (s, 3H), 2.41 (s, 3H), 1.62 (dd, \(J = 6.7, 1.6\) Hz, 3H).

\[ ^1C \text{NMR (150 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 165.6, 148.1, 143.6, 137.8, 137.2, 134.2, 133.4, 131.0, 130.8, 129.4, 128.9, 127.9, 125.8, 125.4, 121.1, 58.9, 52.3, 21.7, 15.7.

HRMS calculated for C\text{\textsubscript{2}}H\text{\textsubscript{2}}N\text{O\textsubscript{6}}S: 431.1277. Found: 431.1274.

**Methyl 2,5-dihydro-2-(2-nitrophenyl)-1-tosyl-1H-pyrrole-3-carboxylate (2a)**

White solid, 87% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 7.90 (d, \(J = 8.0\) Hz, 1H), 7.80 (d, \(J = 8.2\) Hz, 2H), 7.61 – 7.51 (m, 2H), 7.41 (ddd, \(J = 8.5, 5.3, 3.5\) Hz, 1H), 7.34 (d, \(J = 8.0\) Hz, 2H), 6.75 (dd, \(J = 4.0, 2.0\) Hz, 1H), 6.73 – 6.65 (m, 1H), 4.61 (ddd, \(J = 17.4, 6.0, 2.0\) Hz, 1H), 4.36 (dt, \(J = 17.4, 2.7\) Hz, 1H), 3.53 (s, 3H), 2.43 (s, 3H).

\[ ^1C \text{NMR (101 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 162.1, 148.9, 144.3, 136.7, 135.8, 135.2, 133.5, 133.3, 130.2, 129.8, 128.7, 127.9, 124.7, 62.4, 55.8, 52.2, 21.7.

Data in agreement with lit.\textsuperscript{2}

**Methyl 2-(2-chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2b)**

White solid, 91% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 7.59 (d, \(J = 8.2\) Hz, 2H), 7.31 – 7.27 (m, 1H), 7.25 – 7.11 (m, 5H), 6.81 – 6.79 (m, 1H), 6.17 – 6.12 (m, 1H), 4.59 – 4.42 (m, 2H), 3.57 (s, 3H), 2.39 (s, 3H).

\[ ^1C \text{NMR (101 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 161.7, 148.9, 144.3, 136.7, 135.8, 135.2, 133.5, 133.3, 130.0, 129.9, 129.8, 129.2, 127.5, 127.0, 65.5, 55.6, 52.0, 21.6.

Data in agreement with lit.\textsuperscript{3}

**Methyl 2-(2-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2c)**

White solid, 88% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 7.37 (d, \(J = 8.0\) Hz, 2H), 7.23 – 7.17 (m, 2H), 7.11 (d, \(J = 8.0\) Hz, 2H), 6.88 (td, \(J = 7.5, 0.9\) Hz, 1H), 6.76 (dd, \(J = 4.0, 2.0\) Hz, 1H), 6.68 – 6.64 (m, 1H), 6.00 (dt, \(J = 6.0, 1.9\) Hz, 1H), 4.51 (dt, \(J = 16.5, 2.4\) Hz, 1H), 4.37 (ddd, \(J = 16.5, 6.1, 1.9\) Hz, 1H), 3.56 (s, 6H), 2.36 (s, 3H).

\[ ^1C \text{NMR (101 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 162.5, 157.6, 142.9, 136.2, 135.9, 134.3, 130.5, 129.4, 129.3, 127.2, 126.9, 120.6, 111.1, 65.1, 55.5, 55.4, 51.8, 21.6.

Data in agreement with lit.\textsuperscript{4}

**Methyl 2-phenyl-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2d)**

White solid, 92% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 7.42 (d, \(J = 8.0\) Hz, 2H), 7.25 – 7.18 (m, 5H), 7.14 (d, \(J = 8.0\) Hz, 2H), 6.78 (dd, \(J = 3.8, 2.0\) Hz, 1H), 5.74 (dt, \(J = 5.7, 2.0\) Hz, 1H), 4.51 (dt, \(J = 17.1, 2.4\) Hz, 1H), 4.38 (ddd, \(J = 17.1, 5.8, 1.9\) Hz, 1H), 3.58 (s, 3H), 2.37 (s, 3H).

\[ ^1C \text{NMR (101 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 162.3, 143.4, 139.5, 135.8, 135.7, 129.6, 128.4, 128.2, 127.9, 127.2, 69.1, 55.0, 51.9, 21.6.

Data in agreement with lit.\textsuperscript{4}

**Methyl 2-(3-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2e)**

White solid, 52% yield.

\[ ^1H \text{NMR (400 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 7.42 (d, \(J = 7.6\) Hz, 2H), 7.20 – 7.07 (m, 3H), 6.84 (d, \(J = 7.3\) Hz, 1H), 6.77 (s, 2H), 6.67 (s, 1H), 5.71 (s, 1H), 4.51 (d, \(J = 16.9\) Hz, 1H), 4.37 (dd, \(J = 16.9, 4.5\) Hz, 1H), 3.71 (s, 3H), 3.59 (s, 3H), 2.36 (s, 3H).

\[ ^1C \text{NMR (101 MHz, CDCl}_3 \delta \text{ (ppm)} \]
- 162.3, 159.6, 143.4, 140.8, 135.9, 135.8, 129.5, 129.4, 127.2, 120.5, 113.7, 113.4, 69.0, 55.2, 55.1, 52.0, 21.6.
Data in agreement with lit.¹

**Methyl 2-(4-chlorophenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2f)**

White solid, 68% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.45 (d, J = 8.1 Hz, 2H), 7.18 (q, J = 8.6 Hz, 6H), 6.78 (s, 1H), 5.68 (d, J = 5.3 Hz, 1H), 4.50 (d, J = 17.2 Hz, 1H), 4.39 (dd, J = 16.5, 5.0 Hz, 1H), 3.59 (s, 3H), 2.39 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 162.2, 143.8, 138.2, 136.1, 135.5, 135.4, 134.0, 129.7, 129.2, 128.6, 127.2, 68.4, 55.1, 52.0, 21.6.

Data in agreement with lit.¹

**Methyl 2-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate (2g)**

White solid, 81% yield.

¹H NMR (400 MHz, CDCl₃) δ (ppm) 7.43 (d, J = 8.2 Hz, 2H), 7.14 (t, J = 8.1 Hz, 4H), 6.76 (d, J = 8.5 Hz, 3H), 5.70 (d, J = 5.5 Hz, 1H), 4.48 (dt, J = 17.0, 2.3 Hz, 1H), 4.35 (ddd, J = 17.1, 5.7, 1.8 Hz, 1H), 3.77 (s, 3H), 3.59 (s, 3H), 2.37 (s, 3H).

¹³C NMR (101 MHz, CDCl₃) δ (ppm) 162.4, 159.5, 143.3, 135.8, 135.5, 131.7, 129.6, 129.0, 127.2, 113.8, 68.6, 55.4, 54.9, 51.9, 21.6.

Data in agreement with lit.¹

**HPLC chromatograms for the synthesis of 2e and 2f**

Since compounds 2e and 2f could not be isolated in high yields, HPLC chromatograms recorded after the reaction are provided to demonstrate that conversion was almost complete in both cases, with no degradation nor side-products.
NMR spectra of compounds iso-1a and 2a-g

$^1$H NMR of Methyl (E)-2-(((4-methyl-N-(prop-1-en-1-yl)phenyl)sulfonamido)(2-nitrophenyl)methyl) acrylate iso-1a

$^{13}$C NMR of Methyl (E)-2-(((4-methyl-N-(prop-1-en-1-yl)phenyl)sulfonamido)(2-nitrophenyl)methyl) acrylate iso-1a
$^1$H NMR of Methyl 2,5-dihydro-2-(2-nitrophenyl)-1-tosyl-1$H$-pyrrole-3-carboxylate 2a

$^{13}$C NMR of Methyl 2,5-dihydro-2-(2-nitrophenyl)-1-tosyl-1$H$-pyrrole-3-carboxylate 2a
$^1$H NMR of Methyl 2-(2-chlorophenyl)-1-tosyl-2,5-dihydro-$1H$-pyrrole-3-carboxylate 2b

$^{13}$C NMR of Methyl 2-(2-chlorophenyl)-1-tosyl-2,5-dihydro-$1H$-pyrrole-3-carboxylate 2b
$^1$H NMR of Methyl 2-(2-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate 2c

$^{13}$C NMR of Methyl 2-(2-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate 2c
$^1$H NMR of Methyl 2-phenyl-1-tosyl-2,5-dihydro-1$H$-pyrrole-3-carboxylate 2d

$^{13}$C NMR of Methyl 2-phenyl-1-tosyl-2,5-dihydro-1$H$-pyrrole-3-carboxylate 2d
$^1$H NMR of Methyl 2-(3-methoxyphenyl)-1-tosyl-2,5-dihydro-1$H$-pyrrole-3-carboxylate 2e

$^{13}$C NMR of Methyl 2-(2-methoxyphenyl)-1-tosyl-2,5-dihydro-1$H$-pyrrole-3-carboxylate 2e
$^1$H NMR of Methyl 2-(4-chlorophenyl)-1-tosyl-2,5-dihydro-1$H$-pyrrole-3-carboxylate 2f

$^{13}$C NMR of Methyl 2-(4-chlorophenyl)-1-tosyl-2,5-dihydro-1$H$-pyrrole-3-carboxylate 2f
$^1$H NMR of Methyl 2-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate 2g

$^{13}$C NMR of Methyl 2-(4-methoxyphenyl)-1-tosyl-2,5-dihydro-1H-pyrrole-3-carboxylate 2g
References