Supporting Information

Table of Contents

<table>
<thead>
<tr>
<th>Table of Contents</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. General Information</td>
<td>2</td>
</tr>
<tr>
<td>2. Synthesis of substrates 2a-c</td>
<td>3</td>
</tr>
<tr>
<td>3. Asymmetric synthesis of 4</td>
<td>4</td>
</tr>
<tr>
<td>4. Reference</td>
<td>16</td>
</tr>
<tr>
<td>5. NMR Spectra and Chiral HPLC Data</td>
<td>17</td>
</tr>
</tbody>
</table>
1. General information

- Chemicals were purchased from Acros or Aldrich and used without further purification unless otherwise noted. Solvents were predistilled according to standard laboratory methods.
- Chromatographic purification of the products was performed on Merck silica gel 60, particle size 0.040-0.063 mm (230-240 mesh, flash).
- Analytical TLC: SIL G-25 UV254 from MACHEREY&NAGEL. Visualization of the developed TLC plates was performed with ultraviolet irradiation (254 nm) or by staining with basic potassium permanganate solution.
- Optical rotation values were measured on a Perkin-Elmer 241 polarimeter.
- Melting points were determined using a Büchi 510 apparatus and are uncorrected.
- Mass spectra were acquired on a Finnigan SSQ7000 (EI/CI) spectrometer and high resolution mass spectra on a Finnigan MAT 95 (EI/CI) or on a ThermoFisher Scientific LTQOrbitrap XL (ESI). All signals over 10% relative intensity are listed.
- IR spectra were taken on a Perkin-Elmer FT-IR Spectrum 100 using a Diamant/KRS5 ATR. Evaluation was done using the supplementary software. The absorption bands are given in wave numbers (cm⁻¹).
- ¹H- and ¹³C- NMR spectra were recorded at ambient temperature on Varian Mercury 300, VNMRS 600 and Inova 400 instruments. The chemical shifts are reported in ppm downfield of tetramethylsilane (TMS) and referenced to residual solvent peaks resonance as internal standard. The order of citation in parentheses is a) multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, dd= doublet of doublet, ddd= doublet of doublet of doublet, td = triplet of doublet, m = multiplet), b) coupling constants, c) number of protons. Coupling constants (J) are reported in Hertz (Hz).
- Analytical HPLC was performed on a Hewlett-Packard 1100 Series instrument using chiral stationary phases (CHIRALPAK AS, CHIRALPAK AD, CHIRALPAK IA, CHIRALPAK IB, DAICELAD.M, DAICELAS.M).
- Racemic compounds were prepared by using 10 mol% of racemic catalyst B.
- Compounds 2a-c were synthesized according to the literature.¹¹
2. Synthesis of the iminomalonate substrates 2a-c:

2-Oxomalonates (1.0 equiv), 2,2,2-trifluoroethylamine hydrochloride (1.5 equiv) and p-toluenesulfonic acid (0.05 equiv) were dissolved in toluene in a two-necked flask with a water separator and a condenser. The resulting solution was heated to reflux until complete disappearance of the starting materials, after which it was cooled to room temperature, washed with saturated NaHCO₃ solution and dried over anhydrous Na₂SO₄. Then the solvent was evaporated to dryness and the residue was purified by flash chromatography (pentane/Et₂O = 20/1 to 10/1) to provide the desired product 2.

![Image of 2a](image1.png)

**Diethyl 2-((2,2,2-trifluoroethyl)imino)malonate (2a)**

According to the general procedure, 2a was obtained as a colorless oil (2.7 g, 71% yield).

1H NMR (600 MHz, CDCl₃) δ 4.40 – 4.35 (m, 4H), 4.21 (q, J = 9.6 Hz, 2H), 1.35 (t, J = 7.2 Hz, 6H) ppm.

13C NMR (150 MHz, CDCl₃) δ 161.1, 159.8, 156.6, 123.8 (q, J = 275.1 Hz), 62.9, 62.8, 55.1 (q, J = 33.0 Hz), 14.0, 13.9 ppm.

IR (ATR): 3467, 2987, 2322, 1738, 1459, 1385, 1250, 1144, 1077, 928, 856, 777, 674 cm⁻¹.

MS (ESI): m/z = 256.1 [M+H]⁺.

HRMS (ESI): m/z [M+H]⁺ calcd for C₉H₁₃NO₄F₃⁺: 256.0797; found 256.0791.

![Image of 2b](image2.png)

**Dimethyl 2-((2,2,2-trifluoroethyl)imino)malonate (2b)**

According to the general procedure, 2b was obtained as a colorless oil (0.12 g, 53% yield).

1H NMR (600 MHz, CDCl₃) δ 4.22 (q, J = 9.6 Hz, 2H), 3.92 (s, 6H) ppm.

13C NMR (150 MHz, CDCl₃) δ 161.5, 160.0, 155.7, 123.7 (q, J = 275.0 Hz), 55.2 (q, J = 33.0 Hz), 53.5, 53.1 ppm.

IR (ATR): 3470, 2962, 2322, 2102, 1740, 1674, 1440, 1255, 1147, 1078, 925, 851, 800, 675 cm⁻¹.

MS (ESI): m/z = 228.0 [M+H]⁺.

HRMS (ESI): m/z [M+H]⁺ calcd for C₇H₉NO₄F₃⁺: 228.0484; found 228.0478.
Diisopropyl 2-((2,2,2-trifluoroethyl)imino)malonate (2c)

According to the general procedure, 2c was obtained as a colorless oil (0.16 g, 56% yield).

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 5.27 – 5.18 (m, 2H), 4.21 (q, J = 9.6 \text{ Hz}, 2H), 1.34 (d, J = 6.0 \text{ Hz}, 6H), 1.33 (d, J = 6.0 \text{ Hz}, 6H) \text{ ppm}\)

\(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta 160.5, 159.4, 157.2, 123.8 (q, J = 275.1 \text{ Hz}), 71.2, 71.0, 54.9 (q, J = 33.0 \text{ Hz}), 21.6, 21.5 \text{ ppm}\).

IR (ATR): 3466, 2983, 2933, 2325, 2083, 1735, 1461 1378, 1254, 1144, 1079, 913, 829, 674 cm\(^{-1}\).

MS (ESI): \(m/z = 284.1 [\text{M+H}]^+\).

HRMS (ESI): \(m/z [\text{M+H}]^+ \text{ calcd for C}_{11}\text{H}_{17}\text{NO}_4\text{F}_3: 284.1110; \text{ found 284.1104.}\)

3. Asymmetric synthesis of 4:

A 10 mL glass tube equipped with a stirring bar was charged with the \(\alpha,\beta\)-unsaturated-aldehyde 1 (0.48 mmol, 1.2 equiv), the iminomalonate 2 (0.4 mmol, 1.0 equiv), catalyst B (0.02 mmol, 5 mol %) and toluene (4.0 mL). The resulting solution was stirred at room temperature for indicated time and then Ph\(_3\)P=CHCO\(_2\)Me (0.6 mmol, 1.5 equiv) was added. After 4 h the solvent was evaporated to give the crude product, which was directly purified by flash chromatography (pentane/Et\(_2\)O = 4/1 to 1/1) to provide the desired product 4.

![Chemical Structure](image)

Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-phenyl-5-(trifluoromethyl) pyrrolidine-2,2-dicarboxylate (4a)

According to the above general procedure by using 1a (0.063 g, 0.48 mmol), 2a (0.120 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 24 h at room temperature followed by addition of Ph\(_3\)P=CHCO\(_2\)Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et\(_2\)O = 4/1 to 1/1) afforded 4a as a colorless solid (0.163 g, 92% yield).

Melting Point: 105-107 \(^\circ\)C.

\([\alpha]_D^{25} = +59.2 \text{ (c = 1.0, CHCl}_3\text{).}\)

HPLC: CHIRALPAK AS; \(n\)-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 \(^\circ\)C; retention time: 9.26 min (major), 11.51 min (minor), ee: 99%.

\(^1\)H NMR (600 MHz, CDCl\(_3\)): \(\delta 7.33 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.22 – 7.19 (m, 2H), 7.06 (dd, J = 15.6, 9.0 \text{ Hz}, 1H), 5.59 (d, J = 15.6 \text{ Hz}, 1H), 4.30 (q, J = 7.2 \text{ Hz}, 2H), 4.27 – 4.21 (m, 2H), 4.01 – 3.94 (m, 1H), 3.79 (dd, J = 12.0, 9.6 \text{ Hz}, 1H), 3.64 (s, 3H), 3.60 – 3.52 (m, 1H), 3.28 (dd, J = 12.0, 9.0 \text{ Hz}, 1H), 1.27 (t, J = 7.2 \text{ Hz}, 6H) \text{ ppm}\).

\(^13\)C NMR (150 MHz, CDCl\(_3\)): \(\delta 170.0, 168.5, 165.9, 142.7, 136.6, 129.0 (2C), 127.9, 127.7 (2C), 125.3 (q, J = 278.0 \text{ Hz}), 125.1, 73.7, 65.2 (q, J = 30.0 \text{ Hz}), 62.7, 62.0, 56.7, 51.6, 50.6, 14.0, 13.9 ppm.

IR (ATR): 3340, 2922, 2291, 2105, 1720, 1656, 1444, 1370, 1277, 1224, 1142, 1014, 979, 924, 861, 750, 697 cm\(^{-1}\).
MS (ESI): \( m/z = 444.2 \) [M+H].

HRMS (ESI): \( m/z \) [M+H]+ calcld for \( C_{21}H_{25}NO_6F_3+: 444.1634 \); found 444.1645.

The gram scale reaction for the synthesis of 4a was carried out in a similar manner.
A round-bottom flask equipped with a stirring bar was charged with \( \alpha,\beta \)-unsaturated-aldehyde 1a (0.475 g, 3.6 mmol, 1.2 equiv), iminomalonate 2a (0.765 g, 3.0 mmol, 1.0 equiv), catalyst B (49 mg, 0.15 mmol, 5 mol %) and toluene (30 mL). The resulting solution was stirred at room temperature for the indicated time and then Ph₃P=CHCO₂Me (1.50 g, 4.5 mmol, 1.5 equiv) was added. After 4 h the solvent was evaporated to give the crude product, which was directly purified by flash chromatography (pentane/Et₂O = 4/1 to 1/1) to provide the desired product 4a (1.16 g, 88%, dr: > 20:1, ee: > 99%). The analytical data of the gram scale reaction of 4a are consistent with those of the 0.4 mmol scale experiment.

Diethyl (3R,4S,5R)-4-[[1,1'-biphenyl]-4-yl]-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4b)

According to the above general procedure by using 1b (0.100 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4b as a colorless solid (0.187 g, 90% yield).

Melting Point: 99-102 °C.

\([\alpha]_D^{25} = +70.5 \) (c = 1.0, CHCl₃).

HPLC: DAICELAD.M; n-heptane/iPrOH = 9/1; flow rate 1.0 mL/min; T= 30 °C; retention time: 9.83 min (major), 20.87 min (minor), ee: 96%.

\(^1\)H NMR (400 MHz, CDCl₃) \( \delta \) 7.58 – 7.50 (m, 4H), 7.44 – 7.39 (m, 2H), 7.34 – 7.30 (m, 1H), 7.26 (d, \( J = 8.4 \) Hz, 2H), 7.07 (dd, \( J = 15.6, 8.8 \) Hz, 1H), 5.63 (d, \( J = 15.6 \) Hz, 1H), 4.35 – 4.19 (m, 4H), 4.02 – 3.95 (m, 1H), 3.82 (dd, \( J = 11.6, 9.6 \) Hz, 1H), 3.64 (s, 3H), 3.59 – 3.50 (m, 1H), 3.31 (dd, \( J = 11.6, 8.8 \) Hz, 1H), 1.27 (t, \( J = 7.2 \) Hz, 6H) ppm.

\(^{13}\)C NMR (100 MHz, CDCl₃) \( \delta \) 170.0, 168.5, 165.9, 142.6, 140.7, 140.3, 135.6, 128.8 (2C), 128.1 (2C), 127.6 (2C), 127.4, 127.0 (2C), 125.4 (q, \( J = 278.3 \) Hz), 125.2, 73.8, 65.2 (q, \( J = 29.7 \) Hz), 62.8, 62.1, 56.7, 51.6, 50.3, 14.0, 13.9 ppm.

IR (ATR): 3343, 2985, 2323, 2079, 1723, 1439, 1372, 1276, 1227, 1136, 1004, 923, 847, 759, 696 cm⁻¹.

MS (ESI): \( m/z = 520.2 \) [M+H].

HRMS (ESI): \( m/z \) [M+H]+ calcld for \( C_{27}H_{29}NO_6F_3+: 520.1947 \); found 520.2008.
Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(p-tolyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4c)

According to the above general procedure by using 1c (0.070 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4c as a colorless solid (0.172 g, 94% yield).

Melting Point: 98-100 °C.

[α]_{D}^{25} = +64.2 (c = 1.0, CHCl₃).

HPLC: DAICELAD.M; n-heptane/iPrOH = 8/2; flow rate 1.0 mL/min; T= 30 °C; retention time: 8.31 min (major), 24.30 min (minor), ee: >99%.

1H NMR (400 MHz, CDCl₃) δ 7.12 – 6.99 (m, 5H), 5.58 (d, J = 15.6 Hz, 1H), 4.32 – 4.18 (m, 5H), 3.97 – 3.88 (m, 1H), 3.74 (dd, J = 11.6, 9.6 Hz, 1H), 3.63 (s, 3H), 3.24 (dd, J = 11.6, 8.8 Hz, 1H), 2.29 (s, 3H), 1.28 – 1.24 (m, 6H) ppm.

13C NMR (100 MHz, CDCl₃) δ 170.0, 168.5, 165.9, 142.8, 137.5, 133.5, 129.7 (2C), 125.4 (q, J = 278.0 Hz), 125.0, 73.7, 65.2 (q, J = 29.7 Hz), 62.7, 62.0, 56.6, 51.5, 50.2, 21.0, 14.0, 13.9 ppm.

IR (ATR): 3353, 2986, 2324, 2084, 1993, 1726, 1660, 1508, 1441, 1372, 1277, 1220, 1137, 1012, 926, 862, 813, 737 cm⁻¹.

MS (ESI): m/z = 458.2 [M+H]⁺.

HRMS (ESI): m/z [M+H]⁺ calcd for C₂₂H₂₇NO₆F₃⁺: 458.1790; found 458.1797.

Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(4-methoxyphenyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4d)

According to the above general procedure by using 1d (0.078 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 12 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4d as a colorless solid (0.175 g, 92% yield).

Melting Point: 98-100 °C.

[α]_{D}^{25} = +63.8 (c = 1.0, CHCl₃).

HPLC: DAICELAD.M; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 °C; retention time:
11.22 min (major), 28.95 min (minor), ee: >99%.

**1H NMR (600 MHz, CDCl₃)** δ 7.11 (d, J = 8.4 Hz, 2H), 7.05 (dd, J = 15.6, 8.4 Hz, 1H), 6.84 (d, J = 8.4 Hz, 2H), 5.59 (d, J = 15.6 Hz, 1H), 4.31 – 4.21 (m, 4H), 3.91 (s, 1H), 3.77 (s, 3H), 3.76 – 3.72 (m, 3H), 3.53 (d, J = 5.4 Hz, 1H), 3.29 – 3.17 (m, 1H), 1.27 (t, J = 7.2 Hz, 6H) ppm.

**13C NMR (150 MHz, CDCl₃)** δ 170.0, 168.5, 165.9, 159.0, 142.8, 128.7 (2C), 128.4, 125.4 (q, J = 278.0 Hz), 125.1, 114.3 (2C), 73.6, 65.2 (q, J = 29.6 Hz), 62.7, 62.0, 56.7, 55.2, 51.5, 49.9, 14.0, 13.9 ppm.

**IR (ATR):** 3354, 2948, 2304, 2097, 1916, 1723, 1660, 1515, 1439, 1367, 1275, 1130, 1016, 924, 824, 734, 694 cm⁻¹.

**MS (ESI):** m/z = 474.2 [M+H]⁺.

**HRMS (ESI):** m/z [M+H]⁺ calcd for C₂₂H₂₇NO₇F₃⁺: 474.1740; found 474.1749.

Diethyl (3R,4S,5R)-4-(4-(dimethylamino)phenyl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4e)

According to the above general procedure by using 1e (0.085 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4e as a light red solid (0.121 g, 60% yield).

**Melting Point:** 145-147 ºC.

[α]D²⁵ = +75.2 (c = 1.0, CHCl₃).

**HPLC:** CHIRALPAK IA; n-heptane/EtOH = 9/1; flow rate 1.0 mL/min; T= 30 ºC; retention time: 7.16 min (major), 8.75 min (minor), ee: >99%.

**1H NMR (400 MHz, CDCl₃)** δ 7.08 – 6.99 (m, 3H), 6.63 (d, J = 8.8 Hz, 2H), 5.61 (d, J = 15.6 Hz, 1H), 4.34 – 4.15 (m, 4H), 3.93 – 3.83 (m, 1H), 3.71 – 3.66 (m, 1H), 3.63 (s, 3H), 3.47 (d, J = 7.6 Hz, 1H), 3.22 (dd, J = 11.6, 8.8 Hz, 1H), 2.91 (s, 6H), 1.28 – 1.24 (m, 6H) ppm.

**13C NMR (100 MHz, CDCl₃)** δ 170.2, 168.6, 165.9, 150.0, 143.2, 128.3 (2C), 125.5 (q, J = 278.9 Hz), 124.9, 123.7, 112.6 (2C), 73.6, 65.2 (q, J = 29.3 Hz), 62.6, 61.9, 56.5, 51.5, 49.9, 40.4 (2C), 14.0, 13.9 ppm.

**19F NMR (376 MHz, CDCl₃)** δ -74.9 (d, J = 6.4 Hz) ppm.

**IR (ATR):** 3365, 2923, 2640, 2318, 2003, 1937, 1723, 1612, 1526, 1445, 1366, 1271, 1227, 1129, 992, 861, 817, 702 cm⁻¹.

**MS (ESI):** m/z = 487.2 [M+H]⁺.

**HRMS (ESI):** m/z [M+H]⁺ calcd for C₂₃H₃₇N₂O₆F₃⁺: 487.2056; found 487.2067.
Diethyl (3R,4S,5R)-4-(4-fluorophenyl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4f)

According to the above general procedure by using 1f (0.072 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 24 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4f as a colorless solid (0.168 g, 91% yield).

**Melting Point:** 98-100 °C.

$[\alpha]_D^{25} = +54.7$ (c = 1.0, CHCl3).

**HPLC:** DAICELAS.M; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 °C; retention time: 9.54 min (major), 12.62 min (minor), ee: >99%.

**1H NMR (600 MHz, CDCl3)** δ 7.19 – 7.16 (m, 2H), 7.07 – 6.98 (m, 3H), 5.58 (d, J = 15.6 Hz, 1H), 4.33 – 4.20 (m, 4H), 3.95 – 3.90 (m, 1H), 3.80 – 3.75 (m, 1H), 3.65 (s, 3H), 3.57 – 3.51 (m, 1H), 3.21 (dd, J = 11.4, 9.6 Hz, 1H), 1.26 (t, J = 7.2 Hz, 6H) ppm.

**13C NMR (150 MHz, CDCl3)** δ 169.9, 168.4, 165.8, 162.2 (d, J = 245.4 Hz), 142.4, 132.3, 129.3 (d, J = 8.1 Hz, 2C), 125.3, 125.2 (q, J = 278.4 Hz), 116.0 (d, J = 6.5 Hz, 2C), 73.5, 65.2 (q, J = 29.9 Hz), 62.8, 62.1, 56.8, 51.6, 49.9, 14.0, 13.9 ppm.

**IR (ATR):** 3356, 2980, 2321, 2083, 1993, 1924, 1722, 1607, 1514, 1440, 1368, 1277, 1223, 1121, 997, 921, 835, 753, 693 cm$^{-1}$.

**MS (ESI):** m/z = 462.2 [M+H]+.

**HRMS (ESI):** m/z [M+H]+ calcd for C21H24NO6F4+: 462.1540; found 462.1548.

Diethyl (3R,4S,5R)-4-(4-chlorophenyl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4g)

According to the above general procedure by using 1g (0.080 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4g as a colorless solid (0.147 g, 77% yield).

**Melting Point:** 90-92 °C.

$[\alpha]_D^{25} = +71.6$ (c = 1.0, CHCl3).
HPLC: DAICELAS.M; n-heptane/EtOH = 97/3; flow rate 1.0 mL/min; T= 30 °C; retention time: 9.16 min (major), 10.92 min (minor), ee: >99%.

**1H NMR (400 MHz, CDCl₃)** \(\delta\) 7.28 (d, \(J = 8.4\) Hz, 2H), 7.12 (d, \(J = 8.4\) Hz, 2H), 7.02 (dd, \(J = 15.6, 8.8\) Hz, 1H), 5.57 (d, \(J = 15.6\) Hz, 1H), 4.33 – 4.17 (m, 4H), 3.95 – 3.86 (m, 1H), 3.75 (d, \(J = 6.8\) Hz, 1H), 3.20 (dd, \(J = 11.6, 8.8\) Hz, 1H), 1.27 – 1.23 (m, 6H) ppm.

**13C NMR (100 MHz, CDCl₃)** \(\delta\) 169.8, 168.3, 165.7, 142.2, 135.1, 133.7, 129.2 (2C), 129.1 (2C), 125.2 (q, \(J = 278.1\) Hz), 125.3, 73.6, 65.1 (q, \(J = 30.0\) Hz), 62.8, 62.1, 56.6, 51.6, 50.0, 14.0, 13.8 ppm.

**IR (ATR):** 3344, 2984, 2306, 2095, 1720, 1659, 1441, 1372, 1279, 1226, 1139, 1012, 828, 757, 692 cm⁻¹.

**MS (ESI):** \(m/z = 478.1\) [M+H]+.

**HRMS (ESI):** \(m/z\) [M+H]+ calcd for C₂₁H₂₄NO₆ClF₃+: 478.1244; found 478.1232.

**Diethyl (3R,4S,5R)-4-(4-bromophenyl)-3-((E)-3-methoxy-3-oxoprop-1-yl)-5-(trifluoro methyl)pyrrolidine-2,2-dicarboxylate (4h)**

According to the above general procedure by using 1h (0.101 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/iPrOH = 4/1 to 1/1) afforded 4h as a colorless solid (0.169 g, 81% yield).

**Melting Point:** 100-102 °C.

\([\alpha]_{D}^{25} = +74.0\) (c = 1.0, CHCl₃).

**HPLC:** DAICELAS.M; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 °C; retention time: 10.16 min (major), 13.09 min (minor), ee: 94%.

**1H NMR (400 MHz, CDCl₃)** \(\delta\) 7.42 (d, \(J = 8.4\) Hz, 2H), 7.07 (d, \(J = 8.4\) Hz, 2H), 7.01 (dd, \(J = 15.6, 8.8\) Hz, 1H), 5.57 (d, \(J = 15.6\) Hz, 1H), 4.32 – 4.15 (m, 4H), 3.96 – 3.86 (m, 1H), 3.54 (d, \(J = 7.2\) Hz, 1H), 3.20 (dd, \(J = 11.6, 8.8\) Hz, 1H), 1.27 – 1.23 (m, 6H) ppm.

**13C NMR (100 MHz, CDCl₃)** \(\delta\) 169.8, 168.3, 165.7, 142.2, 135.7, 132.2 (2C), 129.4 (2C), 125.4, 125.2 (q, \(J = 278.1\) Hz), 121.8, 73.6, 65.1 (q, \(J = 29.9\) Hz), 62.8, 62.1, 56.6, 51.6, 50.1, 14.0, 13.8 ppm.

**IR (ATR):** 3335, 2986, 2308, 2077, 1723, 1441, 1371, 1278, 1221, 1137, 1006, 856, 745, 693 cm⁻¹.

**MS (ESI):** \(m/z = 520.2\) [M+H]+.

**HRMS (ESI):** \(m/z\) [M+H]+ calcd for C₂₁H₂₄NO₆BrF₃+: 522.0739; found 522.0756.
Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(4-nitrophenyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4i)

According to the above general procedure by using 1i (0.085 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4i as a wax (0.123 g, 63% yield).

$[\alpha]_D^{25} = +40.6$ (c = 1.0, CHCl3).

HPLC: DAICELAD.M; n-heptane/iPrOH = 8/2; flow rate 1.0 mL/min; T= 30 °C; retention time: 8.31 min (major), 24.30 min (minor), ee: 87%.

$^1$H NMR (400 MHz, CDCl3) δ 8.18 (d, $J = 8.8$ Hz, 2H), 7.39 (d, $J = 8.8$ Hz, 2H), 7.02 (dd, $J = 15.6, 8.8$ Hz, 1H), 5.57 (d, $J = 15.6$ Hz, 1H), 4.33 – 4.18 (m, 4H), 3.99 – 3.88 (m, 2H), 3.63 (s, 3H), 3.61 – 3.55 (m, 1H), 3.26 (dd, $J = 11.6, 8.8$ Hz, 1H), 1.26 (t, $J = 7.2$ Hz, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl3) δ 169.5, 168.2, 165.5, 147.6, 144.1, 141.6, 128.8 (2C), 125.0 (q, $J = 278.0$ Hz), 125.7, 124.3 (2C), 73.6, 65.0 (q, $J = 30.5$ Hz), 62.9, 62.2, 56.8, 51.7, 50.4, 14.0, 13.8 ppm.

IR (ATR): 3353, 2979, 2073, 1726, 1602, 1524, 1443, 1352, 1278, 1221, 1131, 1006, 851, 702 cm$^{-1}$.

MS (ESI): $m/z = 489.1$ [M+H]$^+$. 


Diethyl (3R,4S,5R)-4-(4-cyanophenyl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4j)

According to the above general procedure by using 1j (0.075 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4j as a colorless solid (0.170 g, 91% yield).

Melting Point: 109-111 °C.

$[\alpha]_D^{25} = +30.4$ (c = 1.0, CHCl3).

HPLC: DAICELAS.M; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 °C; retention time: 13.37 min (major), 17.78 min (minor), ee: 93%.
\[ ^{1}H \text{NMR (400 MHz, CDCl)}_{3} \delta 7.61 (d, J = 8.4 \text{ Hz}, 2H), 7.32 (d, J = 8.4 \text{ Hz}, 2H), 7.01 (dd, J = 15.6, 9.2 \text{ Hz}, 1H), 5.55 (d, J = 15.6 \text{ Hz}, 1H), 4.32 – 4.18 (m, 4H), 3.91 (s, 1H), 3.88 – 3.79 (m, 1H), 3.63 (s, 3H), 3.57 (d, J = 7.2 \text{ Hz}, 1H), 3.23 (dd, J = 11.2, 9.2 \text{ Hz}, 1H), 1.27 – 1.23 (m, 6H) ppm. \]

\[ ^{13}C \text{NMR (100 MHz, CDCl)}_{3} \delta 169.6, 168.2, 165.6, 142.2, 141.7, 132.8 (2C), 128.7 (2C), 125.6, 125.0 (q, J = 278.2 \text{ Hz}), 118.2, 112.0, 73.6, 64.9 (q, J = 30.2 \text{ Hz}), 62.9, 62.2, 56.7, 51.7, 50.6, 14.0, 13.8 ppm. \]

IR (ATR): 3743, 3331, 2985, 2341, 2109, 1993, 1932, 1718, 1660, 1442, 137, 1276, 1219, 1123, 989, 845, 727 cm\(^{-1}\). 

MS (ESI): \text{m/z} = 469.2 [M+H]\(^{+}\). 

HRMS (ESI): \text{m/z} [M+H]\(^{+}\) calcd for C\(_{22}\)H\(_{24}\)N\(_{2}\)O\(_{6}\)F\(_{3}\): 469.1586; found 469.1599.

Diethyl (3\(R\),4\(S\),5\(R\))-4-(2-chlorophenyl)-3-((\(E\))-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4k)

According to the above general procedure by using 1k (0.080 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph\(_{3}\)P=CHCO\(_{2}\)Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et\(_{2}\)O = 4/1 to 1/1) afforded 4k as a colorless solid (0.141 g, 73% yield).

Melting Point: 158-160 °C. 

[\(\alpha\)]\(_{D}^{25}\) = +20.7 (c = 1.0, CHCl\(_{3}\)).

HPLC: DAICEL AS.M; n-heptane/iPrOH = 9/1; flow rate 1.0 mL/min; T= 30 °C; retention time: 7.57 min (major), 11.38 min (minor), ee: 96%.

\[ ^{1}H \text{NMR (600 MHz, CDCl)}_{3} \delta 7.37 (d, J = 7.8 \text{ Hz}, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.19 (m, 1H), 7.09 (dd, J = 15.6, 8.4 \text{ Hz}, 1H), 5.62 (d, J = 15.6 \text{ Hz}, 1H), 4.51 – 4.46 (m, 1H), 4.30 (q, J = 7.2 \text{ Hz}, 2H), 4.26 (q, J = 7.2 \text{ Hz}, 2H), 4.12 – 4.04 (m, 1H), 3.67 (s, 3H), 3.62 – 3.55 (m, 1H), 3.47 – 3.37 (m, 1H), 1.31 – 1.27 (m, 6H) ppm. \]

\[ ^{13}C \text{NMR (150 MHz, CDCl)}_{3} \delta 169.9, 168.4, 165.9, 142.2, 134.6, 134.1, 130.4, 129.0, 127.4, 125.2 (q, J = 278.0 \text{ Hz}), 125.0, 122.5, 73.7, 64.1, 62.8, 62.1, 56.6, 51.6, 46.0, 14.0, 13.9 ppm. \]

IR (ATR): 3854, 3741, 3323, 2923, 2291, 2193, 2111, 1997, 1923, 1720, 1441, 1368, 1282, 1141, 1001, 864, 757, 701 cm\(^{-1}\).

MS (ESI): \text{m/z} = 478.1 [M+H]\(^{+}\).

HRMS (ESI): \text{m/z} [M+H]\(^{+}\) calcd for C\(_{22}\)H\(_{26}\)NO\(_{6}\)Cl\(_{3}\): 478.1244; found 478.1260.
Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(2-methoxyphenyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4l)

According to the above general procedure by using 1l (0.078 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4l as a colorless solid (0.167 g, 88% yield).

Melting Point: 114-116 °C.

[a]D²⁵ = +49.6 (c = 1.0, CHCl₃).

HPLC: DAICELAD.M; n-heptane/iPrOH = 9/1; flow rate 1.0 mL/min; T = 30 °C; retention time: 6.44 min (major), 25.10 min (minor), ee: 99%.

¹H NMR (400 MHz, CDCl₃) δ 7.23 – 7.19 (m, 1H), 7.13 – 7.05 (m, 2H), 6.91 – 6.82 (m, 2H), 5.59 (d, J = 15.6 Hz, 1H), 4.27 (q, J = 7.2 Hz, 2H), 4.23 – 4.18 (m, 3H), 4.09 – 4.00 (m, 1H), 3.80 (s, 3H), 3.62 (s, 3H), 3.61 – 3.53 (m, 2H), 1.27 – 1.23 (m, 6H) ppm.

¹³C NMR (100 MHz, CDCl₃) δ 170.1, 168.7, 166.1, 157.4, 143.8, 129.8, 128.9, 128.7, 125.7 (q, J = 271.2 Hz), 124.3, 121.0, 111.1, 73.9, 62.6 (q, J = 29.7 Hz), 62.5, 61.9, 55.3, 54.0, 51.4, 46.7, 14.0, 13.8 ppm.

IR (ATR): 3741, 3328, 2985, 2327, 2107, 1995, 1923, 1721, 1658, 1443, 1372, 1282, 1233, 1136, 1017, 866, 757, 696 cm⁻¹.

MS (ESI): m/z = 474.2 [M+H]⁺.

HRMS (ESI): m/z [M+H]⁺ calcd for C₂₃H₂₇NO₇F₃⁺: 474.1740; found 474.1752.

Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(2-methoxyphenyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4m)

According to the above general procedure by using 1m (0.078 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 12 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4m as a colorless solid (0.134 g, 71% yield).

Melting Point: 100-103 °C.

[a]D²⁵ = +48.9 (c = 1.0, CHCl₃).

HPLC: CHIRALPAK IA; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T = 30 °C; retention time:
10.64 min (major), 26.90 min (minor), ee: >99%.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.24 – 7.20 (m, 1H), 7.04 (dd, $J$ = 15.6, 8.8 Hz, 1H), 6.80 – 6.75 (m, 2H), 6.73 – 6.70 (m, 1H), 5.60 (d, $J$ = 15.6 Hz, 1H), 4.34 – 4.16 (m, 4H), 4.01 – 3.90 (m, 1H), 3.77 (s, 3H), 3.64 (s, 3H), 3.56 – 3.49 (m, 1H), 3.24 (dd, $J$ = 11.2, 8.8 Hz, 1H), 1.28 – 1.24 (m, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 169.9, 168.5, 165.9, 159.9, 142.6, 138.2, 130.0, 125.3 (q, $J$ = 278.1 Hz), 125.1, 119.9, 113.9, 112.8, 73.7, 65.2 (q, $J$ = 29.8 Hz), 62.7, 62.0, 56.6, 51.5, 50.6, 14.0 ppm.

IR (ATR): 3329, 2960, 2312, 2102, 1724, 1609, 1442, 1267, 1133, 858, 732 cm$^{-1}$.

MS (ESI): $m/z$ 496.2 [M+Na]$^+$.  
HRMS (ESI): $m/z$ [M+H]$^+$ calcld for C$_{22}$H$_{27}$NO$_7$F$_3$: 474.1740; found 474.1754.

Diethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(naphthalen-2-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4n)

According to the above general procedure by using 1n (0.088 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph$_3$P=CHCO$_2$Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et$_2$O = 4/1 to 1/1) afforded 4n as a colorless solid (0.181 g, 92% yield).

**Melting Point:** 113-115 °C.

$[\alpha]_D^{25} = +39.6$ (c = 1.0, CHCl$_3$).

HPLC: CHIRALPAK AS; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 °C; retention time: 10.81 min (major), 13.38 min (minor), ee: 95%.

$^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 7.83 – 7.76 (m, 3H), 7.69 – 7.65 (m, 1H), 7.50 – 7.43 (m, 2H), 7.31 (dd, $J$ = 8.4, 1.6 Hz, 1H), 7.11 (dd, $J$ = 15.6, 8.8 Hz, 1H), 5.60 (d, $J$ = 15.6 Hz, 1H), 4.35 – 4.20 (m, 4H), 4.15 – 4.04 (m, 1H), 3.98 (dd, $J$ = 11.2, 9.6 Hz, 1H), 3.62 (d, $J$ = 7.6 Hz, 1H), 3.58 (s, 3H), 3.40 (dd, $J$ = 11.2, 8.8 Hz, 1H), 1.30 – 1.26 (m, 6H) ppm.

$^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 170.0, 168.5, 165.8, 142.6, 134.0, 133.4, 132.9, 128.9, 127.8, 127.7, 127.5, 126.4, 126.2, 125.4 (q, $J$ = 278.0 Hz), 125.2, 124.7, 73.8, 65.2 (q, $J$ = 30.0 Hz), 62.7, 62.1, 56.7, 51.5, 50.8, 14.0, 13.9 ppm.


MS (ESI): $m/z$ 494.2 [M+H]$^+$.  
HRMS (ESI): $m/z$ [M+H]$^+$ calcld for C$_{25}$H$_{27}$NO$_7$F$_3$: 494.1790; found 494.1803.
Diethyl (3R,4R,5R)-4-(furan-2-yl)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoromethyl) pyrrolidine-2,2-dicarboxylate (4o)

According to the above general procedure by using 1o (0.059 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 48 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4o as a wax (0.104 g, 57% yield).

$[\alpha]_D^{25} = +50.4$ (c = 1.0, CHCl3).

HPLC: DAICELAD.M; n-heptane/iPrOH = 9/1; flow rate 0.7 mL/min; T= 30 °C; retention time: 8.92 min (major), 13.60 min (minor), ee: 91%.

$^1$H NMR (600 MHz, CDCl3) δ 7.34 – 7.32 (m, 1H), 7.09 (dd, $J = 15.6$, 8.4 Hz, 1H), 6.29 – 6.27 (m, 1H), 6.19 – 6.17 (m, 1H), 5.68 (d, $J = 15.6$ Hz, 1H), 4.32 – 4.18 (m, 4H), 4.12 – 4.05 (m, 1H), 3.94 (dd, $J = 11.4$, 9.6 Hz, 1H), 3.69 (s, 3H), 3.56 (d, $J = 7.8$ Hz, 1H), 3.36 (dd, $J = 11.4$, 8.4 Hz, 1H), 1.28 – 1.25 (m, 6H) ppm.

$^{13}$C NMR (150 MHz, CDCl3) δ 169.7, 168.3, 166.0, 149.3, 142.6, 142.4, 125.1 (q, $J = 278.0$ Hz), 110.5, 108.7, 73.3, 62.8, 62.1 (q, $J = 30.3$ Hz), 62.0, 53.7, 51.6, 44.2, 14.0, 13.9 ppm.

IR (ATR): 3354, 2984, 2328, 2084, 1920, 1726, 1443, 1373, 1277, 1221, 1136, 1010, 927, 861, 736 cm$^{-1}$.


HRMS (ESI): m/z [M+H]$^+$ calcld for C19H23NO7F3$: 434.1427$; found 434.1433.

Diethyl (3R,4R,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(thiophen-2-yl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4p)

According to the above general procedure by using 1p (0.066 g, 0.48 mmol), 2a (0.102 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 24 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4p as a colorless solid (0.174 g, 97% yield).

Melting Point: 108-110 °C.

$[\alpha]_D^{25} = +58.9$ (c = 1.0, CHCl3).

HPLC: CHIRALPAK IB; n-heptane/iPrOH = 97/3; flow rate 1.0 mL/min; T= 30 °C; retention time: 8.57 min (major), 11.01 min (minor), ee: >99%.
**1H NMR (400 MHz, CDCl3)** δ 7.21 – 7.17 (m, 1H), 7.06 (dd, J = 15.6, 8.8 Hz, 1H), 6.91 – 6.89 (m, 2H), 5.69 (d, J = 15.6 Hz, 1H), 4.33 – 4.10 (m, 5H), 4.01 – 3.90 (m, 1H), 3.65 (s, 3H), 3.55 (d, J = 15.6 Hz, 1H), 3.17 (dd, J = 11.2, 8.8 Hz, 1H), 1.287 – 1.23 (m, 6H) ppm.

**13C NMR (100 MHz, CDCl3)** δ 169.7, 168.3, 165.9, 142.2, 139.9, 127.1, 126.6, 125.6, 124.8, 125.1 (q, J = 278.3 Hz), 73.5, 65.7 (q, J = 29.9 Hz), 62.8, 62.1, 57.7, 51.6, 46.0, 14.0, 13.8 ppm.

**IR (ATR):** 3329, 2988, 2060, 1721, 1660, 1436, 1370, 1275, 1230, 1145, 1012, 981, 861, 776, 710 cm⁻¹.

**MS (ESI):** m/z = 450.1 [M+H]⁺.

**HRMS (ESI):** m/z [M+H]⁺ calcld for C₁₉H₂₃NO₆F₃S⁺: 450.1198; found 450.1184.

---

Dimethyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(4-methoxyphenyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4q)

According to the above general procedure by using 1d (0.078 g, 0.48 mmol), 2b (0.091 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 12 h at room temperature followed by addition of Ph₃P=CHCO₂Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et₂O = 4/1 to 1/1) afforded 4q as a colorless solid (0.154 g, 93% yield).

**Melting Point:** 113-115 °C.

[α]D²⁵ = +67.8 (c = 1.0, CHCl₃).

**HPLC:** CHIRALPAK AD; n-heptane/iPrOH = 97/3; flow rate 1.0 mL/min; T= 30 °C; retention time: 5.61 min (major), 9.06 min (minor), ee: >99%.

**1H NMR (600 MHz, CDCl3)** δ 7.11 (d, J = 9.0 Hz, 2H), 7.03 (dd, J = 15.6, 9.0 Hz, 1H), 6.83 (d, J = 9.0 Hz, 2H), 5.58 (d, J = 15.6 Hz, 1H), 3.96 – 3.92 (m, 1H), 3.82 (s, 3H), 3.76 (s, 6H), 3.74 – 3.72 (m, 1H), 3.64 (s, 3H), 3.57 – 3.51 (m, 1H), 3.22 (dd, J = 11.4, 9.0 Hz, 1H) ppm.

**13C NMR (150 MHz, CDCl3)** δ 170.5, 169.0, 165.9, 159.1, 142.5, 128.7 (2C), 128.3, 125.4 (q, J = 278.1 Hz), 125.1, 114.4 (2C), 73.9, 65.2 (q, J = 29.6 Hz), 56.7, 55.1, 53.5, 52.9, 51.5, 49.9 ppm.

**IR (ATR):** 3379, 2954, 2850, 2060, 1727, 1652, 1516, 1437, 1362, 1270, 1129, 1035, 979, 926, 866, 821, 772, 700 cm⁻¹.

**MS (ESI):** m/z = 468.1 [M+Na]⁺.

**HRMS (ESI):** m/z [M+H]⁺ calcld for C₂₀H₂₃NO₇F₃⁺: 446.1427; found 446.1414.
Diisopropyl (3R,4S,5R)-3-((E)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(4-methoxyphenyl)-5-(trifluoromethyl)pyrrolidine-2,2-dicarboxylate (4r)

According to the above general procedure by using 1d (0.078 g, 0.48 mmol), 2c (0.113 g, 0.4 mmol) and catalyst B (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 12 h at room temperature followed by addition of Ph3P=CHCO2Me (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et2O = 4/1 to 1/1) afforded 4r as a colorless solid (0.184 g, 89% yield).

**Melting Point:** 109-112 °C.

$[\alpha]_{D}^{25} = +58.8$ (c = 1.0, CHCl3).

**HPLC:** CHIRALPAK AD; n-heptane/iPrOH = 9/1; flow rate 1.0 mL/min; T = 30 °C; retention time: 4.47 min (major), 8.02 min (minor), ee: >99%.

$^1$H NMR (600 MHz, CDCl3) $\delta$ 7.11 (d, $J = 8.4$ Hz, 2H), 7.07 (dd, $J = 15.6$, 9.0 Hz, 1H), 6.84 (d, $J = 8.4$ Hz, 2H), 5.59 (d, $J = 15.6$ Hz, 1H), 5.16 – 5.07 (m, 2H), 3.95 – 3.88 (m, 1H), 3.77 (s, 3H), 3.77 – 3.72 (m, 1H), 3.64 (s, 3H), 3.49 (d, $J = 7.2$ Hz, 1H), 3.19 (dd, $J = 11.4$, 9.0 Hz, 1H), 1.28 – 1.23 (m, 12H) ppm.

$^{13}$C NMR (150 MHz, CDCl3) $\delta$ 169.5, 168.1, 165.9, 159.0, 143.1, 128.7 (2C), 128.6, 125.5 (q, $J = 278.3$ Hz), 125.0, 114.3 (2C), 73.5, 70.7, 69.8, 65.2 (q, $J = 29.6$ Hz), 56.8, 55.2, 51.5, 49.9, 21.6, 21.4, 21.4, 21.3 ppm.

**IR (ATR):** 3354, 2977, 2936, 2162, 1716, 1659, 1515, 1441, 1375, 1276, 1230, 1104, 1031, 991, 912, 820, 753, 693 cm$^{-1}$.

**MS (ESI):** $m/z$ = 524.2 [M+Na]$^+$.  
**HRMS (ESI):** $m/z$ [M+H]$^+$ calcd for C$_{24}$H$_{31}$NO$_7$F$_3$: 502.2053; found 502.2052.

4. Reference  
5. NMR Spectra and Chiral HPLC Data:

$^1$H NMR of 2a:

$^{13}$C NMR of 2a:
\(^1\)H NMR of \(2b\):

\[^1^3\)C NMR of \(2b\):
$^1$H NMR of $2c$:

$^{13}$C NMR of $2c$: 
$^1$H NMR of 4a:

$^{13}$C NMR of 4a:
Instrument Conditions:  
At Start | At Stop
Temperature in °C: 30.0°C | 30.0°C
Pressure in bar: 22.3 | 23.0
Flow in ml/min: 0.70 | 0.70

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time</th>
<th>Width</th>
<th>Height</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.24</td>
<td>0.13</td>
<td>2.55</td>
<td>15.70</td>
<td>0.20</td>
</tr>
<tr>
<td>2</td>
<td>4.48</td>
<td>0.14</td>
<td>8.35</td>
<td>79.08</td>
<td>0.87</td>
</tr>
<tr>
<td>3</td>
<td>5.50</td>
<td>0.24</td>
<td>16.20</td>
<td>161.03</td>
<td>1.09</td>
</tr>
<tr>
<td>4</td>
<td>7.46</td>
<td>0.34</td>
<td>1.65</td>
<td>28.83</td>
<td>0.29</td>
</tr>
<tr>
<td>5</td>
<td>9.19</td>
<td>0.40</td>
<td>616.17</td>
<td>12990.00</td>
<td>96.65</td>
</tr>
<tr>
<td>6</td>
<td>10.52</td>
<td>0.55</td>
<td>3.41</td>
<td>150.26</td>
<td>1.25</td>
</tr>
<tr>
<td>7</td>
<td>13.67</td>
<td>0.18</td>
<td>1.28</td>
<td>13.18</td>
<td>0.10</td>
</tr>
</tbody>
</table>

Total 13884.45 100.00%
$^1$H NMR of 4b:

![NMR spectrum of 4b](image1)

$^{13}$C NMR of 4b:

![NMR spectrum of 4b](image2)
$^1$H NMR of 4c:

$^{13}$C NMR of 4c:
<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (min)</th>
<th>Height (mAU)</th>
<th>Area (mAU*s)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.21</td>
<td>0.20</td>
<td>4.41</td>
<td>52.32</td>
<td>5.40%</td>
</tr>
<tr>
<td>2</td>
<td>3.55</td>
<td>0.19</td>
<td>13.74</td>
<td>159.35</td>
<td>16.43%</td>
</tr>
<tr>
<td>3</td>
<td>4.47</td>
<td>0.19</td>
<td>322.28</td>
<td>3220.28</td>
<td>33.85%</td>
</tr>
<tr>
<td>4</td>
<td>6.19</td>
<td>0.23</td>
<td>19.26</td>
<td>207.17</td>
<td>2.17%</td>
</tr>
<tr>
<td>5</td>
<td>7.10</td>
<td>0.23</td>
<td>3.65</td>
<td>36.02</td>
<td>0.37%</td>
</tr>
<tr>
<td>6</td>
<td>10.24</td>
<td>0.47</td>
<td>144.55</td>
<td>4036.74</td>
<td>41.16%</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td></td>
<td></td>
<td>9748.26</td>
<td>100.00</td>
</tr>
</tbody>
</table>

Temperature in °C: 30.0
Pressure in bar: 35.7
Flow in ml/min: 1.0
**$^1$H NMR of 4d:**

![H NMR spectrum](image1)

**$^{13}$C NMR of 4d:**

![C NMR spectrum](image2)
$^1$H NMR of 4e:

$^{13}$C NMR of 4e:
Name: YZ K-P101 J roc

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Type</th>
<th>Area%</th>
<th>Area</th>
<th>Height Width [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.15</td>
<td>BB</td>
<td>0.10</td>
<td>2.74</td>
<td>0.52</td>
</tr>
<tr>
<td>4.04</td>
<td>BB</td>
<td>0.21</td>
<td>2.95</td>
<td>0.48</td>
</tr>
<tr>
<td>6.62</td>
<td>BV</td>
<td>10.24</td>
<td>140.56</td>
<td>17.46</td>
</tr>
<tr>
<td>8.15</td>
<td>VB</td>
<td>0.48</td>
<td>5.52</td>
<td>0.09</td>
</tr>
<tr>
<td>7.16</td>
<td>SV</td>
<td>44.12</td>
<td>826.59</td>
<td>66.14</td>
</tr>
<tr>
<td>7.42</td>
<td>VB</td>
<td>0.91</td>
<td>12.51</td>
<td>1.38</td>
</tr>
<tr>
<td>8.75</td>
<td>BB</td>
<td>43.77</td>
<td>821.03</td>
<td>37.89</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>100.00</td>
<td>1418.69</td>
<td></td>
</tr>
</tbody>
</table>

Name: Chiralpak IC, (150 x 4.6) mm, 5μ, SN: IC00CD-QFD15

Pressure at start: 51 bar  Start flow: 1.000 ml/min  Column oven: 20.00 °C

Name: yz-T44

<table>
<thead>
<tr>
<th>RT [min]</th>
<th>Type</th>
<th>Area%</th>
<th>Area</th>
<th>Height Width [min]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5.56</td>
<td>VB</td>
<td>0.10</td>
<td>2.61</td>
<td>0.29</td>
</tr>
<tr>
<td>7.10</td>
<td>BB</td>
<td>69.01</td>
<td>2711.00</td>
<td>260.06</td>
</tr>
<tr>
<td>9.07</td>
<td>BB</td>
<td>0.00</td>
<td>24.58</td>
<td>1.24</td>
</tr>
<tr>
<td>Sum</td>
<td></td>
<td>100.00</td>
<td>2733.19</td>
<td></td>
</tr>
</tbody>
</table>
$^1$H NMR of 4f:

$^{13}$C NMR of 4f:
### Instrument Conditions: 
- **At Start**: 30.0°C
- **At Stop**: 30.0°C
- **Pressure in bar**: 21.6
- **Flow in ml/min**: 0.70

### Table 1

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (min)</th>
<th>Height (mAU)</th>
<th>Area (mAU·sec)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.47</td>
<td>0.19</td>
<td>16.33</td>
<td>212.02</td>
<td>0.57</td>
</tr>
<tr>
<td>2</td>
<td>4.81</td>
<td>0.17</td>
<td>4.44</td>
<td>69.96</td>
<td>0.14</td>
</tr>
<tr>
<td>3</td>
<td>5.49</td>
<td>0.17</td>
<td>32.93</td>
<td>1387.45</td>
<td>3.44</td>
</tr>
<tr>
<td>4</td>
<td>0.14</td>
<td>0.60</td>
<td>9.94</td>
<td>455.66</td>
<td>1.22</td>
</tr>
<tr>
<td>5</td>
<td>9.71</td>
<td>0.49</td>
<td>60.67</td>
<td>2996.80</td>
<td>40.39</td>
</tr>
<tr>
<td>6</td>
<td>12.80</td>
<td>0.71</td>
<td>402.81</td>
<td>17182.07</td>
<td>46.04</td>
</tr>
</tbody>
</table>

**Total** 37278.91 100.00%

### Instrument Conditions: 
- **At Start**: 30.0°C
- **At Stop**: 30.0°C
- **Pressure in bar**: 21.0
- **Flow in ml/min**: 0.70

### Table 2

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (min)</th>
<th>Height (mAU)</th>
<th>Area (mAU·sec)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.50</td>
<td>0.16</td>
<td>2.21</td>
<td>97.66</td>
<td>0.27</td>
</tr>
<tr>
<td>2</td>
<td>5.63</td>
<td>0.17</td>
<td>18.23</td>
<td>221.87</td>
<td>0.38</td>
</tr>
<tr>
<td>3</td>
<td>4.54</td>
<td>0.44</td>
<td>1144.57</td>
<td>37935.63</td>
<td>49.36</td>
</tr>
<tr>
<td>4</td>
<td>12.62</td>
<td>0.55</td>
<td>1.70</td>
<td>52.86</td>
<td>0.19</td>
</tr>
</tbody>
</table>

**Total** 32611.72 100.00%
$^1$H NMR of 4g:

$^{13}$C NMR of 4g:
$^1$H NMR of 4h:

![NMR spectrum of 4h with chemical shifts and peaks]

$^{13}$C NMR of 4h:

![NMR spectrum of 4h with chemical shifts and peaks]
### Instrument Conditions

<table>
<thead>
<tr>
<th></th>
<th>At Start</th>
<th>At Stop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in °C</td>
<td>80.0 °C</td>
<td>80.0 °C</td>
</tr>
<tr>
<td>Pressure in bar</td>
<td>23.4</td>
<td>23.4</td>
</tr>
<tr>
<td>Flow in mL/min</td>
<td>0.70</td>
<td>0.70</td>
</tr>
</tbody>
</table>

### Chromatogram 1

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (sA)</th>
<th>Height (sA)</th>
<th>Area (sA)*</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.81</td>
<td>0.28</td>
<td>6.70</td>
<td>108.08</td>
<td>0.22</td>
</tr>
<tr>
<td>2</td>
<td>6.47</td>
<td>0.20</td>
<td>6.70</td>
<td>82.68</td>
<td>0.19</td>
</tr>
<tr>
<td>3</td>
<td>7.74</td>
<td>0.22</td>
<td>28.88</td>
<td>850.26</td>
<td>1.73</td>
</tr>
<tr>
<td>4</td>
<td>9.36</td>
<td>0.39</td>
<td>6.93</td>
<td>169.62</td>
<td>0.36</td>
</tr>
<tr>
<td>5</td>
<td>9.60</td>
<td>0.24</td>
<td>4.42</td>
<td>22.76</td>
<td>0.27</td>
</tr>
<tr>
<td>6</td>
<td>10.37</td>
<td>0.68</td>
<td>64.67</td>
<td>2440.66</td>
<td>49.75</td>
</tr>
<tr>
<td>7</td>
<td>11.57</td>
<td>0.20</td>
<td>0.11</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>8</td>
<td>13.34</td>
<td>0.94</td>
<td>692.34</td>
<td>22996.72</td>
<td>47.40</td>
</tr>
<tr>
<td>9</td>
<td>14.02</td>
<td>0.30</td>
<td>8.48</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>15.09</td>
<td>0.30</td>
<td>6.48</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Total: 45961.70 100.00

### Instrument Conditions

<table>
<thead>
<tr>
<th></th>
<th>At Start</th>
<th>At Stop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in °C</td>
<td>80.0 °C</td>
<td>80.0 °C</td>
</tr>
<tr>
<td>Pressure in bar</td>
<td>23.6</td>
<td>23.8</td>
</tr>
<tr>
<td>Flow in mL/min</td>
<td>0.70</td>
<td>0.70</td>
</tr>
</tbody>
</table>

### Chromatogram 2

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (sA)</th>
<th>Height (sA)</th>
<th>Area (sA)*</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.53</td>
<td>0.17</td>
<td>5.29</td>
<td>109.46</td>
<td>0.45</td>
</tr>
<tr>
<td>2</td>
<td>5.42</td>
<td>0.22</td>
<td>24.49</td>
<td>242.15</td>
<td>1.00</td>
</tr>
<tr>
<td>3</td>
<td>7.64</td>
<td>0.45</td>
<td>6.23</td>
<td>164.08</td>
<td>0.76</td>
</tr>
<tr>
<td>4</td>
<td>10.16</td>
<td>0.39</td>
<td>69.58</td>
<td>22966.71</td>
<td>94.70</td>
</tr>
<tr>
<td>5</td>
<td>12.09</td>
<td>0.54</td>
<td>12.69</td>
<td>749.72</td>
<td>3.08</td>
</tr>
</tbody>
</table>

Total: 24211.06 100.00
$^1$H NMR of 4i:

![H NMR spectrum of 4i](image)

$^{13}$C NMR of 4i:

![C NMR spectrum of 4i](image)
# Chromatography Data

**Temperature in °C:** 20.0  
**Pressure in bar:** 26.9  
**Flow in ml/min:** 1.0

### First Chromatogram

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width</th>
<th>Height (mAU)</th>
<th>Area (mAU*sec)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.80</td>
<td>0.30</td>
<td>10.80</td>
<td>495.55</td>
<td>0.35</td>
</tr>
<tr>
<td>2</td>
<td>3.25</td>
<td>0.30</td>
<td>10.80</td>
<td>355.04</td>
<td>1.21</td>
</tr>
<tr>
<td>3</td>
<td>5.29</td>
<td>0.30</td>
<td>83.00</td>
<td>1559.34</td>
<td>48.81</td>
</tr>
<tr>
<td>4</td>
<td>5.46</td>
<td>0.30</td>
<td>5.55</td>
<td>5.55</td>
<td>0.05</td>
</tr>
<tr>
<td>5</td>
<td>22.82</td>
<td>0.00</td>
<td>34.09</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>6</td>
<td>24.02</td>
<td>0.00</td>
<td>49.06</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>7</td>
<td>24.28</td>
<td>1.14</td>
<td>105.62</td>
<td>3740.88</td>
<td>47.59</td>
</tr>
<tr>
<td>8</td>
<td>24.68</td>
<td>0.30</td>
<td>62.24</td>
<td>0.20</td>
<td>0.20</td>
</tr>
<tr>
<td>9</td>
<td>24.73</td>
<td>0.00</td>
<td>71.56</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>10</td>
<td>24.95</td>
<td>0.00</td>
<td>64.48</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>11</td>
<td>25.06</td>
<td>0.00</td>
<td>45.67</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>12</td>
<td>25.12</td>
<td>0.00</td>
<td>39.57</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>13</td>
<td>25.40</td>
<td>0.00</td>
<td>38.59</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>14</td>
<td>26.06</td>
<td>0.00</td>
<td>8.76</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>15</td>
<td>26.22</td>
<td>0.00</td>
<td>2.47</td>
<td>0.00</td>
<td>0.00</td>
</tr>
<tr>
<td>16</td>
<td>26.60</td>
<td>0.00</td>
<td>0.52</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Total: 15118.83  100.00

### Second Chromatogram

**Temperature in °C:** 30.0  
**Pressure in bar:** 36.1  
**Flow in ml/min:** 1.0

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width</th>
<th>Height (mAU)</th>
<th>Area (mAU*sec)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.80</td>
<td>0.20</td>
<td>7.80</td>
<td>10.38</td>
<td>0.42</td>
</tr>
<tr>
<td>2</td>
<td>3.17</td>
<td>0.11</td>
<td>0.39</td>
<td>3.31</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>3.22</td>
<td>0.12</td>
<td>0.76</td>
<td>13.37</td>
<td>0.57</td>
</tr>
<tr>
<td>4</td>
<td>5.31</td>
<td>0.16</td>
<td>116.74</td>
<td>2455.55</td>
<td>52.26</td>
</tr>
<tr>
<td>5</td>
<td>24.00</td>
<td>1.16</td>
<td>2.87</td>
<td>176.91</td>
<td>4.64</td>
</tr>
</tbody>
</table>

Total: 2864.35  100.00

---

[Image of chromatograms]
$^1$H NMR of 4j:

![Chemical Structure](image1)

$^{13}$C NMR of 4j:

![Chemical Structure](image2)
### Instrument Conditions: At Start and At Stop

<table>
<thead>
<tr>
<th>Parameter</th>
<th>At Start</th>
<th>At Stop</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature in °C</td>
<td>30.0°C</td>
<td>30.0°C</td>
</tr>
<tr>
<td>Pressure in bar</td>
<td>21.2</td>
<td>21.5</td>
</tr>
<tr>
<td>Flow in ml/min</td>
<td>0.70</td>
<td>0.70</td>
</tr>
</tbody>
</table>

### Data 1: Signal 344.5, Ref 300.160 (Y2/T5/B-A5.0)

<table>
<thead>
<tr>
<th>Ret. Time (min)</th>
<th>Width</th>
<th>Height</th>
<th>Area (μA)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.86</td>
<td>0.21</td>
<td>18.44</td>
<td>290.93</td>
</tr>
<tr>
<td>2</td>
<td>5.49</td>
<td>0.18</td>
<td>26.49</td>
<td>276.71</td>
</tr>
<tr>
<td>3</td>
<td>10.33</td>
<td>0.18</td>
<td>3.62</td>
<td>120.49</td>
</tr>
<tr>
<td>4</td>
<td>12.09</td>
<td>0.22</td>
<td>2.98</td>
<td>89.78</td>
</tr>
<tr>
<td>5</td>
<td>10.23</td>
<td>0.21</td>
<td>110.91</td>
<td>4075.90</td>
</tr>
<tr>
<td>6</td>
<td>17.09</td>
<td>0.79</td>
<td>92.37</td>
<td>3497.82</td>
</tr>
</tbody>
</table>

**Total** 9904.68 100.00

### Data 2: Signal 314.5, Ref 302.160 (Y2/T5/B-A5.0)

<table>
<thead>
<tr>
<th>Ret. Time (min)</th>
<th>Width</th>
<th>Height</th>
<th>Area (μA)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.22</td>
<td>0.17</td>
<td>4.56</td>
<td>49.65</td>
</tr>
<tr>
<td>2</td>
<td>4.46</td>
<td>0.24</td>
<td>9.60</td>
<td>166.40</td>
</tr>
<tr>
<td>3</td>
<td>5.44</td>
<td>0.15</td>
<td>55.54</td>
<td>540.94</td>
</tr>
<tr>
<td>4</td>
<td>12.37</td>
<td>0.58</td>
<td>666.73</td>
<td>21479.62</td>
</tr>
<tr>
<td>5</td>
<td>17.75</td>
<td>0.72</td>
<td>13.82</td>
<td>411.57</td>
</tr>
<tr>
<td>6</td>
<td>19.66</td>
<td>0.75</td>
<td>7.58</td>
<td>459.45</td>
</tr>
</tbody>
</table>

**Total** 23658.66 100.00

---

40
$^1$H NMR of 4k:

$^{13}$C NMR of 4k:
<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time</th>
<th>Width</th>
<th>Height</th>
<th>Area</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.13</td>
<td>0.13</td>
<td>7.82</td>
<td>78.51</td>
<td>0.68</td>
</tr>
<tr>
<td>2</td>
<td>3.30</td>
<td>0.14</td>
<td>5.17</td>
<td>30.42</td>
<td>0.27</td>
</tr>
<tr>
<td>3</td>
<td>3.66</td>
<td>0.12</td>
<td>3.02</td>
<td>102.17</td>
<td>0.98</td>
</tr>
<tr>
<td>4</td>
<td>4.52</td>
<td>0.22</td>
<td>1.25</td>
<td>19.04</td>
<td>0.18</td>
</tr>
<tr>
<td>5</td>
<td>7.69</td>
<td>0.87</td>
<td>172.00</td>
<td>6262.99</td>
<td>46.79</td>
</tr>
<tr>
<td>6</td>
<td>11.88</td>
<td>0.74</td>
<td>114.49</td>
<td>6578.87</td>
<td>48.28</td>
</tr>
</tbody>
</table>

Total: 11348.34  
100.00

---

Instrument Conditions:  
Temperature in ºC: 30.0ºC  
Pressure in bar: 0.8  
Flow in ml/min: 1.69

---

Instrument Conditions:  
Temperature in ºC: 30.0ºC  
Pressure in bar: 0.8  
Flow in ml/min: 1.69
$^1$H NMR of 4l:

$^{13}$C NMR of 4l:
$^1$H NMR of 4m:

$^{13}$C NMR of 4m:
Column: Chiraflow IA, (250 x 4.6) mm, 5μ, SR: IA00E-C028
Pressure at start: 36 bar  Start flow: 0.700 ml/min  Column oven: 20.00 °C

Name               k-p101N
RT [min]  Type  Area%  Area      Height Width [min]
  9.37  BB       0.34  74.25  6.07     0.19
 10.84  BB       49.93  10908.02  827.34  0.21
 13.18  VV       1.13  250.10  14.13  0.28
 16.24  VB       1.01  222.79  13.63  0.25
 26.90  VV       48.20  10856.86  297.15  0.55
  Sum       100.00  22112.38

Column: Chiraflow IA, (250 x 4.6) mm, 5μ, SR: IA00E-C035
Pressure at start: 36 bar  Start flow: 0.700 ml/min  Column oven: 20.00 °C

Name               YZ T 49
RT [min]  Type  Area%  Area      Height Width [min]
 10.94  BV       59.56  18581.08  1105.24  0.21
 27.36  BBA      3.44  72.31  1.52  0.66
  Sum       100.00  19420.90
$^1$H NMR of 4n:

$^{13}$C NMR of 4n:
$^1$H NMR of 4o:

$^{13}$C NMR of 4o:
<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (s)</th>
<th>Height (mAU)</th>
<th>Area (nA*s)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>5.34</td>
<td>0.24</td>
<td>23.17</td>
<td>341.08</td>
<td>2.44</td>
</tr>
<tr>
<td>2</td>
<td>6.66</td>
<td>0.37</td>
<td>33.18</td>
<td>776.76</td>
<td>5.86</td>
</tr>
<tr>
<td>3</td>
<td>7.28</td>
<td>0.31</td>
<td>34.42</td>
<td>737.82</td>
<td>5.24</td>
</tr>
<tr>
<td>4</td>
<td>8.52</td>
<td>0.32</td>
<td>473.55</td>
<td>921.55</td>
<td>6.58</td>
</tr>
<tr>
<td>5</td>
<td>9.63</td>
<td>0.29</td>
<td>32.90</td>
<td>538.06</td>
<td>4.02</td>
</tr>
<tr>
<td>6</td>
<td>10.14</td>
<td>0.51</td>
<td>15.98</td>
<td>432.02</td>
<td>3.09</td>
</tr>
<tr>
<td>7</td>
<td>12.80</td>
<td>0.62</td>
<td>10.09</td>
<td>437.23</td>
<td>3.12</td>
</tr>
<tr>
<td>8</td>
<td>15.52</td>
<td>0.55</td>
<td>25.92</td>
<td>1751.47</td>
<td>12.83</td>
</tr>
</tbody>
</table>

Total: 13981.68 100.00
$^1$H NMR of 4p:

$^{13}$C NMR of 4p:
$^1$H NMR of 4q:

$^{13}$C NMR of 4q:
### Table 1: Analysis Results 1

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (mAU)</th>
<th>Height (mAU)</th>
<th>Area (mAU²)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.75</td>
<td>0.22</td>
<td>96.83</td>
<td>1306.98</td>
<td>10.64</td>
</tr>
<tr>
<td>2</td>
<td>1.27</td>
<td>0.27</td>
<td>80.78</td>
<td>6499.69</td>
<td>48.08</td>
</tr>
<tr>
<td>3</td>
<td>0.40</td>
<td>0.40</td>
<td>210.02</td>
<td>13404.41</td>
<td>45.82</td>
</tr>
</tbody>
</table>

Total: 12490.97 100.00%

---

### Table 2: Analysis Results 2

<table>
<thead>
<tr>
<th>#</th>
<th>Ret. Time (min)</th>
<th>Width (mAU)</th>
<th>Height (mAU)</th>
<th>Area (mAU²)</th>
<th>Area %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.66</td>
<td>0.23</td>
<td>40.60</td>
<td>884.28</td>
<td>3.01</td>
</tr>
<tr>
<td>2</td>
<td>5.61</td>
<td>0.29</td>
<td>924.83</td>
<td>16448.07</td>
<td>94.59</td>
</tr>
</tbody>
</table>

Total: 17127.12 100.00%
$^1$H NMR of 4r:

$^{13}$C NMR of 4r: