Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

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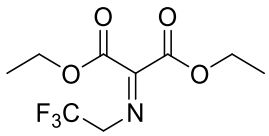
1. General information

- 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}).
- ^{1}H- and ^{13}C- 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.[1]

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 $NaHCO_3$ solution and dried over anhydrous Na_2SO_4. Then the solvent was evaporated to dryness and the residue was purified by flash chromatography (pentane/Et_2O = 20/1 to 10/1) to provide the desired product **2**.



2a

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).

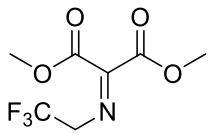
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.40 – 4.35 (m, 4H), 4.21 (q, *J* = 9.6 Hz, 2H), 1.35 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) 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, 2100, 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 $C_9H_{13}NO_4F_3^+$: 256.0797; found 256.0791.



2b

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).

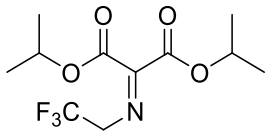
^{1}H NMR (600 MHz, $CDCl_3$) δ 4.22 (q, *J* = 9.6 Hz, 2H), 3.92 (s, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_7H_9NO_4F_3^+$: 228.0484; found 228.0478.



2c

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, $CDCl_3$) δ 5.27 – 5.18 (m, 2H), 4.21 (q, *J* = 9.6 Hz, 2H), 1.34 (d, *J* = 6.0 Hz, 6H), 1.33 (d, *J* = 6.0 Hz, 6H) ppm

^{13}C NMR (150 MHz, $CDCl_3$) δ 160.5, 159.4, 157.2, 123.8 (q, *J* = 275.1 Hz), 71.2, 71.0, 54.9 (q, *J* = 33.0 Hz), 21.6, 21.5 ppm.

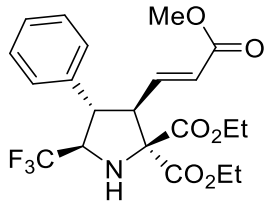
IR (ATR): 3466, 2983, 2933, 2325, 2083, 1735, 1461 1378, 1254, 1144, 1079, 913, 829, 674 cm^{-1}.

MS (ESI): *m/z* = 284.1 $[M+H]^+$.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{11}H_{17}NO_4F_3^+$: 284.1110; found 284.1104.

3. Asymmetric synthesis of 4:

A 10 mL glass tube equipped with a stirring bar was charged with the α,β-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 $Ph_3P{=}CHCO_2Me$ (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_2O = 4/1 to 1/1) to provide the desired product **4**.



4a

Diethyl (3*R*,4*S*,5*R*)-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4a** as a colorless solid (0.163 g, 92% yield).

Melting Point: 105-107 °C.

$[\alpha]_D^{25}$ = +59.2 (c = 1.0, $CHCl_3$).

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

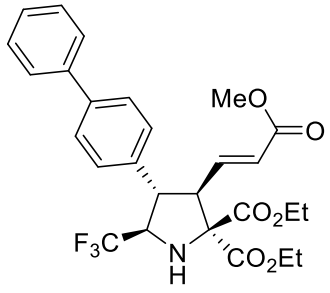
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 – 7.31 (m, 2H), 7.27 – 7.23 (m, 1H), 7.22 – 7.19 (m, 2H), 7.06 (dd, *J* = 15.6, 9.0 Hz, 1H), 5.59 (d, *J* = 15.6 Hz, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.27 – 4.21 (m, 2H), 4.01 – 3.94 (m, 1H), 3.79 (dd, *J* = 12.0, 9.6 Hz, 1H), 3.64 (s, 3H), 3.60 – 3.52 (m, 1H), 3.28 (dd, *J* = 12.0, 9.0 Hz, 1H), 1.27 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 170.0, 168.5, 165.9, 142.7, 136.6, 129.0 (2C), 127.9, 127.7 (2C), 125.3 (q, *J* = 278.0 Hz), 125.1, 73.7, 65.2 (q, *J* = 30.0 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}.

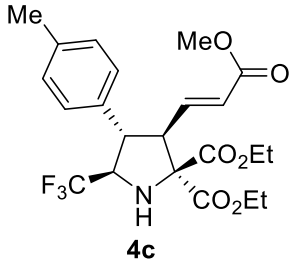
MS (ESI): *m/z* = 444.2 $[M+H]^+$.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{25}NO_6F_3^+$: 444.1634; found 444.1645.

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 α,β-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 $Ph_3P{=}CHCO_2Me$ (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/Et_2O = 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.



4b

Diethyl (3*R*,4*S*,5*R*)-4-([1,1'-biphenyl]-4-yl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(tri fluoromethyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).
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, $CDCl_3$) δ 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, $CDCl_3$) δ 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, 1654, 1439, 1372, 1276, 1227, 1136, 1004, 923, 847, 759, 696 cm^{-1}.
MS (ESI): *m/z* = 520.2 $[M+H]^+$.
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{27}H_{29}NO_6F_3^+$: 520.1947; found 520.2008.



4c

Diethyl (3*R*,4*S*,5*R*)-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4c** as a colorless solid (0.172 g, 94% yield).

Melting Point: 98-100 °C.

$[\alpha]_D^{25}$ = +64.2 (c = 1.0, $CHCl_3$).

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%.

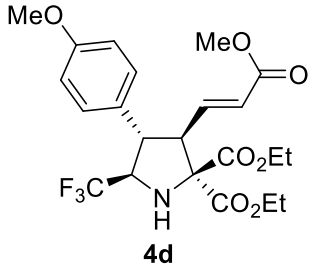
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 – 6.99 (m, 5H), 5.58 (d, *J* = 15.6 Hz, 1H), 4.32 – 4.18 (m, 5H), 3.97 – 3.88 (m, 1H), 3.74 (dd, *J* = 11.6, 9.6 Hz, 1H), 3.63 (s, 3H), 3.24 (dd, *J* = 11.6, 8.8 Hz, 1H), 2.29 (s, 3H), 1.28 – 1.24 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 170.0, 168.5, 165.9, 142.8, 137.5, 133.5, 129.7 (2C), 127.5 (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 $C_{22}H_{27}NO_6F_3^+$: 458.1790; found 458.1797.



4d

Diethyl (3*R*,4*S*,5*R*)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(4-methoxyphenyl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4d** as a colorless solid (0.175 g, 92% yield).

Melting Point: 98-100 °C.

$[\alpha]_D^{25}$ = +63.8 (c = 1.0, $CHCl_3$).

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%.

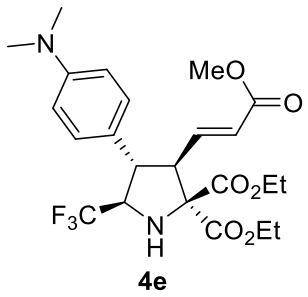
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.11 (d, *J* = 8.4 Hz, 2H), 7.05 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.84 (d, *J* = 8.4 Hz, 2H), 5.59 (d, *J* = 15.6 Hz, 1H), 4.31 – 4.21 (m, 4H), 3.91 (s, 1H), 3.77 (s, 3H), 3.76 – 3.72 (m, 1H), 3.65 (s, 3H), 3.53 (d, *J* = 5.4 Hz, 1H), 3.29 – 3.17 (m, 1H), 1.27 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{22}H_{27}NO_7F_3^+$: 474.1740; found 474.1749.



4e

Diethyl (3*R*,4*S*,5*R*)-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4e** as a light red solid (0.121 g, 60% yield).

Melting Point: 145-147 °C.

$[\alpha]_D^{25}$ = +75.2 (c = 1.0, $CHCl_3$).

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

^{1}H NMR (400 MHz, $CDCl_3$) 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.

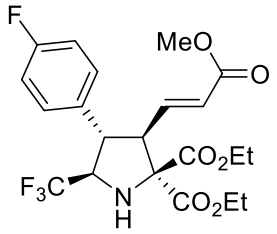
^{13}C NMR (100 MHz, $CDCl_3$) δ 170.2, 168.6, 166.0, 150.0, 143.2, 128.3 (2C), 125.5 (q, *J* = 278.9 Hz), 124.9, 123.7, 112.6 (2C), 73.6, 65.2 (q, *J* = 29.3 Hz), 62.6, 61.9, 56.5, 51.5, 49.9, 40.4 (2C), 14.0, 13.9 ppm.

^{19}F NMR (376 MHz, $CDCl_3$) 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 $C_{23}H_{30}N_2O_6F_3^+$: 487.2056; found 487.2067.



4f

Diethyl (3*R*,4*S*,5*R*)-4-(4-fluorophenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).

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%.

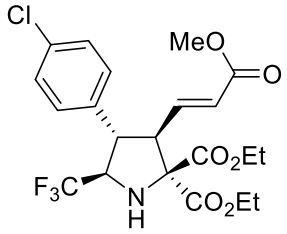
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.19 – 7.16 (m, 2H), 7.07 – 6.98 (m, 3H), 5.58 (d, *J* = 15.6 Hz, 1H), 4.33 – 4.20 (m, 4H), 3.95 – 3.90 (m, 1H), 3.80 – 3.75 (m, 1H), 3.65 (s, 3H), 3.57 – 3.51 (m, 1H), 3.21 (dd, *J* = 11.4, 9.6 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) 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 $C_{21}H_{24}NO_6F_4^+$: 462.1540; found 462.1548.



4g

Diethyl (3*R*,4*S*,5*R*)-4-(4-chlorophenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).

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%.

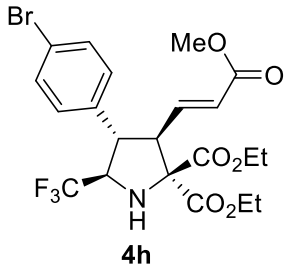
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 (d, *J* = 8.4 Hz, 2H), 7.12 (d, *J* = 8.4 Hz, 2H), 7.02 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.57 (d, *J* = 15.6 Hz, 1H), 4.33 – 4.17 (m, 4H), 3.95 – 3.86 (m, 1H), 3.75 (dd, *J* = 11.6, 9.6 Hz, 1H), 3.64 (s, 3H), 3.52 (d, *J* = 6.8 Hz, 1H), 3.20 (dd, *J* = 11.6, 8.8 Hz, 1H), 1.27 – 1.23 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 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 $C_{21}H_{24}NO_6ClF_3^+$: 478.1244; found 478.1232.



4h

Diethyl (3*R*,4*S*,5*R*)-4-(4-bromophenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).

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%.

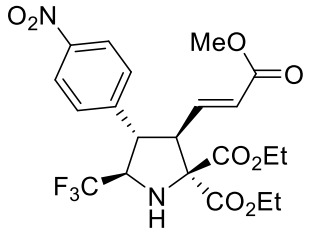
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.42 (d, *J* = 8.4 Hz, 2H), 7.07 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.57 (d, *J* = 15.6 Hz, 1H), 4.32 – 4.15 (m, 4H), 3.96 – 3.86 (m, 1H), 3.74 (dd, *J* = 11.6, 9.6 Hz, 1H), 3.63 (s, 3H), 3.53 (d, *J* = 7.2 Hz, 1H), 3.20 (dd, *J* = 11.6, 8.8 Hz, 1H), 1.27 – 1.23 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 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 $C_{21}H_{24}NO_6BrF_3^+$: 522.0739; found 522.0756.



4i

Diethyl (3*R*,4*S*,5*R*)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(4-nitrophenyl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4i** as a wax (0.123 g, 63% yield).

$[\alpha]_D^{25}$ = +40.6 (c = 1.0, $CHCl_3$).

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%.

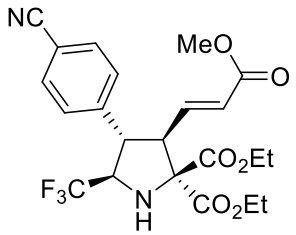
^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.8 Hz, 2H), 7.39 (d, *J* = 8.8 Hz, 2H), 7.02 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.57 (d, *J* = 15.6 Hz, 1H), 4.33 – 4.18 (m, 4H), 3.99 – 3.88 (m, 2H), 3.63 (s, 3H), 3.61 – 3.55 (m, 1H), 3.26 (dd, *J* = 11.6, 8.8 Hz, 1H), 1.26 (t, *J* = 7.2 Hz, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) 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 $[M+H]^+$.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{24}N_2O_8F_3^+$: 489.1485; found 489.1493.



4j

Diethyl (3*R*,4*S*,5*R*)-4-(4-cyanophenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).

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%.

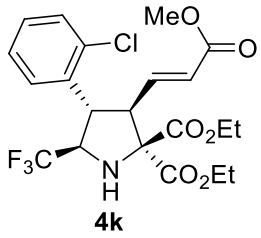
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.61 (d, *J* = 8.4 Hz, 2H), 7.32 (d, *J* = 8.4 Hz, 2H), 7.01 (dd, *J* = 15.6, 9.2 Hz, 1H), 5.55 (d, *J* = 15.6 Hz, 1H), 4.32 – 4.18 (m, 4H), 3.91 (s, 1H), 3.88 – 3.79 (m, 1H), 3.63 (s, 3H), 3.57 (d, *J* = 7.2 Hz, 1H), 3.23 (dd, *J* = 11.2, 9.2 Hz, 1H), 1.27 – 1.23 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 169.6, 168.2, 165.6, 142.2, 141.7, 132.8 (2C), 128.7 (2C), 125.6, 125.0 (q, *J* = 278.2 Hz), 118.2, 112.0, 73.6, 64.9 (q, *J* = 30.2 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, 1371, 1276, 1219, 1123, 989, 845, 727 cm^{-1}.

MS (ESI): *m/z* = 469.2 $[M+H]^+$.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{22}H_{24}N_2O_6F_3^+$: 469.1586; found 469.1599.



4k

Diethyl (3*R*,4*S*,5*R*)-4-(2-chlorophenyl)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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: DAICELAS.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%.

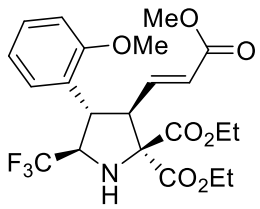
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.37 (d, *J* = 7.8 Hz, 1H), 7.28 – 7.24 (m, 2H), 7.22 – 7.19 (m, 1H), 7.09 (dd, *J* = 15.6, 8.4 Hz, 1H), 5.62 (d, *J* = 15.6 Hz, 1H), 4.51 – 4.46 (m, 1H), 4.30 (q, *J* = 7.2 Hz, 2H), 4.26 (q, *J* = 7.2 Hz, 2H), 4.12 – 4.04 (m, 1H), 3.67 (s, 3H), 3.62 – 3.55 (m, 1H), 3.47 – 3.37 (m, 1H), 1.31 – 1.27 (m, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.9, 168.4, 165.9, 142.2, 134.6, 134.1, 130.4, 129.0, 127.4, 125.2 (q, *J* = 278.0 Hz), 125.0, 122.5, 73.7, 64.1, 62.8, 62.1, 56.6, 51.6, 46.6, 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): *m/z* = 478.1 $[M+H]^+$.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{21}H_{24}NO_6ClF_3^+$: 478.1244; found 478.1260.



4l

Diethyl (3*R*,4*S*,5*R*)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(2-methoxyphenyl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4l** as a colorless solid (0.167 g, 88% yield).

Melting Point: 114-116 °C.

$[\alpha]_D^{25}$ = +49.6 (c = 1.0, $CHCl_3$).

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%.

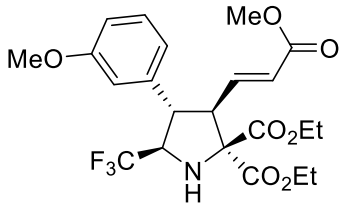
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 – 7.19 (m, 1H), 7.13 – 7.05 (m, 2H), 6.91 – 6.82 (m, 2H), 5.59 (d, *J* = 15.6 Hz, 1H), 4.27 (q, *J* = 7.2 Hz, 2H), 4.23 – 4.18 (m, 3H), 4.09 – 4.00 (m, 1H), 3.80 (s, 3H), 3.62 (s, 3H), 3.61 – 3.53 (m, 2H), 1.27 – 1.23 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) 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 $C_{22}H_{27}NO_7F_3^+$: 474.1740; found 474.1752.



4m

Diethyl (3*R*,4*S*,5*R*)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(3-methoxyphenyl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4m** as a colorless solid (0.134 g, 71% yield).

Melting Point: 100-103 °C.

$[\alpha]_D^{25}$ = +48.9 (c = 1.0, $CHCl_3$).

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%.

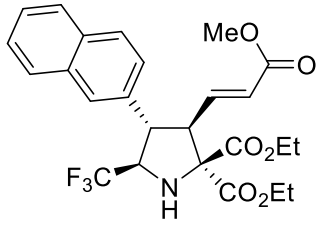
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.24 – 7.20 (m, 1H), 7.04 (dd, *J* = 15.6, 8.8 Hz, 1H), 6.80 – 6.75 (m, 2H), 6.73 – 6.70 (m, 1H), 5.60 (d, *J* = 15.6 Hz, 1H), 4.34 – 4.16 (m, 4H), 4.01 – 3.90 (m, 1H), 3.77 (s, 3H), 3.76 – 3.70 (m, 1H), 3.64 (s, 3H), 3.56 – 3.49 (m, 1H), 3.24 (dd, *J* = 11.2, 8.8 Hz, 1H), 1.28 – 1.24 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 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, 55.2, 51.5, 50.6, 14.0, 13.9 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* $[M+H]^+$ calcd for $C_{22}H_{27}NO_7F_3^+$: 474.1740; found 474.1754.



4n

Diethyl (3*R*,4*S*,5*R*)-3-((*E*)-3-methoxy-3-oxoprop-1-en-1-yl)-4-(naphthalen-2-yl)-5-(trifluoro methyl)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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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%.

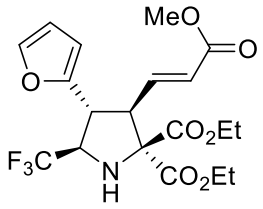
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 – 7.76 (m, 3H), 7.69 – 7.65 (m, 1H), 7.50 – 7.43 (m, 2H), 7.31 (dd, *J* = 8.4, 1.6 Hz, 1H), 7.11 (dd, *J* = 15.6, 8.8 Hz, 1H), 5.60 (d, *J* = 15.6 Hz, 1H), 4.35 – 4.20 (m, 4H), 4.15 – 4.04 (m, 1H), 3.98 (dd, *J* = 11.2, 9.6 Hz, 1H), 3.62 (d, *J* = 7.6 Hz, 1H), 3.58 (s, 3H), 3.40 (dd, *J* = 11.2, 8.8 Hz, 1H), 1.30 – 1.26 (m, 6H) ppm.

^{13}C NMR (100 MHz, $CDCl_3$) δ 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.

IR (ATR): 3733, 3343, 2989, 2650, 2324, 2109, 2058, 1916, 1727, 1515, 1442, 1368, 1277, 1225, 1137, 985, 857, 743 cm^{-1}.

MS (ESI): *m/z* = 494.2 $[M+H]^+$.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{25}H_{27}NO_6F_3^+$: 494.1790; found 494.1803.



4o

Diethyl (3*R*,4*R*,5*R*)-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4o** as a wax (0.104 g, 57% yield).

$[\alpha]_D^{25}$ = +50.4 (c = 1.0, $CHCl_3$).

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%.

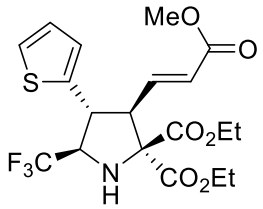
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.34 – 7.32 (m, 1H), 7.09 (dd, *J* = 15.6, 8.4 Hz, 1H), 6.29 – 6.27 (m, 1H), 6.19 – 6.17 (m, 1H), 5.68 (d, *J* = 15.6 Hz, 1H), 4.32 – 4.18 (m, 4H), 4.12 – 4.05 (m, 1H), 3.94 (dd, *J* = 11.4, 9.6 Hz, 1H), 3.69 (s, 3H), 3.56 (d, *J* = 7.8 Hz, 1H), 3.36 (dd, *J* = 11.4, 8.4 Hz, 1H), 1.28 – 1.25 (m, 6H) ppm.

^{13}C NMR (150 MHz, $CDCl_3$) δ 169.7, 168.3, 166.0, 149.3, 142.6, 142.4, 125.2, 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}.

MS (ESI): *m/z* = 456.1 $[M+Na]^+$.

HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{19}H_{23}NO_7F_3^+$: 434.1427; found 434.1433.



4p

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

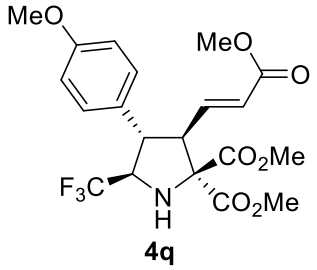
According to the above general procedure by using **1p** (0.066 g, 0.48 mmol), **2a** (0.102 g, 0.4 mmol) and catalyst **B** (6.5 mg, 0.02 mmol) in toluene (4.0 mL) for 24 h at room temperature followed by addition of $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).

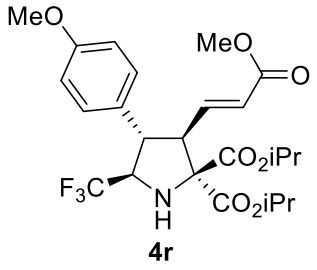
HPLC: CHIRALPAK IB; *n*-heptane/iPrOH = 97/3; flow rate 1.0 mL/min; T= 30 °C; retention time: 8.57 min (major), 11.01 min (minor), ee: >99%.

^{1}H NMR (400 MHz, $CDCl_3$) 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* = 7.6 Hz, 1H), 3.17 (dd, *J* = 11.2, 8.8 Hz, 1H), 1.287 – 1.23 (m, 6H) ppm.
^{13}C NMR (100 MHz, $CDCl_3$) 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* $[M+H]^+$ calcd for $C_{19}H_{23}NO_6F_3S^+$: 450.1198; found 450.1184.



4q

Dimethyl (3*R*,4*S*,5*R*)-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 4/1 to 1/1) afforded **4q** as a colorless solid (0.154 g, 93% yield).
Melting Point: 113-115 °C.
$[\alpha]_D^{25}$ = +67.8 (c = 1.0, $CHCl_3$).
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%.
^{1}H NMR (600 MHz, $CDCl_3$) 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.
^{13}C NMR (150 MHz, $CDCl_3$) 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* $[M+H]^+$ calcd for $C_{20}H_{23}NO_7F_3^+$: 446.1427; found 446.1414.



4r

Diisopropyl (3*R*,4*S*,5*R*)-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 $Ph_3P{=}CHCO_2Me$ (0.20 g, 0.6 mmol), the chromatographic purification (pentane/Et_2O = 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, $CHCl_3$).

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, $CDCl_3$) δ 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, $CDCl_3$) δ 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 $[M+Na]^+$.

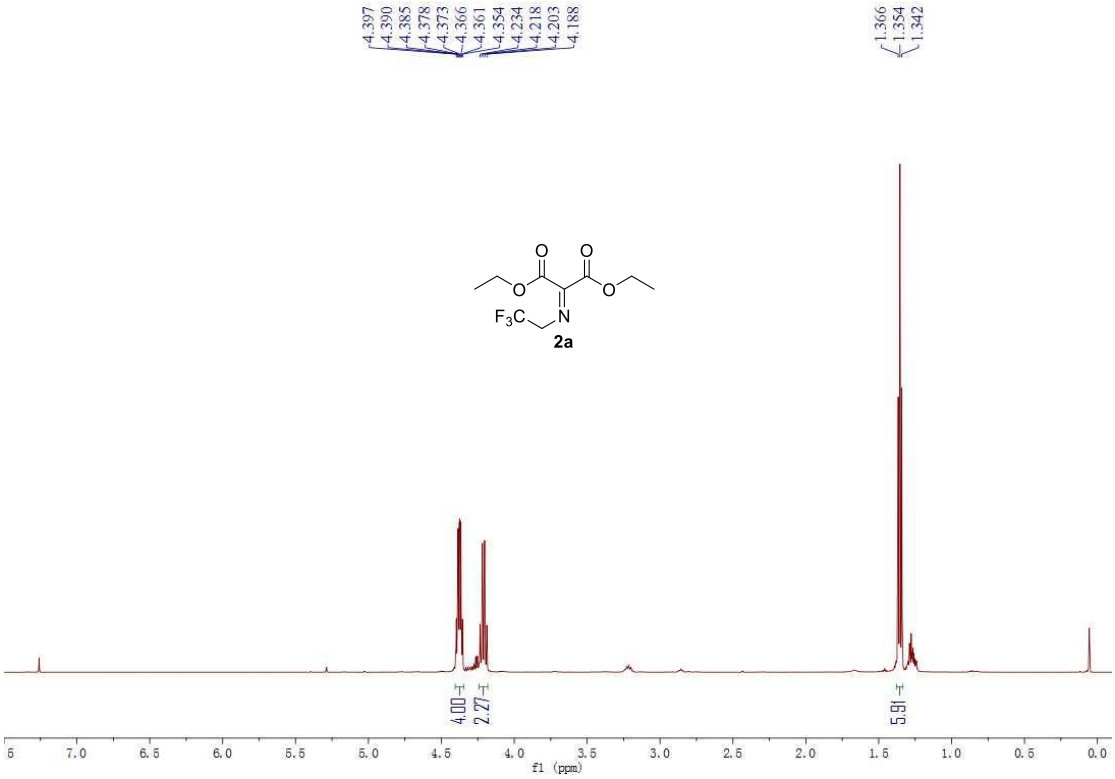
HRMS (ESI): *m/z* $[M+H]^+$ calcd for $C_{24}H_{31}NO_7F_3^+$: 502.2053; found 502.2052.

4. Reference

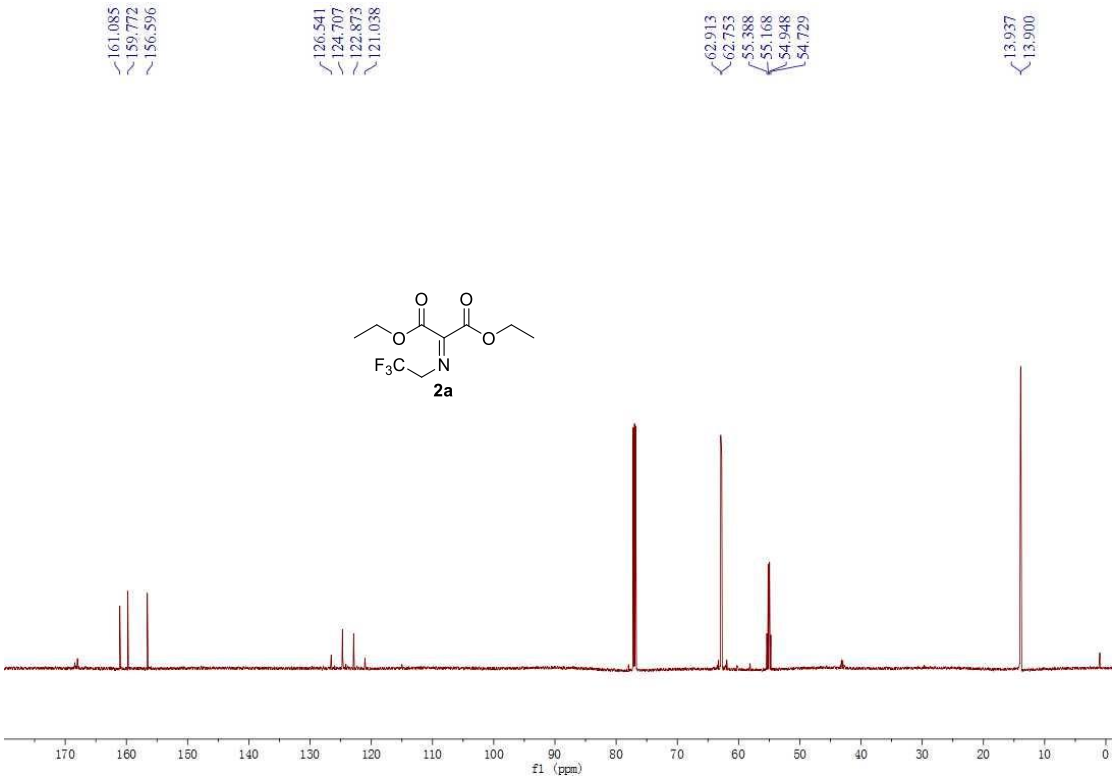
[1] Q. Sun, X. Li, J. Su, L. Zhao, M. Ma, Y. Zhu, Y. Zhao, R. Zhu, W. Yan, K. Wang and R. Wang, *Adv. Synth. Catal.*, **2015**, *357*, 3187-3196.

5. NMR Spectra and Chiral HPLC Data:

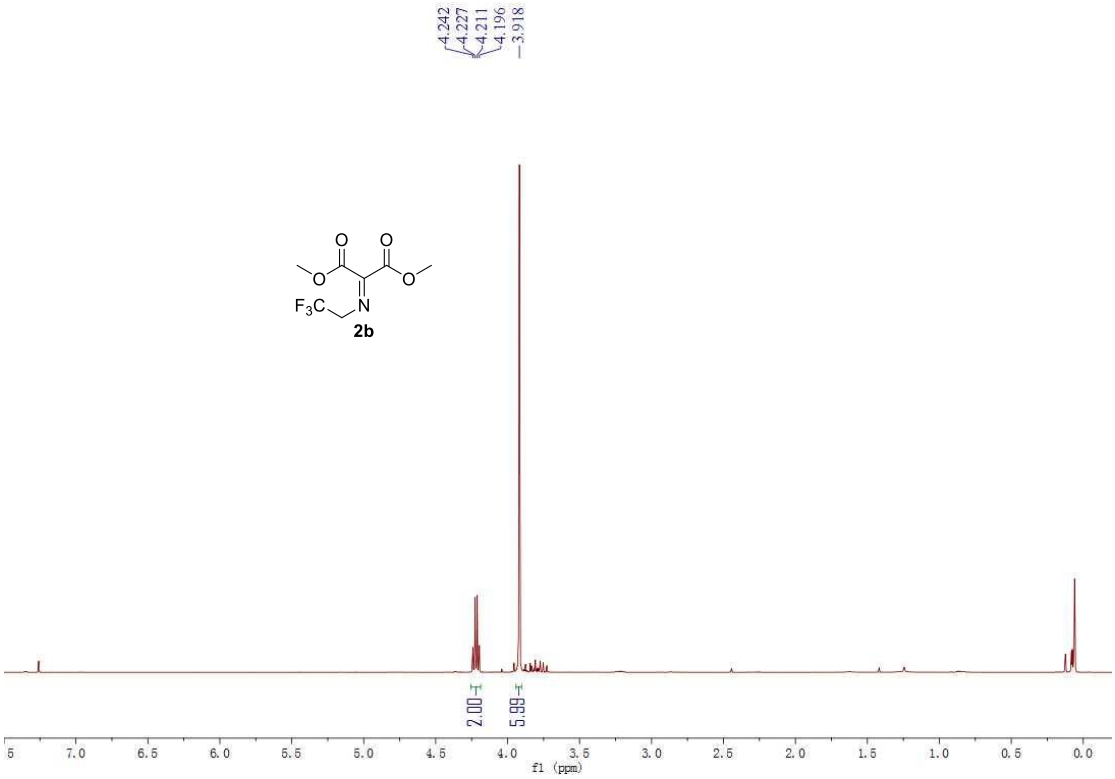
^{1}H NMR of **2a:**



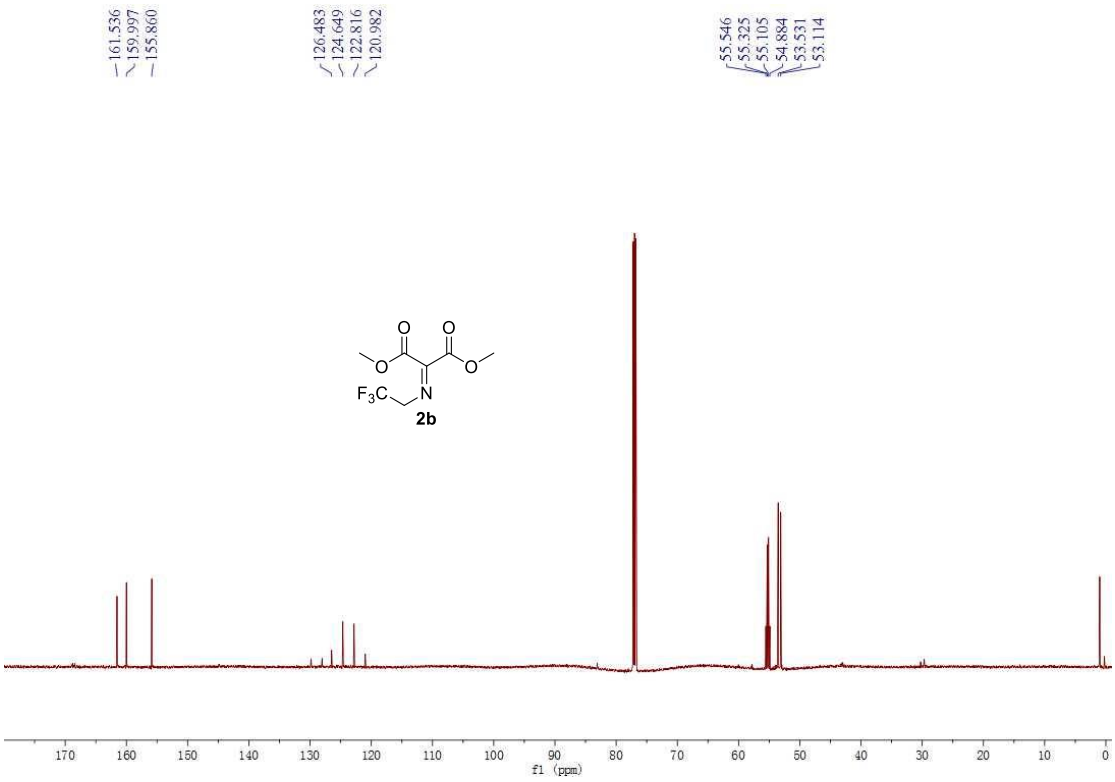
^{13}C NMR of **2a:**



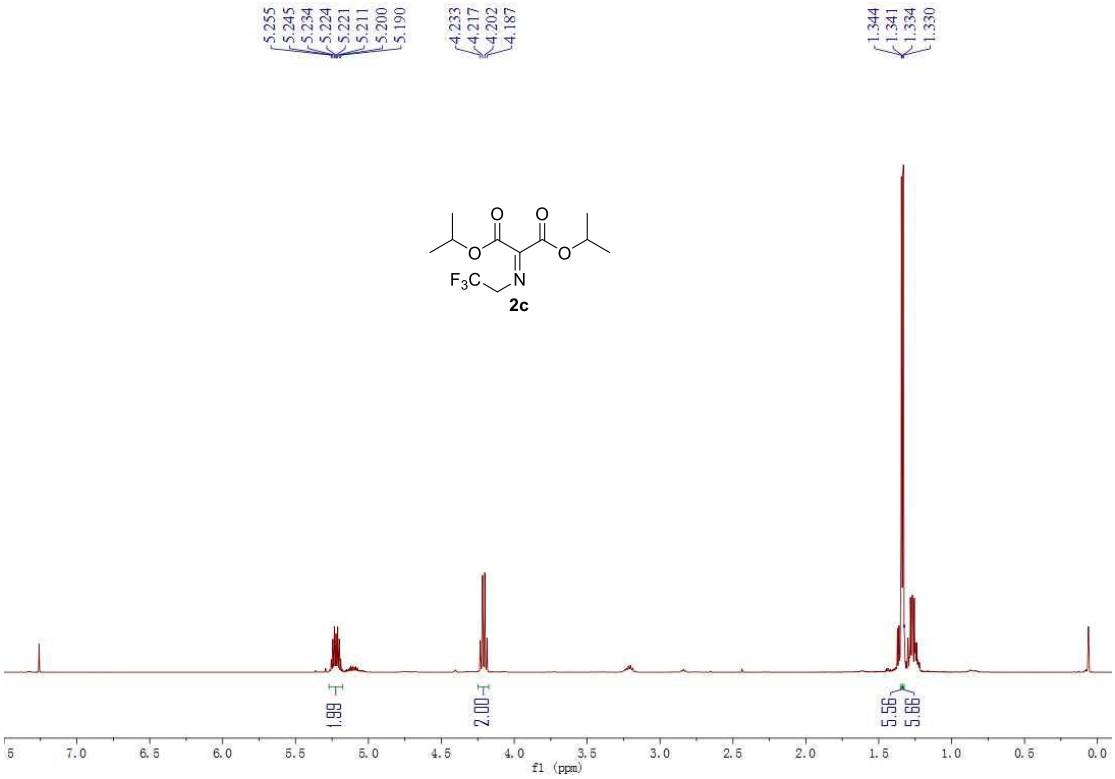
^{1}H NMR of **2b:**



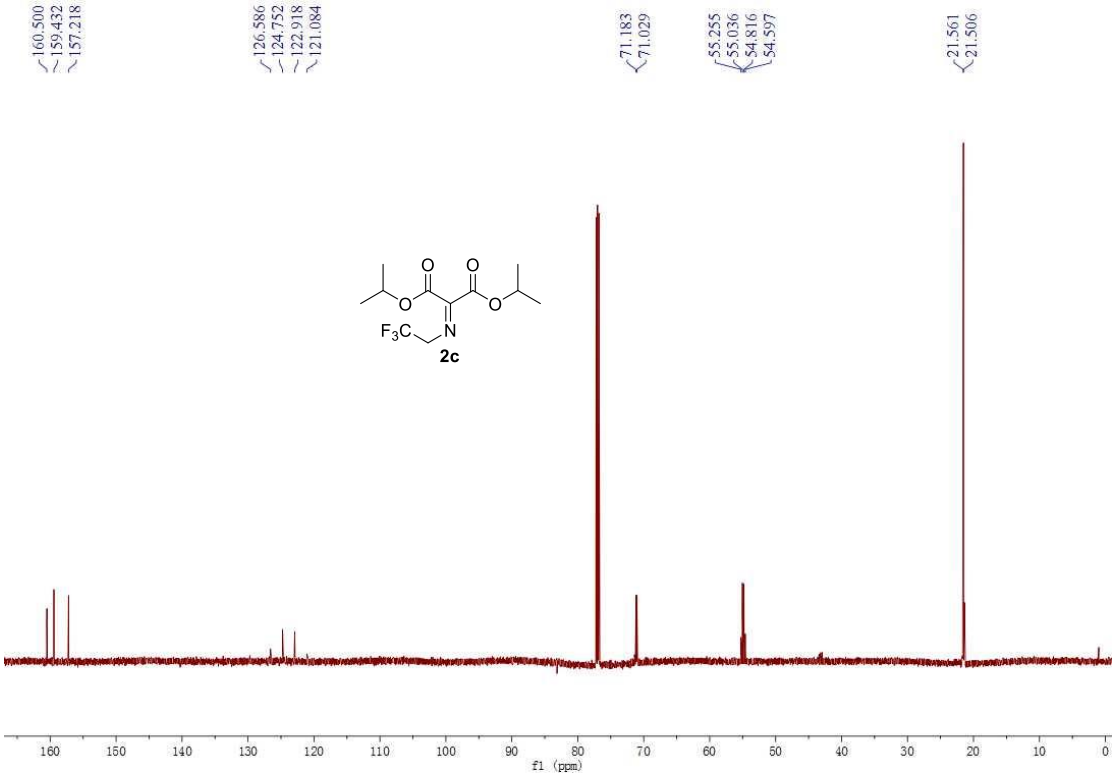
^{13}C NMR of **2b:**



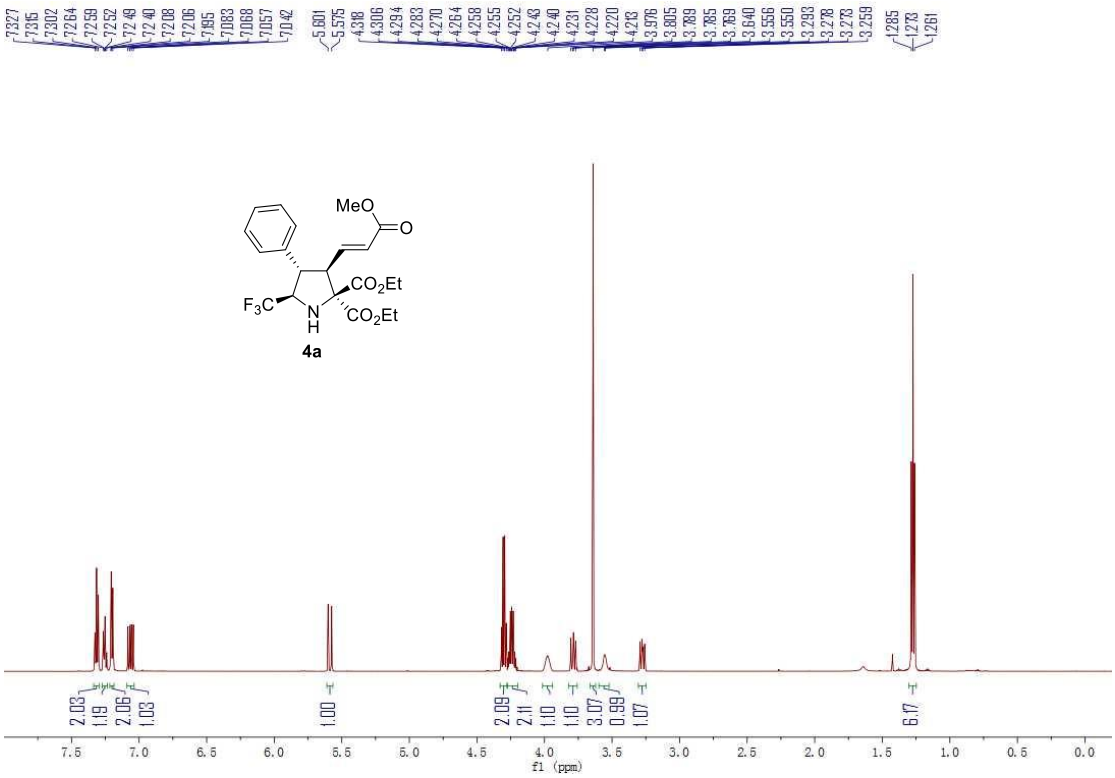
^{1}H NMR of **2c:**



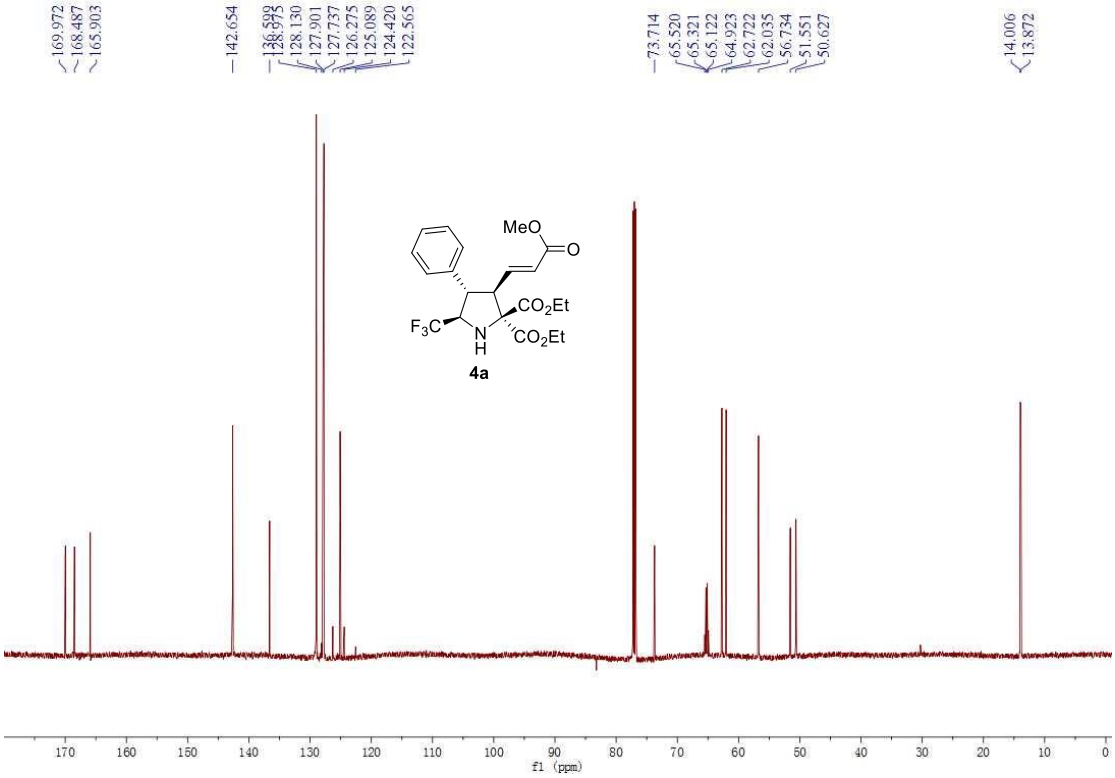
^{13}C NMR of **2c:**



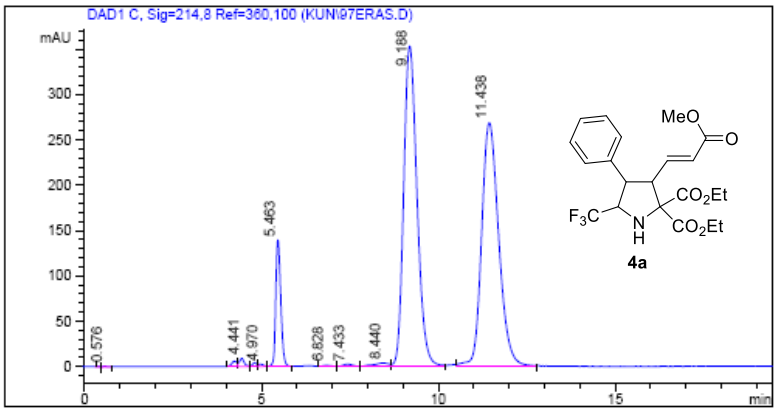
^{1}H NMR of **4a:**



^{13}C NMR of **4a:**

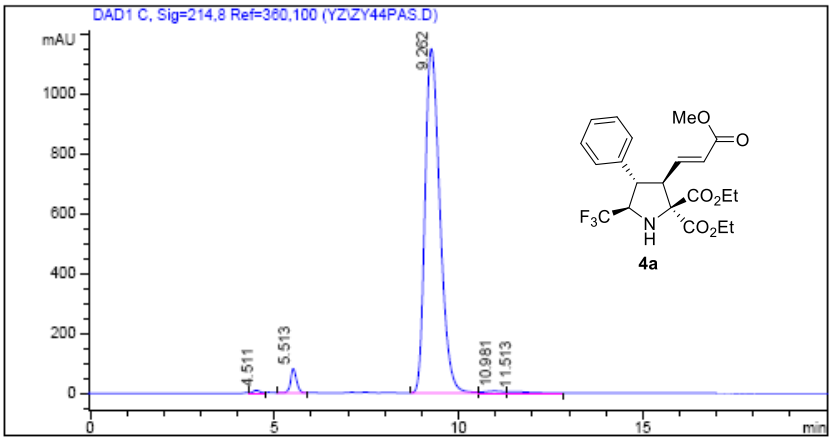


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.0	21.7
Flow in ml/min:	0.70	0.70



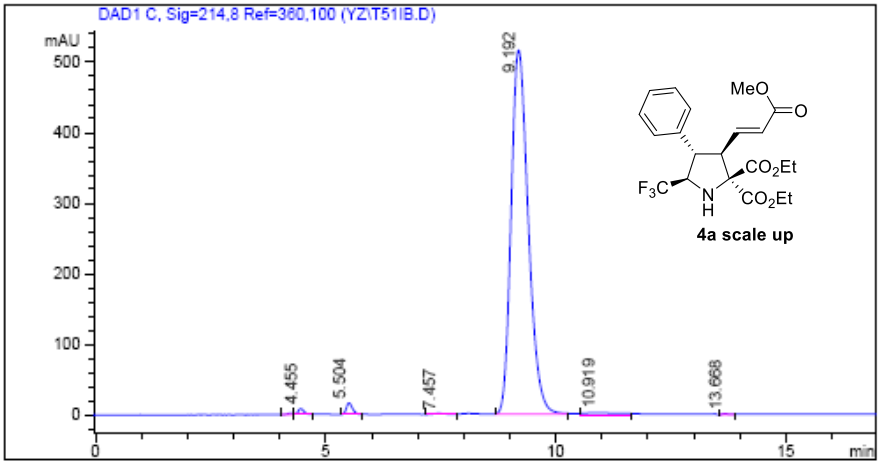
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	0.39	0.07	1.15	5.18	0.03
2	0.58	0.13	1.26	12.29	0.06
3	4.23	0.17	5.82	63.11	0.32
4	4.44	0.14	9.08	85.70	0.43
5	4.81	0.13	4.07	37.17	0.19
6	4.97	0.14	2.59	22.98	0.11
7	5.46	0.16	139.15	1379.70	6.90
8	6.83	0.21	0.94	14.92	0.07
9	7.43	0.27	2.30	39.73	0.20
10	8.44	0.40	3.61	106.76	0.53
11	9.19	0.40	353.12	9229.97	46.15
12	11.44	0.52	268.43	9001.37	45.01
Total				19998.88	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	20.9	21.5
Flow in ml/min:	0.70	0.70



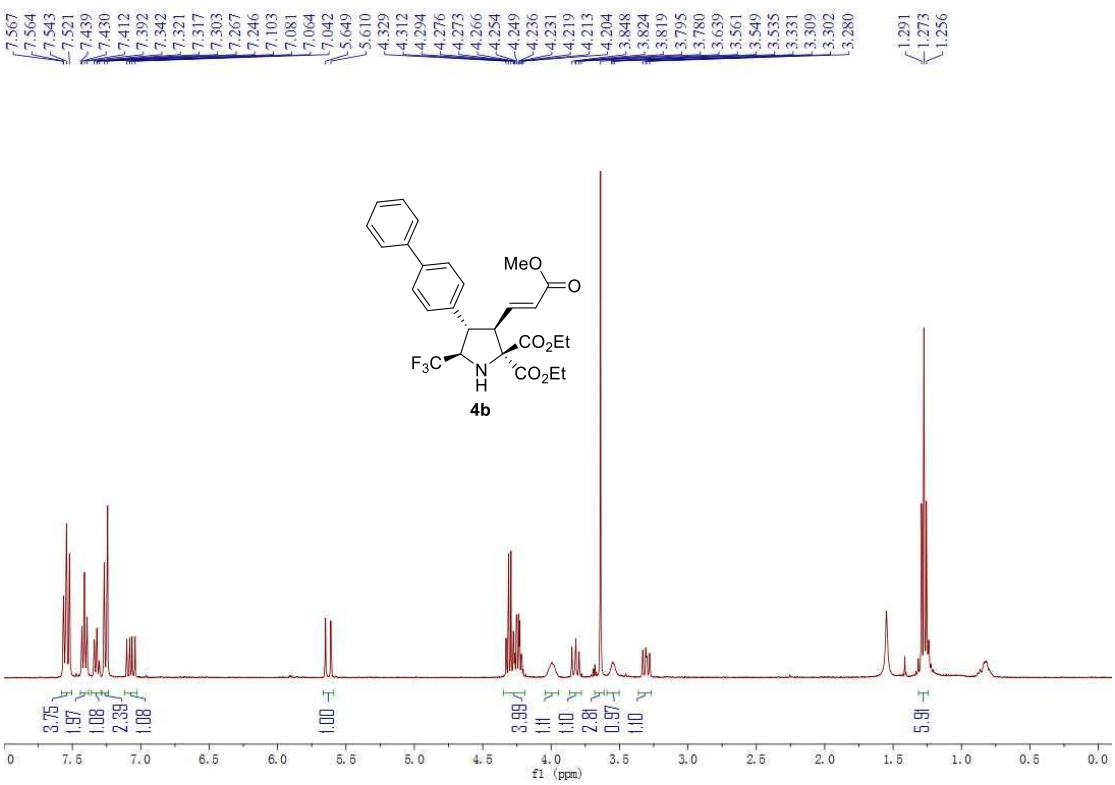
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.51	0.20	9.23	121.63	0.36
2	5.51	0.17	81.31	931.56	2.75
3	9.26	0.44	1150.11	32343.18	95.65
4	10.98	0.57	6.70	229.89	0.68
5	11.51	0.66	4.80	188.56	0.56
Total				33814.83	100.00

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

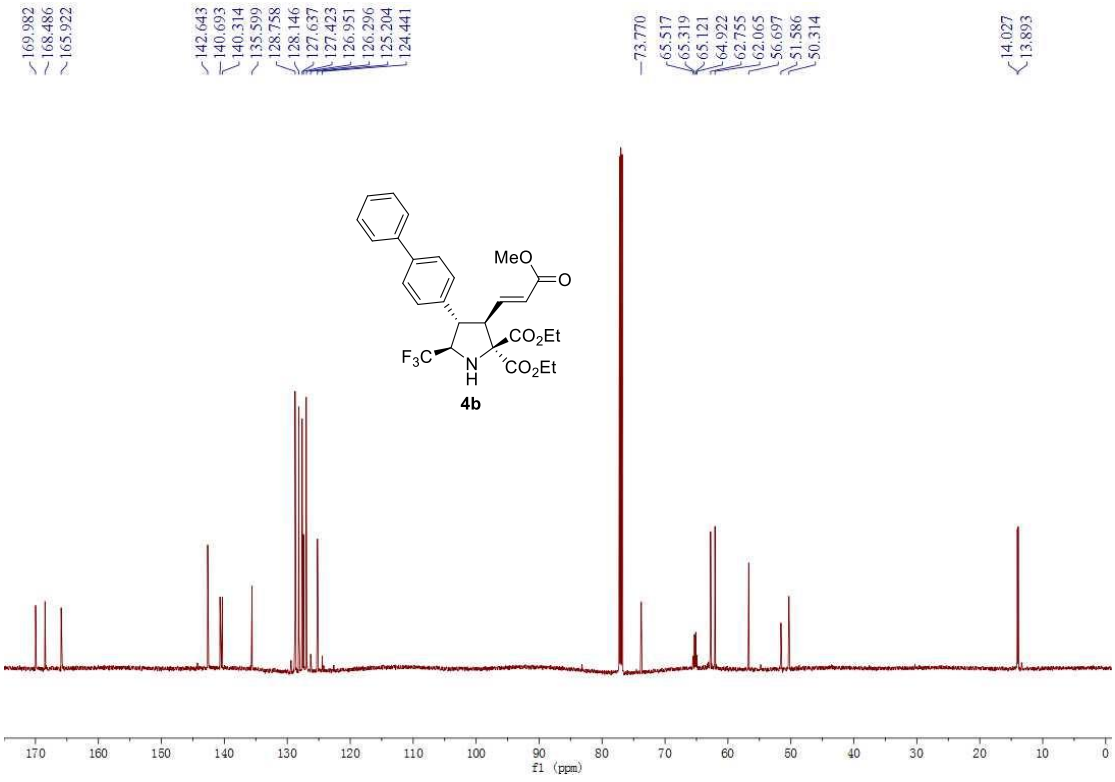


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.24	0.13	1.89	15.78	0.11
2	4.46	0.14	8.38	79.08	0.57
3	5.50	0.14	16.23	151.33	1.09
4	7.46	0.24	1.50	25.83	0.19
5	9.19	0.40	516.17	13388.00	96.55
6	10.92	0.95	3.41	193.26	1.39
7	13.67	0.15	1.29	13.18	0.10
Total				13866.45	100.00

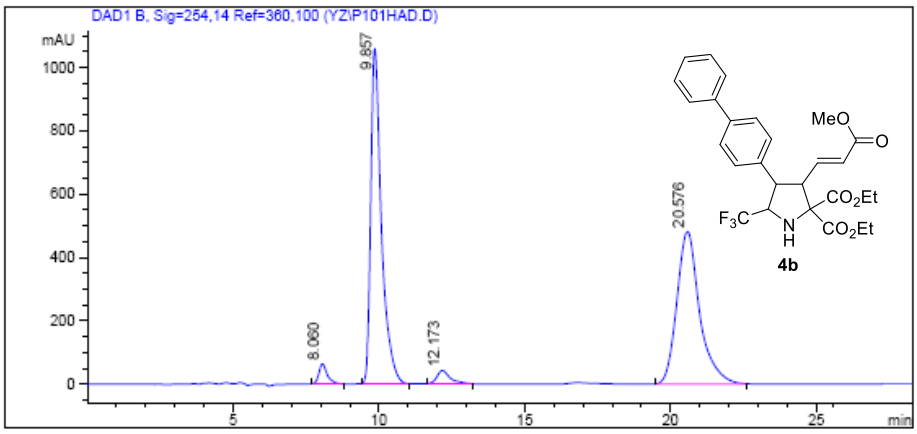
^{1}H NMR of **4b:**



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

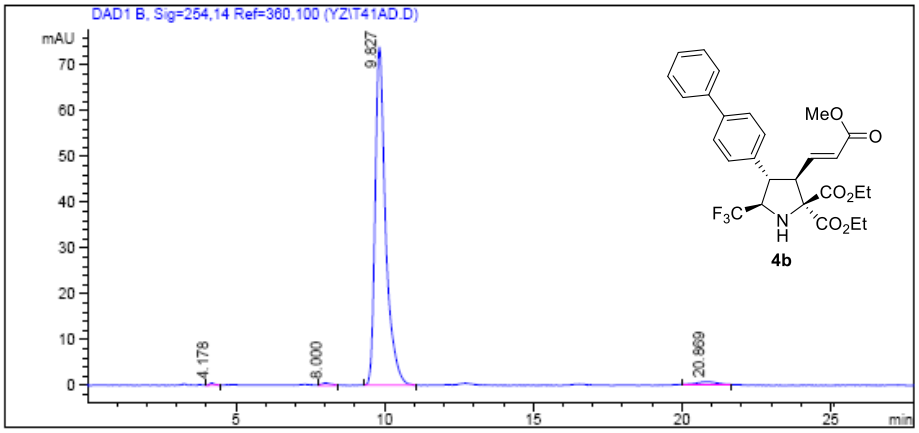


Temperature in°C:	30.0	30.0
Pressure in bar:	33.9	33.2
Flow in ml/min:	1.0	1.0



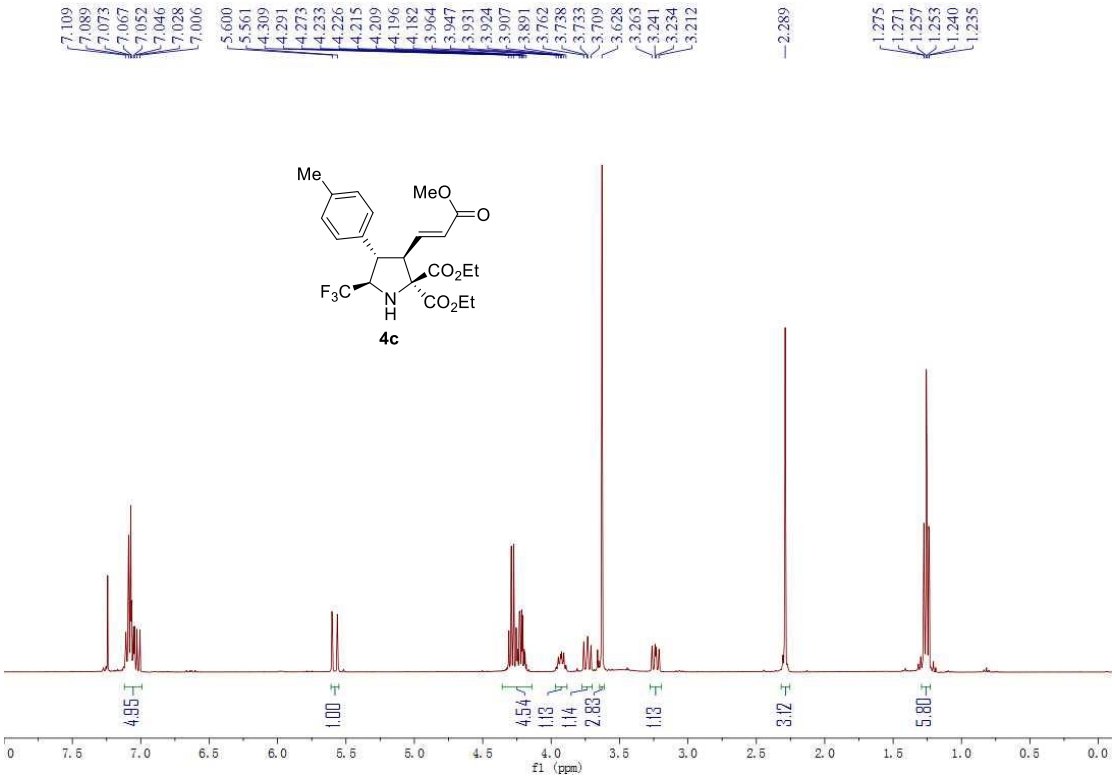
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	8.06	0.30	63.85	1294.06	2.32
2	9.86	0.38	1057.79	26917.53	48.36
3	12.17	0.47	41.81	1347.29	2.42
4	20.58	0.82	481.77	26106.68	46.90
Total				55665.56	100.00

Temperature in°C:	30.0	30.0
Pressure in bar:	33.1	32.1
Flow in ml/min:	1.0	1.0

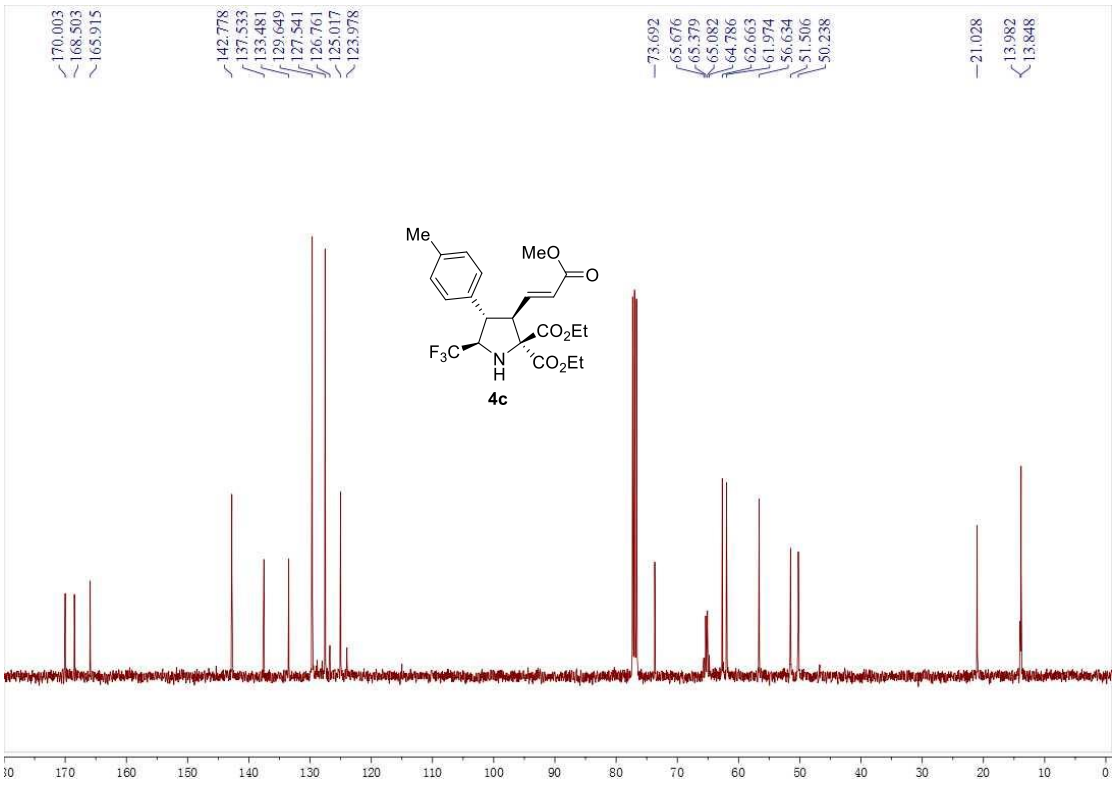


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.18	0.20	0.50	6.07	0.32
2	8.00	0.34	0.59	11.89	0.64
3	9.83	0.41	73.92	1816.28	97.10
4	10.46	0.00	3.84	0.00	0.00
5	10.76	0.00	0.49	0.00	0.00
6	20.87	0.85	0.71	36.37	1.94
Total				1870.61	100.00

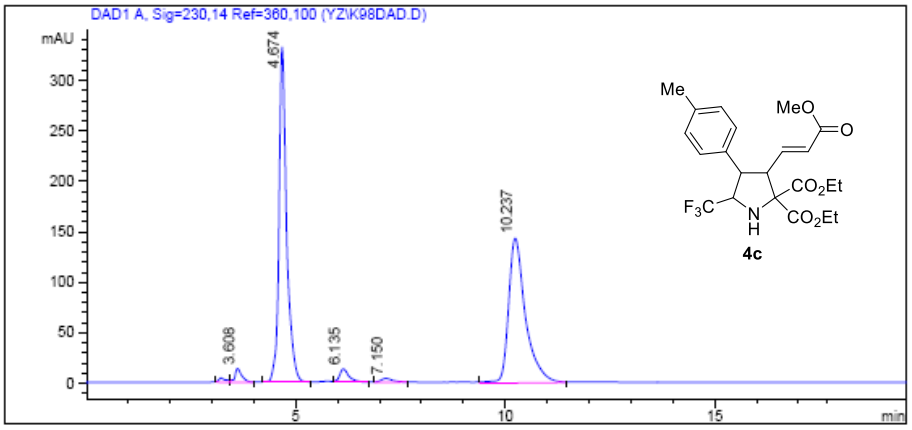
^{1}H NMR of **4c:**



^{13}C NMR of **4c:**

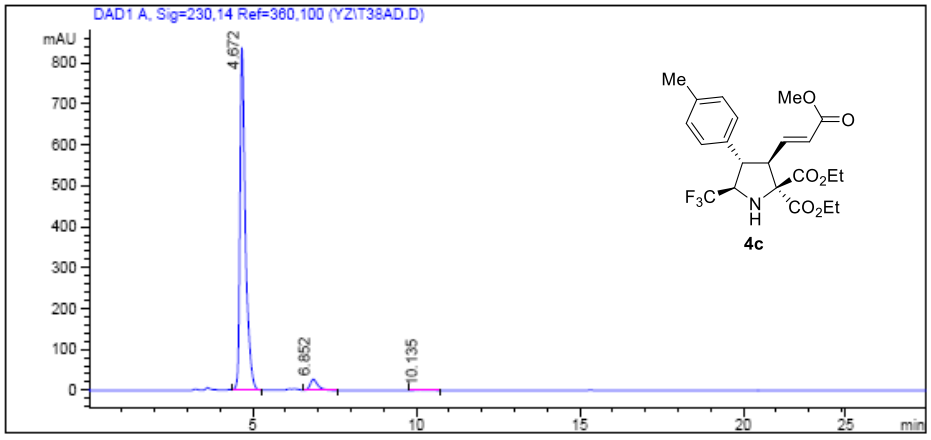


Temperature in°C:	30.0	30.0
Pressure in bar:	37.2	36.7
Flow in ml/min:	1.0	1.0



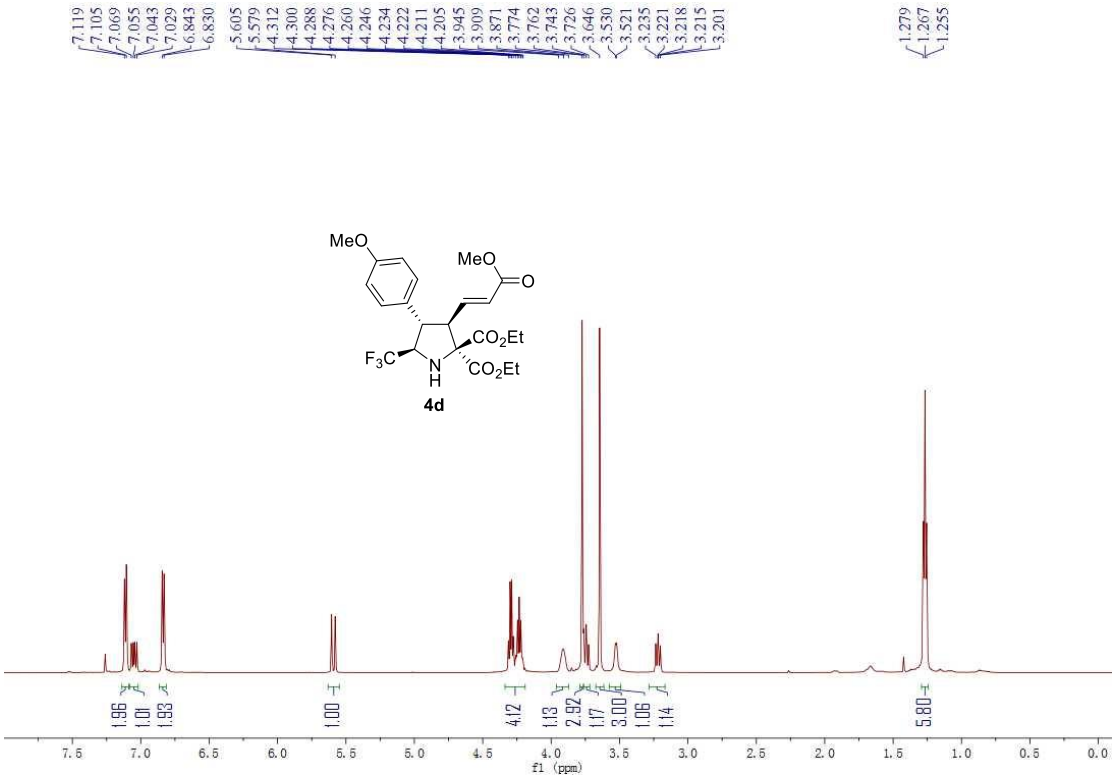
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.21	0.20	4.41	52.32	0.60
2	3.61	0.19	13.74	159.95	1.83
3	4.67	0.18	332.16	4213.26	48.18
4	6.14	0.23	13.24	207.17	2.37
5	7.15	0.29	3.80	75.82	0.87
6	10.24	0.47	143.55	4036.74	46.16
Total				8745.26	100.00

Temperature in°C:	30.0	30.0
Pressure in bar:	35.7	35.8
Flow in ml/min:	1.0	1.0

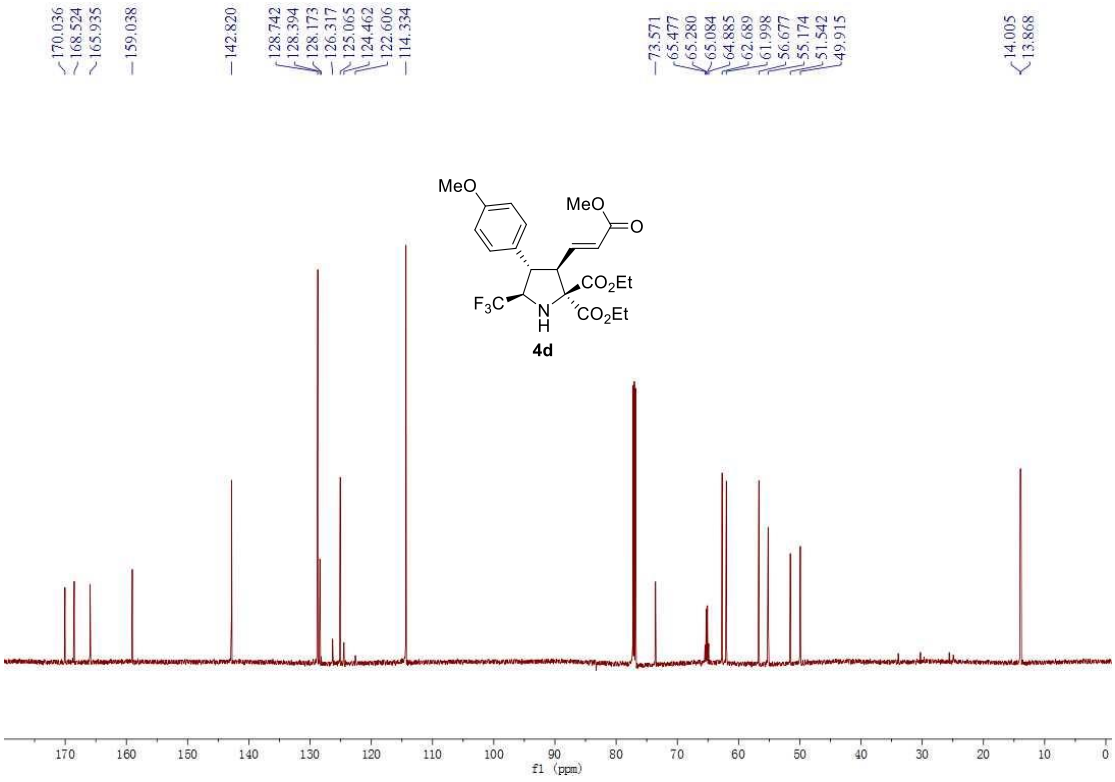


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.67	0.17	838.02	9793.49	95.10
2	6.85	0.26	27.10	469.37	4.56
3	10.13	0.28	1.57	34.79	0.34
Total				10297.64	100.00

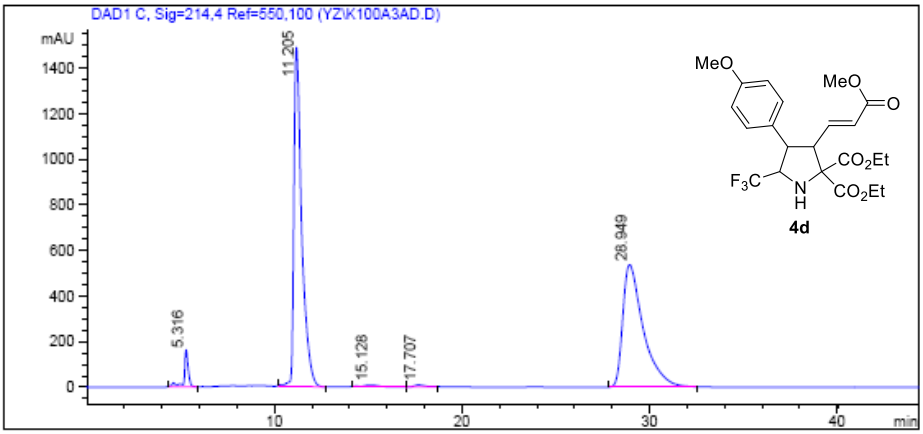
^{1}H NMR of **4d:**



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

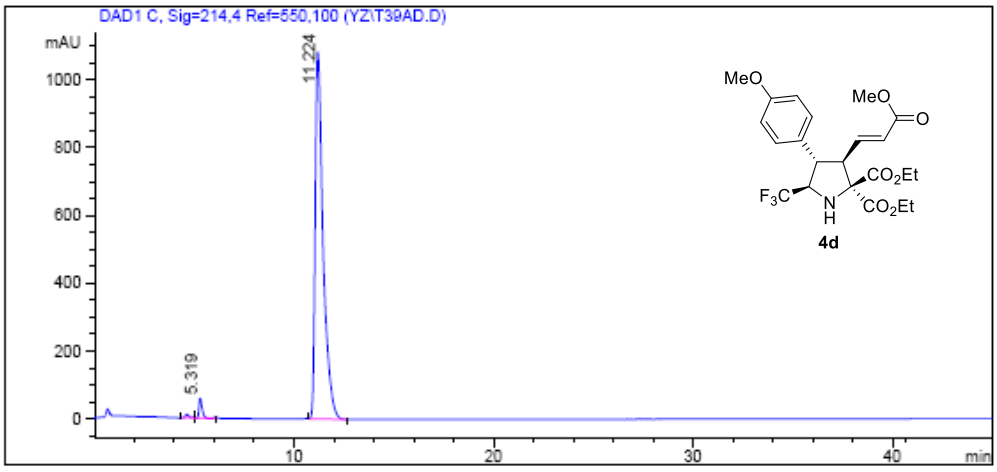


Temperature in°C:	30.0	30.0
Pressure in bar:	23.3	22.3
Flow in ml/min:	0.7	0.7



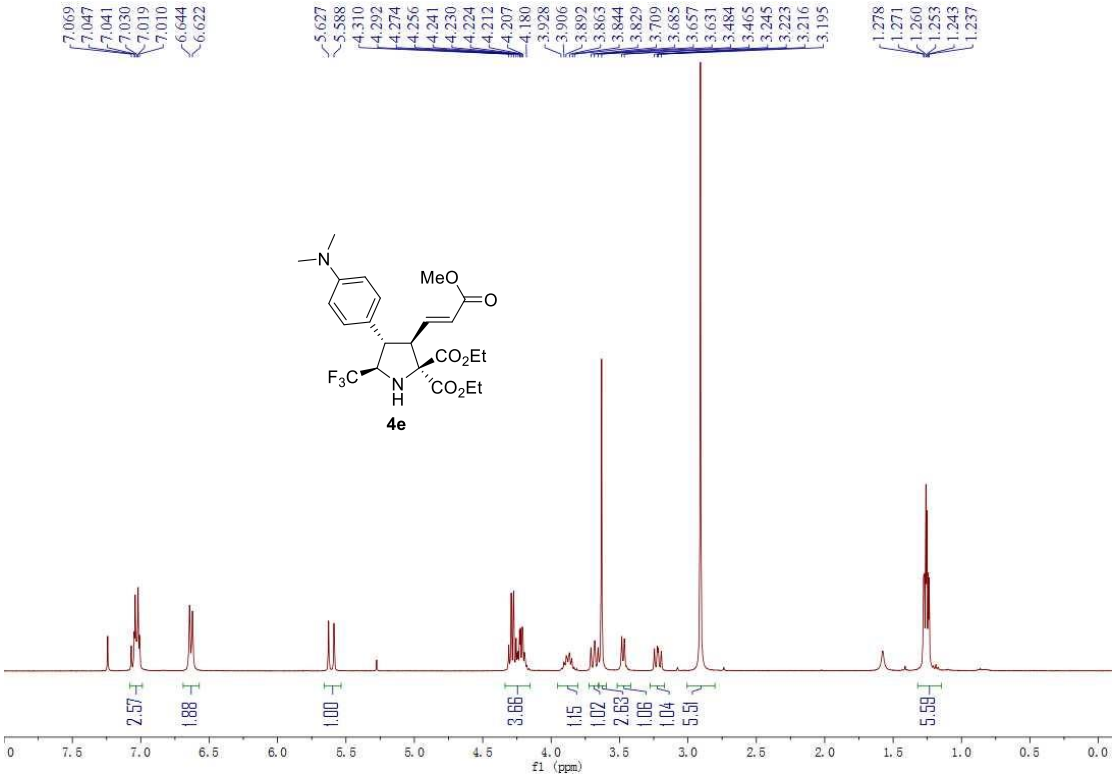
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.32	0.26	155.42	2463.87	2.82
2	11.20	0.45	1427.31	43022.87	49.18
3	15.13	1.04	7.36	527.55	0.60
4	17.71	0.65	9.19	400.55	0.46
5	28.95	1.15	537.36	41071.17	46.95
Total				87486.01	100.00

Temperature in°C:	30.0	30.0
Pressure in bar:	23.8	23.6
Flow in ml/min:	0.7	0.7

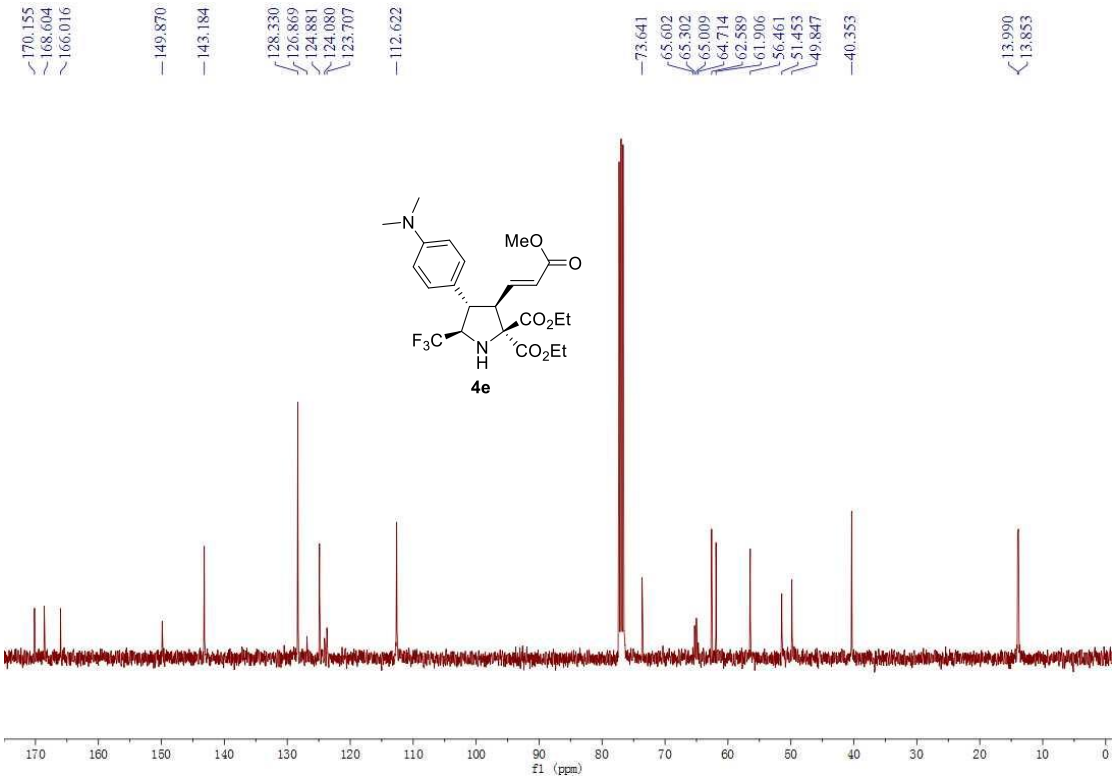


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.64	0.20	10.07	114.08	0.37
2	5.32	0.21	55.20	617.56	2.02
3	11.22	0.43	1053.90	29825.51	97.61
Total				30557.15	100.00

^{1}H NMR of **4e:**

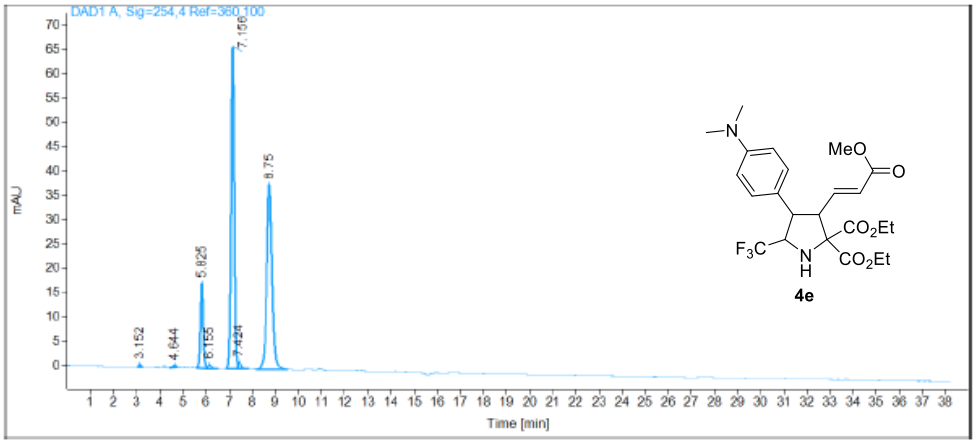


^{13}C NMR of **4e:**



Column: Chiralpak IA, (250 x 4.6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 51 bar Start flow: 1.000 ml/min Column oven: 29.97 °C

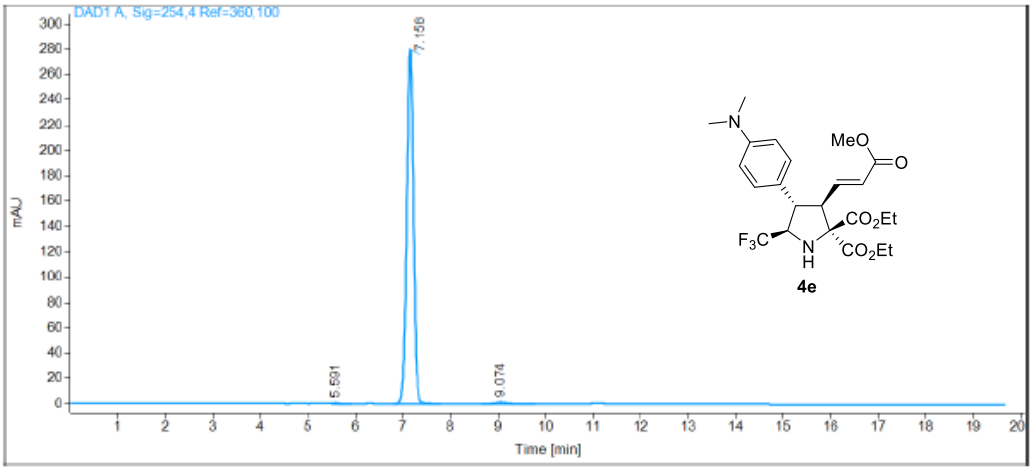


Name YZ K-P101 J rac

RT [min]	Type	Area%	Area	Height	Width [min]
3.15	BB	0.19	2.74	0.52	0.09
4.64	BB	0.21	2.95	0.43	0.10
5.82	BV	10.34	146.66	17.49	0.13
6.15	VB	0.46	6.52	0.69	0.14
7.16	BV	44.12	625.89	66.14	0.15
7.42	VB	0.91	12.91	1.36	0.14
8.75	BB	43.77	621.03	37.89	0.25
	Sum	100.00	1418.69		

Column: Chiralpak IC, (150 x 4.6) mm, 5µ, SN: IC00CD-QF015

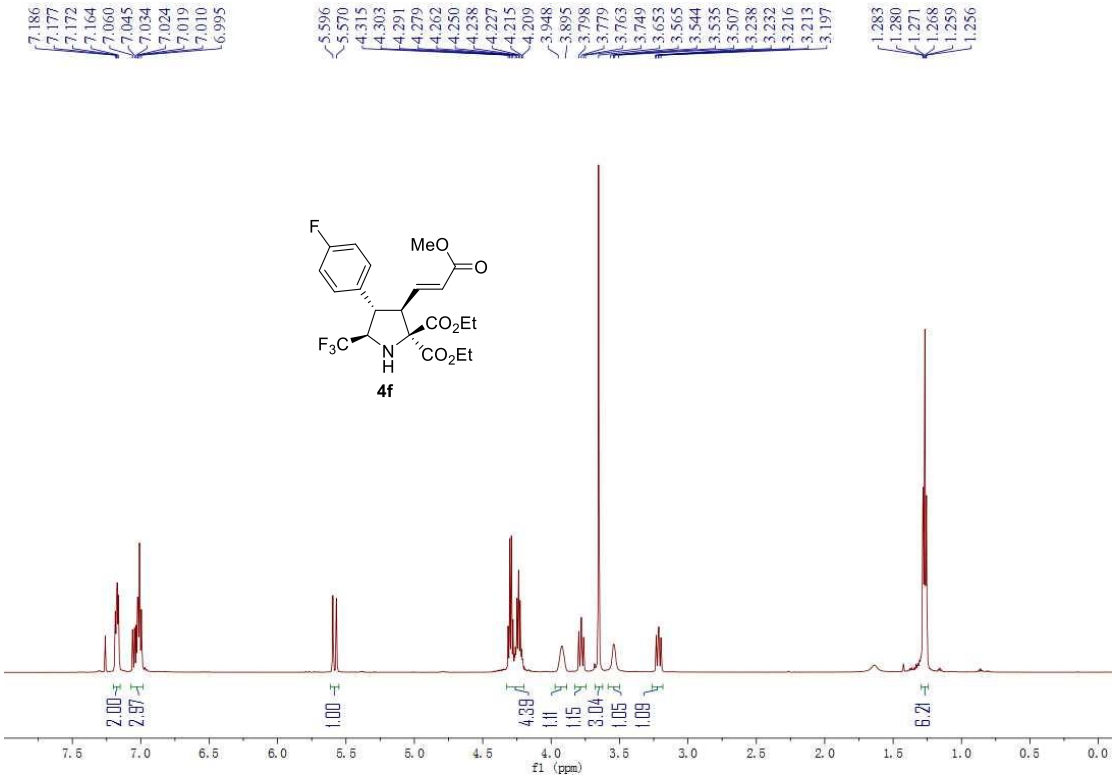
Pressure at start: 51 bar Start flow: 1.000 ml/min Column oven: 29.99 °C



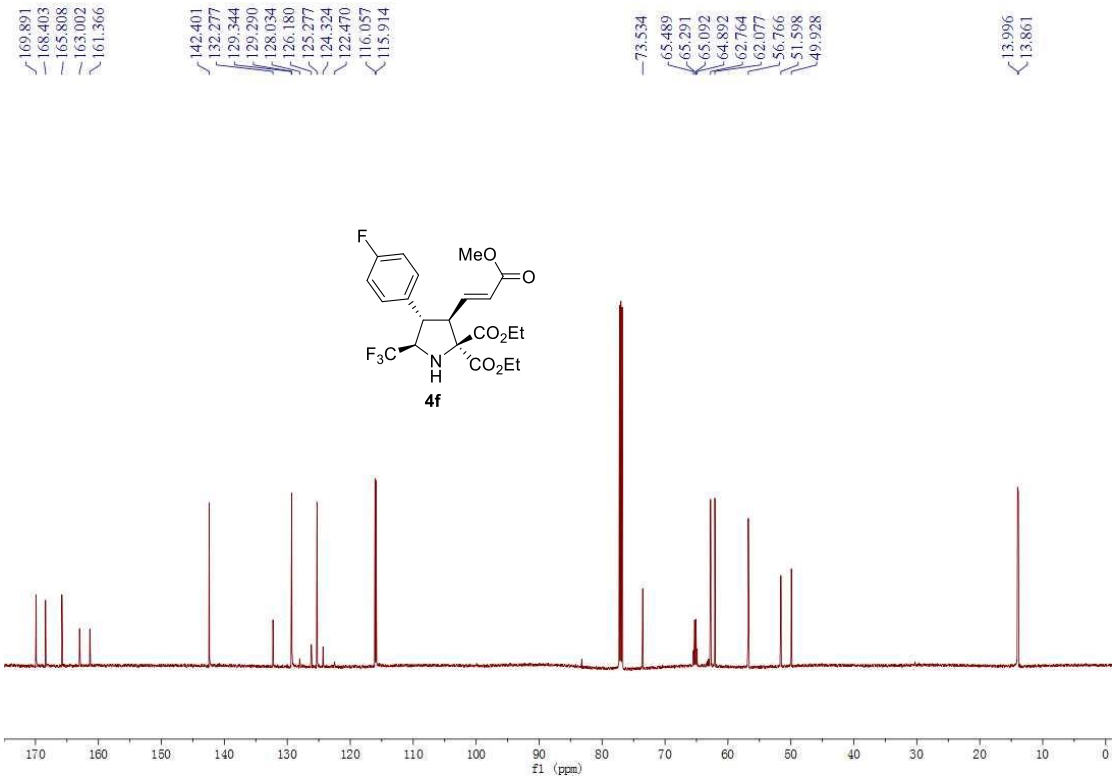
Name yz-T44

RT [min]	Type	Area%	Area	Height	Width [min]
5.59	VB	0.10	2.61	0.29	0.13
7.16	BB	99.01	2711.00	280.08	0.15
9.07	BB	0.90	24.58	1.34	0.27
	Sum	100.00	2738.19		

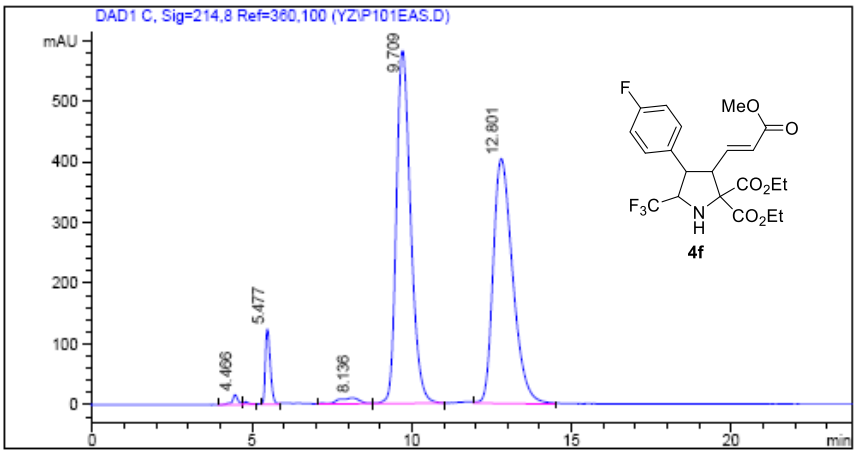
^{1}H NMR of **4f:**



^{13}C NMR of **4f:**

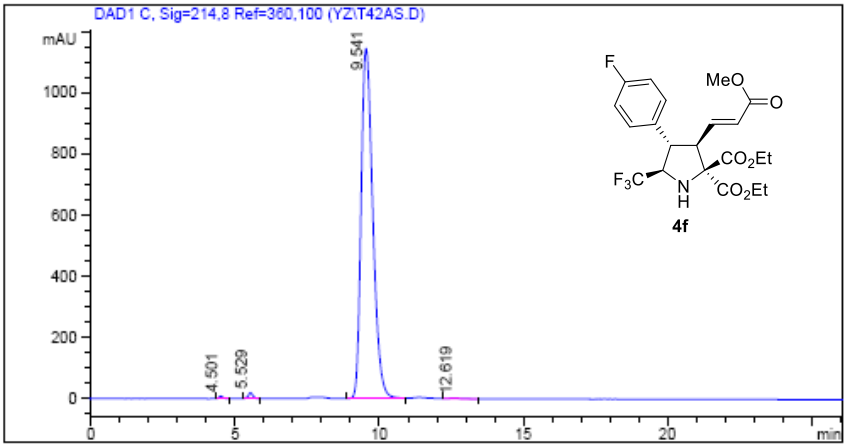


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.6	22.0
Flow in ml/min:	0.70	0.70



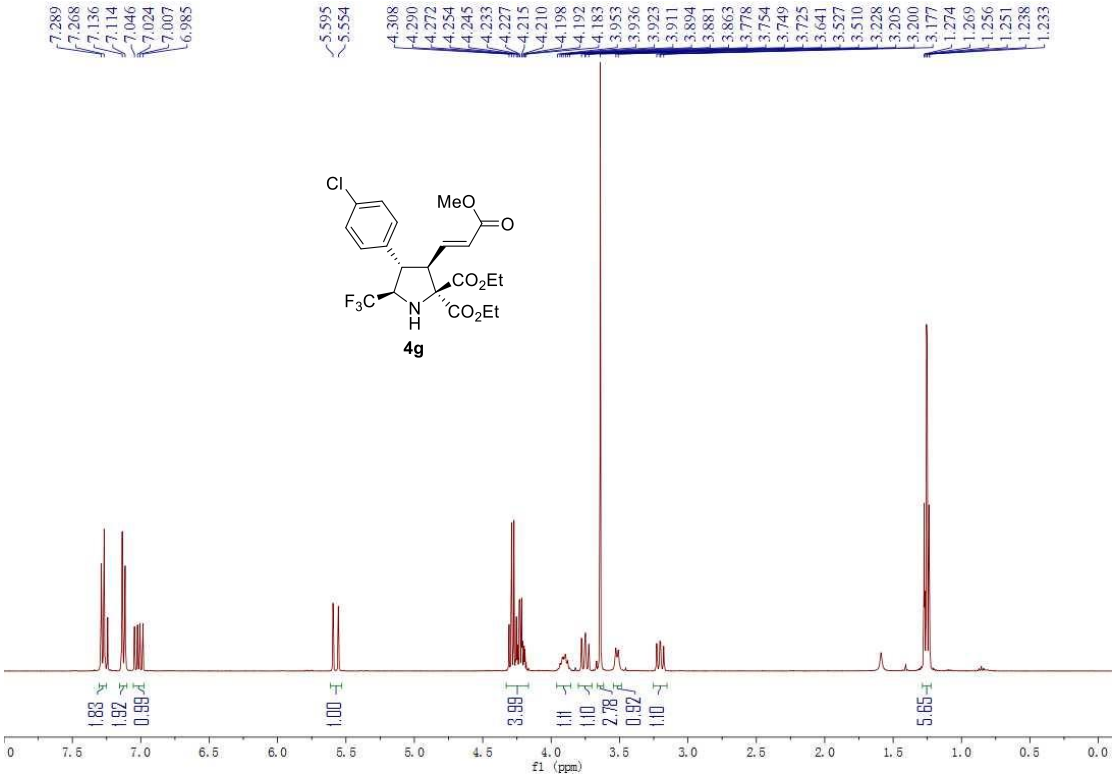
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.47	0.19	16.33	212.02	0.57
2	4.81	0.17	4.46	53.96	0.14
3	5.48	0.17	123.83	1357.49	3.64
4	8.14	0.63	9.94	456.56	1.22
5	9.71	0.48	580.67	18036.80	48.38
6	12.80	0.71	402.81	17162.07	46.04
Total				37278.91	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.0	21.1
Flow in ml/min:	0.70	0.70

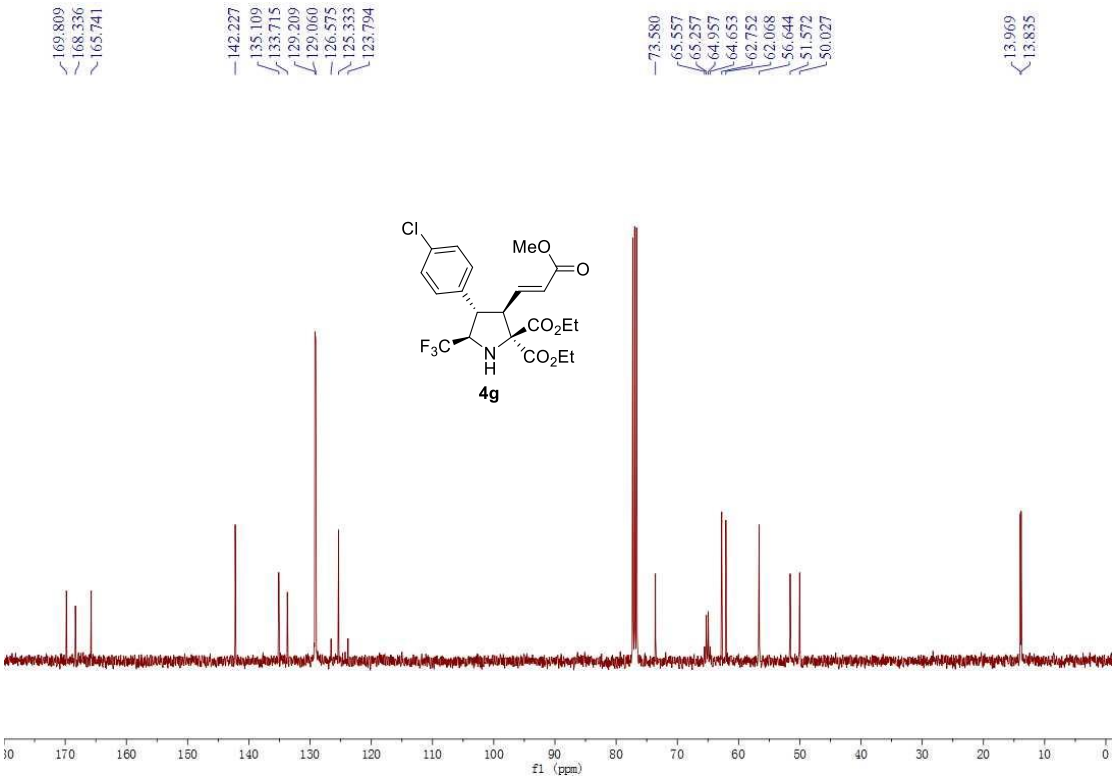


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.50	0.16	8.21	87.65	0.27
2	5.53	0.17	19.23	221.87	0.68
3	9.54	0.44	1144.87	32239.63	98.86
4	12.62	0.59	1.78	62.56	0.19
Total				32611.72	100.00

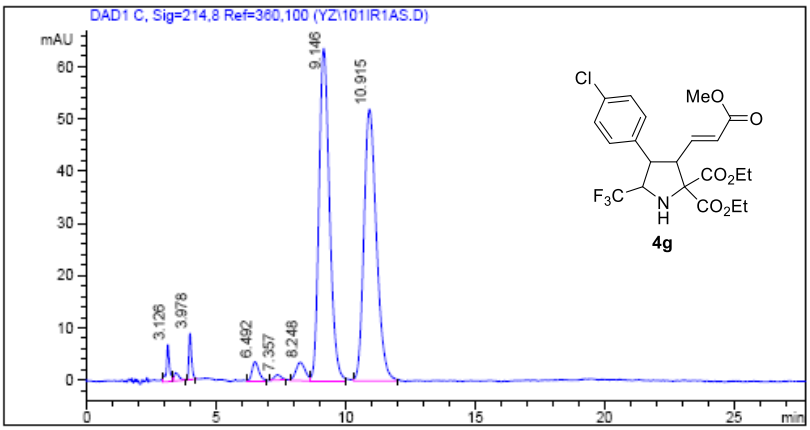
^{1}H NMR of **4g:**



^{13}C NMR of **4g:**

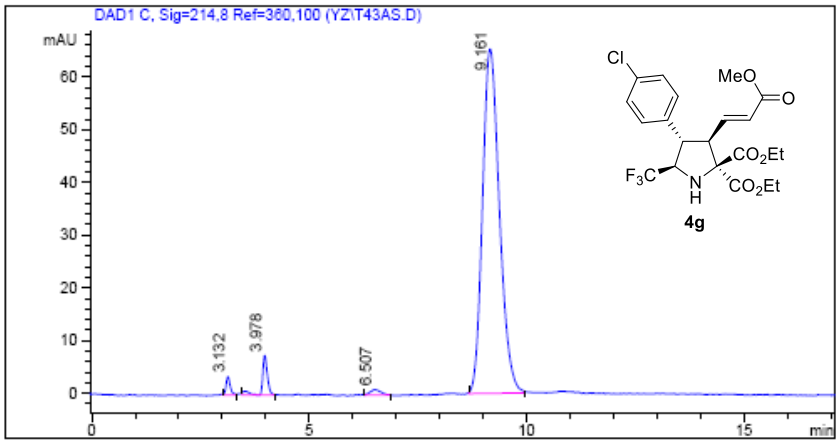


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	29.3	29.6
Flow in ml/min:	1.00	1.00



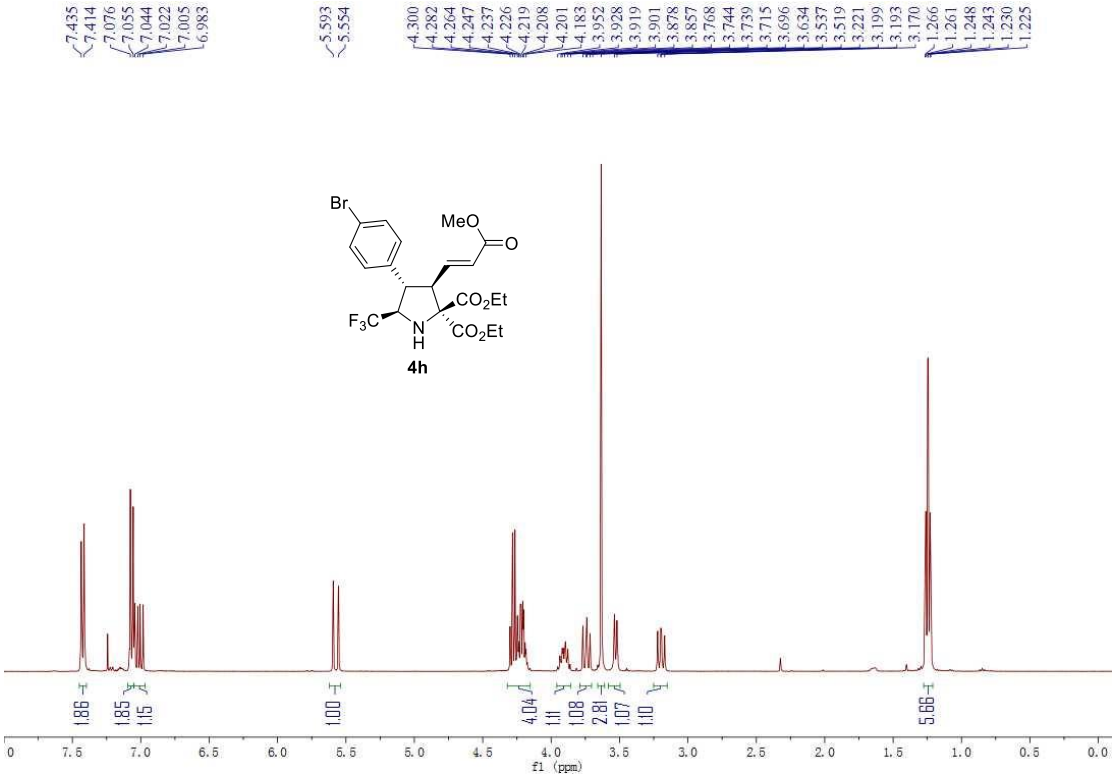
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.13	0.12	7.03	60.26	1.56
2	3.42	0.17	1.54	20.71	0.54
3	3.98	0.11	8.86	65.16	1.69
4	6.49	0.28	3.60	65.20	1.69
5	7.36	0.30	1.01	18.47	0.48
6	8.25	0.35	3.53	88.77	2.30
7	9.15	0.44	63.64	1797.33	46.54
8	10.92	0.52	51.97	1746.32	45.22
Total				3862.22	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	28.9	28.9
Flow in ml/min:	1.00	1.00

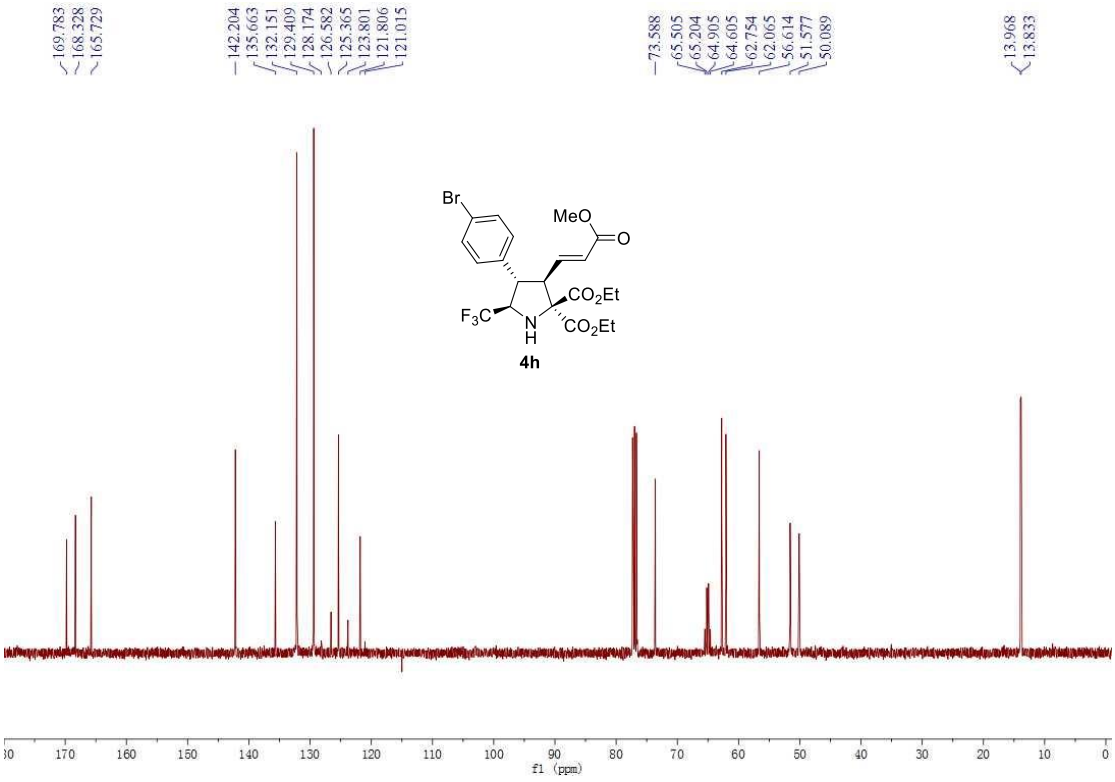


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.13	0.10	3.48	23.83	1.28
2	3.98	0.12	7.49	60.90	3.26
3	6.51	0.29	1.05	18.43	0.99
4	9.16	0.41	65.31	1765.09	94.48
Total				1868.24	100.00

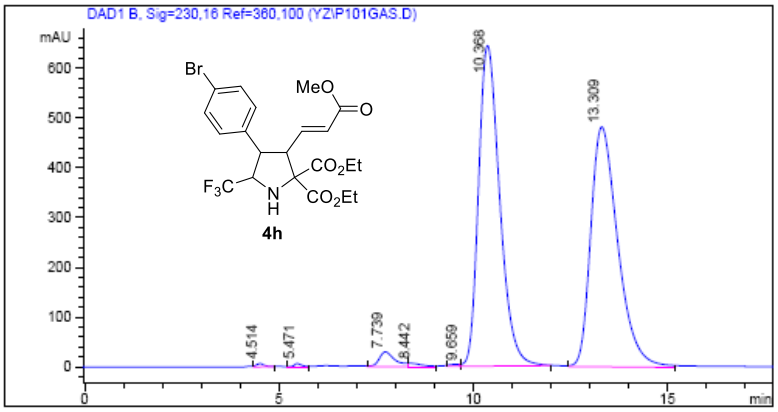
^{1}H NMR of **4h:**



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

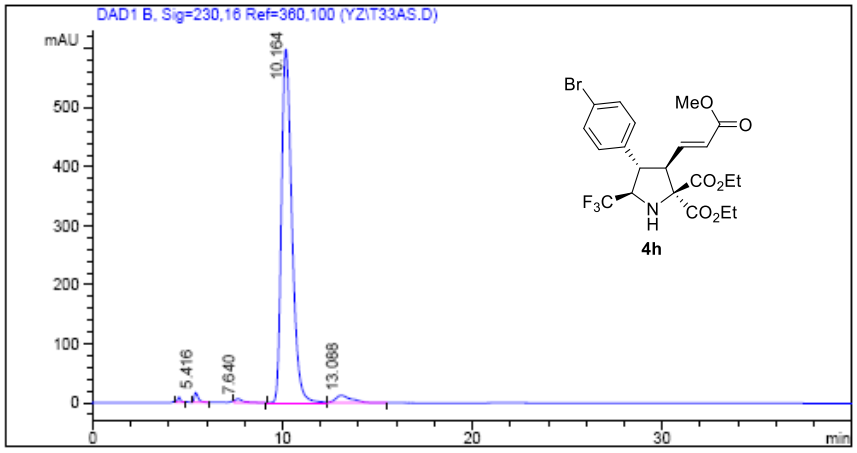


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.4	21.4
Flow in ml/min:	0.70	0.70



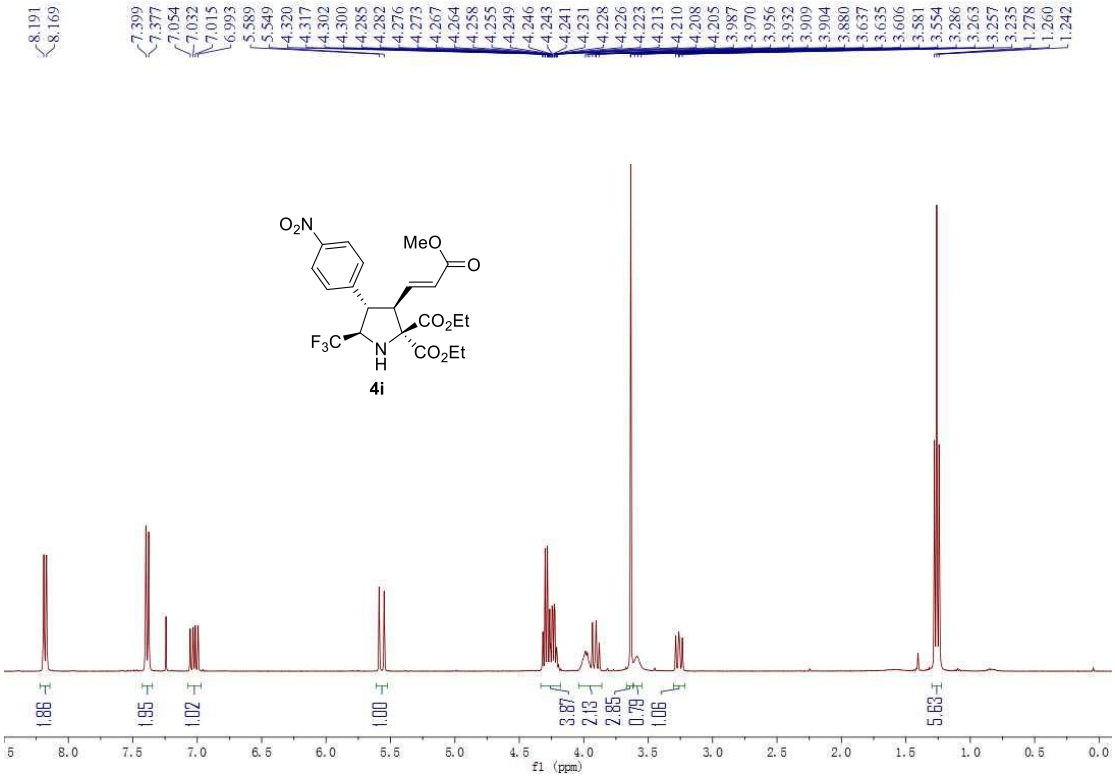
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.51	0.23	6.70	105.03	0.21
2	5.47	0.20	6.73	92.83	0.19
3	7.74	0.42	29.95	850.26	1.73
4	8.44	0.38	6.83	169.52	0.35
5	9.66	0.31	4.42	81.76	0.17
6	10.37	0.63	644.27	24407.66	49.75
7	11.87	0.00	0.15	0.00	0.00
8	13.31	0.81	481.81	23354.72	47.60
9	14.82	0.00	8.48	0.00	0.00
10	15.03	0.00	6.49	0.00	0.00
Total				49061.78	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.6	21.8
Flow in ml/min:	0.70	0.70

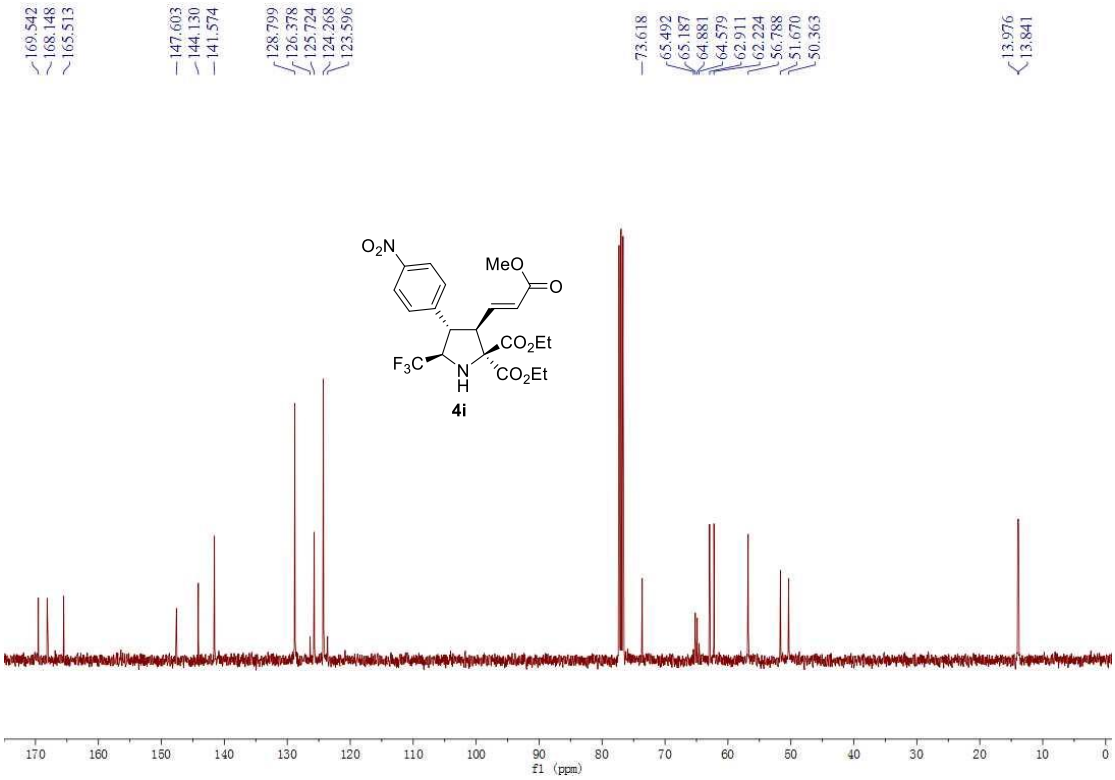


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.53	0.17	9.28	109.46	0.45
2	5.42	0.22	16.45	242.12	1.00
3	7.64	0.43	6.25	184.05	0.76
4	10.16	0.59	599.55	22946.71	94.70
5	13.09	0.84	12.60	748.72	3.09
Total				24231.06	100.00

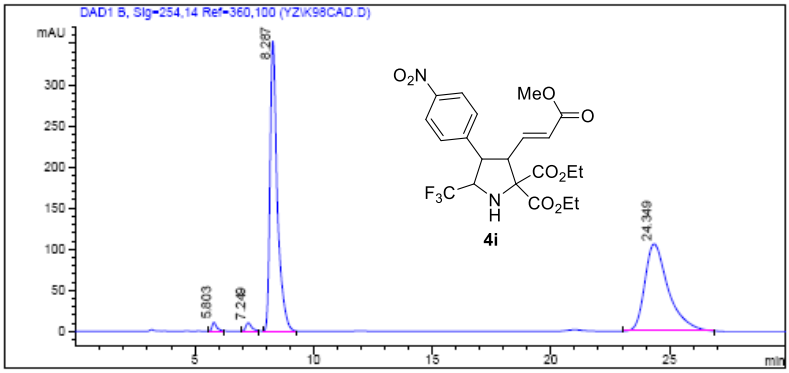
^{1}H NMR of **4i:**



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

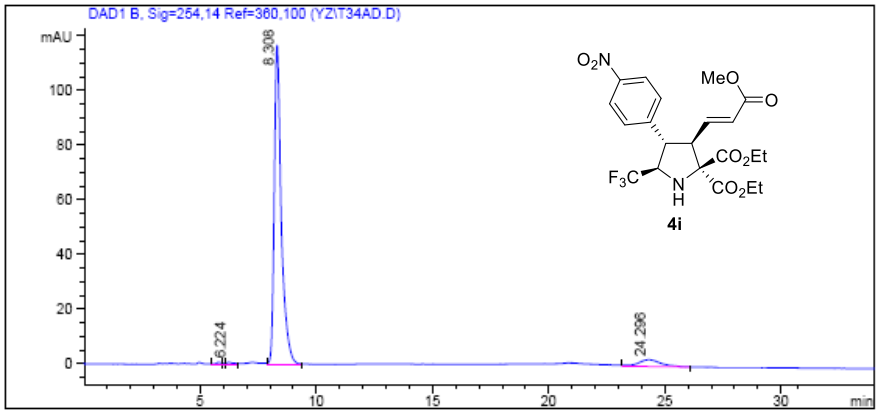


Temperature in°C:	30.0	30.0
Pressure in bar:	36.9	36.9
Flow in ml/min:	1.0	1.0



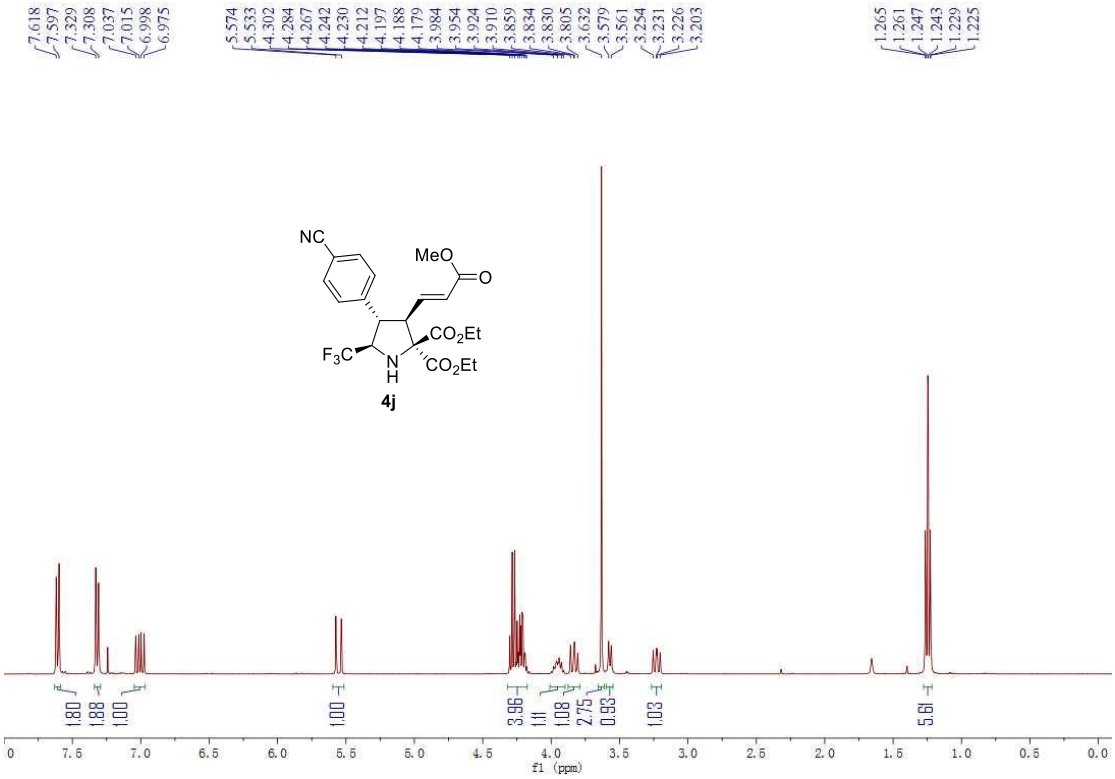
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.80	0.20	10.78	149.59	0.99
2	7.25	0.26	10.36	183.06	1.21
3	8.29	0.32	353.00	7545.34	49.91
4	23.33	0.00	0.81	0.00	0.00
5	23.43	0.00	2.55	0.00	0.00
6	23.92	0.00	51.09	0.00	0.00
7	24.02	0.00	69.96	0.00	0.00
8	24.35	1.14	105.62	7240.65	47.89
9	24.66	0.00	82.36	0.00	0.00
10	24.75	0.00	71.56	0.00	0.00
11	24.85	0.00	60.40	0.00	0.00
12	25.00	0.00	45.67	0.00	0.00
13	25.13	0.00	35.67	0.00	0.00
14	25.48	0.00	18.65	0.00	0.00
15	25.86	0.00	8.75	0.00	0.00
16	26.21	0.00	3.47	0.00	0.00
17	26.32	0.00	2.47	0.00	0.00
18	26.58	0.00	0.82	0.00	0.00
Total				15118.63	100.00

Temperature in°C:	30.0	30.0
Pressure in bar:	36.1	36.5
Flow in ml/min:	1.0	1.0

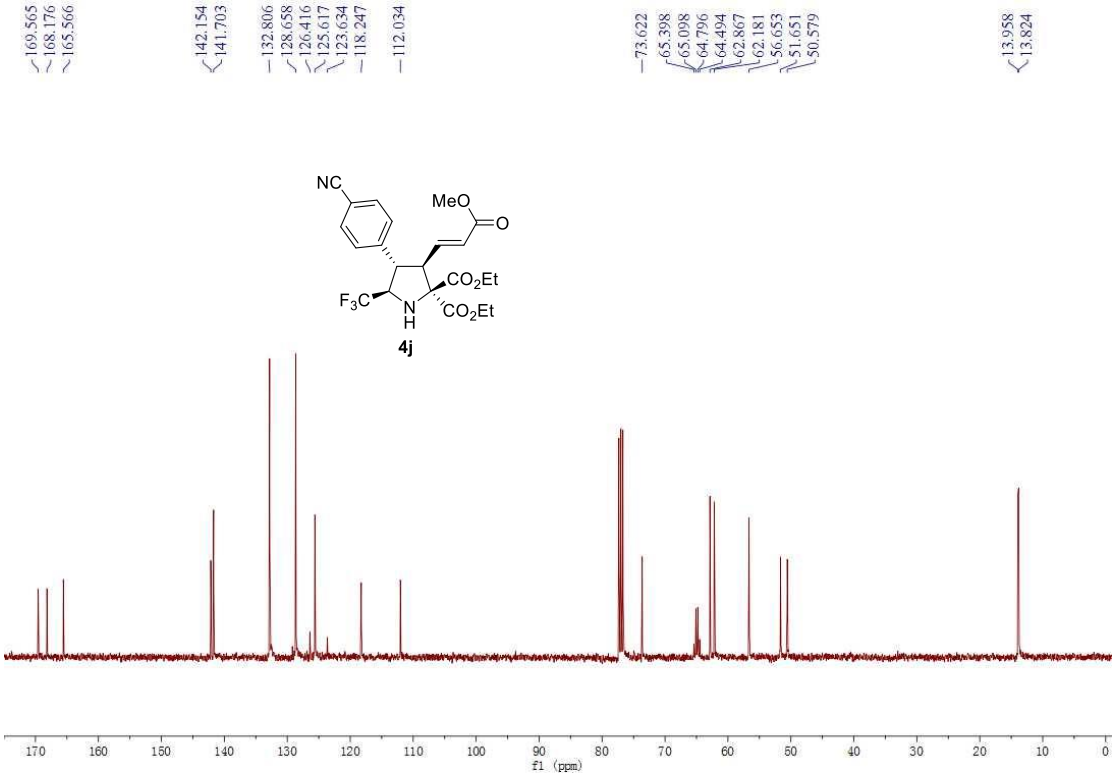


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.80	0.20	0.75	10.85	0.41
2	5.97	0.11	0.39	3.31	0.12
3	6.22	0.26	0.76	15.24	0.57
4	8.31	0.31	116.74	2455.88	92.26
5	24.30	1.14	2.57	176.67	6.64
Total				2661.95	100.00

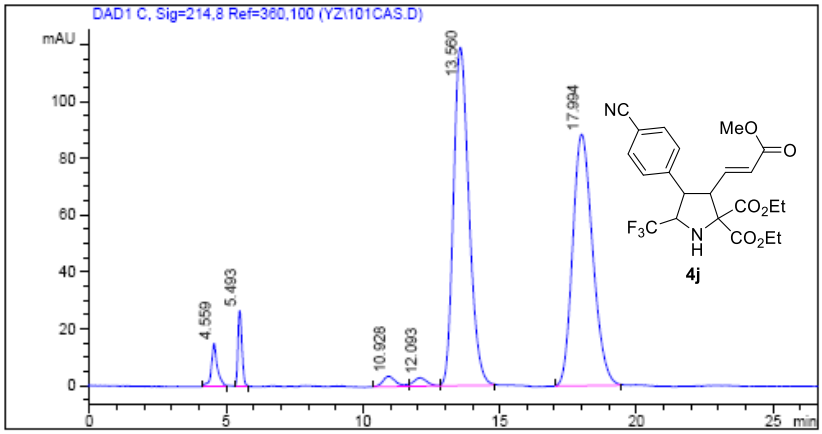
^{1}H NMR of **4j:**



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

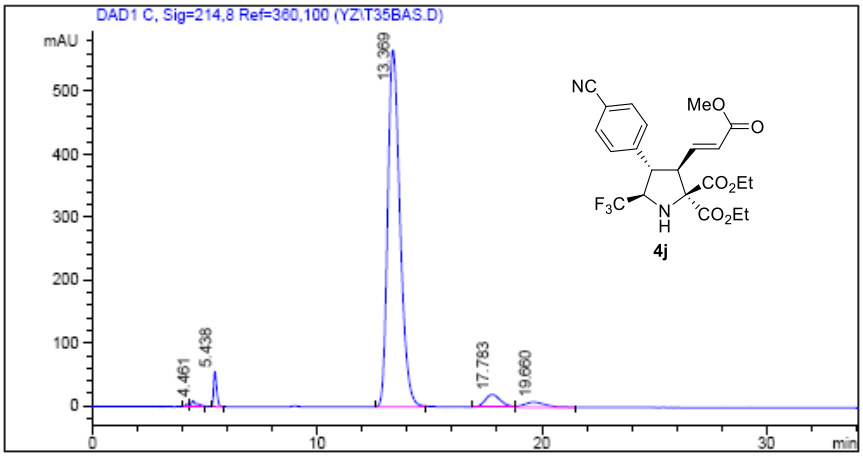


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.2	21.5
Flow in ml/min:	0.70	0.70



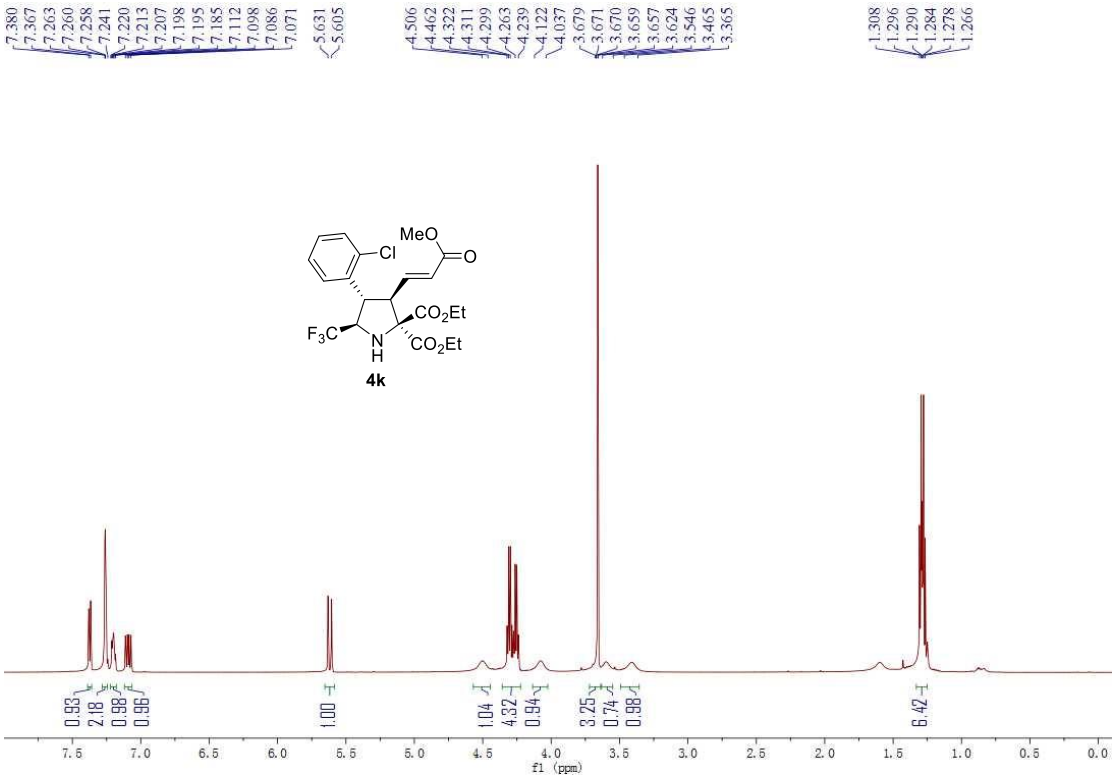
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.56	0.21	15.18	234.93	2.37
2	5.49	0.16	26.69	276.73	2.79
3	10.93	0.45	3.62	120.49	1.22
4	12.09	0.43	2.95	98.78	1.00
5	13.56	0.61	118.91	4675.93	47.21
6	17.99	0.79	88.37	4497.81	45.41
Total				9904.68	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.6	21.9
Flow in ml/min:	0.70	0.70

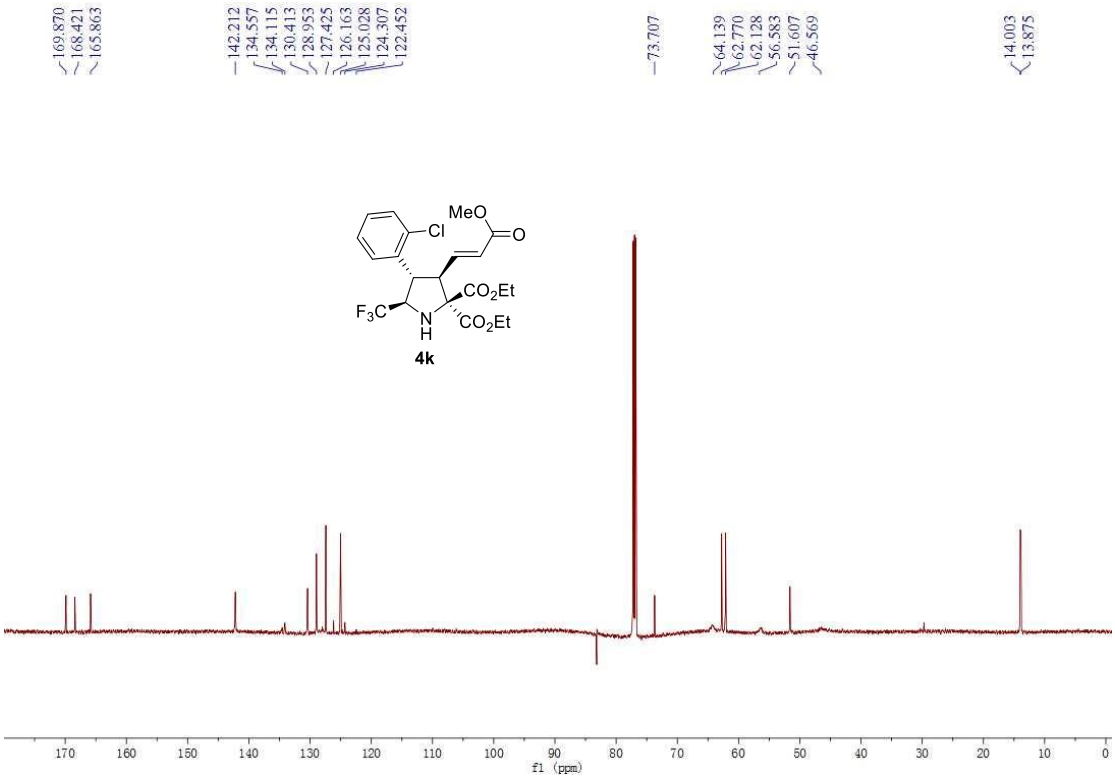


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.22	0.17	4.56	49.69	0.21
2	4.46	0.24	9.50	166.44	0.70
3	5.44	0.15	55.56	540.84	2.28
4	13.37	0.58	566.73	21477.68	90.64
5	17.78	0.72	19.92	961.57	4.06
6	19.66	0.75	7.98	499.44	2.11
Total				23695.66	100.00

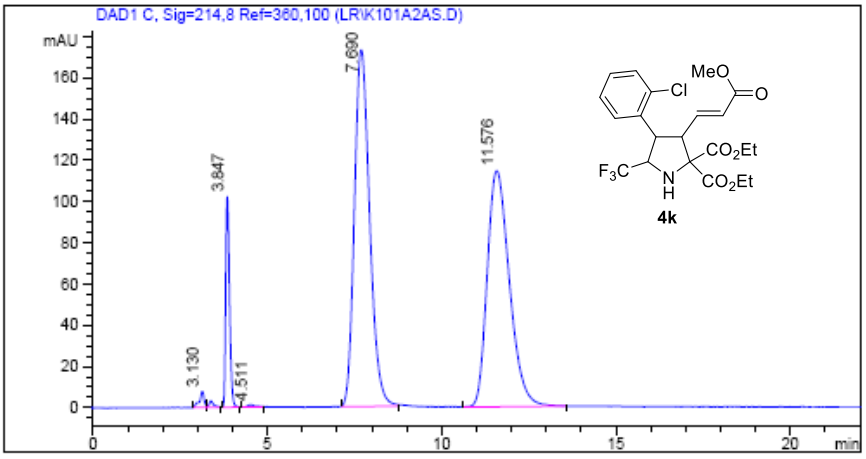
^{1}H NMR of **4k:**



^{13}C NMR of **4k:**

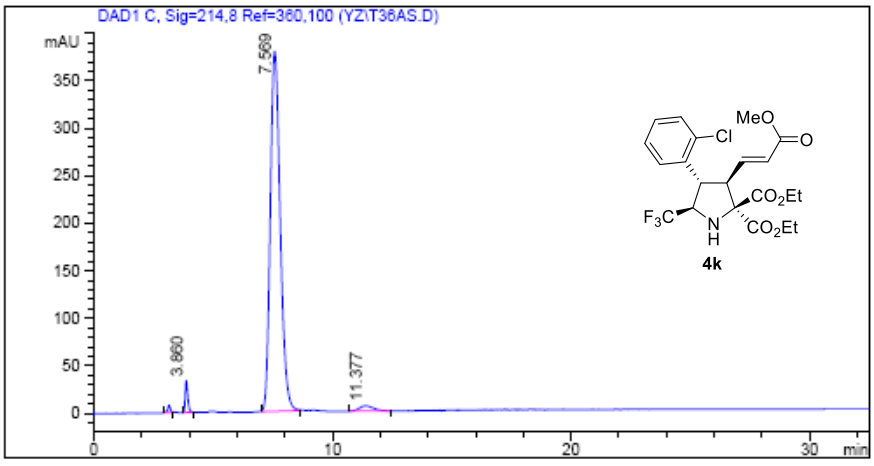


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	29.5	30.7
Flow in ml/min:	1.00	1.00



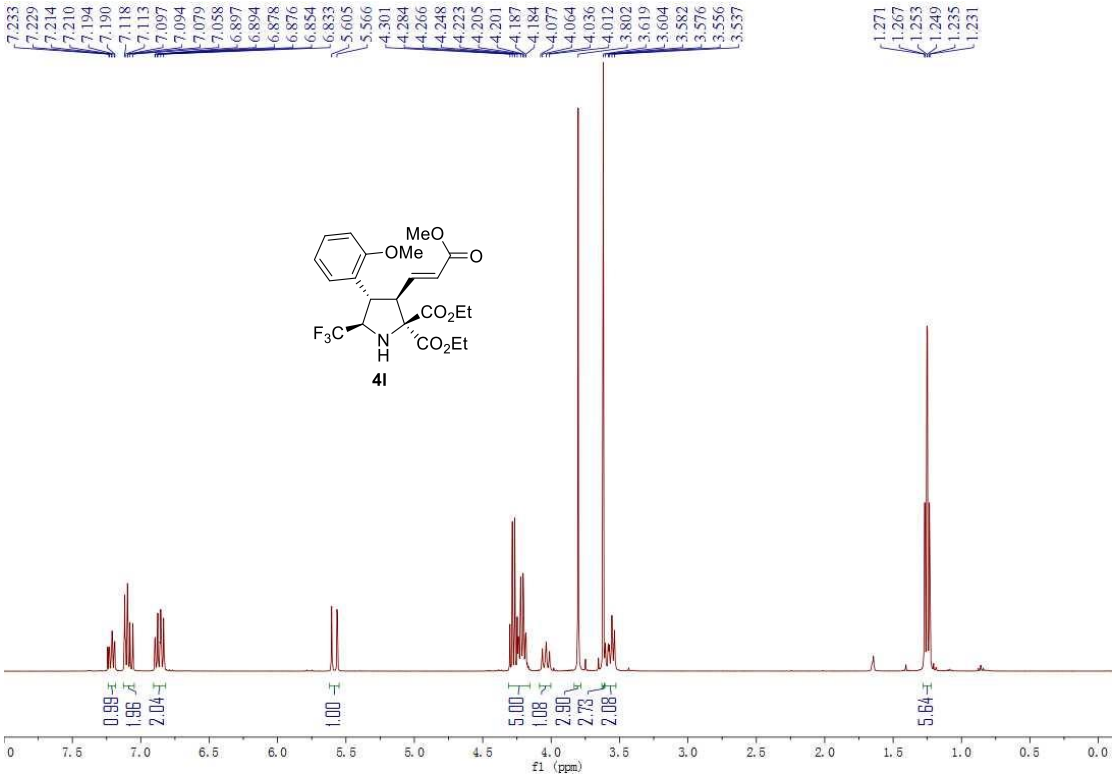
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.13	0.13	7.82	73.51	0.65
2	3.38	0.14	3.17	30.42	0.27
3	3.85	0.12	102.17	785.60	6.98
4	4.51	0.22	1.25	19.84	0.18
5	7.69	0.47	173.00	5262.99	46.79
6	11.58	0.74	114.49	5075.97	45.13
Total				11248.34	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	30.5	31.1
Flow in ml/min:	1.00	1.00

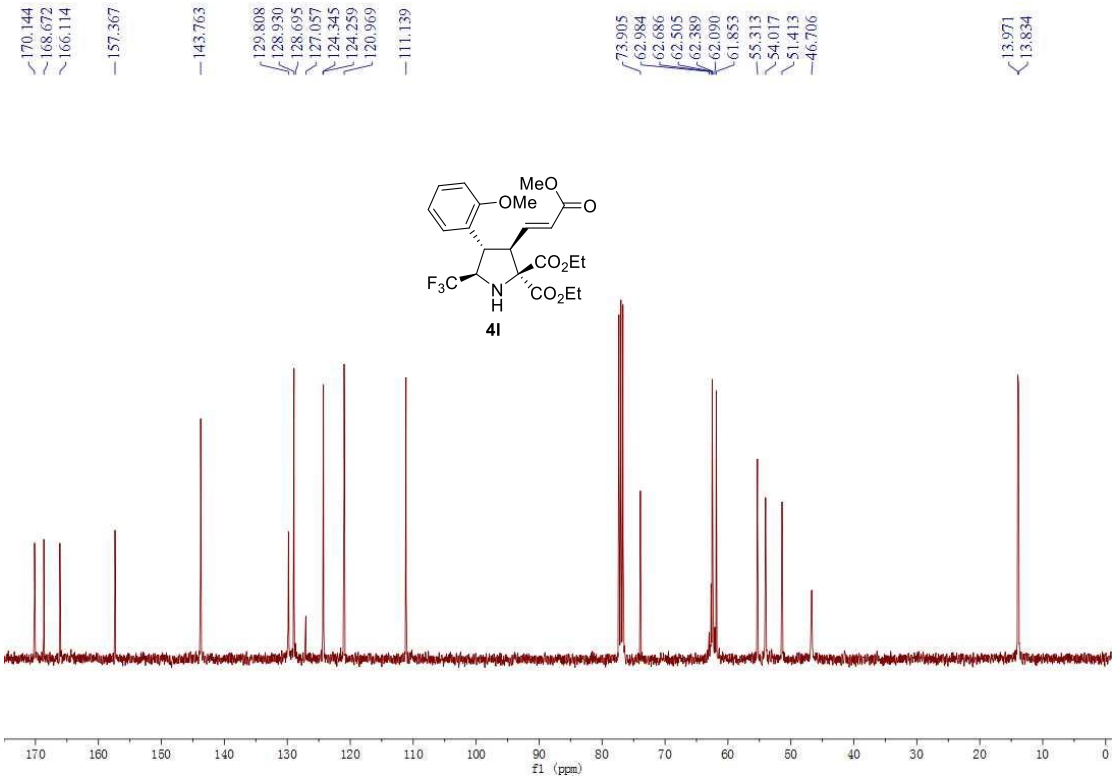


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.14	0.13	7.97	68.23	0.59
2	3.86	0.12	33.35	251.80	2.19
3	7.57	0.44	378.97	10942.84	95.24
4	11.38	0.59	5.55	226.55	1.97
Total				11489.42	100.00

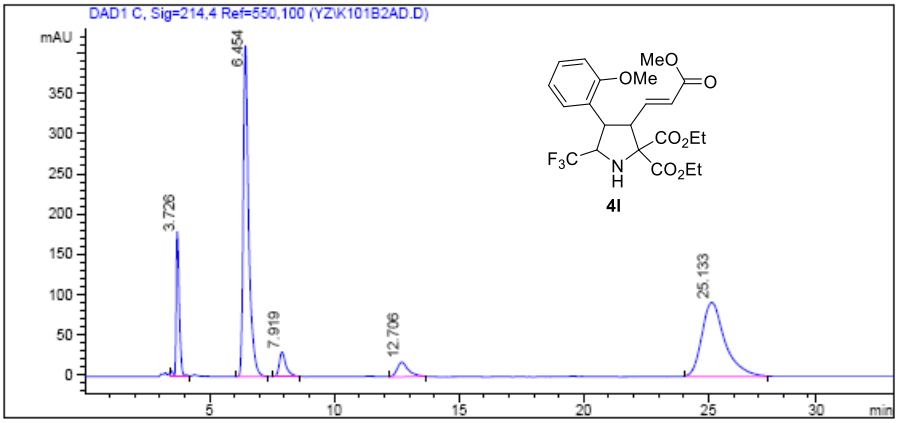
^{1}H NMR of **4l:**



^{13}C NMR of **4l:**

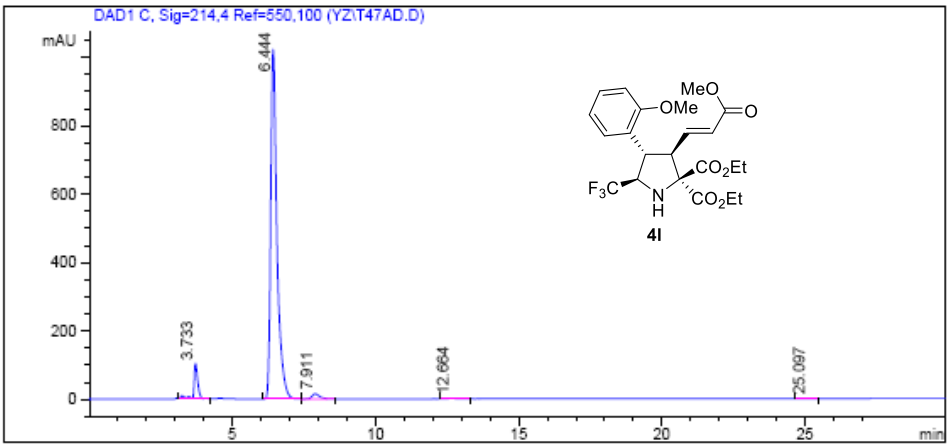


Temperature in°C:	30.0	30.0
Pressure in bar:	32.9	32.5
Flow in ml/min:	1.0	1.0



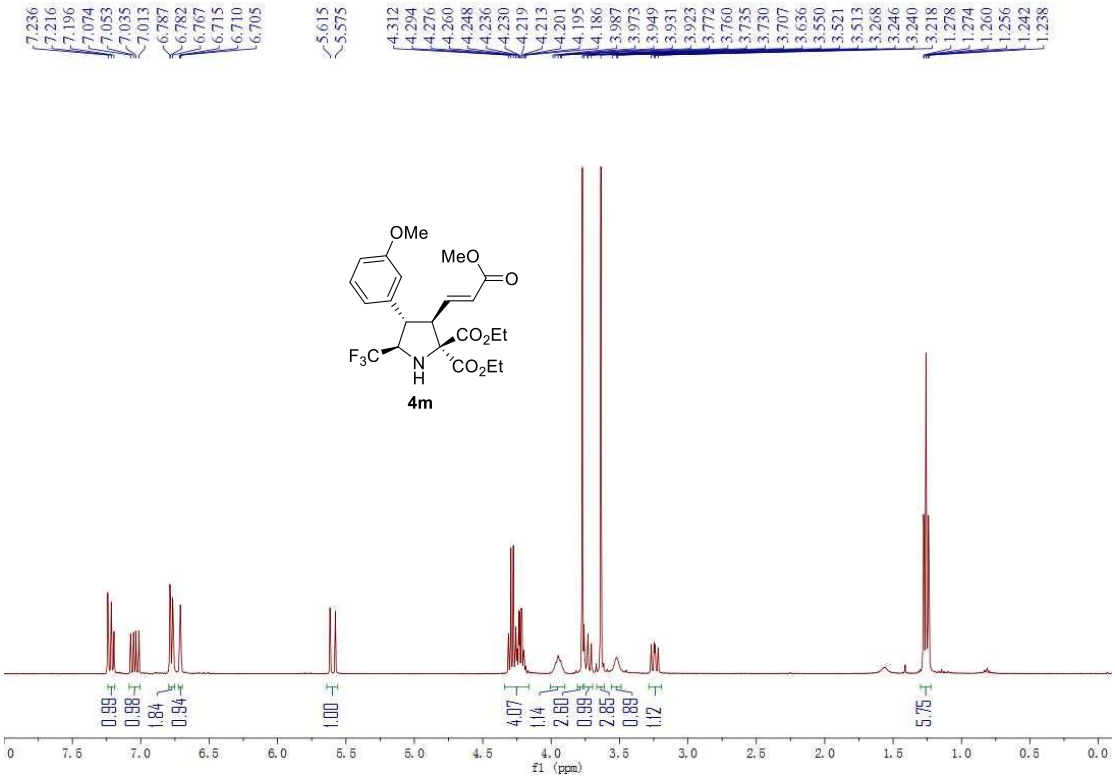
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.73	0.17	175.56	1613.99	10.73
2	6.45	0.26	407.47	6272.40	41.71
3	7.92	0.30	30.01	576.97	3.84
4	12.71	0.52	18.33	572.15	3.80
5	25.13	0.98	92.14	6002.86	39.92
Total				15038.37	100.00

Temperature in°C:	30.0	30.0
Pressure in bar:	34.9	32.7
Flow in ml/min:	1.0	1.0

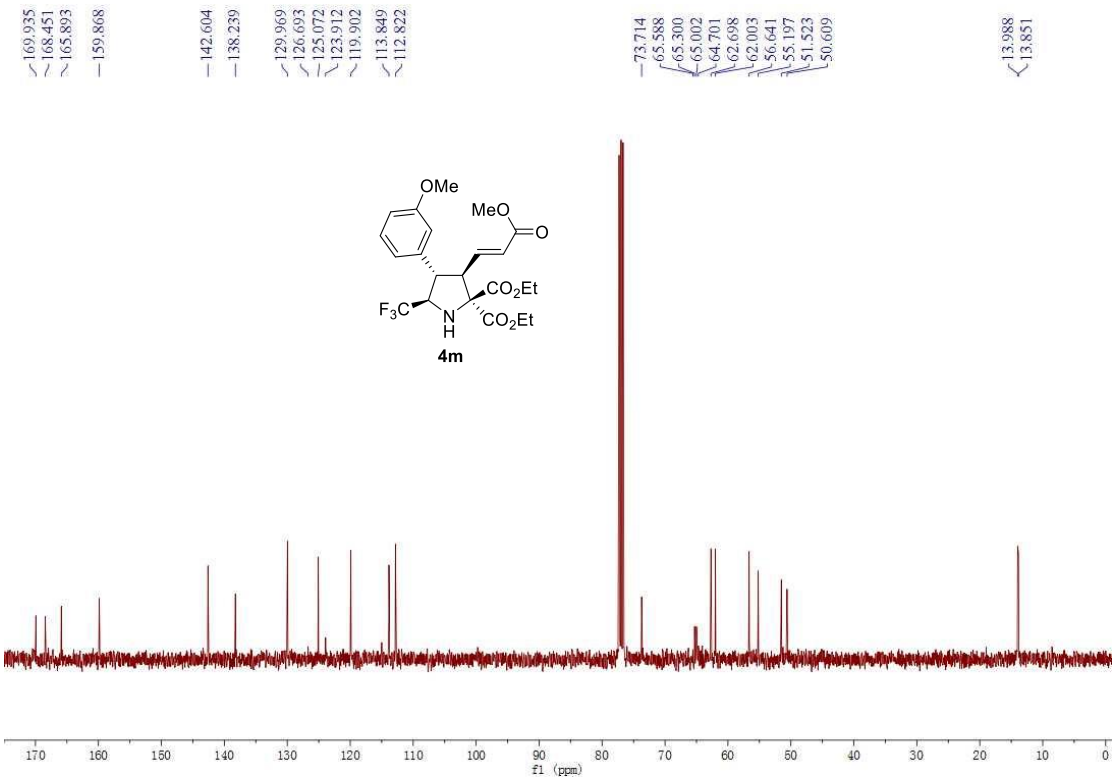


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.73	0.18	100.22	1032.14	6.06
2	6.44	0.26	1007.97	15527.05	91.20
3	7.91	0.33	14.41	283.42	1.66
4	12.66	0.62	2.31	86.38	0.51
5	25.10	0.74	2.17	96.42	0.57
Total				17025.41	100.00

^{1}H NMR of **4m:**

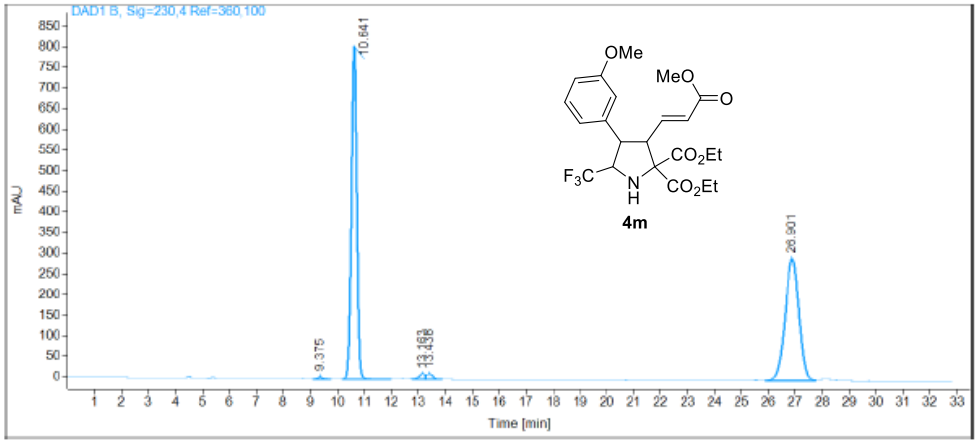


^{13}C NMR of **4m:**



Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

Pressure at start: 35 bar Start flow: 0.700 ml/min Column oven: 29.99 °C

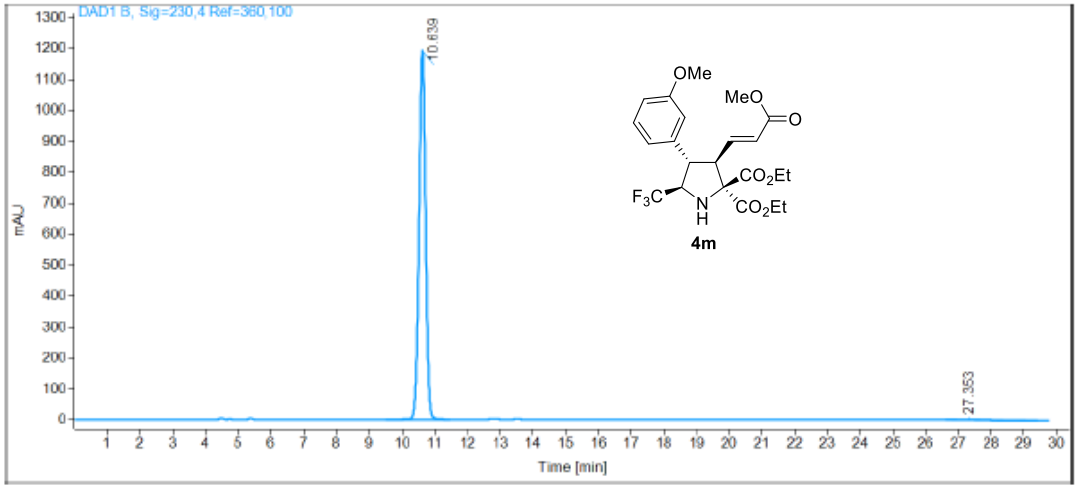


Name k-p101N

RT [min]	Type	Area%	Area	Height	Width [min]
9.37	BB	0.34	74.25	6.07	0.19
10.64	BB	49.33	10908.02	807.34	0.21
13.16	VV	1.13	250.10	14.13	0.26
13.44	VB	1.01	222.73	13.63	0.25
26.90	VV	48.20	10656.98	297.13	0.55
	Sum	100.00	22112.08		

Column: Chiralpak IA, (250 x 4,6) mm, 5µ, SN: IA00CE-RC036

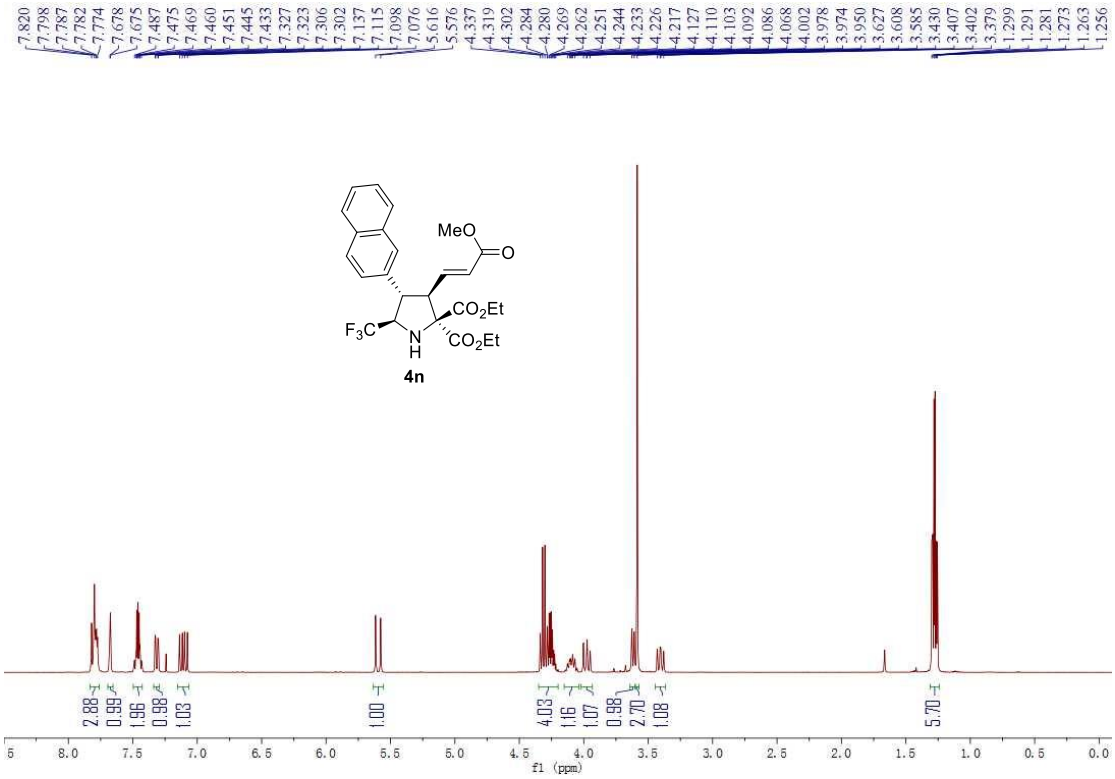
Pressure at start: 36 bar Start flow: 0.700 ml/min Column oven: 29.99 °C



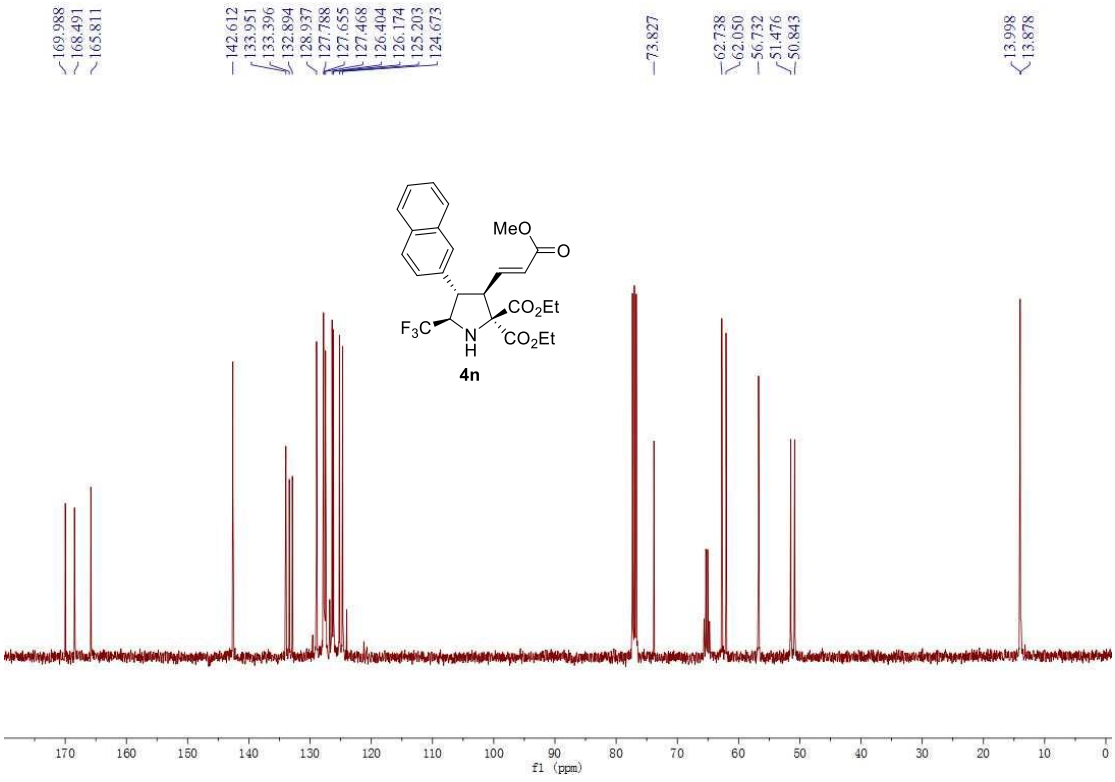
Name YZ T 49

RT [min]	Type	Area%	Area	Height	Width [min]
10.64	BV	99.56	16351.08	1195.24	0.21
27.35	BBA	0.44	72.81	1.52	0.68
	Sum	100.00	16423.90		

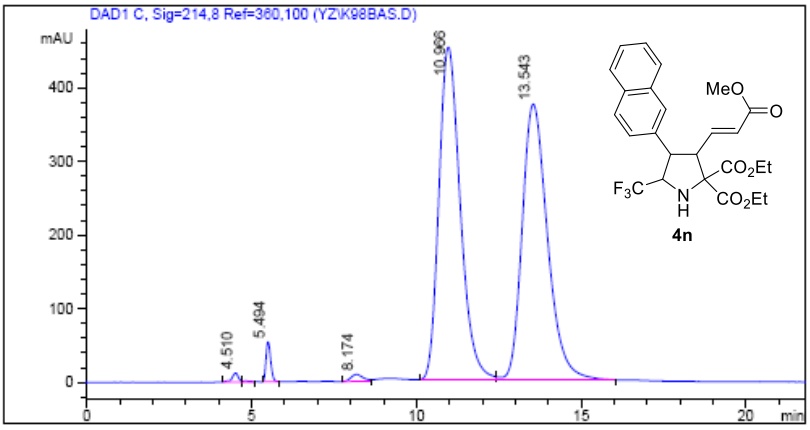
^{1}H NMR of **4n:**



^{13}C NMR of **4n:**

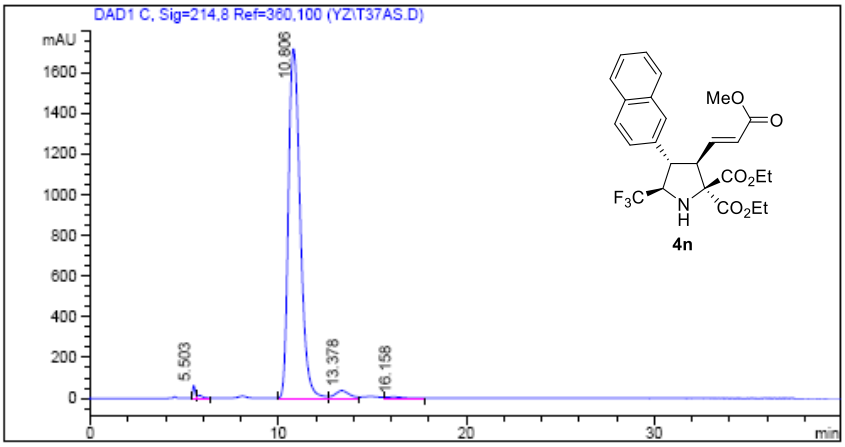


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	20.9	21.5
Flow in ml/min:	0.70	0.70



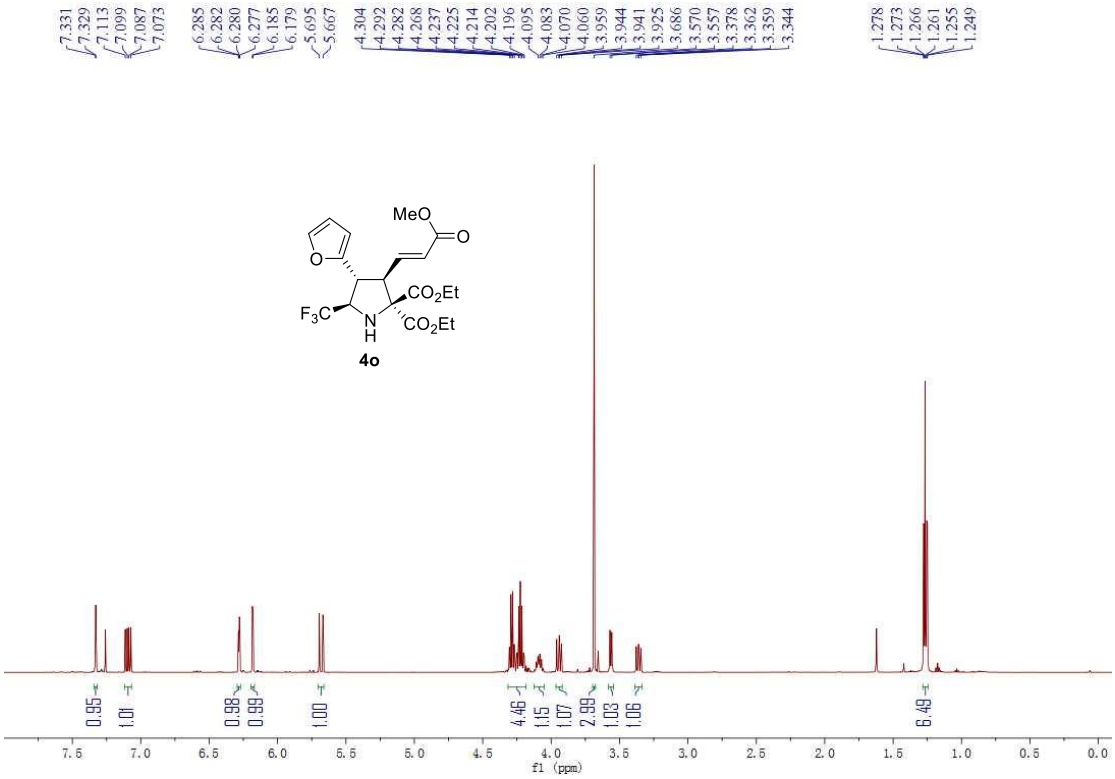
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.51	0.21	12.27	166.08	0.40
2	4.81	0.18	1.60	20.56	0.05
3	5.49	0.16	54.22	546.30	1.31
4	8.17	0.40	9.50	249.90	0.60
5	10.97	0.76	452.90	20516.65	49.15
6	13.54	0.90	375.42	20243.14	48.50
Total				41742.64	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	21.3	21.9
Flow in ml/min:	0.70	0.70

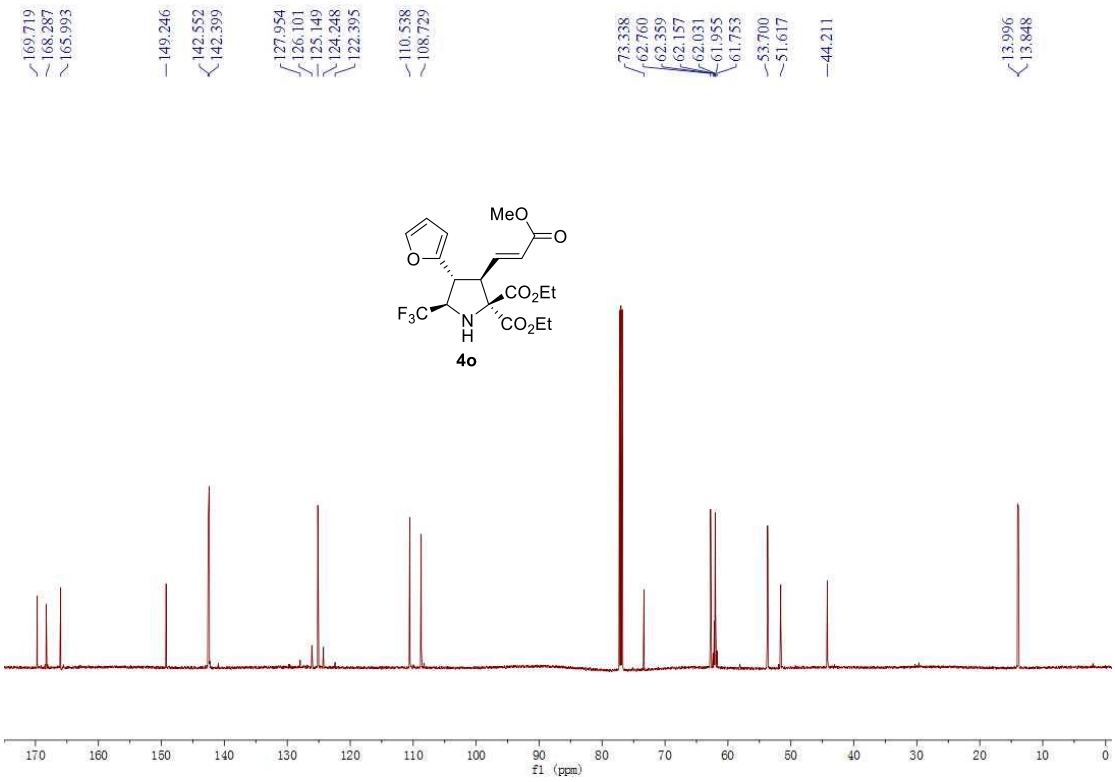


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.50	0.15	62.07	608.60	0.78
2	5.81	0.27	13.06	244.53	0.32
3	10.81	0.67	1714.77	74521.16	96.00
4	13.38	0.76	36.92	1921.91	2.48
5	16.16	0.64	6.18	329.54	0.42
Total				77625.73	100.00

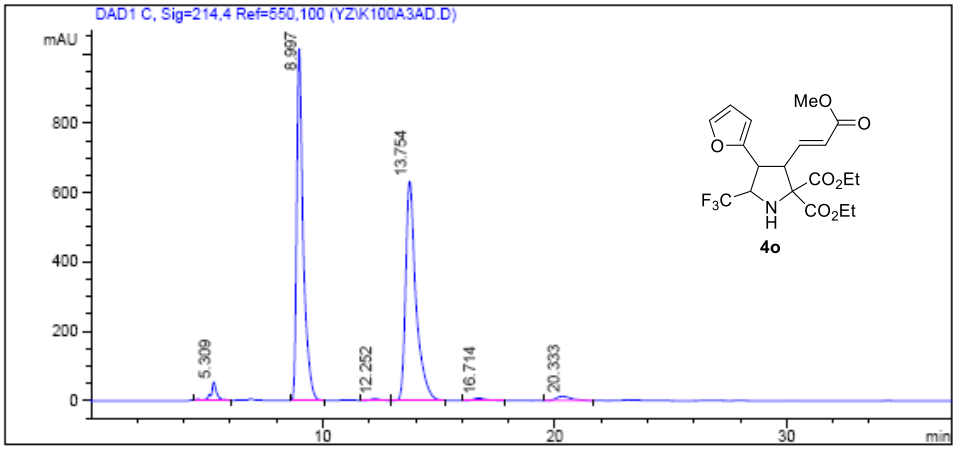
^{1}H NMR of **4o:**



^{13}C NMR of **4o:**

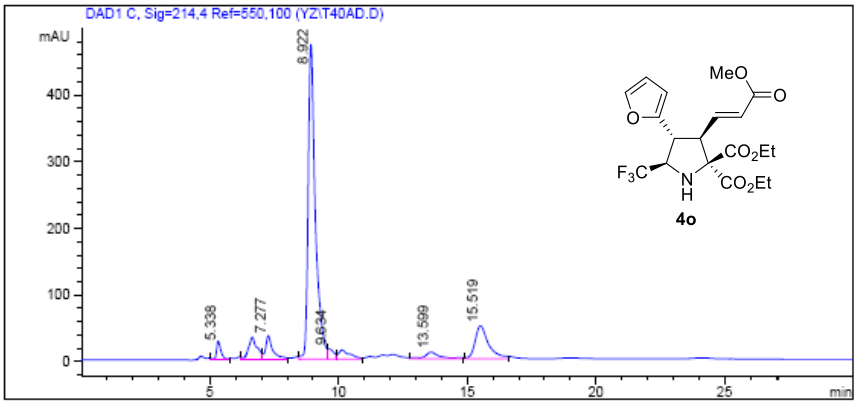


Temperature in°C:	30.0	30.0
Pressure in bar:	23.0	22.8
Flow in ml/min:	0.7	0.7



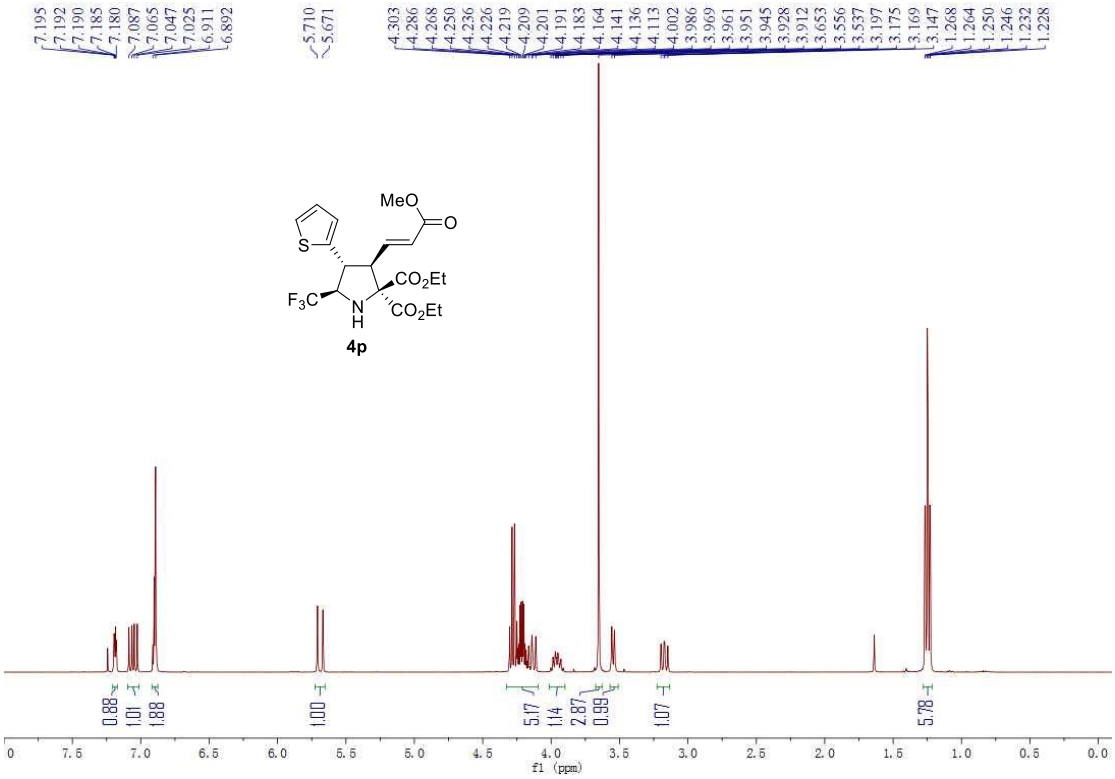
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.31	0.31	52.76	1035.02	2.48
2	9.00	0.31	1001.86	19938.11	47.86
3	12.25	0.48	6.12	203.44	0.49
4	13.75	0.47	632.01	19609.75	47.07
5	16.71	0.62	7.39	309.36	0.74
6	20.33	0.70	12.29	566.30	1.36
Total				41661.98	100.00

Temperature in°C:	30.0	30.0
Pressure in bar:	22.3	22.4
Flow in ml/min:	0.7	0.7

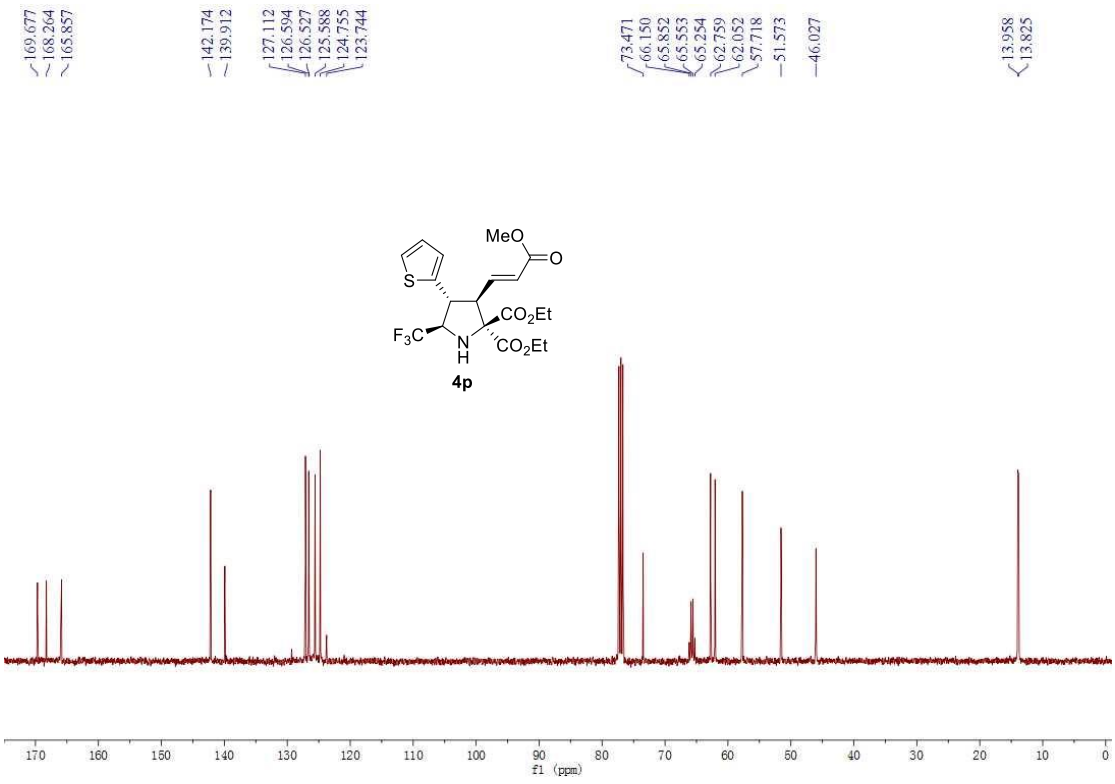


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	5.34	0.24	23.17	341.08	2.44
2	6.65	0.37	33.15	776.76	5.56
3	7.28	0.31	34.61	717.62	5.14
4	8.92	0.32	473.55	9211.55	65.98
5	9.63	0.28	15.10	253.86	1.82
6	10.14	0.51	14.08	432.08	3.09
7	13.60	0.62	10.00	437.23	3.13
8	15.52	0.55	49.32	1791.47	12.83
Total				13961.65	100.00

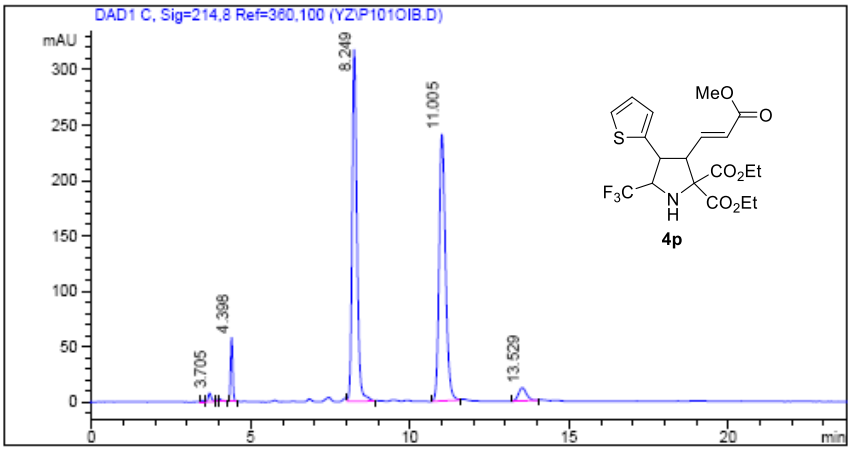
^{1}H NMR of **4p:**



^{13}C NMR of **4p:**

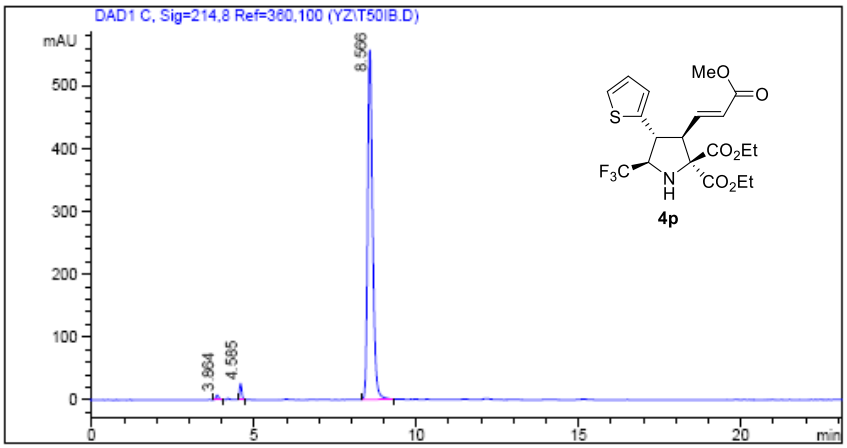


Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	38.3	36.8
Flow in ml/min:	1.00	1.00



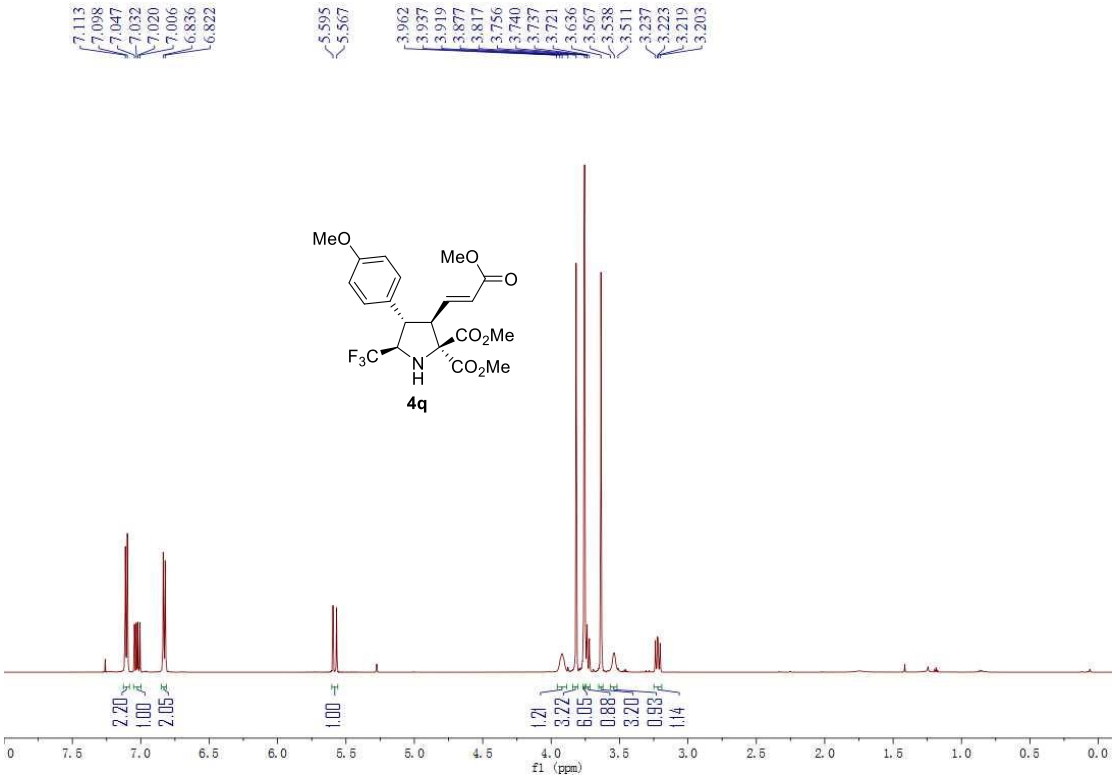
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.48	0.07	1.36	6.10	0.08
2	3.71	0.10	7.94	53.21	0.73
3	3.93	0.07	1.65	7.59	0.10
4	4.02	0.09	2.82	19.36	0.27
5	4.40	0.08	58.00	281.68	3.87
6	8.25	0.16	317.78	3329.81	45.74
7	11.00	0.22	240.70	3372.39	46.33
8	13.53	0.27	11.81	209.08	2.87
Total				7279.23	100.00

Instrument Conditions:	At Start	At Stop
Temperature in°C:	30.0°C	30.0°C
Pressure in bar:	36.5	35.8
Flow in ml/min:	1.00	1.00

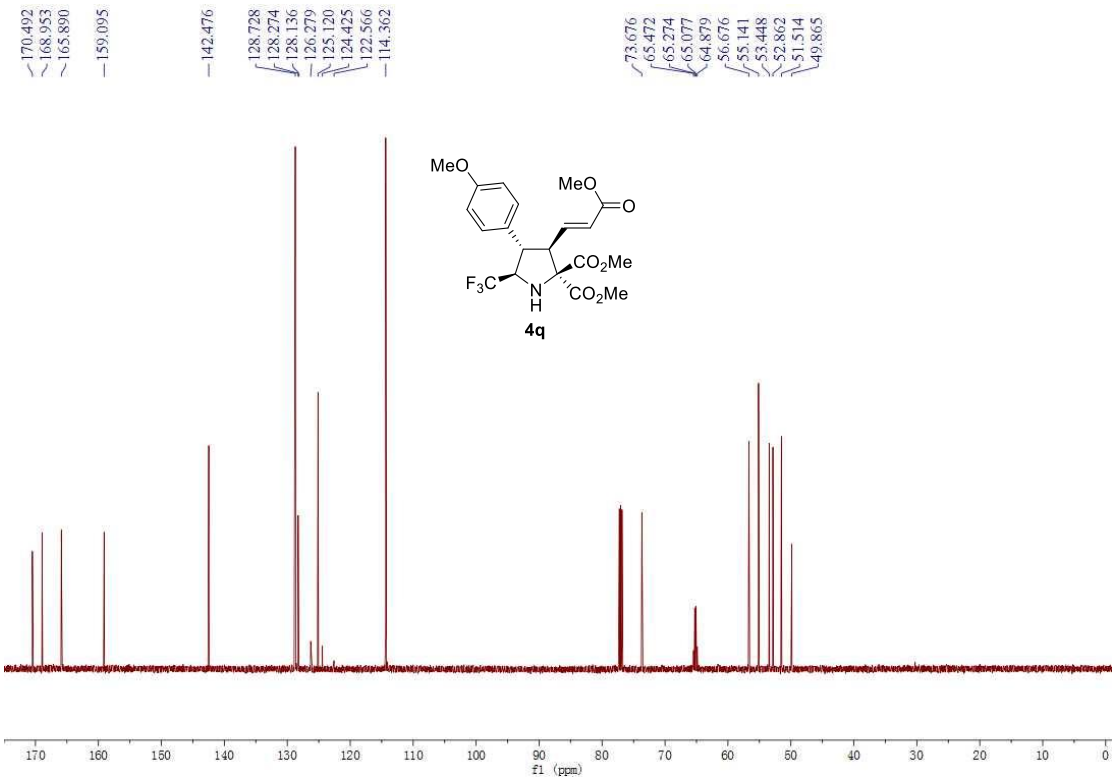


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.86	0.10	7.53	49.00	0.80
2	4.59	0.08	26.20	129.40	2.11
3	8.57	0.16	556.94	5941.96	97.09
Total				6120.36	100.00

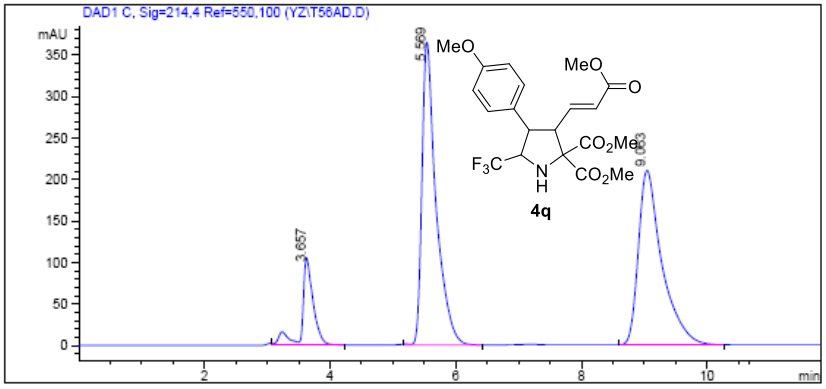
^{1}H NMR of **4q:**



^{13}C NMR of **4q:**

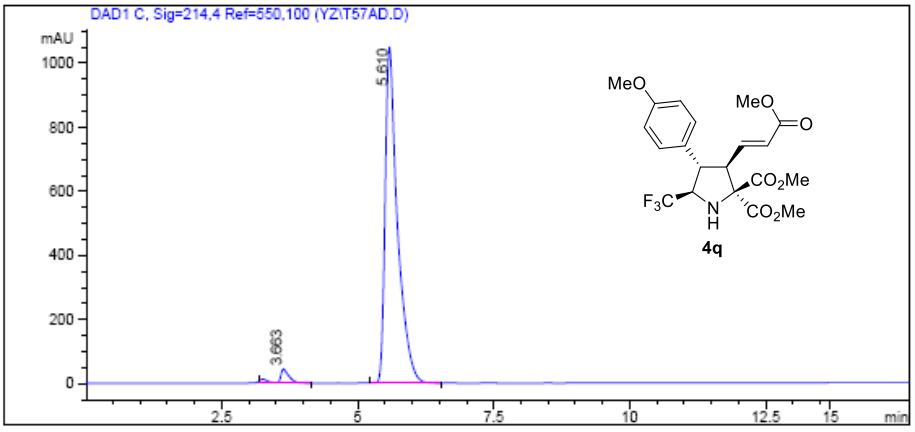


Temperature in°C:	30.7	30.8
Pressure in bar:	36.4	35.9
Flow in ml/min:	1.0	1.0



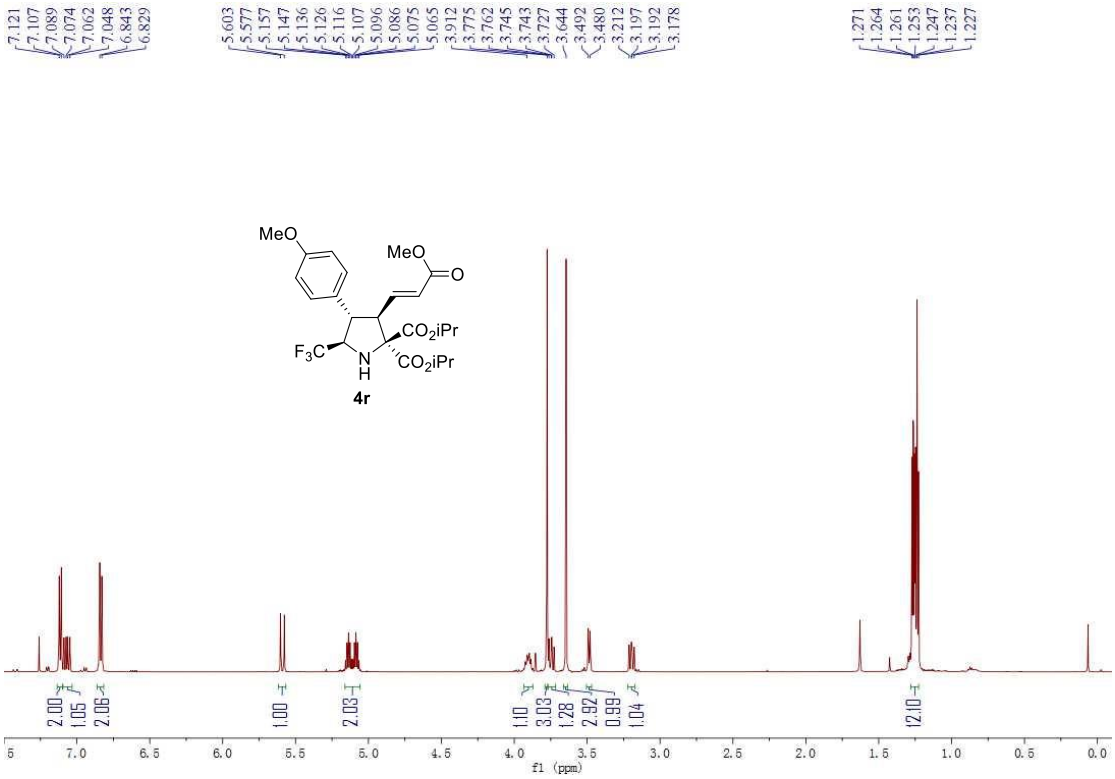
#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.66	0.22	96.53	1306.95	10.46
2	5.57	0.27	341.78	5699.59	45.63
3	9.06	0.40	210.92	5484.43	43.91
Total				12490.97	100.00

Temperature in°C:	30.0	30.1
Pressure in bar:	36.7	36.3
Flow in ml/min:	1.0	1.0

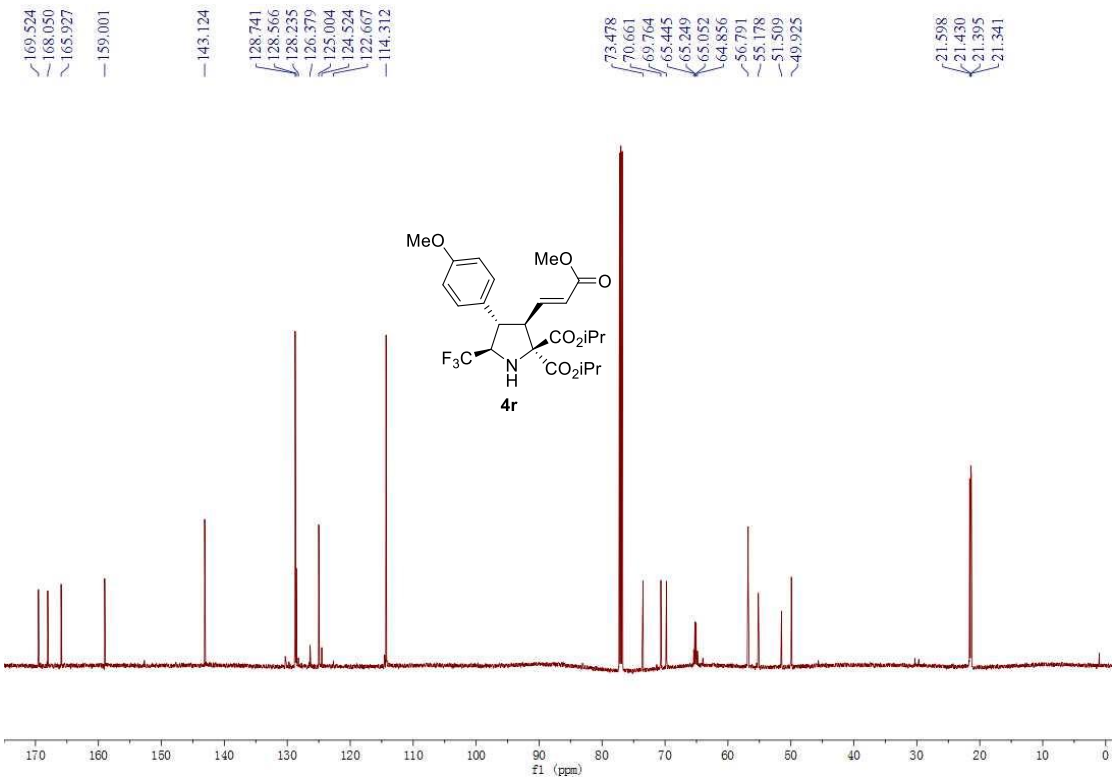


#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.66	0.23	40.50	584.05	3.41
2	5.61	0.29	916.53	16543.07	96.59
Total				17127.12	100.00

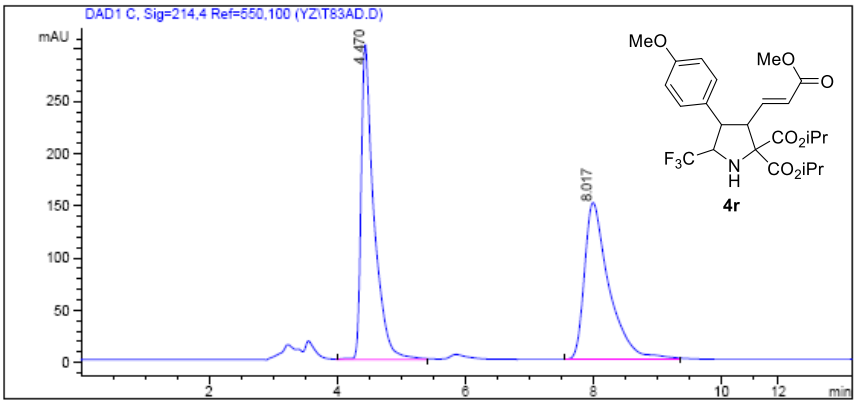
^{1}H NMR of **4r:**



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

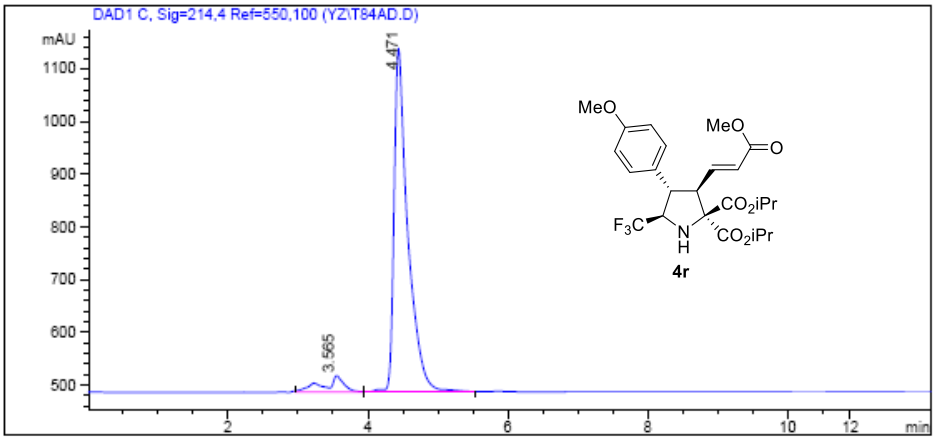


Temperature in°C: Start Temperature n-> End Temperature not available
Pressure in bar: Start Pressure not -> End Pressure not available
Flow in ml/min: Start Flow not -> End Flow not available



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	4.47	0.25	294.36	4193.13	51.02
2	8.02	0.42	146.85	4026.15	48.98
Total				8219.28	100.00

Temperature in°C: 30.0 30.0
Pressure in bar: 42.8 42.2
Flow in ml/min: 1.0 1.0



#	Ret. Time (min)	Width	Height (mAU)	Area (mAU*s)	Area %
1	3.56	0.33	30.01	634.13	6.60
2	4.47	0.25	621.85	8970.82	93.40
Total				9604.95	100.00