Electronic Supplementary Material (ESI) for Organic Chemistry Frontiers.

Cu(I)-Catalyzed Michael Addition of Ketiminoesters to *β*-Trifluoromethyl *β*, *β*-Disubstituted Enones: A Rapid Access to 1-Pyrrolines Bearing a Quaternary All-Carbon Stereocenter

Bing Liu, Zhan-Ming Zhang, Bing Xu, Shan Xu, Hai-Hong Wu, Yuanyuan Liu* and Junliang Zhang*

Shanghai Key Laboratory of Green Chemistry and Chemical Process, School of Chemistry and Molecular Engineering, East China Normal University, 3663 N. Zhongshan Road, Shanghai 200062, China.

Fax:(+86)-021-6223-3213; E-mail: yyliu@chem.ecnu.edu.cn; jlzhang@chem.ecnu.edu.cn.

Supporting Information

Table Contents

1. General Information

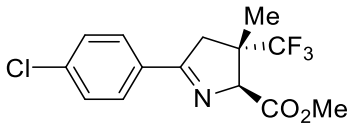
All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra, ^{19}F NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 300, 400 and 500 MHz spectrometer in $CDCl_3$. All signals are reported in ppm with the internal TMS signal at 0 ppm as a standard. Data for ^{1}H NMR spectra are reported as follows: chemical shift (ppm, referenced to TMS; s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, coupling constant(s) in Hz, integration), coupling constant (Hz), and intergration. Data for ^{13}C NMR are reported in terms of chemical shift (ppm) relative to residual solvent peak ($CDCl_3$: 77.0 ppm). Reactions were monitored by thin layer chromatography (TLC) using silica gel plates. Flash column chromatography was performed over silica gel (300-400 mesh). Dichloromethane, toluene were freshly distilled from CaH_2; THF, Et_2O and MTBE were freshly distilled from sodium metal prior to use. The ligands **M1**-**M5** were synthesized according to the procedure of reference.[1] The substrate **1a-1q**[2] were synthesized according to the procedure of references. **2a**-**2c** were commercially available. And the spectral data of the substrates were consisted with the literature.

2. General Procedure for the Synthesis of products 3-10

Typical procedure for asymmetric copper-catalyzed Michael addition initiated cycloaddition of enones with glycine ketoimino ester.

The solution of CuOAc (5 mol%) and (*S*,*S*)-^{i}Pr-PHOXAP (6.0 mol%) in MTBE (2 mL) was stirred at room temperature for 2 h. After the reaction temperature was dropped to -30 ℃, glycine ketoimino ester **2** (0.4 mmol), Cs_2CO_3 (0.1 mmol) and alkene **1** (0.2 mmol) were added sequentially. After the alkene **1** was consumed completely, remove the solvent under reduced pressure. The crude product was analyzed with ^{1}H NMR and ^{19}F NMR to determine the chemicalselective and diastereomeric ratio. Then the crude product was purified by flash column chromatography on silica gel to afford the desired product. The enantionmeric excesses of the products were determined by chiral stationary phase HPLC.

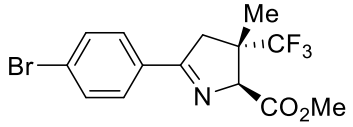
2.1 Synthesis of methyl (2*S*,3*S*)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3aa**).



3aa

The reaction of alkene **1a** (49.6 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3aa** as a colorless ropy liquid (57.4 mg, 90% yield) with >20:1 dr and 97% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.80-7.76 (m, 2H), 7.43-7.39 (m, 2H), 5.12 (t, J = 1.6 Hz, 1H), 3.80 (s, 3H), 3.43-3.37 (m, 1H), 3.01-2.94 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.07. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.35, 169.85, 137.74, 129.26, 129.12, 128.88, 128.00 (q, $J_{C\text{-}F}$ = 281.0 Hz), 77.44 (d, J = 1.8 Hz), 52.29, 50.12 (q, J = 26.2 Hz), 44.80 (d, J = 1.8 Hz), 17.15 (d, J = 2.7 Hz). MS (EI): m/z (%) = 319 (M^+, 11.07), 260 (100)； HRMS calculated for $[C_{14}H_{13}NO_2F_3Cl]^+$: 319.0587 found: 319.0583. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 8.7 min, minor enantiomer tr = 15.6 min. $[\alpha]_D^{25}$ = +54.3 (*c* = 0.50, $CHCl_3$).

2.2 Synthesis of methyl (2*S*,3*S*)-5-(4-bromophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ba**).

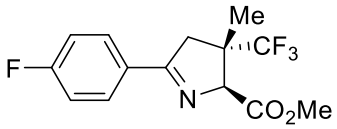


3ba

The reaction of alkene **1a** (58.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ba** as a colorless ropy liquid (63.9 mg, 88% yield) with >20:1 dr and 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2H), 7.57-7.54 (m, 2H), 5.10 (t, J = 1.5 Hz, 1H), 3.79 (s, 3H), 3.42-3.37 (m, 1H), 2.99-2.94 (m, 1H), 1.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.08. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.42, 169.74,

131.82, 131.70, 129.41, 127.99 (q, $J_{C\text{-}F}$ = 282.0 Hz), 126.19, 77.47, 52.22 (d, *J* = 1.7 Hz), 50.12 (q, *J* = 26.2 Hz), 44.72 (d, *J* = 2.2 Hz), 17.11 (d, *J* = 2.9 Hz). MS (EI): m/z (%) = 363 (M^+, 12.4), 304 (100)； HRMS calculated for $[C_{14}H_{13}NO_2F_3Br]^+$: 363.0082 found: 363.0078. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 9.0 min, minor enantiomer tr = 17.1 min. $[\alpha]_D^{25}$ = +56.8 (*c* = 0.50, $CHCl_3$).

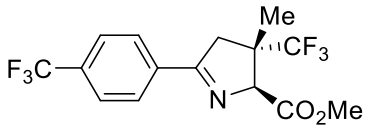
2.3 Synthesis of methyl (2*S*,3*S*)-5-(4-fluorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ca**)



3ca

The reaction of alkene **1a** (46.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ca** as a colorless ropy liquid (49.1 mg, 81% yield) with >20:1 dr and 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86-7.82 (m, 2H), 7.12-7.08 (m, 2H), 5.11 (t, *J* = 1.5 Hz, 1H), 3.79 (s, 3H), 3.42-3.38 (m, 1.2 Hz, 1H), 3.00-2.95 (m, 1.8 Hz, 1H), 1.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.10, -107.97. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.16, 169.91, 164.77 (d, *J* = 252.4 Hz), 130.12 (d, *J* = 8.8 Hz), 129.17 (d, *J* = 32.0 Hz), 128.03 (q, $J_{C\text{-}F}$ = 282.0 Hz), 115.67 (d, *J* = 21.9 Hz), 77.40, 52.18 (d, *J* = 2.0 Hz), 50.14 (q, *J* = 26.2 Hz), 44.83 (d, *J* = 1.8 Hz), 17.12 (d, *J* = 2.9 Hz). ESI-MS calculated for $C_{14}H_{13}F_4NNaO_2$: m/z (%): 326.0775 ($M+Na^+$), found: 326.0773. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 9.4 min, minor enantiomer tr = 14.7 min. $[\alpha]_D^{25}$ = +56.1 (*c* = 0.50, $CHCl_3$).

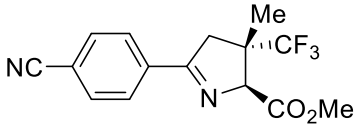
2.4 Synthesis of methyl (2*S*,3*S*)-3-methyl-3-(trifluoromethyl)-5-(4-(trifluoromethyl) phenyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3da**).



3da

The reaction of alkene **1a** (56.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3da** as a ropy liquid (63.9 mg, 85% yield) with >20:1 dr and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.96 (d, *J* = 8.1 Hz, 2H), 7.69 (d, *J* = 8.2 Hz, 2H), 5.16 (t, *J* = 1.5 Hz, 1H), 3.81 (s, 3H), 3.47-3.42 (m, 1H), 3.04-2.99 (m, 1H), 1.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -63.04, -77.23. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.33, 169.59, 136.00, 133.10 (q, *J* = 32.6 Hz), 128.30, 127.98 (q, $J_{C\text{-}F}$ = 281.9 Hz), 125.56 (q, *J* = 3.7 Hz), 123.72 (q, $J_{C\text{-}F}$ = 273.4 Hz), 77.61, 52.27 (d, *J* = 2.4 Hz), 50.19 (q, *J* = 26.4 Hz), 44.86 (d, *J* = 2.0 Hz), 17.09 (d, *J* = 2.8 Hz). ESI-MS calculated for $C_{15}H_{13}F_6NNaO_2$: m/z (%): 376.0743 ($M+Na^+$), found: 376.0740. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 5.3 min, minor enantiomer tr = 6.6 min. $[\alpha]_D^{25}$ = +57.4 (*c* = 0.50, $CHCl_3$).

2.5 Synthesis of methyl (2*S*,3*S*)-5-(4-cyanophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ea**).

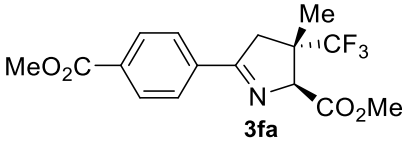


3ea

The reaction of alkene **1a** (47.8 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 2:1) afforded the product **3ea** as a colorless ropy liquid (51.5 mg, 83% yield) with >20:1 dr and 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, *J* = 8.2 Hz, 2H), 7.73-7.71 (m, 2H), 5.16 (s, 1H), 3.81 (s, 3H), 3.44-3.40 (m, 1H), 3.02-3.97 (m, 1H), 1.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.25. ^{13}C NMR (126 MHz, $CDCl_3$) δ 172.02, 169.43, 136.59, 132.35, 128.48, 127.87 (q, $J_{C\text{-}F}$ = 281.1 Hz), 118.11, 114.88, 77.62, 52.37, 50.20 (q, *J* = 26.3 Hz), 44.71, 17.08. ESI-MS calculated for $C_{15}H_{13}F_3N_2NaO_2$: m/z (%): 333.0821

(M+Na^+), found: 333.0817. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 70:30, 0.8 mL/min, 254 nm); major enantiomer tr = 11.1 min, minor enantiomer tr = 17.4 min. $[\alpha]_D^{25}$ = +54.4 (*c* = 0.50, $CHCl_3$).

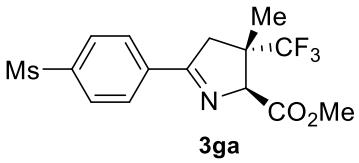
2.6 Synthesis of methyl (2*S*,3*S*)-5-(4-(methoxycarbonyl)phenyl)-3-methyl-3-(trifluoro methyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3fa**).



3fa

The reaction of alkene **1a** (54.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 2:1) afforded the product **3fa** as a white solid (65.9 mg, 96% yield) with >20:1 dr and 98% *ee*. mp: 86-87 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.91 (d, *J* = 8.2 Hz, 2H), 5.15 (s, 1H), 3.94 (s, 3H), 3.81 (s, 3H), 3.47-3.43 (m, 1H), 3.05-3.00 (m, 1H), 1.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.09. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.72, 169.66, 166.33, 136.66, 132.62, 129.78, 128.00 (q, $J_{C\text{-}F}$ = 281.9 Hz), 127.92, 77.63, 52.29, 52.29, 50.16 (q, *J* = 26.1 Hz), 44.96, 17.15. ESI-MS calculated for $C_{16}H_{16}F_3NNaO_4$: m/z (%): 366.0924 (M+Na^+), found: 366.0926. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 254 nm); major enantiomer tr = 13.8 min, minor enantiomer tr = 16.9 min. $[\alpha]_D^{25}$ = +74.2 (*c* = 0.50, $CHCl_3$).

2.7 Synthesis of methyl (2*S*,3*S*)-3-methyl-5-(4-(methylsulfonyl)phenyl)-3-(trifluoro methyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ga**).

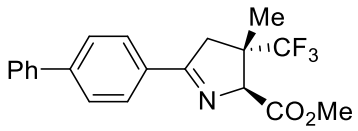


3ga

The reaction of alkene **1a** (58.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 2:1) afforded

the product **3ga** as a colorless ropy liquid (68.2 mg, 94% yield) with >20:1 dr and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.03-7.97 (m, 4H), 5.15 (s, 1H), 3.79 (s, 3H), 3.46-3.41 (m, 1H), 3.04 (s, 3H), 3.03-3.00 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.25. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.03, 169.35, 142.82, 137.51, 128.81, 127.60, 127.36 (q, $J_{C\text{-}F}$ = 281.9 Hz), 77.63, 52.28 (d, J = 2.4 Hz), 50.20 (q, J = 26.3 Hz), 44.79 (d, J = 1.8 Hz), 44.29, 17.00 (d, J = 2.6 Hz). ESI-MS calculated for $C_{15}H_{16}F_3NNaO_4S$: m/z (%): 386.0644 ($M+Na^+$), found: 386.0645. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 60:40, 0.8 mL/min, 254 nm); major enantiomer tr = 39.0 min, minor enantiomer tr = 48.3 min. $[\alpha]_D^{25}$ = +60.0 (*c* = 0.50, $CHCl_3$).

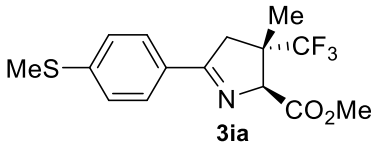
2.8 Synthesis of methyl (2*S*,3*S*)-5-([1,1'-biphenyl]-4-yl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ha**).



3ha

The reaction of alkene **1a** (58.0 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ha** as a white solid (55.6 mg, 77% yield) with >20:1 dr and 97% *ee*. mp: 113-114 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.93 (d, J = 8.4 Hz, 2H), 7.68-7.61 (m, 4H), 7.49-7.45 (m, 2H), 7.41-7.37 (m, 1H), 5.16 (s, 1H), 3.82 (s, 3H), 3.50-3.45 (m, 1H), 3.07-3.02 (m, 1H), 1.35 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.97. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.06, 170.01, 144.28, 140.09, 131.74, 128.90, 128.47, 128.14 (q, $J_{C\text{-}F}$ = 281.5 Hz), 127.97, 127.25, 127.16, 77.54, 52.10, 50.09 (q, J = 26.2 Hz), 44.87, 17.22. ESI-MS calculated for $C_{20}H_{19}F_3NO_2$: m/z (%): 362.1362 ($M+H^+$), found: 362.1369. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 9.4 min, minor enantiomer tr = 18.1 min. $[\alpha]_D^{25}$ = +72.2 (*c* = 0.50, $CHCl_3$).

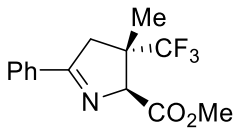
2.9 Synthesis of methyl (2*S*,3*S*)-3-methyl-5-(4-(methylthio)phenyl)-3-(trifluoro methyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ia**).



3ia

The reaction of alkene **1a** (52.0 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 3:1) afforded the product **3ia** as a white solid (56.3 mg, 85% yield) with >20:1 dr and 98% *ee*. mp: 109-110 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75 (d, *J* = 8.5 Hz, 2H), 7.26-7.24 (m, 2 H), 5.11 (s, 1H), 3.79 (s, 3 H), 3.42-3.37 (m, 1H), 2.99-2.95 (m, 1 H), 2.51 (s, 3H), 1.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.96. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.71, 170.04, 143.49, 129.25, 128.23, 128.08 (q, J_{C-F} = 282.0 Hz), 125.47, 77.32, 52.19, 50.01 (q, *J* = 26.2 Hz), 44.74, 17.16, 15.03. ESI-MS calculated for $C_{15}H_{17}F_3NO_2S$: m/z (%): 332.0927 ($M+H^+$), found: 332.0929. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 275 nm); major enantiomer tr = 11.1 min, minor enantiomer tr = 36.7 min. $[\alpha]_D^{25}$ = +71.7 (*c* = 0.50, $CHCl_3$).

2.10 Synthesis of methyl (2*S*,3*S*)-3-methyl-5-phenyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ja**).

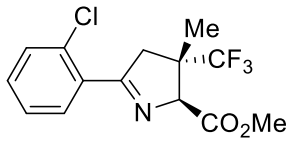


3ja

The reaction of alkene **1a** (42.8 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ja** as a colorless ropy liquid (45.0 mg, 79% yield) with >20:1 dr and 95% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.86-7.83 (m, 2H), 7.51-7.40 (m, 3H), 5.13 (s, 1H), 3.80 (s, 3H), 3.47-3.41 (m, 1H), 3.04-2.98 (m, 1H), 1.33 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.00. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.40, 169.98, 132.80, 131.51, 128.57, 127.93, 127.37 (q, J_{C-F} = 281.6 Hz), 77.43, 52.21, 49.97 (q, *J* = 26.2 Hz),

44.86 (d, J = 1.8 Hz), 17.16 (d, J = 2.7 Hz). ESI-MS calculated for $C_{14}H_{14}F_3NNaO_2$: m/z (%): 308.0869 ($M+Na^+$), found: 308.0872. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 14.2 min, minor enantiomer tr = 19.0 min. $[\alpha]_D^{25}$ = +56.0 (c = 0.50, $CHCl_3$).

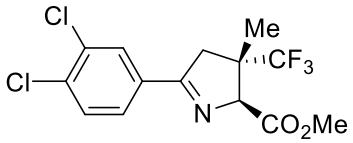
2.11 Synthesis of methyl (2*S*,3*S*)-5-(2-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ka**).



3ka

The reaction of alkene **1a** (49.6 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ka** as a colorless ropy liquid (54.2 mg, 85% yield) with >20:1 dr and 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.72-7.69 (m, 1H), 7.43-7.40 (m, 1H), 7.39-7.35 (m, 1H), 7.33-7.29 (m, 1H), 5.09 (s, 1H), 3.81 (s, 3H), 3.55-3.50 (m, 1H), 3.19-3.14 (m, 1H), 1.34 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.92. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.66, 169.54, 133.31, 132.68, 131.45, 130.84, 130.33, 127.97 (q, $J_{C\text{-}F}$ = 279.0 Hz), 126.99, 77.21, 52.29, 50.75 (q, J = 26.2 Hz), 47.74 (d, J = 1.9 Hz), 16.81 (d, J = 2.9 Hz). ESI-MS calculated for $C_{14}H_{13}ClF_3NNaO_2$: m/z (%): 342.0479 ($M+Na^+$), found: 342.0493. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 10.4 min, minor enantiomer tr = 11.5 min. $[\alpha]_D^{25}$ = +64.1 (c = 0.50, $CHCl_3$).

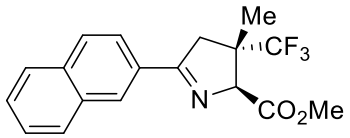
2.12 Synthesis of methyl (2*S*,3*S*)-5-(3,4-dichlorophenyl)-3-methyl-3-(trifluoro methyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3la**).



3la

The reaction of alkene **1a** (56.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3la** as a colorless ropy liquid (67.1 mg, 95% yield) with >20:1 dr and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.94 (d, J = 2.0 Hz, 1H), 7.66-7.63 (m, 1H), 7.49 (d, J = 8.3 Hz, 1H), 5.12 (s, 1H), 3.80 (s, 3H), 3.40-3.35 (m, 1H), 2.98-2.93 (m, 1H), 1.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.19. ^{13}C NMR (101 MHz, $CDCl_3$) δ 171.42, 169.56, 135.80, 133.10, 132.66, 130.59, 129.79, 127.91 (q, $J_{C\text{-}F}$ = 279.0 Hz), 126.99, 77.49, 52.28 (d, J = 2.0 Hz), 50.21 (q, J = 26.2 Hz), 44.67 (d, J = 2.0 Hz), 17.07 (d, J = 2.6 Hz). ESI-MS calculated for $C_{14}H_{12}Cl_2F_3NNaO_2$: m/z (%): 376.0089 ($M+Na^+$), found: 376.0092. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 7.8 min, minor enantiomer tr = 13.3 min. $[\alpha]_D^{25}$ = +74.0 (c = 0.50, $CHCl_3$).

2.13 Synthesis of methyl (2*S*,3*S*)-3-methyl-5-(naphthalen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ma**).

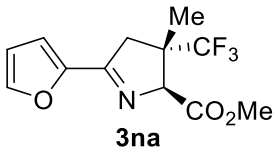


3ma

The reaction of alkene **1a** (52.8 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ma** as a white solid (65.0 mg, 97% yield) with >20:1 dr and 96% *ee*. Mp: 118-119 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18-8.17 (m, 1H), 8.10-8.08 (m, 1H), 7.90-7.85 (m, 3H), 7.58-7.50 (m, 2H), 5.20 (s, 1H), 3.82 (s, 3H), 3.61-3.13 (m, 2H), 1.38 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.87. ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.38, 170.04, 134.79, 132.72, 130.32, 128.93, 128.78, 128.41, 128.12 (q, $J_{C\text{-}F}$ = 281.3 Hz), 127.79, 127.66, 126.66, 124.28, 77.51, 52.26, 50.09 (q, J = 26.1 Hz), 44.92 (d, J = 1.9 Hz), 17.23 (d, J = 2.7 Hz). ESI-MS calculated for $C_{18}H_{17}F_3NO_2$: m/z (%): 336.1206 ($M+H^+$), found: 336.1208. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major

enantiomer tr = 8.1 min, minor enantiomer tr = 20.8 min. $[\alpha]_D^{25}$ = +99.6 (*c* = 0.50, $CHCl_3$).

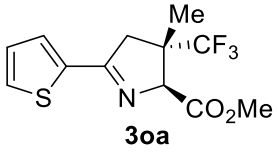
2.14 Synthesis of methyl (2*S*,3*S*)-5-(furan-2-yl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3na**).



3na

The reaction of alkene **1a** (40.8 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3na** as a colorless ropy liquid (36.3 mg, 66% yield) with >20:1 dr and 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (d, *J* = 1.5 Hz, 1H), 6.94 (d, *J* = 3.5 Hz, 1H), 6.52-6.50 (m, 1H), 5.10 (s, 1H), 3.78 (s, 3H), 3.38-3.34 (m, 1H), 2.95-2.90 (m, 1H), 1.31 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.06. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.71, 163.95, 148.44, 145.43, 127.94 (q, $J_{C\text{-}F}$ = 280.9 Hz), 114.58, 111.96, 77.57, 52.23 (d, *J* = 2.5 Hz), 49.83 (q, *J* = 26.3 Hz), 44.54 (d, *J* = 2.0 Hz), 16.99 (d, *J* = 2.8 Hz). ESI-MS calculated for $C_{12}H_{12}F_3NNaO_3$: m/z (%): 298.0661 ($M+Na^+$), found: 298.0664. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 254 nm); major enantiomer tr = 12.6 min, minor enantiomer tr = 20.9 min. $[\alpha]_D^{25}$ = +51.3 (*c* = 0.50, $CHCl_3$).

2.15 Synthesis of methyl (2*S*,3*S*)-3-methyl-5-(thiophen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3oa**).

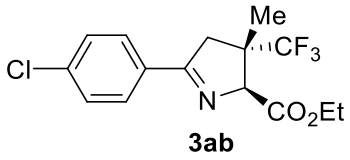


3oa

The reaction of alkene **1a** (44.0mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3oa** as a colorless ropy liquid (53.0 mg, 91% yield) with >20:1 dr and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50-7.48 (m, 1H), 7.38-7.36 (m, 1H), 7.10-7.07 (m,

1H), 5.08 (s, 1H), 3.78 (s, 3H), 3.44-3.39 (m, 1H), 3.01-2.96 (m, 1H), 1.32 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.11. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.77, 167.81, 137.39, 130.67, 130.54, 127.97 (q, J_{C-F} = 282.0 Hz), 127.60, 77.32, 52.18 (d, J = 2.4 Hz), 50.33 (q, J = 26.2 Hz), 45.22 (d, J = 2.0 Hz), 17.07 (d, J = 2.8 Hz). ESI-MS calculated for $C_{12}H_{12}F_3NNaO_2S$: m/z (%): 314.0433 ($M+Na^+$), found: 314.0436. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 13.2 min, minor enantiomer tr = 17.7 min. $[\alpha]_D^{25}$ = +56.1 (c = 0.50, $CHCl_3$).

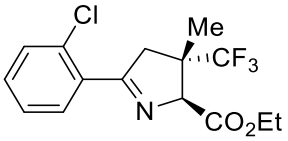
2.16 Synthesis of ethyl (2*S*,3*S*)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ab**).



3ab

The reaction of alkene **1a** (49.6mg, 0.2 mmol) and glycine ketoimino ester **2a** (106.8 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ab** as a colorless ropy liquid (59.9 mg, 90% yield) with >20:1 dr and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40-7.37 (m, 2H), 7.59-7.30 (m, 2H), 5.08 (s, 1H), 4.29-4.23 (m, 2H), 3.41-3.36 (m, 1H), 2.98-2.93 (m, 1H), 1.33 (s, 3H), 1.31 (t, J = 1.80 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.01. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.17, 169.31, 137.63, 131.33, 129.22, 128.80, 128.02 (q, J_{C-F} = 281.9 Hz), 77.36, 61.36, 50.13 (q, J = 26.2 Hz), 44.78 (d, J = 1.8 Hz), 17.07 (q, J = 2.6 Hz), 14.13. ESI-MS calculated for $C_{15}H_{15}ClF_3NNaO_2$: m/z (%): 356.0636 ($M+Na^+$), found: 356.0644. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 8.5 min, minor enantiomer tr = 14.9 min. $[\alpha]_D^{25}$ = +56.7 (c = 0.50, $CHCl_3$).

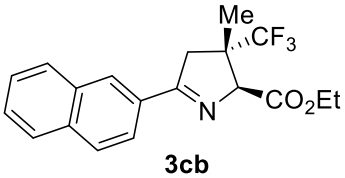
2.17 Synthesis of ethyl (2*S*,3*S*)-5-(2-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3bb**).



3bb

The reaction of alkene **1a** (49.6mg, 0.2 mmol) and glycine ketoimino ester **2b** (106.8 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3bb** as a colorless ropy liquid (47.3 mg, 71% yield) with >20:1 dr and 93% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.42-7.40 (m, 1H), 7.38-7.34 (m, 1H), 7.32-7.28 (m, 1H), 5.06 (t, *J* = 1.5 Hz, 1H), 4.31-4.25 (m, 2H), 3.54-3.50 (m, 1H), 3.18-3.13 (m, 1H), 1.35 (s, 3H), 1.32 (t, *J* = 7.2 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.92. ^{13}C NMR (101 MHz, $CDCl_3$) δ 174.60, 169.03, 133.34, 132.59, 131.38, 130.78, 130.26, 127.95 (q, *J* = 280.9 Hz), 126.94, 76.57, 61.42, 50.69 (q, *J* = 26.1 Hz), 47.67, 16.71 (d, *J* = 2.4 Hz), 14.15. ESI-MS calculated for $C_{15}H_{16}ClF_3NO_2$: m/z (%): 334.0816 ($M+H^+$), found: 334.0823. Enantiomeric excess was determined by HPLC with a Chiralpak IA column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 11.2 min, minor enantiomer tr = 12.8 min. $[\alpha]_D^{25}$ = +15.9 (*c* = 0.50, $CHCl_3$).

2.18 Synthesis of ethyl (2*S*,3*S*)-3-methyl-5-(naphthalen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3cb**).

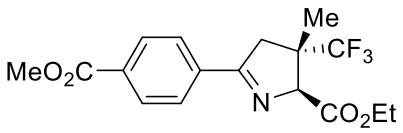


3cb

The reaction of alkene **1a** (52.8 mg, 0.2 mmol) and glycine ketoimino ester **2a** (106.8 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3cb** as a white solid (53.2 mg, 76% yield) with 13:1 cr, >20:1 dr and 98% *ee*. mp: 96-97 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.11-8.08 (m, 1H), 7.90-7.85 (m, 3H), 7.58-7.50 (m, 2H), 5.17 (s, 1H), 4.33-4.27 (m, 2H), 3.60-3.55 (m, 1H), 3.17-3.12 (m, 1H), 1.39 (s, 3H), 1.34 (t, *J* = 7.1 Hz, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.77 (s). ^{13}C NMR (126 MHz, $CDCl_3$) δ 173.26, 169.58, 134.77, 132.72, 130.38,

128.89, 128.76, 128.37, 128.16 (q, $J_{C\text{-}F}$ = 282.5 Hz), 127.78, 127.62, 126.63, 124.31, 77.41, 61.37, 50.09 (q, J = 26.1 Hz), 44.94, 17.18, 14.18. ESI-MS calculated for $C_{19}H_{19}F_3NO_2$: m/z (%): 350.1367 ($M+H^+$), found: 350.1362. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 7.8 min, minor enantiomer tr = 19.7 min. $[\alpha]_D^{25}$ = +97.0 (c = 0.50, $CHCl_3$).

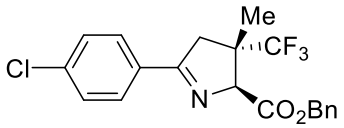
2.19 Synthesis of ethyl (2*S*,3*S*)-5-(4-(methoxycarbonyl)phenyl)-3-methyl-3-(trifluoro methyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3db**).



3db

The reaction of alkene **1a** (54.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (106.8 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3db** as a white solid (62.1 mg, 87% yield) with >20:1 dr and 98% *ee*. mp: 70-71 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10-8.08 (m, 2H), 7.92-7.90 (m, 2H), 5.13 (d, J = 0.8 Hz, 1H), 4.31-4.25 (m, 2H), 3.94-3.93 (m, 3H), 3.47-3.42 (m, 1H), 3.04-2.99 (m, 1H), 1.35 (s, 3H), 1.35-1.30 (m, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -77.00. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.61, 169.22, 166.36, 136.72, 132.57, 129.77, 128.02 (q, $J_{C\text{-}F}$ = 281.9 Hz), 127.92, 77.55, 61.47, 52.32, 50.16 (q, J = 26.1 Hz), 44.99, 17.14, 14.19. ESI-MS calculated for $C_{17}H_{18}F_3NNaO_4$: m/z (%): 380.1080 ($M+Na^+$), found: 380.1081. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 16.6 min, minor enantiomer tr = 19.9 min. $[\alpha]_D^{25}$ = +63.8 (c = 0.50, $CHCl_3$).

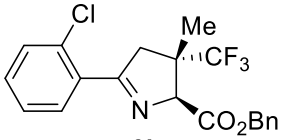
2.20 Synthesis of benzyl (2*S*,3*S*)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3ac**).



3ac

The reaction of alkene **1a** (49.6mg, 0.2 mmol) and glycine ketoimino ester **2a** (131.6 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3ac** as a white solid (70.3 mg, 89% yield) with >20:1 dr and 98% *ee*. mp: 50-51 ºC. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.77 (m, 2H), 7.42-7.33 (m, 7H), 5.25 (s, 2H), 5.16 (s, 1H), 3.42-2.93 (m, 2H), 1.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.90. ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.32, 169.23, 137.69, 135.10, 131.29, 129.24, 128.83, 128.53, 128.53, 128.46, 127.98 (q, $J_{C\text{-}F}$ = 282.1 Hz), 77.32, 67.11, 50.27 (q, J = 26.2 Hz), 44.84 (d, J = 2.0 Hz), 17.03 (d, J = 2.7 Hz). ESI-MS calculated for $C_{20}H_{17}F_3NNaO_2$: m/z (%): 418.0792 ($M+Na^+$), found: 418.0794. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 8.9 min, minor enantiomer tr = 18.1 min. $[\alpha]_D^{25}$ = +32.4 (*c* = 0.50, $CHCl_3$).

2.21 Synthesis of benzyl (2*S*,3*S*)-5-(2-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3bc**).

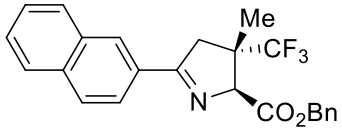


3bc

The reaction of alkene **1a** (49.6mg, 0.2 mmol) and glycine ketoimino ester **2c** (131.6 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3bc** as a white solid (75.1 mg, 95% yield) with >20:1 dr and 95% *ee*. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.71-7.69 (m, 1H), 7.41-7.28 (m, 8H), 5.24 (q, J = 12.2 Hz, 2H), 5.12 (s, 1H), 3.54-3.50 (m, 1H), 3.15-3.11 (m, 1H), 1.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.90. ^{13}C NMR (126 MHz, $CDCl_3$) δ 174.95, 168.91, 135.14, 133.23, 132.71, 131.57, 130.91, 130.37, 128.65, 128.62, 128.56, 127.97 (q, $J_{C\text{-}F}$ = 281.6 Hz), 127.04, 76.51, 67.25, 50.86 (q, J = 26.1 Hz), 47.77 (d, J = 1.4 Hz), 16.73 (d, J = 2.4 Hz). ESI-MS calculated for $C_{20}H_{18}ClF_3NO_2$: m/z (%): 396.0973 ($M+H^+$), found: 396.0980.

Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 254 nm); major enantiomer tr = 8.2 min, minor enantiomer tr = 9.6 min. $[\alpha]_D^{25}$ = +86.5 (*c* = 0.50, $CHCl_3$).

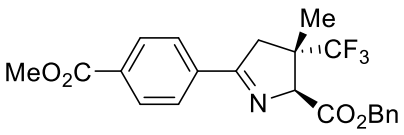
2.22 Synthesis of benzyl (2*S*,3*S*)-3-methyl-5-(naphthalen-2-yl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3cc**).



3cc

The reaction of alkene **1a** (52.8 mg, 0.2 mmol) and glycine ketoimino ester **2a** (131.6 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3cc** as a white solid (68.2 mg, 83% yield) with >20:1 dr and 96% *ee*. mp: 96-97 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 8.18 (s, 1H), 8.11 (d, *J* = 8.6 Hz, 1H), 7.91-7.86 (m, 3H), 7.59-7.51 (m, 2H), 7.43-7.34 (m, 5H), 5.28 (s, 2H), 5.25 (s, 1H), 3.60-3.56 m, 1H), 3.16-3.11 (m, 1H), 1.30 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.73. ^{13}C NMR (101 MHz, $CDCl_3$) δ 173.36, 169.43, 135.20, 134.79, 132.73, 130.38, 128.89, 128.76, 128.53, 128.53, 128.42, 128.37, 128.12 (q, $J_{C\text{-}F}$ = 281.5 Hz), 127.78, 127.62, 126.63, 124.31, 77.39, 67.07, 50.25 (q, *J* = 26.2 Hz), 44.99, 17.13 (d, *J* = 2.8 Hz). ESI-MS calculated for $C_{24}H_{20}F_3NNaO_2$: m/z (%): 434.1338 ($M+Na^+$), found: 434.1338. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 8.2 min, minor enantiomer tr = 25.5 min. $[\alpha]_D^{25}$ = +52.1 (*c* = 0.50, $CHCl_3$).

2.23 Synthesis of benzyl (2*S*,3*S*)-5-(4-(methoxycarbonyl)phenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**3dc**).

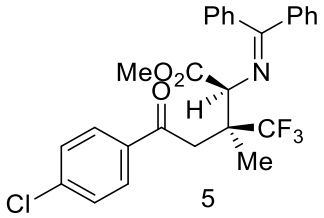


3dc

The reaction of alkene **1a** (54.4 mg, 0.2 mmol) and glycine ketoimino ester **2a** (131.6

mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 5:1) afforded the product **3dc** as a white solid (72.9 mg, 87% yield) with >20:1 dr and 97% *ee*. mp: 68-69 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.10 (d, *J* = 8.5 Hz, 2H), 7.91 (d, *J* = 8.5 Hz, 2H), 7.41-7.33 (m, 5H), 5.25 (s, 1H), 5.19 (s, 1H), 3.94 (s, 3H), 3.47-3.42 (m, 1H), 3.02-2.98 (m, 1H), 1.24 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -76.90 (d, *J* = 3.3 Hz). ^{13}C NMR (101 MHz, $CDCl_3$) δ 172.76, 169.09, 166.32, 136.62, 135.06, 132.57, 129.74, 128.54, 128.47, 128.42 (q, J_{C-F} = 281.9 Hz), 127.91, 126.88, 77.43, 67.16, 52.29, 50.25 (q, *J* = 26.3 Hz), 44.99 (d, *J* = 2.0 Hz), 17.03. ESI-MS calculated for $C_{22}H_{20}F_3NNaO_4$: m/z (%): 442.1237 ($M+Na^+$), found: 442.1237. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 85:15, 0.8 mL/min, 254 nm); major enantiomer tr = 16.5 min, minor enantiomer tr = 21.6 min. $[\alpha]_D^{25}$ = +40.1 (*c* = 0.50, $CHCl_3$).

2.24 Synthesis of methyl (2*S*,3*S*)-5-(4-chlorophenyl)-2-((diphenylmethylene)amino)-3-methyl-5-oxo-3-(trifluoromethyl)pentanoate (**5**).

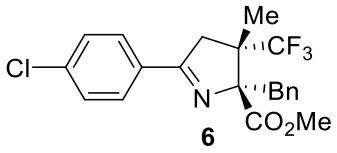


5

The reaction of alkene **1a** (49.6 mg, 0.2 mmol) and glycine ketoimino ester **2a** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 10:1) afforded the product **5** as a colorless ropy liquid (78.2 mg, 78% yield) with >20:1 dr and 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.92 (d, *J* = 8.6 Hz, 2H), 7.63-7.61 (m, 2H), 7.48-7.46 (m, 3H), 7.42-7.39 (m, 3H), 7.35-7.31 (m, 2H), 7.11-7.09 (m, 2H), 4.64 (s, 1H), 3.78 (d, *J* = 16.0 Hz, 1H), 3.55 (s, 3H), 3.42 (d, *J* = 16.0 Hz, 1H), 1.52 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.29. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.15, 171.94, 170.17, 139.36, 139.18, 136.38, 135.96, 130.69, 129.67, 128.89, 128.86, 128.75 (q, J_{C-F} = 283.6 Hz), 128.74, 128.57, 128.05, 127.32, 65.98, 51.87, 48.59 (q, *J* = 22.8 Hz), 37.89, 16.79 (d, *J* = 2.6 Hz). ESI-MS calculated for $C_{27}H_{23}ClF_3NNaO_3$: m/z (%): 524.1211 ($M+Na^+$), found: 524.1204. Enantiomeric excess was determined by HPLC with a

Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); minor enantiomer tr = 6.6 min, major enantiomer tr = 8.4 min. $[\alpha]_D^{25}$ = +10.2 (*c* = 0.50, $CHCl_3$).

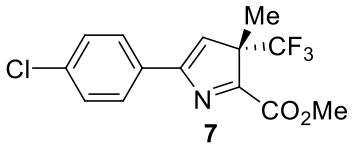
2.25 Synthesis of methyl (2*S*,3*S*)-2-benzyl-5-(4-chlorophenyl)-3-methyl-3-(trifluoro methyl)-3,4-dihydro-2*H*-pyrrole-2-carboxylate (**6**).



6

The reaction of alkene **3aa** (63.8 mg, 0.2 mmol) and BrBn (51.3 mg, 0.3 mmol) in DMF (4 mL) under the NaH (12 mg, 0.3 mmol) was stired at room tempreture. Then the reaction was determined by TLC analysis. After the **3aa** was consumed completely, the reaction mixture was quenched by the addition of NH_4Cl aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 10:1) afforded the product **6** as a colorless ropy liquid (62.2 mg, 76% yield) with 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83 (d, *J* = 8.5 Hz, 2H), 7.43-7.41 (m, 2H), 7.39-7.36 (m, 2H), 7.28-7.19 (m, 3H), 3.59 (s, 3H), 3.47-3.42 (m, 2H), 2.97 (d, *J* = 13.3 Hz, 1H), 2.85 (d, *J* = 16.7 Hz, 1H), 1.51 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.34. ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.93, 170.19, 137.57, 136.34, 131.79, 131.01, 129.69 (q, $J_{C\text{-}F}$ = 281.4 Hz), 129.18, 128.84, 127.86, 126.62, 83.71, 55.50 (q, *J* = 24.6 Hz), 52.29, 43.73, 40.47, 17.20 (d, *J* = 2.8 Hz). ESI-MS calculated for $C_{21}H_{19}ClF_3NNaO_2$: m/z (%): 432.0949 ($M+Na^+$), found: 432.0952. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 6.1 min, minor enantiomer tr = 6.9 min. $[\alpha]_D^{25}$ = +124.1 (*c* = 0.50, $CHCl_3$).

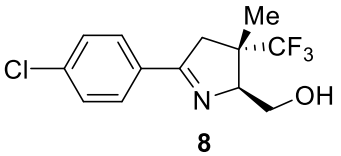
2.26 Synthesis of methyl (*S*)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3*H*-pyrrole-2-carboxylate (**7**).



7

The solution of compound **3aa** (63.8 mg, 0.2 mmol) in toluene (4 mL) was stirred at 75 ^{o}C in a sealed tube. Subsequently, DDQ (113.5 mg, 0.5 mmol) added to the above solution. Then the reaction was determined by TLC analysis. After the **3aa** was consumed completely, the reaction mixture was quenched by the addition of NaCl aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 10:1) to afford the desired product **7** as a colorless ropy liquid (52.6 mg, 83% yield) and 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84 (d, J = 8.6 Hz, 2H), 7.40 (d, J = 8.6 Hz, 2H), 6.57 (s, 1H), 3.98 (s, 3H), 1.76 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -68.45. ^{13}C NMR (126 MHz, $CDCl_3$) δ 169.07, 160.66, 154.83, 135.59, 130.05, 128.98, 128.05, 124.29 (q, $J_{C\text{-}F}$ = 280.8 Hz), 122.97 (d, J = 1.8 Hz), 66.39 (q, J = 28.6 Hz), 53.00, 15.41. ESI-MS calculated for $C_{14}H_{11}ClF_3NNaO_2$: m/z (%): 340.0323 ($M+Na^+$), found: 340.0323. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 6.6 min, minor enantiomer tr = 8.8 min. $[\alpha]_D^{25}$ = -3.5 (c = 0.50, $CHCl_3$).

2.27 Synthesis of ((2*S*,3*S*)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-yl)methanol (**8**).

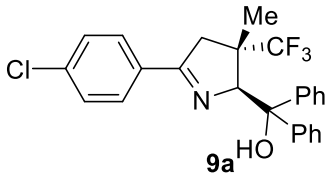


8

The solution of compound **3aa** (63.8 mg, 0.2 mmol) in MeOH (4 mL) was stirred at 25 ^{o}C in a sealed tube. Subsequently, $NaBH_4$ (75.6 mg, 2 mmol) added to the above solution. Then the reaction was determined by TLC analysis. After the **3aa** was consumed completely, the reaction mixture was quenched by the addition of NH_4Cl

aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 5:1) afforded the product **8** as a white solid (41.3 mg, 71% yield) with 90% *ee*. mp: 66-67 ^oC. ^1H NMR (300 MHz, $CDCl_3$) δ 7.71-7.67 (m, 2H), 7.39-7.36 (m, 2H), 4.42-4.39 (m, 1H), 4.08-4.03 (m, 1H), 3.84-3.78 (m, 1H), 3.37-3.31 (m, 1H), 2.91-2.85 (m, 1H), 1.94 (d, J = 37.7 Hz, 1H), 1.35 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -77.10. ^{13}C NMR (126 MHz, $CDCl_3$) δ 170.22, 137.36, 131.52, 128.94, 128.80, 128.61 (q, J_{C-F} = 281.1 Hz), 75.82, 62.04, 48.84 (q, J = 25.1 Hz), 45.41 (d, J = 1.9 Hz), 15.78 (d, J = 2.8 Hz). ESI-MS calculated for $C_{13}H_{14}ClF_3NO$: m/z (%): 292.0711 ($M+H^+$), found: 292.0714. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 18.2 min, minor enantiomer tr = 40.1 min. $[\alpha]_D^{25}$ = +75.5% (*c* = 0.50, $CHCl_3$).

2.28 Synthesis of ((2*S*,3*S*)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-yl)diphenylmethanol (**9a**).

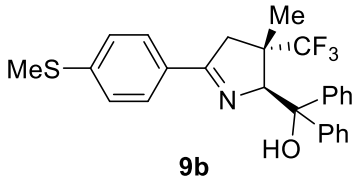


9a

The solution of compound **3aa** (63.8 mg, 0.2 mmol) in THF (4 mL) was stirred at -50 ^oC in a sealed tube. Subsequently, PhLi (0.6 mmol) added to the above solution. Then the reaction was determined by TLC analysis. After the **3aa** was consumed completely, the reaction mixture was quenched by the addition of NH_4Cl aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 5:1) afforded the product **9a** as a white solid (66.5 mg, 75% yield) with 90% *ee*. mp: 120-121 ^oC. ^1H NMR (400 MHz,

$CDCl_3$) δ 7.68-7.63 (m, 6H), 7.35-7.29 (m, 6H), 7.21-7.16 (m, 2H), 5.82 (d, *J* = 2.1 Hz, 1H), 3.38 (d, *J* = 17.7 Hz, 1H), 2.98-2.93 (m, 1H), 2.38 (s, 1H), 1.04 (s, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -78.42. ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.42, 147.95, 144.38, 137.30, 131.57, 129.15, 129.11 (q, J_{C-F} = 280.8 Hz), 128.74, 128.17, 128.17, 126.60, 126.46, 125.54, 125.23, 80.38, 78.70, 50.60 (q, *J* = 23.9 Hz), 46.33 (d, *J* = 2.0 Hz), 17.40 (d, *J* = 2.9 Hz). ESI-MS calculated for $C_{25}H_{22}ClF_3NO$: m/z (%): 444.1337 ($M+H^+$), found: 444.1348. Enantiomeric excess was determined by HPLC with a Chiralpak OJH column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 254 nm); major enantiomer tr = 20.8 min, minor enantiomer tr = 12.1 min. $[\alpha]_D^{25}$ = -10.7 (*c* = 0.50, $CHCl_3$).

2.29 Synthesis of ((2*S*,3*S*)-3-methyl-5-(4-(methylthio)phenyl)-3-(trifluoromethyl)-3,4-dihydro-2*H*-pyrrol-2-yl)diphenylmethanol (**9b**).

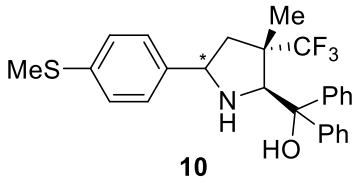


9b

The solution of compound **3aa** (66.2 mg, 0.2 mmol) in THF (4 mL) was stirred at -50 ^oC in a sealed tube. Subsequently, PhLi (0.6 mmol) added to the above solution. Then the reaction was determined by TLC analysis. After the **3aa** was consumed completely, the reaction mixture was quenched by the addition of NH_4Cl aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 5:1) afforded the product **9b** as a white solid (77.4 mg, 85% yield) with 96% *ee*. mp: 61-62 ^oC. ^1H NMR (500 MHz, $CDCl_3$) δ 7.70-7.64 (m, 6H), 7.34-7.31 (m, 4H), 7.21 (d, *J* = 8.3 Hz, 4H), 5.84 (s, 1H), 3.42-3.39 (m, 1H), 2.97 (d, *J* = 17.7 Hz, 1H), 2.48 (s, 1H), 2.43-2.42 (m, 1H), 1.06 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -78.27 (d, *J* = 3.2 Hz). ^{13}C NMR (126 MHz, $CDCl_3$) δ 171.87, 148.12, 144.46, 142.92, 129.60, 128.76 (q, J_{C-F} = 280.7 Hz), 128.15, 128.12,

127.88, 126.52, 126.35, 125.55, 125.44, 125.25, 80.35, 78.57, 50.48 (q, J = 24.0 Hz), 46.30, 17.43, 15.06. MS (EI): m/z (%) = 455 (M^+, 0.43), 183 (100); HRMS calculated for $[C_{26}H_{24}NOF_3S]^+$: 455.1531 found: 455.1527. Enantiomeric excess was determined by HPLC with a Chiralpak IF column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 210 nm); major enantiomer tr = 7.1 min, minor enantiomer tr = 8.1 min. $[\alpha]_D^{25}$ = -80.7 (c = 0.50, $CHCl_3$).

2.30 Synthesis of ((2*S*,3*S*)-3-methyl-5-(4-(methylthio)phenyl)-3-(trifluoromethyl)-pyrrolidin-2-yl)diphenylmethanol (**10**).

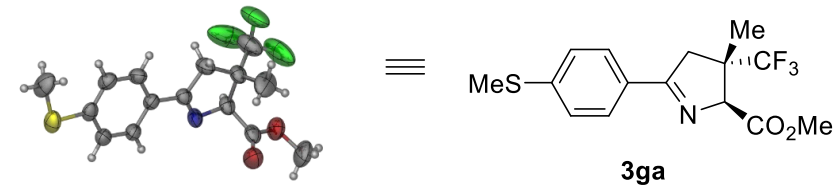


10

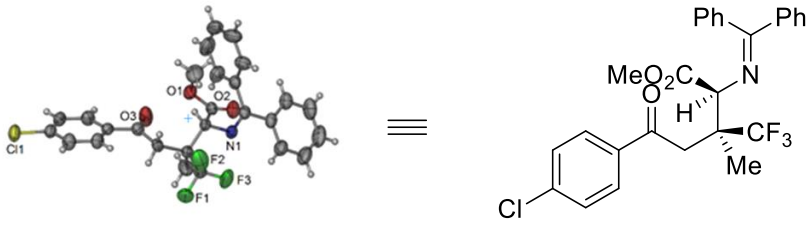
The solution of compound **9b** (45.5 mg, 0.1 mmol) in EtOH/AcOH (10:1, 2 mL) was stirred at rt in a sealed tube. Subsequently, $NaBCNH_3$ (0.6 mmol) added to the above solution. Then the reaction was determined by TLC analysis. After the **9b** was consumed completely, the reaction mixture was quenched by the addition of $NaHCO_3$ aq. and diluted with EtOAc. The organic layer was separated, and the aqueous layer was extracted twice with EtOAc. The combined organic layers were dried over Na_2SO_4, filtered, concentrated. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 5:1) afforded the product **10** as a ropy liquid (42.5 mg, 93% total yield) with 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.63 (d, J = 7.5 Hz, 4H), 7.24-7.07 (m, 10H), 4.87 (s, 1H), 4.76 (s, 1H), 4.32-4.26 (m, 1H), 2.44-2.39 (m, 1H), 2.42 (s, 3H), 2.09 (s, 1H), 1.68-1.62 (m, 1H), 0.95 (s, 3H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -74.38. ^{13}C NMR (126 MHz, $CDCl_3$) δ 149.19, 143.28, 139.13, 137.60, 129.60 (q, $J_{C\text{-}F}$ = 283.5 Hz), 128.62, 127.83, 126.86, 126.85, 126.51, 126.44, 125.40, 124.97, 78.34, 63.95, 57.65, 50.50 (q, J = 23.6 Hz), 46.26, 17.96, 15.99. ESI-MS calculated for $C_{26}H_{27}F_3NOS$: m/z (%): 458.1760 ($M+H^+$), found: 458.1762. Enantiomeric excess was determined by HPLC with a Chiralpak ASH column (hexanes: 2-propanol = 95:5, 0.8 mL/min, 210 nm); major enantiomer tr = 10.2 min, minor

enantiomer tr = 9.1 min. $[\alpha]_D^{25}$ = -33.4 (*c* = 0.50, $CHCl_3$).

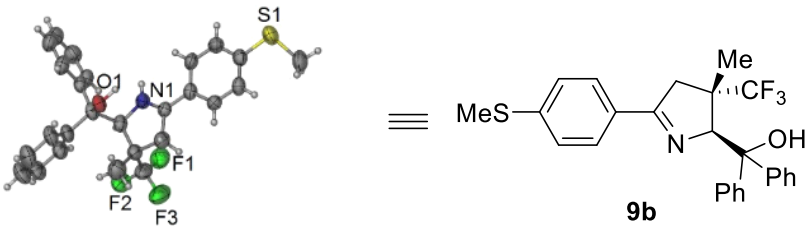
3. X-ray crystallographic analysis of 3ga, 5, 9b



3ga



5



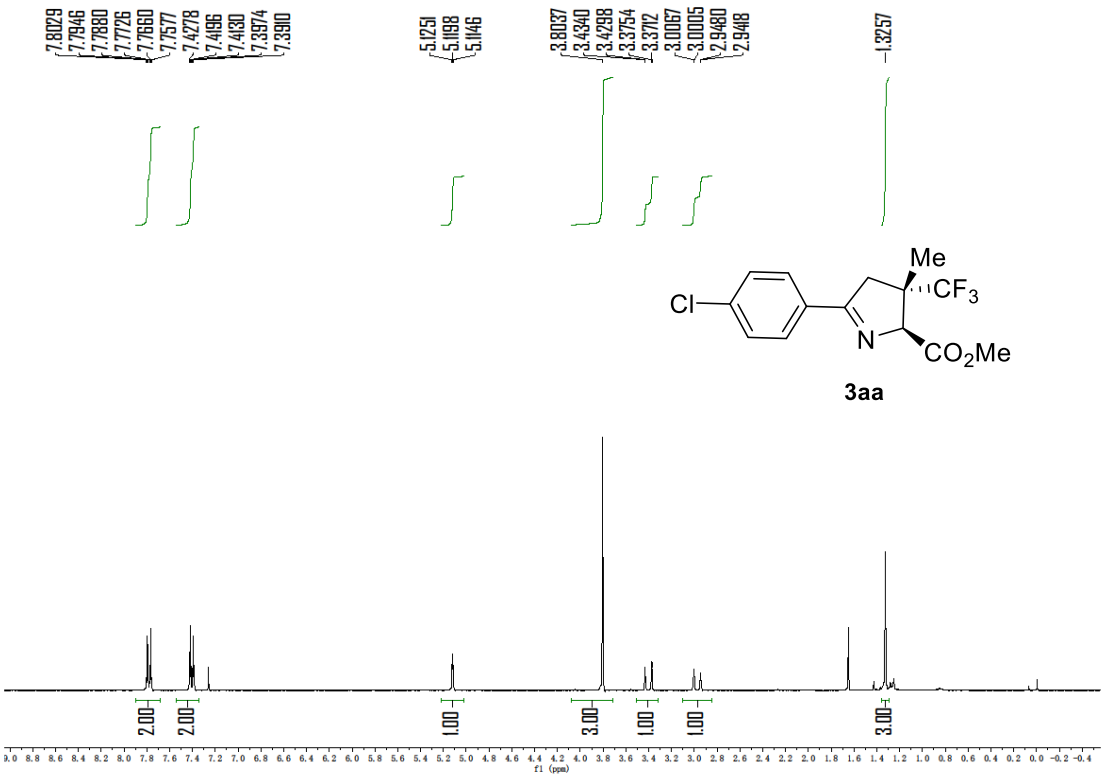
9b

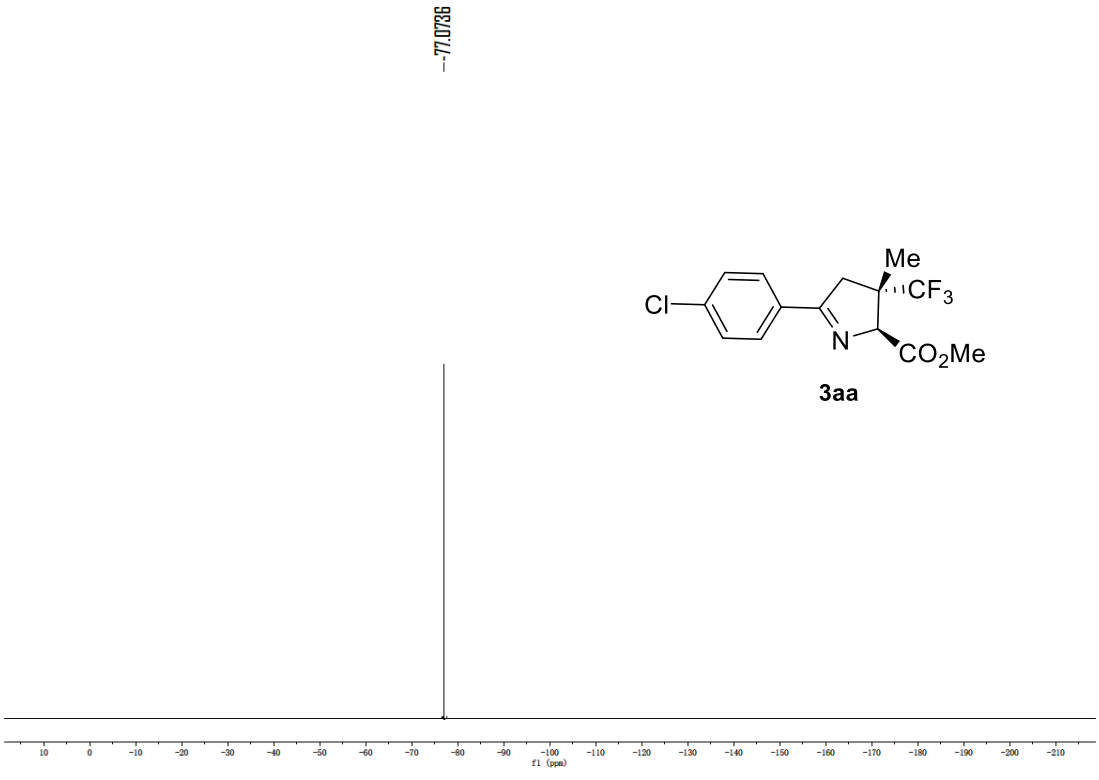
4. References

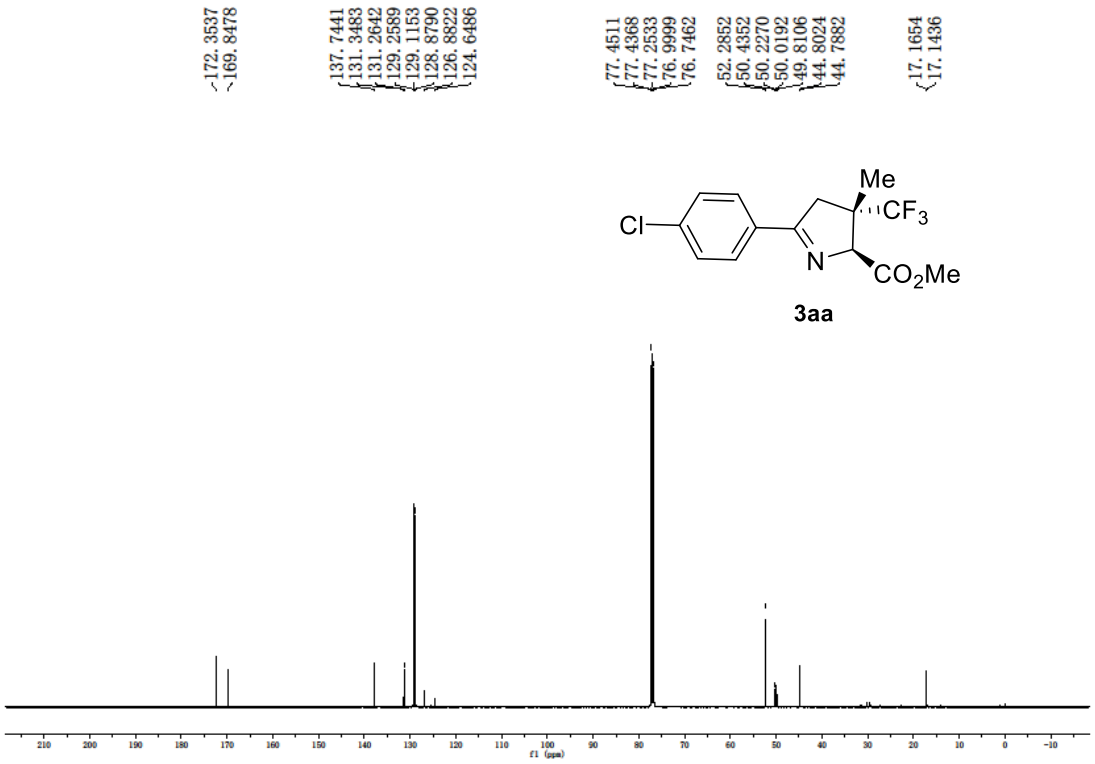
(1) (a) Ellman, J. A. *Tetrahedron* **1999**, *55*, 8883. (b) Ellman, J. A. *Org. Lett.* **2003**, *5*, 545. (c) Zhang, Z.-M.; Chen, P.; Li, W.; Niu, Y.; Zhao, X.-L.; Zhang, J. *Angew. Chem. Int. Ed.* **2014**, *53*, 4350.

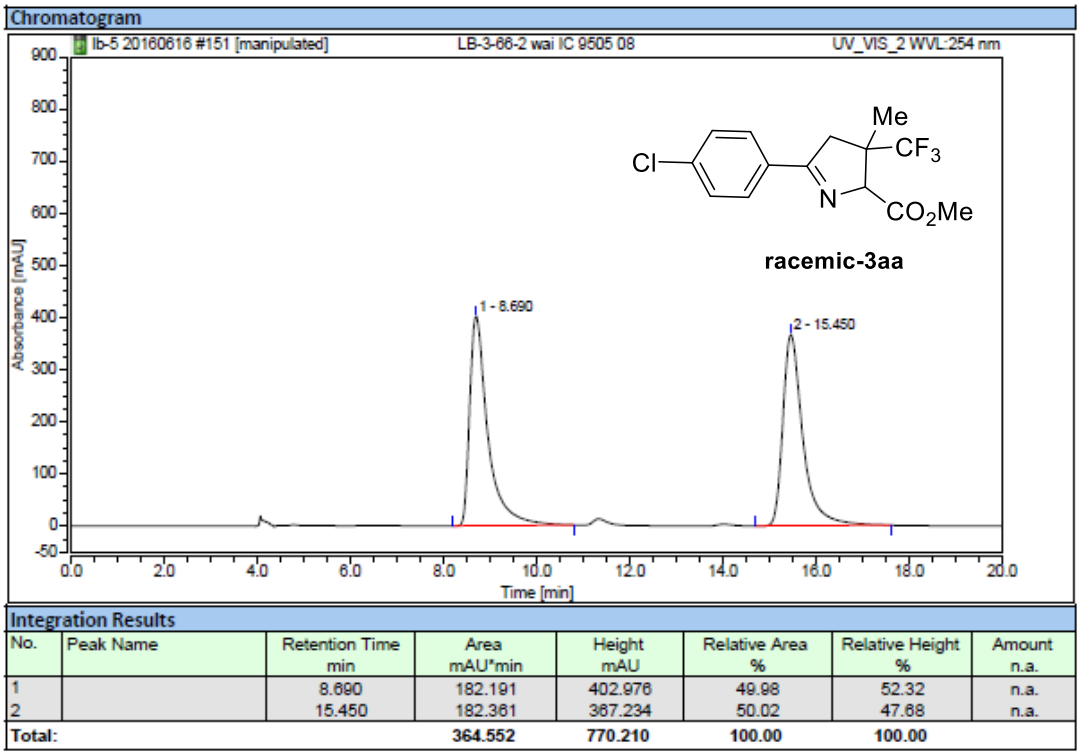
(2) (a) Kawai, H.; Okusu, S.; Tokunaga, E.; Sato, H.; Shiro, M.; Shibata, N. *Angew. Chem. Int. Ed.* **2012**, *51*, 4959. (b) Kawai, H.; Yuan, Z.; Kitayama, T.; Tokunaga, E.; Shibata, N. *Angew. Chem. Int. Ed.* **2013**, *52*, 5575.

5. ^{1}H , ^{19}F, ^{31}P, ^{13}C NMR and HPLC Spectra



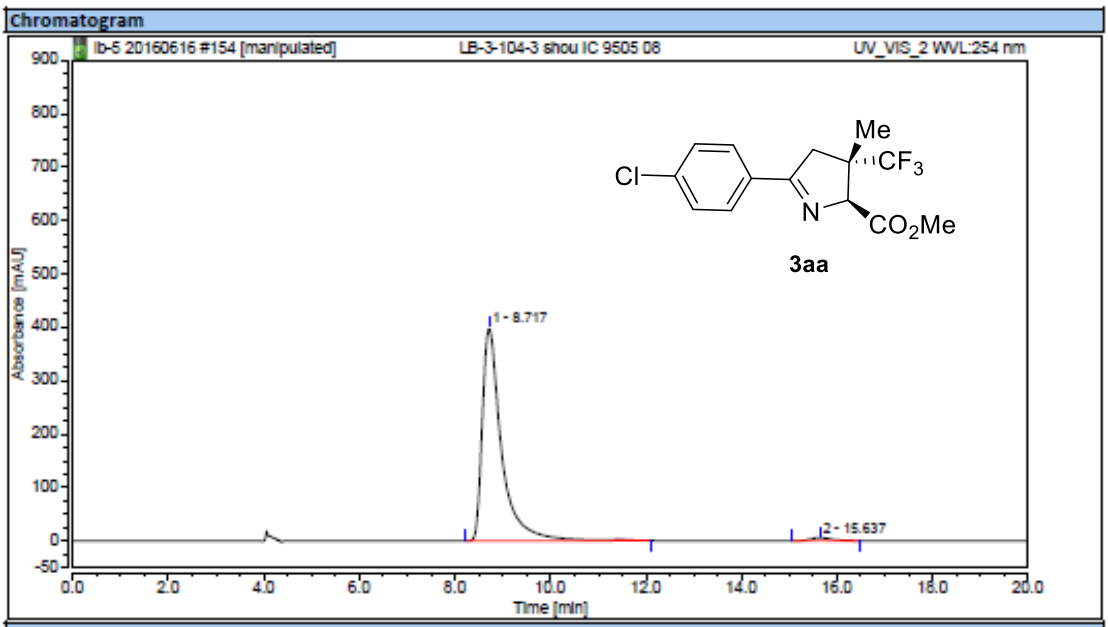






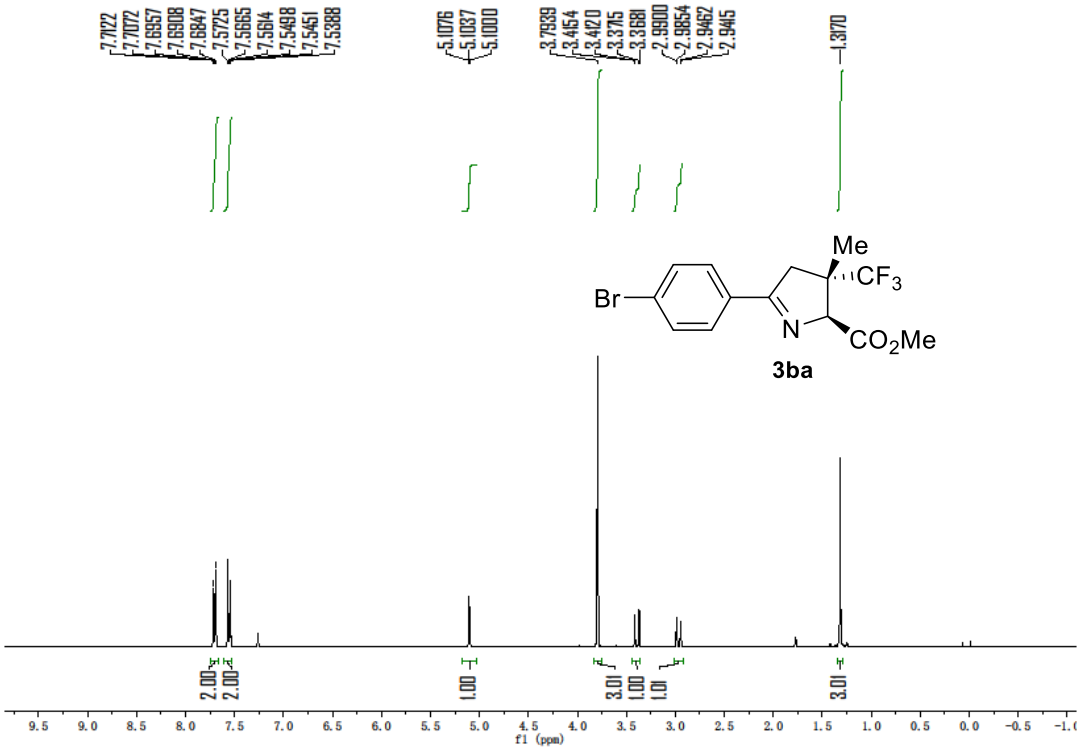
Integration Results

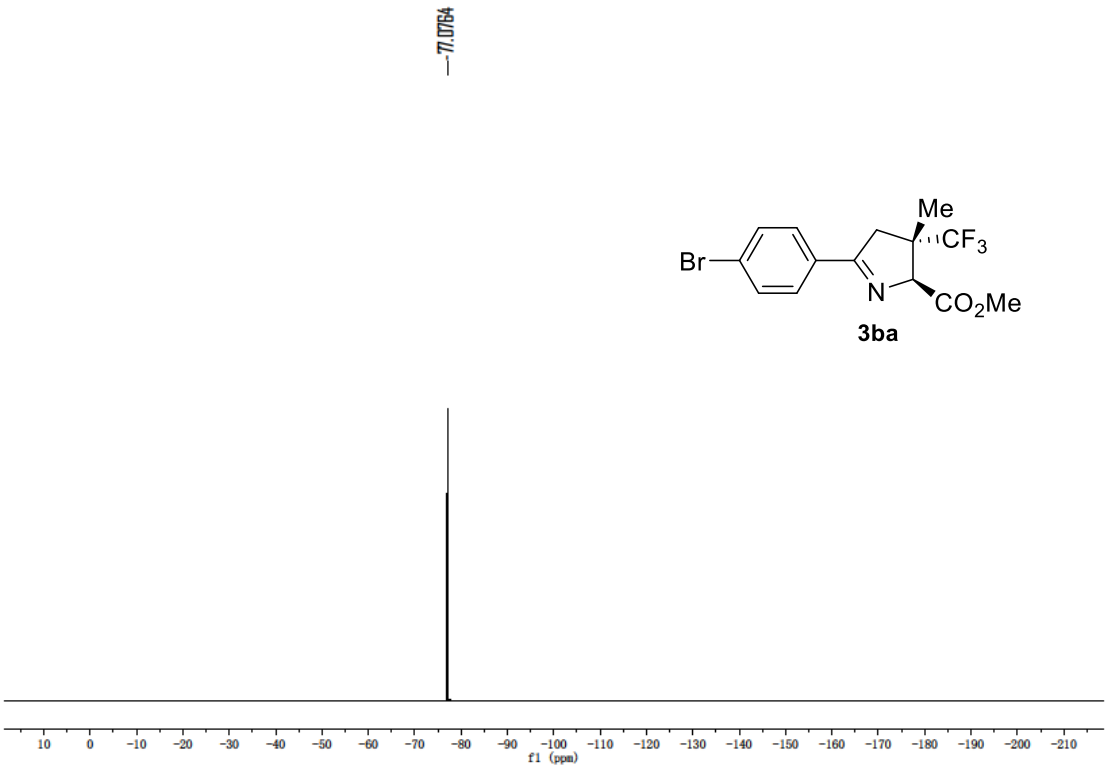
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.690	182.191	402.976	49.98	52.32	n.a.
2		15.450	182.361	367.234	50.02	47.68	n.a.
Total:			**364.552**	**770.210**	**100.00**	**100.00**	

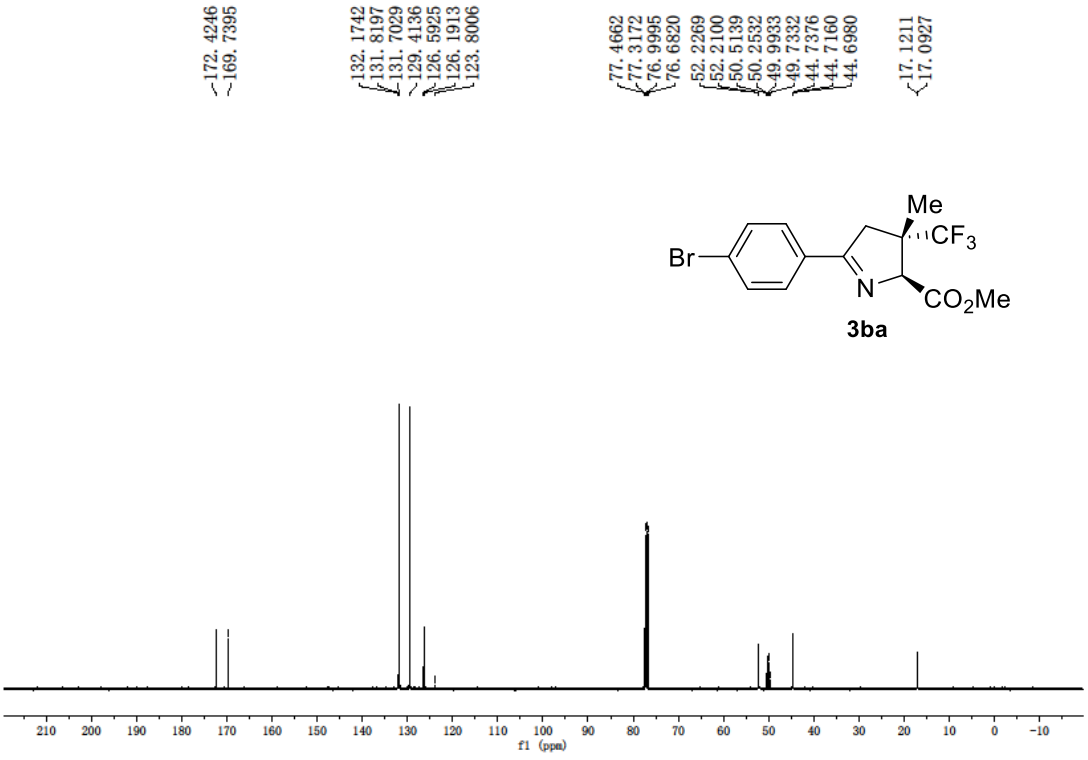


Integration Results

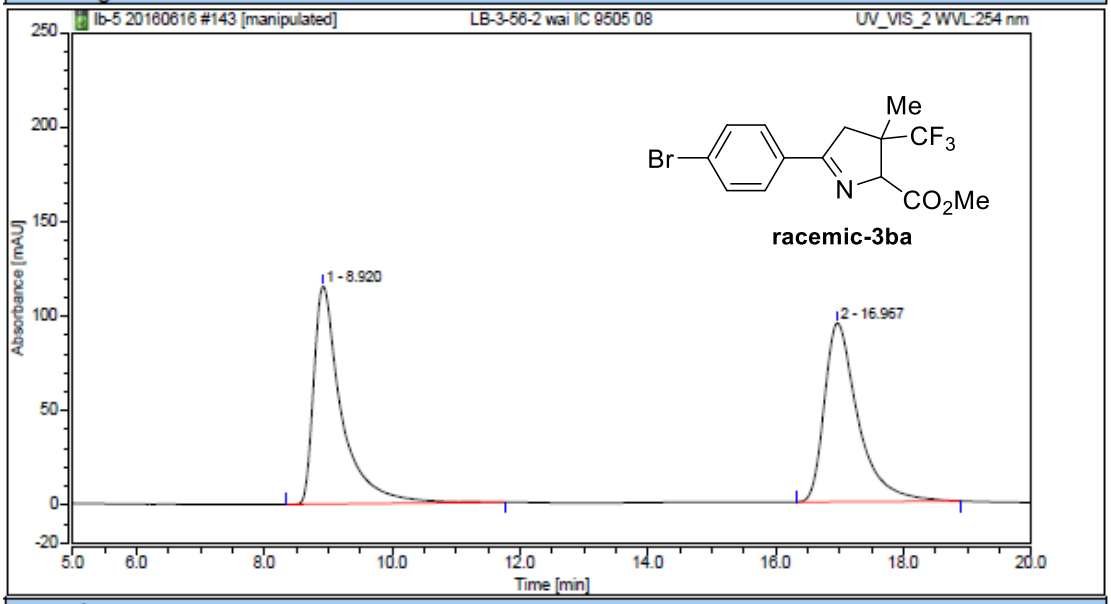
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.717	187.258	398.876	98.37	98.55	n.a.
2		15.637	3.095	5.866	1.63	1.45	n.a.
Total:			**190.354**	**404.742**	**100.00**	**100.00**	




-77.0764
Me
CF3
Br
N
CO2Me
3ba
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


172.4246
169.7395
132.1742
131.8197
131.7029
129.4136
126.5925
126.1913
123.8006
77.4662
77.3172
76.9995
76.6820
52.2269
52.2100
50.5139
50.2532
49.9933
49.7332
44.7376
44.7160
44.6980
17.1211
17.0927
Me
CF3
Br
N
CO2Me
3ba
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

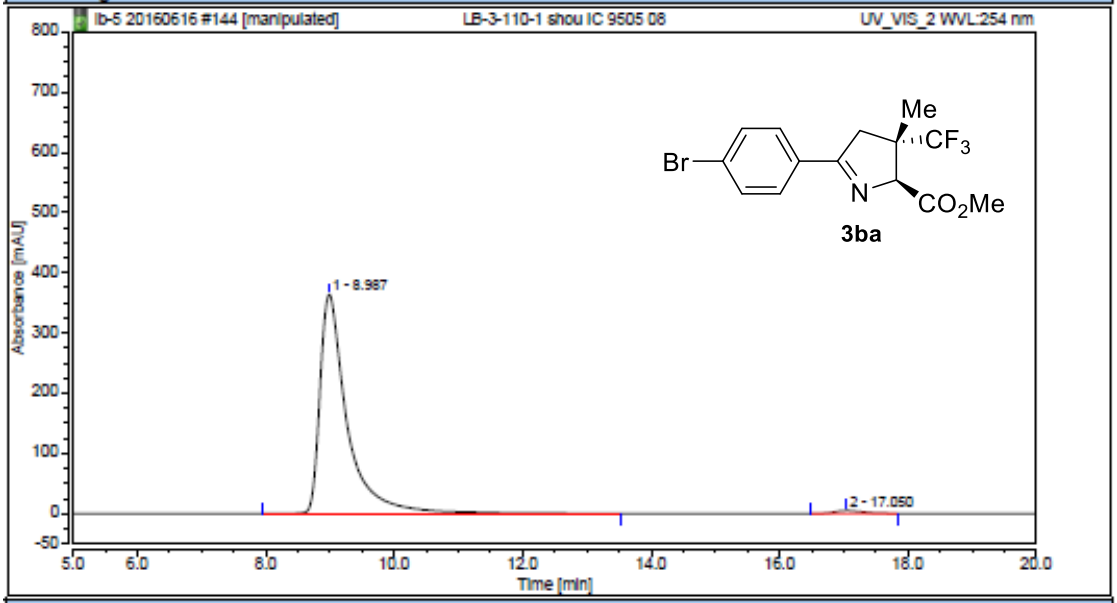
Chromatogram



Integration Results

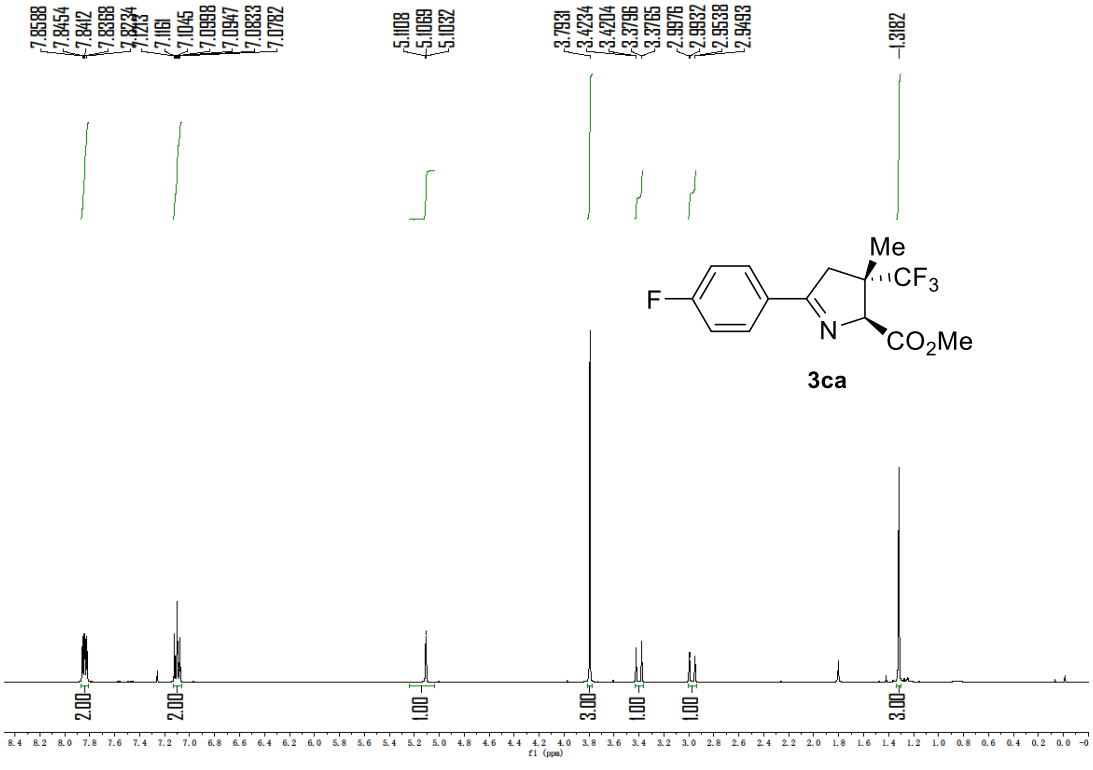
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.920	57.874	115.354	50.04	54.94	n.a.
2		16.967	57.787	94.608	49.96	45.06	n.a.
Total:			**115.661**	**209.961**	**100.00**	**100.00**	

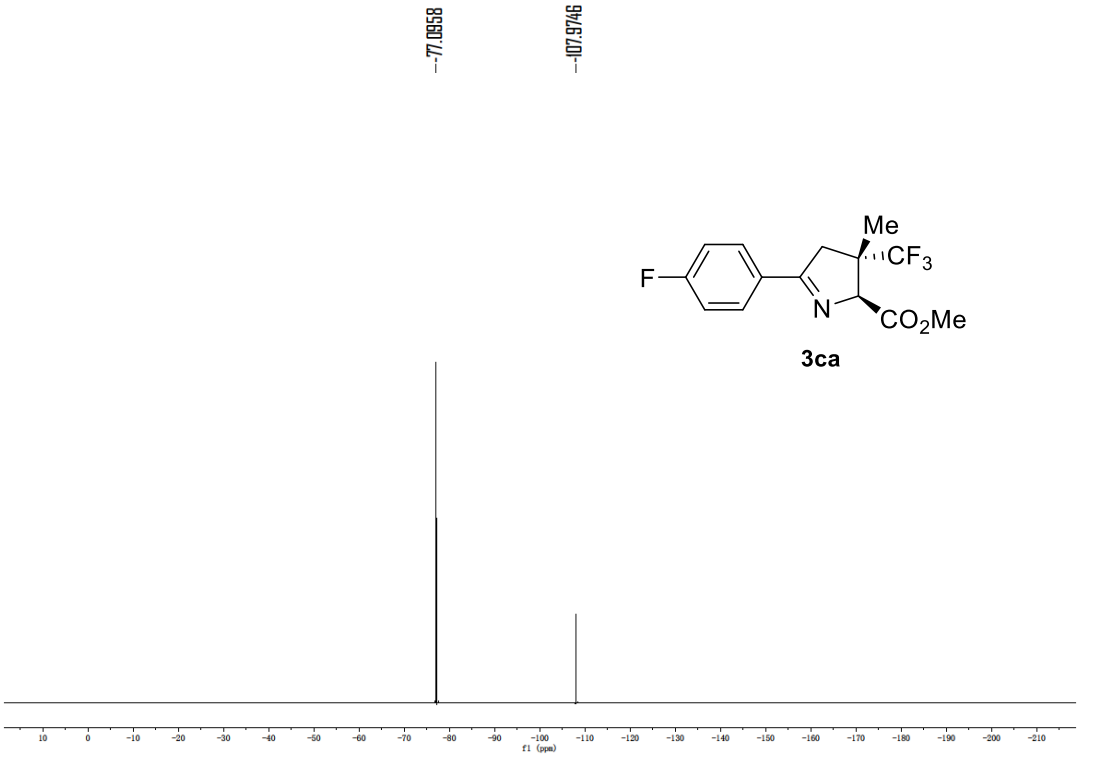
Chromatogram



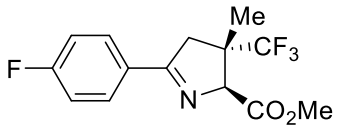
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.987	179.149	363.988	98.63	98.63	n.a.
2		17.050	2.485	5.059	1.37	1.37	n.a.
Total:			**181.633**	**369.047**	**100.00**	**100.00**	

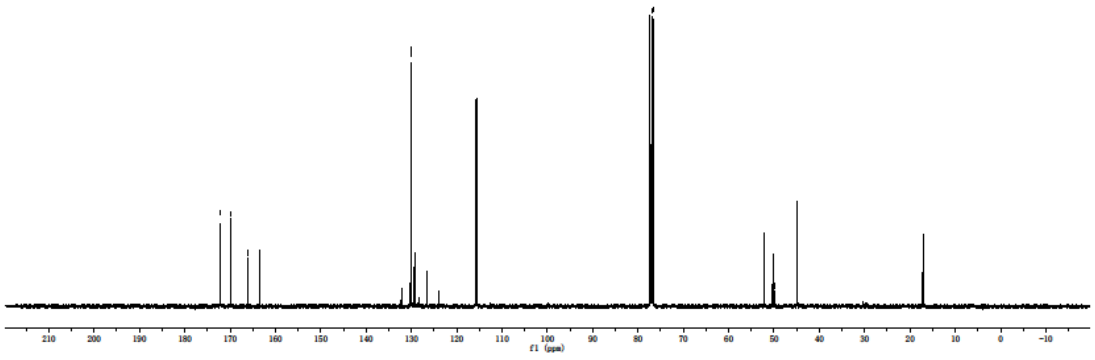

7.8588
7.8454
7.8412
7.8368
7.8234
7.1213
7.1161
7.1045
7.0998
7.0947
7.0833
7.0782
5.1108
5.1069
5.1032
3.7931
3.4234
3.4204
3.3796
3.3765
2.9876
2.9832
2.9538
2.9493
1.3182
Me
CF3
F
N
CO2Me
3ca
2.00
2.00
1.00
3.00
1.00
1.00
3.00
f1 (ppm)

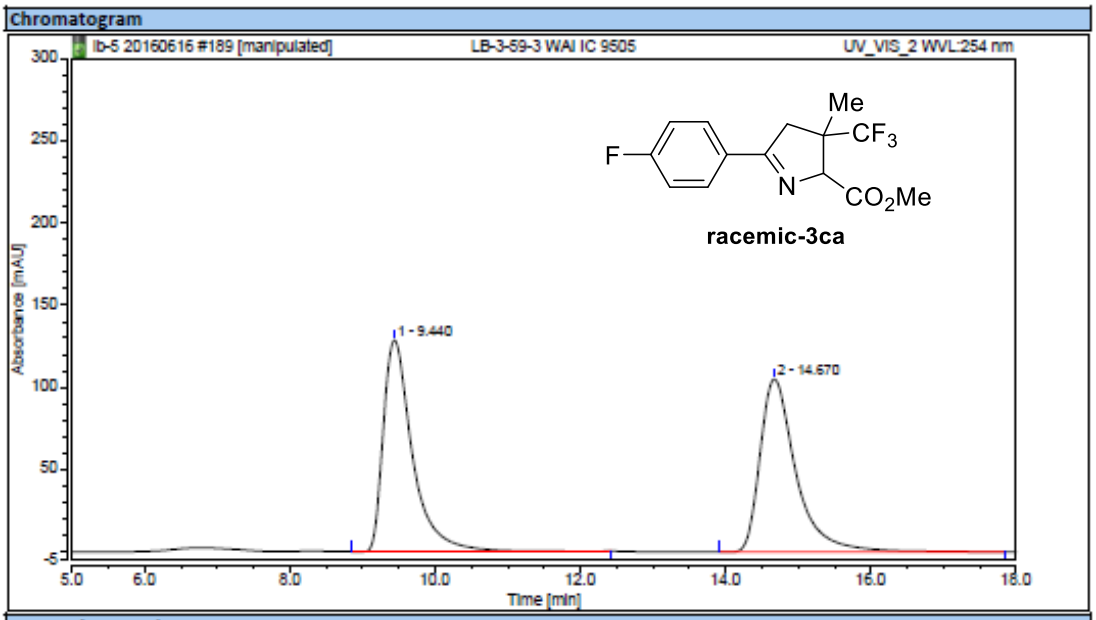

-77.0858
-107.9746
Me
CF3
F
N
CO2Me
3ca
f1 (ppm)

172.1587
169.9051
166.0195
163.5109
132.2213
130.1681
130.0804
129.4303
129.1934
129.1614
126.6392
123.8476
115.7791
115.5612
77.4021
77.3179
77.0001
76.6818
52.1913
52.1718
50.5295
50.2697
50.0105
49.7499
44.8430
44.8249
17.1313
17.1026



3ca

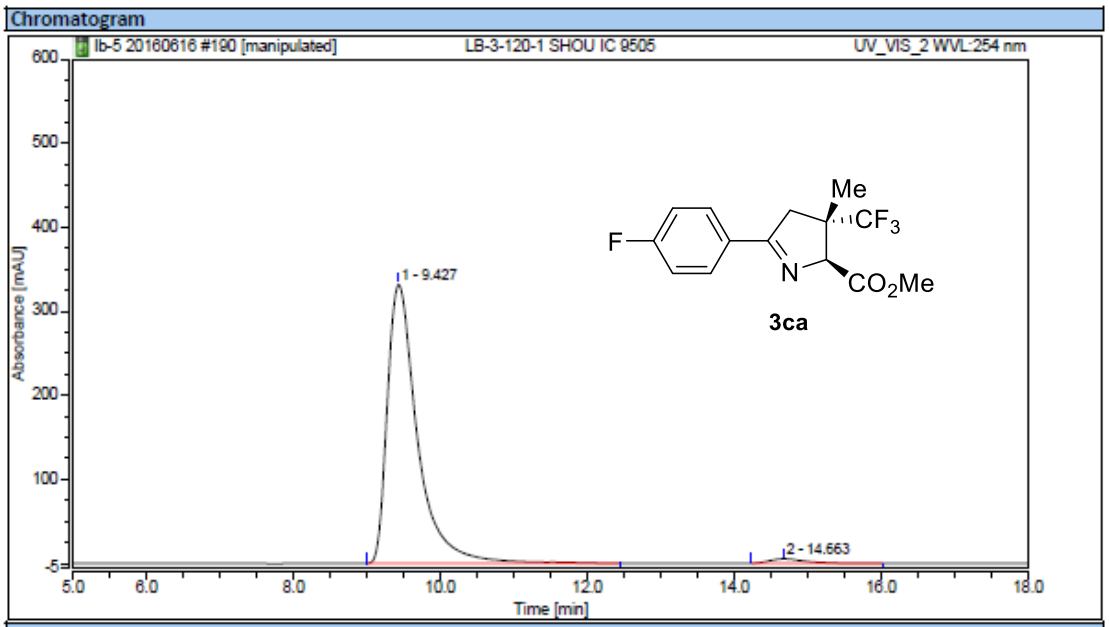




racemic-3ca

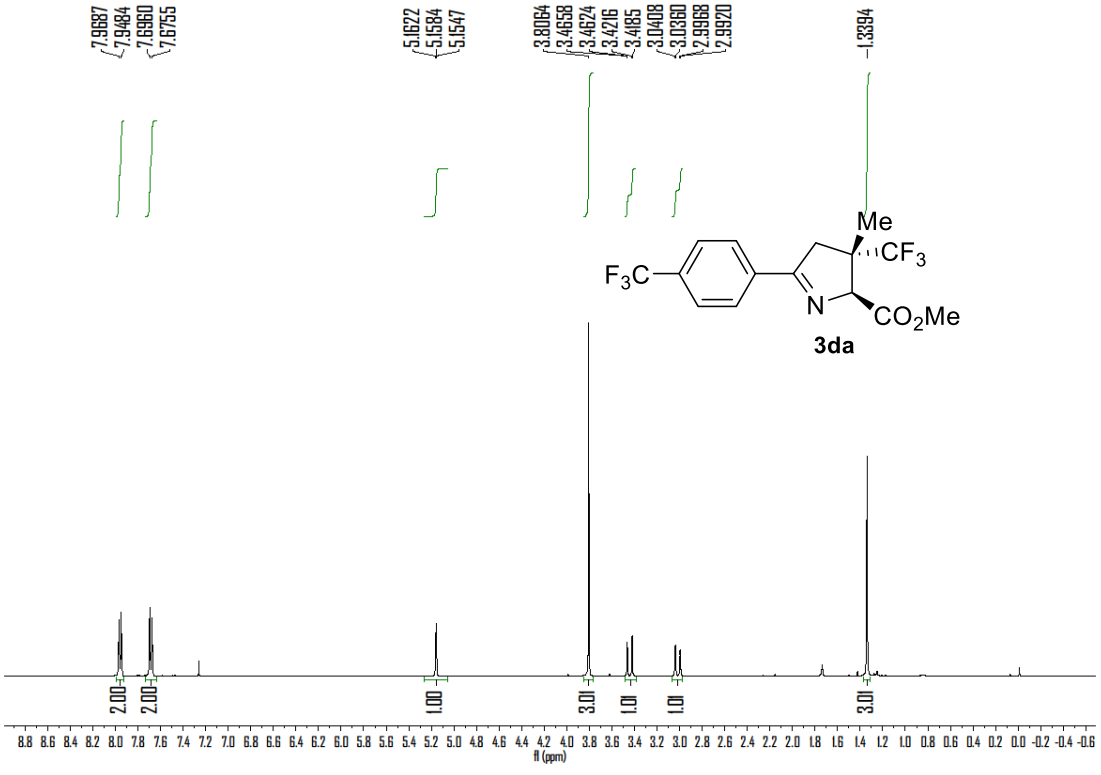
Integration Results

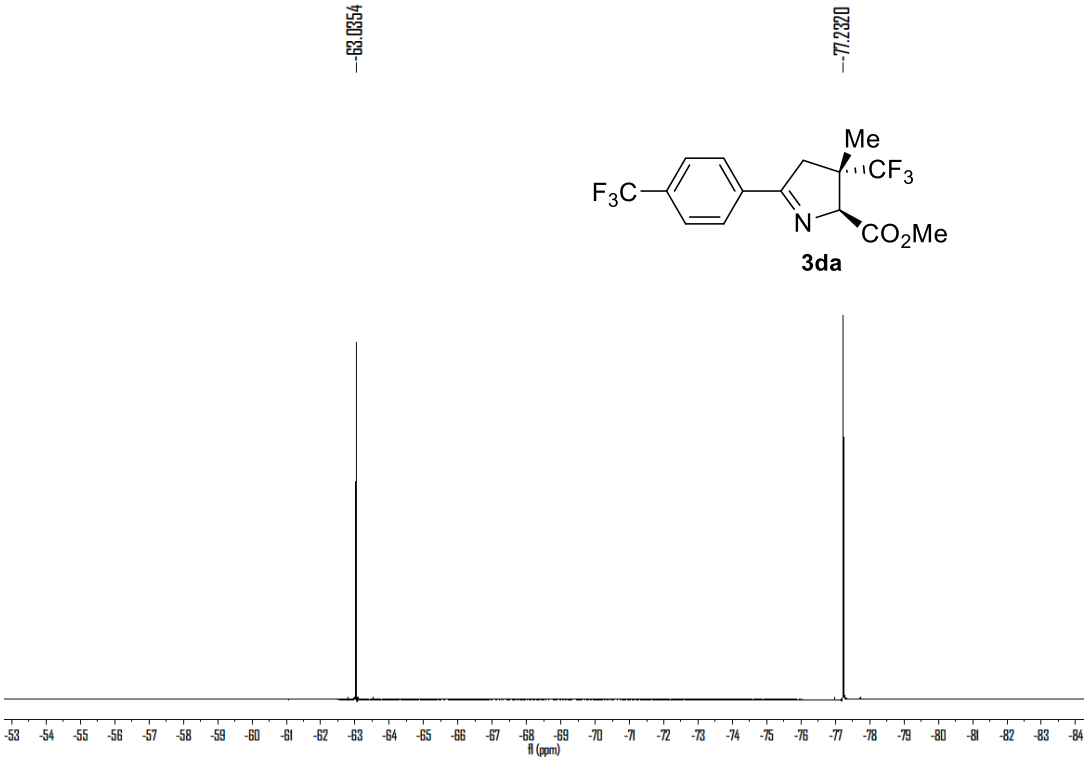
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.440	59.919	128.793	49.70	55.02	n.a.
2		14.670	60.637	105.308	50.30	44.98	n.a.
Total:			**120.555**	**234.100**	**100.00**	**100.00**	

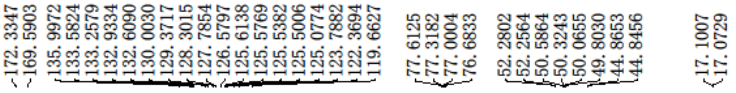


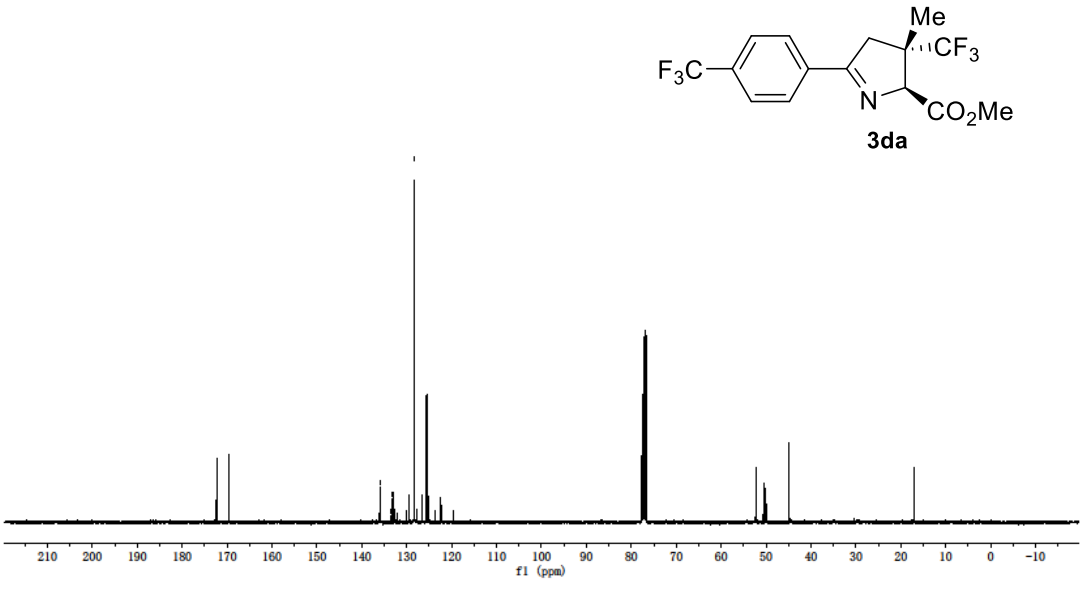
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.427	157.566	332.044	98.25	98.47	n.a.
2		14.663	2.802	5.167	1.75	1.53	n.a.
Total:			**160.368**	**337.211**	**100.00**	**100.00**	

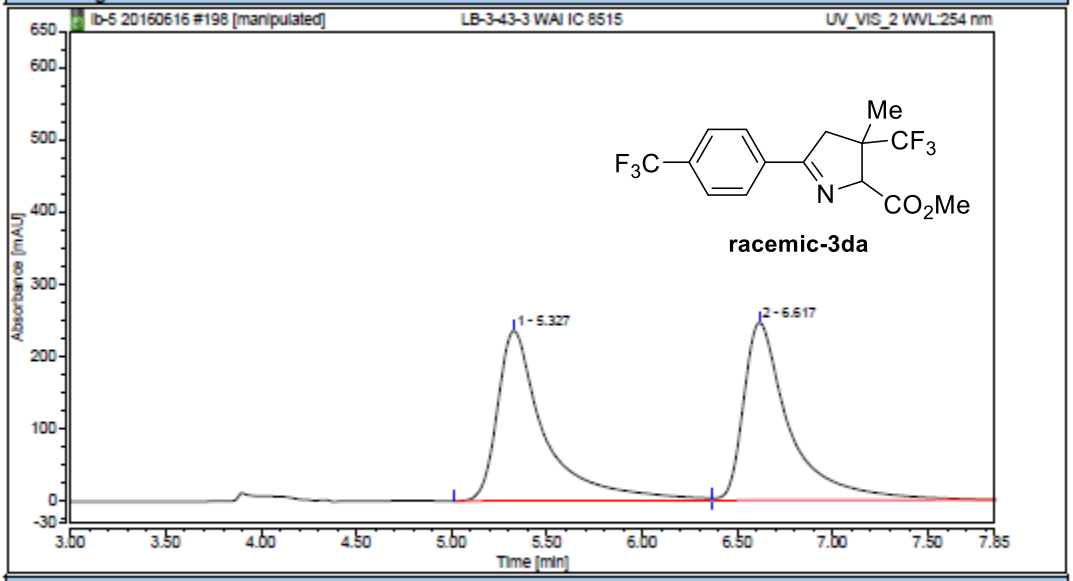



-63.0354
-77.2320
Me
CF3
F3C
N
CO2Me
3da
f1 (ppm)


172.3347
169.5903
135.9972
133.5824
133.2579
132.9334
132.6090
130.0030
129.3717
128.3015
127.7854
126.5797
125.6138
125.5769
125.5382
125.5006
125.0774
123.7882
122.3694
119.6627
77.6125
77.3182
77.0004
76.6833
52.2802
52.2564
50.5864
50.3243
50.0655
49.8030
44.8653
44.8456
17.1007
17.0729


Me
CF3
F3C
N
CO2Me
3da
f1 (ppm)

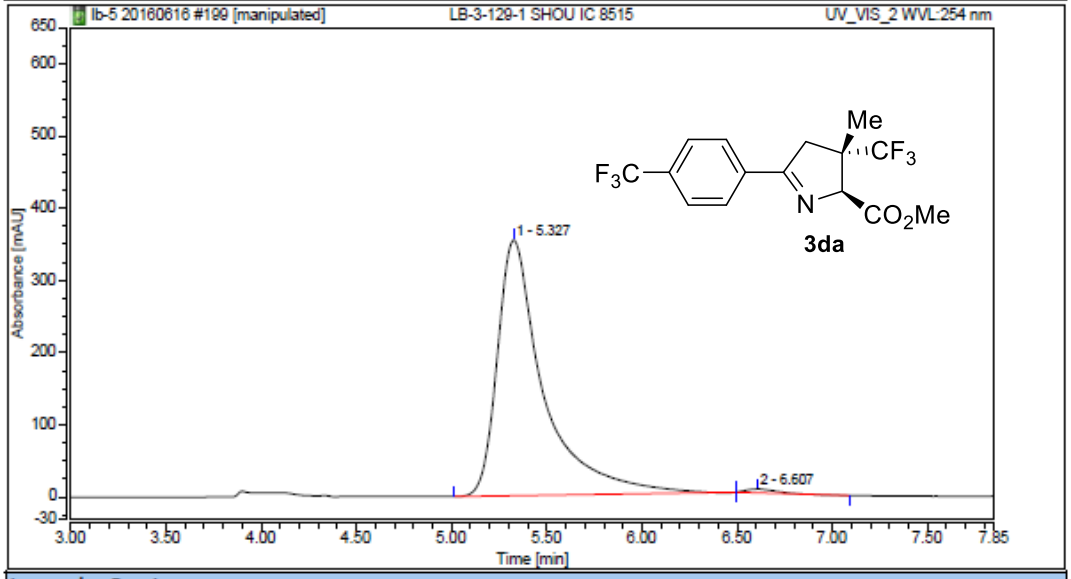
Chromatogram



Integration Results

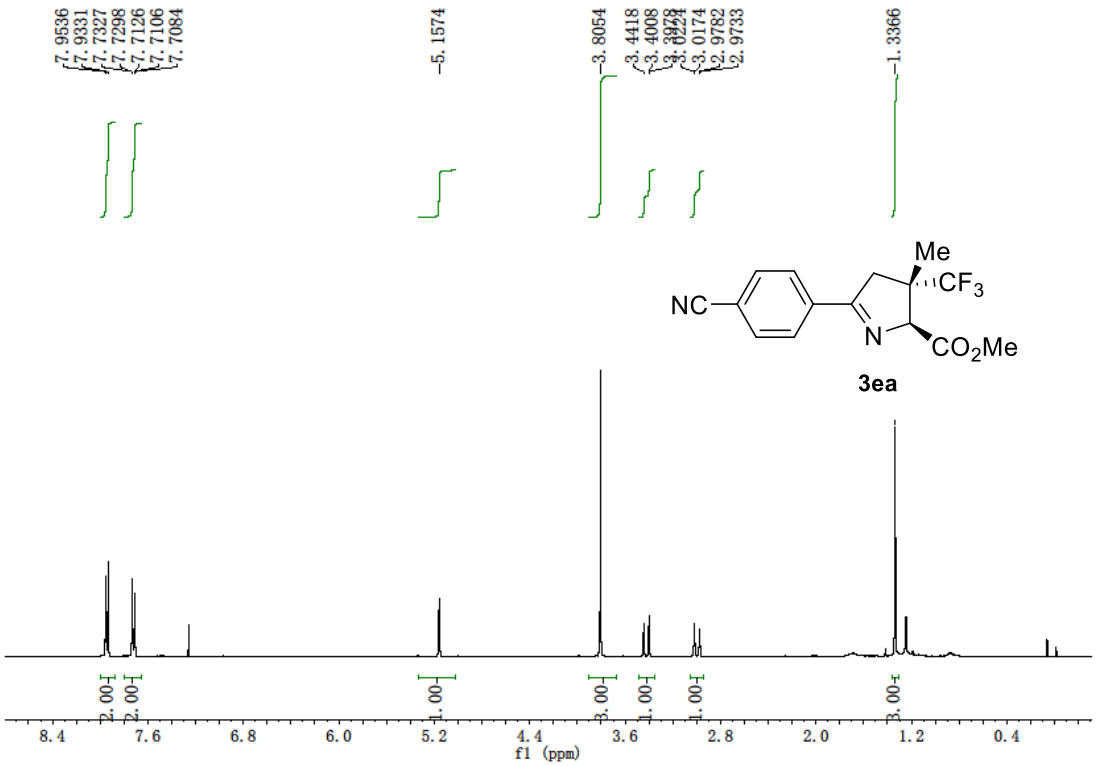
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.327	67.742	235.536	49.63	48.93	n.a.
2		6.617	68.761	245.868	50.37	51.07	n.a.
Total:			**136.503**	**481.404**	**100.00**	**100.00**	

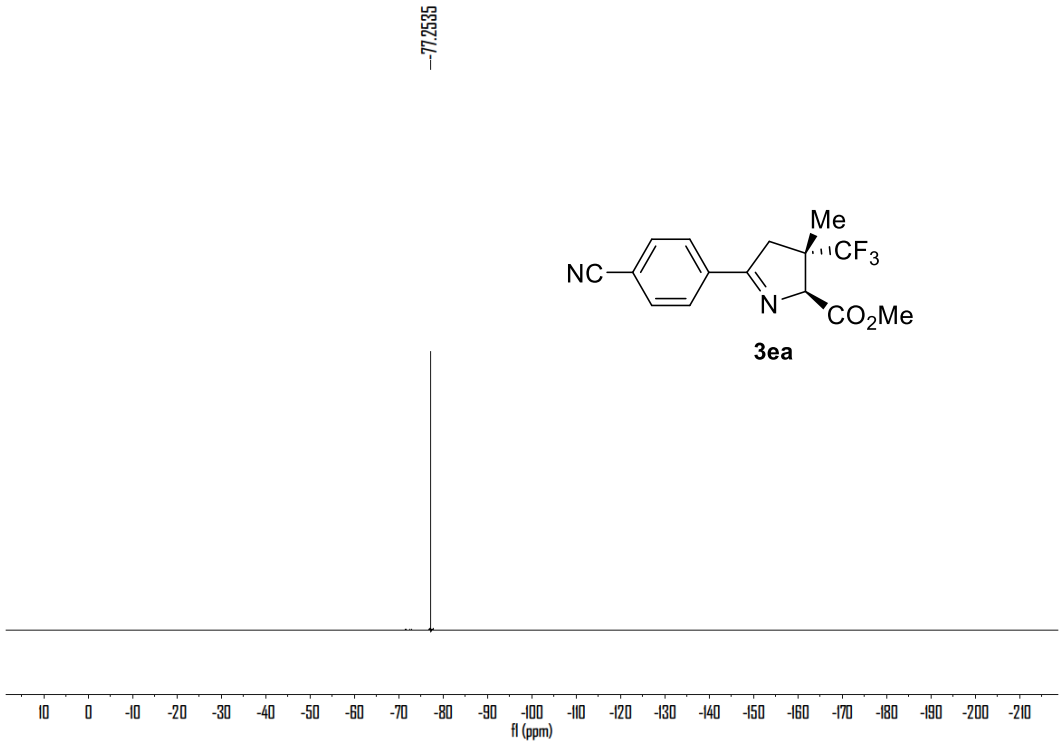
Chromatogram

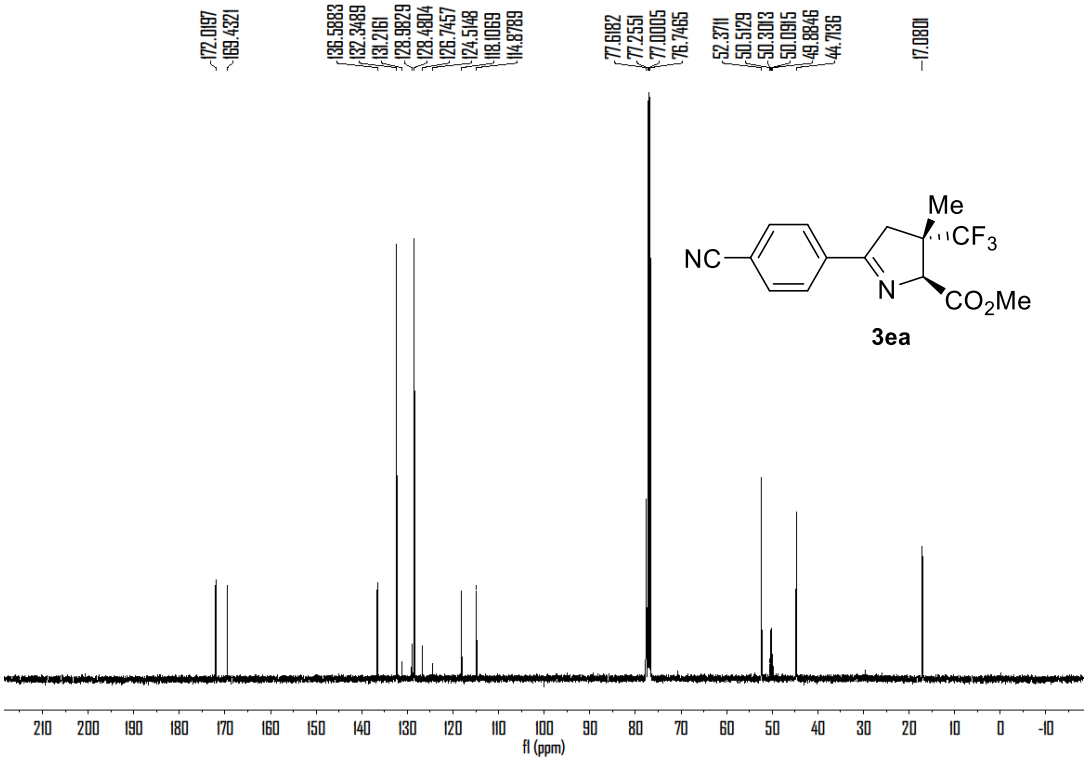


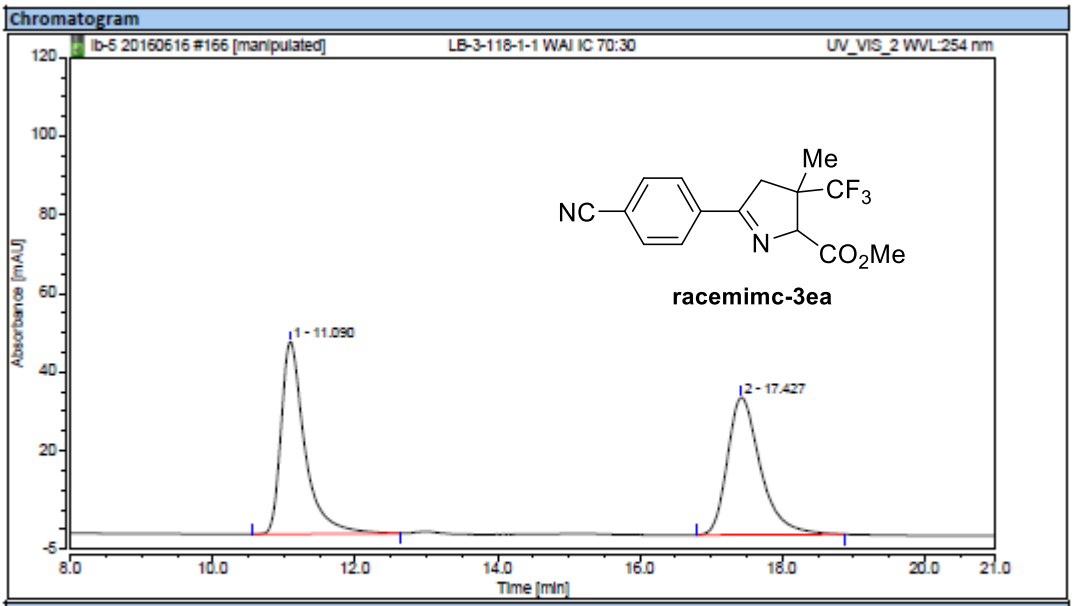
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		5.327	99.558	354.245	99.06	98.53	n.a.
2		6.607	0.941	5.298	0.94	1.47	n.a.
Total:			**100.499**	**359.542**	**100.00**	**100.00**	


7.9536
7.9331
7.7327
7.7298
7.7126
7.7106
7.7084
5.1574
3.8054
3.4418
3.4008
3.0174
2.9782
2.9733
1.3366
Me
CF3
NC
N
CO2Me
3ea
2.00
2.00
1.00
3.00
1.00
1.00
3.00
8.4
7.6
6.8
6.0
5.2
4.4
3.6
2.8
2.0
1.2
0.4
f1 (ppm)

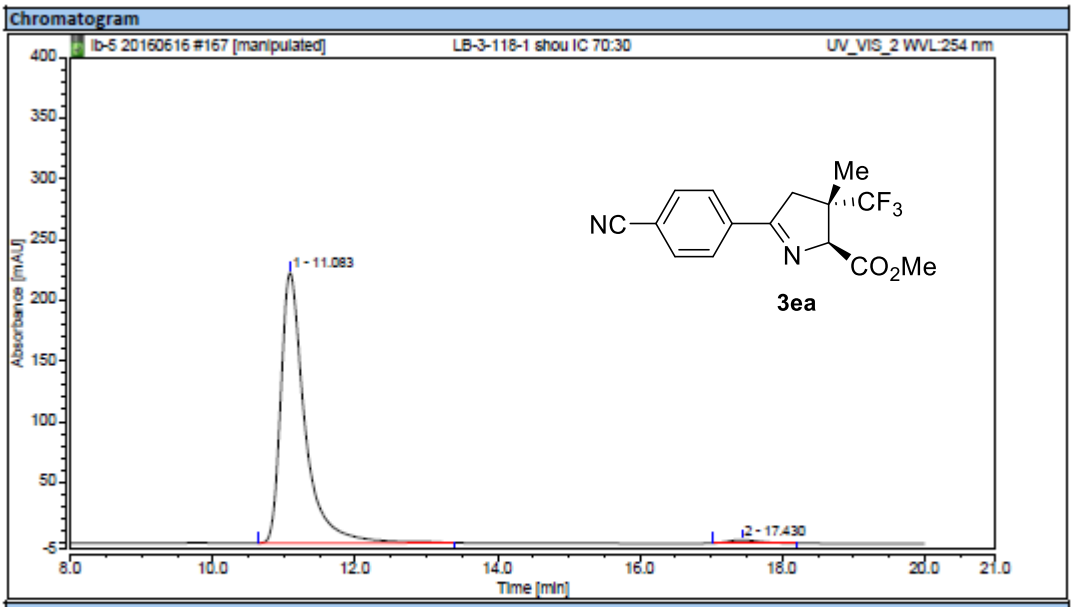

77.2535
Me
CF3
NC
N
CO2Me
3ea
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)





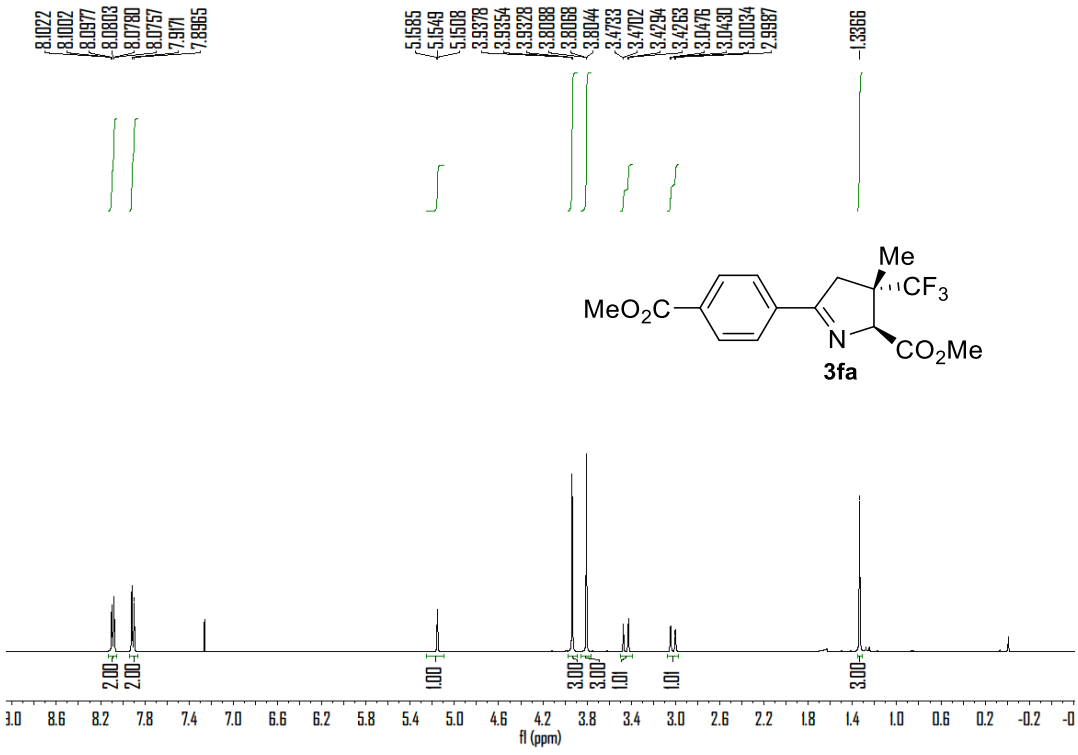
Integration Results

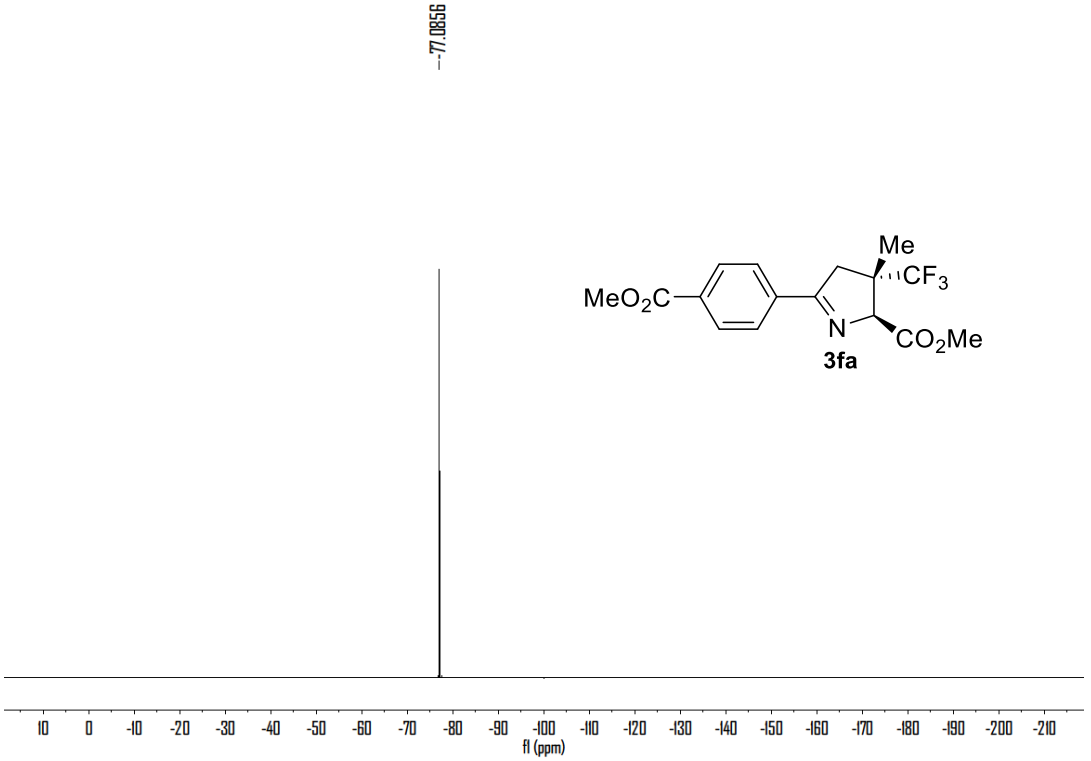
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.090	18.943	48.957	50.10	58.33	n.a.
2		17.427	18.865	34.981	49.90	41.67	n.a.
Total:			**37.808**	**83.938**	**100.00**	**100.00**	

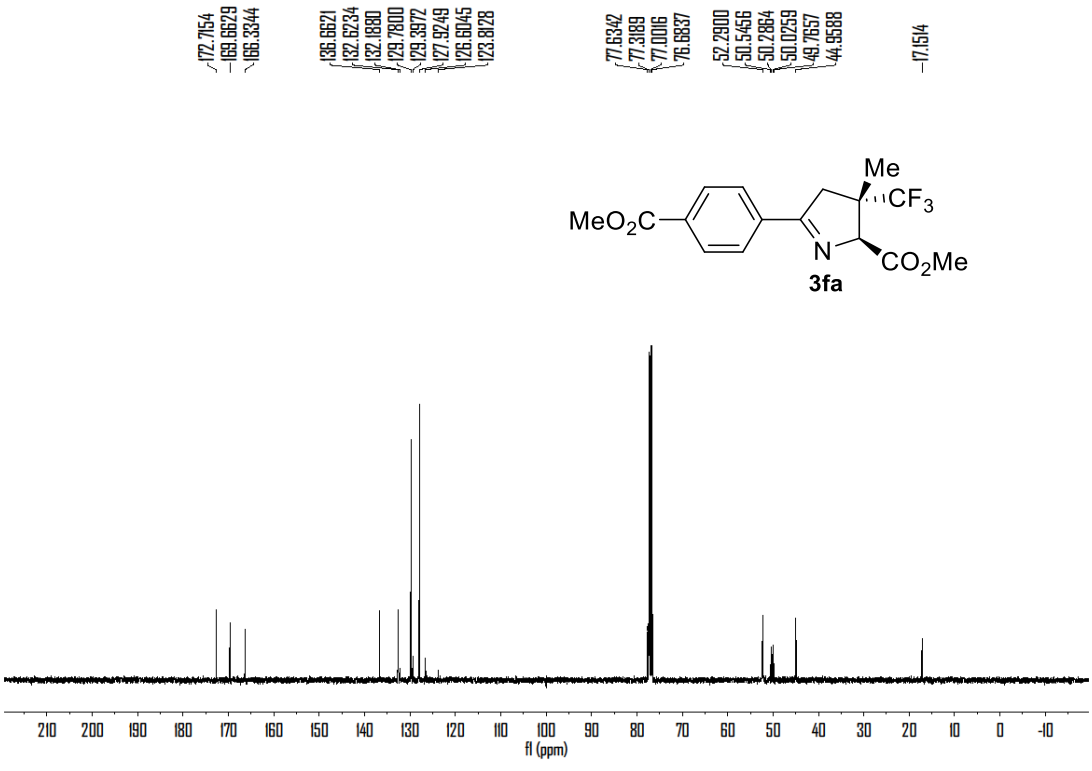


Integration Results

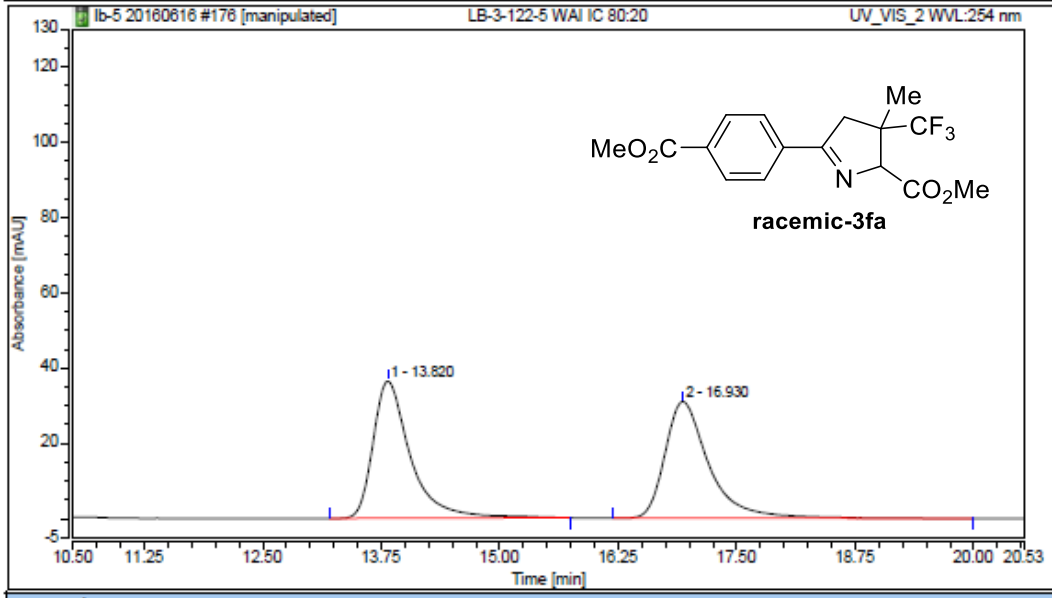
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.083	87.340	222.855	98.44	98.78	n.a.
2		17.430	1.389	2.753	1.56	1.22	n.a.
Total:			**88.728**	**225.608**	**100.00**	**100.00**	




-77.0856
Me
CF3
MeO2C
N
CO2Me
3fa
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


172.7154
169.6629
166.3344
136.6621
132.6234
132.1880
129.7800
129.3972
127.9249
126.6045
123.8128
77.6342
77.3189
77.0016
76.6837
52.2900
50.5456
50.2864
50.0259
49.7657
44.8588
17.1514
Me
CF3
MeO2C
N
CO2Me
3fa
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

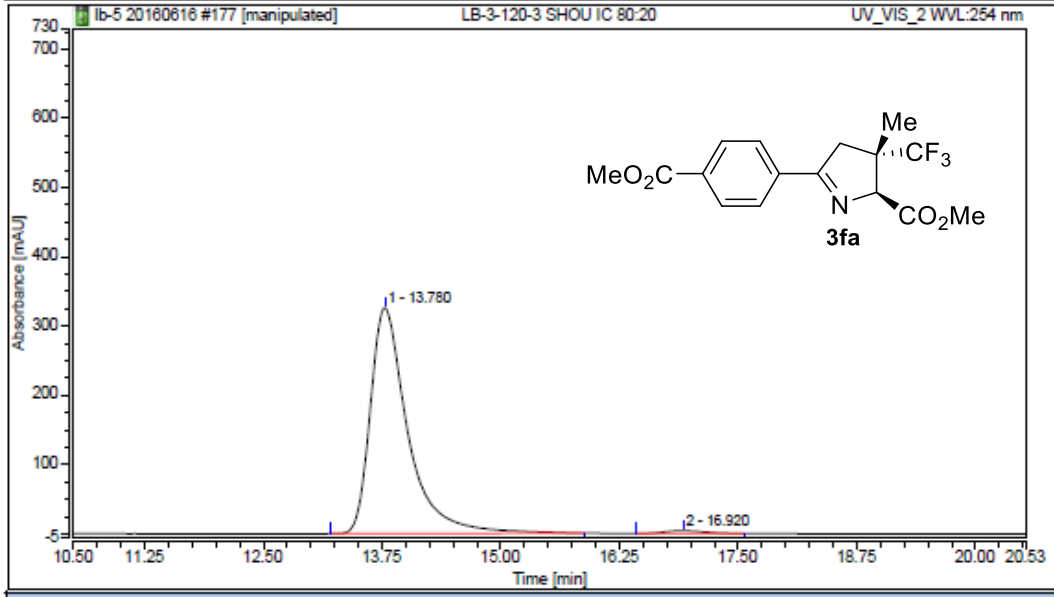
Chromatogram



Integration Results

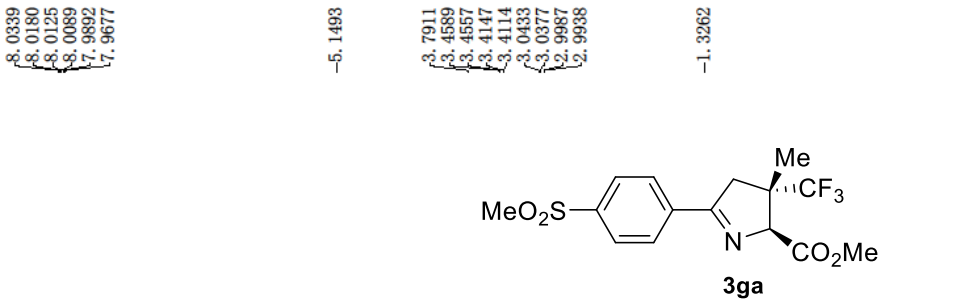
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.820	16.651	36.415	49.98	54.08	n.a.
2		16.930	16.667	30.915	50.02	45.92	n.a.
Total:			**33.318**	**67.330**	**100.00**	**100.00**	

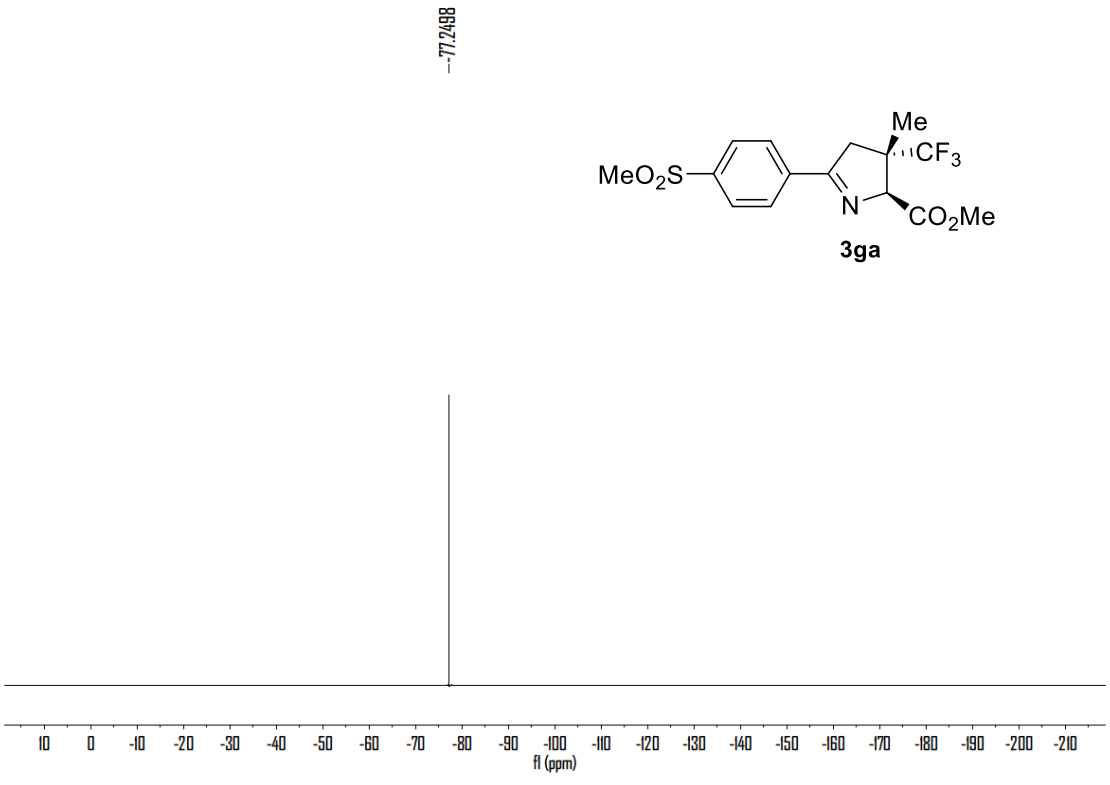
Chromatogram

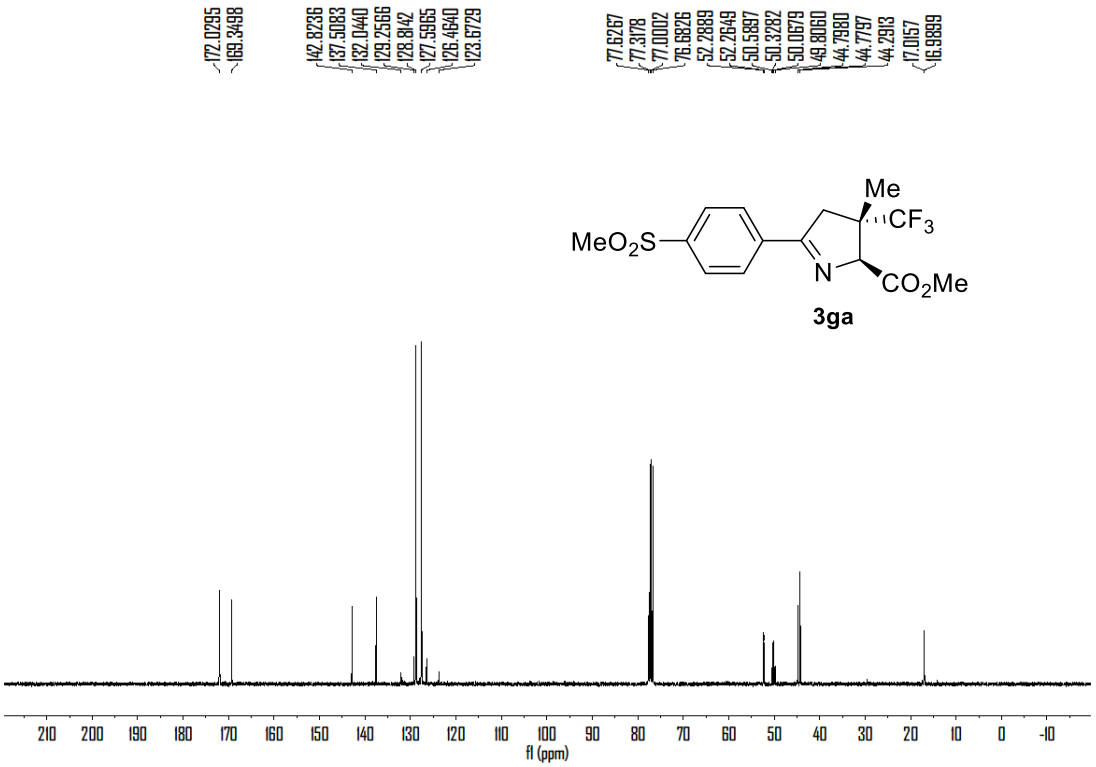


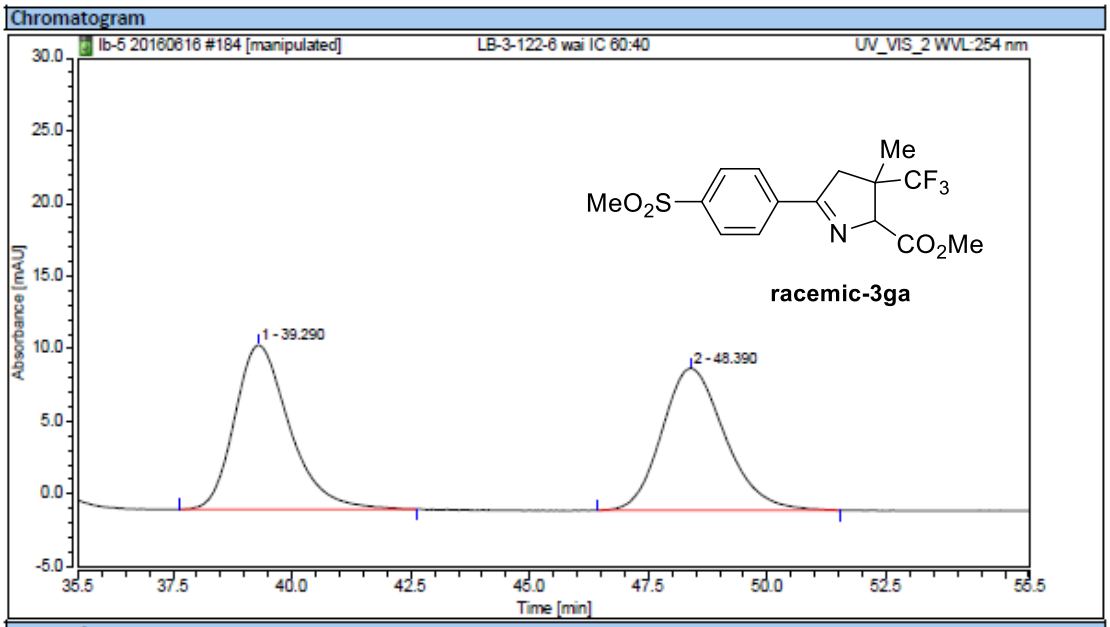
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.780	149.107	326.100	98.75	98.77	n.a.
2		16.920	1.891	4.057	1.25	1.23	n.a.
Total:			**150.997**	**330.157**	**100.00**	**100.00**	


8.0339
8.0180
8.0125
8.0089
7.9892
7.9677
5.1493
3.7911
3.4589
3.4557
3.4147
3.4114
3.0433
3.0377
2.9987
2.9938
1.3262
Me
CF3
MeO2S
N
CO2Me
3ga
4.01
1.00
3.00
2.02
3.00
1.00
3.00
9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

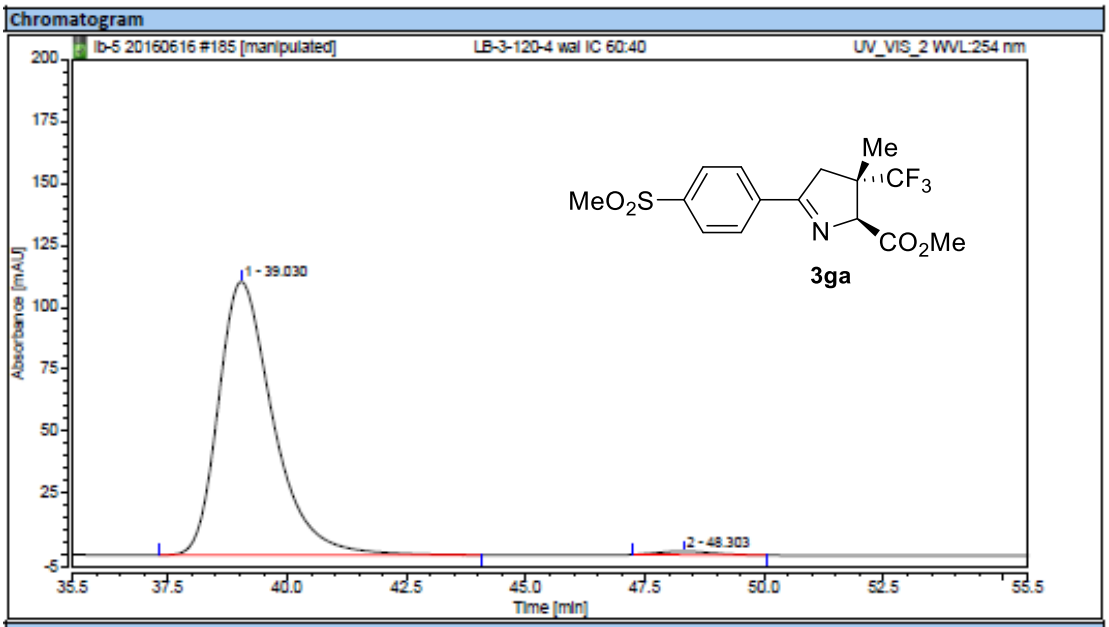

77.2498
Me
CF3
MeO2S
N
CO2Me
3ga
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)





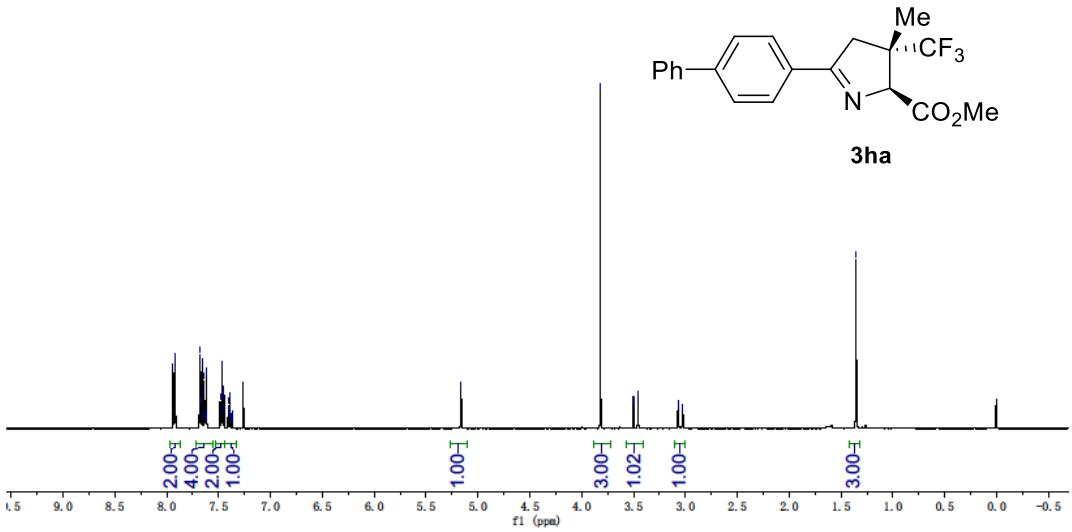
Integration Results

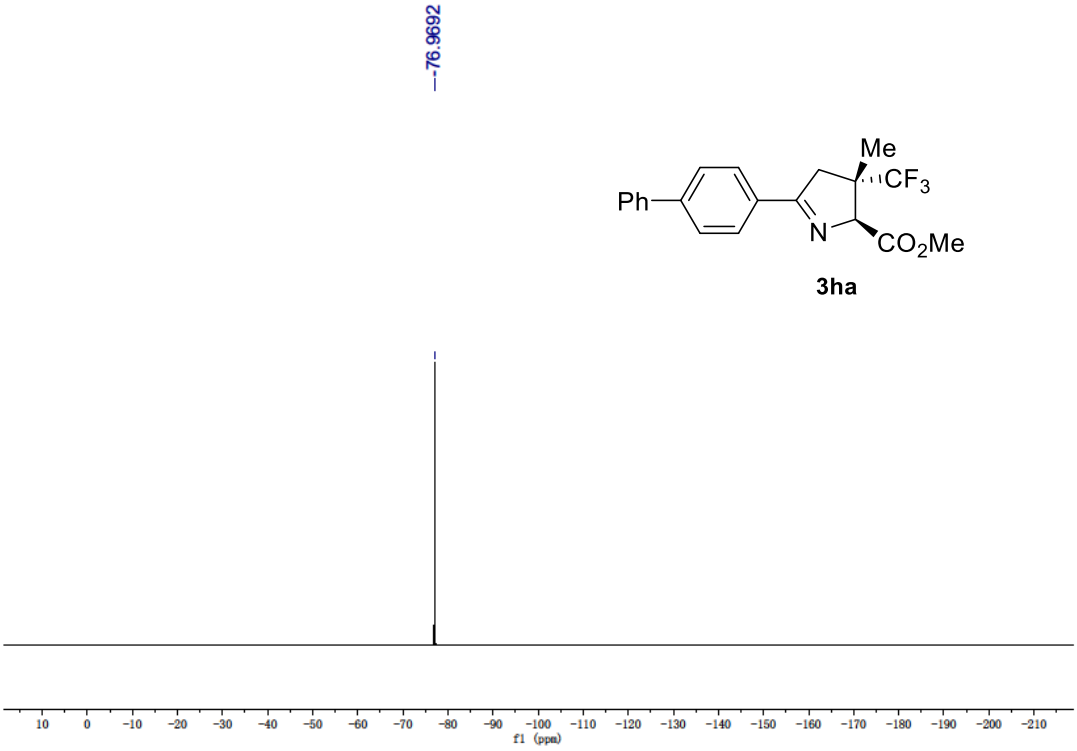
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		39.290	15.162	11.304	50.14	53.61	n.a.
2		48.390	15.077	9.782	49.86	46.39	n.a.
Total:			**30.240**	**21.085**	**100.00**	**100.00**	

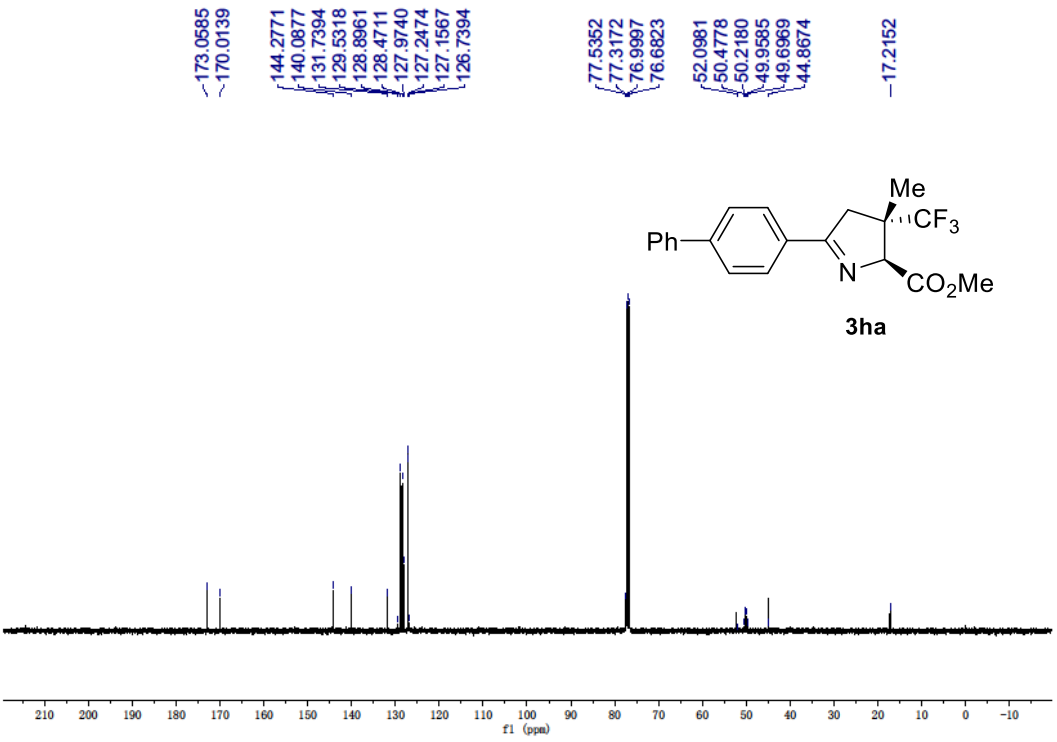


Integration Results

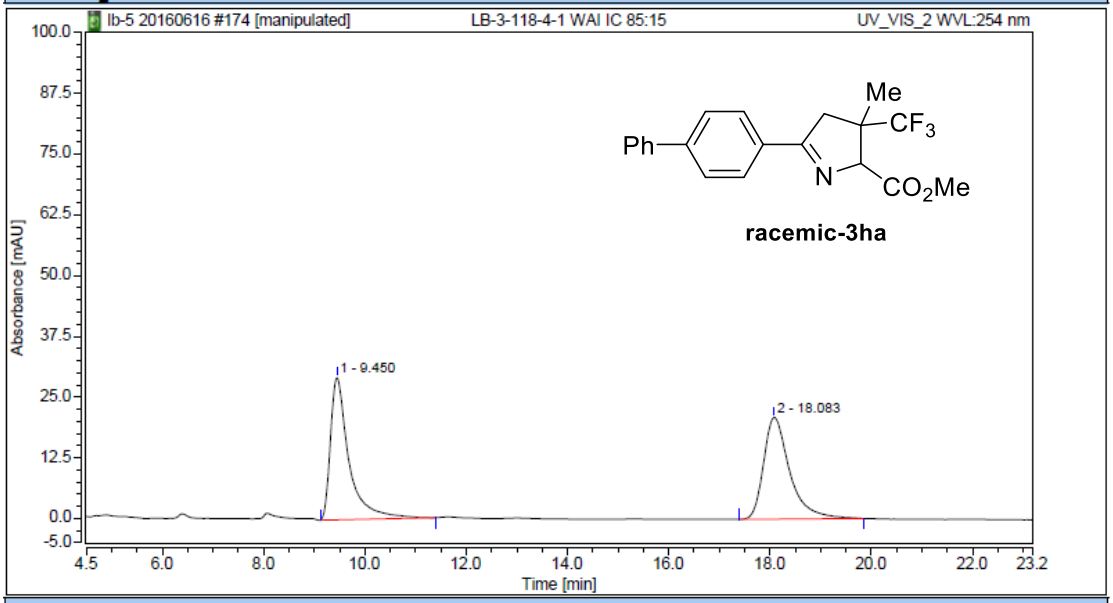
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		39.030	146.644	110.311	98.77	98.76	n.a.
2		48.303	1.825	1.390	1.23	1.24	n.a.
Total:			**148.470**	**111.702**	**100.00**	**100.00**	




-76.9692
Me
CF3
Ph
N
CO2Me
3ha
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


173.0585
170.0139
144.2771
140.0877
131.7394
129.5318
128.8961
128.4711
127.9740
127.2474
127.1567
126.7394
77.5352
77.3172
76.9997
76.6823
52.0981
50.4778
50.2180
49.9585
49.6969
44.8674
17.2152
Me
CF3
Ph
N
CO2Me
3ha
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

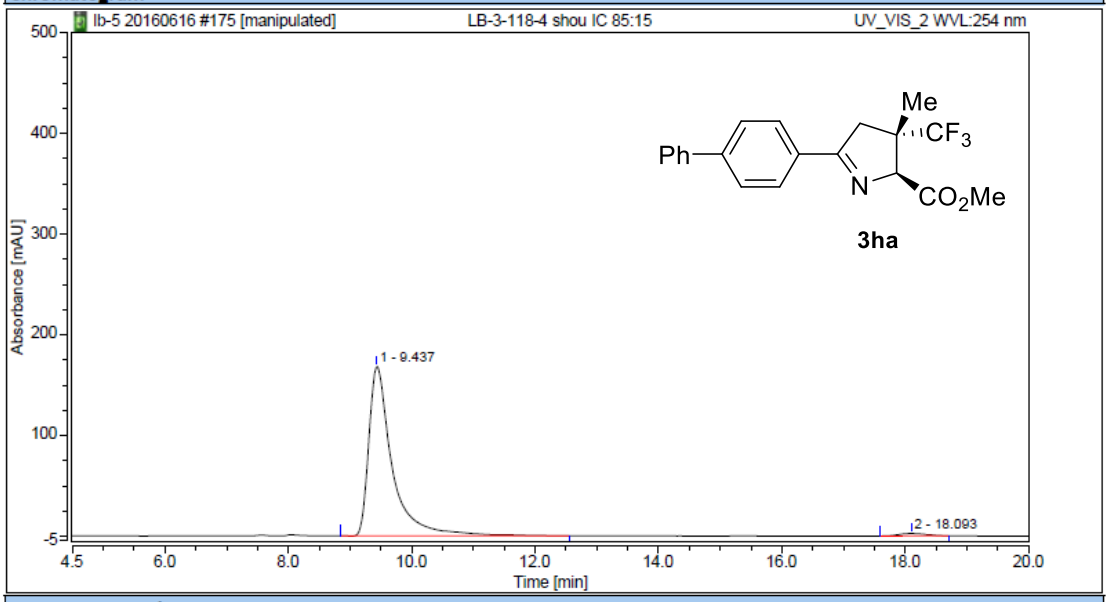
Chromatogram



Integration Results

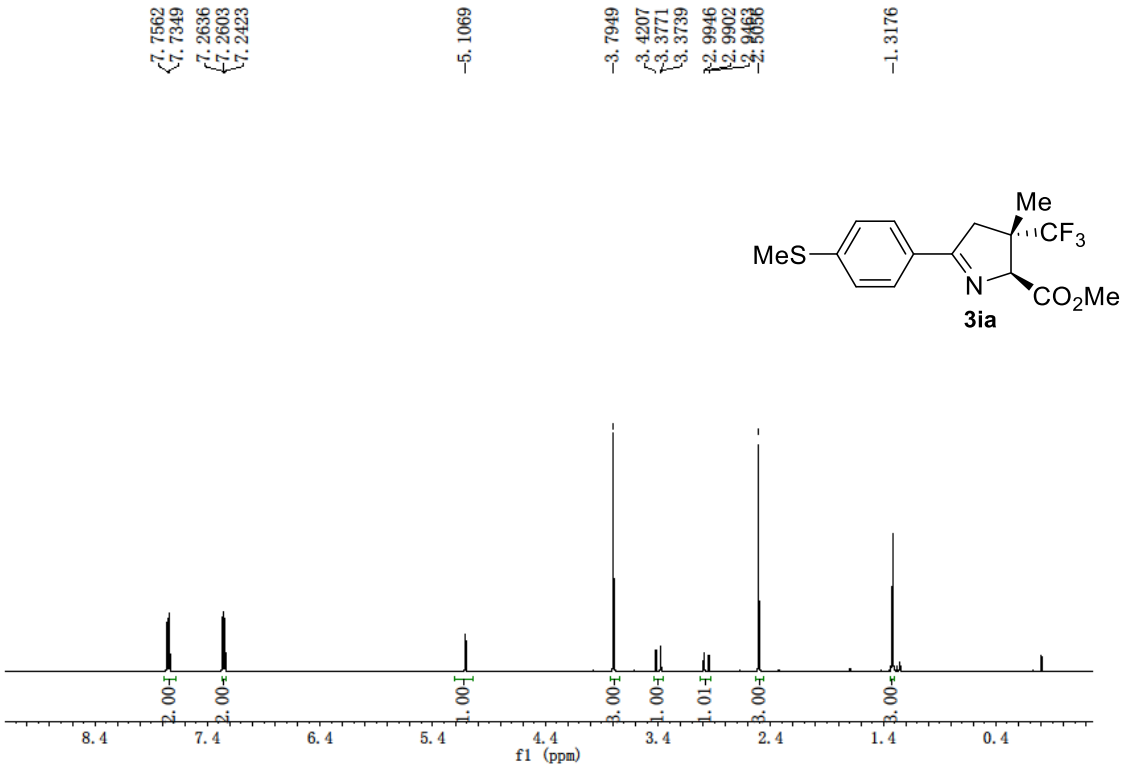
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.450	12.403	29.283	49.79	58.32	n.a.
2		18.083	12.507	20.929	50.21	41.68	n.a.
Total:			**24.910**	**50.212**	**100.00**	**100.00**	

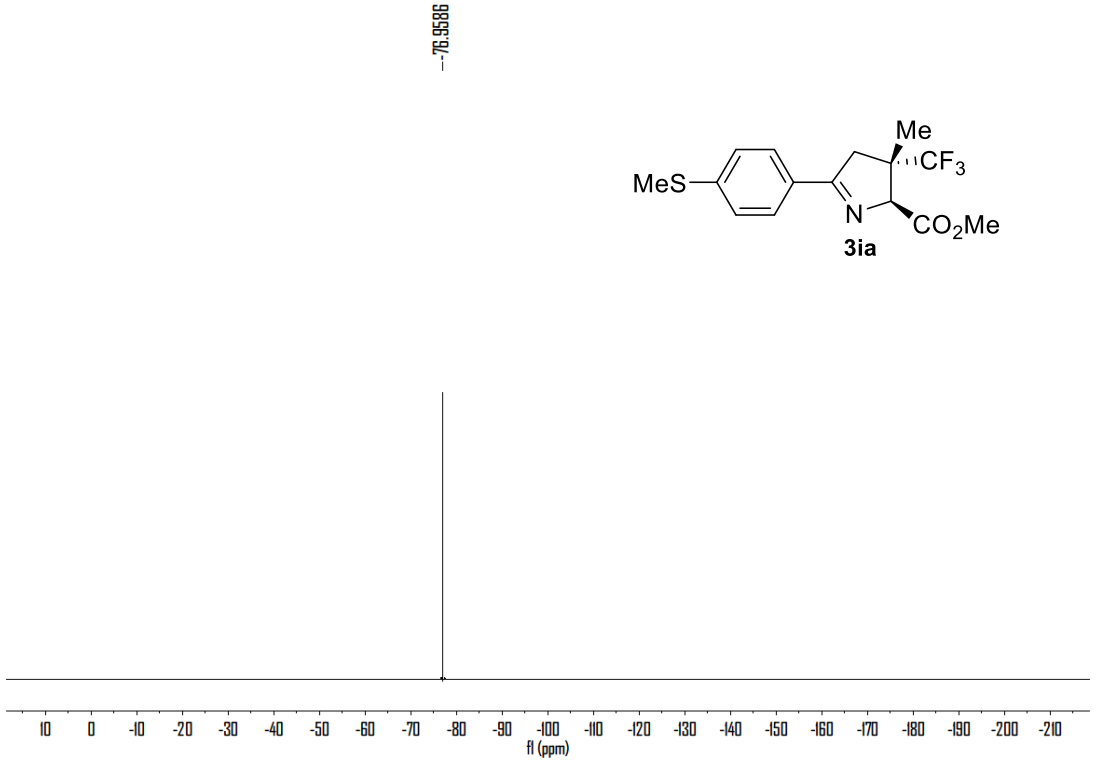
Chromatogram

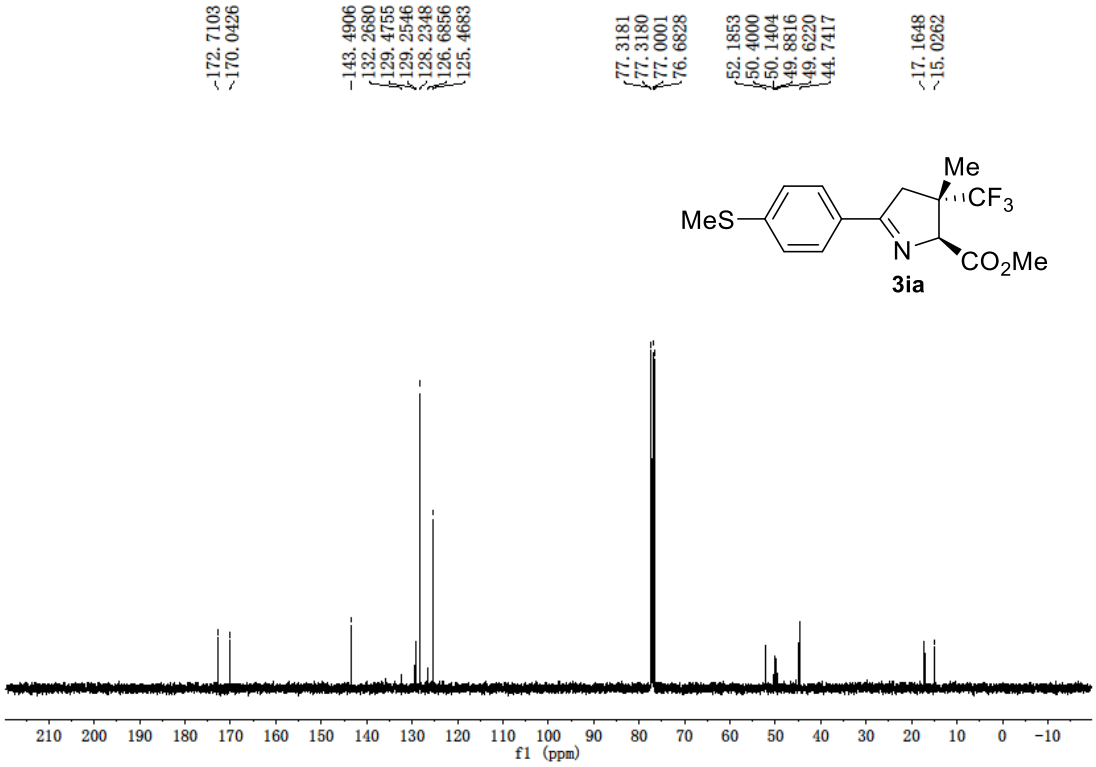


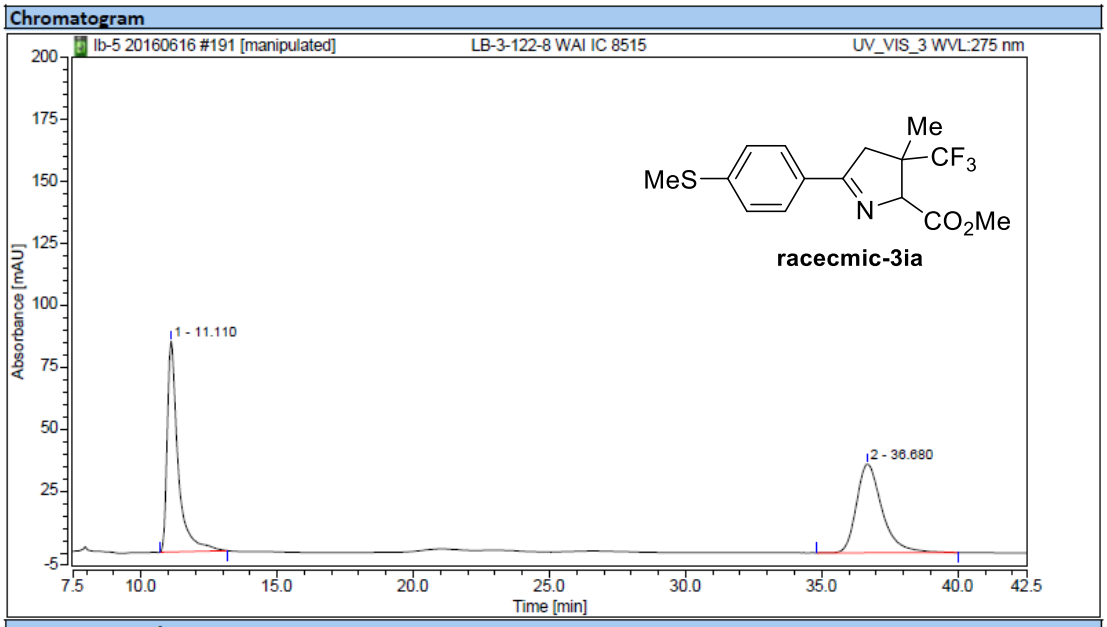
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.437	74.253	168.499	98.35	98.56	n.a.
2		18.093	1.242	2.457	1.65	1.44	n.a.
Total:			**75.495**	**170.957**	**100.00**	**100.00**	


7.7562
7.7349
7.2636
7.2603
7.2423
5.1069
3.7949
3.4207
3.3771
3.3739
2.9946
2.9902
1.3176
Me
CF3
MeS
N
CO2Me
3ia
2.00
2.00
1.00
3.00
1.00
1.01
3.00
3.00
8.4
7.4
6.4
5.4
4.4
3.4
2.4
1.4
0.4
f1 (ppm)


-76.9586
Me
CF3
MeS
N
CO2Me
3ia
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

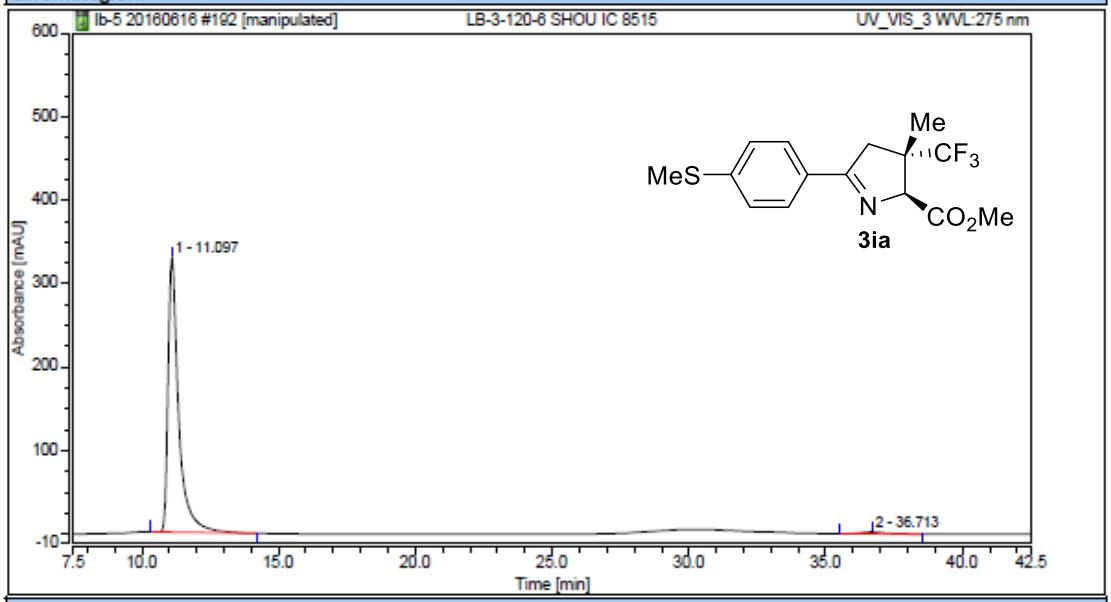




Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.110	39.356	85.081	50.23	70.38	n.a.
2		36.680	38.994	35.807	49.77	29.62	n.a.
Total:			**78.350**	**120.889**	**100.00**	**100.00**	

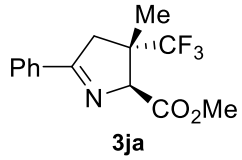
Chromatogram

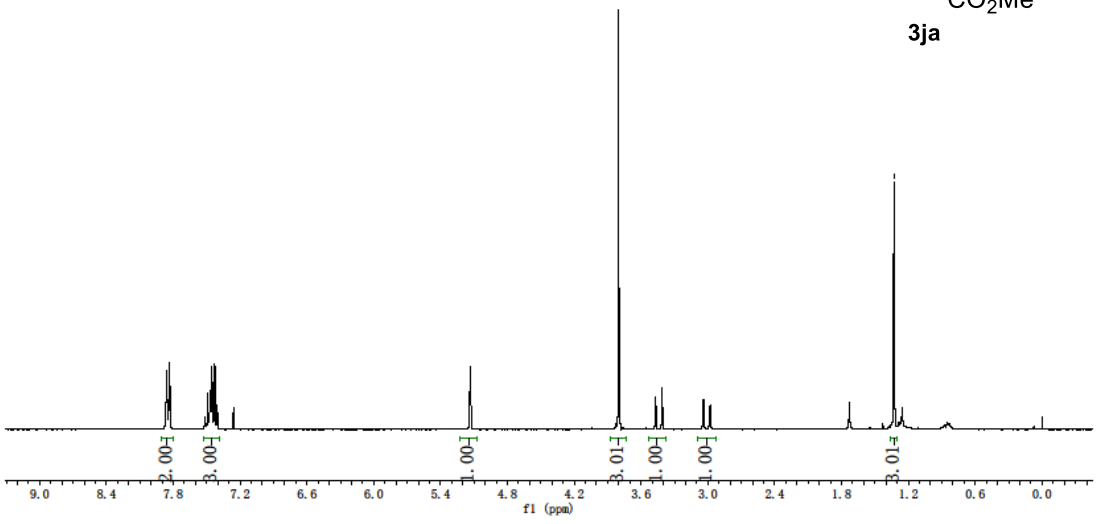


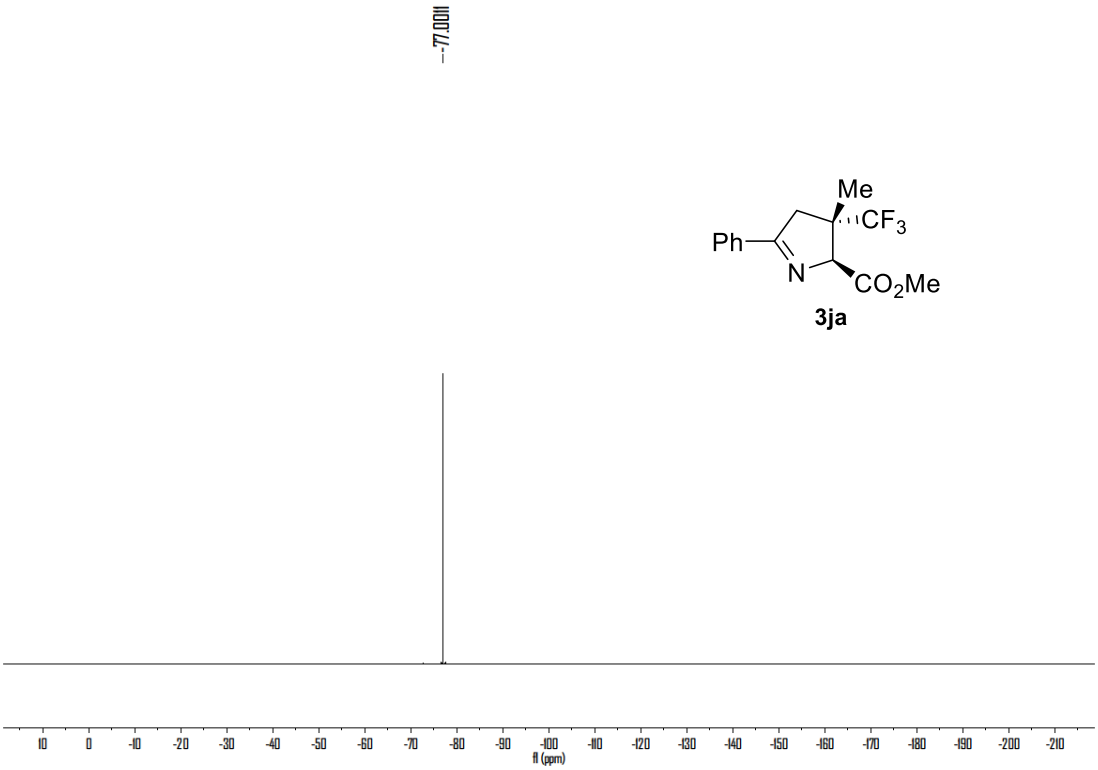
Integration Results

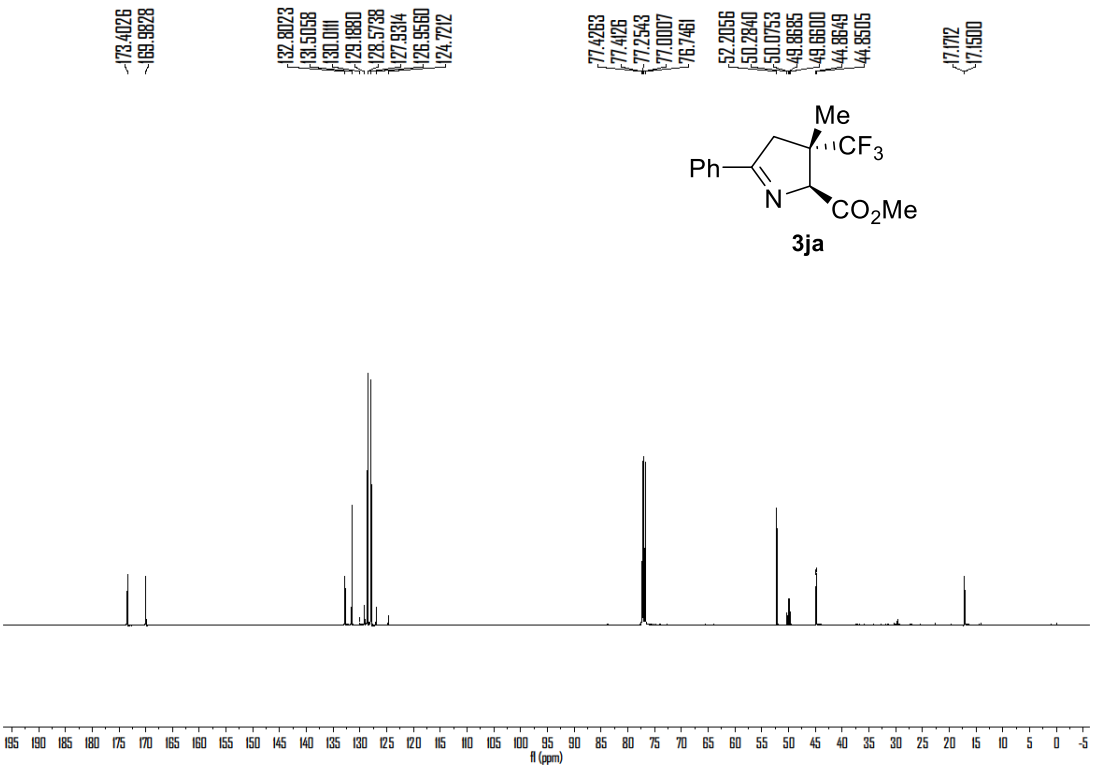
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.097	147.910	329.443	98.63	99.37	n.a.
2		36.713	2.056	2.087	1.37	0.63	n.a.
Total:			**149.966**	**331.530**	**100.00**	**100.00**	

7.8635 7.8588 7.8534 7.8442 7.8369 7.8309 7.5147 7.4902 7.4811 7.4725 7.4672 7.4613 7.4539 7.4515 7.4469 7.4339 7.4276 7.4250 7.4198 7.4109 7.4050 7.3983 5.1332 3.8007 3.4717 3.4674 3.4131 3.4089 3.0434 3.0374 2.9849 2.9788 1.3295

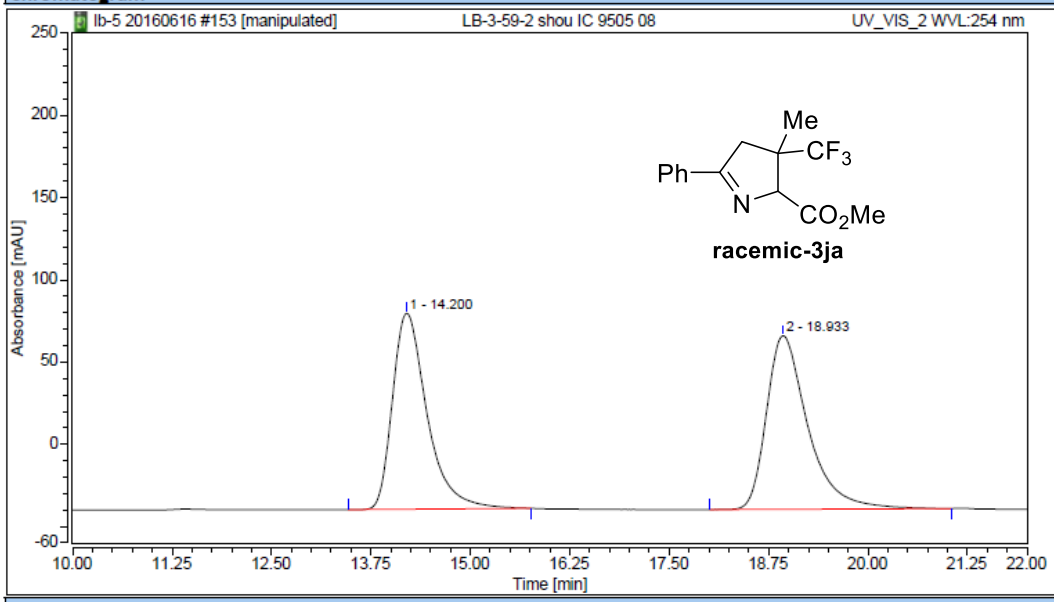





-77.0011
Me
CF3
Ph
N
CO2Me
3ja
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


173.4026
169.9828
132.8023
131.5058
131.0111
129.1880
128.5738
127.9394
126.9560
124.7212
77.4263
77.4126
77.2543
77.0007
76.7461
52.2056
50.2840
50.0753
49.8685
49.6600
44.8649
44.8505
17.1712
17.1500
Me
CF3
Ph
N
CO2Me
3ja
195 190 185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0 -5
f1 (ppm)

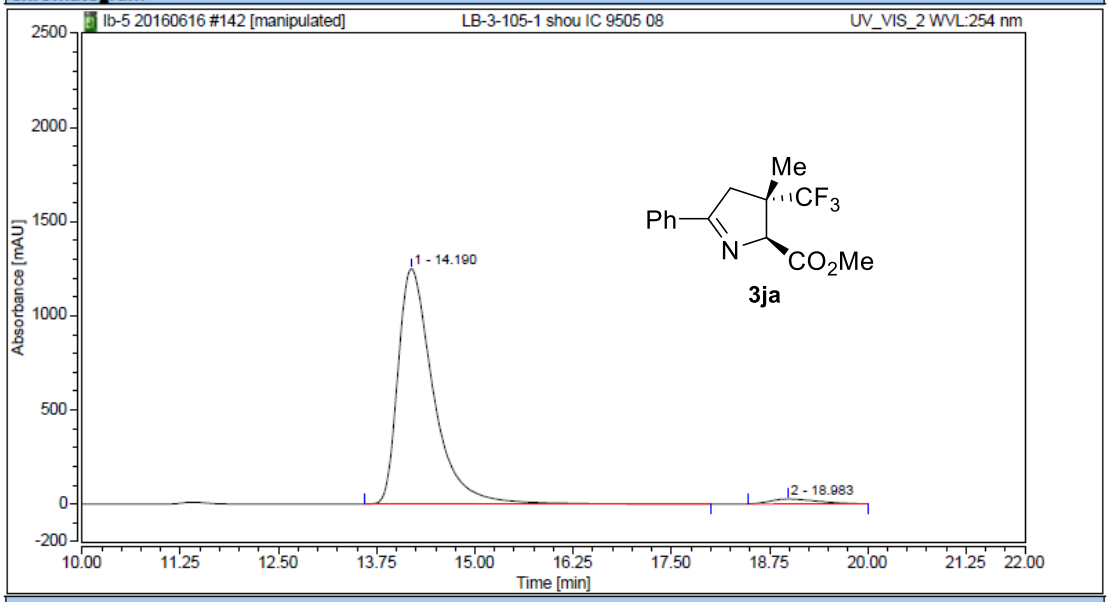
Chromatogram



Integration Results

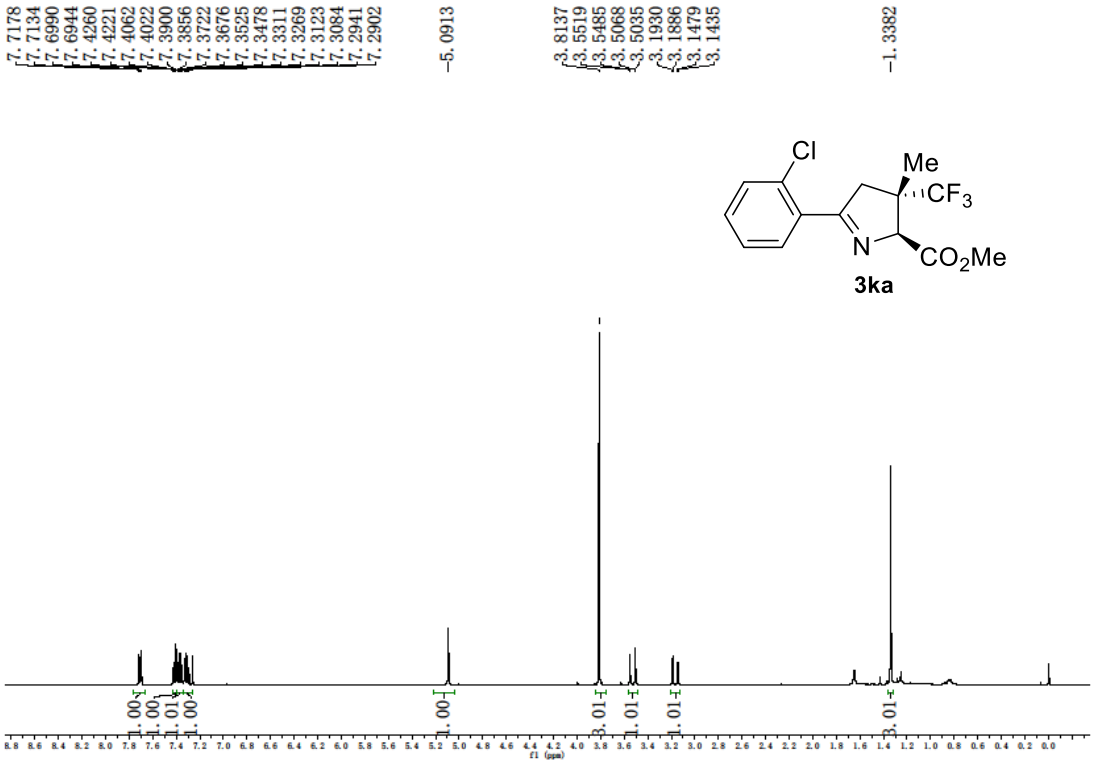
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.200	60.077	119.278	48.62	53.06	n.a.
2		18.933	63.492	105.515	51.38	46.94	n.a.
Total:			**123.569**	**224.793**	**100.00**	**100.00**	

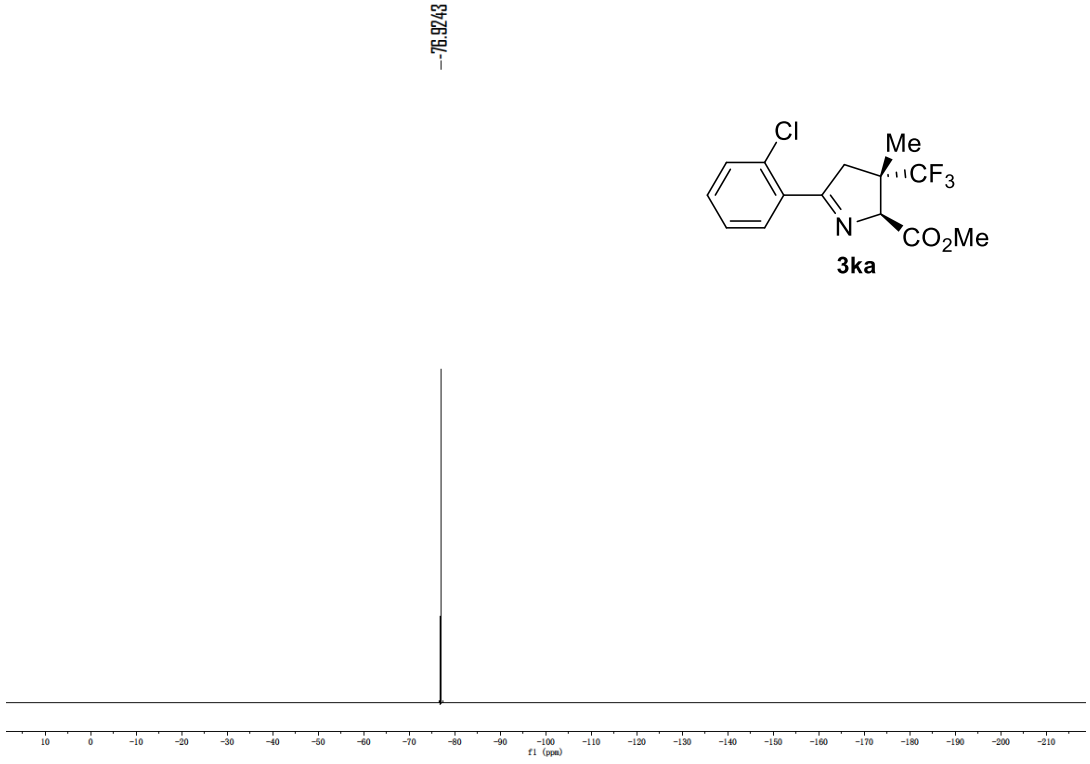
Chromatogram

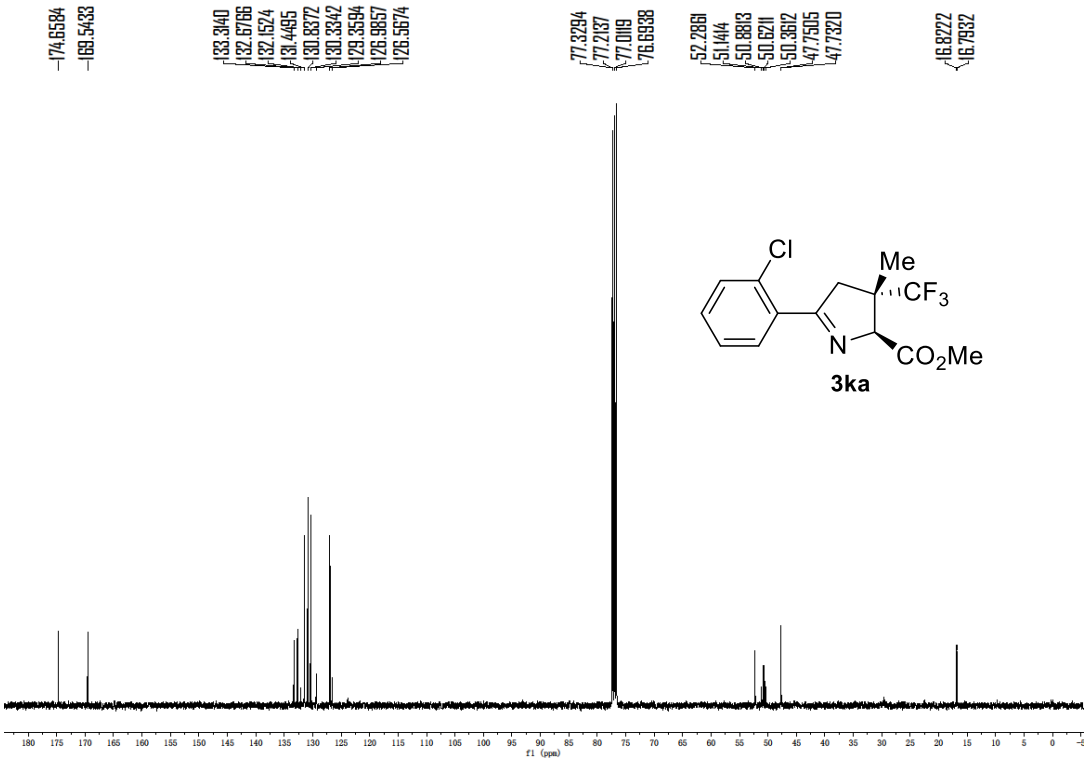


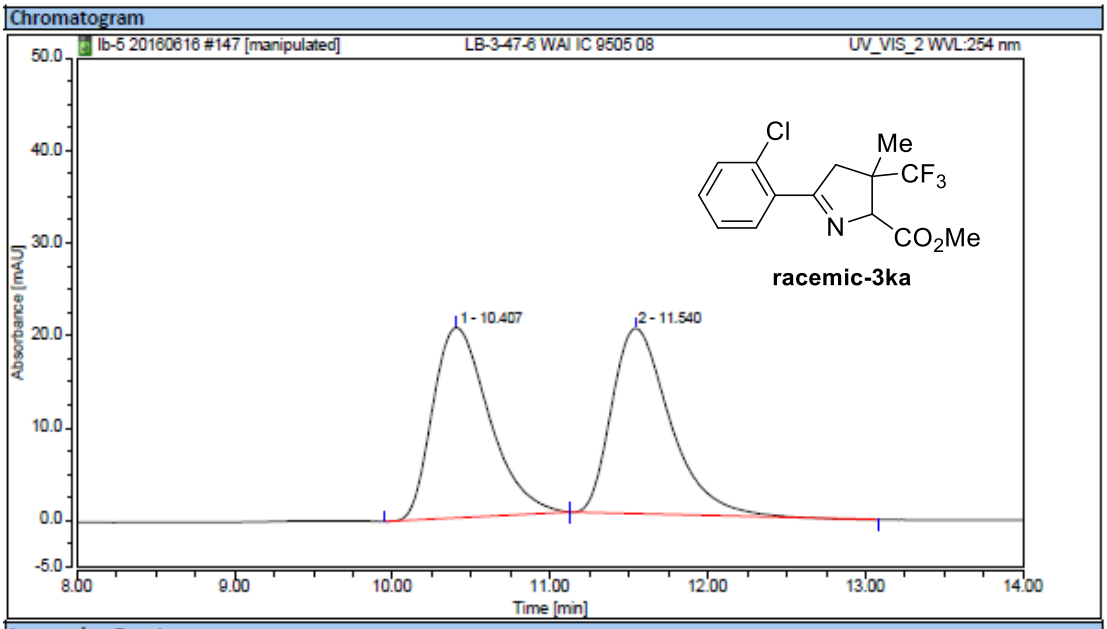
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		14.190	651.766	1248.808	97.40	97.97	n.a.
2		18.983	17.415	25.831	2.60	2.03	n.a.
Total:			**669.181**	**1274.638**	**100.00**	**100.00**	


7.7178
7.7134
7.6990
7.6944
7.4260
7.4221
7.4062
7.4022
7.3900
7.3856
7.3722
7.3676
7.3525
7.3478
7.3311
7.3269
7.3123
7.3084
7.2941
7.2902
5.0913
3.8137
3.5519
3.5485
3.5068
3.5035
3.1930
3.1886
3.1479
3.1435
1.3382
Cl
Me
CF3
N
CO2Me
3ka
1.00
1.00
1.01
1.00
1.00
3.01
1.01
1.01
3.01
f1 (ppm)


-76.8243
Cl
Me
CF3
N
CO2Me
3ka
f1 (ppm)

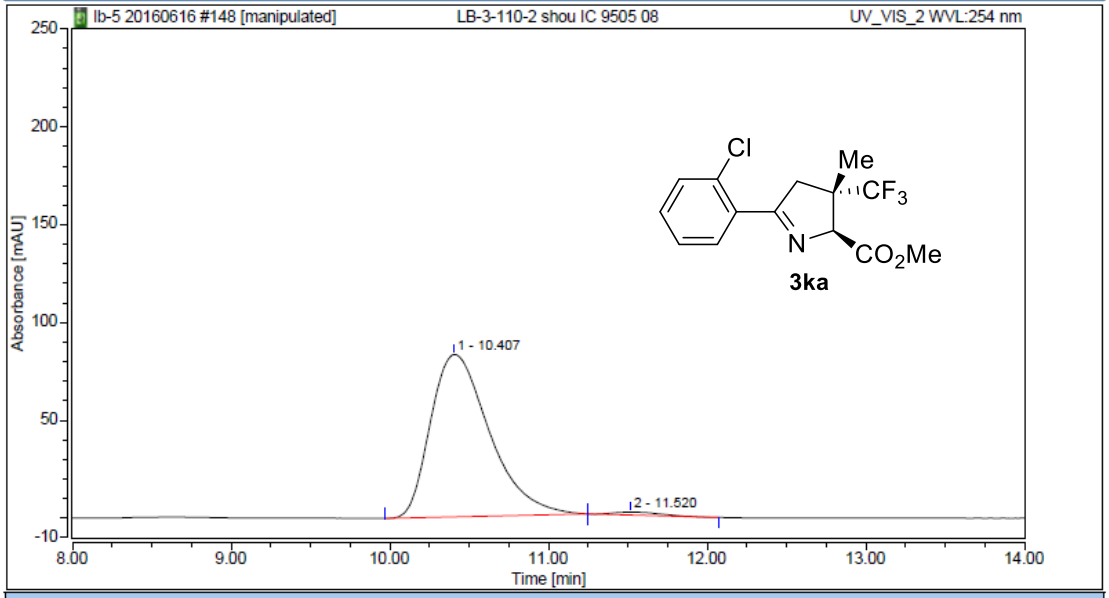




Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.407	8.534	20.576	49.74	50.62	n.a.
2		11.540	8.623	20.070	50.26	49.38	n.a.
Total:			**17.157**	**40.646**	**100.00**	**100.00**	

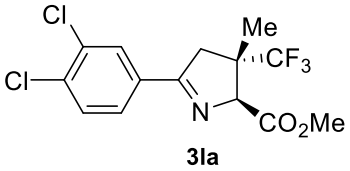
Chromatogram

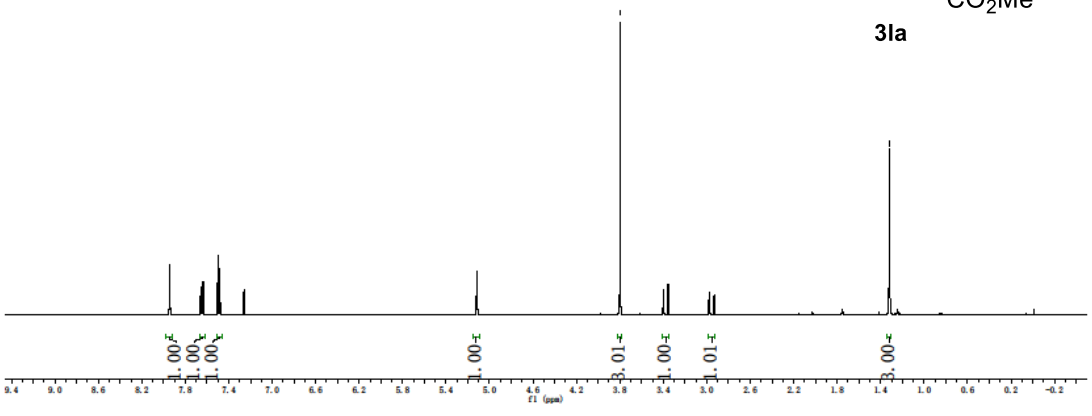


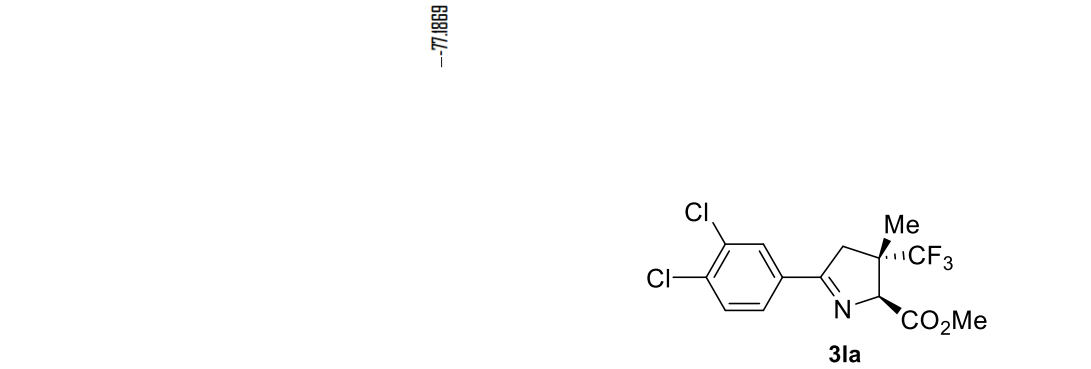
Integration Results

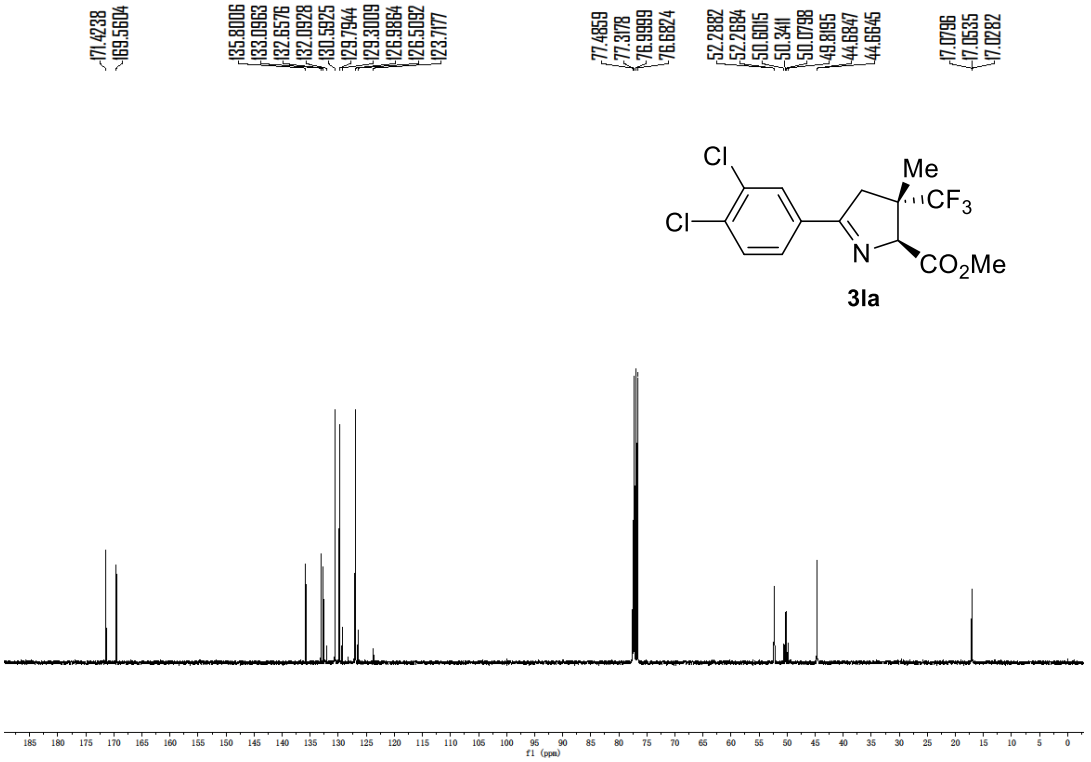
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		10.407	35.799	83.010	98.48	98.12	n.a.
2		11.520	0.553	1.589	1.52	1.88	n.a.
Total:			36.351	84.600	100.00	100.00	

7.9461 7.9411 7.6590 7.6540 7.6381 7.6331 7.5014 7.4806 5.1159 3.7984 3.4018 3.3579 3.3546 3.3496 2.9748 2.9355 2.9308 1.3194

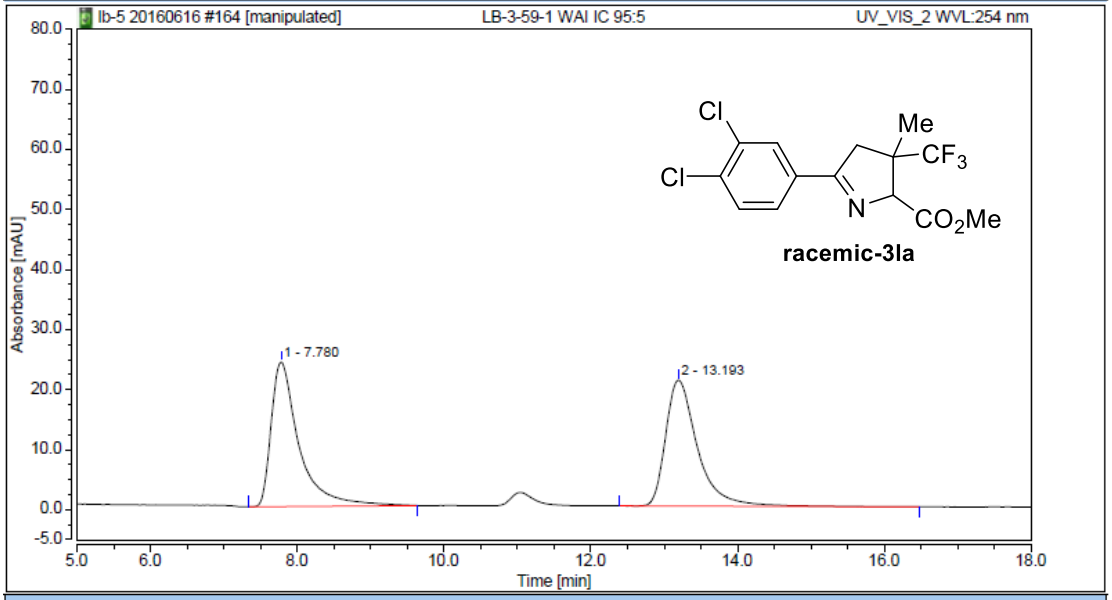





-77.1869
Cl
Cl
Me
CF3
N
CO2Me
3la
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


171.4238
169.5604
135.8006
133.0963
132.6576
132.0928
130.5925
129.7944
129.3009
126.9864
126.5092
123.7177
77.4859
77.3178
76.9999
76.6824
52.2882
52.2684
50.6015
50.3411
50.0798
49.8195
44.6847
44.6645
17.0796
17.0535
17.0282
Cl
Cl
Me
CF3
N
CO2Me
3la
185 180 175 170 165 160 155 150 145 140 135 130 125 120 115 110 105 100 95 90 85 80 75 70 65 60 55 50 45 40 35 30 25 20 15 10 5 0
f1 (ppm)

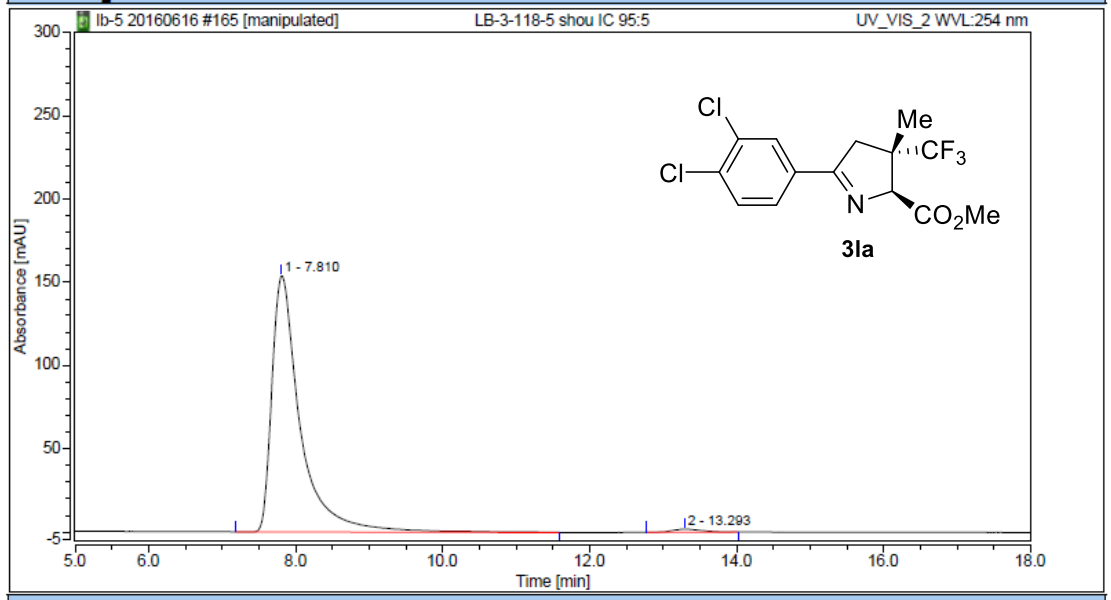
Chromatogram



Integration Results

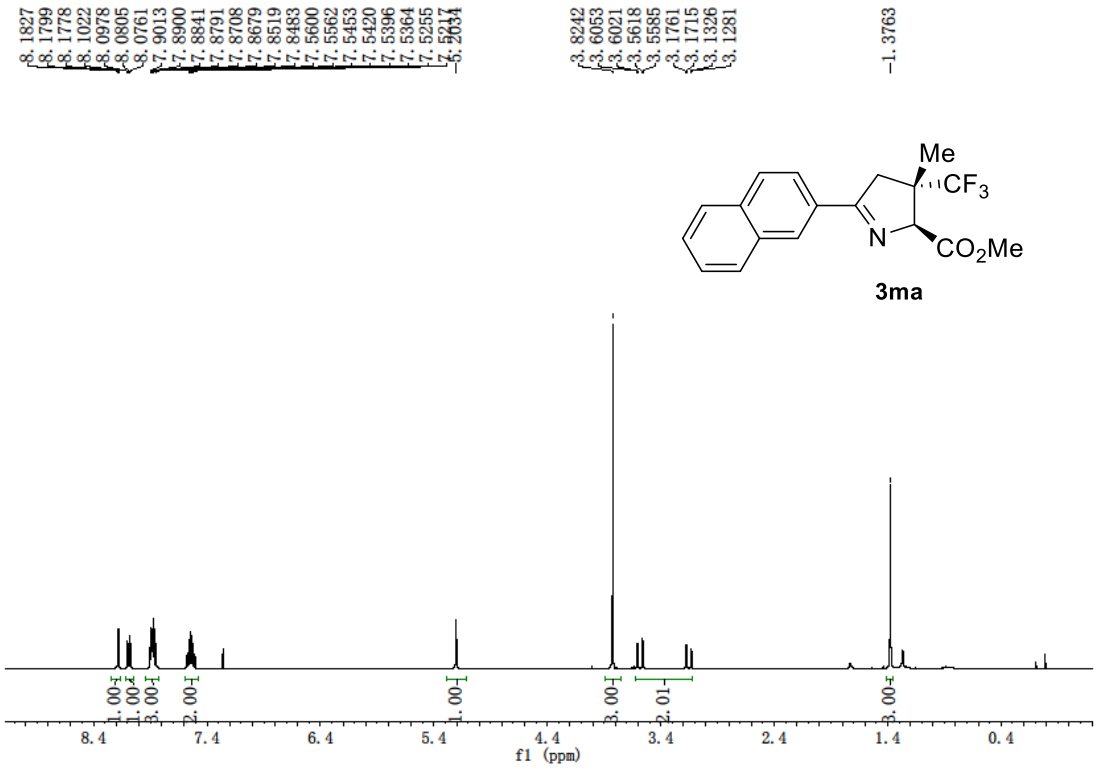
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.780	10.621	24.109	50.17	53.46	n.a.
2		13.193	10.550	20.992	49.83	46.54	n.a.
Total:			**21.170**	**45.100**	**100.00**	**100.00**	

Chromatogram

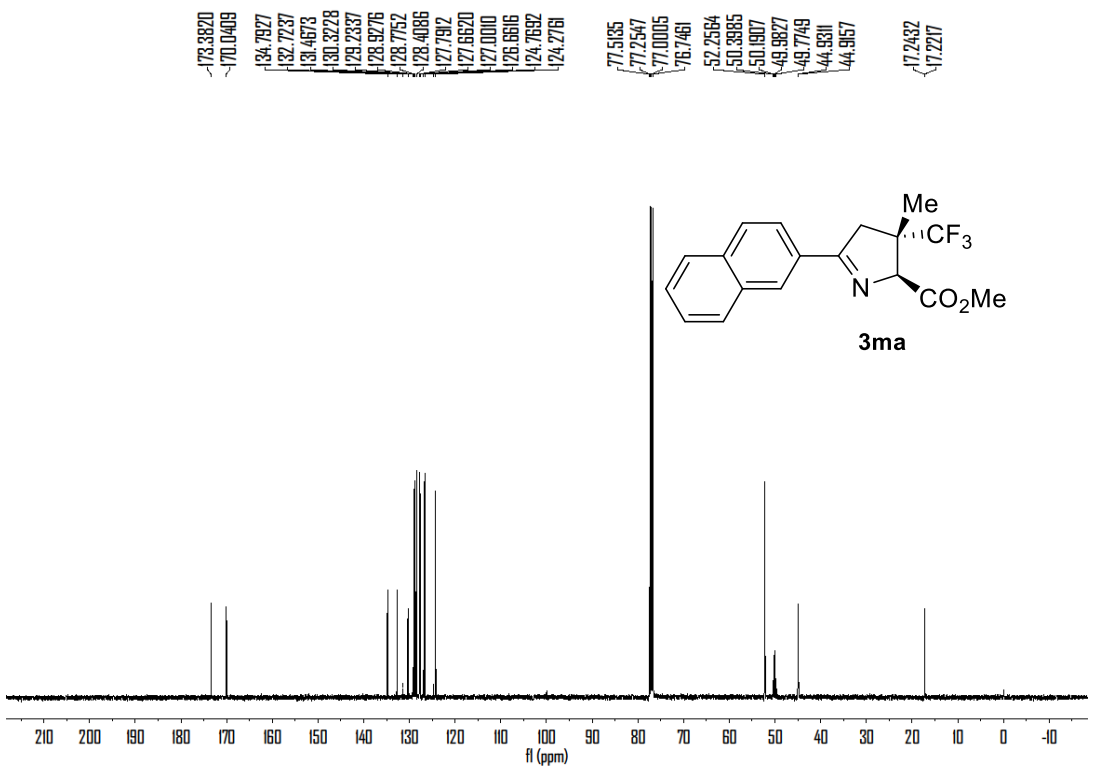


Integration Results

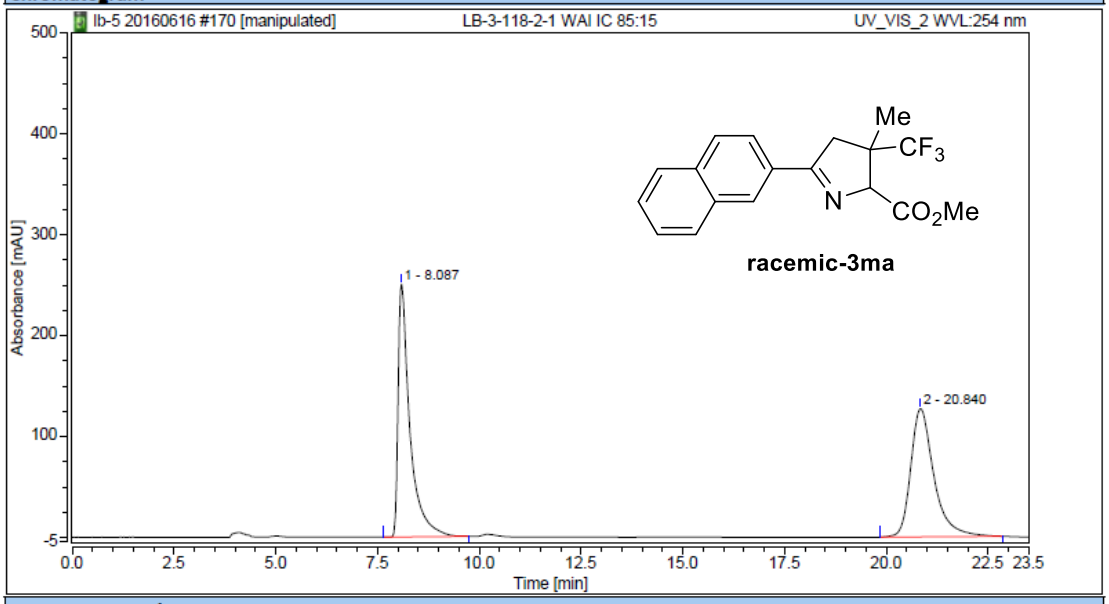
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.810	68.898	153.939	98.78	98.82	n.a.
2		13.293	0.850	1.832	1.22	1.18	n.a.
Total:			**69.748**	**155.771**	**100.00**	**100.00**	


8.1827
8.1799
8.1778
8.1022
8.0978
8.0805
8.0761
7.9013
7.8900
7.8841
7.8791
7.8708
7.8679
7.8519
7.8483
7.5600
7.5562
7.5453
7.5420
7.5396
7.5364
7.5255
5.2034
3.8242
3.6053
3.6021
3.5618
3.5585
3.1761
3.1715
3.1326
3.1281
1.3763
Me
CF3
N
CO2Me
3ma
1.00
1.00
3.00
2.00
1.00
3.00
2.01
3.00
8.4
7.4
6.4
5.4
4.4
3.4
2.4
1.4
0.4
f1 (ppm)


-76.8668
Me
CF3
N
CO2Me
3ma
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



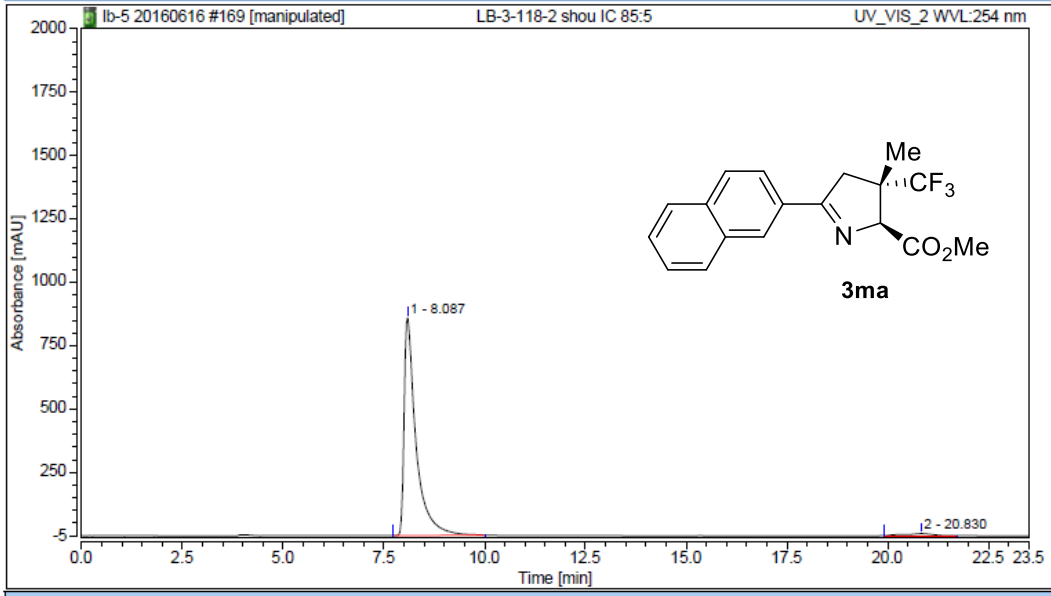
Chromatogram



Integration Results

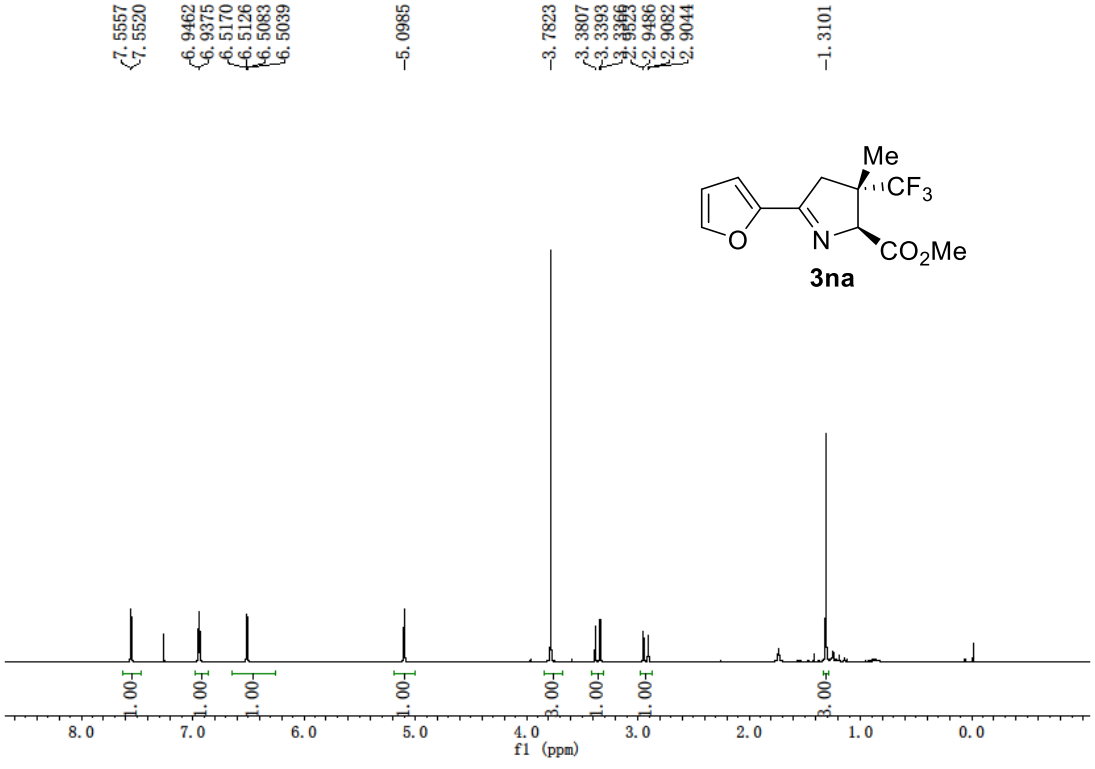
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.087	83.599	250.766	49.88	66.33	n.a.
2		20.840	84.013	127.312	50.12	33.67	n.a.
Total:			**167.612**	**378.078**	**100.00**	**100.00**	

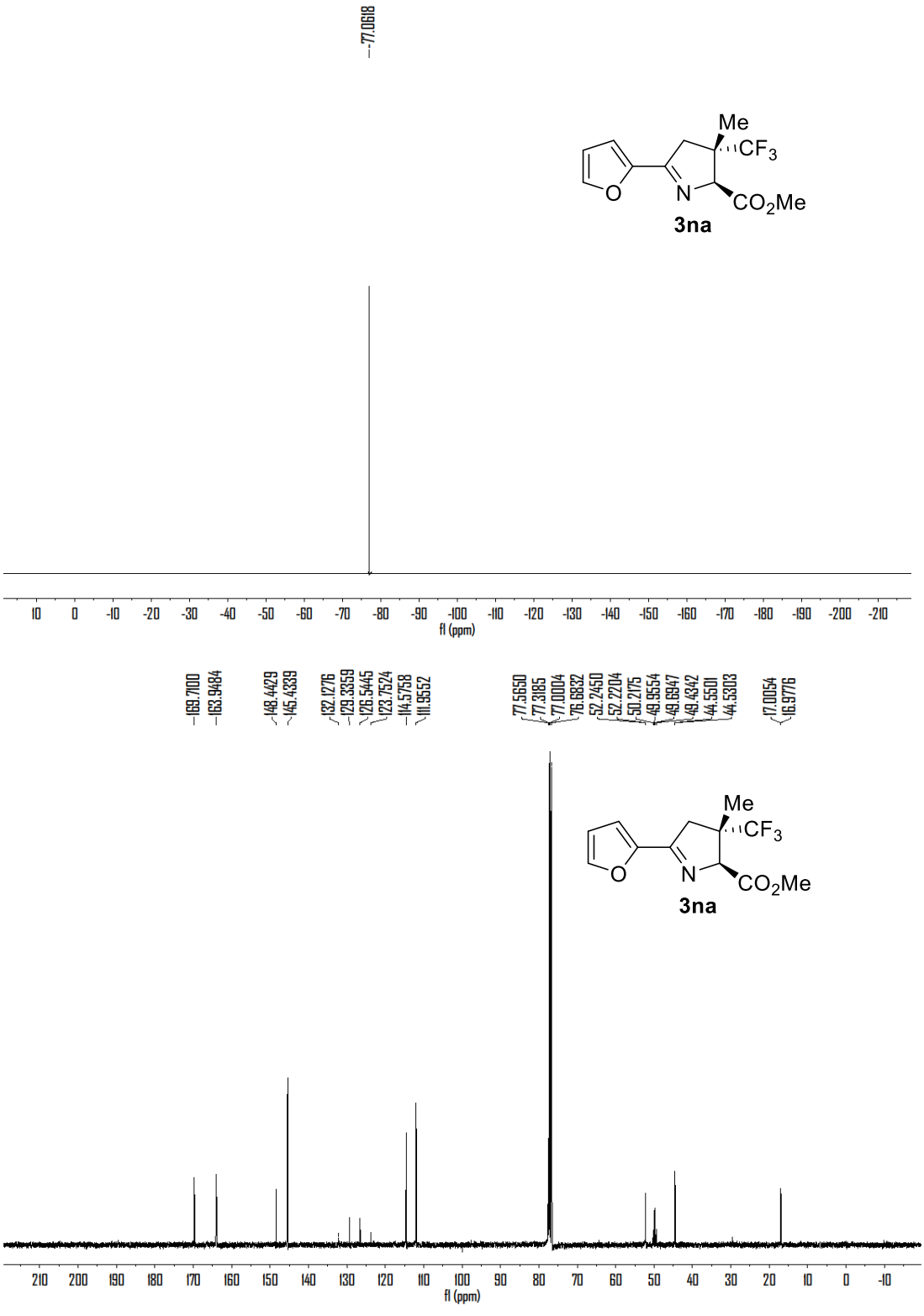
Chromatogram

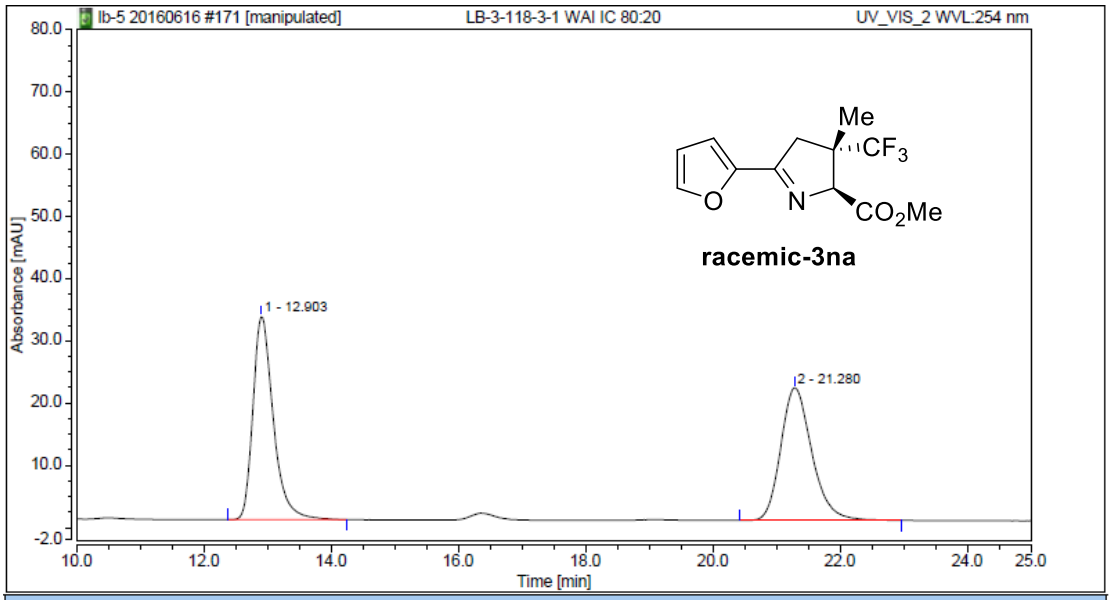


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.087	291.548	859.288	97.95	99.13	n.a.
2		20.830	6.104	7.505	2.05	0.87	n.a.
Total:			**297.652**	**866.793**	**100.00**	**100.00**	

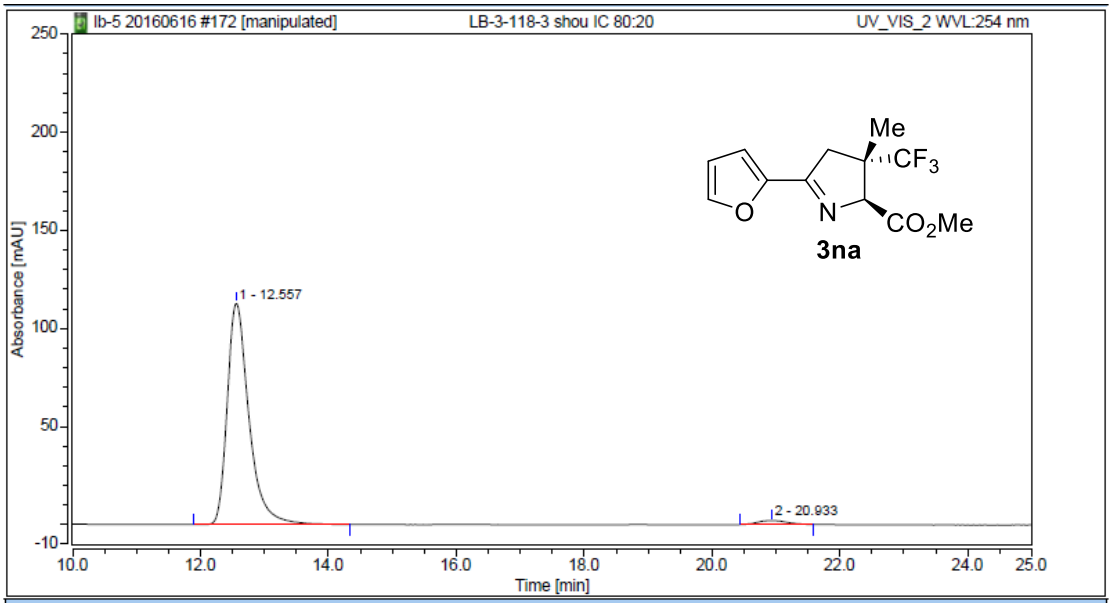



-77.0618
Me
CF3
O
N
CO2Me
3na
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.7100
163.9484
148.4429
145.4339
132.1276
129.3359
126.5445
123.7524
114.5758
111.9552
77.5650
77.3185
77.0004
76.8832
52.2450
52.2204
50.2175
49.9554
49.6947
49.4342
44.5501
44.5303
17.0054
16.9776
Me
CF3
O
N
CO2Me
3na
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



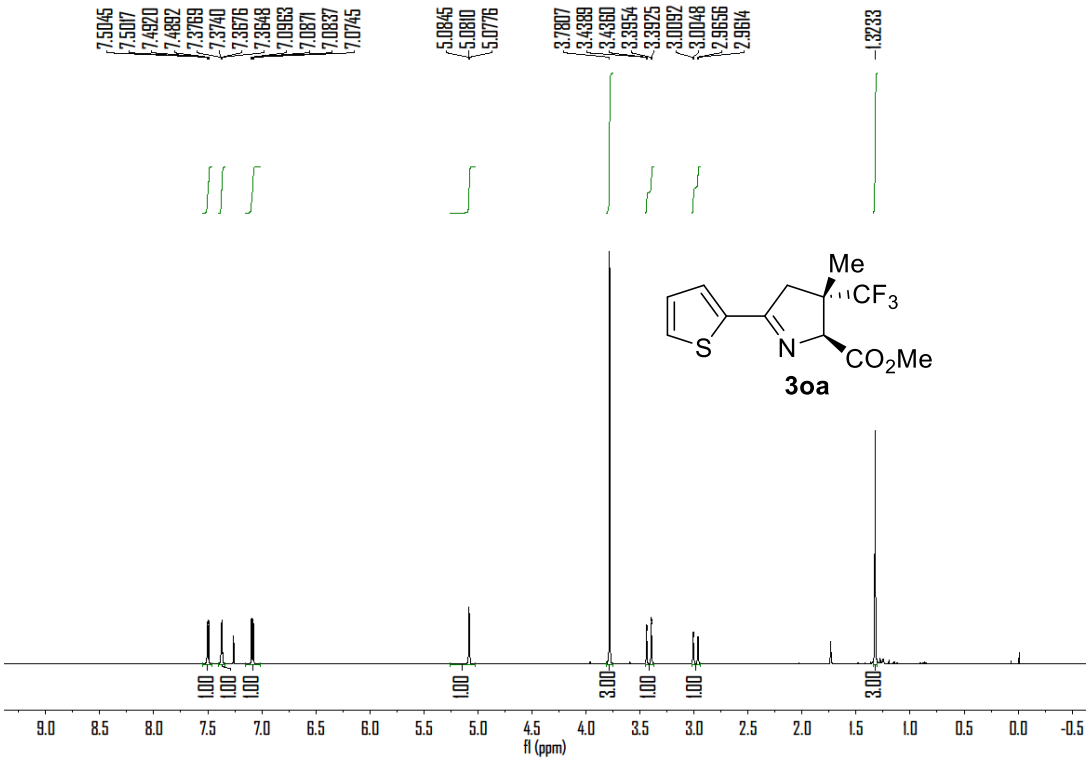
Integration Results

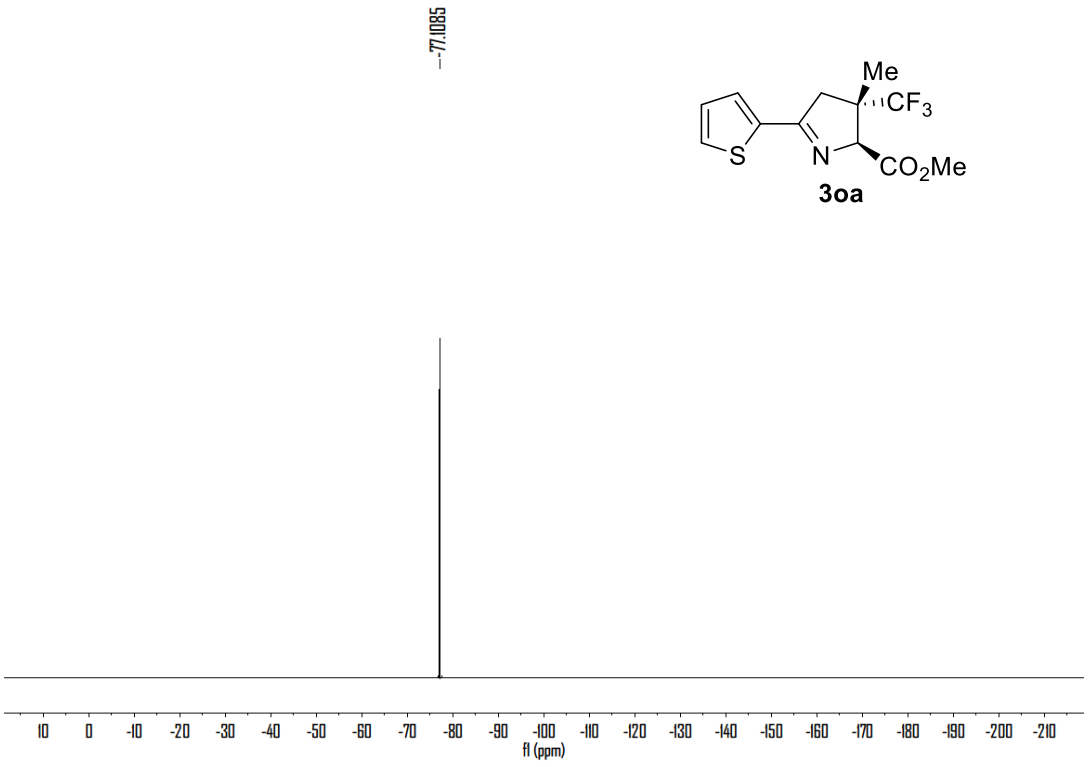
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.903	12.095	32.648	50.03	60.51	n.a.
2		21.280	12.080	21.308	49.97	39.49	n.a.
Total:			**24.175**	**53.955**	**100.00**	**100.00**	

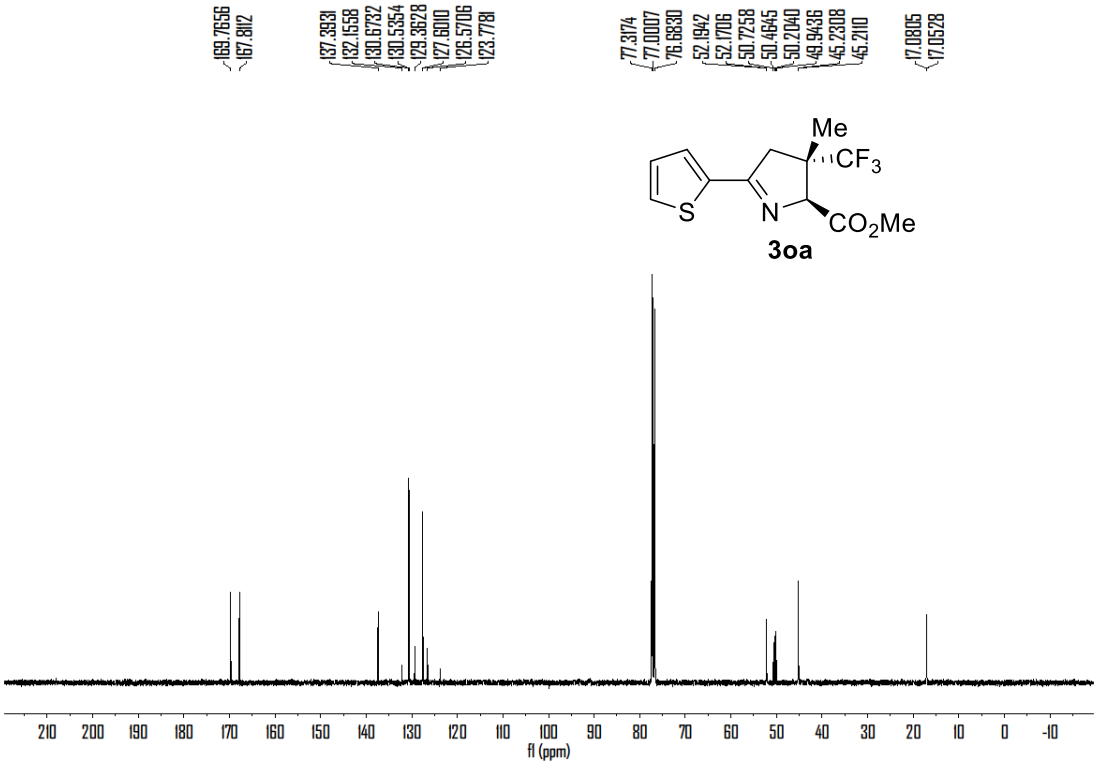


Integration Results

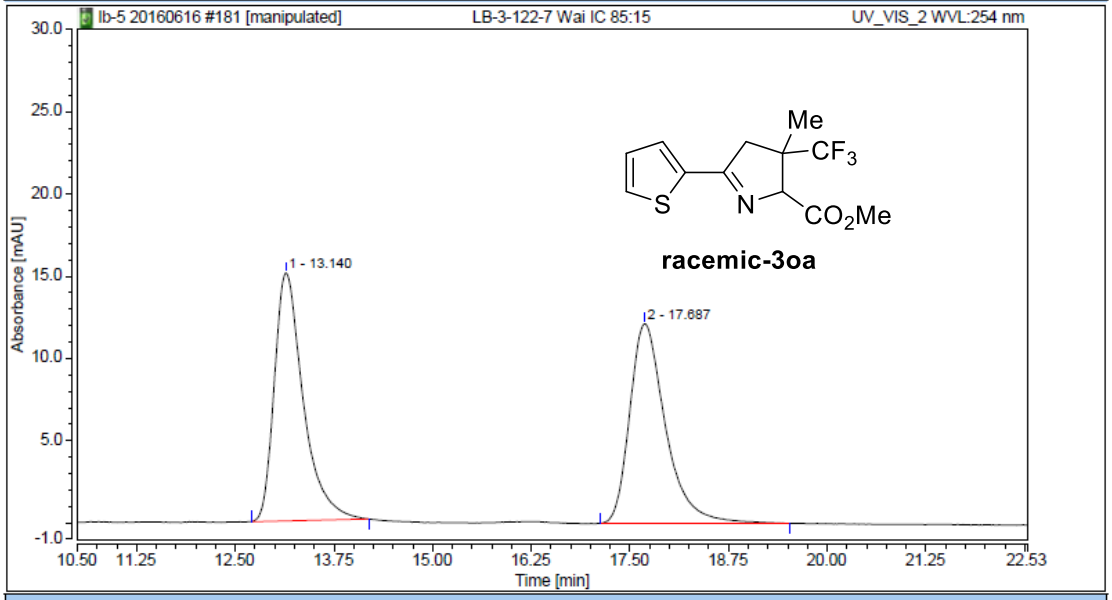
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.557	44.412	112.947	97.55	98.17	n.a.
2		20.933	1.115	2.106	2.45	1.83	n.a.
Total:			**45.527**	**115.053**	**100.00**	**100.00**	


7.5045
7.5017
7.4920
7.4882
7.3769
7.3740
7.3676
7.3648
7.0963
7.0871
7.0837
7.0745
5.0845
5.0810
5.0776
3.7807
3.4388
3.4360
3.3954
3.3925
3.0092
3.0048
2.9656
2.9614
1.3233
Me
CF3
S
N
CO2Me
3oa
1.00
1.00
1.00
1.00
3.00
1.00
1.00
3.00
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


77.1085
Me
CF3
S
N
CO2Me
3oa
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)



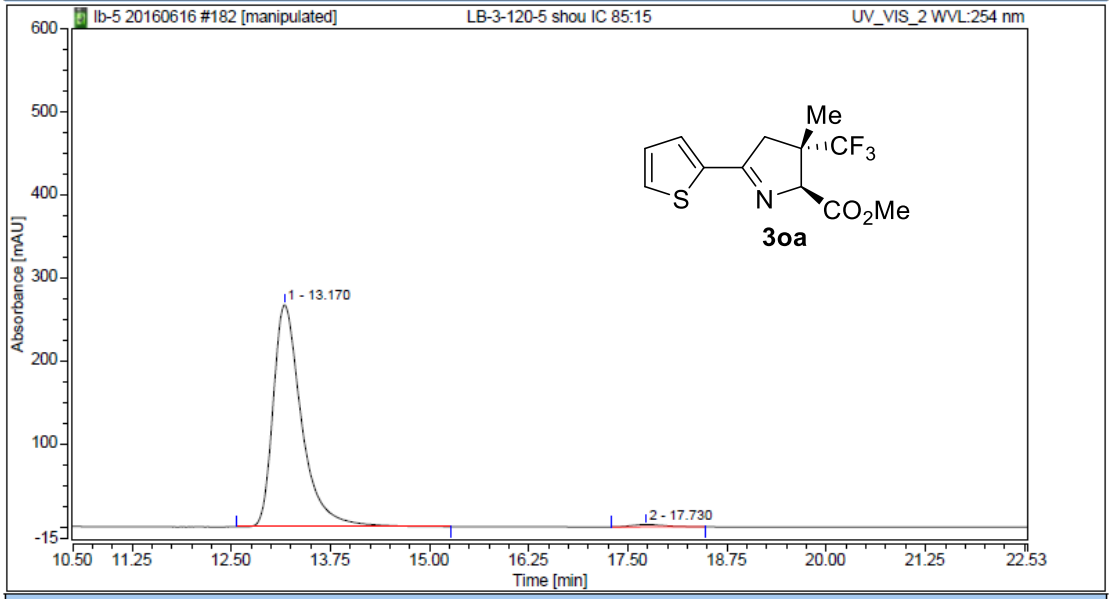
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.140	6.395	15.084	49.99	55.40	n.a.
2		17.687	6.398	12.142	50.01	44.60	n.a.
Total:			**12.793**	**27.226**	**100.00**	**100.00**	

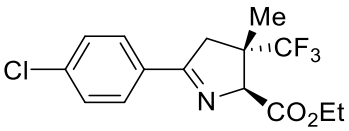
Chromatogram



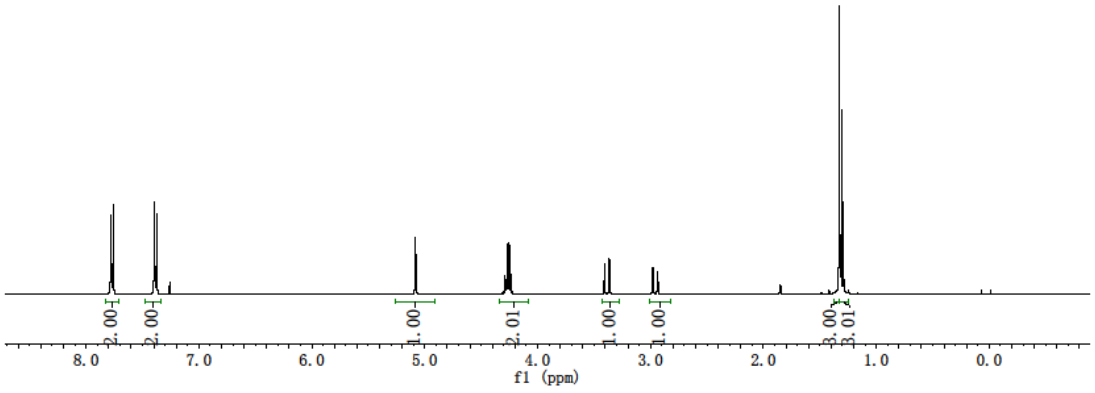
Integration Results

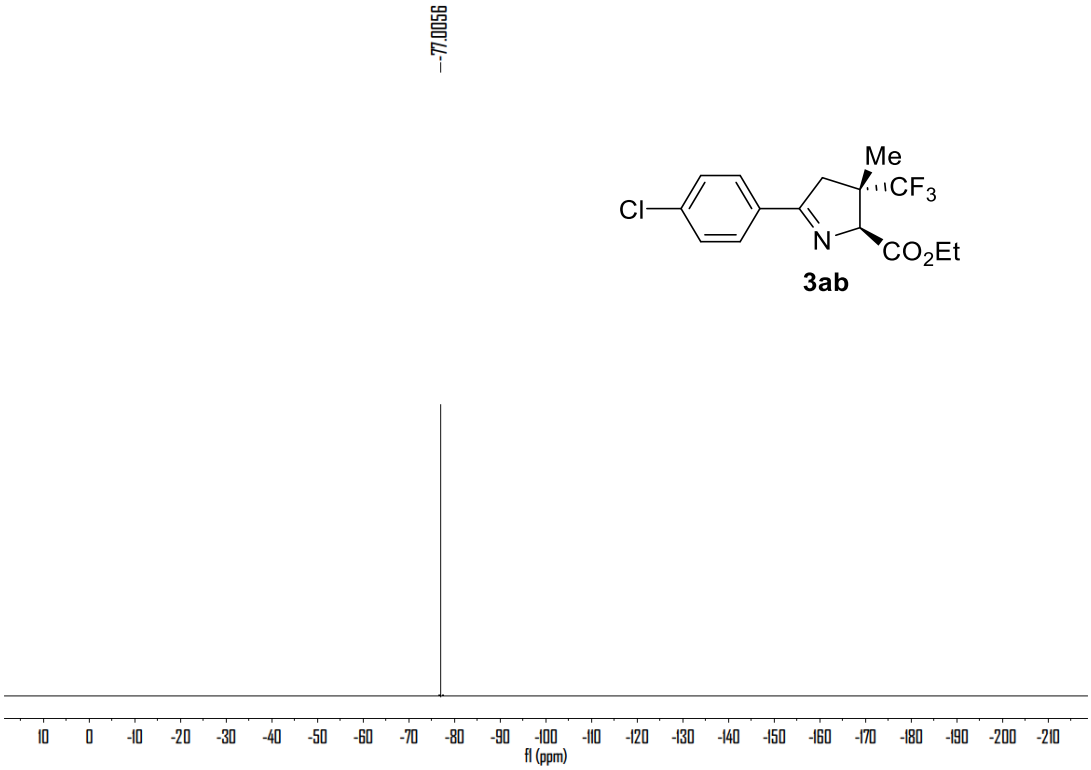
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		13.170	111.309	267.752	98.86	98.99	n.a.
2		17.730	1.279	2.721	1.14	1.01	n.a.
Total:			**112.588**	**270.473**	**100.00**	**100.00**	

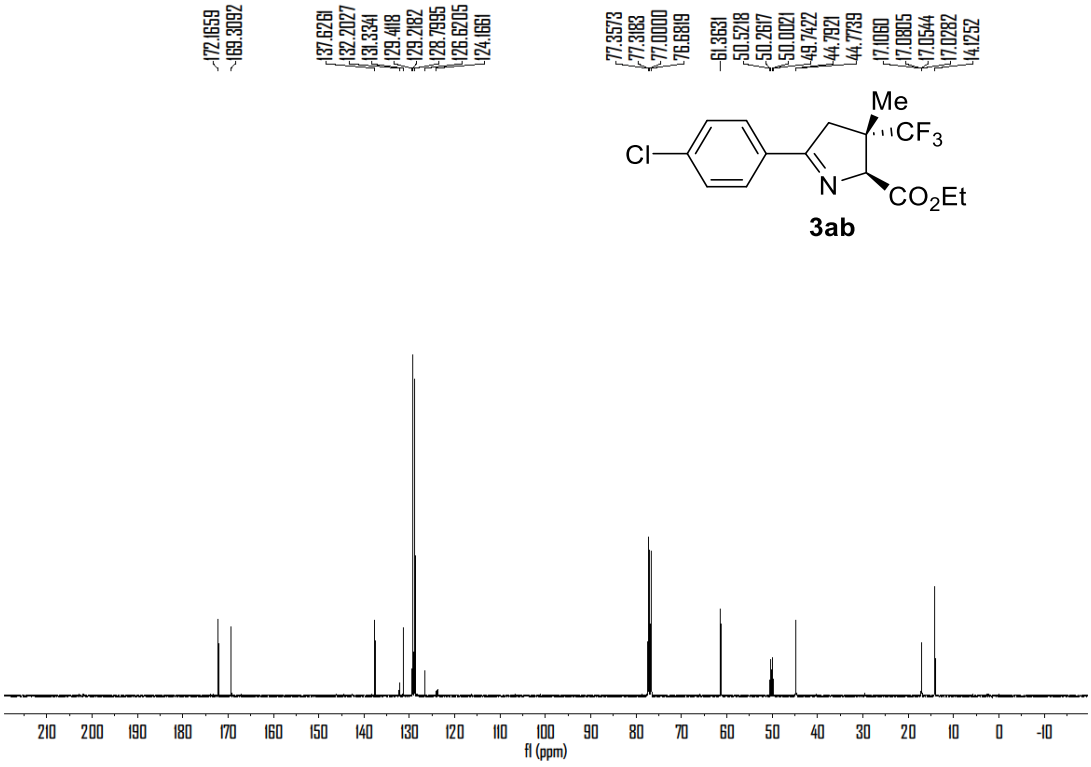
7.7875 7.7812 7.7762 7.7647 7.7597 7.7533 7.4020 7.3958 7.3907 7.3792 7.3743 7.3679 5.0808 4.2892 4.2860 4.2714 4.2683 4.2535 4.2505 4.2356 3.4087 3.3650 2.9780 2.9388 2.9342 1.3263 1.3080 1.2902



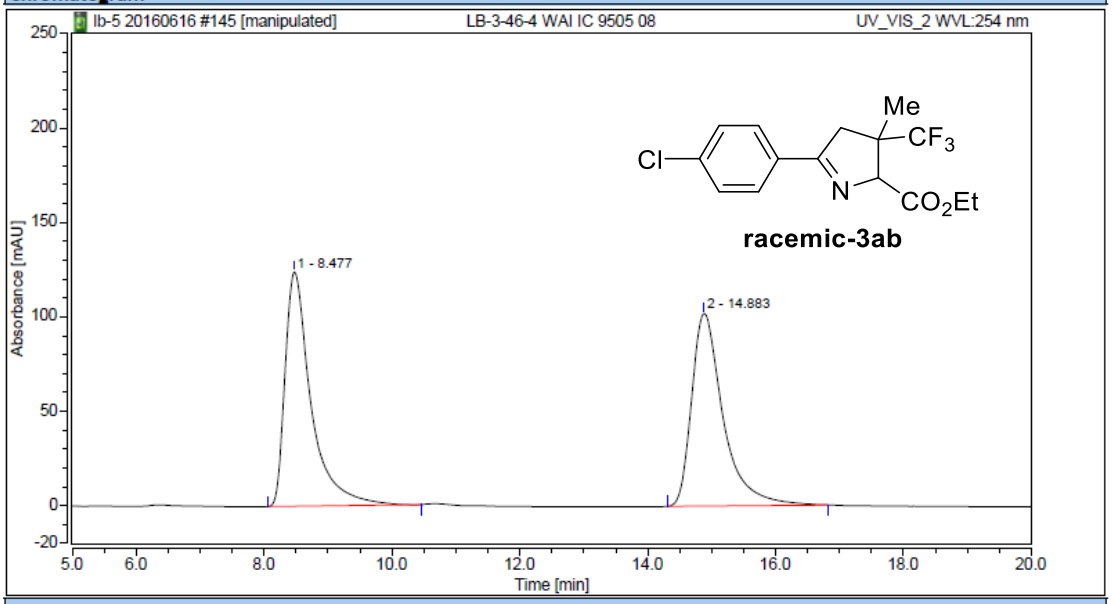
3ab




-77.0056
Me
CF3
Cl
N
CO2Et
3ab
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


172.1659
169.3092
137.6226
132.2027
131.3341
129.4118
129.2182
128.7995
126.6205
124.1661
77.3573
77.3183
77.0000
76.6819
61.3631
50.5218
50.2617
50.0021
49.7422
44.7921
44.7739
17.1080
17.0805
17.0544
17.0282
14.1252
Me
CF3
Cl
N
CO2Et
3ab
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

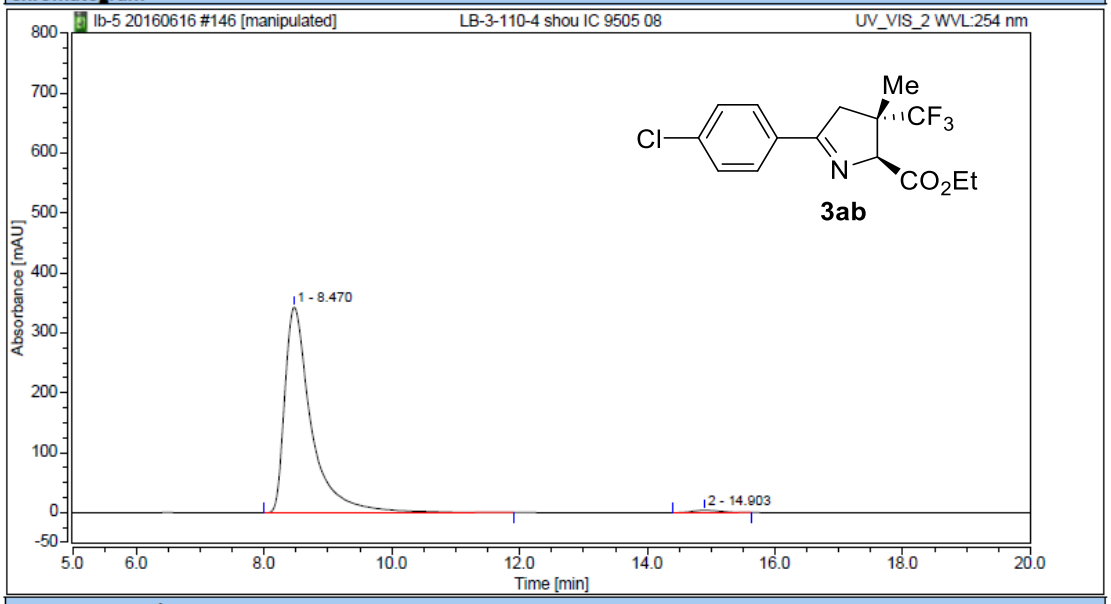
Chromatogram



Integration Results

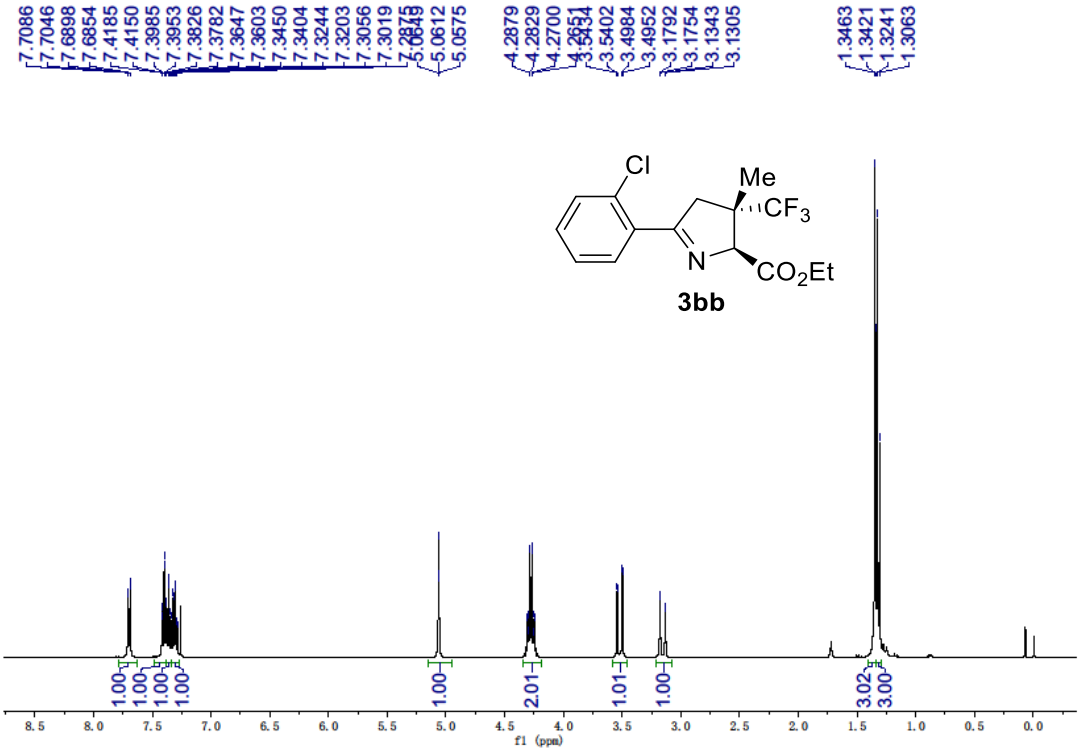
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.477	58.192	124.072	50.01	54.89	n.a.
2		14.883	58.165	101.984	49.99	45.11	n.a.
Total:			**116.357**	**226.056**	**100.00**	**100.00**	

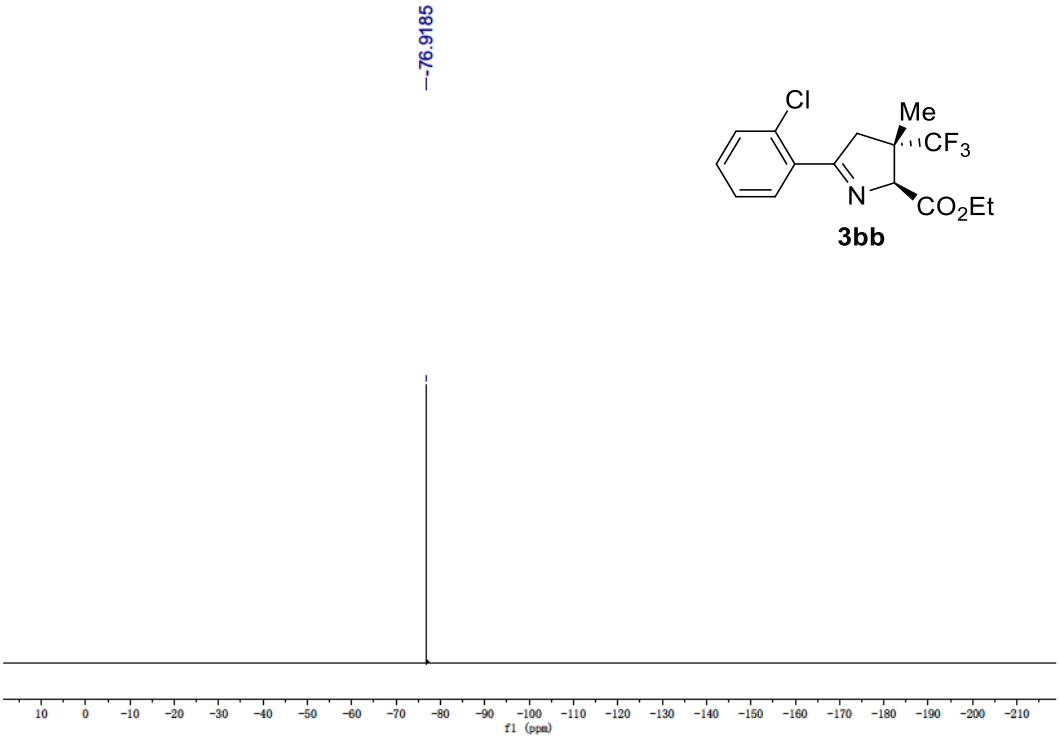
Chromatogram

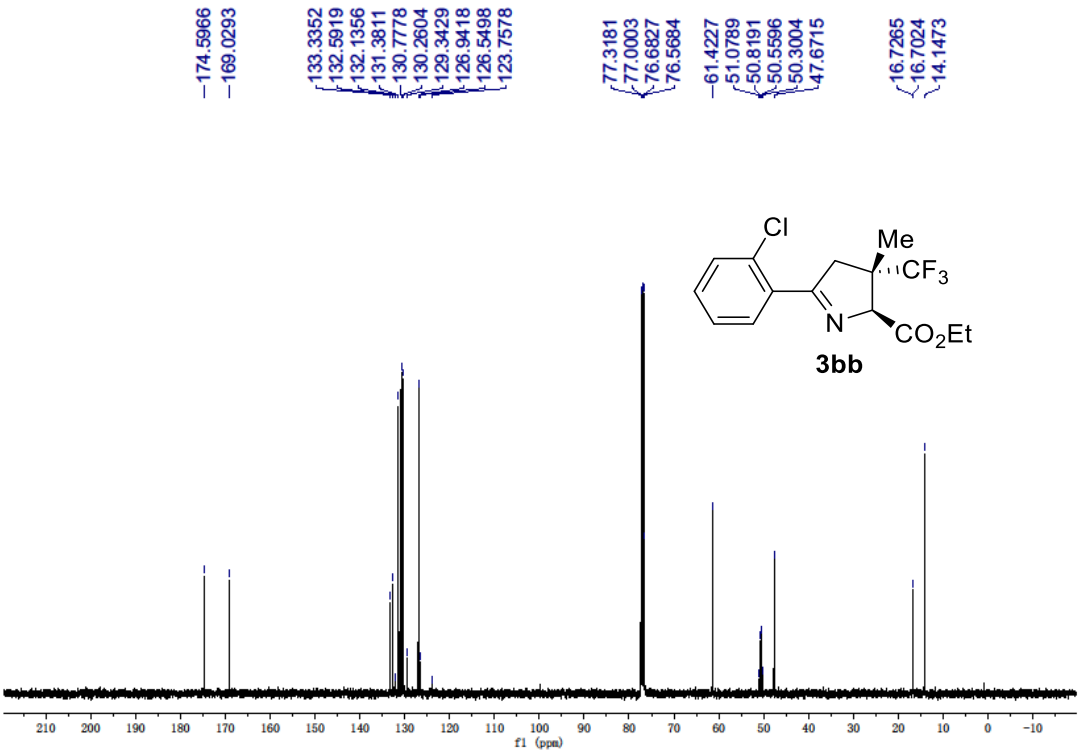


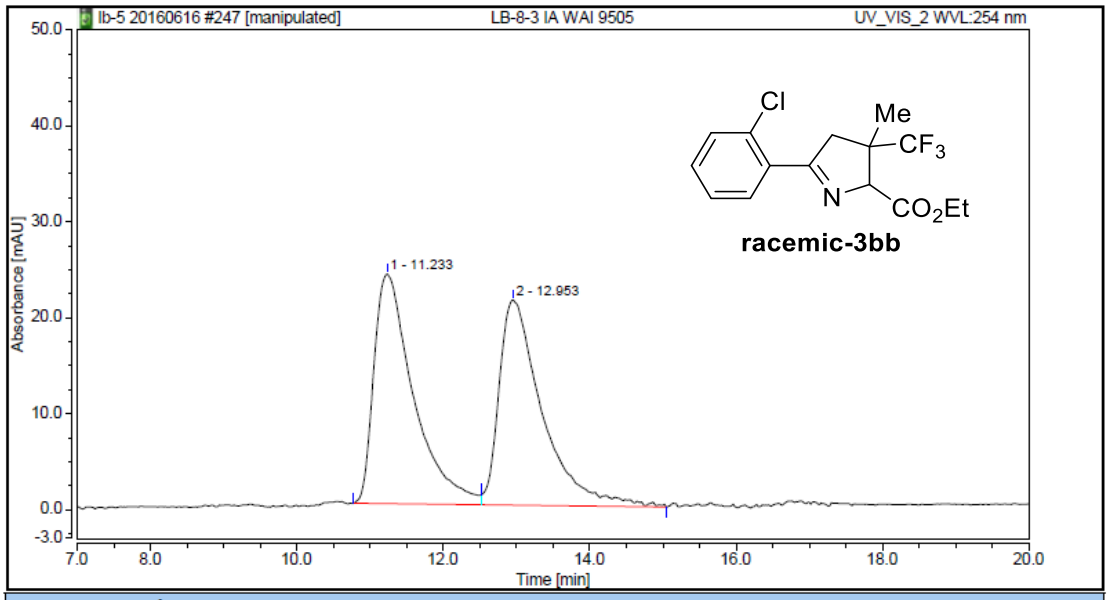
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.470	166.271	343.594	98.77	98.83	n.a.
2		14.903	2.071	4.081	1.23	1.17	n.a.
Total:			**168.341**	**347.676**	**100.00**	**100.00**	


7.7086
7.7046
7.6898
7.6854
7.4185
7.4150
7.3985
7.3953
7.3826
7.3782
7.3647
7.3603
7.3450
7.3404
7.3244
7.3203
7.3056
7.3019
5.0612
5.0575
4.2879
4.2829
4.2700
3.5402
3.4984
3.4952
3.1792
3.1754
3.1343
3.1305
1.3463
1.3421
1.3241
1.3063
Cl
Me
CF3
N
CO2Et
3bb
1.00
1.00
1.00
1.00
1.00
2.01
1.01
1.00
3.02
3.00
f1 (ppm)

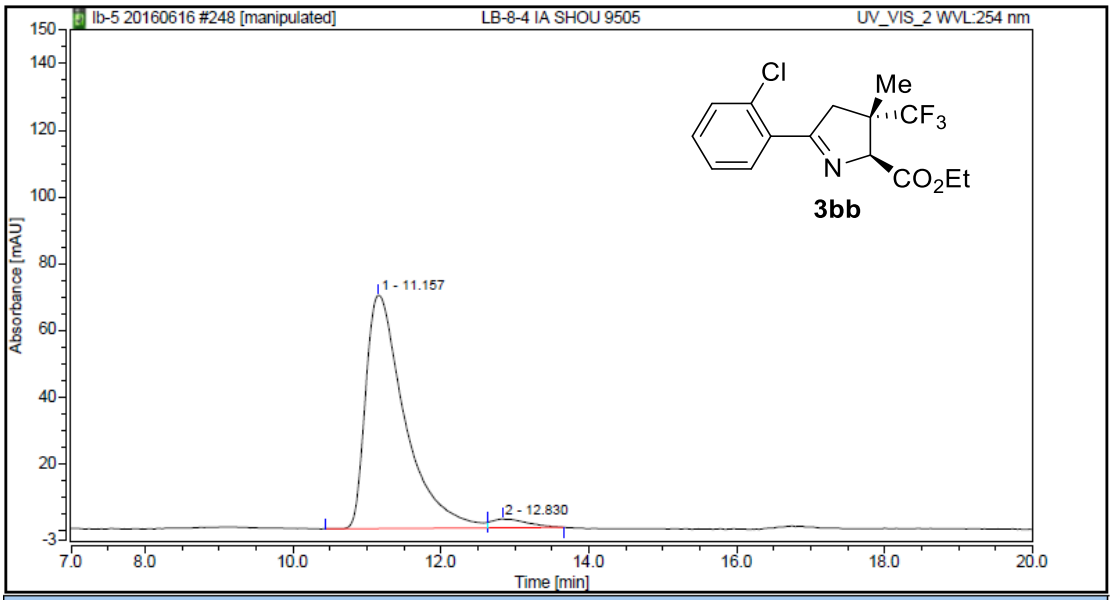

-76.9185
Cl
Me
CF3
N
CO2Et
3bb
f1 (ppm)





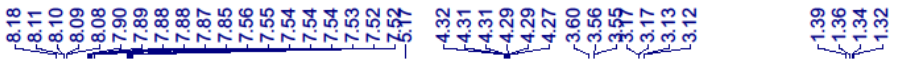
Integration Results

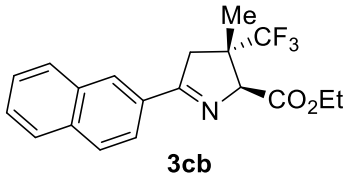
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.233	14.934	23.939	50.68	52.83	n.a.
2		12.953	14.534	21.371	49.32	47.17	n.a.
Total:			**29.468**	**45.310**	**100.00**	**100.00**	



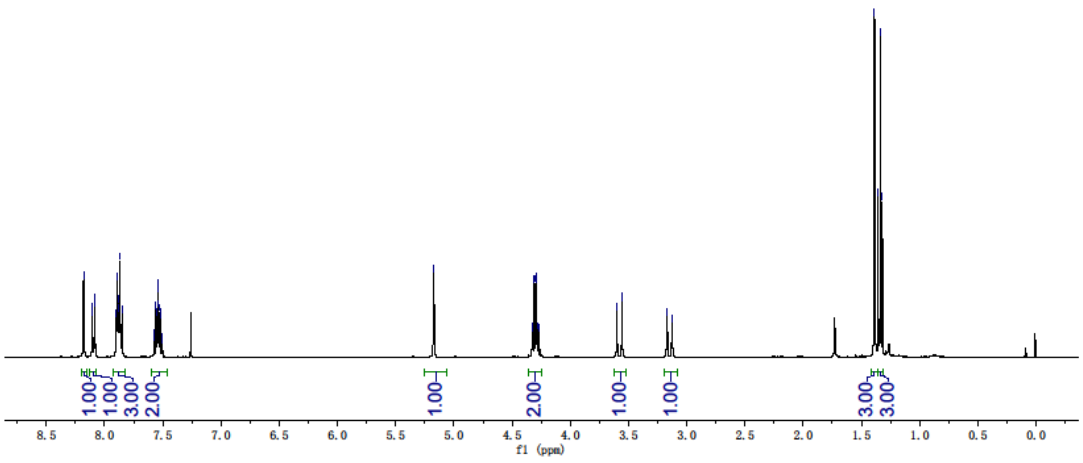
Integration Results

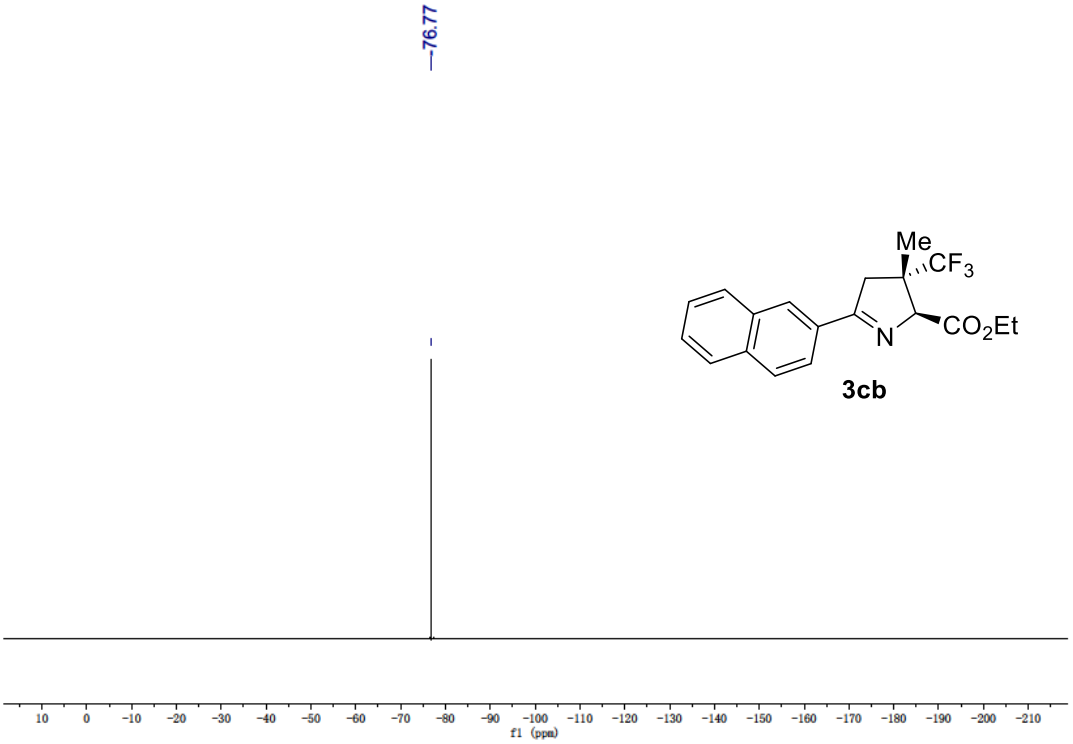
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		11.157	42.760	69.873	96.68	96.36	n.a.
2		12.830	1.470	2.636	3.32	3.64	n.a.
Total:			**44.231**	**72.509**	**100.00**	**100.00**	

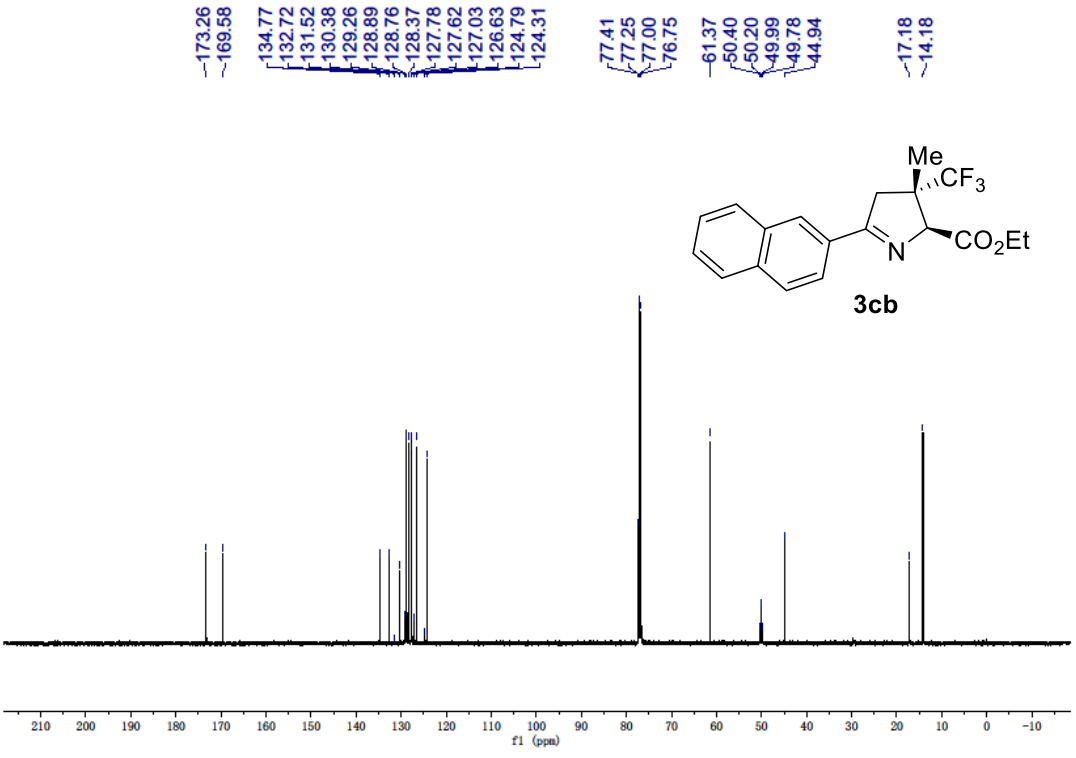




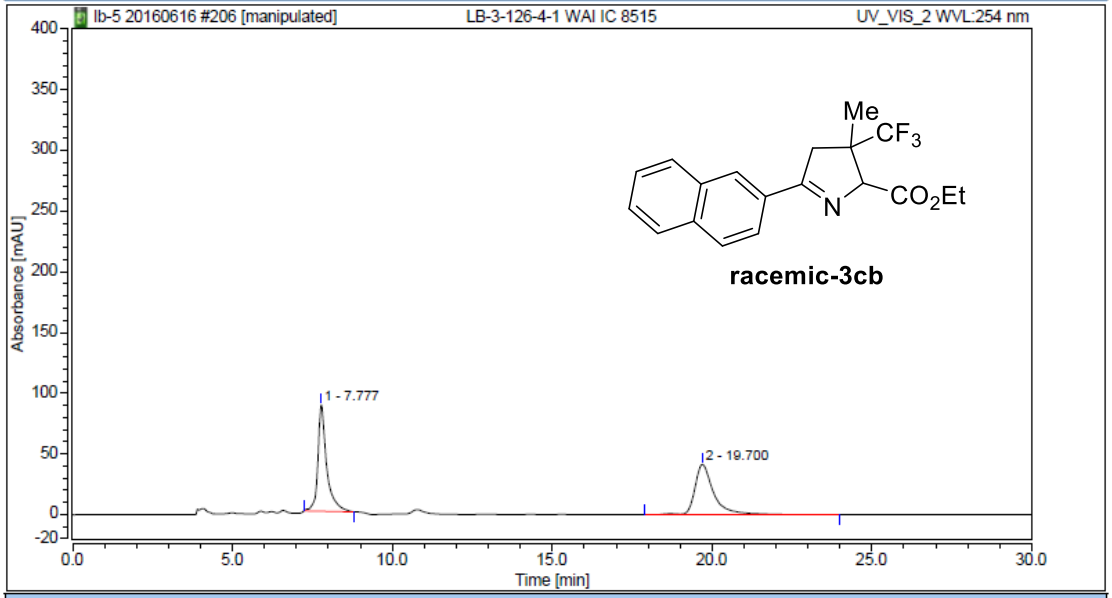
3cb




-76.77
Me
CF3
CO2Et
N
3cb
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


173.26
169.58
134.77
132.72
131.52
130.38
129.26
128.89
128.76
128.37
127.78
127.62
127.03
126.63
124.79
124.31
77.41
77.25
77.00
76.75
61.37
50.40
50.20
49.99
49.78
44.94
17.18
14.18
Me
CF3
CO2Et
N
3cb
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

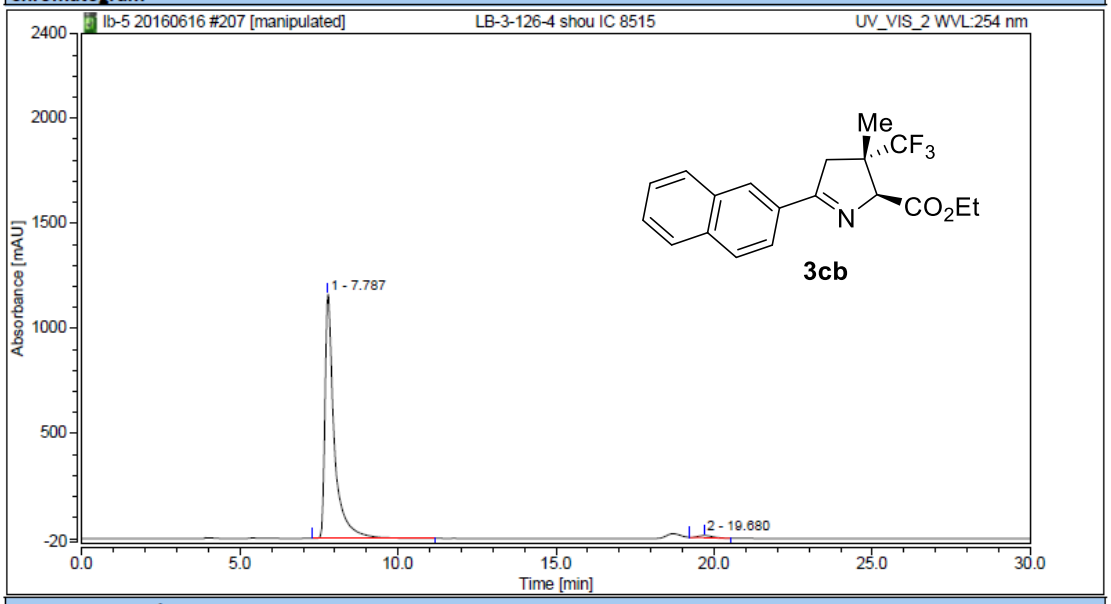
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.777	28.053	87.657	49.99	67.92	n.a.
2		19.700	28.063	41.399	50.01	32.08	n.a.
Total:			**56.116**	**129.056**	**100.00**	**100.00**	

Chromatogram

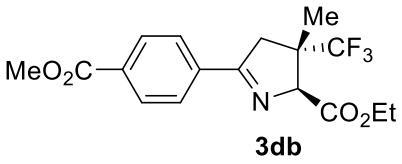


Integration Results

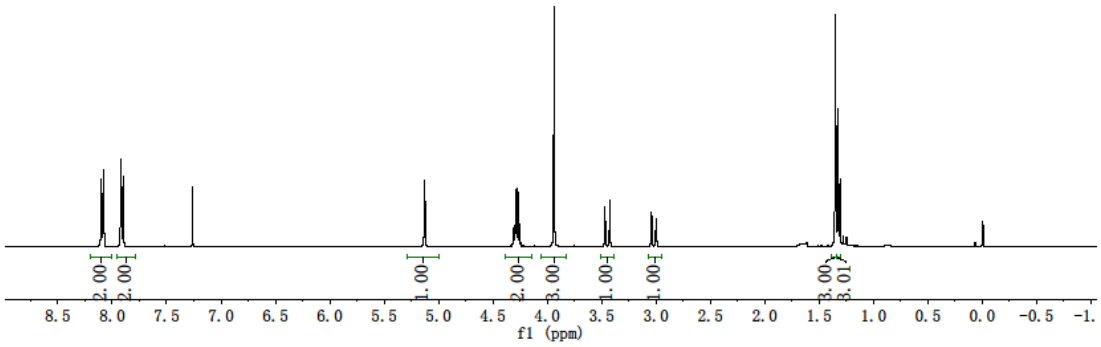
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.787	398.707	1163.013	98.76	99.15	n.a.
2		19.680	4.992	9.971	1.24	0.85	n.a.
Total:			**403.700**	**1172.984**	**100.00**	**100.00**	

8.1027
8.1002
8.0977
8.0811
8.0778
8.0763
7.9225
7.9191
7.9013
7.8982

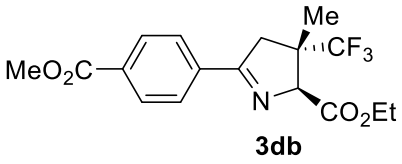
5.1275
5.1254
4.2926
4.2881
4.2747
4.2703
3.9390
3.9361
3.9340
3.4683
3.0417
3.0382
3.0010
2.9978
2.9942
1.3494
1.3452
1.3418
1.3263
1.3235
1.3216
1.3084
1.3056
1.3038



3db

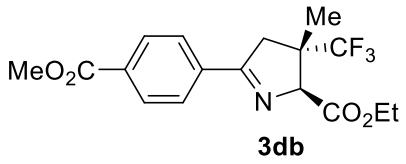


-76.8965

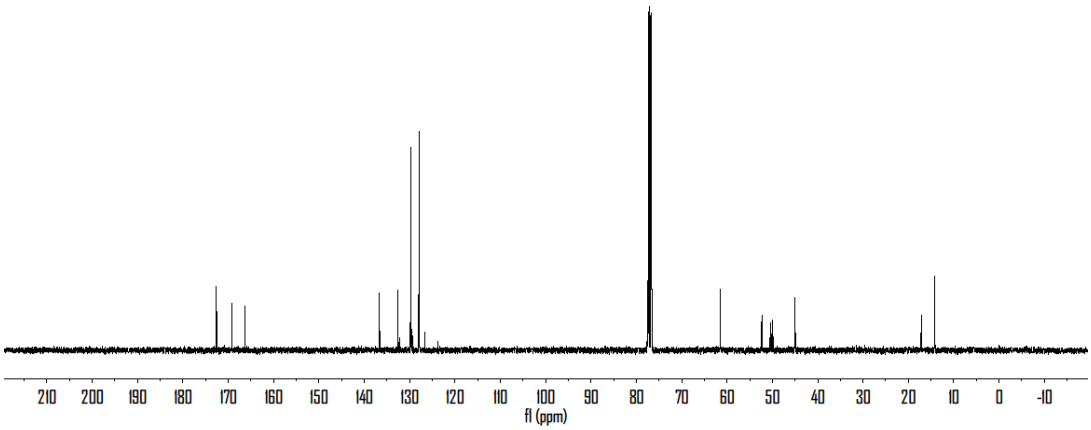


3db

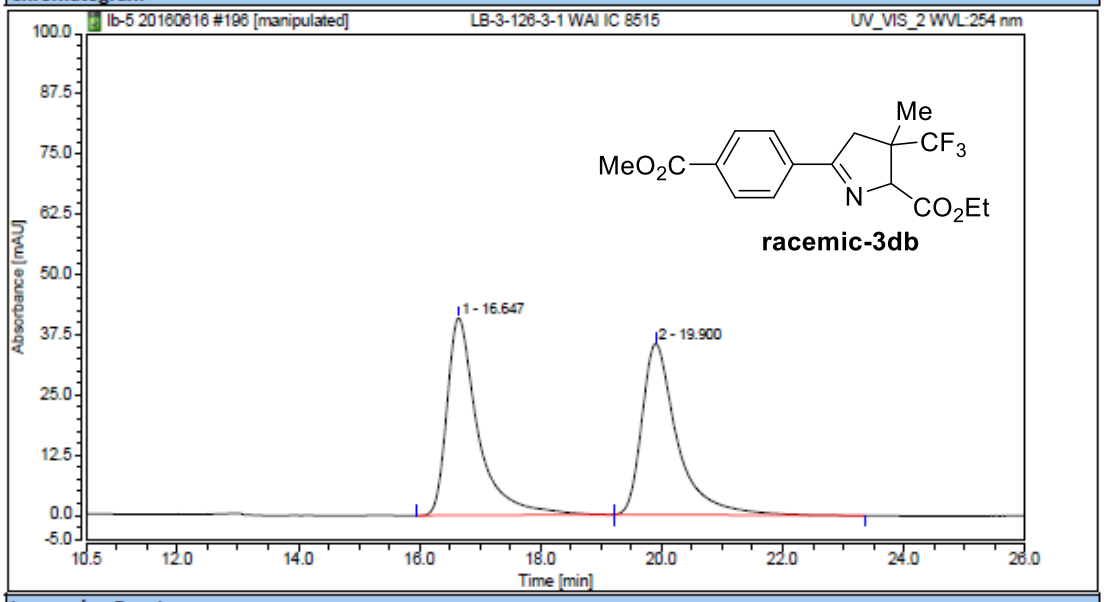
172.6055
169.2172
166.3569
136.7778
132.5688
132.2018
129.7661
129.4495
127.9222
126.6293
123.8506
77.5506
77.3178
77.0007
76.6832
61.4669
52.3180
50.5553
50.2951
50.0343
49.7758
44.9946
17.1371
14.1861



3db



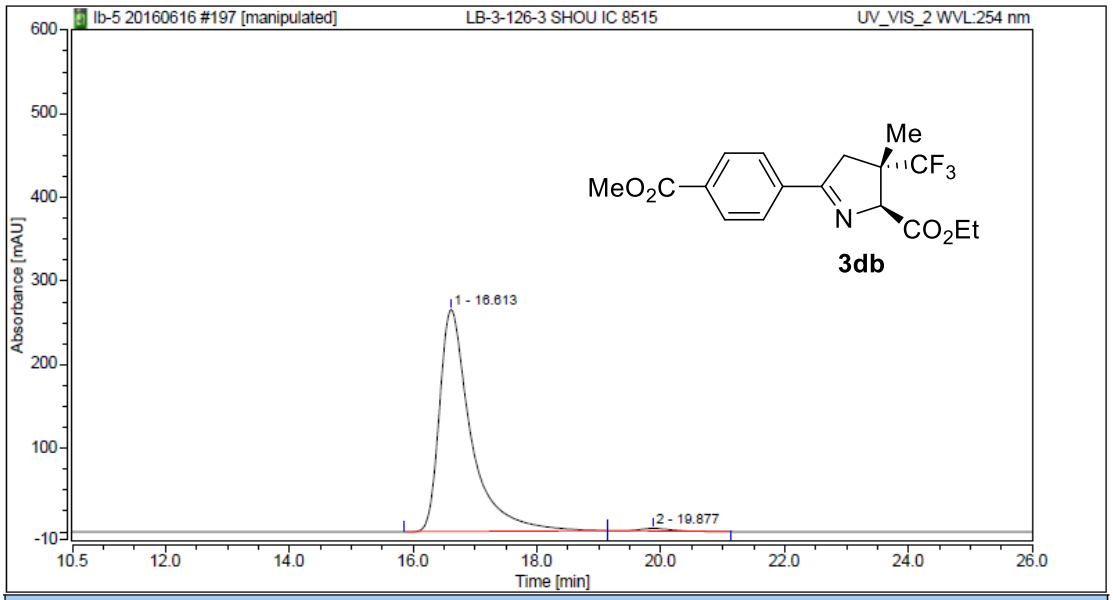
Chromatogram



racemic-3db

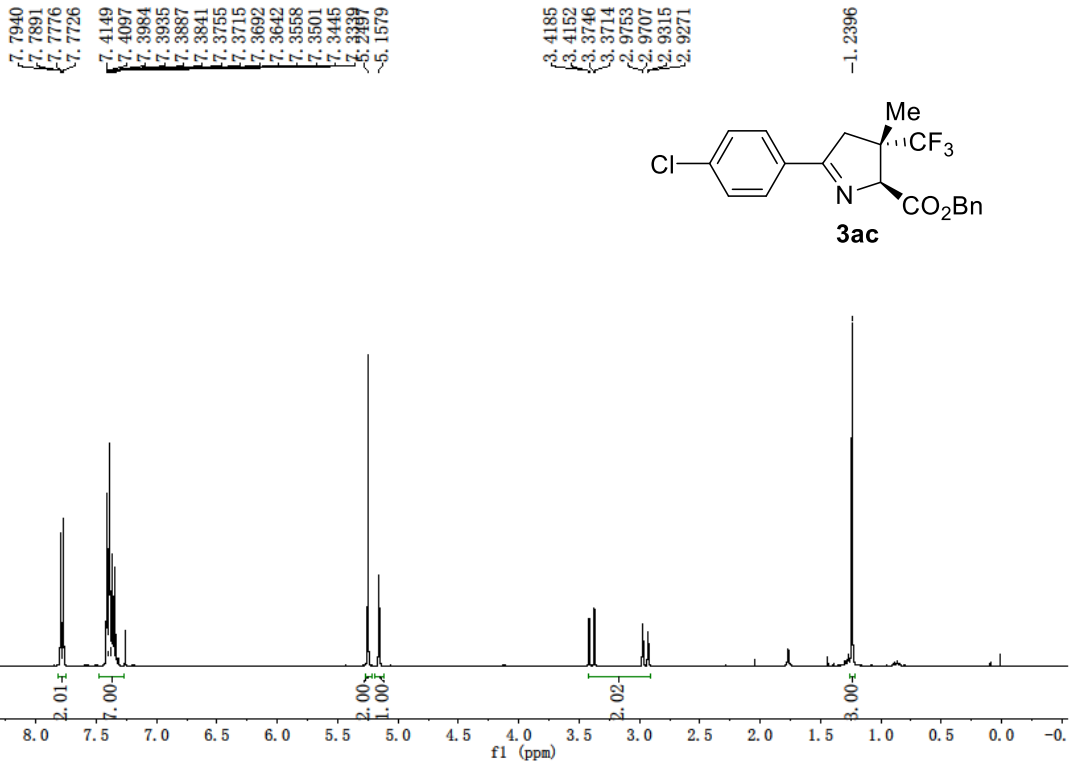
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.647	24.297	40.967	50.19	53.56	n.a.
2		19.900	24.114	35.521	49.81	46.44	n.a.
Total:			**48.411**	**76.489**	**100.00**	**100.00**	

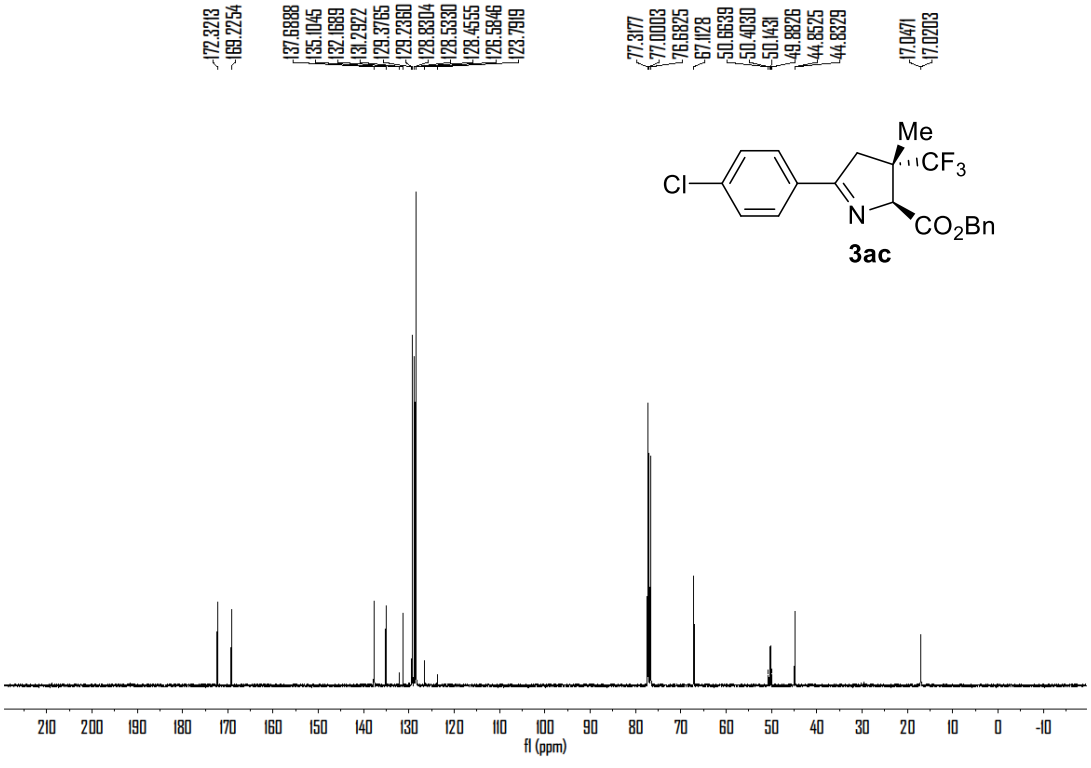


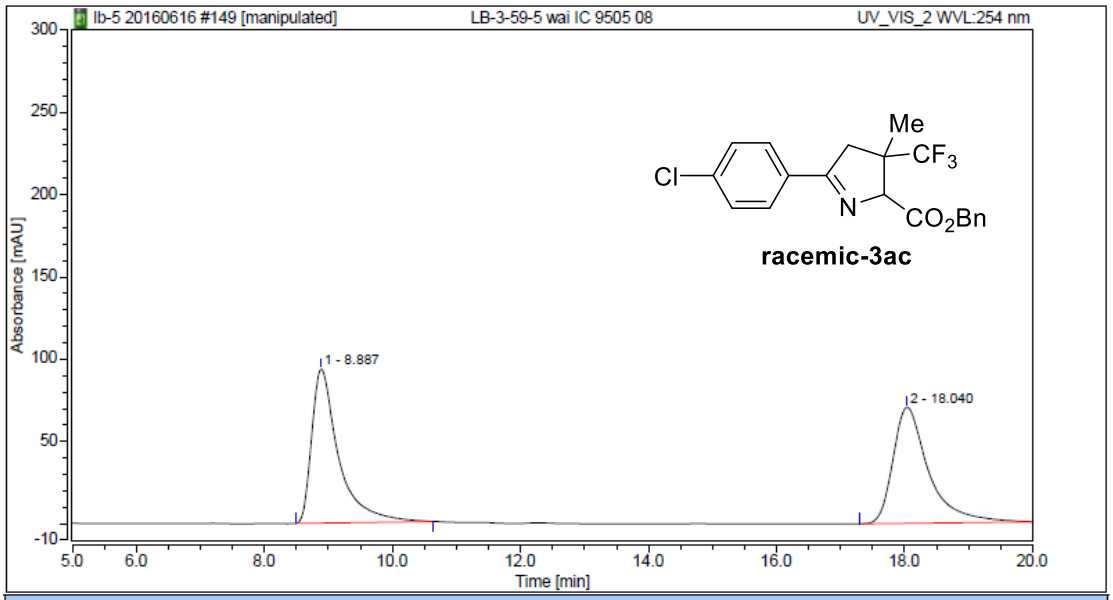
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.613	156.745	265.433	98.89	98.82	n.a.
2		19.877	1.762	3.171	1.11	1.18	n.a.
Total:			**158.507**	**268.604**	**100.00**	**100.00**	



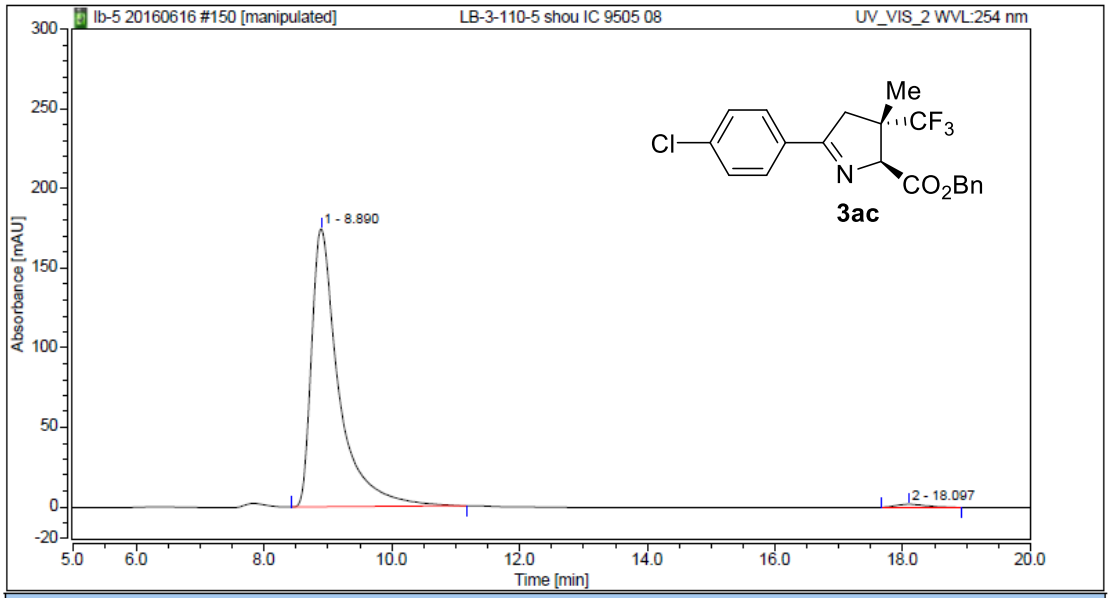

-76.8868
Me
CF3
Cl
N
CO2Bn
3ac
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


172.3213
169.2754
137.6888
135.1045
132.1688
131.2922
129.3765
129.2360
128.8304
128.5330
128.4555
126.5846
123.7919
77.3177
77.0003
76.6825
67.1128
50.6639
50.4030
50.1431
49.8826
44.8525
44.8329
17.0471
17.0203
Me
CF3
Cl
N
CO2Bn
3ac
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



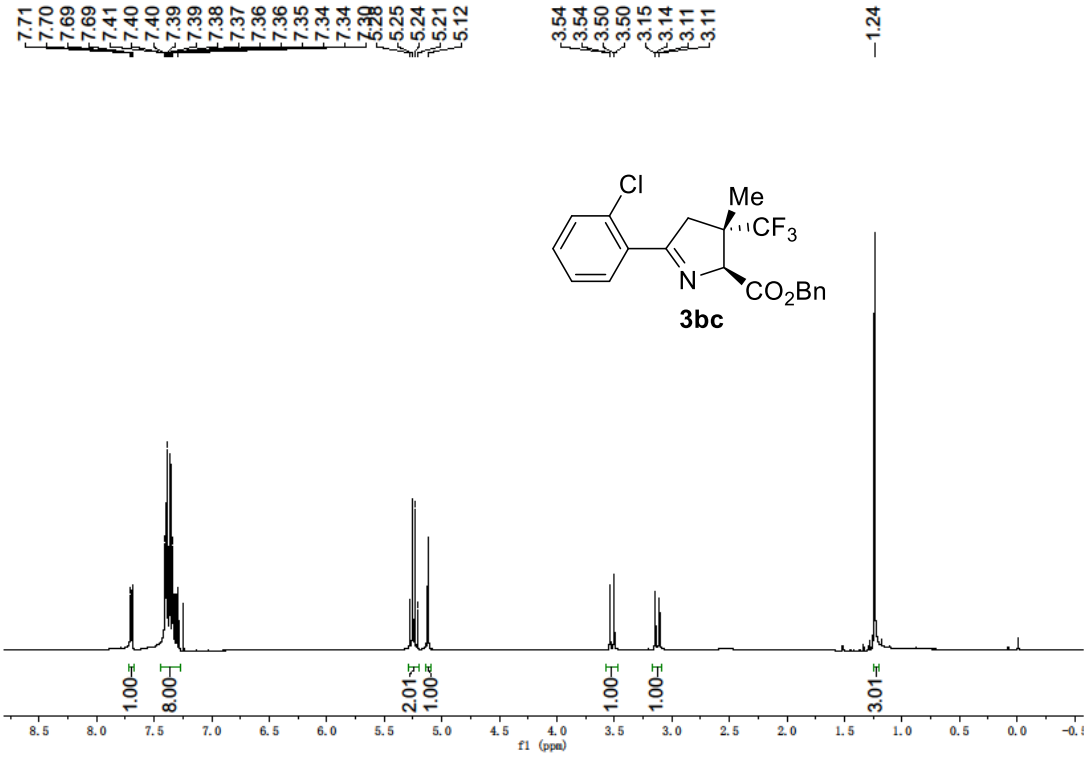
Integration Results

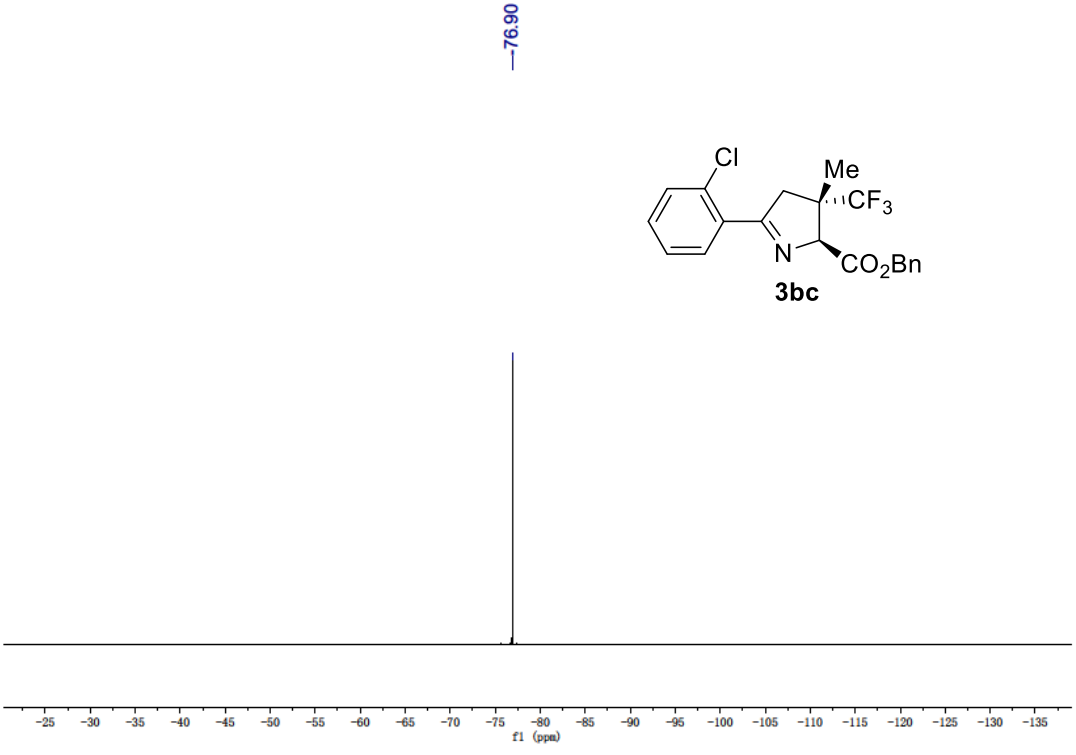
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.887	45.406	93.530	50.01	57.03	n.a.
2		18.040	45.393	70.478	49.99	42.97	n.a.
Total:			**90.799**	**164.008**	**100.00**	**100.00**	

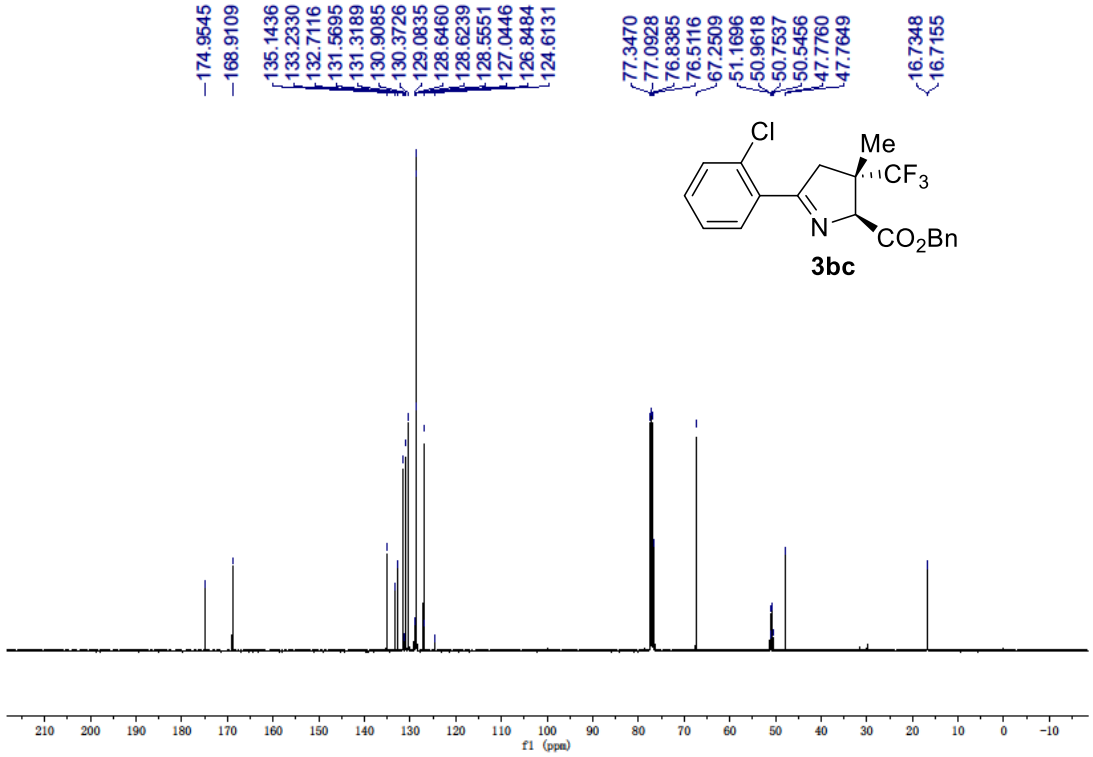


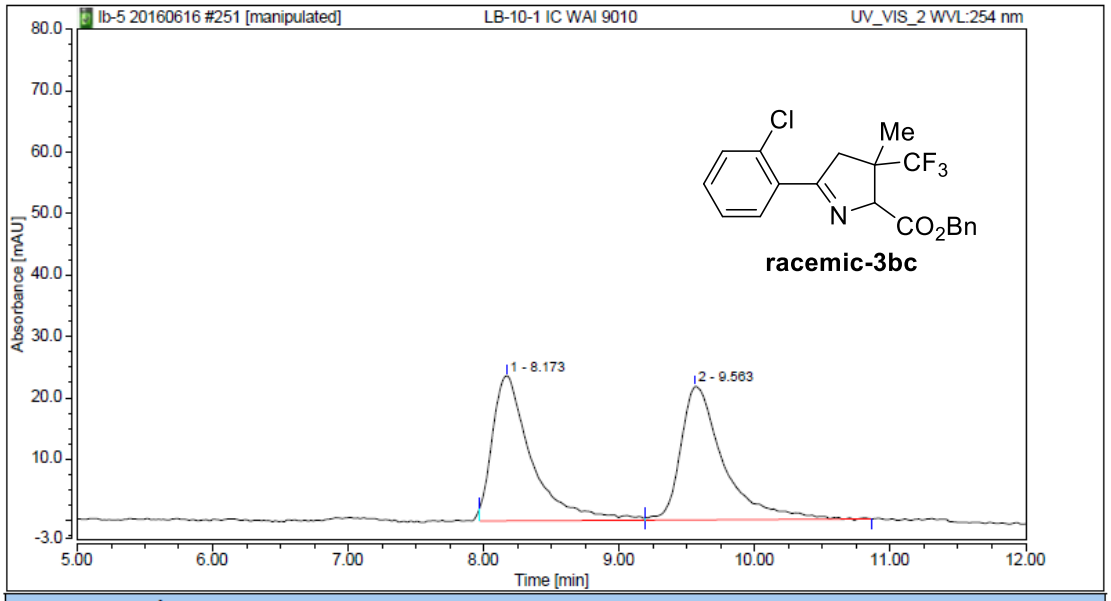
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.890	86.470	174.776	98.74	98.86	n.a.
2		18.097	1.103	2.008	1.26	1.14	n.a.
Total:			**87.573**	**176.785**	**100.00**	**100.00**	


7.71
7.70
7.69
7.69
7.41
7.40
7.40
7.39
7.39
7.38
7.37
7.36
7.36
7.35
7.34
7.34
5.25
5.24
5.21
5.12
3.54
3.54
3.50
3.50
3.15
3.14
3.11
3.11
1.24
Cl
Me
CF3
N
CO2Bn
3bc
1.00
8.00
2.01
1.00
1.00
1.00
3.01
f1 (ppm)

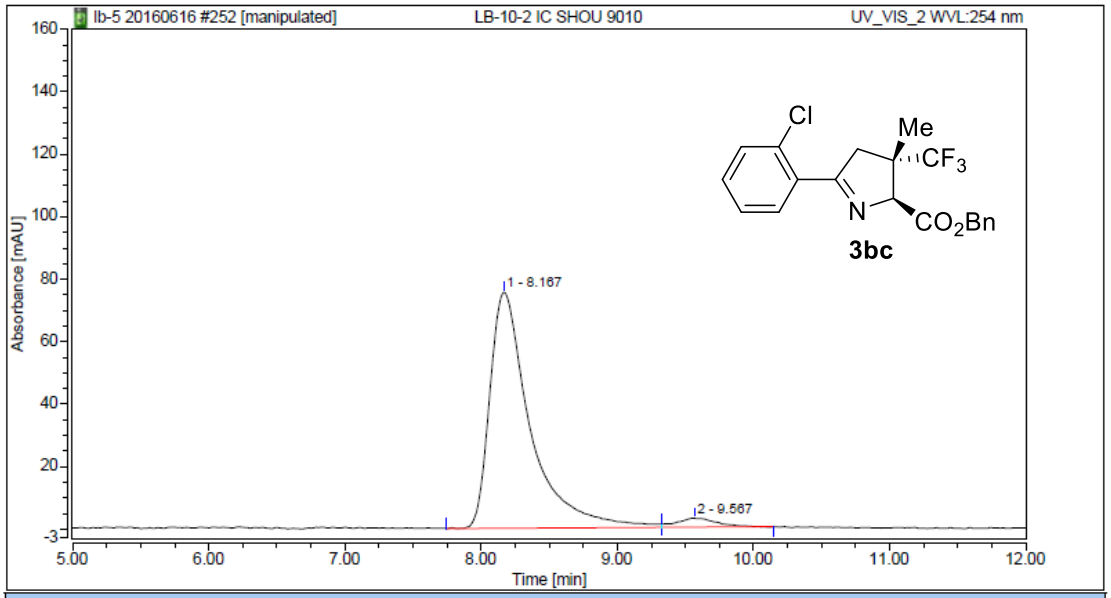

76.90
Cl
Me
CF3
N
CO2Bn
3bc
f1 (ppm)





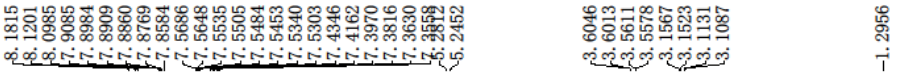
Integration Results

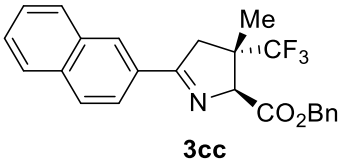
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.173	7.906	23.618	49.81	52.05	n.a.
2		9.563	7.967	21.757	50.19	47.95	n.a.
Total:			**15.873**	**45.375**	**100.00**	**100.00**	

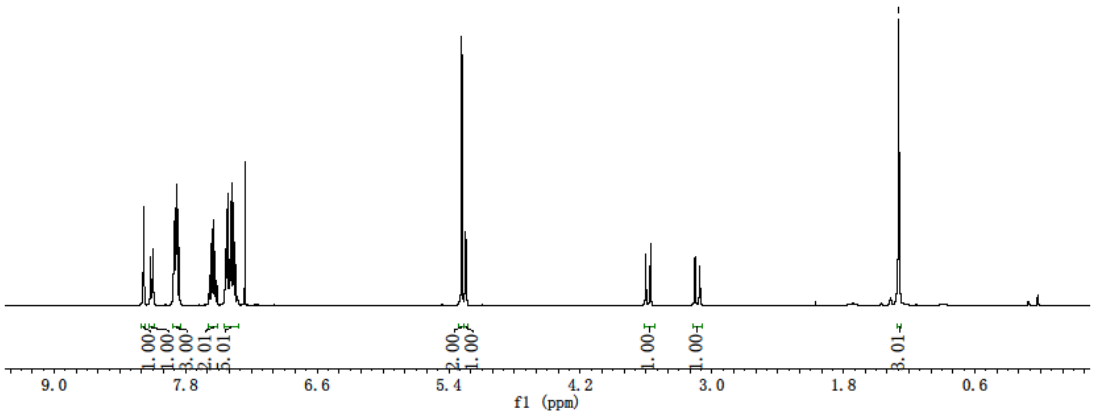


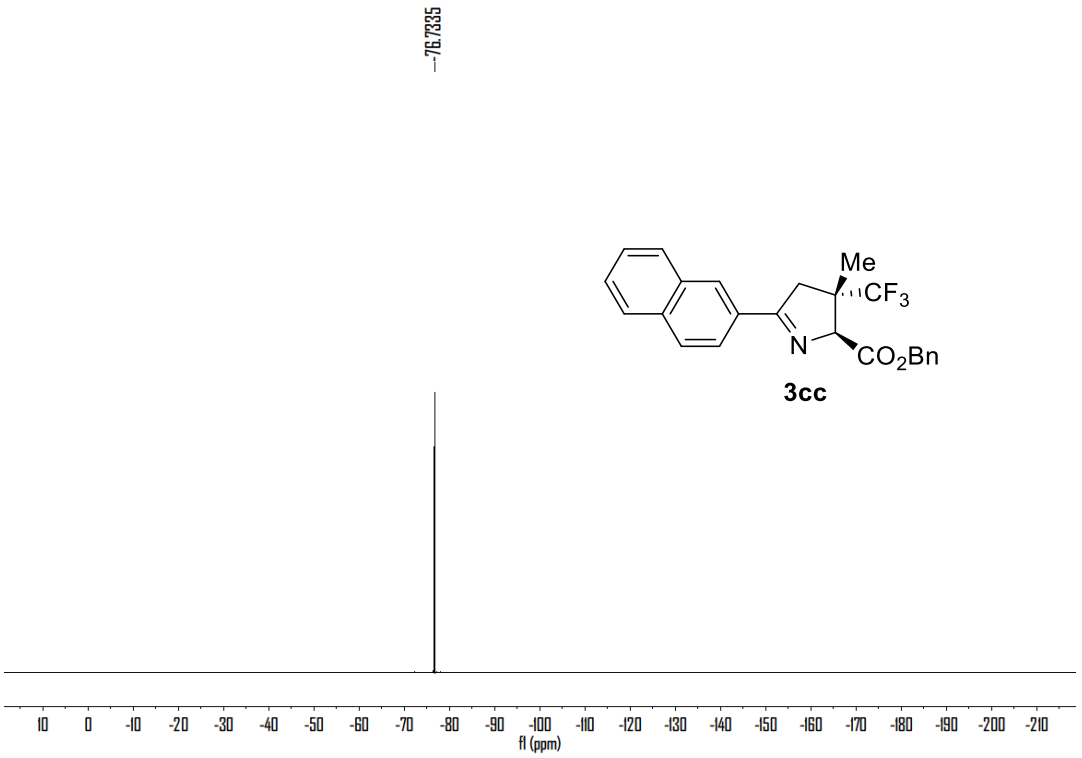
Integration Results

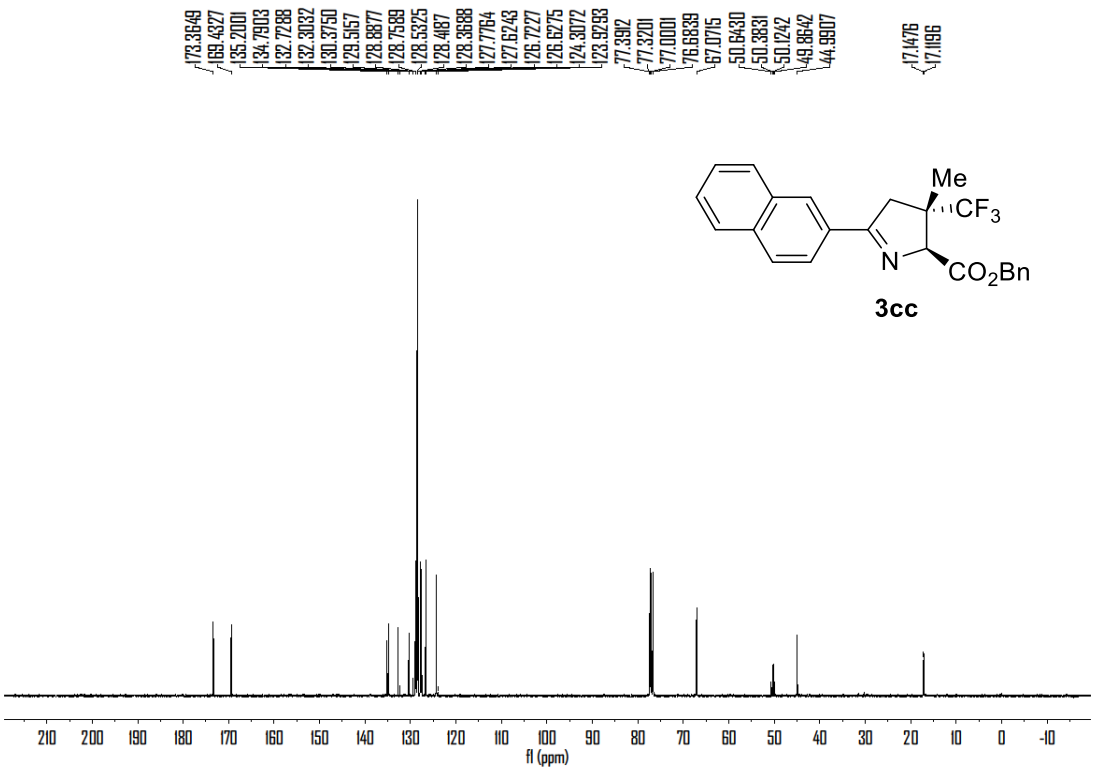
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.167	26.027	75.611	96.45	96.39	n.a.
2		9.567	0.958	2.829	3.55	3.61	n.a.
Total:			**26.985**	**78.439**	**100.00**	**100.00**	

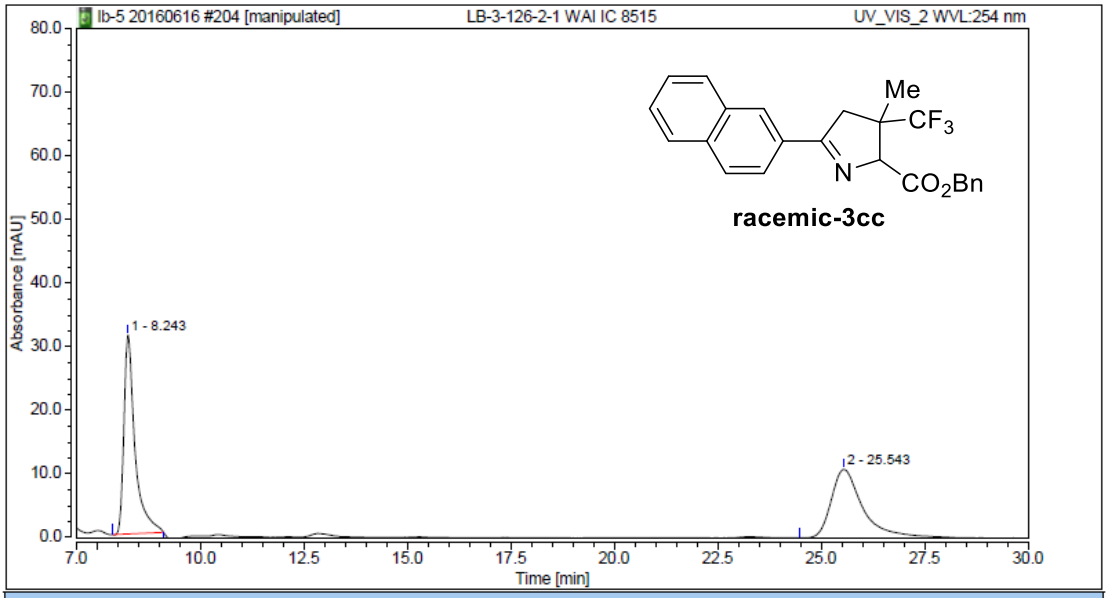






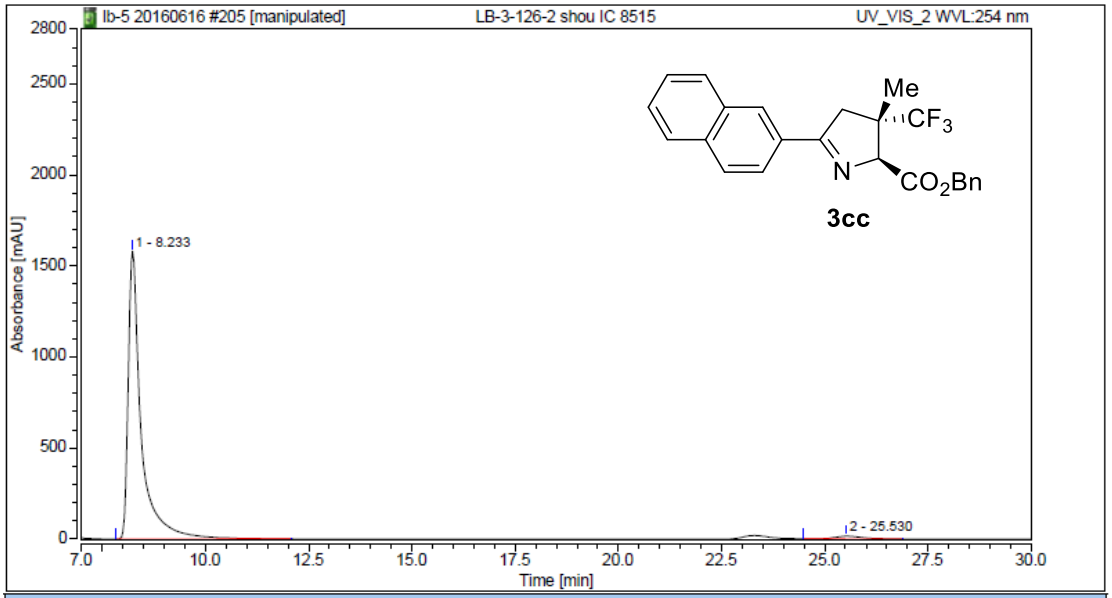

-76.7335
Me
CF3
N
CO2Bn
3cc
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


173.3649
169.4327
135.2001
134.7903
132.7288
132.3032
131.3750
129.5157
128.8877
128.7589
128.5325
128.4187
128.3688
127.7764
127.6243
126.7227
126.6275
124.3072
123.9293
77.3982
77.3201
77.0001
76.6639
67.0715
50.6430
50.3831
50.1242
49.8642
44.9907
17.1476
17.1196
Me
CF3
N
CO2Bn
3cc
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



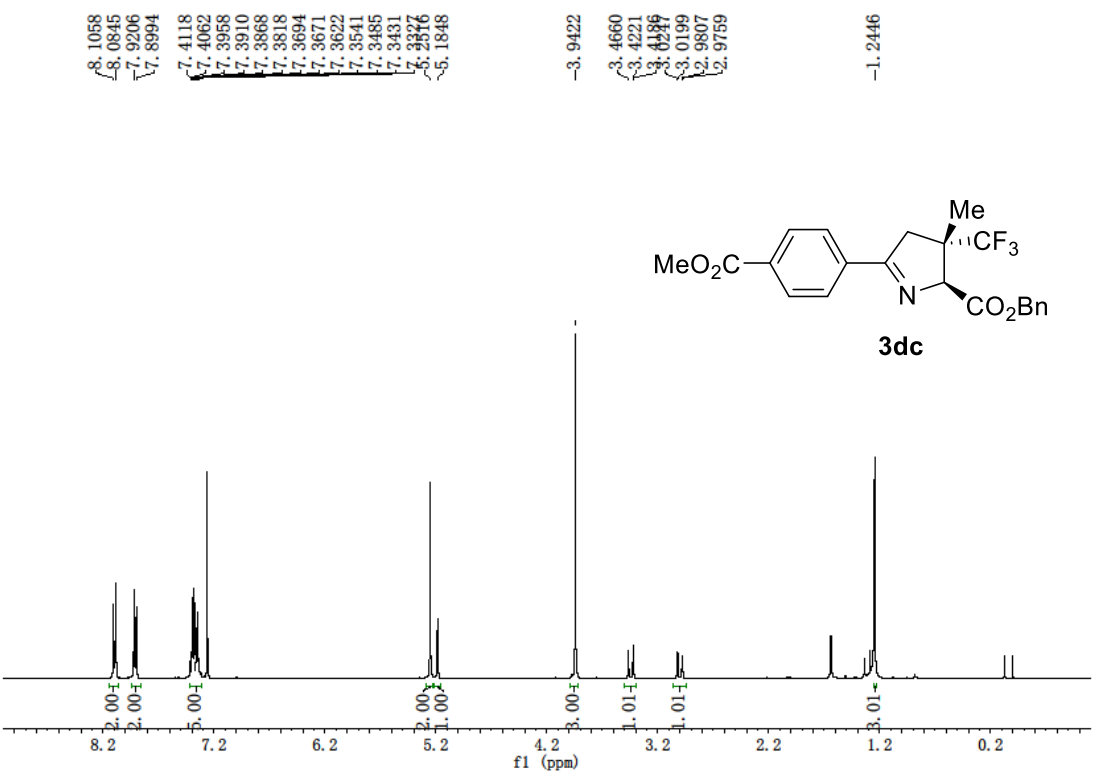
Integration Results

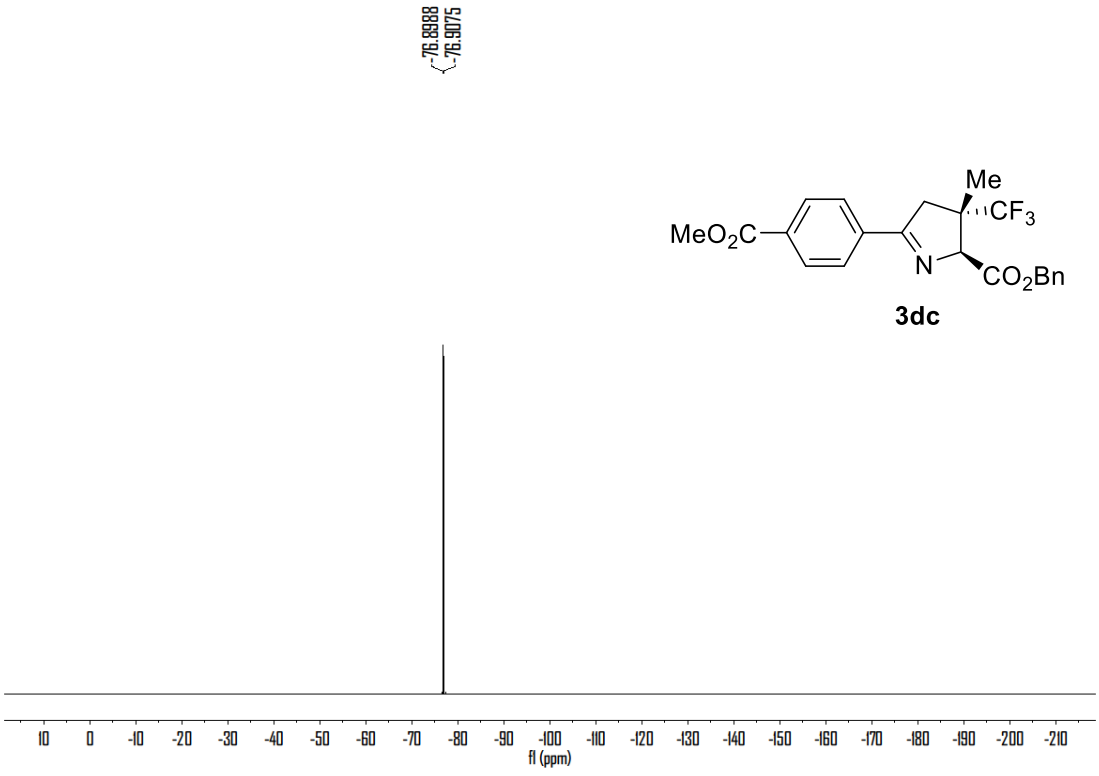
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.243	9.692	31.270	50.30	74.35	n.a.
2		25.543	9.574	10.785	49.70	25.65	n.a.
Total:			**19.266**	**42.055**	**100.00**	**100.00**	

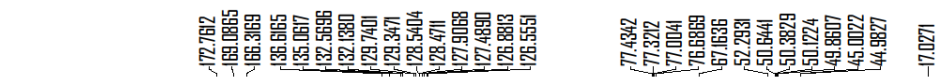


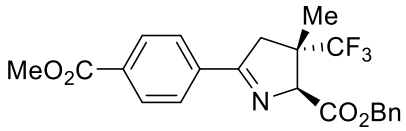
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		8.233	578.919	1580.992	98.06	99.05	n.a.
2		25.530	11.464	15.113	1.94	0.95	n.a.
Total:			**590.383**	**1596.105**	**100.00**	**100.00**	

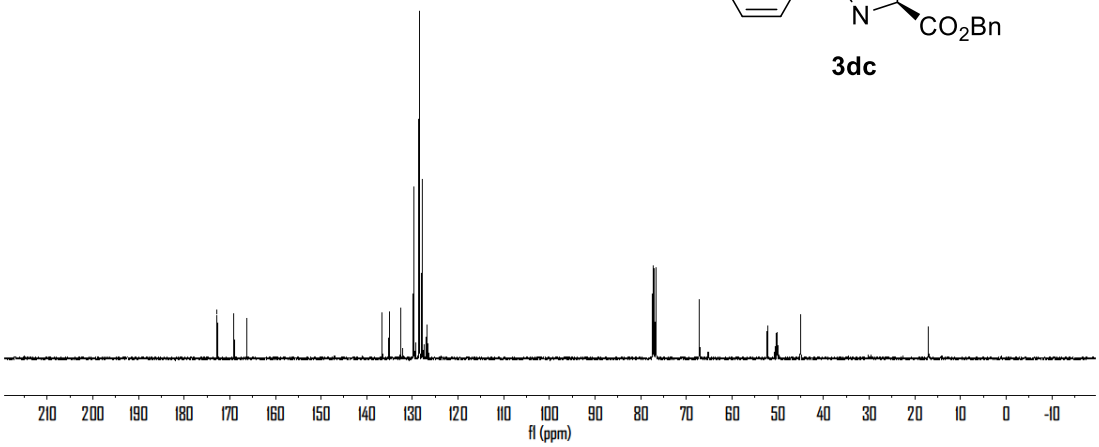

8.1058
8.0845
7.9206
7.8994
7.4118
7.4062
7.3958
7.3910
7.3868
7.3818
7.3694
7.3671
7.3622
7.3541
7.3485
7.3431
5.2516
5.1848
3.9422
3.4660
3.4221
3.0199
2.9807
2.9759
1.2446
Me
CF3
MeO2C
N
CO2Bn
3dc
2.00
2.00
5.00
2.00
1.00
3.00
1.01
1.01
3.01
8.2
7.2
6.2
5.2
4.2
3.2
2.2
1.2
0.2
f1 (ppm)

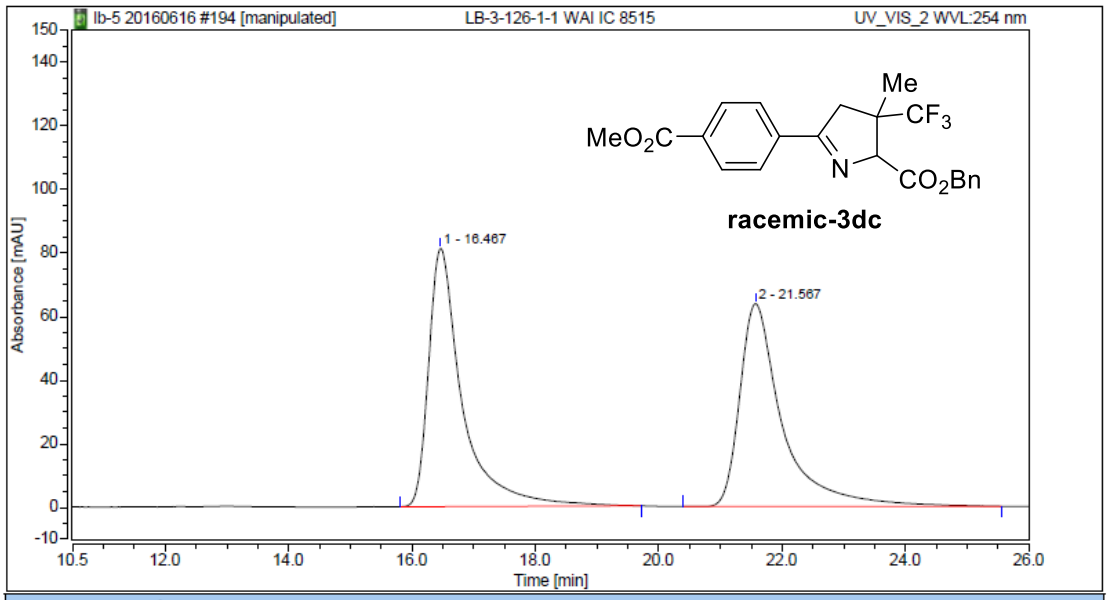

76.8988
76.9075
Me
CF3
MeO2C
N
CO2Bn
3dc
10
0
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)





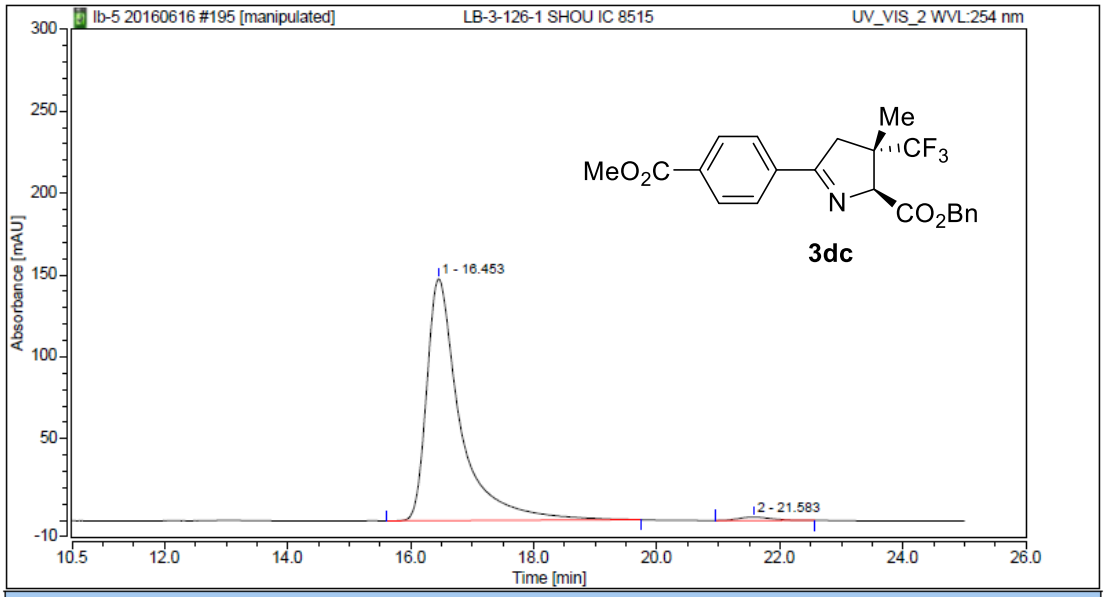
3dc





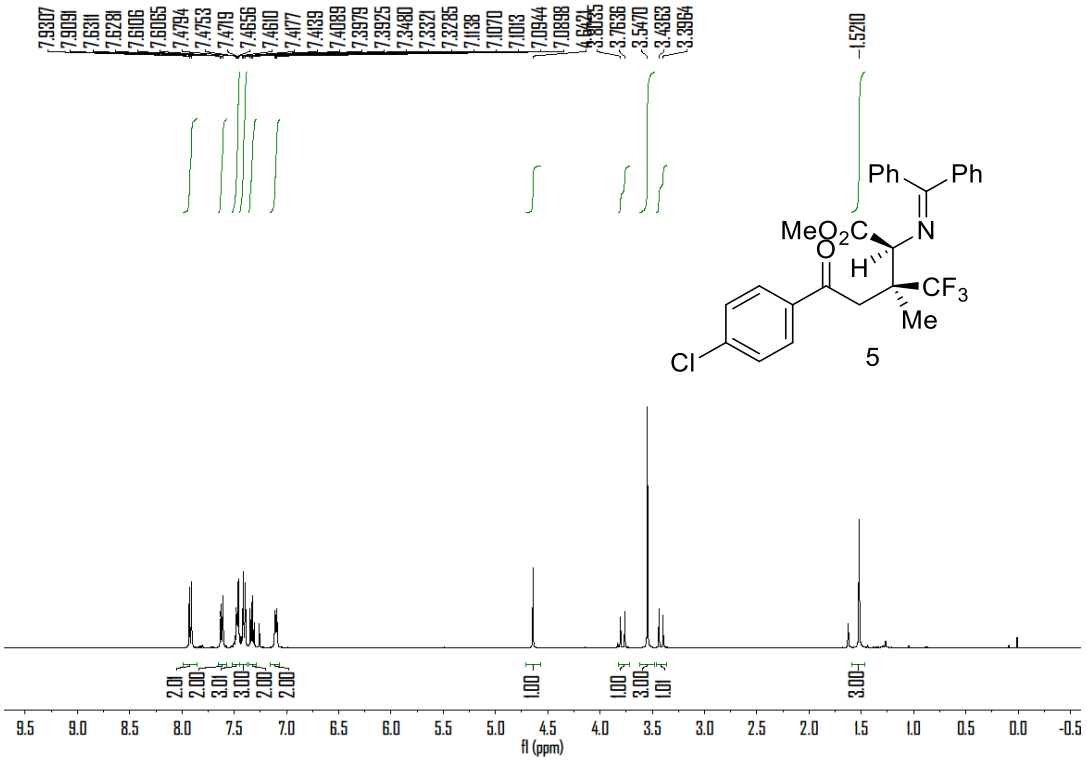
Integration Results

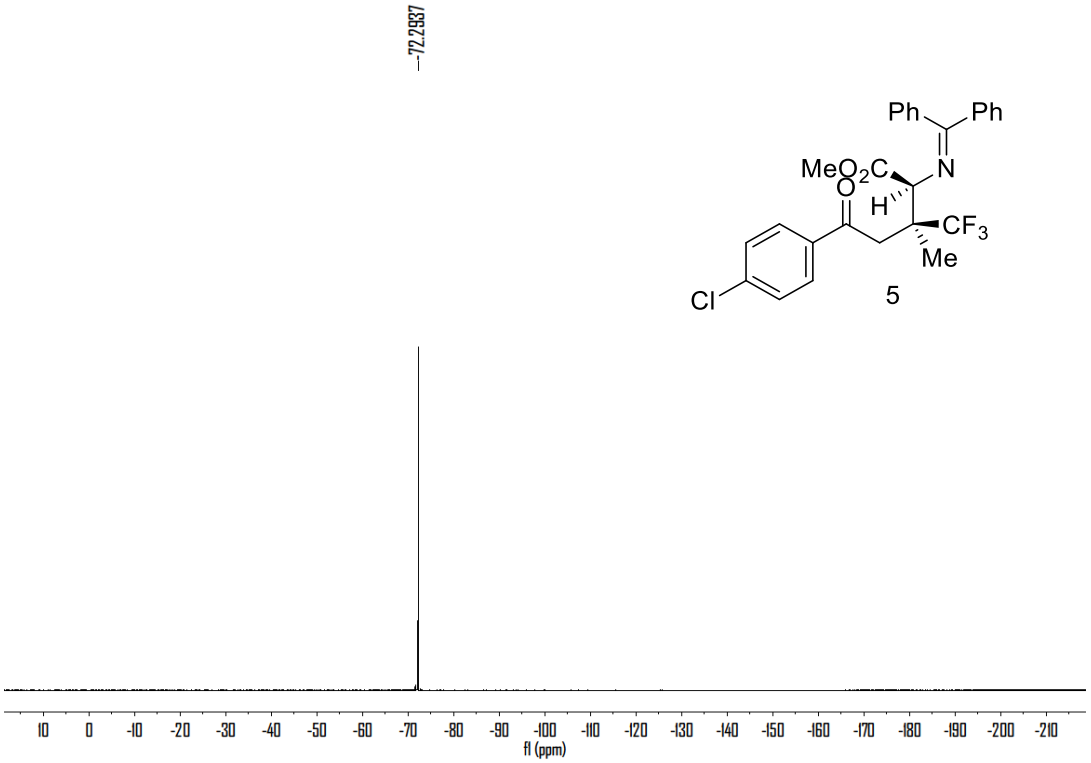
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.467	51.222	81.214	50.14	56.01	n.a.
2		21.567	50.930	63.783	49.86	43.99	n.a.
Total:			**102.151**	**144.997**	**100.00**	**100.00**	

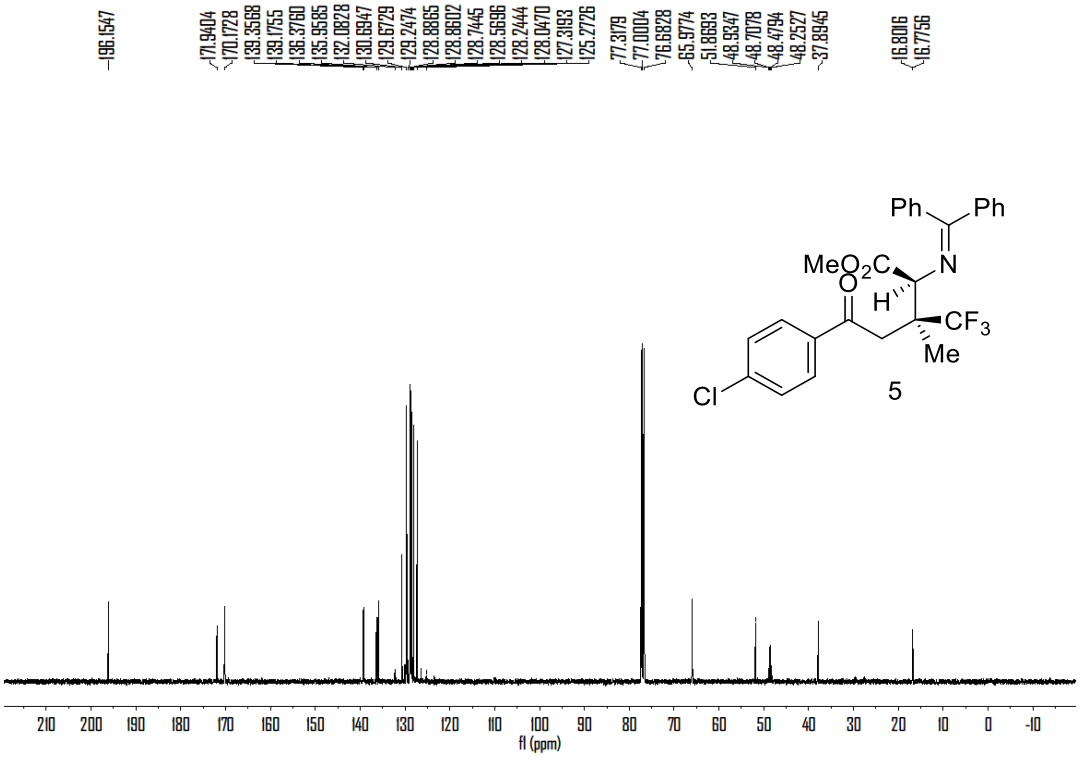


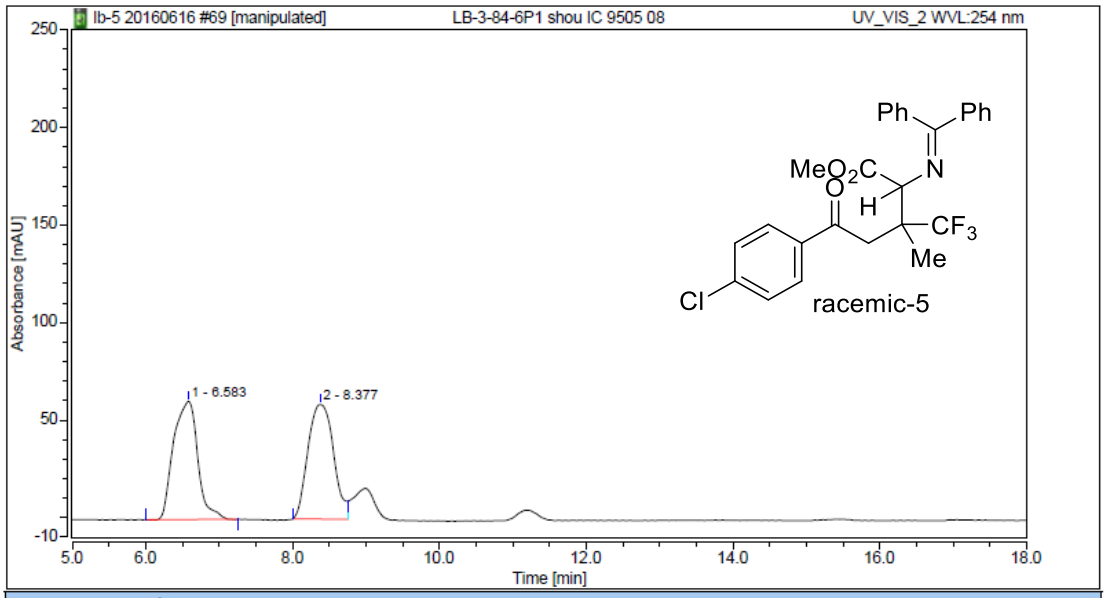
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		16.453	93.174	147.731	98.65	98.63	n.a.
2		21.583	1.275	2.057	1.35	1.37	n.a.
Total:			**94.450**	**149.787**	**100.00**	**100.00**	



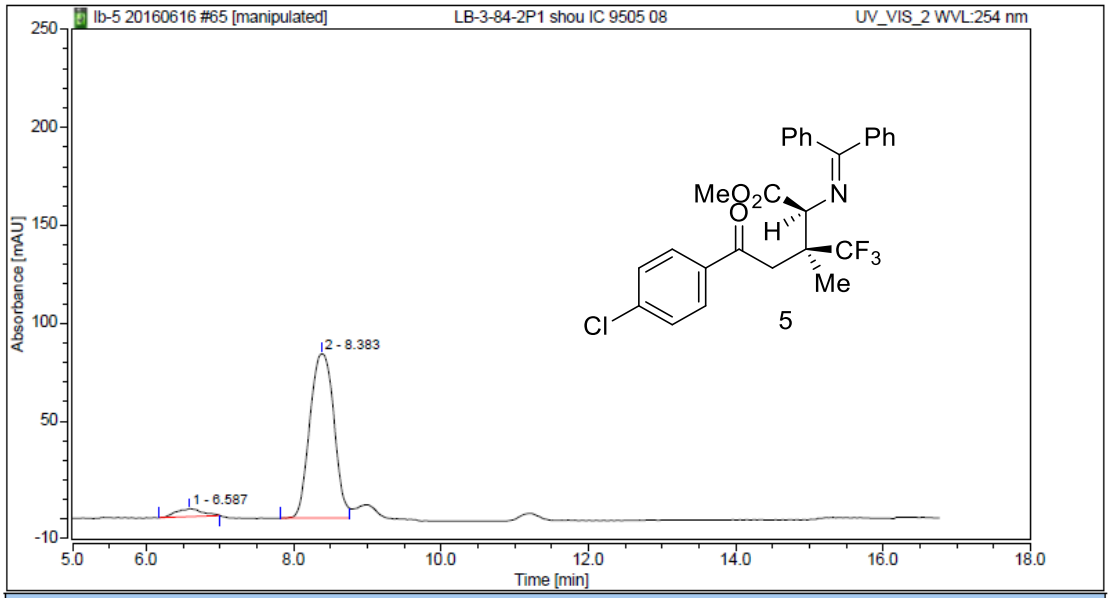

-72.2937
Ph
Ph
N
MeO2C
O
H
CF3
Me
Cl
5
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)


196.1547
171.9404
170.1728
139.3568
133.1755
136.3760
135.9585
132.0828
130.6947
129.6729
129.2474
128.8865
128.8602
128.7445
128.5696
128.2444
128.0470
127.3193
125.2726
77.3179
77.0004
76.6828
65.9774
51.8693
48.8347
48.7078
48.4794
48.2527
37.8945
16.8016
16.7756
Ph
Ph
N
MeO2C
O
H
CF3
Me
Cl
5
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



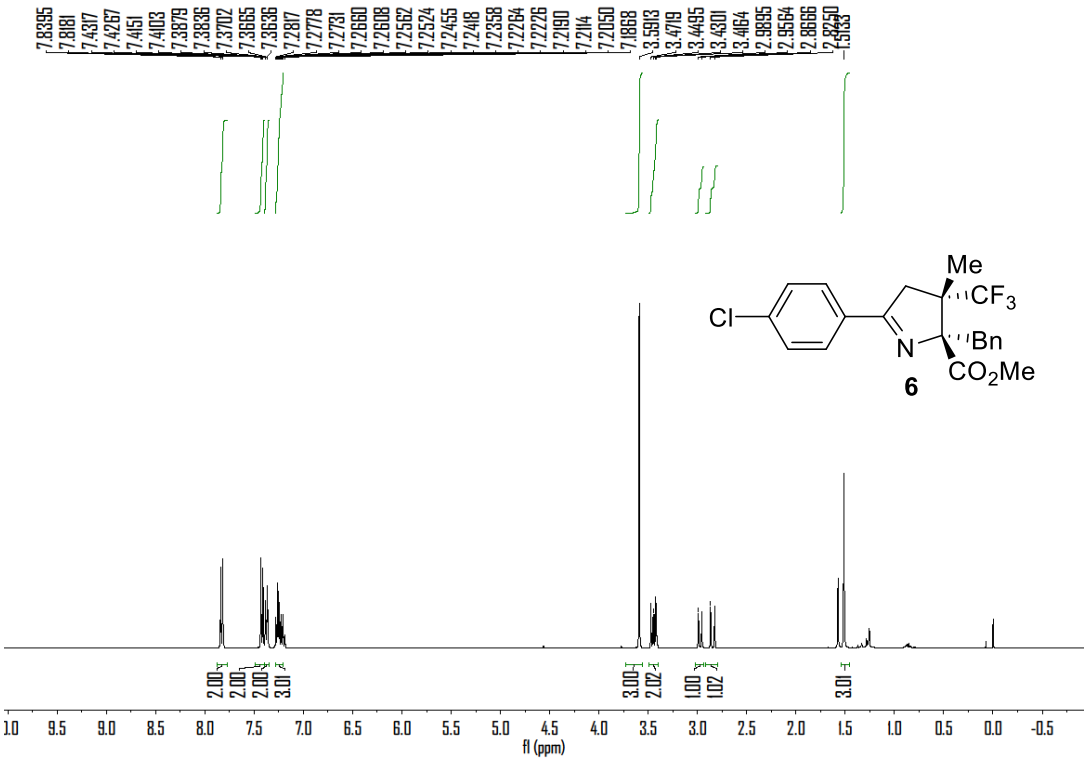
Integration Results

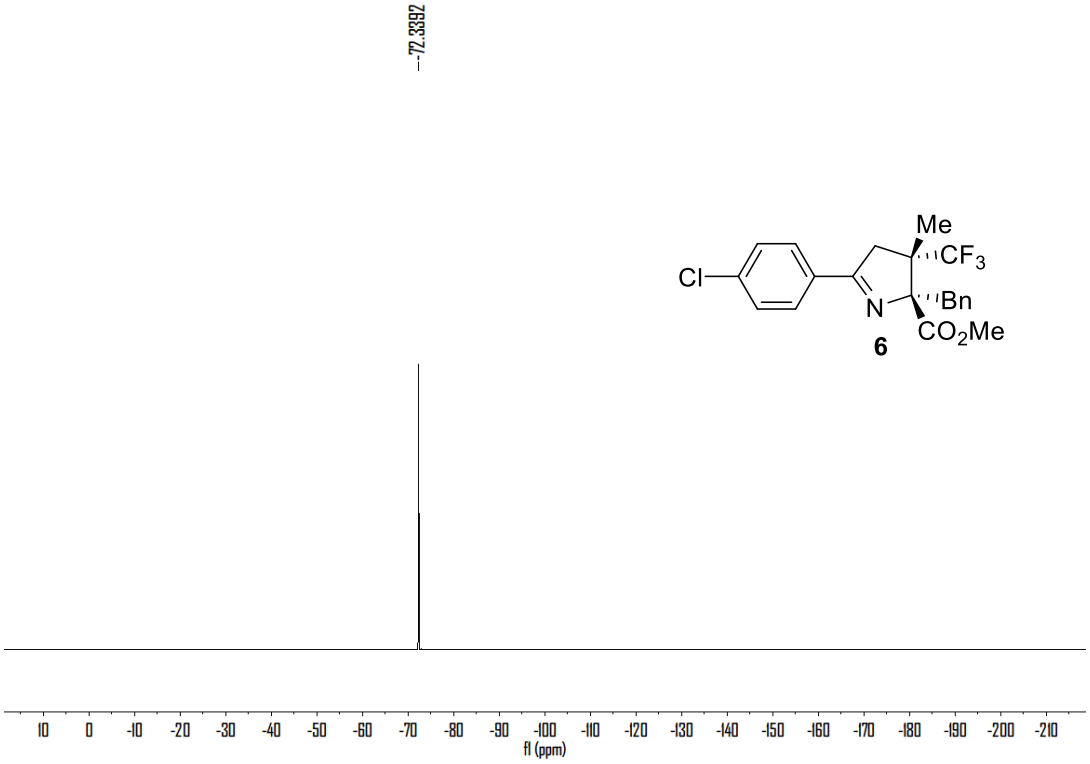
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.583	23.215	60.647	49.37	50.82	n.a.
2		8.377	23.811	58.698	50.63	49.18	n.a.
Total:			**47.026**	**119.345**	**100.00**	**100.00**	

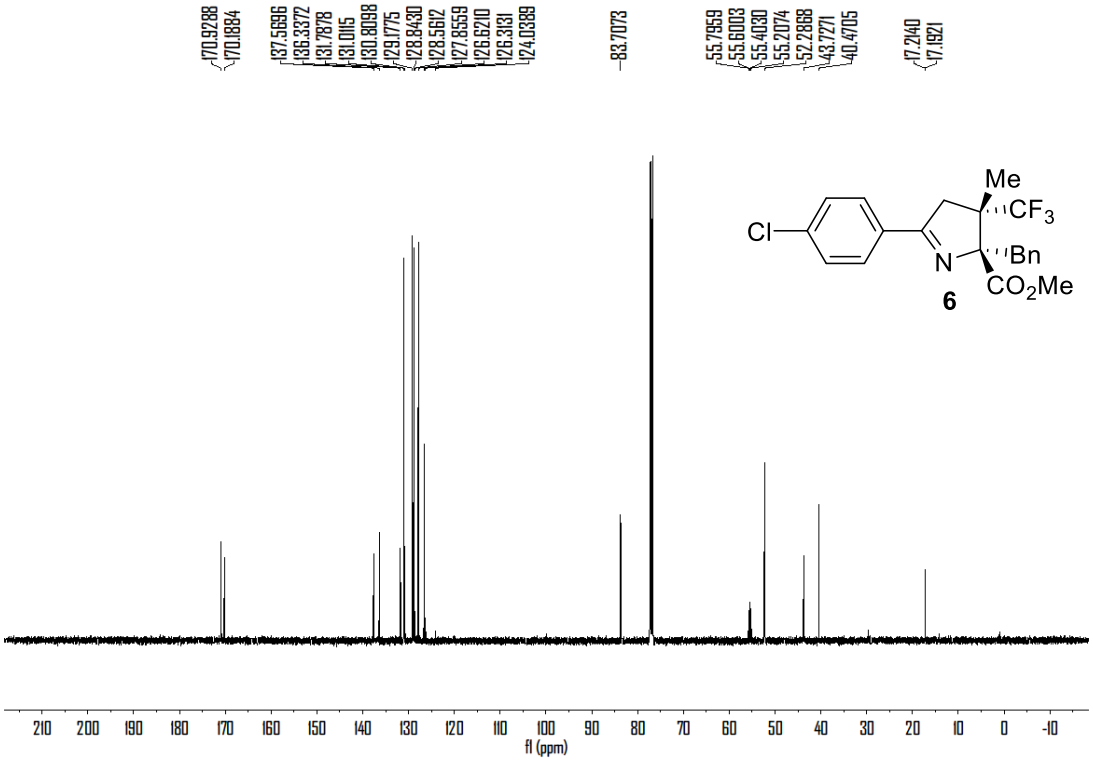


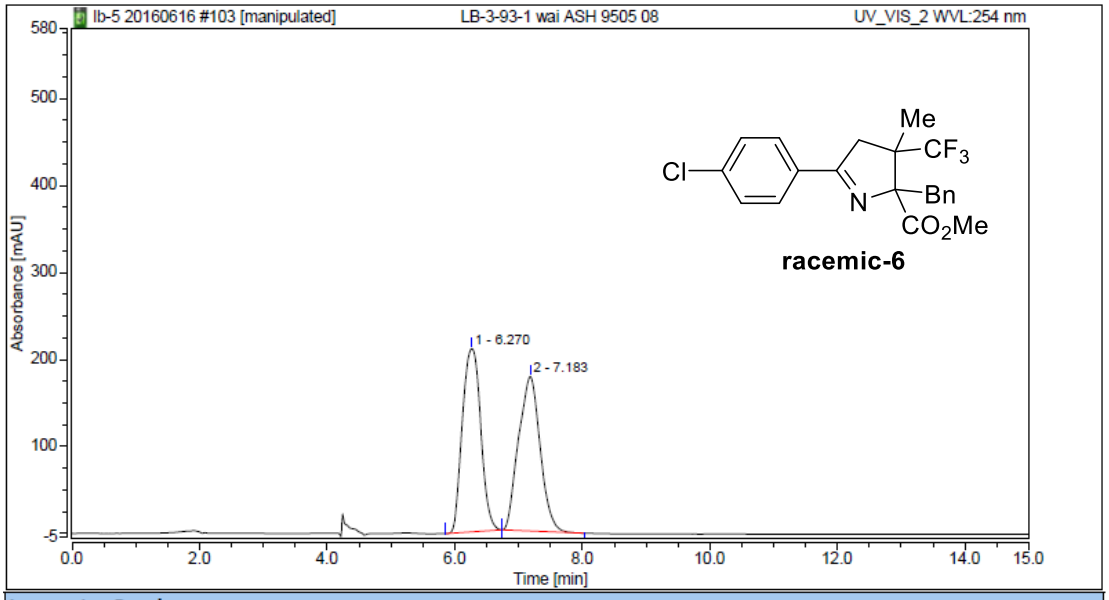
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.587	1.639	4.019	4.90	4.57	n.a.
2		8.383	31.842	83.877	95.10	95.43	n.a.
Total:			**33.481**	**87.895**	**100.00**	**100.00**	


7.8395
7.8181
7.4317
7.4267
7.4151
7.4103
7.3879
7.3836
7.3702
7.3665
7.3638
7.2817
7.2778
7.2731
7.2660
7.2608
7.2562
7.2524
7.2455
7.2418
7.2358
7.2264
7.2226
7.2190
7.2114
7.2050
7.1868
3.5913
3.4719
3.4435
3.4301
3.4164
2.9895
2.9564
2.8666
2.8250
1.5133
Me
CF3
Cl
N
Bn
CO2Me
6
2.00
2.00
2.00
3.01
3.00
2.02
1.00
1.02
3.01
fl (ppm)

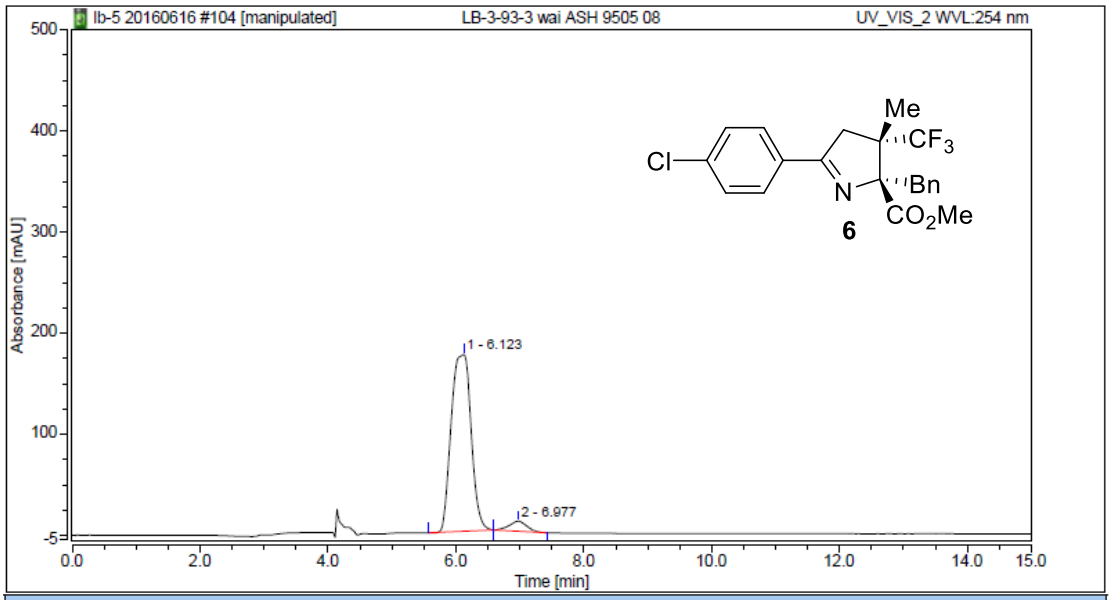

-72.3392
Me
CF3
Cl
N
Bn
CO2Me
6
fl (ppm)





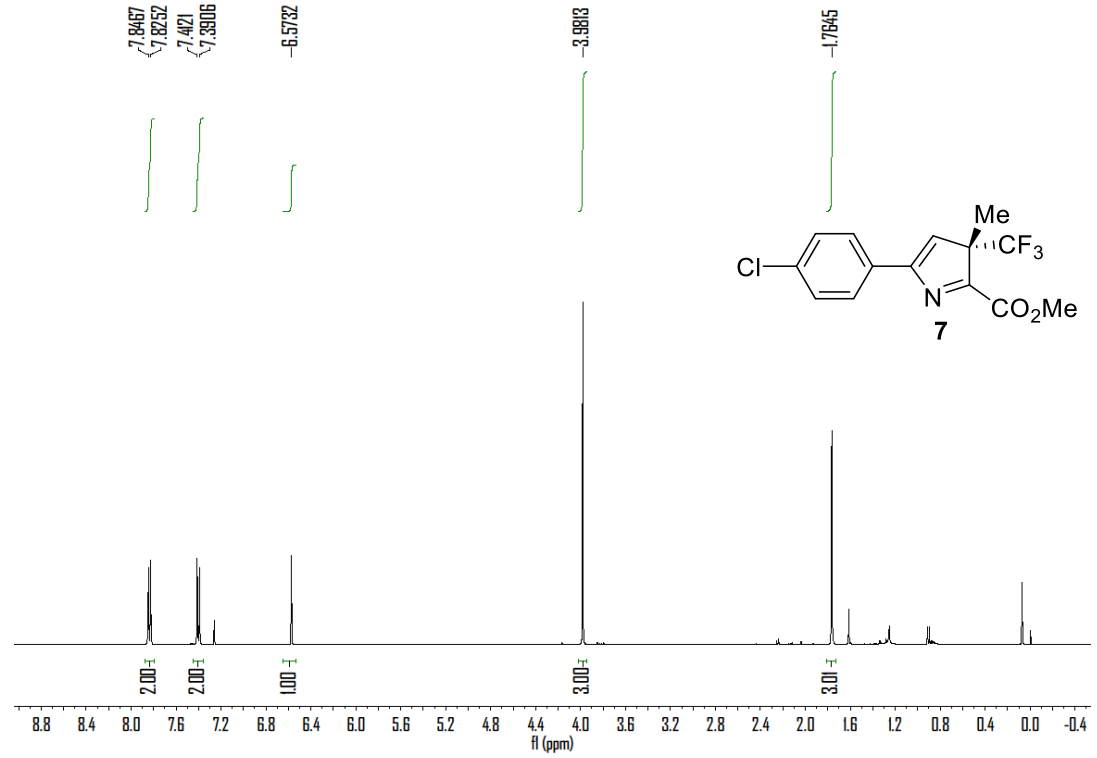
Integration Results

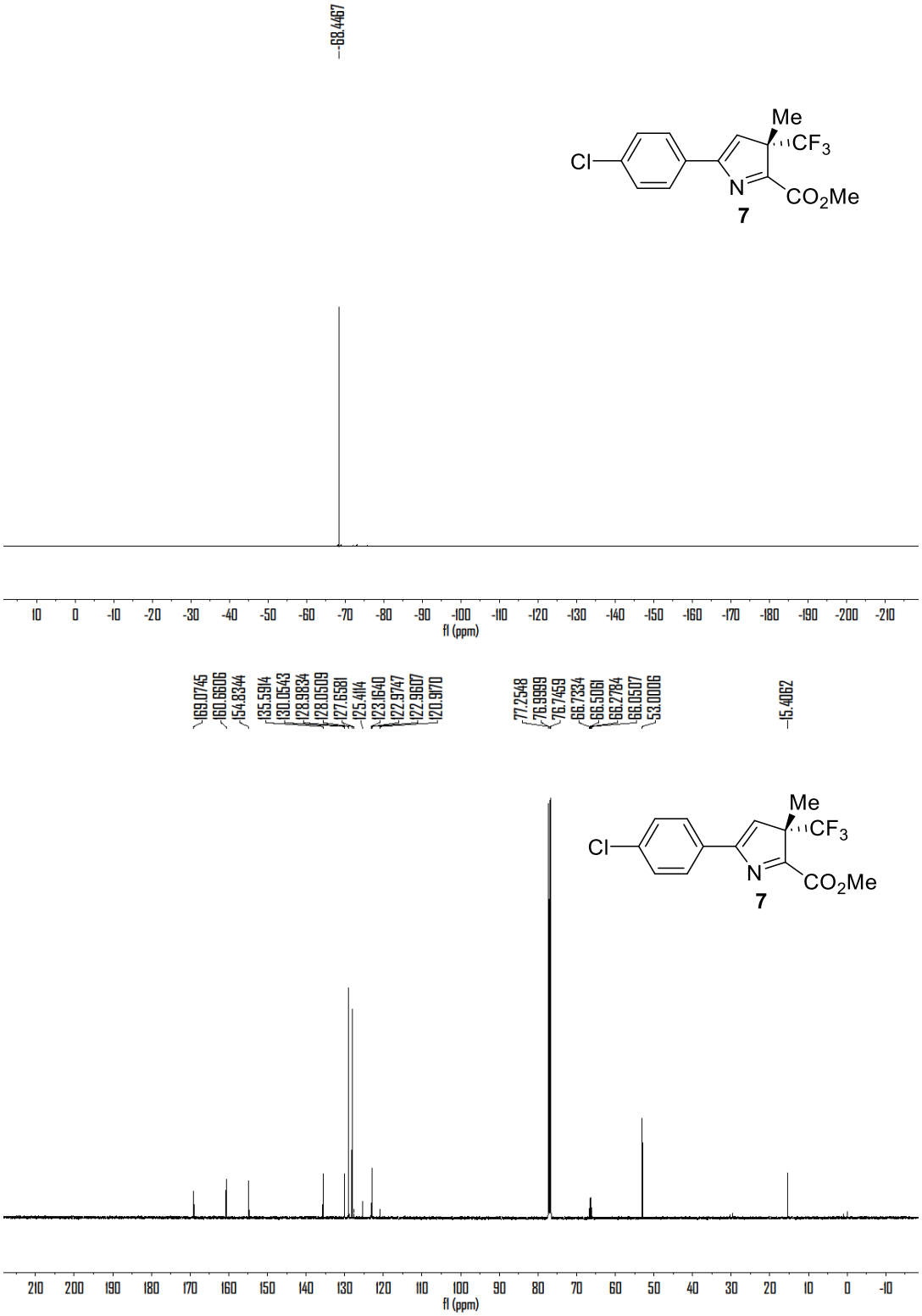
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.270	70.460	210.882	50.19	54.22	n.a.
2		7.183	69.920	178.087	49.81	45.78	n.a.
Total:			**140.380**	**388.969**	**100.00**	**100.00**	

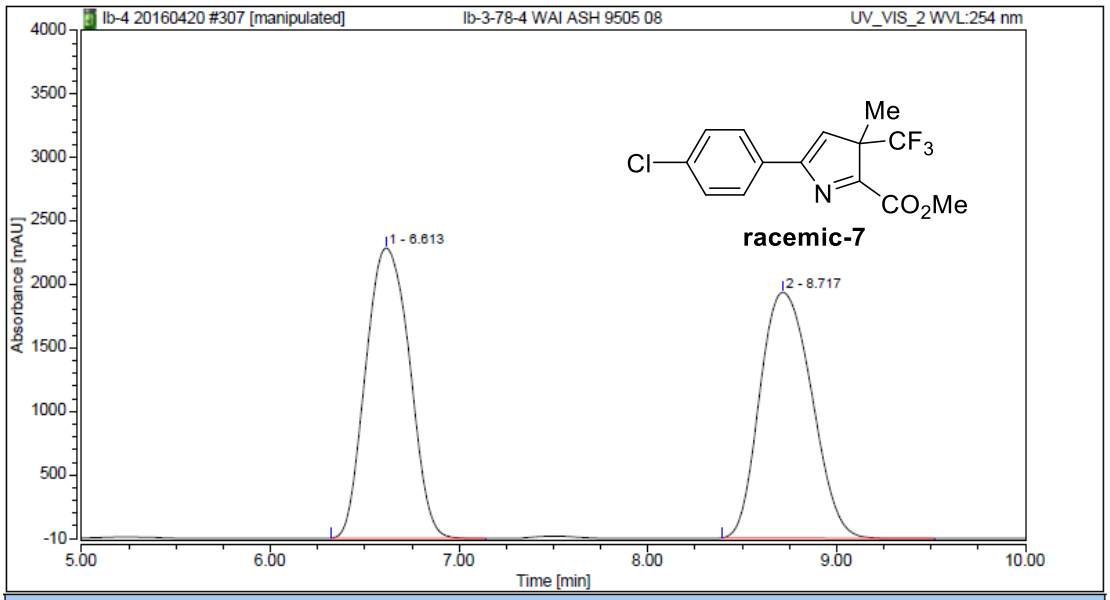


Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.123	63.095	175.053	95.17	94.60	n.a.
2		6.977	3.200	9.986	4.83	5.40	n.a.
Total:			**66.295**	**185.039**	**100.00**	**100.00**	

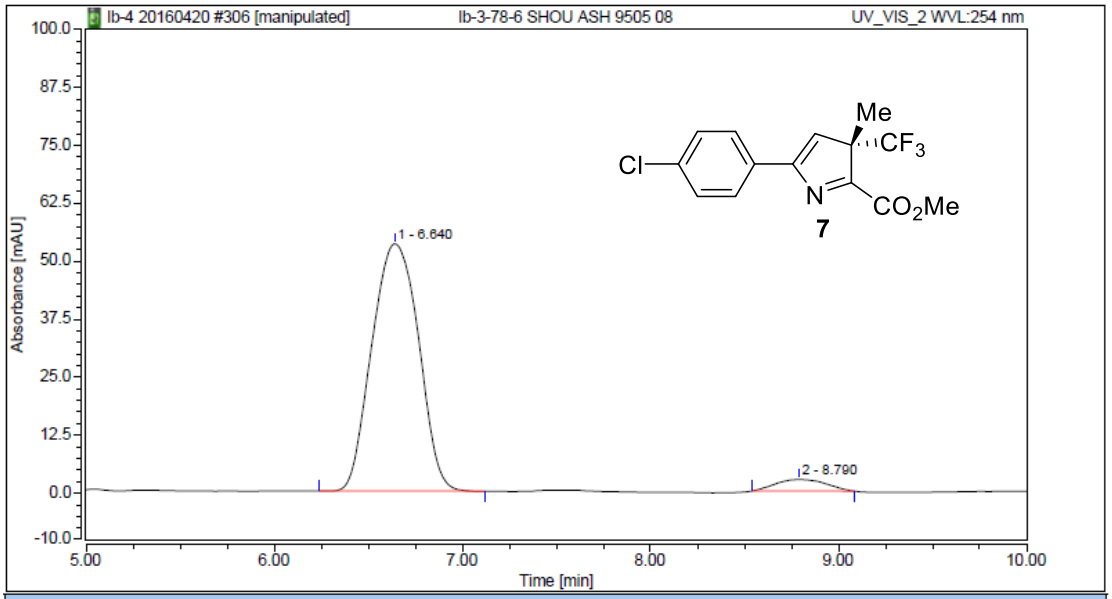



-68.4467
Me
CF3
Cl
N
CO2Me
7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
169.0745
160.6606
154.8344
135.5914
130.0543
128.9834
128.0509
127.6381
125.4114
123.1640
122.9747
122.9607
120.9770
77.2548
76.9999
76.7459
66.7334
66.5061
66.2784
66.0507
53.0006
15.4062
Me
CF3
Cl
N
CO2Me
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



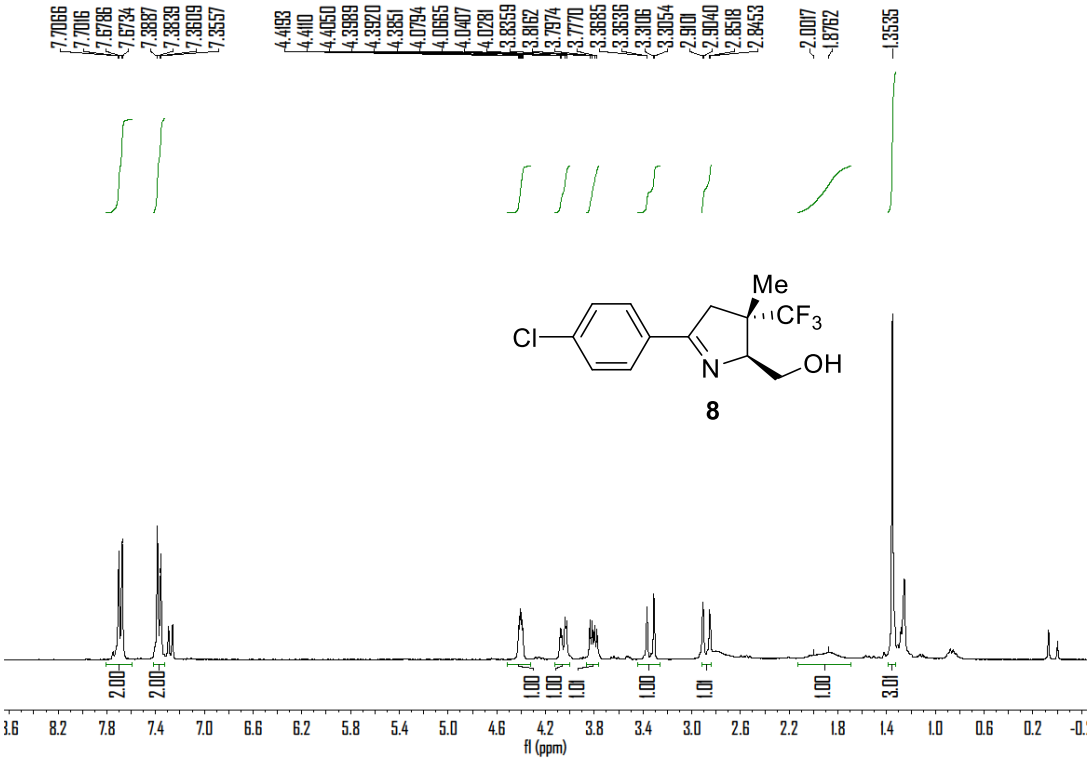
Integration Results

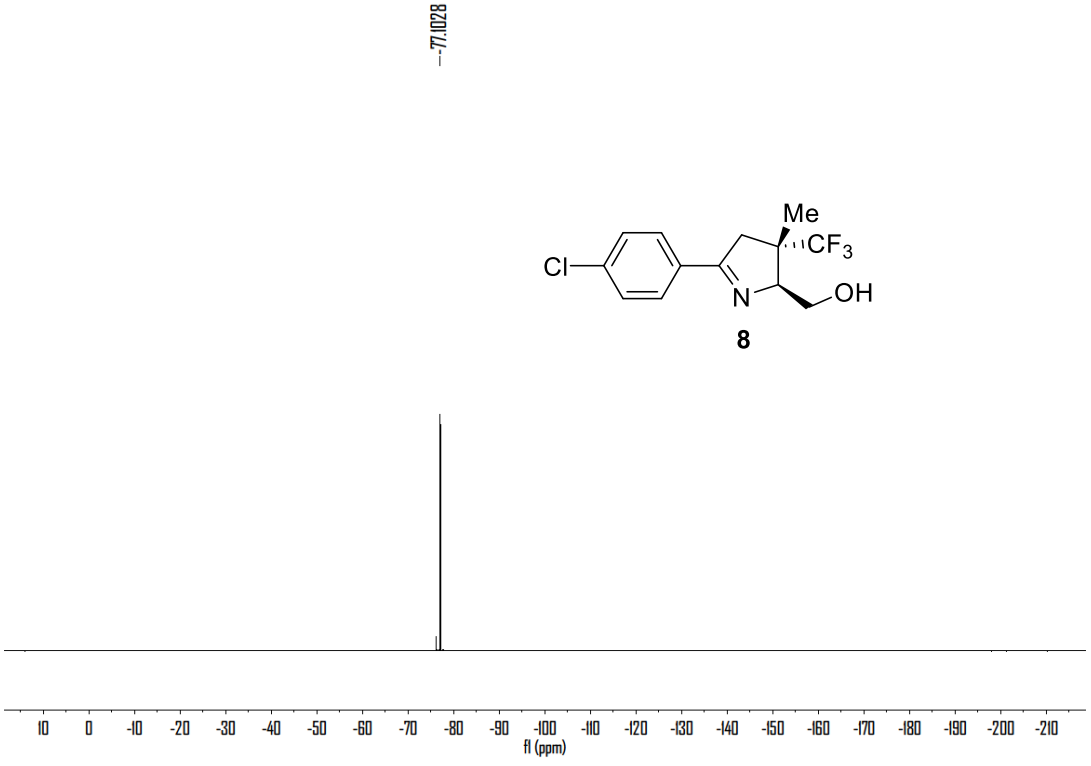
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.613	614.367	2284.670	49.99	54.16	n.a.
2		8.717	614.516	1933.898	50.01	45.84	n.a.
Total:			**1228.883**	**4218.568**	**100.00**	**100.00**	

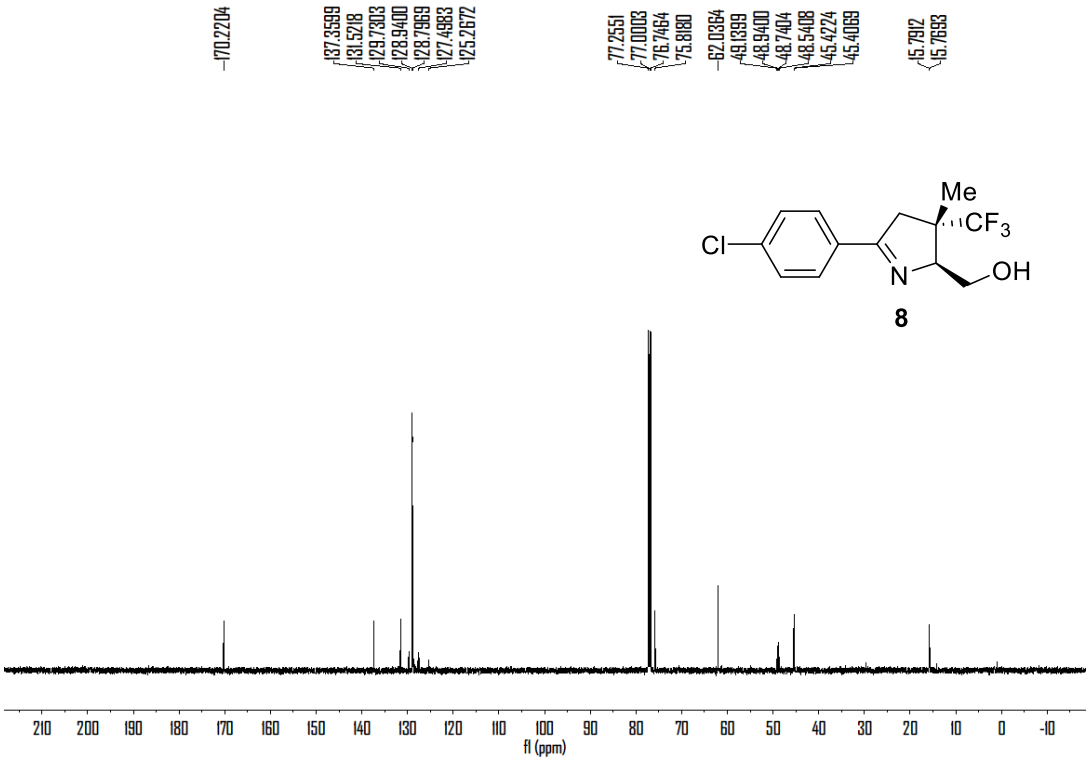


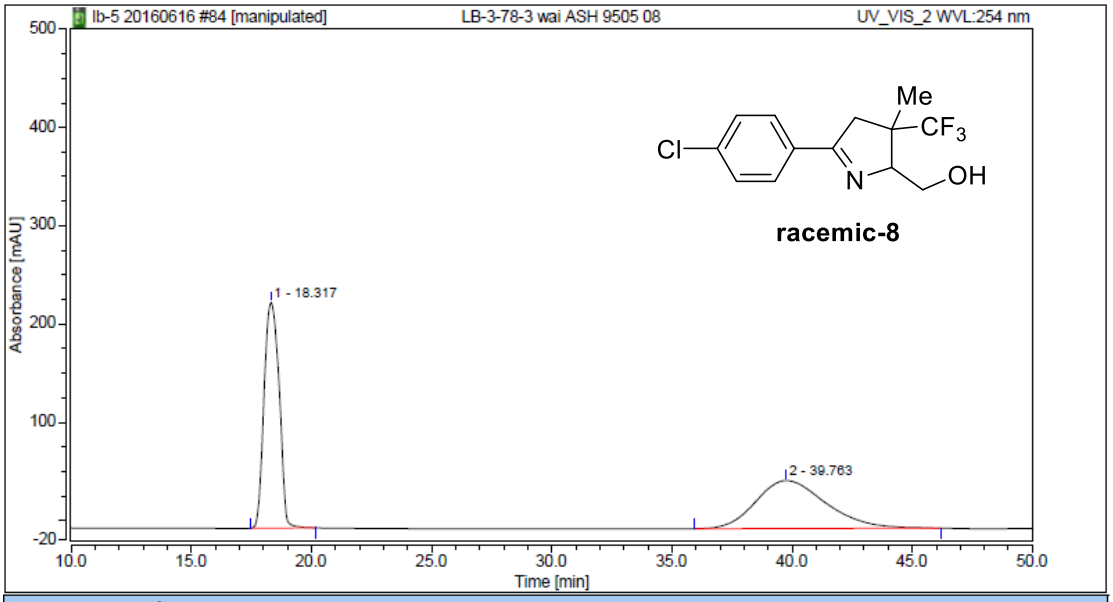
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		6.640	15.361	53.329	95.21	95.51	n.a.
2		8.790	0.773	2.505	4.79	4.49	n.a.
Total:			**16.134**	**55.835**	**100.00**	**100.00**	


7.7066
7.7016
7.6786
7.6734
7.3887
7.3839
7.3609
7.3557
4.4193
4.4110
4.4050
4.3989
4.3920
4.3851
4.0794
4.0665
4.0407
4.0281
3.8359
3.8162
3.7974
3.7770
3.3685
3.3636
3.3106
3.3054
2.9101
2.9040
2.8518
2.8453
2.0017
1.8762
1.3535
Me
CF3
Cl
N
OH
8
2.00
2.00
1.00
1.00
1.01
1.00
1.01
1.00
3.01
f1 (ppm)

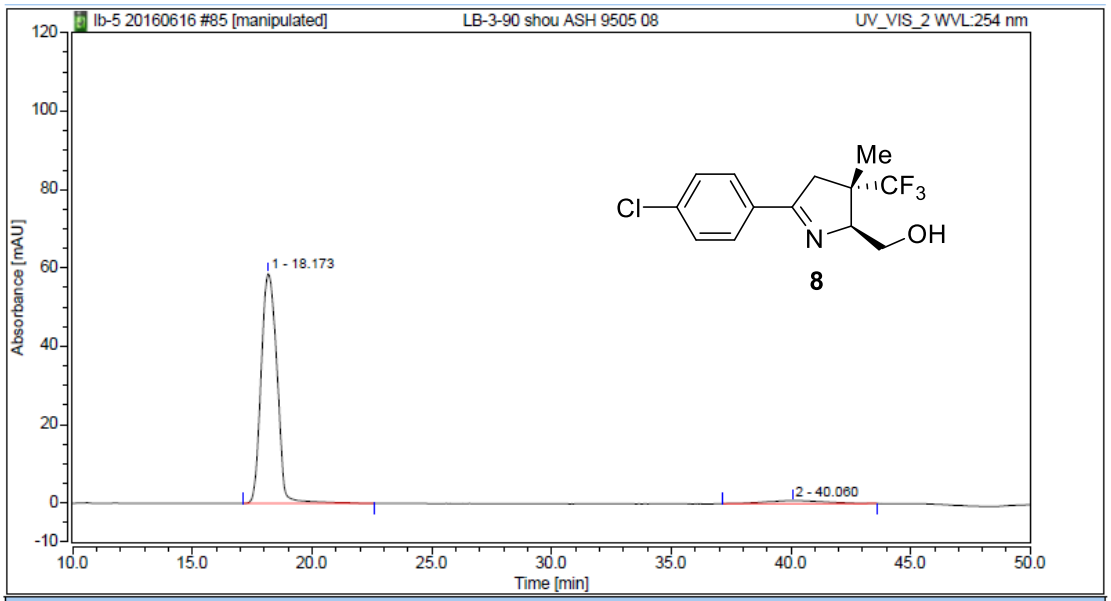

-77.1028
Me
CF3
Cl
N
OH
8
f1 (ppm)





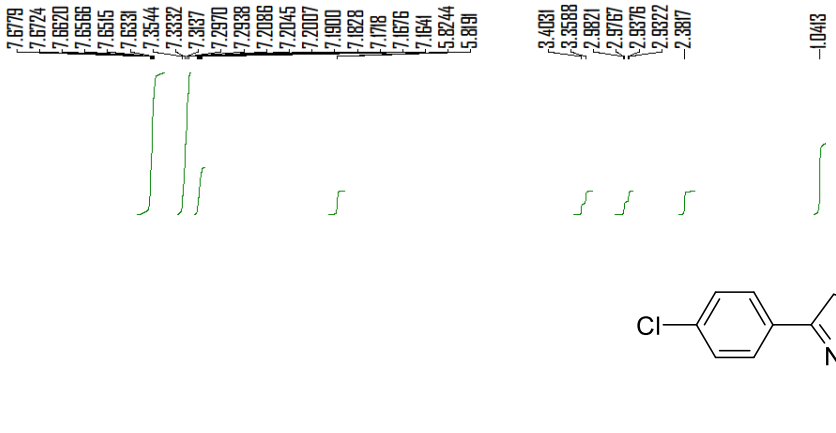
Integration Results

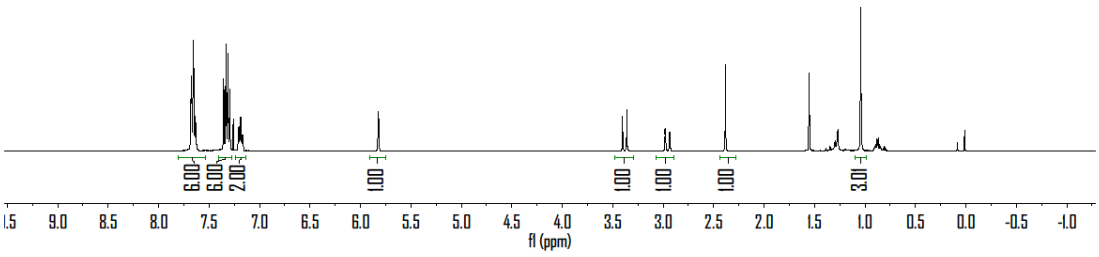
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.317	167.194	229.861	50.28	82.47	n.a.
2		39.763	165.345	48.854	49.72	17.53	n.a.
Total:			**332.539**	**278.715**	**100.00**	**100.00**	

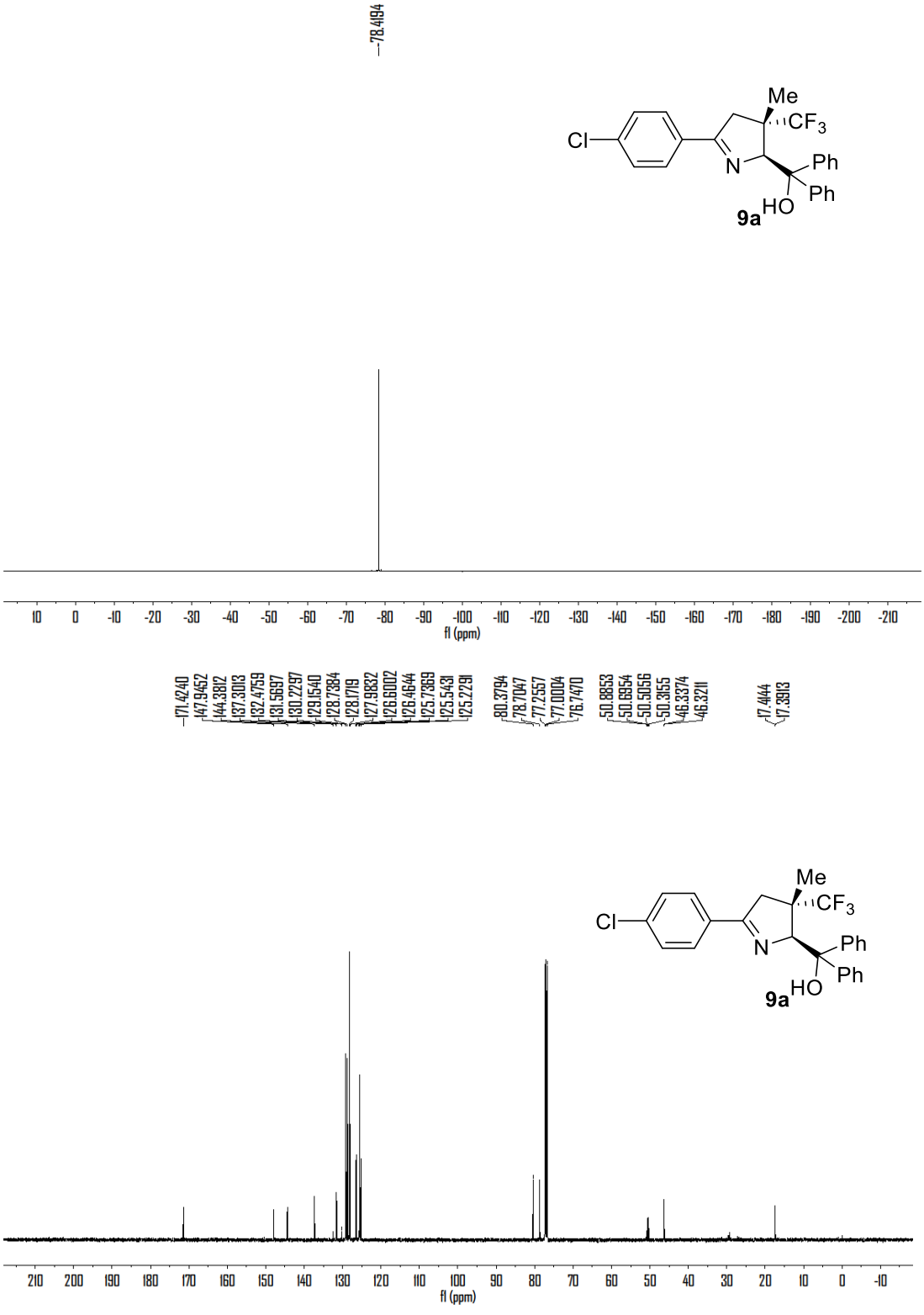


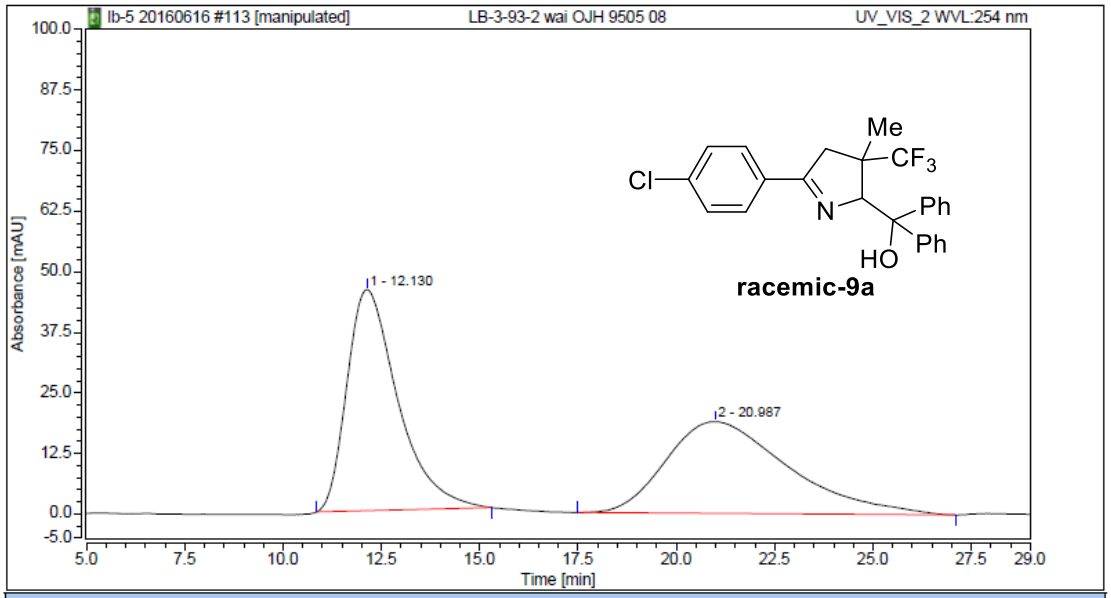
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		18.173	45.041	58.662	95.24	98.71	n.a.
2		40.060	2.251	0.765	4.76	1.29	n.a.
Total:			**47.292**	**59.427**	**100.00**	**100.00**	



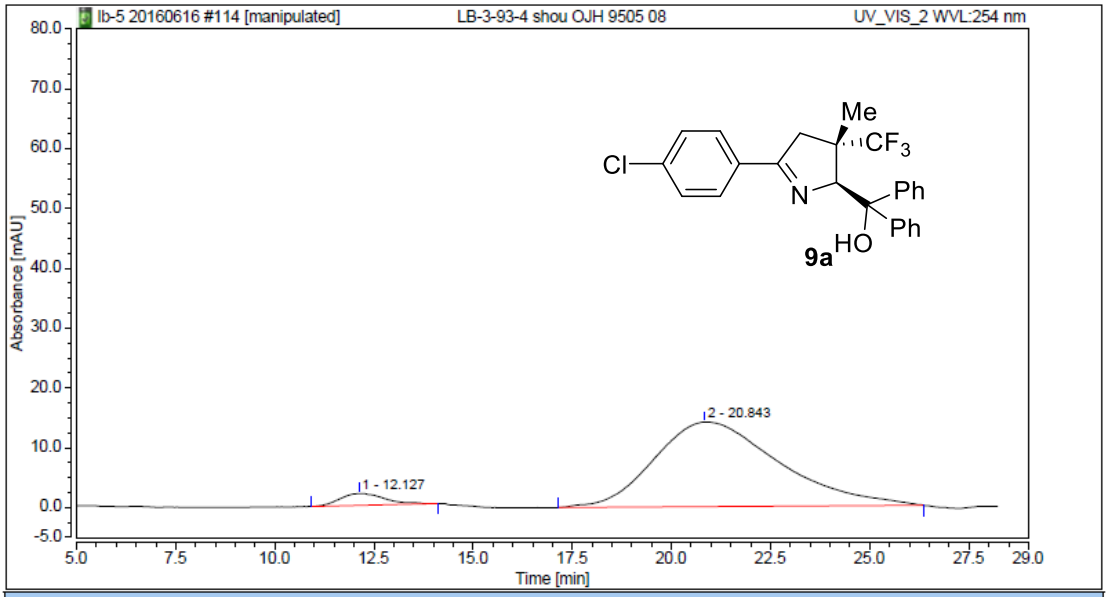



-78.4194
Me
CF3
Cl
N
Ph
Ph
HO
9a
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)
171.4240
147.9452
144.3812
137.3013
132.4759
131.5697
130.2297
129.1540
128.7384
128.1719
127.9832
126.6002
126.4644
125.7369
125.5431
125.2291
80.3794
78.7047
77.2557
77.0004
76.7470
50.8853
50.6954
50.5056
50.3155
46.3374
46.3211
17.4444
17.3913
Me
CF3
Cl
N
Ph
Ph
HO
9a
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)



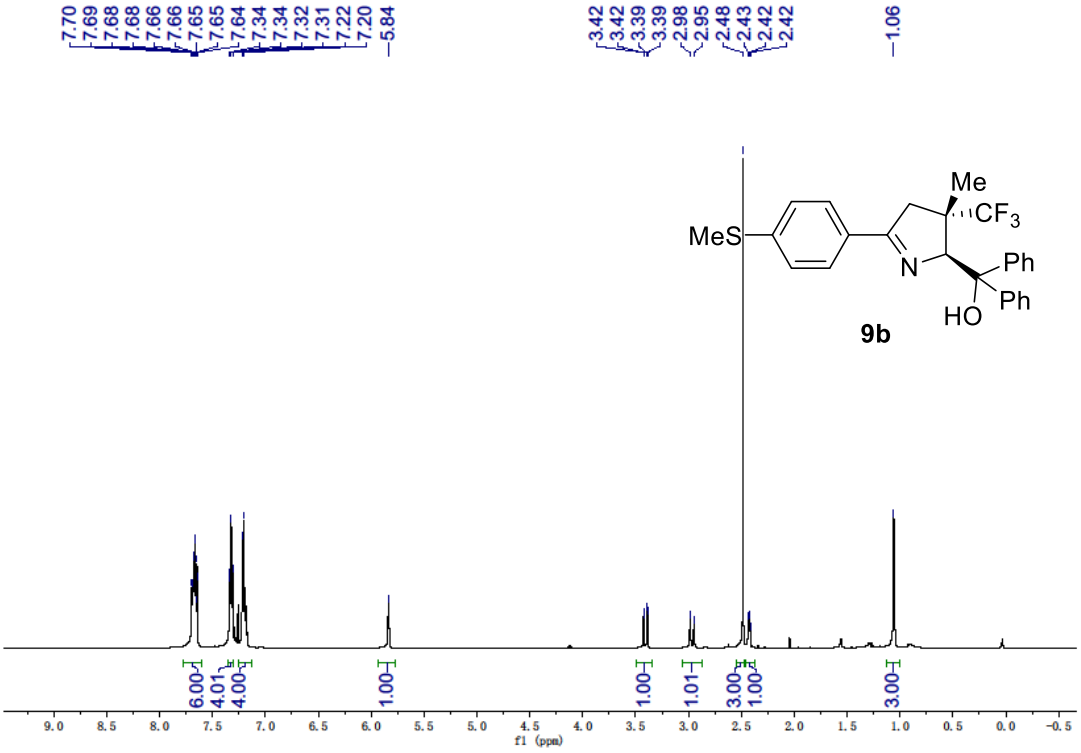
Integration Results

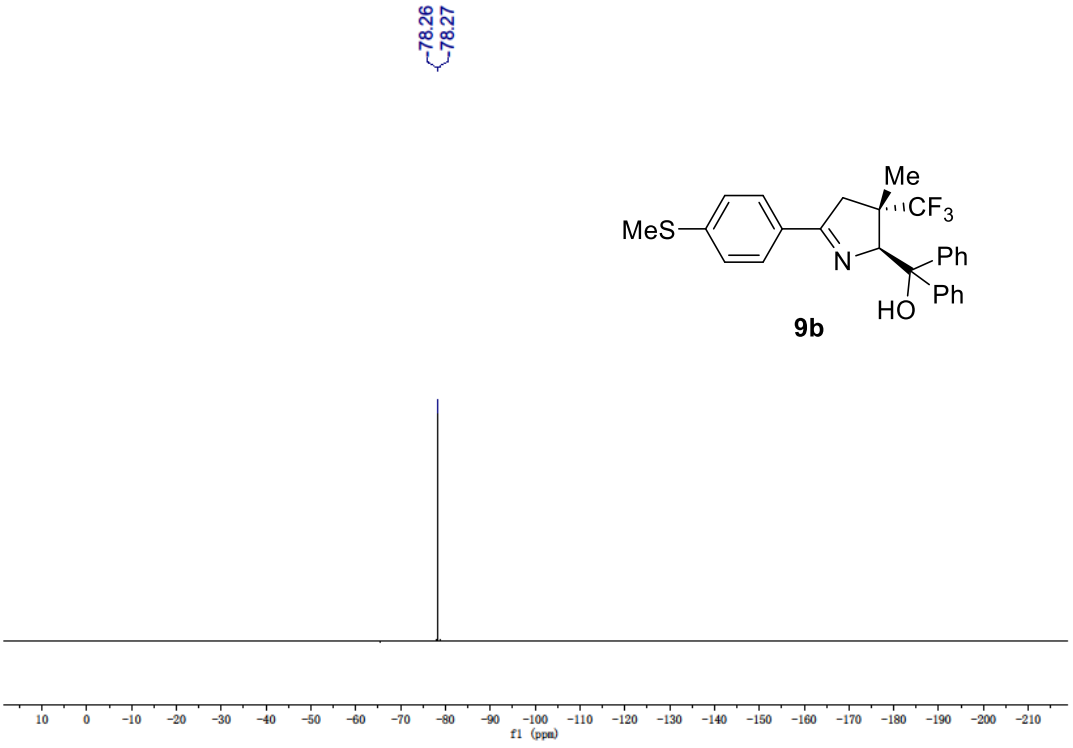
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.130	68.417	45.612	50.09	70.66	n.a.
2		20.987	68.184	18.939	49.91	29.34	n.a.
Total:			**136.602**	**64.551**	**100.00**	**100.00**	

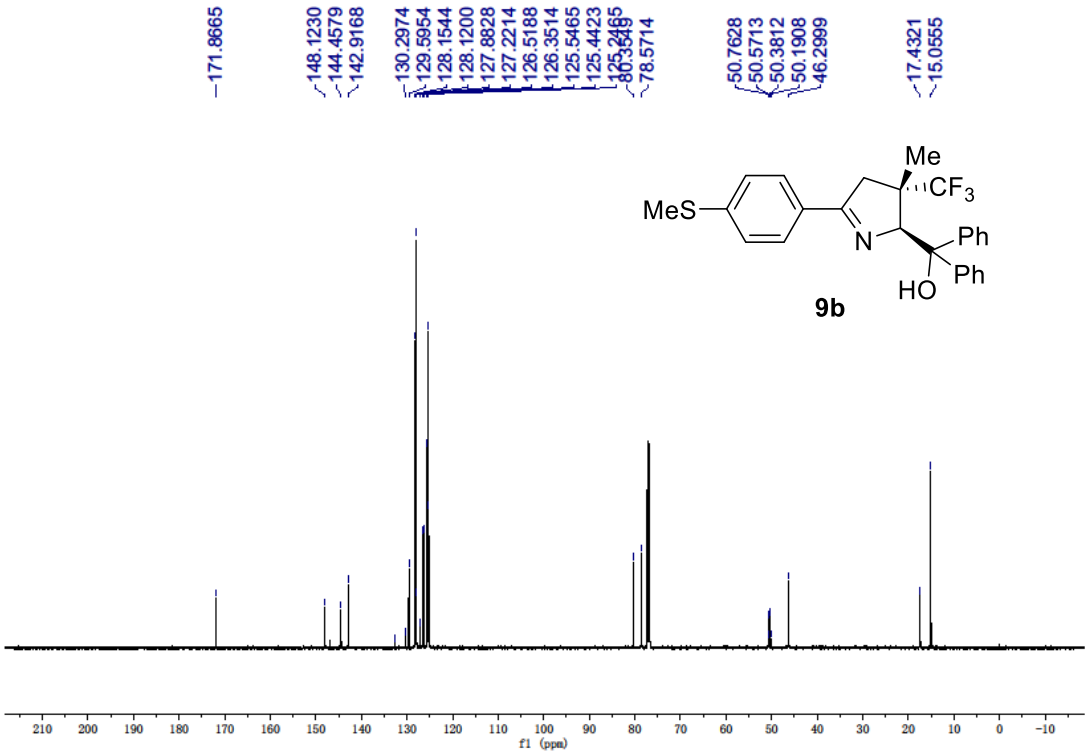


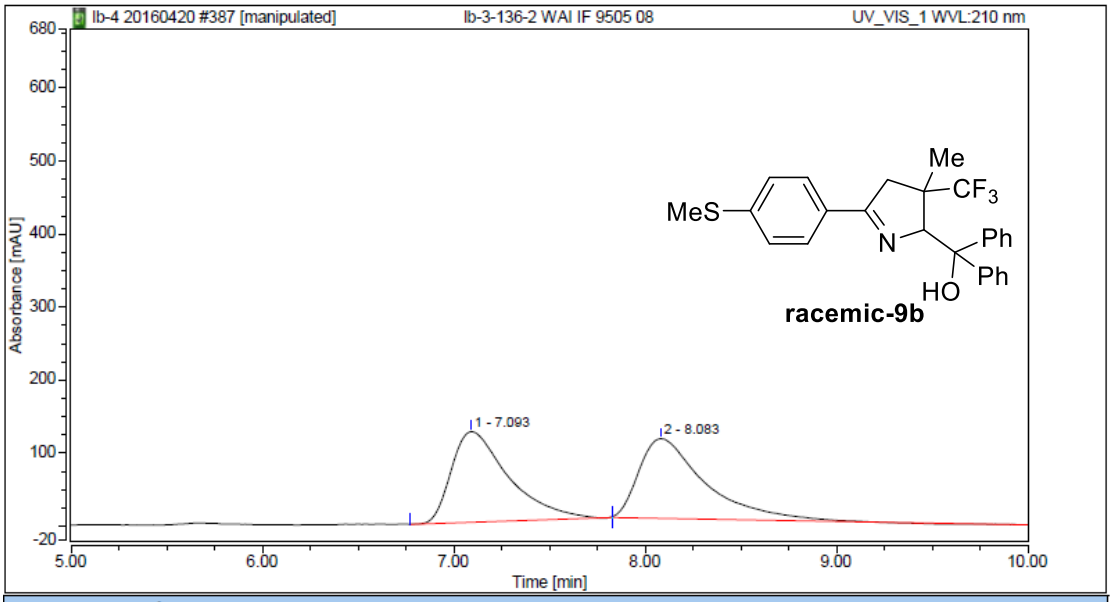
Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		12.127	2.555	1.980	4.71	12.25	n.a.
2		20.843	51.696	14.182	95.29	87.75	n.a.
Total:			**54.251**	**16.162**	**100.00**	**100.00**	


7.70
7.69
7.68
7.68
7.66
7.66
7.65
7.65
7.64
7.34
7.34
7.32
7.31
7.22
7.20
5.84
3.42
3.42
3.39
3.39
2.98
2.95
2.48
2.43
2.42
2.42
1.06
Me
CF3
MeS
N
Ph
Ph
HO
9b
6.00
4.01
4.00
1.00
1.00
1.01
3.00
1.00
3.00
f1 (ppm)

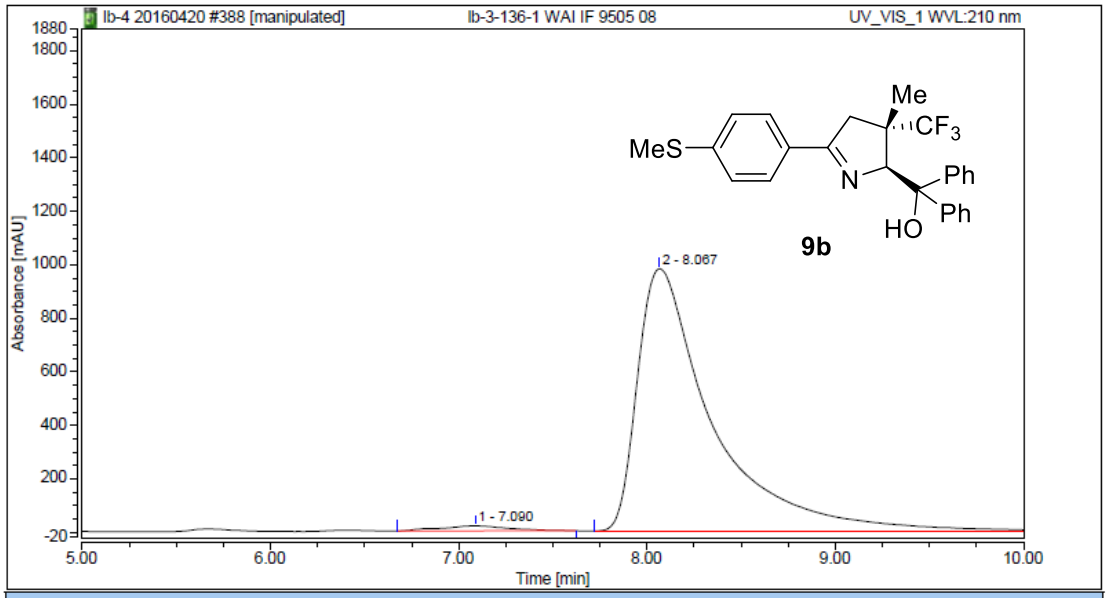

78.26
78.27
Me
CF3
MeS
N
Ph
Ph
HO
9b
f1 (ppm)





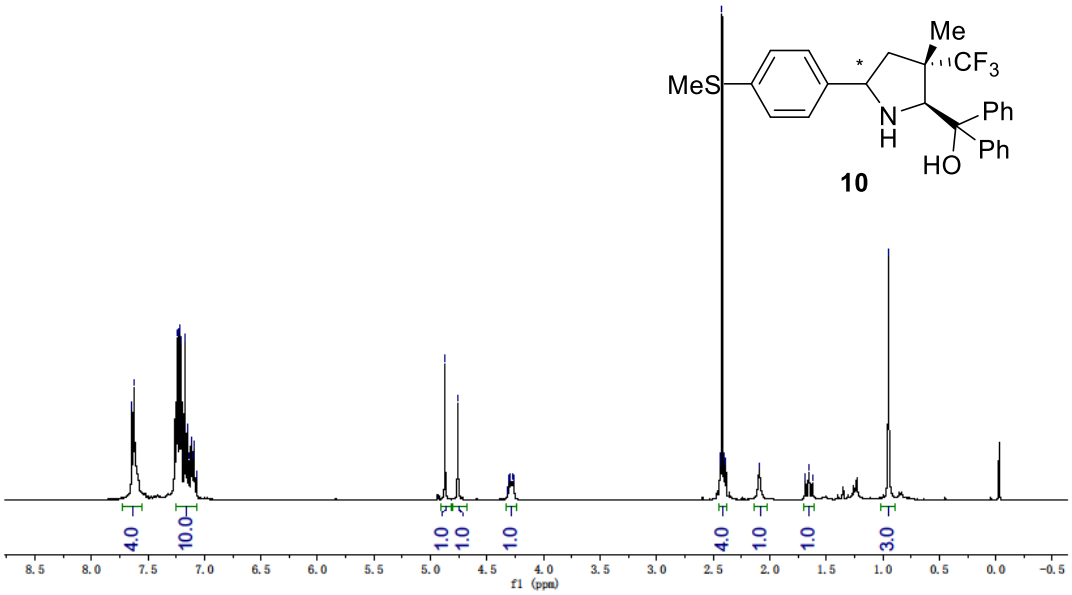
Integration Results

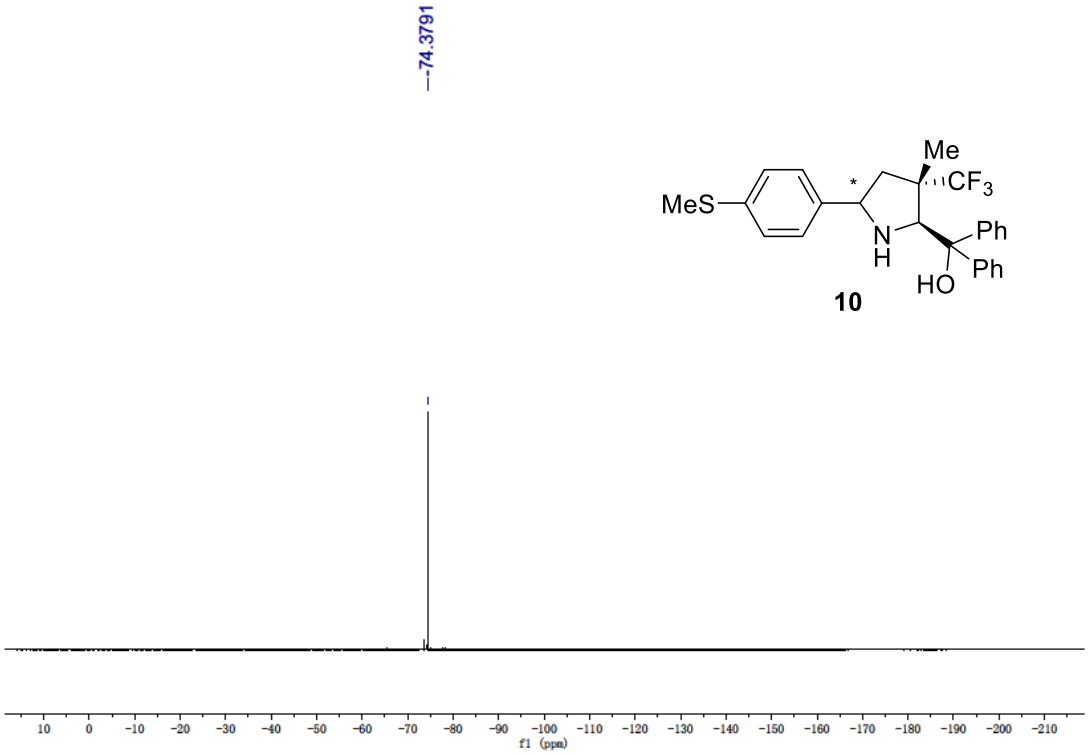
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.093	42.853	124.148	49.62	53.21	n.a.
2		8.083	43.503	109.179	50.38	46.79	n.a.
Total:			**86.356**	**233.326**	**100.00**	**100.00**	

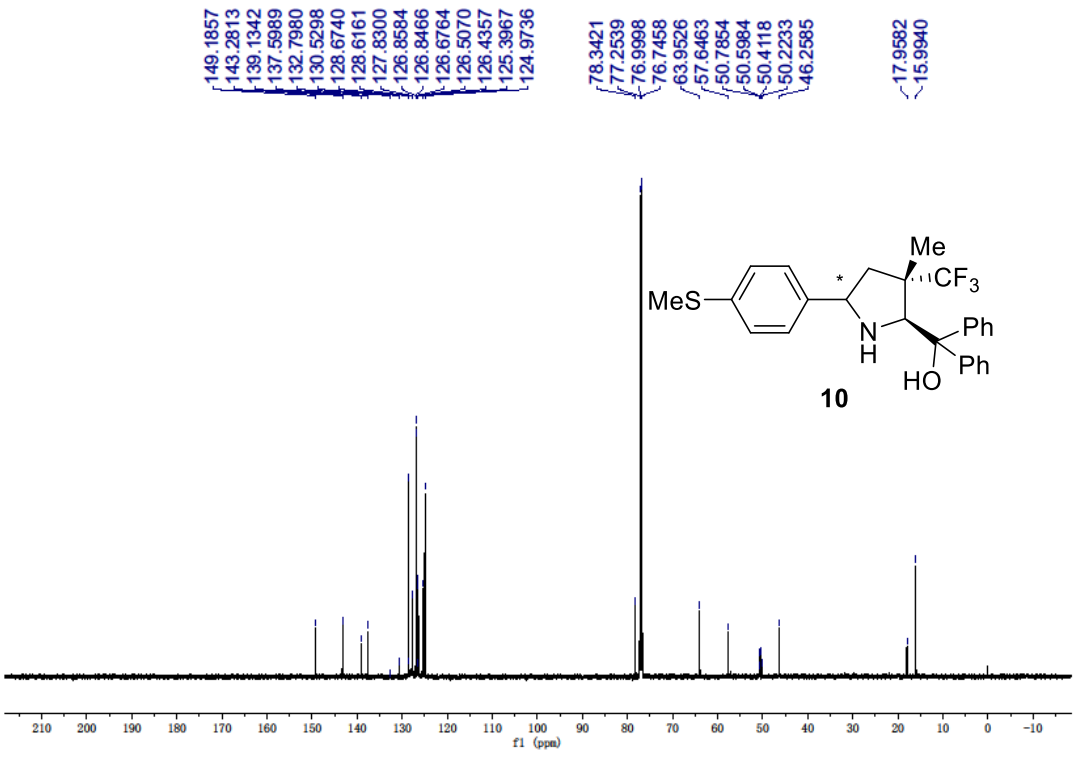


Integration Results

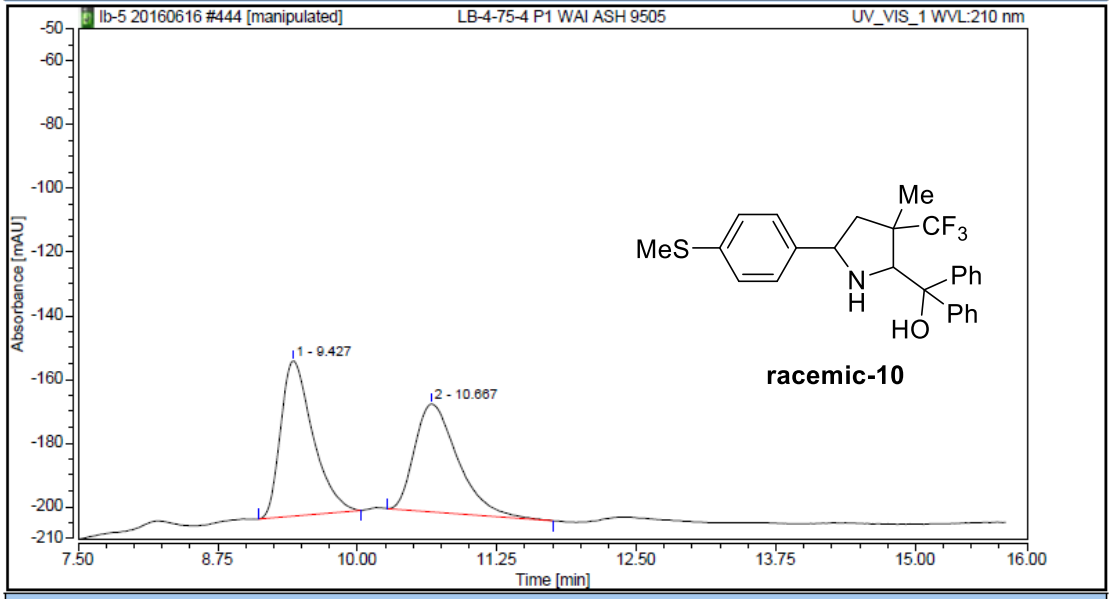
No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		7.090	7.945	18.681	1.72	1.87	n.a.
2		8.067	455.046	980.911	98.28	98.13	n.a.
Total:			**462.991**	**999.592**	**100.00**	**100.00**	




-74.3791
Me
CF3
MeS
N
H
Ph
Ph
HO
10
f1 (ppm)


149.1857
143.2813
139.1342
137.5989
132.7980
130.5298
128.6740
128.6161
127.8300
126.8584
126.8466
126.6764
126.5070
126.4357
125.3967
124.9736
78.3421
77.2539
76.9998
76.7458
63.9526
57.6463
50.7854
50.5984
50.4118
50.2233
46.2585
17.9582
15.9940
Me
CF3
MeS
N
H
Ph
Ph
HO
10
f1 (ppm)

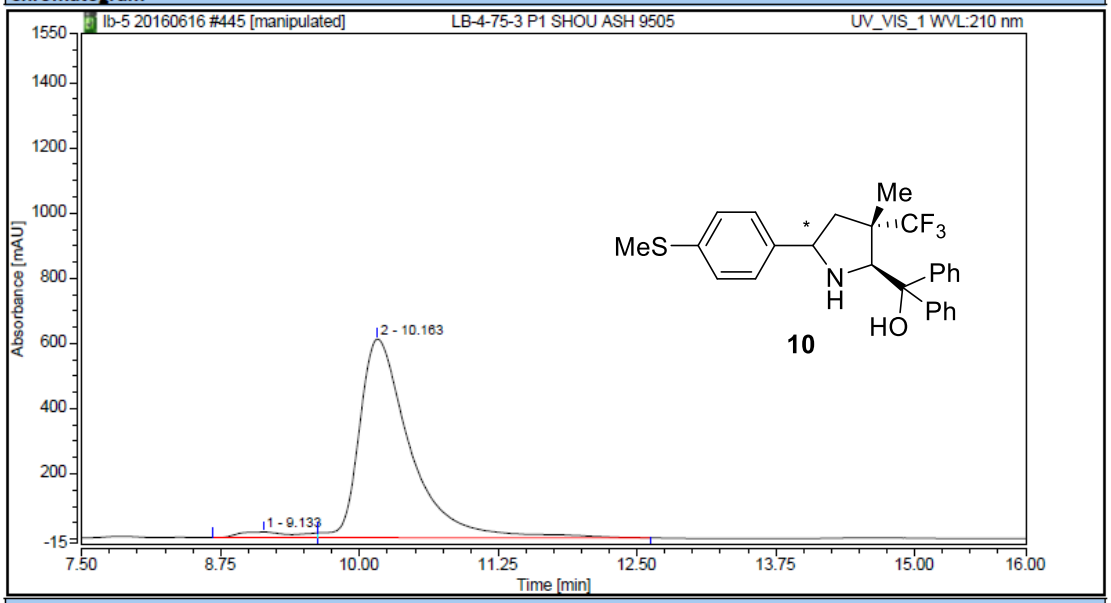
Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.427	16.307	48.766	51.71	59.03	n.a.
2		10.667	15.231	33.843	48.29	40.97	n.a.
Total:			**31.538**	**82.608**	**100.00**	**100.00**	

Chromatogram



Integration Results

No.	Peak Name	Retention Time min	Area mAU*min	Height mAU	Relative Area %	Relative Height %	Amount n.a.
1		9.133	10.559	17.077	3.16	2.72	n.a.
2		10.163	323.655	609.706	96.84	97.28	n.a.
Total:			**334.214**	**626.784**	**100.00**	**100.00**	