Supporting Information

Copper(I)-Catalyzed Asymmetric *Exo*-selective [3+2] Cycloaddition of Azomethine Ylides with β-Trifluoromethyl β, β-Disubstituted Enones

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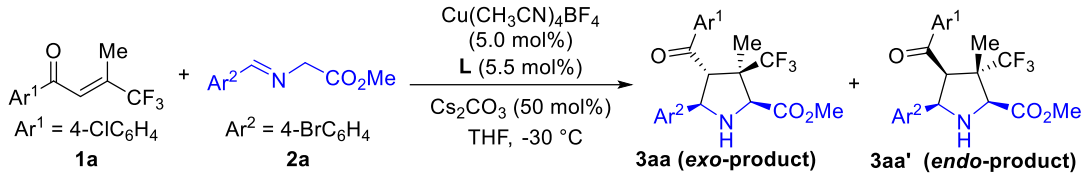
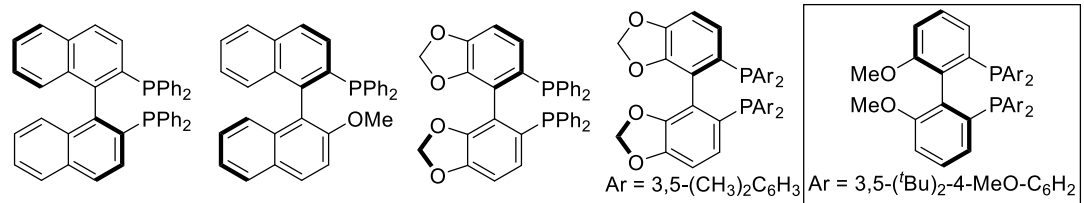
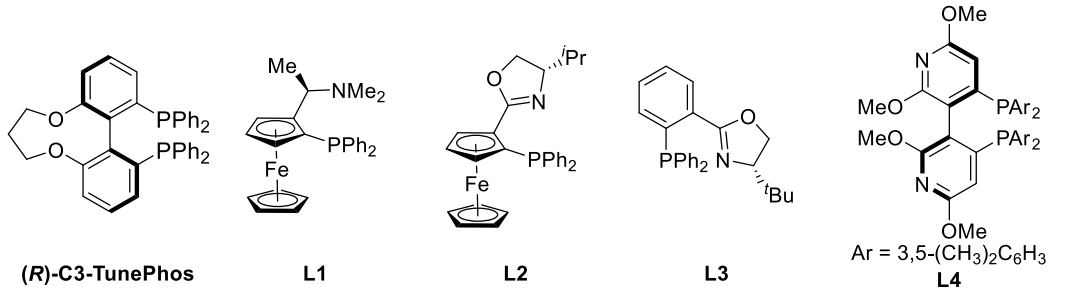
1. General Information

All reactions were carried out under an atmosphere of nitrogen in flame-dried glassware with magnetic stirring. ^{1}H NMR spectra, ^{13}C NMR spectra were recorded on a Bruker 300, and 400 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, dd = doublet of doublets, m = multiplet), 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, dichloroethane, toluene were freshly distilled from CaH_2; THF and MTBE was freshly distilled from sodium metal prior to use. The substrate **1a-1l**,[1] **2a-2o**,[2] **1m**,[3] were synthesized according to the procedure of references. In addition, the spectral data of the substrates were consisted with the literature.

2. Scr*ee*ning the Known Ligands[a]

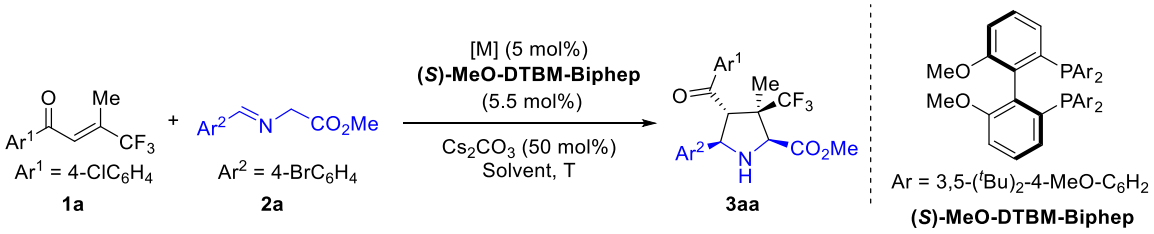






[a] All reactions were carried out with 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol% of catalyst ([Cu] to Ligand = 1:1.1) in 2.0 mL THF at -30 °C for 2-8 h. [b] The yield of **3aa** (*exo*-product). [c] The yield of **3aa'** (*endo*-product). [d] NMR yield with CH_2Br_2 as an internal standard. [e] The diastereomeric ratios were determined by ^1H, ^{19}F NMR analysis of the crude products. [f] The *ee* of **3aa** (*exo*-product). Determined by chiral HPLC.

3. Table S1. Optimization of Reaction Conditions[a]



Entry	[M]	Solvent	T (°C)	Dr[b]	Yield (*Ee*) [%][c,d]
1	$Cu(CH_3CN)_4BF_4$	THF	-30	>20:1	99(98)
2	$Cu(CH_3CN)_4PF_6$	THF	-30	>20:1	98(98)
3	$Cu(CH_3CN)_4NTf_2$	THF	-30	>20:1	98(98)
4	$Cu(CH_3CN)_4ClO_4$	THF	-30	>20:1	98(98)
5	$(CuOTf)_2$•Tol	THF	-30	>20:1	97(97)
6	AgOAc	THF	-30	4:1	78(94)
7	$Cu(CH_3CN)_4BF_4$	Acetone	-30	>20:1	93(95)

8	$Cu(CH_3CN)_4BF_4$	Toluene	-30	>20:1	80(99)
9	$Cu(CH_3CN)_4BF_4$	$^{i}Pr_2O$	-30	>20:1	88(99)
10	$Cu(CH_3CN)_4BF_4$	MTBE	-30	>20:1	89(98)
11	$Cu(CH_3CN)_4BF_4$	Et_2O	-30	>20:1	87(98)
12	$Cu(CH_3CN)_4BF_4$	THF	-20	>20:1	93(98)
13	$Cu(CH_3CN)_4BF_4$	THF	0	>20:1	92(97)
14	$Cu(CH_3CN)_4BF_4$	THF	20	>20:1	80(94)

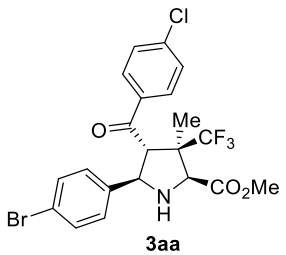
[a] All reactions were carried out with 0.1 mmol of **1a**, 0.2 mmol of **2a**, 5 mol% of catalyst ([Cu] to Ligand = 1:1.1) in 2.0 mL THF at -30 ºC for 4-12 h. [b] The diastereomeric ratios were determined by ^{1}H, ^{19}F NMR analysis of the crude products. [c] NMR yield with CH_2Br_2 as an internal standard. [d] Determined by chiral HPLC.

4. General Procedure for the Synthesis of products 3aa-3ma.

Typical procedure for asymmetric copper-catalyzed cycloaddition of enones with azomethine ylides.

The solution of ligand (5.5 mol%) and $Cu(CH_3CN)_4BF_4$ (5 mol%) in THF (4 mL) was stirred at room temperature for 2 h. After the reaction temperature was dropped to -30 °C, azomethine ylides **2** (0.4 mmol), Cs_2CO_3 (0.1 mmol) and enones **1** (0.2 mmol) were added sequentially. The reaction was determined by TLC analysis. After the enones **1** were consumed completely, the solvent was removed under reduced pressure. The crude product was analyzed with ^{1}H NMR and ^{19}F NMR to determine the diastereomeric ratio. Then the crude product was then 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 using a Chiralpak IC, IE, IF, OZ-3 and AD-H.

4.1 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(4-chlorobenzoyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3aa**).

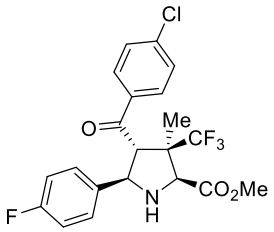


3aa

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and iminoester **2a** (102.4 mg, 0.4 mmol),

after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3aa** as a colorless ropy liquid (99.6 mg, 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.72 (m, 2 H), 7.43-7.37 (m, 4 H), 7.25-7.23 (m, 2 H), 4.76 (d, J = 8.9 Hz, 1 H), 4.18 (d, J = 9.0 Hz, 1 H), 3.82 (s, 1 H), 3.81 (s, 3 H), 2.68 (s, 1 H), 1.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.15. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.22, 169.87, 140.61, 138.21, 135.46, 132.02, 129.73, 129.19, 128.18, 126.35 (q, J_{C-F} = 282.1 Hz), 122.09, 68.97, 65.33, 57.46 (q, J = 23.8 Hz), 56.13, 52.57, 16.91 (d, J = 2.6 Hz). MS (EI): m/z (%) = 503 (M^+, 9.54), 139 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_3ClBr]^+$: 503.0111 found: 503.0105. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 19.9 min, major enantiomer tr = 17.2 min. $[\alpha]_D^{20}$ = 13.0 (c = 0.25, $CHCl_3$).

4.2 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-5-(4-fluorophenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ab**).

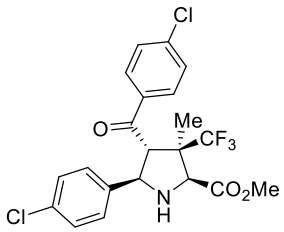


3ab

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2b** (78.0 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ab** as a colorless ropy liquid (87.7 mg, 99% yield) with > 20:1 d.r. and 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2 H), 7.40-7.33 (m, 4 H), 7.00-6.95 (m, 2 H), 4.77 (d, J = 9.0 Hz, 1 H), 4.20 (d, J = 9.0 Hz, 1 H), 3.83-3.81 (m, 4 H), 2.66 (s, 1 H), 1.36 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.16, -113.67. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.34, 169.94, 162.42 (d, J = 246.9 Hz), 140.54, 135.55, 134.87 (d, J = 3.2 Hz), 129.70, 129.15, 128.22 (d, J = 8.2 Hz), 127.83 (q, J_{C-F} = 281.8 Hz), 115.84 (d, J = 21.4 Hz), 69.04, 65.45, 57.54 (q, J = 23.7 Hz), 56.33, 52.56, 16.95 (d, J = 2.7 Hz). MS (EI): m/z (%) = 443 (M^+, 18.12), 139 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_4Cl]^+$: 443.0911 found: 443.0907. Enantiomeric excess was determined by

HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 21.2 min, major enantiomer tr = 15.6 min. $[\alpha]_D^{20} = 5.7$ (*c* = 0.50, $CHCl_3$).

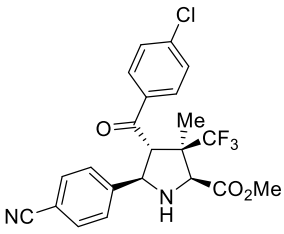
4.3 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-5-(4-chlorophenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ac**).



3ac

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2c** (84.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ac** as a colorless ropy liquid (89.6 mg, 98% yield) with > 20:1 d.r. and 99% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2 H), 7.41-7.39 (m, 2 H), 7.33-7.26 (m, 4 H), 4.79 (d, *J* = 8.7 Hz, 1 H), 4.20 (d, *J* = 8.9 Hz, 1 H), 3.85-3.81 (m, 4 H), 2.71 (s, 1 H), 1.36 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.15. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.24, 169.89, 140.59, 137.65, 135.45, 133.94, 129.72, 129.17, 129.07, 127.85, 126.35 (q, $J_{C\text{-}F}$ = 281.8 Hz), 68.96, 65.30, 57.46 (q, *J* = 23.4 Hz), 56.18, 52.57, 16.91. MS (EI): m/z (%) = 459 (M^+, 14.34), 139 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_3Cl_2]^+$: 459.0616 found: 459.0613. Enantiomeric excess was determined by HPLC with a Chiralpak IE column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 25.0 min, major enantiomer tr = 34.6 min. $[\alpha]_D^{20} = 10.3$ (*c* = 0.50, $CHCl_3$).

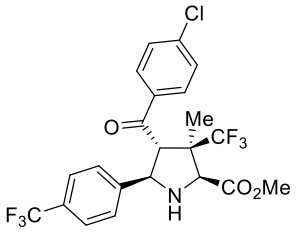
4.4 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-5-(4-cyanophenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ad**).



3ad

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2d** (80.8 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ad** as a colorless ropy liquid (87.0 mg, 97% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 2 H), 7.57 (d, *J* = 8.2 Hz, 2 H), 7.50 (d, *J* = 8.1 Hz, 2 H), 7.40-7.37 (m, 2 H), 4.89 (d, *J* = 8.8 Hz, 1 H), 4.18 (d, *J* = 8.9 Hz, 1 H), 3.85 (s, 1 H), 3.80 (s, 3 H), 2.71 (s, 1 H), 1.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.10. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.79, 169.96, 144.96, 140.82, 135.27, 132.64, 129.70, 129.24, 127.47 (q, $J_{C\text{-}F}$ = 281.5 Hz), 127.28, 118.35, 112.00, 68.58, 64.90, 57.13 (q, *J* = 25.1, 24.6 Hz), 55.71, 52.57, 16.82 (d, *J* = 2.7 Hz). MS (EI): m/z (%) = 450 (M^+, 18.42), 139 (100); HRMS calculated for $[C_{22}H_{18}N_2O_3F_3Cl]^+$: 450.0958 found: 450.0955. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 254 nm); minor enantiomer tr = 40.6 min, major enantiomer tr = 24.7 min. $[\alpha]_D^{20}$ = 1.8 (*c* = 0.25, $CHCl_3$).

4.5 Synthesis of methyl (2*S*, 3R, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-3-methyl-3-(trifluoro methyl)-5-(4-(trifluoromethyl)phenyl)pyrrolidine-2-carboxylate (**3ae**).

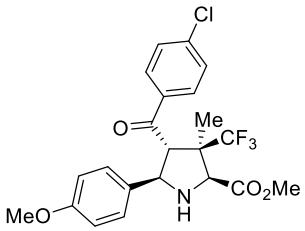


3ae

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2e** (98.0 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ae** as a colorless ropy liquid (93.5 mg, 95% yield) with > 20:1 d.r. and 99% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2 H), 7.55 (d, *J* = 8.2 Hz, 2 H), 7.49 (d, *J* = 8.2 Hz, 2 H), 7.42-7.38 (m, 2 H), 4.90 (d, *J* = 8.8 Hz, 1 H), 4.22 (d, *J* = 9.0 Hz, 1 H), 3.86 (s, 1 H), 3.82 (s, 3 H), 2.74 (s, 1 H), 1.36 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -62.69, -71.14. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.44, 170.15, 143.69, 141.09, 135.71, 130.69 (q, *J* = 32.5 Hz), 130.10, 129.57, 128.05 (q, $J_{C\text{-}F}$ = 281.8 Hz), 127.19, 126.20 (q, *J* = 3.8 Hz), 124.15 (q, $J_{C\text{-}F}$ = 270.52 Hz), 69.25, 65.52, 57.74 (q, *J* = 23.9 Hz), 56.38, 52.92, 17.19 (d, *J* = 2.7 Hz). MS (EI): m/z (%) = 493 (M^+, 16.25), 139 (100);

HRMS calculated for $[C_{22}H_{18}NO_3F_6Cl]^+$: 493.0879 found: 493.0876. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 12.5 min, major enantiomer tr = 11.2 min. $[\alpha]_D^{20}$ = 15.2 (*c* = 0.25, $CHCl_3$).

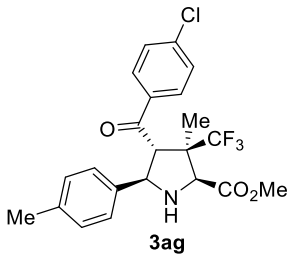
4.6 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-5-(4-methoxyphenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3af**).



3af

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2f** (83.0 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3af** as a colorless ropy liquid (90.1 mg, 99% yield) with > 20:1 d.r. and 96% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2 H), 7.38-7.35 (m, 2 H), 7.30-7.26 (m, 2 H), 6.83-6.79 (m, 2 H), 4.72 (d, *J* = 8.9 Hz, 1 H), 4.22 (d, *J* = 9.0 Hz, 1 H), 3.81-3.80 (m, 4 H), 3.73 (s, 3 H), 2.64 (s, 1 H), 1.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.16. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.60, 169.89, 159.34, 140.30, 135.68, 130.85, 129.69, 129.05, 127.95 (q, $J_{C\text{-}F}$ = 281.8 Hz), 127.65, 114.20, 69.22, 65.92, 57.71 (q, *J* = 23.5 Hz), 56.43, 55.13, 52.48, 16.96 (d, *J* = 2.5 Hz). MS (EI): m/z (%) = 455 (M^+, 25.23), 139 (100); HRMS calculated for $[C_{22}H_{21}NO_4F_3Cl]^+$: 455.1111 found: 455.1107. Enantiomeric excess was determined by HPLC with a Chiralpak IE column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 210 nm); minor enantiomer tr = 22.5 min, major enantiomer tr = 35.1 min. $[\alpha]_D^{20}$ = 8.5 (*c* = 0.50, $CHCl_3$).

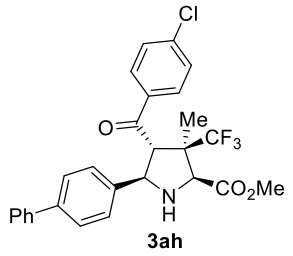
4.7 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-3-methyl -5-(p-tolyl)-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ag**).



3ag

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2g** (76.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ag** as a colorless ropy liquid (85.8 mg, 98% yield) with > 20:1 d.r. and 94% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.77-7.74 (m, 2 H), 7.39-7.36 (m, 2 H), 7.23 (d, J = 7.9 Hz, 2 H), 7.10 (d, J = 7.7 Hz, 2 H), 4.75 (d, J = 8.9 Hz, 1 H), 4.24 (d, J = 8.9 Hz, 1 H), 3.82-3.81 (m, 4 H), 2.76 (s, 1 H), 2.28 (s, 3 H), 1.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.15. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.62, 169.79, 140.32, 137.93, 135.80, 135.65, 129.74, 129.56, 129.06, 127.98 (q, $J_{C\text{-}F}$ = 281.2 Hz), 126.28, 69.31, 66.13, 57.77 (q, J = 21.5 Hz), 56.44, 52.51, 21.03, 16.95. MS (EI): m/z (%) = 439 (M^+, 23.93), 139 (100); HRMS calculated for $[C_{22}H_{21}NO_3F_3Cl]^+$: 439.1162 found: 439.1165. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 37.3 min, major enantiomer tr = 30.5 min. $[\alpha]_D^{20}$ = 12.4 (c = 0.50, $CHCl_3$).

4.8 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-([1,1'-biphenyl]-4-yl)-4- (4-chlorobenzoyl) -3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ah**).

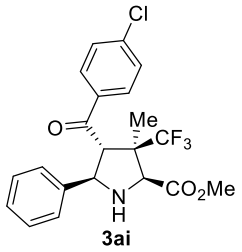


3ah

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2h** (101.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ah** as a colorless ropy liquid (99.9 mg, > 99% yield) with > 20:1 d.r. and 97% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.83-7.79 (m, 2 H), 7.55-7.53 (m, 4 H), 7.45-7.38 (m, 6 H), 7.35-7.31 (m, 1 H), 4.87 (d, J = 8.9 Hz, 1 H), 4.31 (d, J = 9.0 Hz, 1 H), 3.87 (s, 1

H), 3.83 (s, 3 H), 2.82 (s, 1 H), 1.39 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.08. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.54, 169.81, 141.01, 140.44, 140.28, 137.95, 135.61, 129.78, 129.12, 128.73, 127.95 (q, $J_{C\text{-}F}$ = 281.2 Hz), 127.57, 127.39, 126.93, 126.85, 69.26, 65.90, 57.72 (q, J = 23.5 Hz), 56.34, 52.53, 16.94 (d, J = 2.6 Hz). MS (EI): m/z (%) = 501 (M^+, 30.27), 44 (100); HRMS calculated for $[C_{27}H_{23}NO_3F_3Cl]^+$: 501.1319 found: 501.1314. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 34.0 min, major enantiomer tr = 27.4 min. $[\alpha]_D^{20}$ = -3.5 (c = 0.50, $CHCl_3$).

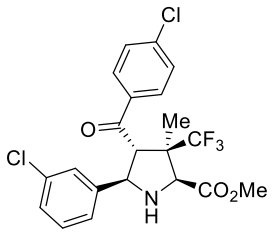
4.9 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-3-methyl-5-phenyl- 3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ai**).



3ai

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2i** (70.8 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ai** as a colorless ropy liquid (84.6 mg, > 99% yield) with > 20:1 d.r. and 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.74 (m, 2 H), 7.39-7.34 (m, 4 H), 7.32-7.24 (m, 3 H), 4.80 (d, J = 8.9 Hz, 1 H), 4.26 (d, J = 9.0 Hz, 1 H), 3.85-3.84 (m, 1 H), 3.81 (s, 3 H), 2.78 (s, 1 H), 1.37 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.16. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.55, 169.78, 140.37, 138.93, 135.65, 129.72, 129.08, 128.91, 128.20, 127.96 (q, $J_{C\text{-}F}$ = 281.8 Hz), 126.40, 69.28, 66.26, 57.73 (q, J = 23.6 Hz), 56.44, 52.50, 16.94 (q, J = 2.6 Hz). MS (EI): m/z (%) = 425 (M^+, 20.47), 139 (100); HRMS calculated for $[C_{21}H_{19}NO_3F_3Cl]^+$: 425.1006 found: 425.1004. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 28.5 min, major enantiomer tr = 21.0 min. $[\alpha]_D^{20}$ = -13.9 (c = 0.25, $CHCl_3$).

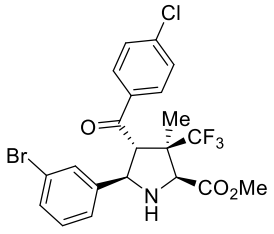
4.10 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-5-(3-chlorophenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3aj**).



3aj

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2j** (84.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3aj** as a colorless ropy liquid (90.8 mg, 99% yield) with > 20:1 d.r. and 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.79-7.75 (m, 2 H), 7.41-7.38 (m, 3 H), 7.24-7.20 (m, 3 H), 4.78 (d, *J* = 8.9 Hz, 1 H), 4.20 (d, *J* = 8.9 Hz, 1 H), 3.83-3.82 (m, 4 H), 2.70 (s, 1 H), 1.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.13. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.19, 169.78, 141.28, 140.62, 135.48, 134.80, 130.18, 129.78, 129.19, 128.43, 126.76, 126.37 (q, $J_{C\text{-}F}$ = 281.8 Hz), 124.67, 68.99, 65.35, 57.43 (q, *J* = 23.8 Hz), 56.12, 52.59, 16.91-16.86 (m, 1 C). MS (EI): m/z (%) = 459 (M^+, 14.63), 139 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_3Cl_2]^+$: 459.0616 found: 459.0608. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 18.3 min, major enantiomer tr = 16.8 min. $[\alpha]_D^{20}$ = 17.5 (*c* = 0.25, $CHCl_3$).

4.11 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(3-bromophenyl)-4-(4-chlorobenzoyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ak**).

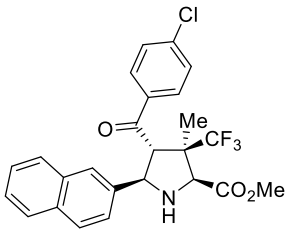


3ak

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2k** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ak** as a colorless ropy liquid (99.3 mg, 98% yield) with > 20:1 d.r. and 92% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.78-7.75 (m, 2 H), 7.55 (t, *J* = 1.8 Hz, 1 H), 7.42-7.37 (m, 3 H), 7.26 (t, *J* = 3.9 Hz, 1 H), 7.15 (t, *J* = 7.8 Hz, 1 H), 4.78 (d, *J* = 8.9 Hz, 1

H), 4.19 (d, J = 8.9 Hz, 1 H), 3.84-3.82 (s, 4 H), 2.70 (s, 1 H), 1.34 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.12. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.17, 169.76, 141.51, 140.62, 135.44, 131.37, 130.45, 129.79, 129.66, 129.19, 126.34 (q, $J_{C\text{-}F}$ = 281.2 Hz), 125.11, 122.98, 68.94, 65.25, 57.39 (q, J = 25.1, 24.6 Hz), 56.07, 52.60, 16.89. MS (EI): m/z (%) = 503 (M^+, 9.08), 139 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_3ClBr]^+$: 503.0111 found: 503.0094. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 19.1 min, major enantiomer tr = 16.6 min. $[\alpha]_D^{20}$ = 2.1 (c = 0.50, $CHCl_3$).

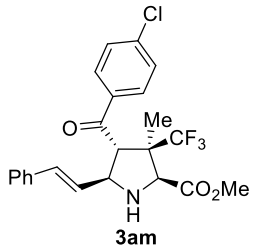
4.12 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-chlorobenzoyl)-3-methyl-5-(naphtha lene-2-yl)-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3al**).



3al

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2l** (91.0 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3al** as a colorless ropy liquid (94.6 mg, > 99% yield) with > 20:1 d.r. and 95% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.81-7.76 (m, 6 H), 7.51-7.43 (m, 3 H), 7.37-7.34 (m, 2 H), 4.99 (d, J = 8.9 Hz, 1 H), 4.36 (d, J = 8.9 Hz, 1 H), 3.91 (s, 1 H), 3.84 (s, 3 H), 2.91 (s, 1 H), 1.40 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.08. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.57, 169.86, 140.42, 136.29, 135.59, 133.17, 133.02, 129.74, 129.08, 128.93, 127.97 (q, $J_{C\text{-}F}$ = 281.9 Hz), 127.92, 127.58, 126.36, 126.19, 125.60, 123.94, 69.27, 66.30, 57.69 (q, J = 23.6 Hz), 56.40, 52.56, 16.99 (d, J = 2.7 Hz). MS (EI): m/z (%) = 475 (M^+, 31.26), 139 (100); HRMS calculated for $[C_{25}H_{21}NO_3F_3Cl]^+$: 475.1162 found: 475.1160. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 26.6 min, major enantiomer tr = 23.2 min. $[\alpha]_D^{20}$ = 26.1 (c = 0.25, $CHCl_3$).

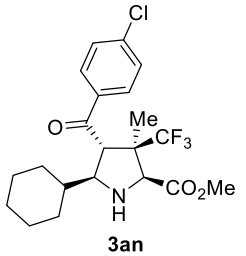
4.13 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*S*)-4-(4-chlorobenzoyl)-3-methyl-5-((E)-styryl)-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3am**).



3am

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2m** (81.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3am** as a colorless ropy liquid (89.3 mg, 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91-7.87 (m, 2 H), 7.46-7.42 (m, 2 H), 7.31-7.20 (m, 5 H), 6.57-6.53 (m, 1 H), 6.25-6.19 (m, 1 H), 4.40 (t, J = 7.9 Hz, 1 H), 4.10 (d, J = 8.3 Hz, 1 H), 3.81 (s, 3 H), 3.79 (d, J = 1.5 Hz, 1 H), 2.47 (s, 1 H), 1.34 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.32. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.39, 169.94, 140.55, 135.86, 135.70, 133.13, 129.85, 129.20, 128.54, 128.05, 127.75 (q, $J_{C\text{-}F}$ = 281.8 Hz), 126.72, 126.50, 69.10, 64.86, 57.56 (q, J = 23.4 Hz), 54.89, 52.56, 16.81 (d, J = 2.7 Hz). MS (EI): m/z (%) = 451 (M^+, 27.48), 139 (100); HRMS calculated for $[C_{23}H_{21}NO_3F_3Cl]^+$: 451.1162 found: 451.1158. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90:10, 0.5 mL/min, 254 nm); minor enantiomer tr = 23.3 min, major enantiomer tr = 32.9 min. $[\alpha]_D^{20}$ = 13.3(*c* = 0.25, $CHCl_3$).

4.14 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*S*)-4-(4-chlorobenzoyl)-5-cyclohexyl-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3an**).

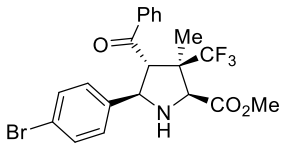


3an

The reaction of enone **1a** (50.0 mg, 0.2 mmol) and azomethine ylide **2n** (73.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3an** as a colorless ropy liquid (79.3 mg, 92% yield) with > 20:1 d.r. and 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.95-7.91 (m, 2 H), 7.49-7.45 (m, 2 H), 3.89 (d, J =

7.9 Hz, 1 H), 3.76 (s, 3 H), 3.65 (d, J = 1.6 Hz, 1 H), 3.55 (t, J = 8.3 Hz, 1 H), 2.32 (s, 1 H), 1.98-1.94 (m, 1 H), 1.73-1.68 (m, 1 H), 1.61-1.55 (m, 2 H), 1.39-1.21 (m, 4 H), 1.18 (s, 3 H), 1.12-1.04 (m, 2 H), 0.90-0.84 (m, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.19. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.96, 169.41, 140.42, 135.26, 129.89, 129.28, 128.28 (q, $J_{C\text{-}F}$ = 282.2 Hz), 69.20, 68.71, 57.32 (q, J = 22.6 Hz), 53.47, 52.40, 42.25, 30.83, 30.63, 26.11, 25.85, 25.64, 16.31 (d, J = 2.8 Hz). MS (EI): m/z (%) = 431 (M^+, 13.60), 139 (100); HRMS calculated for $[C_{21}H_{25}NO_3F_3Cl]^+$: 431.1475 found: 431.1473. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 17.1 min, major enantiomer tr = 11.0 min. $[\alpha]_D^{20}$ = 35.1 (c = 0.25, $CHCl_3$).

4.15 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-benzoyl-5-(4-bromophenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ba**).

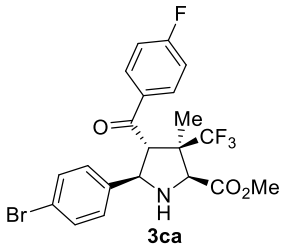


3ba

The reaction of enone **1b** (42.8 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ba** as a colorless ropy liquid (89.9 mg, 96% yield) with > 20:1 d.r. and 90% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.84-7.82 (m, 2 H), 7.69-7.55 (m, 1 H), 7.45-7.41 (m, 4 H), 7.28-7.25 (m, 2 H), 4.81 (d, J = 8.8 Hz, 1 H), 4.27 (d, J = 8.9 Hz, 1 H), 3.84 (s, 1 H), 3.81 (s, 3 H), 2.71 (s, 1 H), 1.36 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.17. ^{13}C NMR (101 MHz, $CDCl_3$) δ 198.48, 169.82, 138.34, 137.16, 133.90, 131.95, 128.81, 128.34, 128.22, 127.85 (q, $J_{C\text{-}F}$ = 281.8 Hz), 121.95, 69.03, 65.27, 57.41 (q, J = 23.7 Hz), 56.08, 52.53, 16.84 (d, J = 2.6 Hz). MS (EI): m/z (%) = 469 (M^+, 9.80), 105 (100); HRMS calculated for $[C_{21}H_{19}NO_3F_3Br]^+$: 469.0500 found: 469.0497. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 21.8 min, major enantiomer tr = 17.2 min. $[\alpha]_D^{20}$ = 0.7 (c = 0.25, $CHCl_3$).

4.16 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(4-fluorobenzoyl)-3-

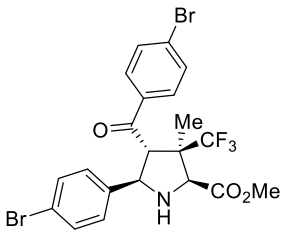
methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ca**).



3ca

The reaction of enone **1c** (46.1 mg, 0.20 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ca** as a colorless ropy liquid (97.3 mg, > 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.87-7.83 (m, 2 H), 7.41-7.38 (m, 2 H), 7.26-7.23 (m, 2 H), 7.11-7.06 (m, 2 H), 4.77 (d, J = 8.8 Hz, 1 H), 4.19 (d, J = 9.0 Hz, 1 H), 3.82 (s, 1 H), 3.80 (s, 3 H), 2.69 (s, 1 H), 1.34 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.15, -103.34. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.72, 169.85, 166.15 (d, J = 256.9 Hz), 138.26, 133.59 (d, J = 2.9 Hz), 131.96, 131.11 (d, J = 9.6 Hz), 128.17, 127.78 (q, $J_{C\text{-}F}$ = 281.2 Hz), 122.00, 116.01 (d, J = 22.0 Hz), 68.94, 65.26, 57.36 (q, J = 23.8 Hz), 56.05, 52.53, 16.85-16.80 (m, 1 C). MS (EI): m/z (%) = 487 (M^+, 8.66), 123 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_4Br]^+$: 487.0406 found: 487.0403. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 17.7 min, major enantiomer tr = 15.4 min. $[\alpha]_D^{20}$ = 1.0 (c = 0.25, $CHCl_3$)

4.17 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-4-(4-bromobenzoyl)-5-(4-bromophenyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3da**).

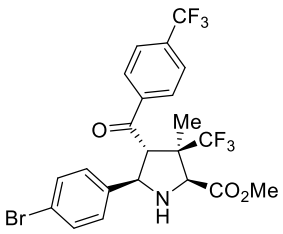


3da

The reaction of enone **1d** (58.4 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3da** as a colorless ropy liquid (102.1 mg, 93% yield) with 12:1 d.r. and 98%

ee. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.65 (m, 2 H), 7.56-7.53 (m, 2 H), 7.41-7.38 (m, 2 H), 7.25-7.23 (m, 2 H), 4.76 (d, J = 8.9 Hz, 1 H), 4.17 (d, J = 9.0 Hz, 1 H), 3.82 (s, 1 H), 3.80 (s, 3 H), 2.69 (s, 1 H), 1.34 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.12. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.39, 169.83, 138.16, 135.78, 132.13, 131.97, 129.75, 129.42, 128.14, 127.70 (q, $J_{C\text{-}F}$ = 282.0 Hz), 122.04, 68.89, 65.26, 57.38 (q, J = 23.8 Hz), 56.04, 52.54, 16.86 (d, J = 2.6 Hz). MS (EI): m/z (%) = 547 (M^+, 10.44), 183 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_3Br_2]^+$: 546.9606 found: 546.9603. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 20.8 min, major enantiomer tr = 18.2 min. $[\alpha]_D^{20}$ = 17.9 (c = 0.25, $CHCl_3$).

4.18 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-3-methyl-3-(trifluoro methyl)-4-(4-(trifluoromethyl)benzoyl)pyrrolidine-2-carboxylate (**3ea**).

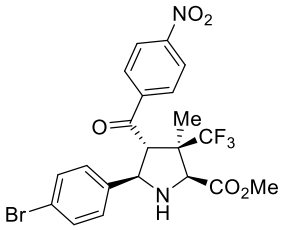


3ea

The reaction of enone **1e** (56.4 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ea** as a colorless ropy liquid (107.1 mg, >99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.91 (d, J = 8.1 Hz, 2 H), 7.69 (d, J = 8.2 Hz, 2 H), 7.45-7.42 (m, 2 H), 7.29-7.27 (m, 2 H), 4.79 (t, J = 9.2 Hz, 1 H), 4.25 (d, J = 9.1 Hz, 1 H), 3.87-3.83 (m, 4 H), 2.72 (t, J = 9.7 Hz, 1 H), 1.38 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -63.29, -71.18. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.74, 169.90, 139.72, 138.06, 134.97 (q, J = 32.7 Hz), 132.09, 128.61, 128.20, 127.66 (q, $J_{C\text{-}F}$ = 281.7 Hz), 125.90 (q, J = 3.7 Hz), 123.29 (q, $J_{C\text{-}F}$ = 271.4 Hz), 122.22, 68.92, 65.39, 57.53 (q, J = 24.0 Hz), 56.52, 52.61, 17.07-16.83 (m, 1 C). MS (EI): m/z (%) = 537 (M^+, 10.84), 173 (100); HRMS calculated for $[C_{22}H_{18}NO_3F_6Br]^+$: 537.0374 found: 537.0377. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 13.1 min, major enantiomer tr = 12.0

min. $[\alpha]_D^{20}$ = -9.0 (*c* = 0.50, $CHCl_3$).

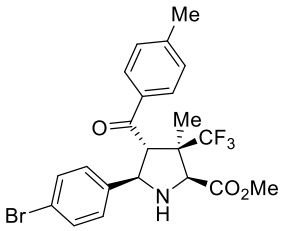
4.19 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-3-methyl-4-(4-nitro benzoyl)-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3fa**).



3fa

The reaction of enone **1f** (52.0 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3fa** as a colorless ropy liquid (102.5 mg, > 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.26-8.23 (m, 2 H), 7.93-7.89 (m, 2 H), 7.44-7.41 (m, 2 H), 7.30-7.27 (m, 2 H), 4.76 (d, *J* = 9.2 Hz, 1 H), 4.23 (d, *J* = 9.2 Hz, 1 H), 3.85 (s, 1 H), 3.82 (s, 3 H), 2.69 (s, 1 H), 1.38 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.14. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.33, 170.00, 150.56, 141.49, 137.92, 132.17, 129.24, 128.21, 127.53 (q, $J_{C\text{-}F}$ = 281.5 Hz), 124.02, 122.38, 68.85, 65.52, 57.62 (q, *J* = 23.9 Hz), 56.87, 52.66, 17.14 (d, *J* = 2.4 Hz). MS (EI): m/z (%) = 514 (M^+, 16.85), 150 (100); HRMS calculated for $[C_{21}H_{18}N_2O_5F_3Br]^+$: 514.0351 found: 514.0355. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 90:10, 0.5 mL/min, 254 nm); minor enantiomer tr = 29.1 min, major enantiomer tr = 32.5 min. $[\alpha]_D^{20}$ = 17.0 (*c* = 0.25, $CHCl_3$).

4.20 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-3-methyl-4-(4-methy lbenzoyl)-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ga**).

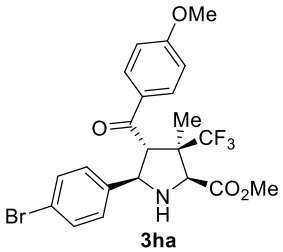


3ga

The reaction of enone **1g** (45.6 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the

product **3ga** as a colorless ropy liquid (95.0 mg, 98% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.75-7.73 (m, 2 H), 7.42-7.38 (m, 2 H), 7.25-7.21 (m, 4 H), 4.79 (t, *J* = 8.4 Hz, 1 H), 4.23 (d, *J* = 8.9 Hz, 1 H), 3.84-3.80 (m, 4 H), 2.71-2.66 (m, 1 H), 2.37 (s, 3 H), 1.34 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.16. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.88, 169.84, 145.04, 138.44, 134.71, 131.90, 129.53, 128.54, 128.20, 127.91 (q, $J_{C\text{-}F}$ = 282.0 Hz), 121.87, 69.04, 65.22, 57.38 (q, *J* = 23.7 Hz), 55.91, 52.51, 21.62, 16.79 (d, *J* = 2.6 Hz). MS (EI): m/z (%) = 483 (M^+, 9.48), 119 (100); HRMS calculated for $[C_{22}H_{21}NO_3F_3Br]^+$: 483.0657 found: 483.0659. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 22.3 min, major enantiomer tr = 19.1 min. $[\alpha]_D^{20}$ = -0.2 (*c* = 0.25, $CHCl_3$).

4.21 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(4-methoxybenzoyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ha**).

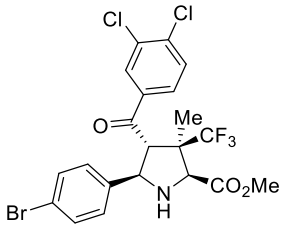


3ha

The reaction of enone **1h** (48.8 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ha** as a colorless ropy liquid (92.5 mg, 93% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.85-7.82 (m, 2 H), 7.41-7.39 (m, 2 H), 7.24-7.22 (m, 2 H), 6.91-6.87 (m, 2 H), 4.79 (d, *J* = 8.6 Hz, 1 H), 4.19 (d, *J* = 8.8 Hz, 1 H), 3.86-3.79 (m, 7 H), 2.68 (s, 1 H), 1.34 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.14. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.54, 169.93, 164.24, 138.61, 131.96, 130.96, 130.29, 128.26, 128.05 (q, $J_{C\text{-}F}$ = 281.6 Hz), 121.90, 114.07, 69.12, 65.26, 57.40 (q, *J* = 23.4 Hz), 55.79, 55.56, 52.58, 16.81. MS (EI): m/z (%) = 499 (M^+, 8.96), 135 (100); HRMS calculated for $[C_{22}H_{21}NO_4F_3Br]^+$: 499.0606 found: 499.0610. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 35.2 min, major enantiomer tr = 26.5 min.

$[\alpha]_D^{20}$ = 22.2 (*c* = 0.25, $CHCl_3$).

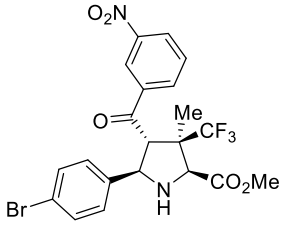
4.22 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(3,4-dichlorobenzoyl)- 3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ia**).



3ia

The reaction of enone **1i** (56.4 mg, 0.2 mmol) and azomethine ylide **2a** (102.6 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ia** as as a colorless ropy liquid (106.9 mg, > 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.90 (d, *J* = 2.1 Hz, 1 H), 7.59-7.57 (m, 1 H), 7.48 (d, *J* = 8.4 Hz, 1 H), 7.43-7.40 (m, 2 H), 7.25-7.23 (m, 2 H), 4.74 (d, *J* = 9.0 Hz, 1 H), 4.12 (d, *J* = 9.1 Hz, 1 H), 3.81 (s, 4 H), 2.69 (s, 1 H), 1.35 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.10. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.25, 169.85, 138.74, 137.99, 136.51, 133.71, 132.08, 130.89, 130.19, 128.15, 127.65 (q, $J_{C\text{-}F}$ = 281.8 Hz), 127.24, 122.21, 68.88, 65.37, 57.49 (q, *J* = 23.8 Hz), 56.27, 52.61, 16.96-16.91 (m, 1 C). MS (EI): m/z (%) = 537 (M^+, 11.65), 173 (100); HRMS calculated for $[C_{21}H_{17}NO_3F_3Cl_2Br]^+$: 536.9721 found: 536.9718. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 15.3 min, major enantiomer tr = 13.4 min. $[\alpha]_D^{20}$ = -20.0 (*c* = 0.25, $CHCl_3$).

4.23 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-3-methyl-4-(3-nitro benzoyl)-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ja**).

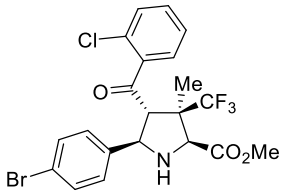


3ja

The reaction of enone **1j** (52.0 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4

mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ja** as a colorless ropy liquid (102.1 mg, > 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (t, *J* = 2.0 Hz, 1 H), 8.41-8.39 (m, 1 H), 8.08-8.05 (m, 1 H), 7.63 (t, *J* = 8.0 Hz, 1 H), 7.44-7.41 (m, 2 H), 7.30-7.26 (m, 2 H), 4.78 (t, *J* = 9.2 Hz, 1 H), 4.22 (d, *J* = 9.2 Hz, 1 H), 3.86-3.80 (m, 4 H), 2.72 (t, *J* = 9.6 Hz, 1 H), 1.38 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -71.09. ^{13}C NMR (101 MHz, $CDCl_3$) δ 196.48, 169.90, 148.53, 138.32, 137.86, 133.59, 132.17, 130.16, 128.24, 127.98, 127.59 (q, $J_{C\text{-}F}$ = 282.0 Hz), 123.15, 122.36, 68.90, 65.50, 57.62 (q, *J* = 24.0 Hz), 56.65, 52.68, 17.11 (d, *J* = 2.6 Hz). MS (EI): m/z (%) = 514 (M^+, 1.07), 84 (100); HRMS calculated for $[C_{21}H_{18}N_2O_5F_3Br]^+$: 514.0351 found: 514.0356. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 210 nm); minor enantiomer tr = 43.0 min, major enantiomer tr = 38.9 min. $[\alpha]_D^{20}$ = -9.0 (*c* = 0.25, $CHCl_3$).

4.24 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(2-chlorobenzoyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3ka**).

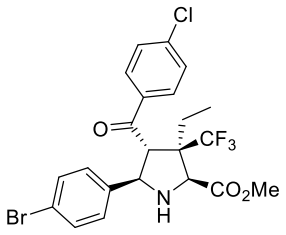


3ka

The reaction of enone **1k** (50.0 mg, 0.2 mmol) and azomethine ylide **2a** (73.2 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ka** as a colorless ropy liquid (99.7 mg, 99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.48-7.46 (m, 2 H), 7.36-7.32 (m, 4 H), 7.24-7.19 (m, 1 H), 7.15-7.12 (m, 1 H), 4.75 (d, *J* = 9.3 Hz, 1 H), 4.19 (d, *J* = 9.3 Hz, 1 H), 3.79 (s, 4 H), 2.65 (s, 1 H), 1.45 (s, 3 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -72.00. ^{13}C NMR (101 MHz, $CDCl_3$) δ 199.88, 169.70, 138.26, 138.05, 132.53, 131.98, 131.65, 131.12, 129.17, 128.68, 127.51 (q, $J_{C\text{-}F}$ = 282.0 Hz), 126.81, 122.20, 68.93, 64.70, 60.42, 57.32 (q, *J* = 24.0 Hz), 52.53, 17.33. MS (EI): m/z (%) = 503 (M^+, 10.76), 139 (100); HRMS calculated for $[C_{21}H_{18}NO_3F_3ClBr]^+$: 503.0111 found: 503.0101. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5

mL/min, 210 nm); minor enantiomer tr = 21.5 min, major enantiomer tr = 18.4 min. $[\alpha]_D^{20}$ = -109.0 (*c* = 0.50, $CHCl_3$).

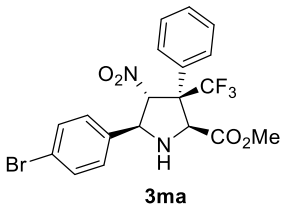
4.25 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(4-chlorobenzoyl)-3-ethyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**3la**).



3la

The reaction of enone **1l** (52.4 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4 mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3la** as a colorless ropy liquid (102.9 mg, >99% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.74-7.72 (m, 2 H), 7.41-7.35 (m, 4 H), 7.26-7.20 (m, 2 H), 4.62 (t, *J* = 8.2 Hz, 1 H), 4.18 (d, *J* = 9.4 Hz, 1 H), 3.90 (d, *J* = 6.4 Hz, 1 H), 3.81 (s, 3 H), 2.72 (s, 1 H), 2.14-2.04 (m, 1 H), 2.00-1.90 (m, 1 H), 0.85-0.80 (m, 3H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.52. ^{13}C NMR (101 MHz, $CDCl_3$) δ 197.42, 169.98, 140.49, 137.77, 135.74, 132.03, 129.51, 129.20, 128.21, 127.89 (q, $J_{C\text{-}F}$ = 283.3 Hz), 122.19, 68.17, 66.61, 62.13 (q, *J* = 22.3 Hz), 56.26, 52.60, 24.66, 9.86 (d, *J* = 1.8 Hz). MS (EI): m/z (%) = 517 (M^+, 8.16), 139 (100); HRMS calculated for $[C_{22}H_{20}NO_3F_3ClBr]^+$: 517.0267 found: 517.0272. Enantiomeric excess was determined by HPLC with a Chiralpak IC column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 16.2 min, major enantiomer tr = 12.9 min. $[\alpha]_D^{20}$ = -30.9 (*c* = 0.25, $CHCl_3$).

4.26 Synthesis of methyl (2*S*, 3*S*, 4*R*, 5*S*)-5-(4-bromophenyl)-4-nitro-3-phenyl-3-(triflu oromethyl)pyrrolidine-2-carboxylate (**3ma**).

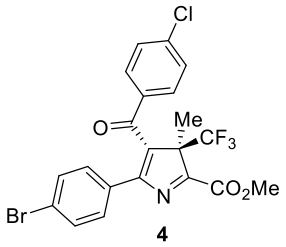


3ma

The reaction of enone **1m** (43.4 mg, 0.2 mmol) and azomethine ylide **2a** (102.4 mg, 0.4

mmol), after a flash column chromatography (hexanes: AcOEt = 6:1) afforded the product **3ma** as a colorless ropy liquid (71.7 mg, 76% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.67-7.64 (m, 2 H), 7.58-7.55 (m, 2 H), 7.43-7.39 (m, 3 H), 7.29-7.26 (m, 2 H), 5.44 (d, *J* = 7.4 Hz, 1 H), 4.94 (m, 2 H), 3.82 (s, 3 H), 3.09 (s, 1 H). ^{19}F NMR (282 MHz, $CDCl_3$) δ -66.19. ^{13}C NMR (101 MHz, $CDCl_3$) δ 168.11, 135.17, 132.52, 131.13, 129.43, 128.76, 128.11, 127.83 (q, *J* = 2.0 Hz), 126.15 (q, $J_{C\text{-}F}$ = 284.7 Hz), 123.30, 96.54, 66.92, 66.62, 66.13 (d, *J* = 22.7 Hz), 53.14. ESI-MS calculated for C19H17BrF3N2O4: m/z (%): 473.0318 ($M+Na^+$), found: 473.0315. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 80:20, 0.8 mL/min, 210 nm); minor enantiomer tr = 18.6 min, major enantiomer tr = 11.2 min. $[\alpha]_D^{20}$ = 31.1 (*c* = 0.25, $CHCl_3$).

4.27 Synthesis of methyl (*R*)-5-(4-bromophenyl)-4-(4-chlorobenzoyl)-3-methyl-3-(trifluoromethyl)-3H-pyrrole-2-carboxylate (**4**).

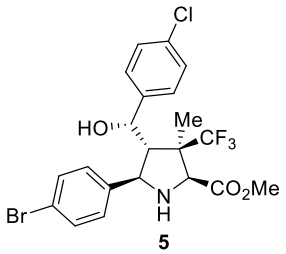


4

The solution of compound **3aa** (100.6 mg, 0.2 mmol) in Toluene (2 mL) was stirred at 70 °C in a sealed tube. Subsequently, DDQ (2.0 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 $NaHCO_3$ 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. The crude product was analyzed with ^{1}H NMR and ^{19}F NMR to determine the diastereomeric ratio. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 20:1) to afford the desired product **4** as a brown liquid (90.0 mg, 90% yield) with > 20:1 d.r. and 98% *ee*. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.4 Hz, 2 H), 7.45-7.41 (m, 2 H), 7.38-7.36 (m, 2 H), 7.29 (d, *J* = 8.4 Hz, 2 H), 4.01 (s, 3 H), 2.08 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -

67.28. ^{13}C NMR (101 MHz, $CDCl_3$) δ 191.35, 169.50, 160.49, 154.57, 140.86, 133.75, 131.81, 131.34, 130.61, 130.36, 129.82, 129.26, 126.64 (q, J_{C-F} = 282.2 Hz), 125.00, 70.65 (q, J = 28.1, 27.6 Hz), 53.30, 16.29. MS (EI): m/z (%) = 499 (M^+, 13.16), 139 (100); HRMS calculated for $[C_{21}H_{14}NO_3F_3ClBr]^+$: 498.9798 found: 498.9793. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 97:3, 0.5 mL/min, 233 nm); minor enantiomer tr = 15.4 min, major enantiomer tr = 17.1 min. $[\alpha]_D^{20}$ = 197.0 (*c* = 0.50, $CHCl_3$).

4.28 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-((*S*)-(4-chlorophenyl) (hydroxy)methyl)-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**5**).

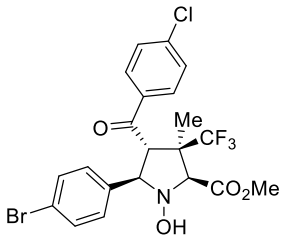


5

The solution of compound **3aa** (100.6 mg, 0.2 mmol) in ^{i}PrOH (2 mL) was stirred at 0 ^{o}C in a sealed tube. Subsequently, $LiBH_4$ (4.8 mg, 0.22 mmol) added to the above solution. The reaction was determined by TLC analysis. After the **3aa** 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 diastereomeric ratio. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 2:1) to afford the desired product **5** as a white solid (72.7 mg, 72% yield) with 7:1 d.r. and >99% *ee*. Mp: 74-75 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.20-7.18 (m, 2 H), 7.00-6.97 (m, 2 H), 6.92-6.89 (m, 2 H), 6.63-6.59 (m, 2 H), 4.54 (d, J = 9.0 Hz, 1 H), 3.75 (s, 3 H), 3.50 (s, 1 H), 3.37 (d, J = 9.1 Hz, 1 H), 2.76 (t, J = 9.1 Hz, 1 H), 2.65 (s, 1 H), 2.37 (s, 1 H), 1.64 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -71.87. ^{13}C NMR (101 MHz, $CDCl_3$) δ 169.31, 139.34, 138.63, 134.22, 131.38, 128.84, 128.43, 128.33 (q, J_{C-F} = 281.5 Hz), 128.19, 121.26, 72.92, 69.14, 64.76, 56.96, 56.07 (q, J = 23.1 Hz), 52.44 (d, J = 2.2 Hz), 15.28. MS (EI): m/z (%) = 505 (M^+, 6.10), 255 (100); HRMS calculated for $[C_{21}H_{20}NO_3F_3ClBr]^+$: 505.0267 found: 505.0256. Enantiomeric excess was determined by HPLC with a Chiralpak OZ-3 column (hexanes: 2-propanol = 95:5, 0.5

mL/min, 210 nm); minor enantiomer tr = 54.9 min, major enantiomer tr = 25.2 min. $[\alpha]_D^{20}$ = -66.9 (*c* = 0.25, $CHCl_3$).

4.29 Synthesis of methyl (2*S*, 3*R*, 4*R*, 5*R*)-5-(4-bromophenyl)-4-(4-chlorobenzoyl)-1-hydroxy-3-methyl-3-(trifluoromethyl)pyrrolidine-2-carboxylate (**6**).

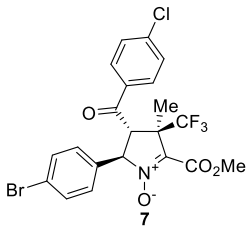


6

The solution of compound **3aa** (100.6 mg, 0.2 mmol) in DCM (2 mL) was stirred at 25 ^oC in a sealed tube. Subsequently, MCPBA (0.22 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 $NaHCO_3$ 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. The crude product was analyzed with ^1H NMR and ^{19}F NMR to determine the diastereomeric ratio. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 6:1) to afford the desired product **6** as a white solid (62.3 mg, 60% yield) with > 20:1 d.r. and 99% *ee*. Mp: 119-120 ^oC. ^1H NMR (400 MHz, $CDCl_3$) δ 7.71-7.68 (m, 2 H), 7.45-7.37 (m, 4 H), 7.33-7.30 (m, 2 H), 5.37 (s, 1 H), 4.51 (d, *J* = 9.5 Hz, 1 H), 4.05 (d, *J* = 9.5 Hz, 1 H), 3.82 (s, 3 H), 3.72 (s, 1 H), 1.31 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.29. ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.81, 168.14, 140.87, 137.33, 135.38, 132.00, 129.84, 129.23, 128.94, 127.23 (q, $J_{C\text{-}F}$ = 281.9 Hz), 122.28, 75.89, 71.01, 52.46, 52.01, 49.83 (q, *J* = 26.2 Hz), 17.30-17.25 (m, 1 C). ESI-MS calculated for $C_{21}H_{18}BrClF_3NO_4Na$: m/z: 541.9958 ($M+Na^+$), found: 541.9852. Enantiomeric excess was determined by HPLC with a Chiralpak IF column (hexanes: 2-propanol = 95:5, 0.5 mL/min, 254 nm); minor enantiomer tr = 40.5 min, major enantiomer tr = 31.5 min. $[\alpha]_D^{20}$ = 21.6 (*c* = 0.25, $CHCl_3$).

4.30 Synthesis of (2*R*,3*R*,4*R*)-2-(4-bromophenyl)-3-(4-chlorobenzoyl)-5-(methoxy-

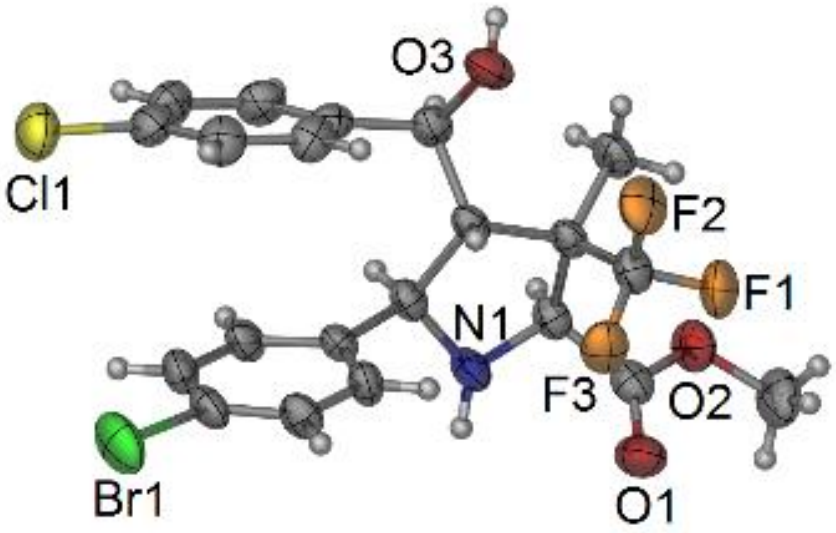
carbonyl)-4-methyl-4-(trifluoromethyl)-3,4-dihydro-2H-pyrrole 1-oxide (**7**).



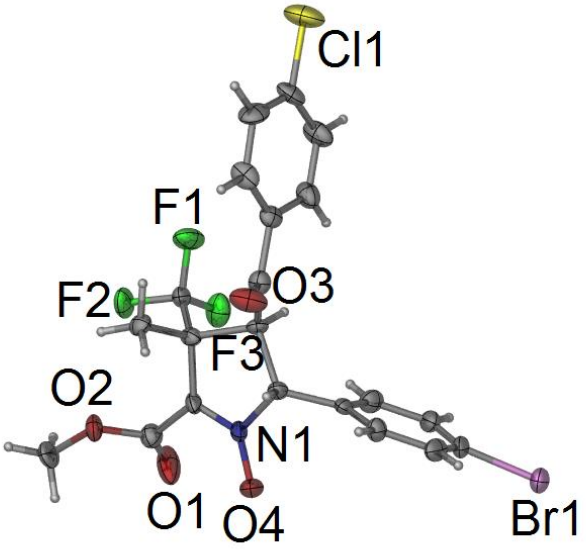
7

The solution of compound **3aa** (100.6 mg, 0.2 mmol) in DCM (2 mL) was stirred at 25 ^{o}C in a sealed tube. Subsequently, MCPBA (0.42 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 $NaHCO_3$ 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. The crude product was analyzed with ^{1}H NMR and ^{19}F NMR to determine the diastereomeric ratio. Then the crude product was then purified by flash column chromatography on silica gel (hexanes: AcOEt = 6:1) to afford the desired product **7** as a white solid (51.7 mg, 50% yield) with >20:1 d.r. and >99% *ee*. Mp: 70-71 ^{o}C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.76-7.73 (m, 2 H), 7.54-7.51 (m, 2 H), 7.46-7.42 (m, 2 H), 7.16-7.12 (m, 2 H), 5.76 (d, J = 8.6 Hz, 1 H), 4.54 (d, J = 8.6 Hz, 1 H), 3.93 (s, 3 H), 1.57 (s, 3 H). ^{19}F NMR (376 MHz, $CDCl_3$) δ -72.61. ^{13}C NMR (126 MHz, $CDCl_3$) δ 193.86, 159.40, 141.55, 134.51, 133.14, 132.56, 129.92, 129.64 (q, $J_{C\text{-}F}$ = 281.8 Hz), 129.45, 129.24, 123.94, 79.03, 54.54 (q, J = 28.6 Hz), 52.97, 49.94, 29.68, 15.86. MS (EI): m/z (%) = 517 (M^+, 1.23), 139 (100); HRMS calculated for $[C_{21}H_{16}NO_4F_3ClBr]^+$: 516.9903 found: 516.9897. Enantiomeric excess was determined by HPLC with a Chiralpak AD-H column (hexanes: 2-propanol = 90:10, 0.8 mL/min, 254 nm); minor enantiomer tr = 37.3 min, major enantiomer tr = 25.1 min. $[\alpha]_D^{20}$ = -39.0 (c = 0.25, $CHCl_3$).

5. X-ray structures of 5 and 7.

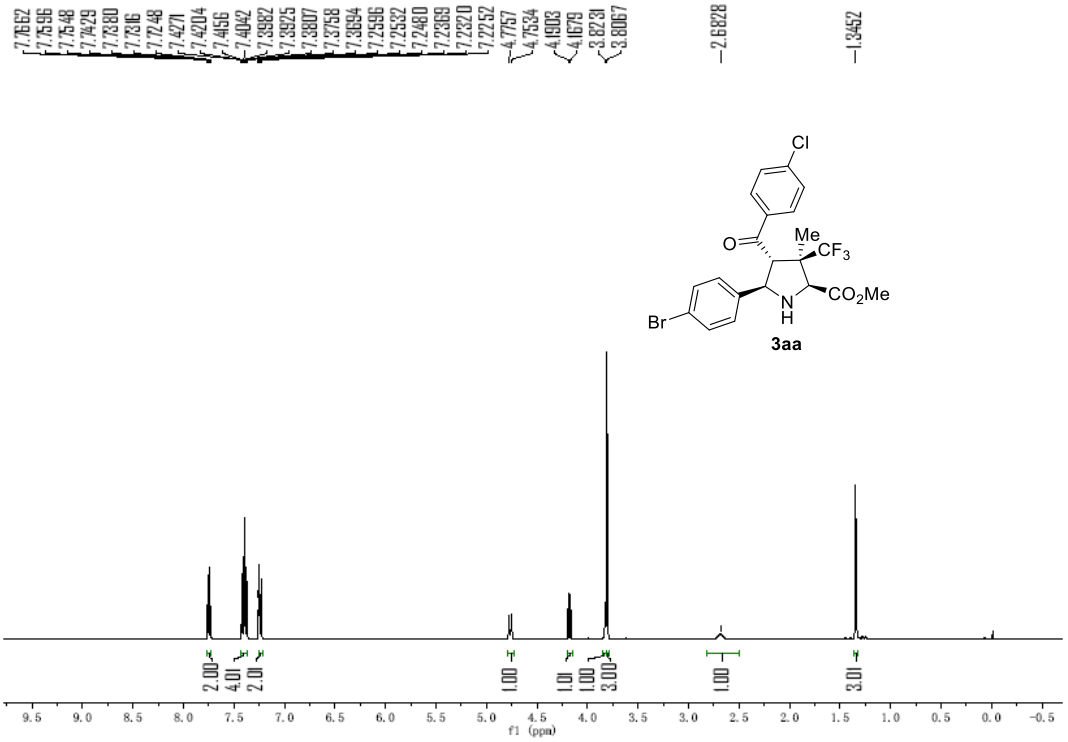


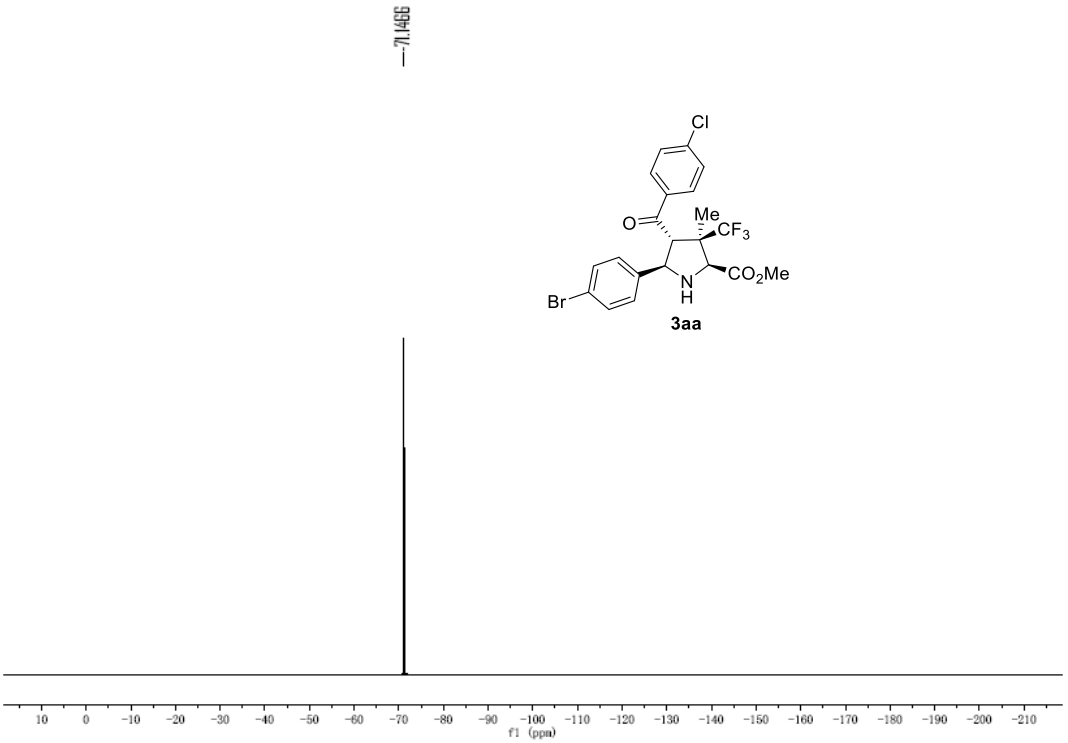
Compound 5

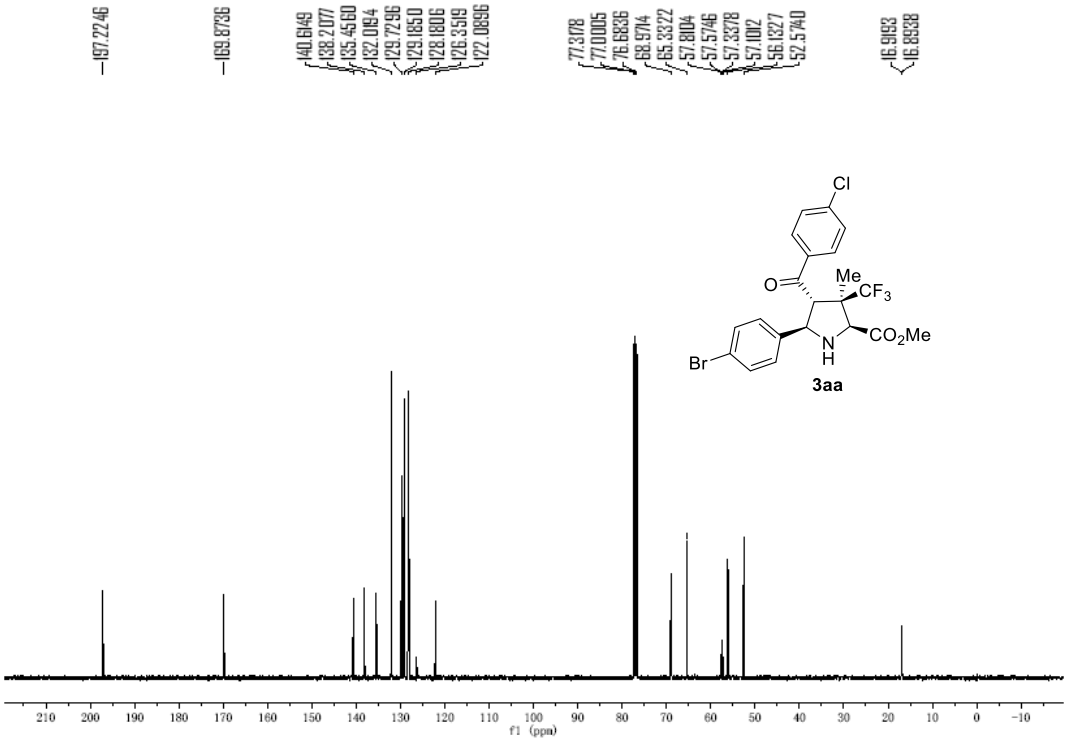


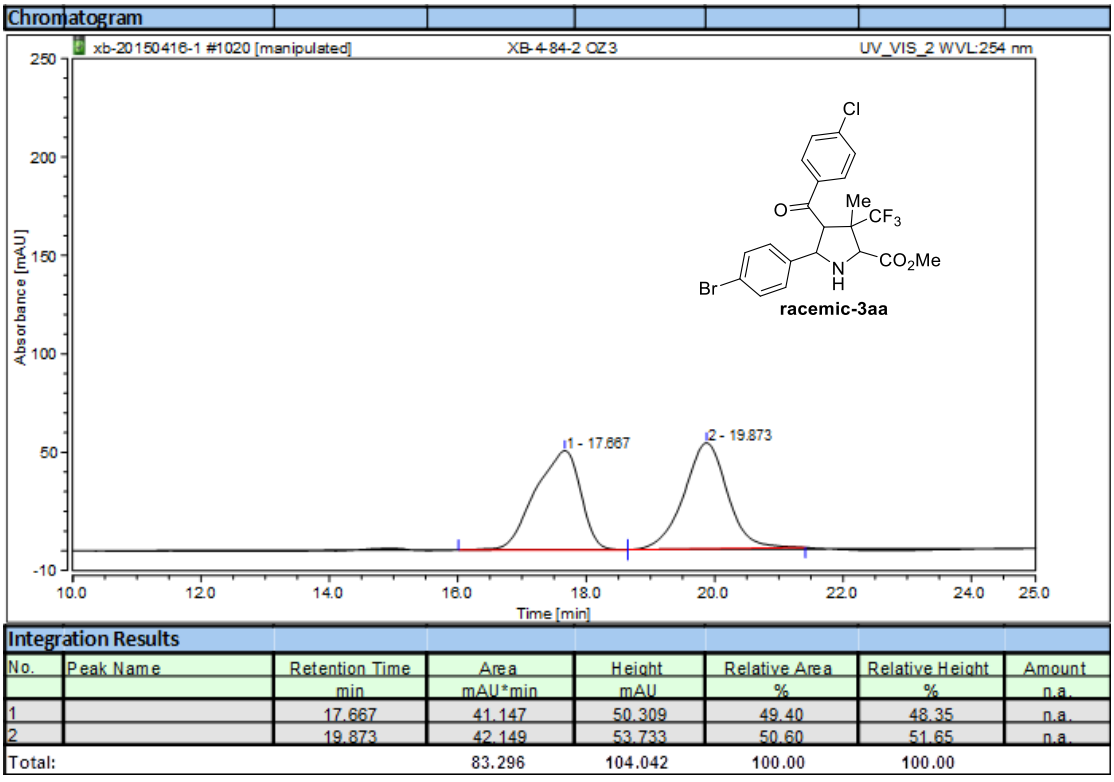
Compound 7

6. ^{1}H , ^{19}F, ^{31}P, ^{13}C NMR and HPLC Spectra





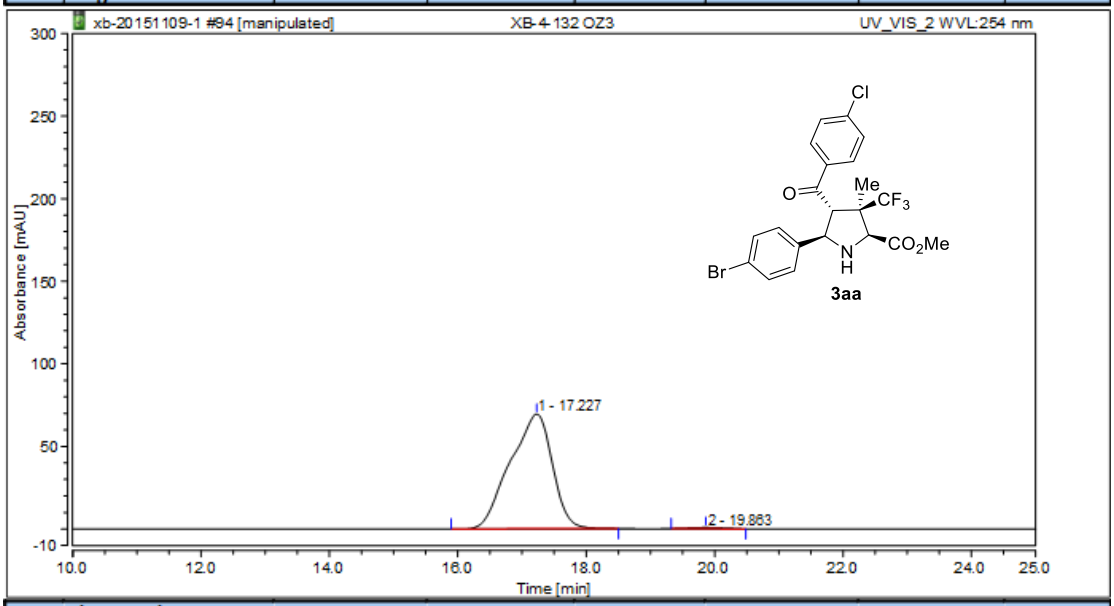




Integration Results

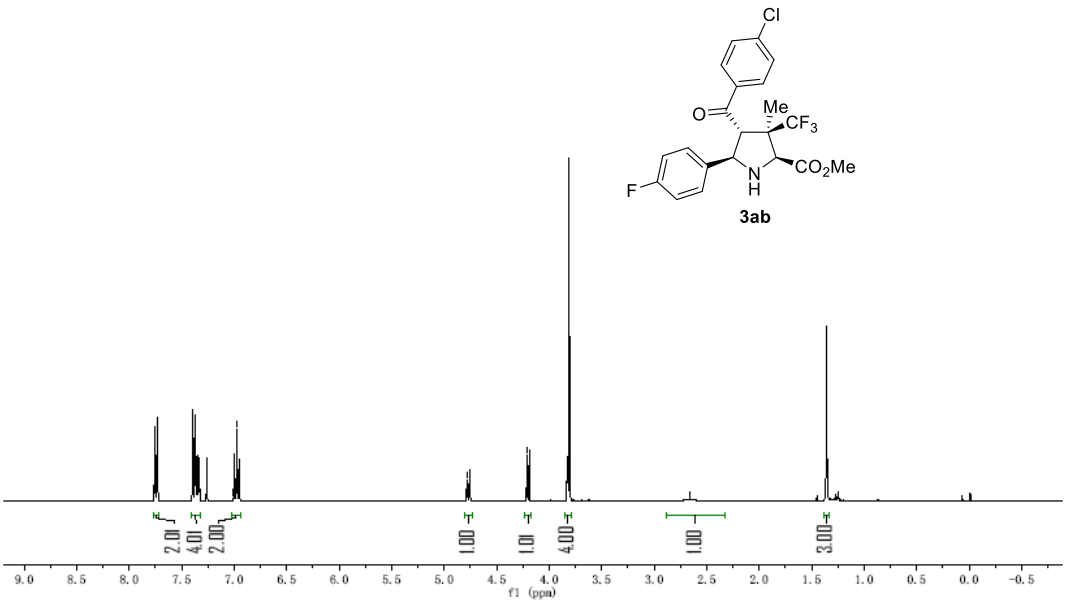
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		17.667	41.147	50.309	49.40	48.35	n.a.
2		19.873	42.149	53.733	50.60	51.65	n.a.
Total:			83.296	104.042	100.00	100.00	

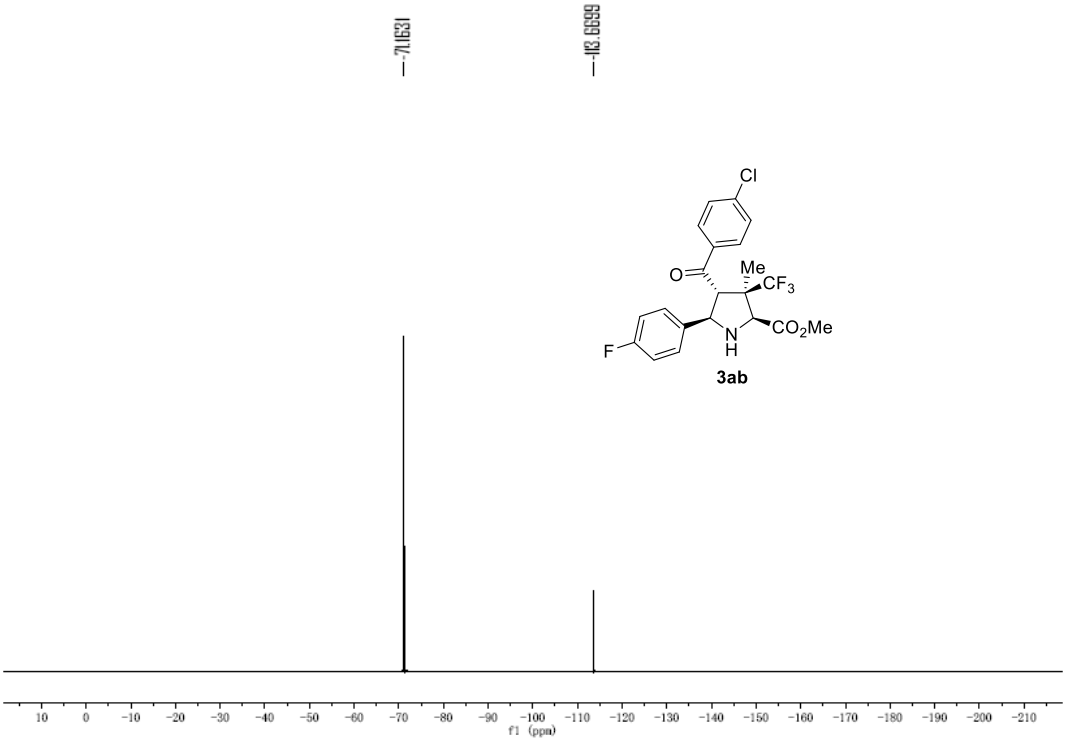
Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		17.227	52.796	69.448	99.17	98.93	n.a.
2		19.863	0.445	0.752	0.83	1.07	n.a.
Total:			53.240	70.200	100.00	100.00	

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Me
CF3
CO2Me
N
H
F
3ab
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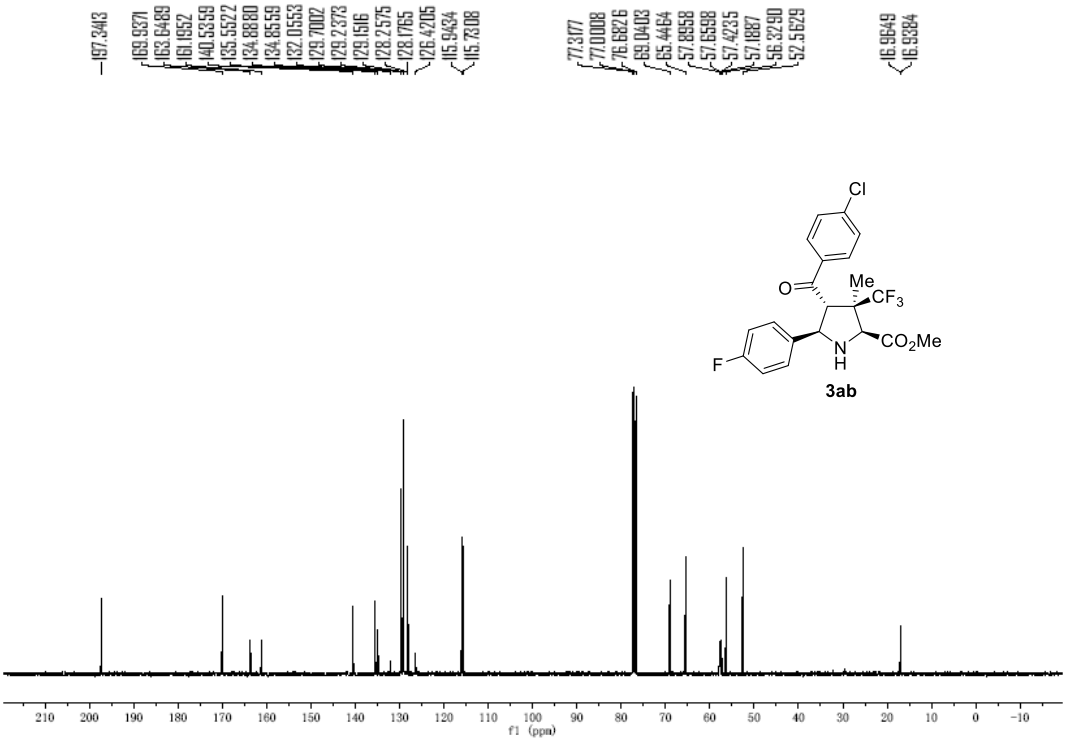
f1 (ppm)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163.6489
161.1952
140.5359
135.5522
134.8880
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132.0553
129.7002
129.2373
129.1516
128.2575
128.1765
126.4205
115.9434
115.7308
77.3177
77.0008
76.6826
69.0403
65.4464
57.8858
57.6598
57.4235
57.1887
56.3290
52.5629
16.9549
16.9384
Cl
O
Me
CF3
CO2Me
N
H
F
3ab
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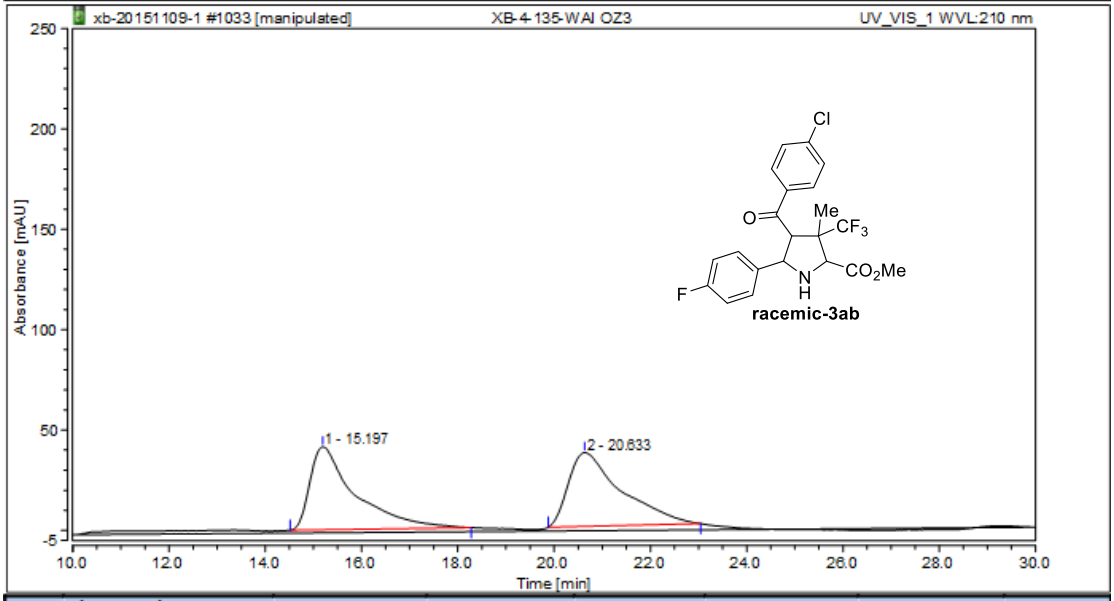
f1 (ppm)

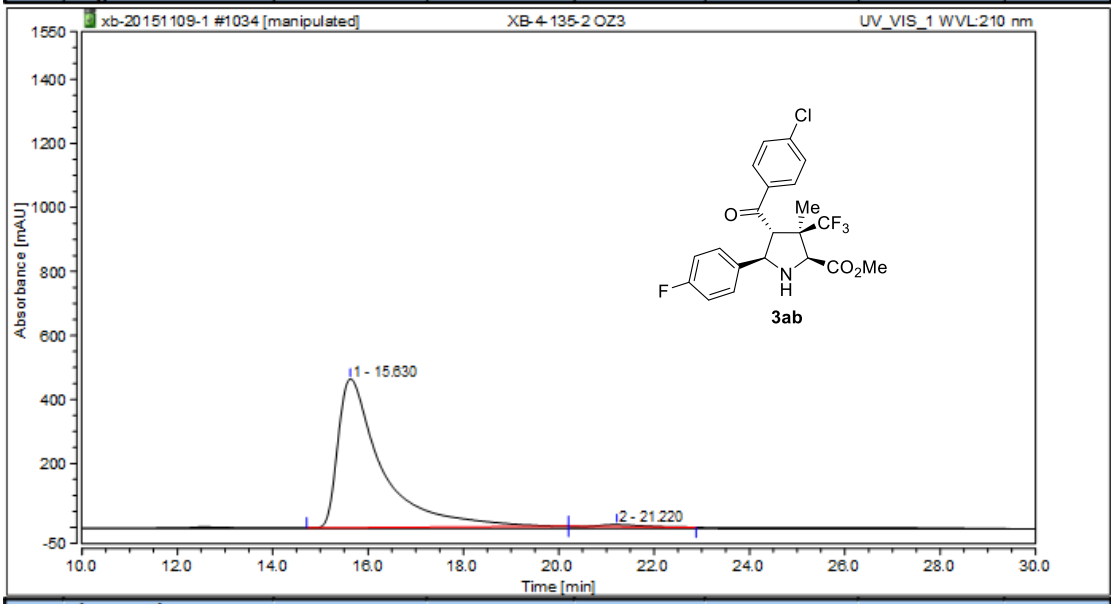
Chromatogram



Integration Results

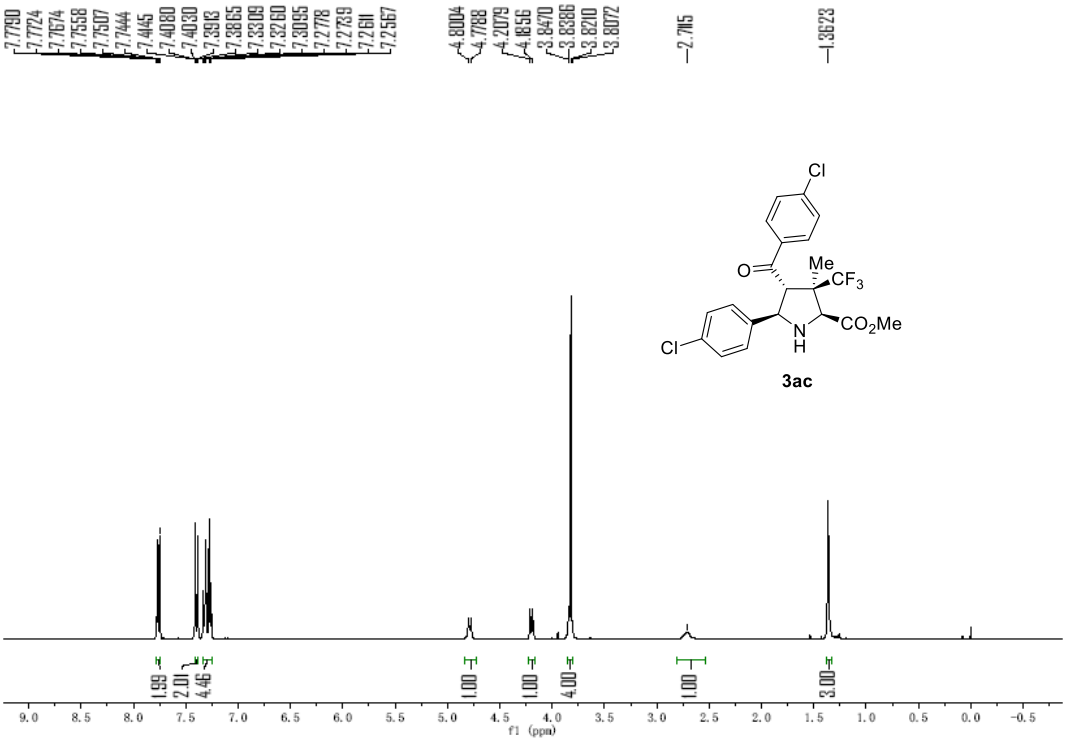
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		15.197	44.834	41.286	49.14	52.91	n.a.
2		20.633	46.394	36.742	50.86	47.09	n.a.
Total:			91.228	78.028	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		15.630	495.078	464.379	98.68	98.52	n.a.
2		21.220	6.626	6.984	1.32	1.48	n.a.
Total:			501.704	471.363	100.00	100.00	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4.8004
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4.2079
4.1856
3.8470
3.8386
3.8210
3.8072
2.765
1.3623
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O
Me
CF3
CO2Me
N
H
Cl
3ac
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2.01
4.46
1.00
1.00
4.00
1.00
3.00
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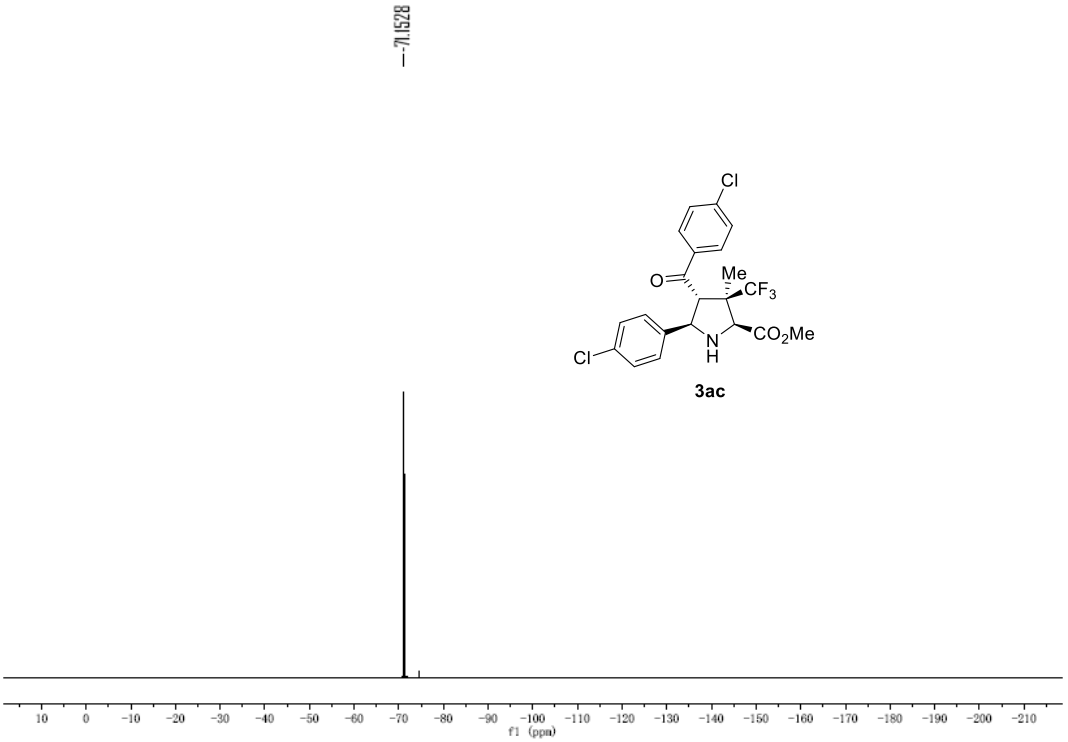
f1 (ppm)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Me
CF3
CO2Me
N
H
Cl
3ac
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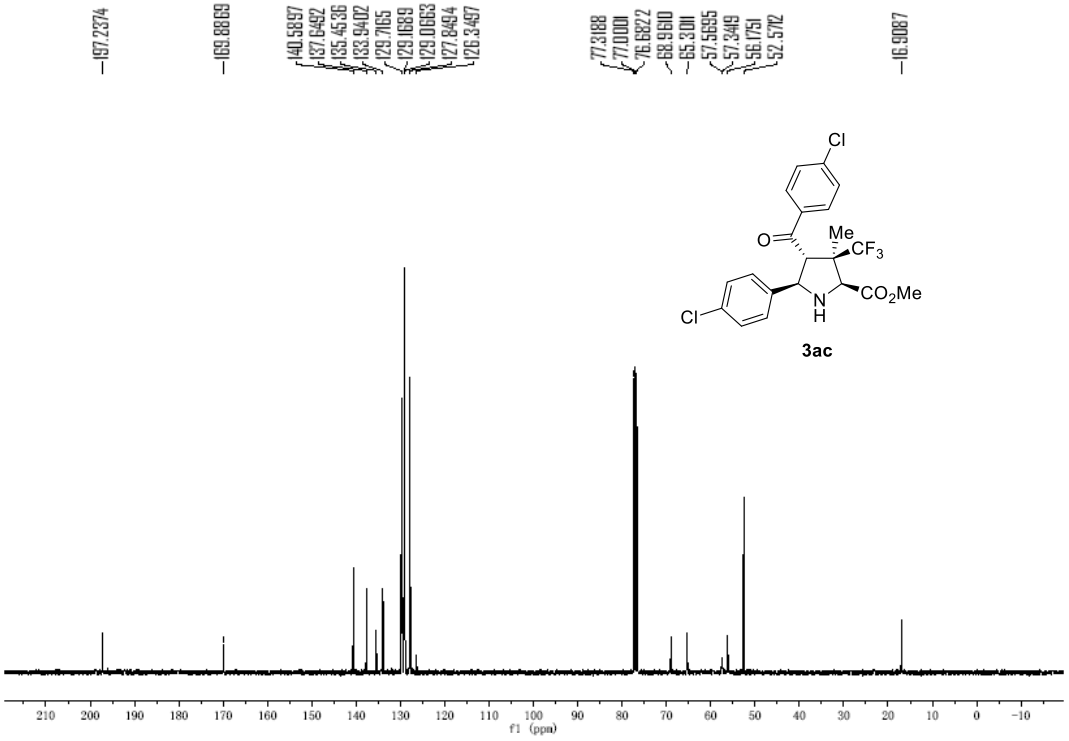
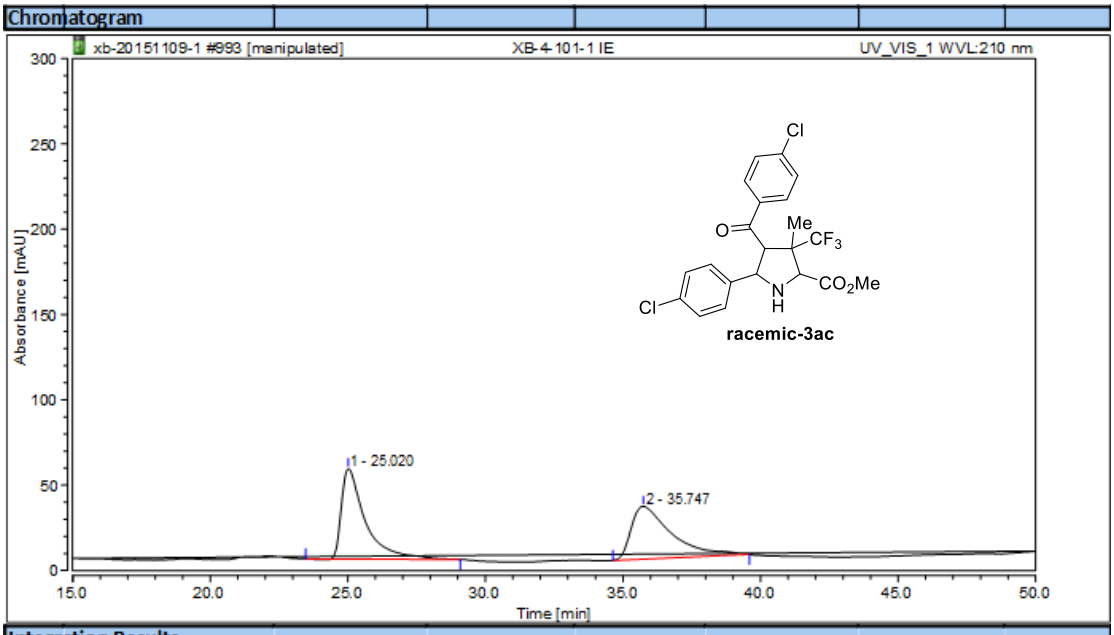
f1 (ppm)

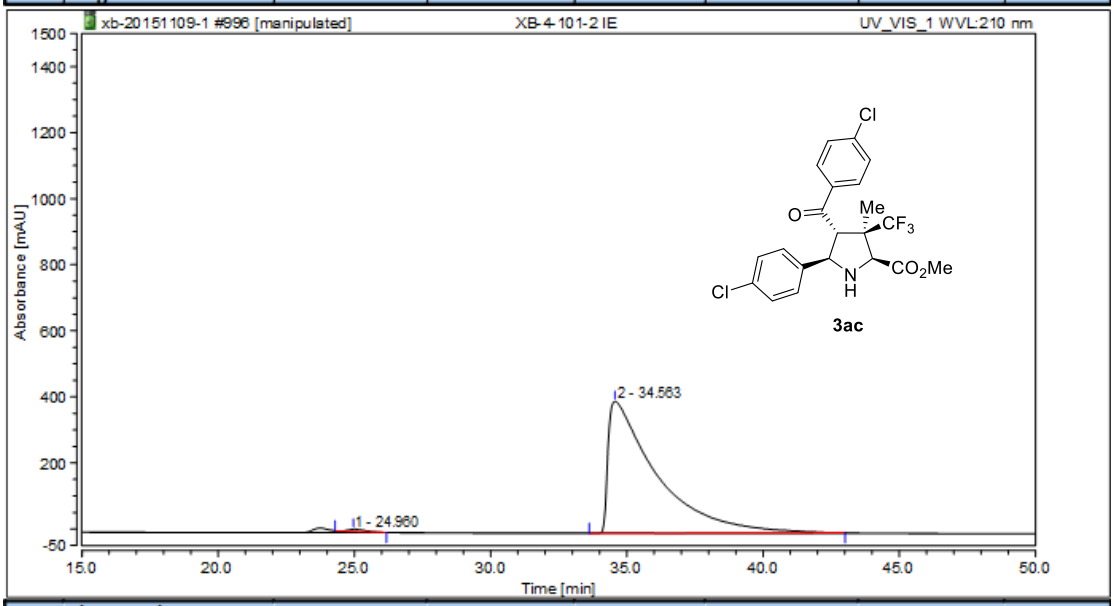




Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		25.020	53.110	52.948	50.33	63.10	n.a.
2		35.747	52.411	30.967	49.67	36.90	n.a.
Total:			105.522	83.916	100.00	100.00	

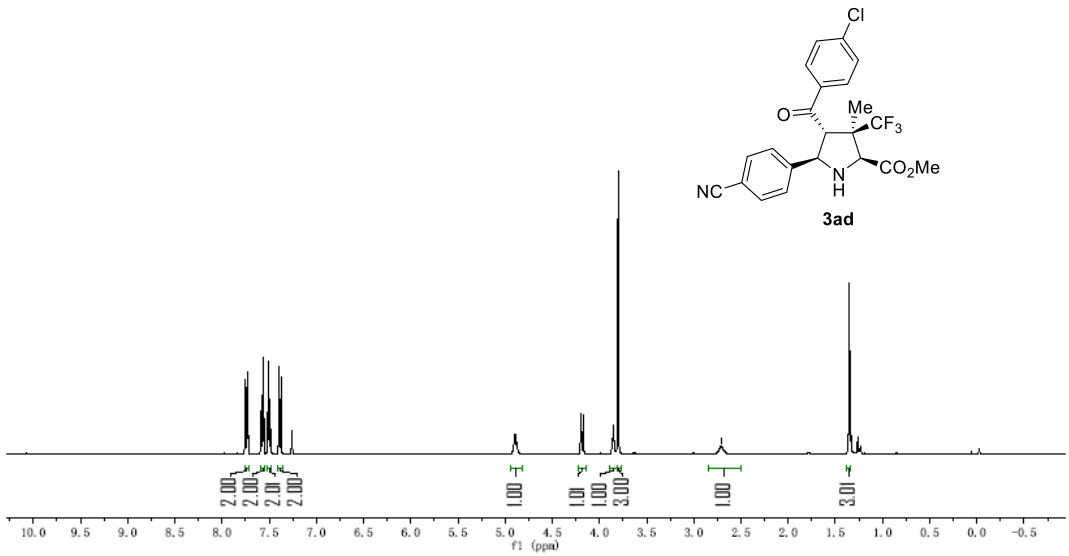
Chromatogram



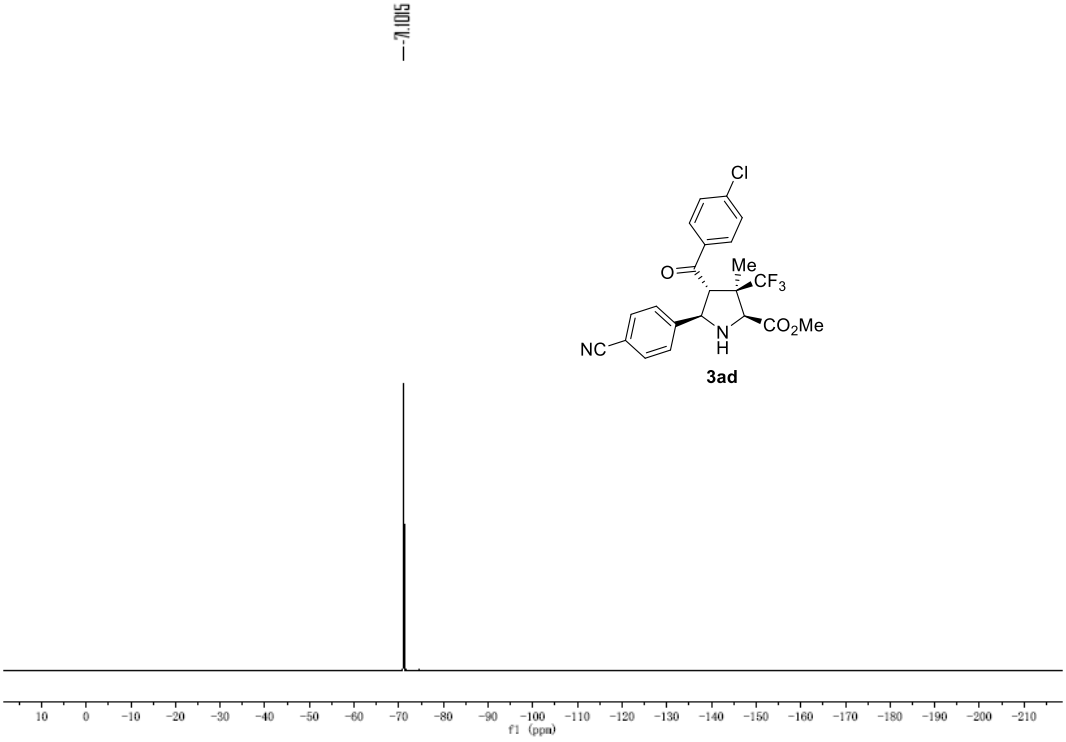
3ac

Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		24.960	4.452	6.774	0.54	1.67	n.a.
2		34.563	822.924	399.639	99.46	98.33	n.a.
Total:			827.376	406.413	100.00	100.00	



3ad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CO2Me
N
H
NC
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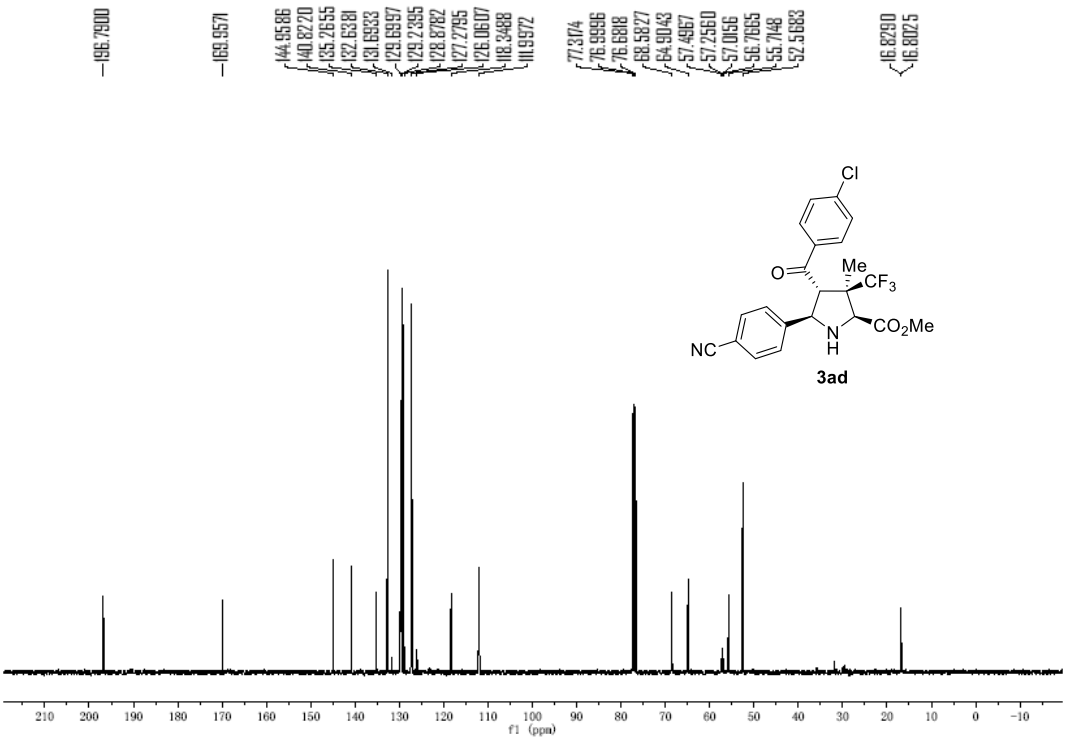
f1 (ppm)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NC
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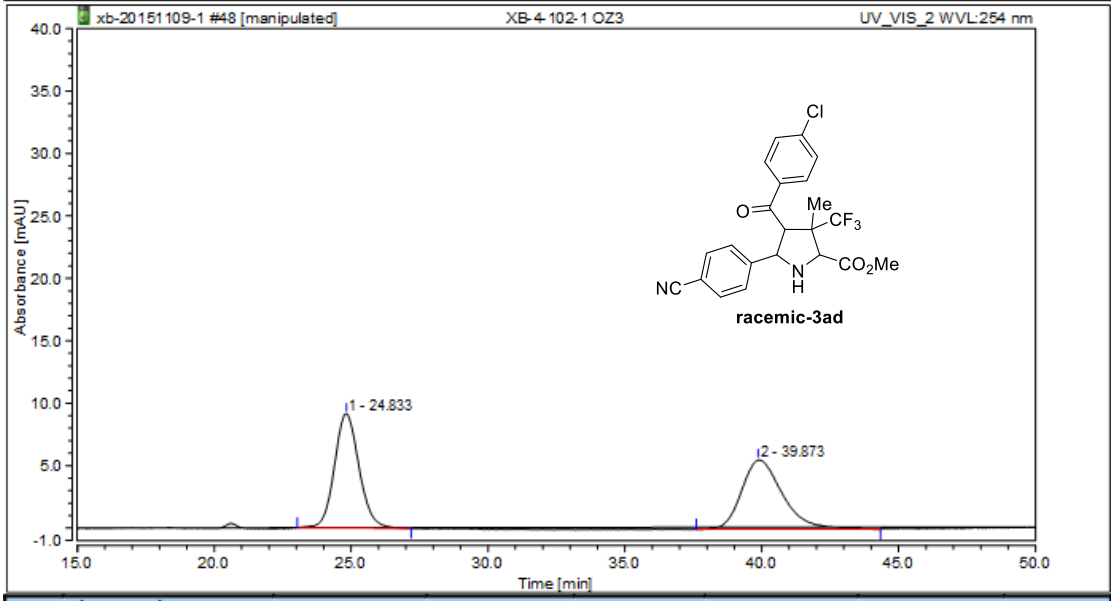
f1 (ppm)

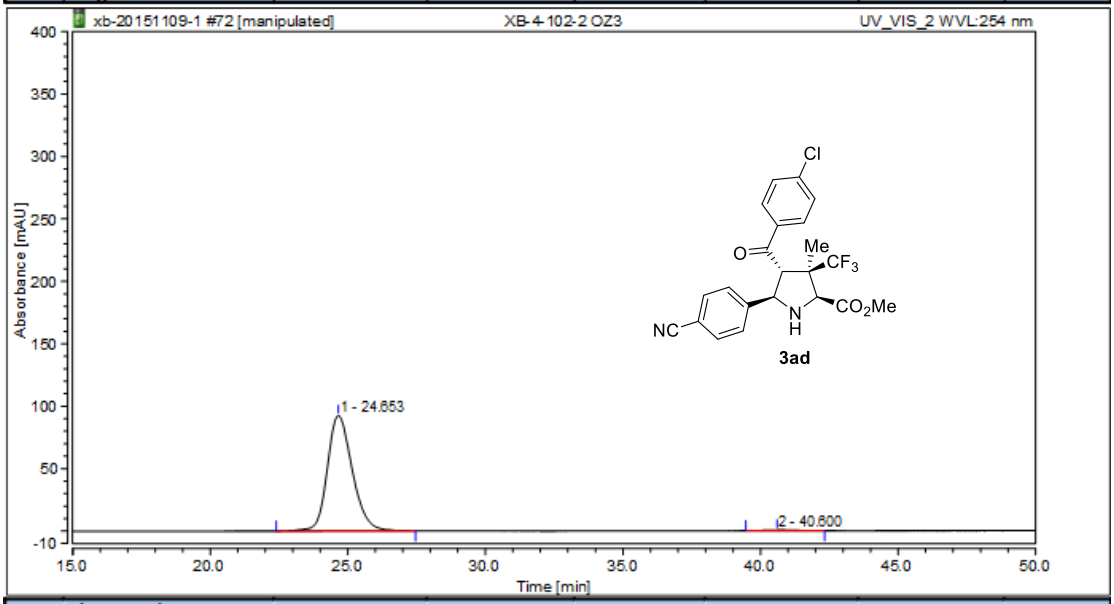
Chromatogram



Integration Results

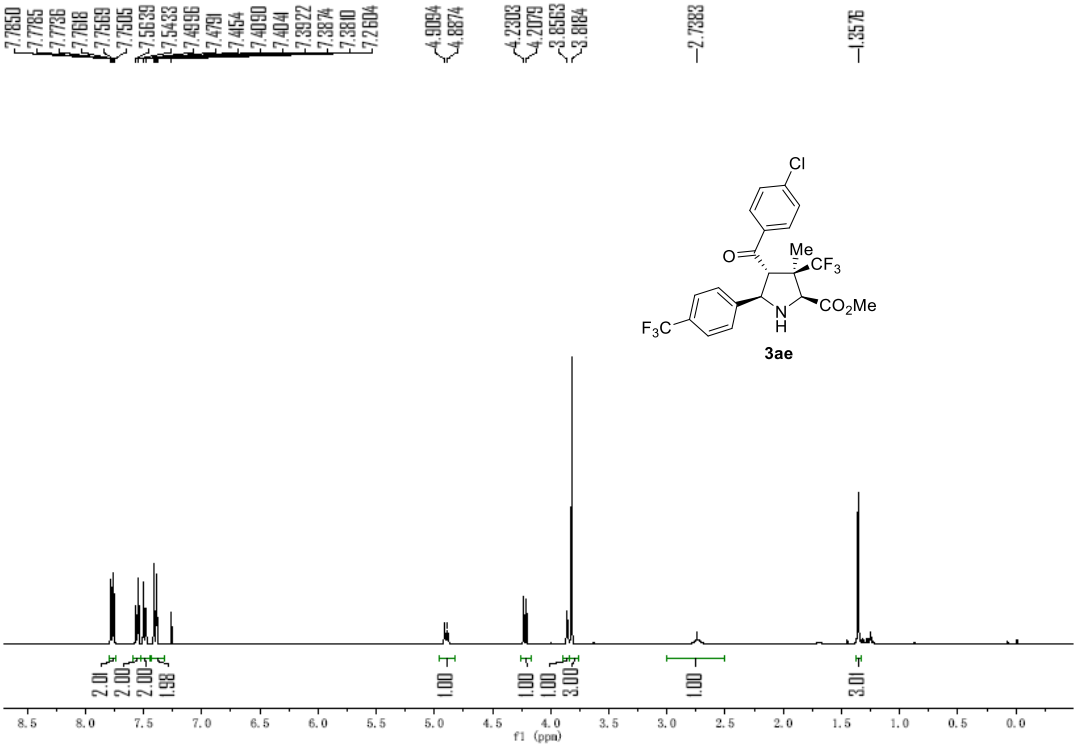
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		24.833	9.543	9.159	49.88	62.19	n.a.
2		39.873	9.591	5.568	50.12	37.81	n.a.
Total:			19.134	14.728	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		24.653	97.308	92.565	99.08	99.33	n.a.
2		40.600	0.902	0.624	0.92	0.67	n.a.
Total:			98.209	93.190	100.00	100.00	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7.2604
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4.8874
4.2303
4.2079
3.8563
3.8184
2.7383
1.3576
Cl
O
Me
CF3
N
H
CO2Me
F3C
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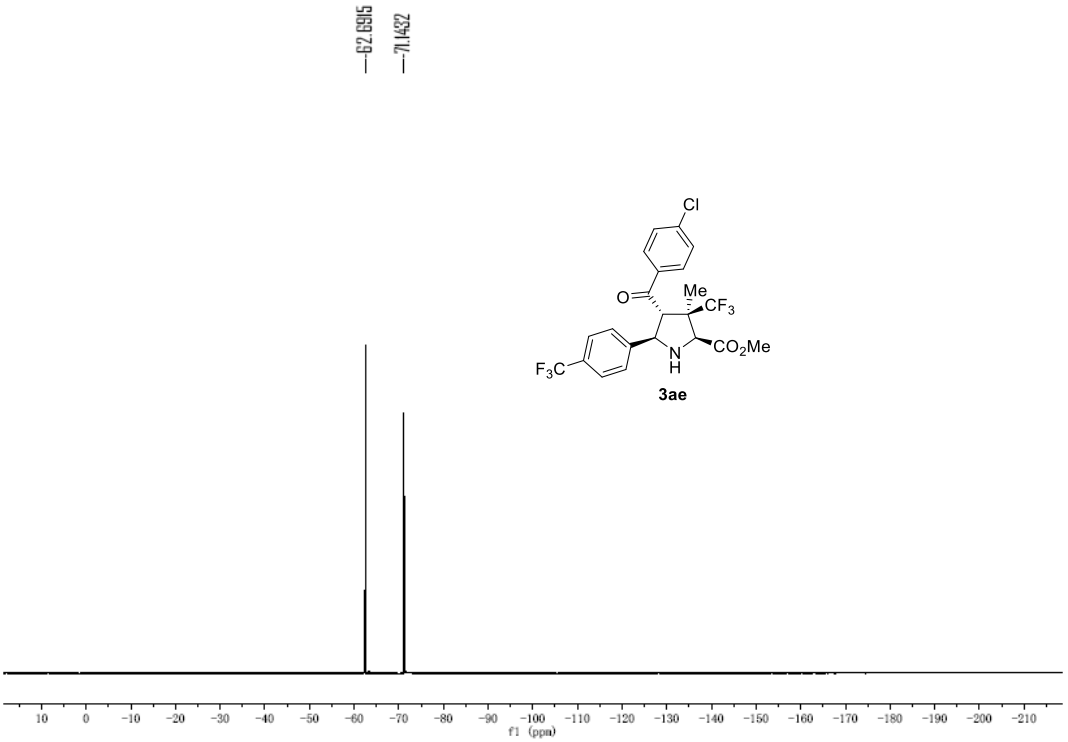
1.98
1.00
1.00
1.00
3.00
1.00
3.01
f1 (ppm)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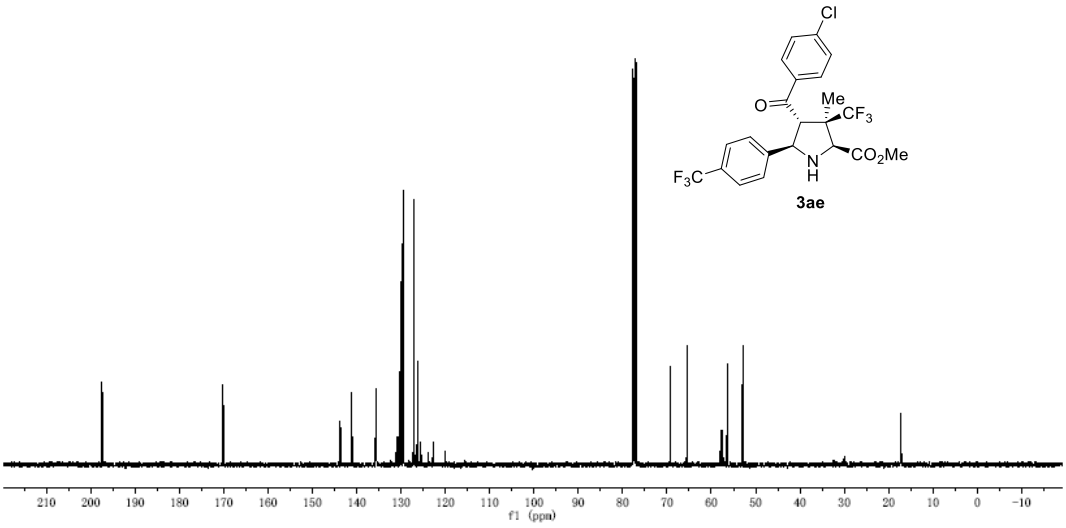
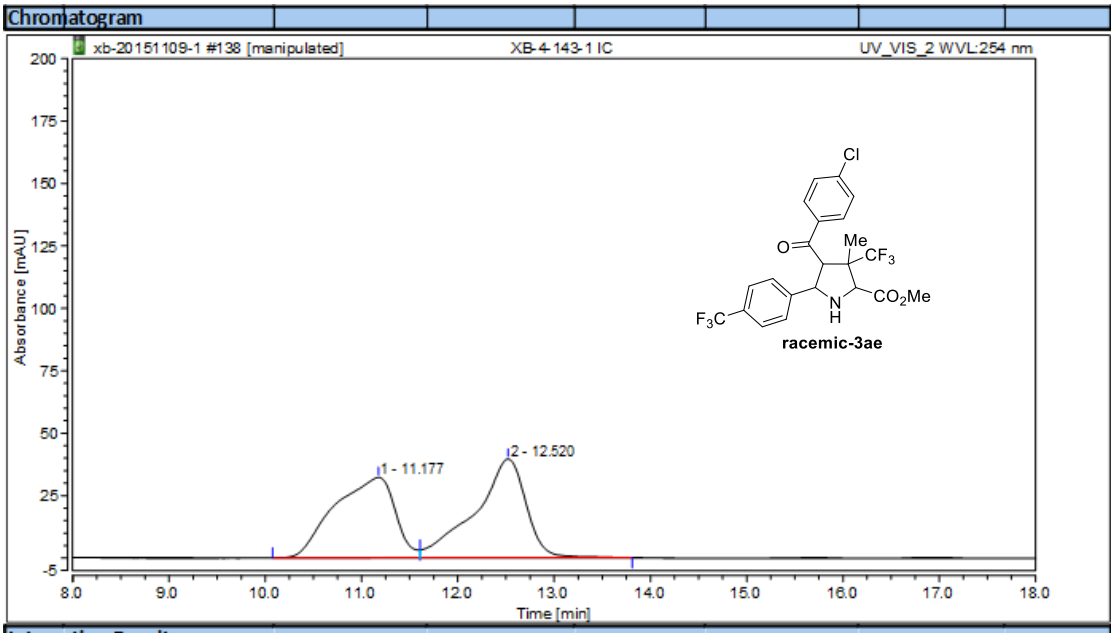
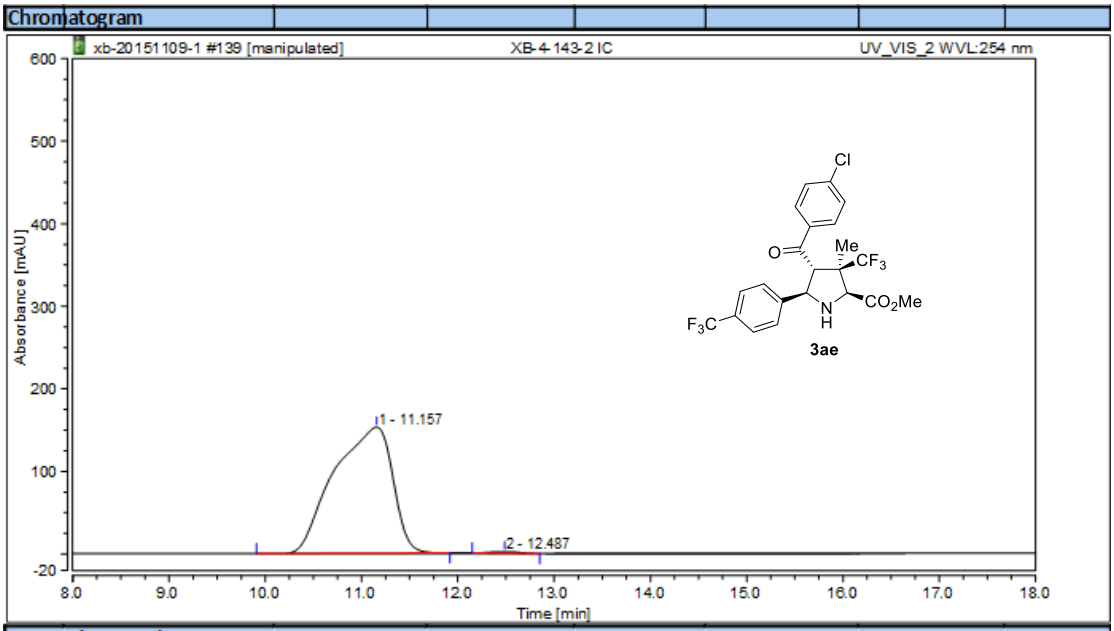
Me
CF3
N
H
CO2Me
F3C
3ae
f1 (ppm)





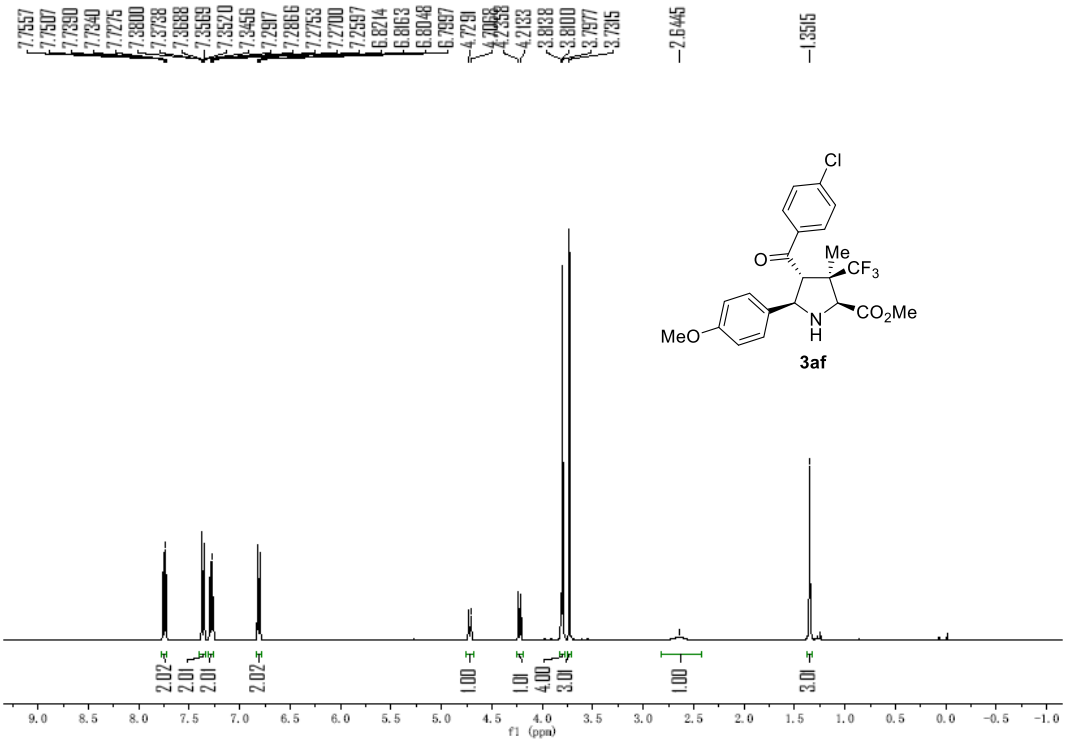
Integration Results

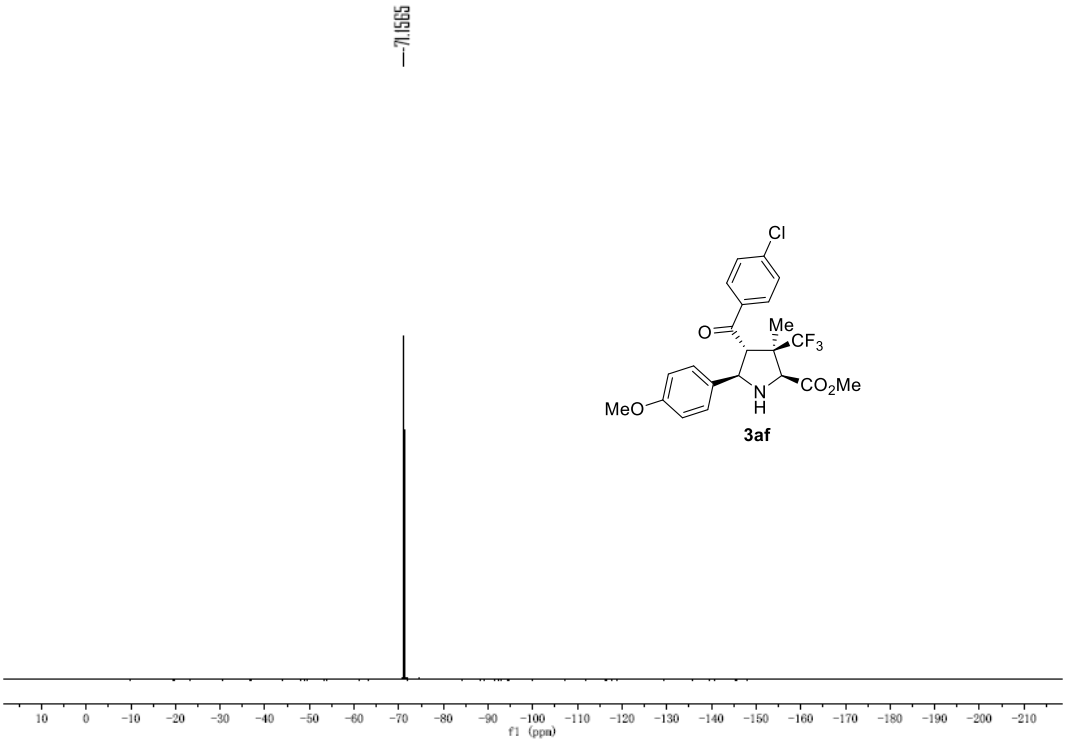
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.177	23.473	32.172	49.29	44.85	n.a.
2		12.520	24.153	39.555	50.71	55.15	n.a.
Total:			47.626	71.726	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.157	107.564	152.529	99.43	98.85	n.a.
2		12.487	0.613	1.780	0.57	1.15	n.a.
Total:			108.177	154.308	100.00	100.00	

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CF3
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N
H
MeO
3af
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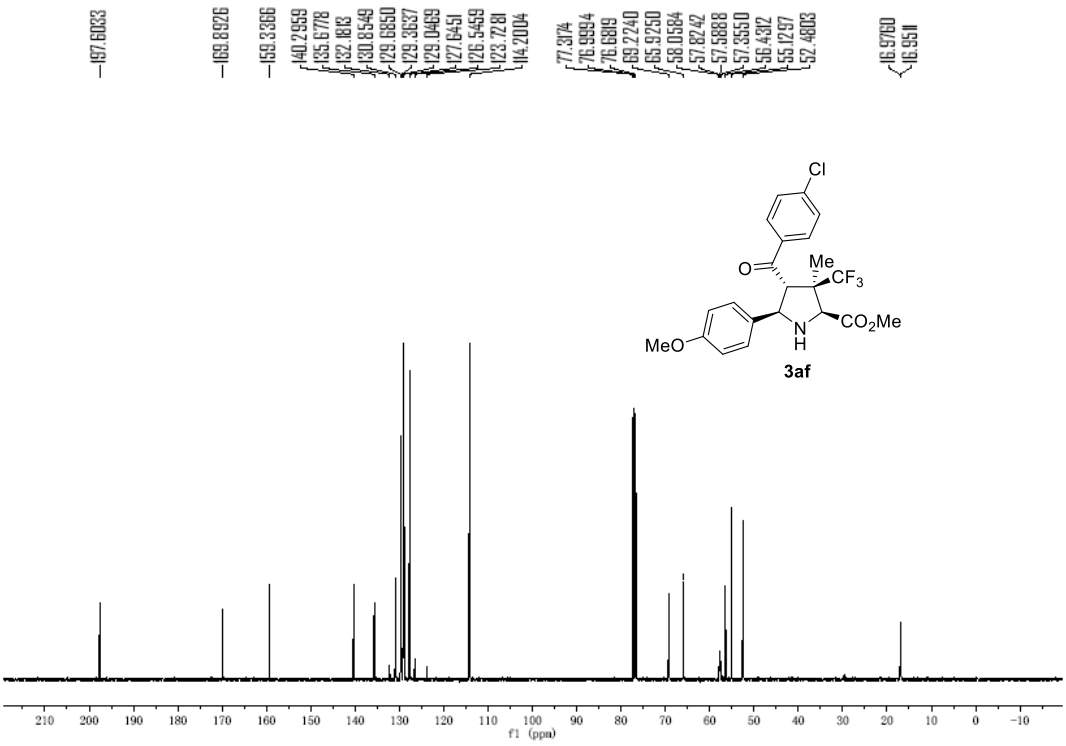
f1 (ppm)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56.4312
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16.9760
16.9511
Cl
O
Me
CF3
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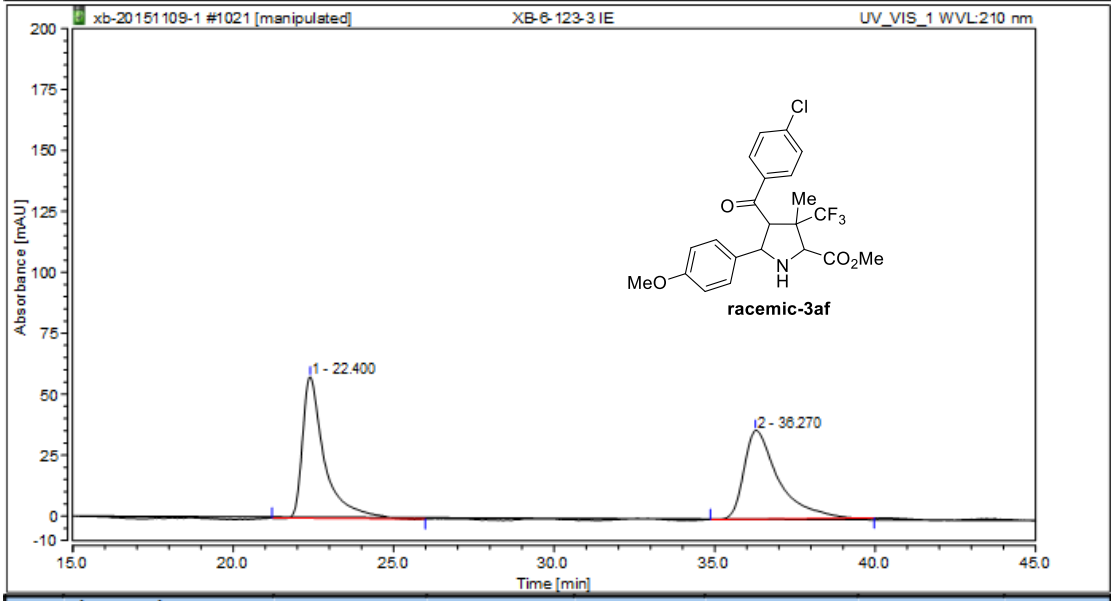
H
MeO
3af
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

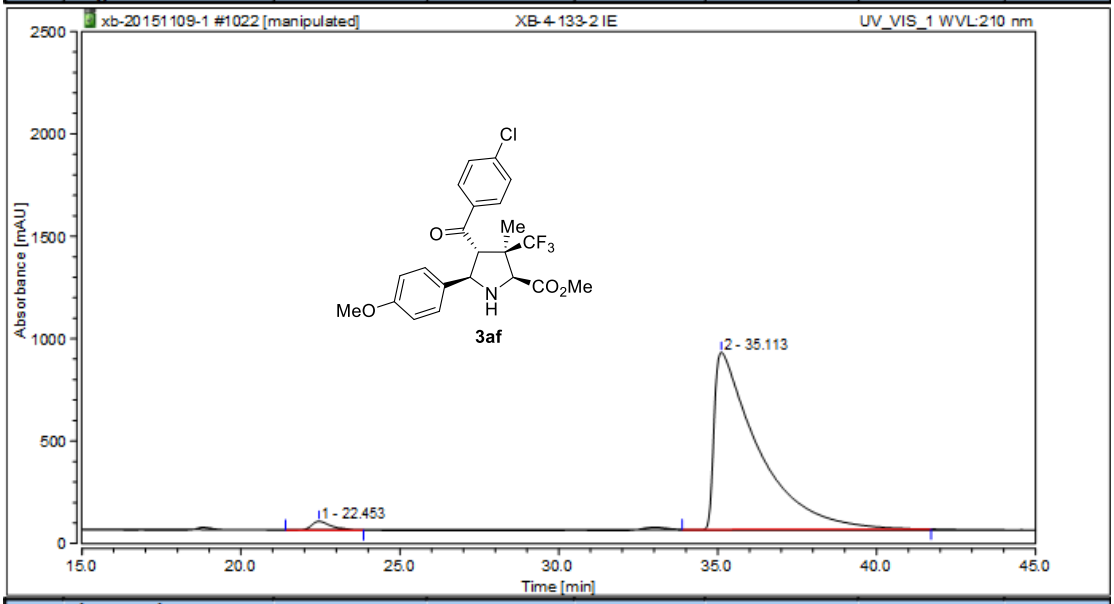
Chromatogram



Integration Results

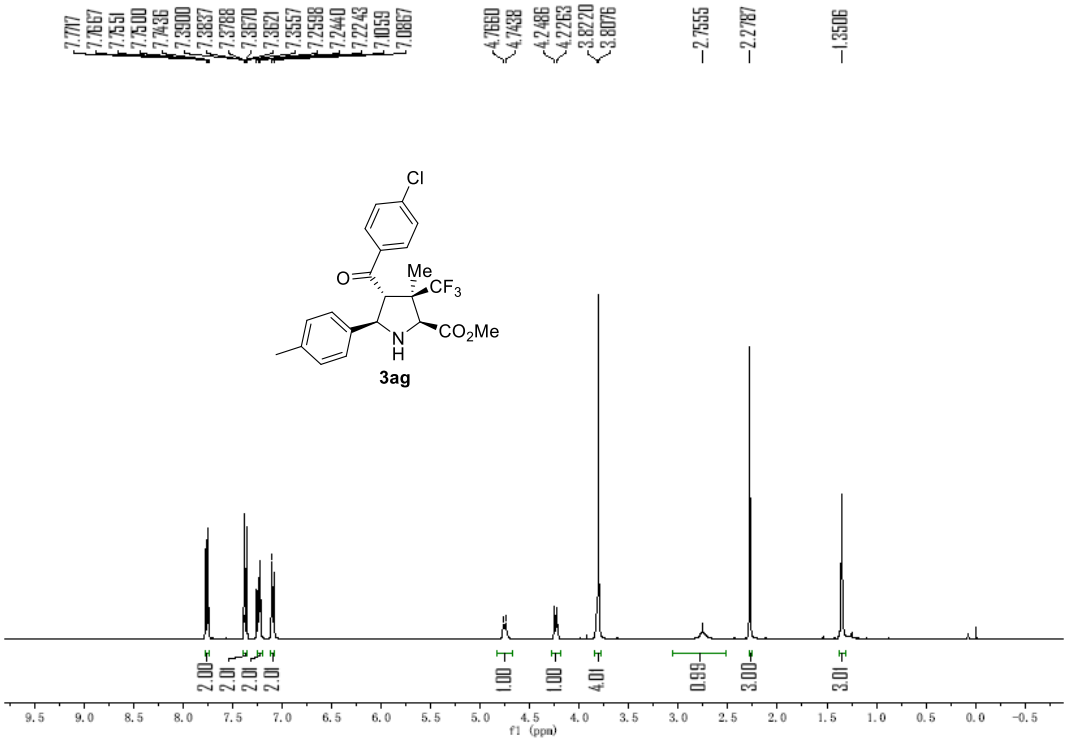
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		22.400	45.800	57.959	50.24	61.38	n.a.
2		36.270	45.360	36.466	49.76	38.62	n.a.
Total:			91.161	94.425	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		22.453	30.981	42.916	2.18	4.73	n.a.
2		35.113	1391.191	865.177	97.82	95.27	n.a.
Total:			1422.171	908.093	100.00	100.00	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7.2440
7.2243
7.1059
7.0867
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4.7458
4.2486
4.2263
3.8220
3.8076
2.7555
2.2787
1.3506
Cl
O
Me
CF3
CO2Me
N
H
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2.01
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1.00
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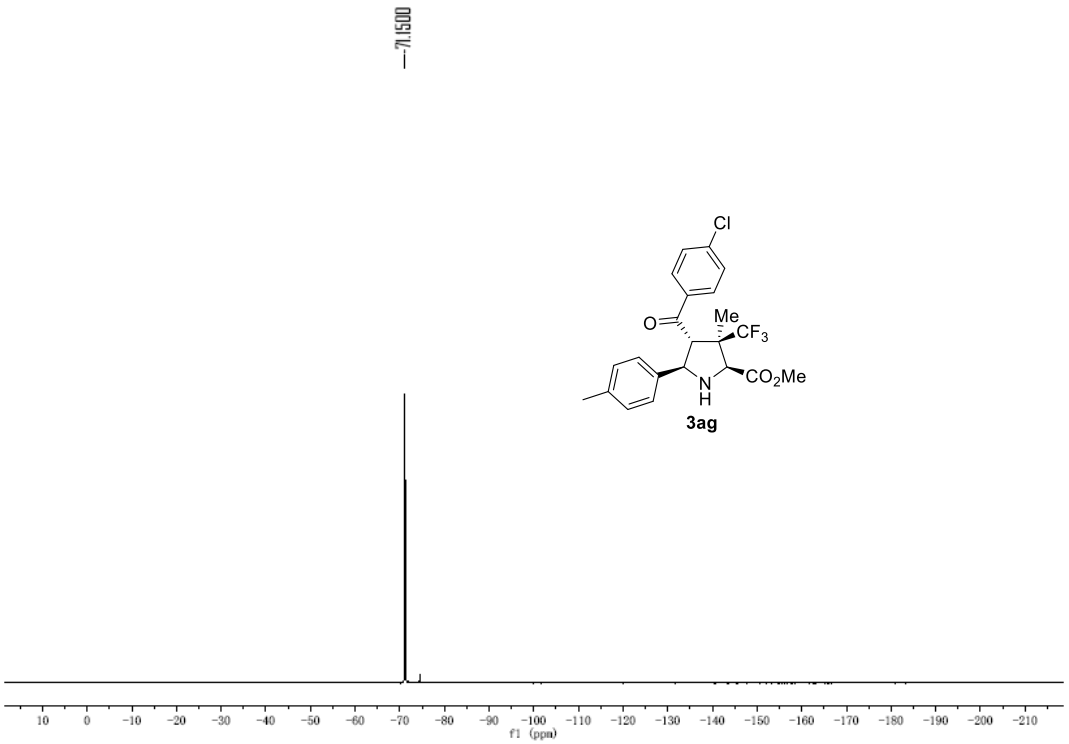
3.01
f1 (ppm)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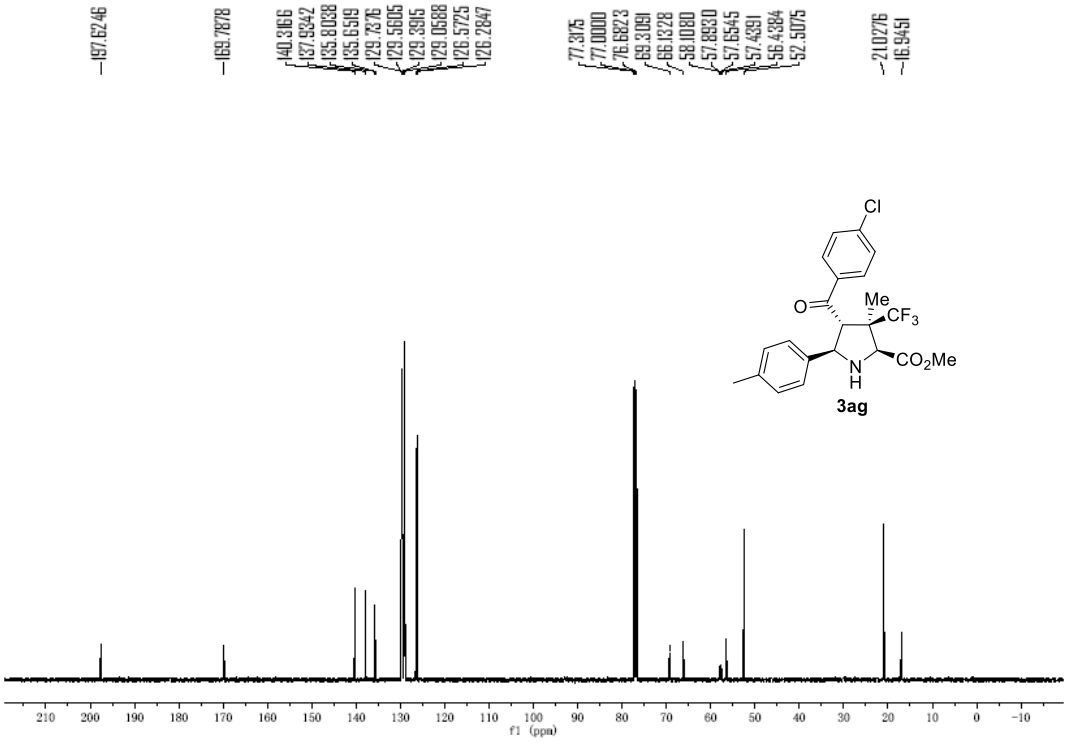
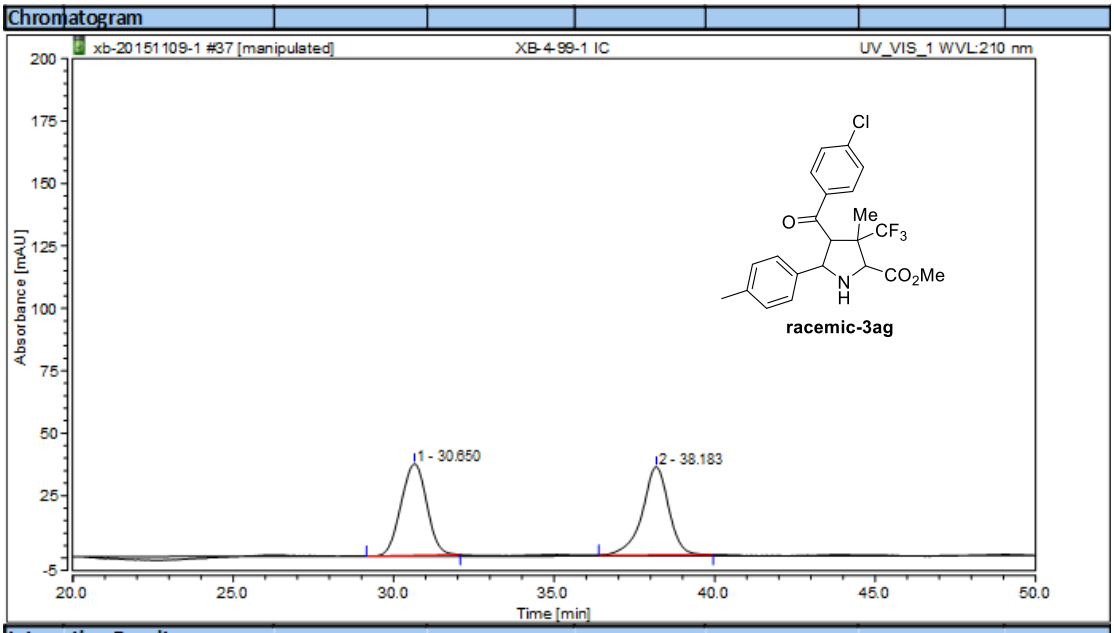
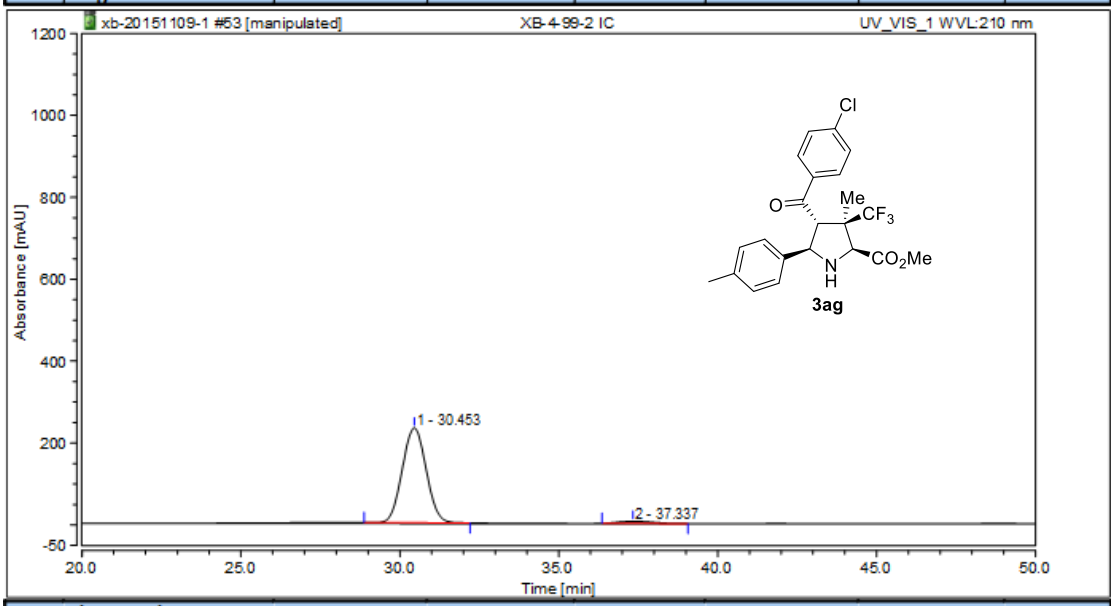




Integration Results

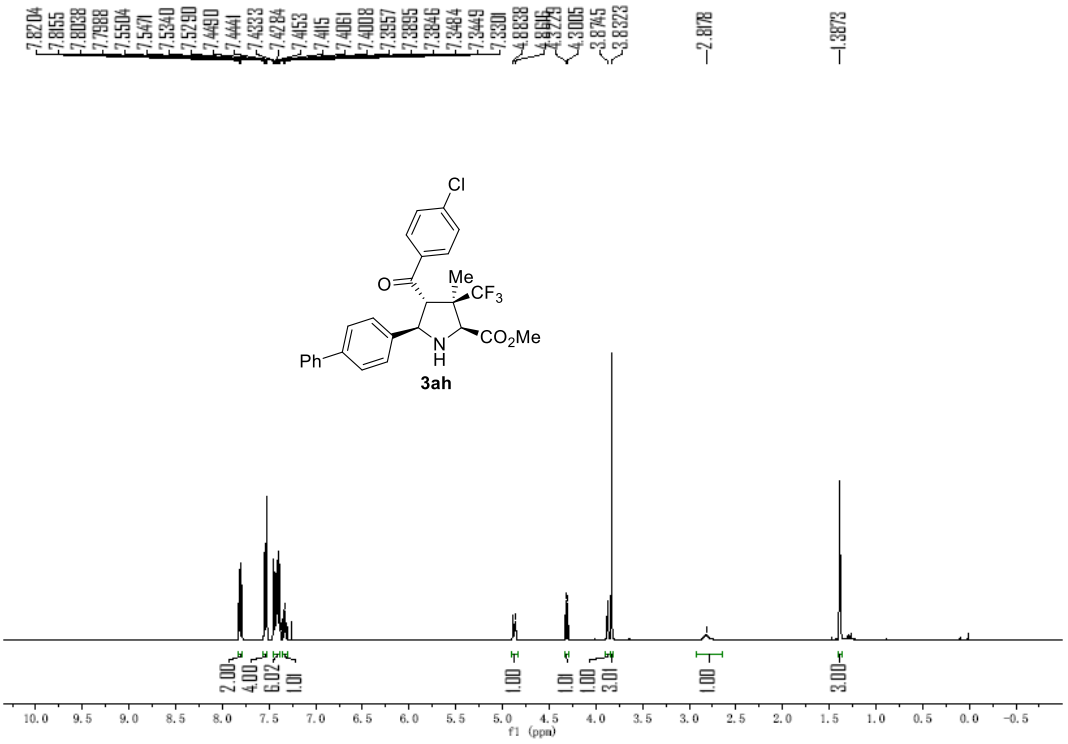
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		30.650	34.006	36.600	50.31	50.95	n.a.
2		38.183	33.586	35.241	49.69	49.05	n.a.
Total:			67.592	71.841	100.00	100.00	

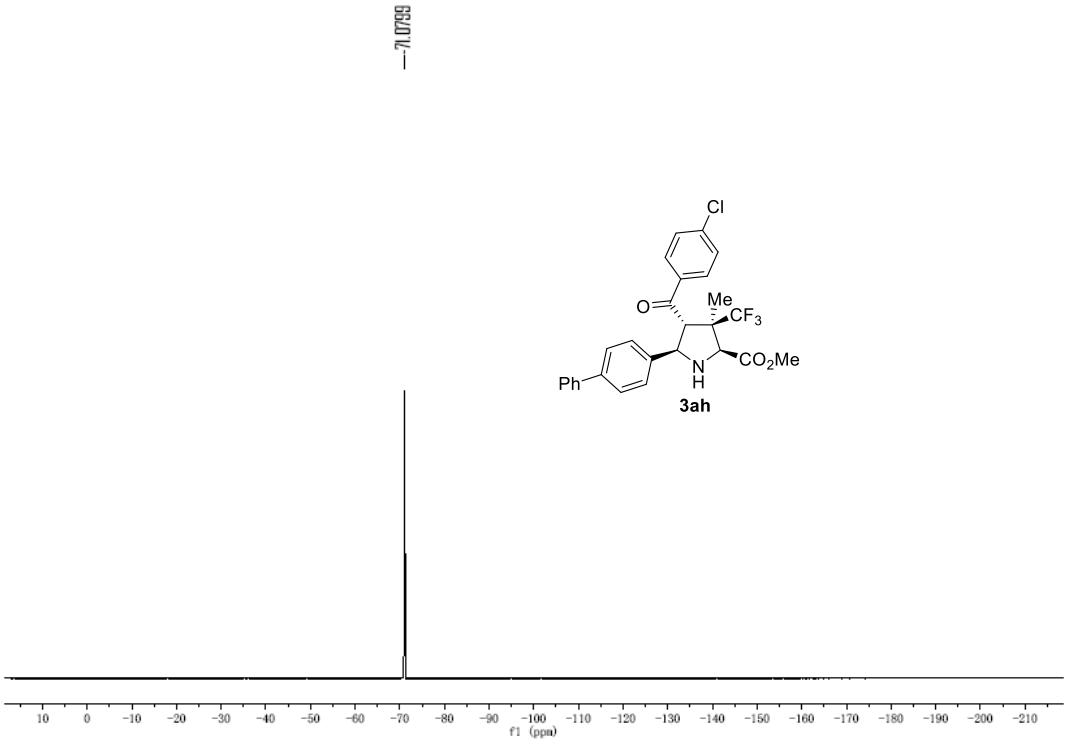
Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		30.453	201.391	231.283	96.77	97.75	n.a.
2		37.337	6.730	5.332	3.23	2.25	n.a.
Total:			208.121	236.615	100.00	100.00	

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N
H
Ph
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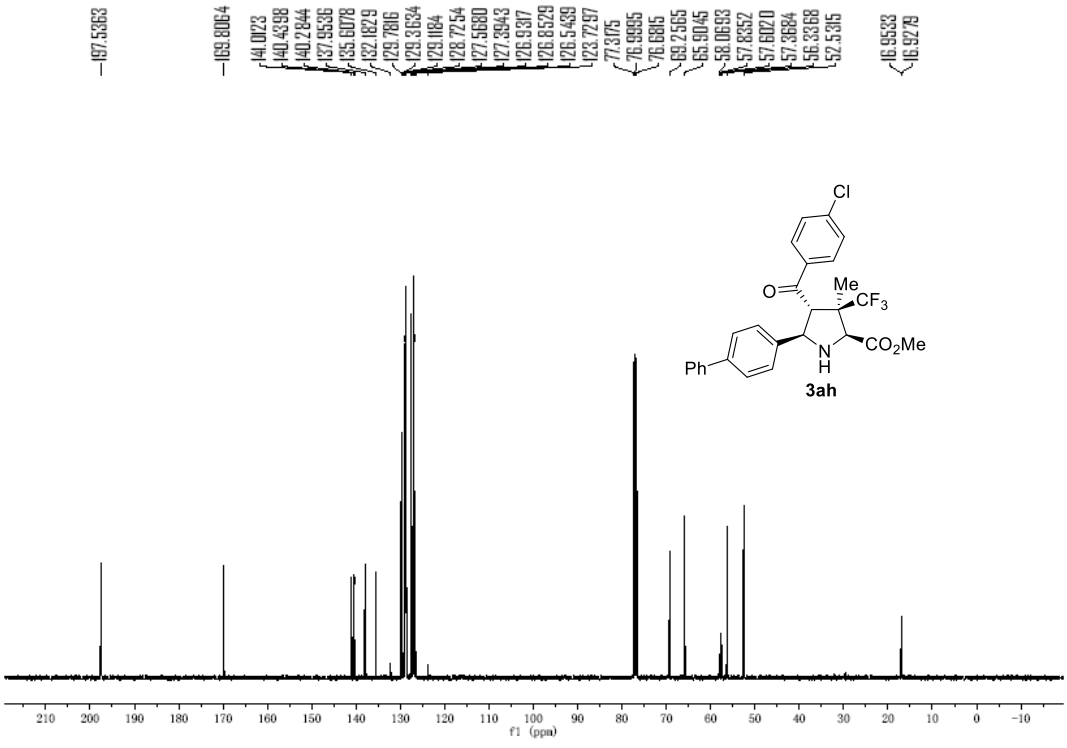
f1 (ppm)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123.7297
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76.9985
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69.2565
65.5045
58.0693
57.8352
57.6020
57.3684
56.3368
52.5315
16.9533
16.9279
Cl
O
Me
CF3
CO2Me
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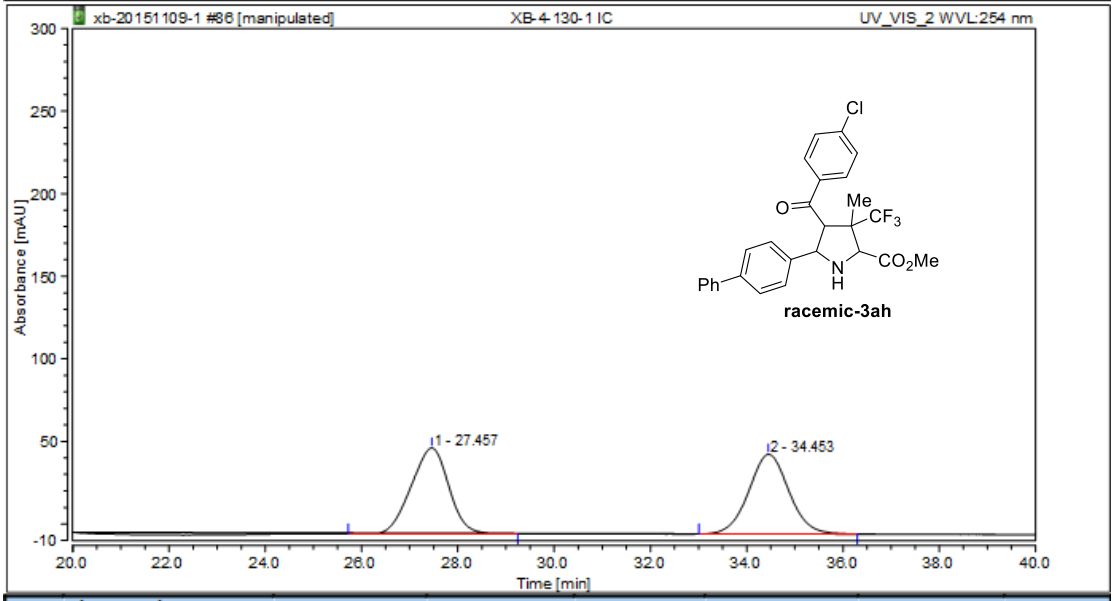
H
Ph
3ah
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

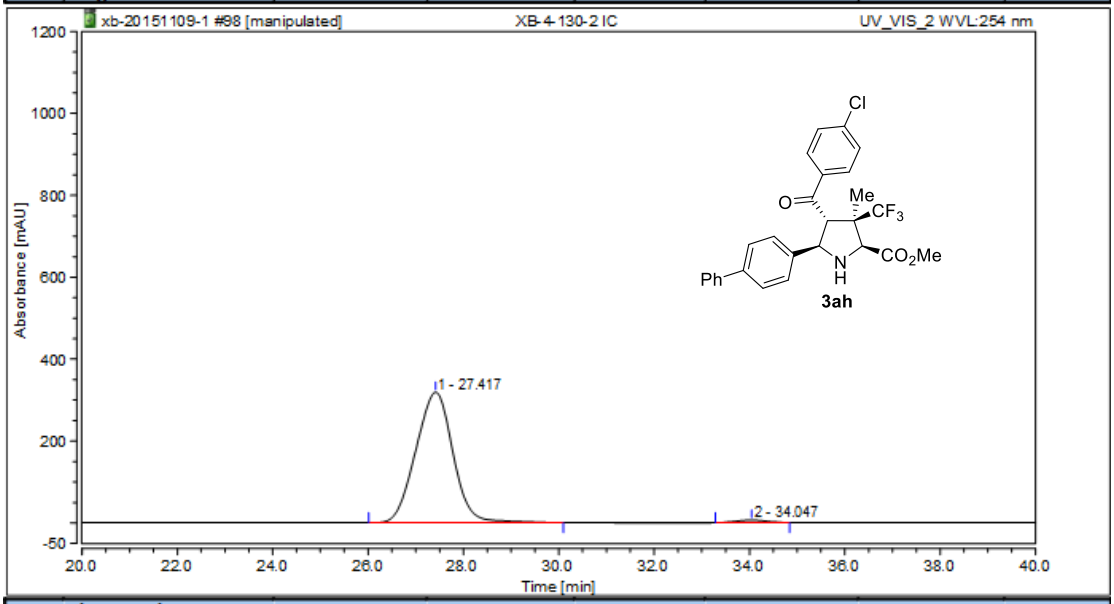
Chromatogram



Integration Results

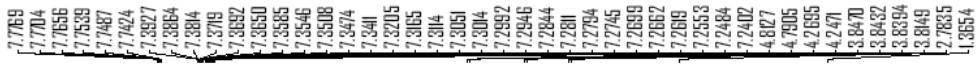
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		27.457	47.293	52.003	50.28	51.87	n.a.
2		34.453	46.760	48.260	49.72	48.13	n.a.
Total:			94.053	100.263	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		27.417	287.916	318.606	98.36	98.04	n.a.
2		34.047	4.807	6.371	1.64	1.96	n.a.
Total:			292.723	324.977	100.00	100.00	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7.2946
7.2844
7.2811
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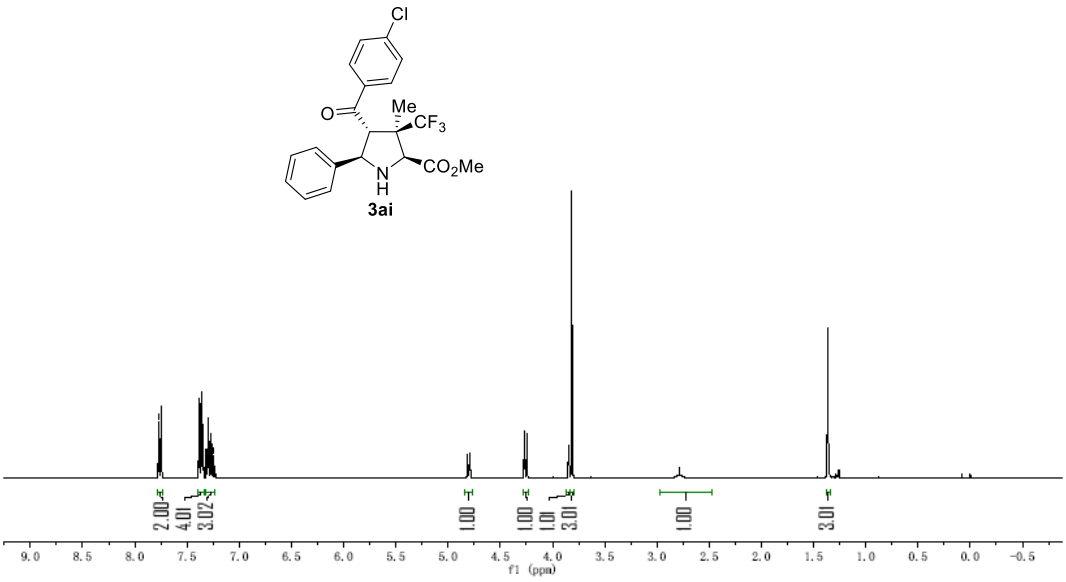
2.7835
1.3654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CF3
CO2Me
N
H
3ai
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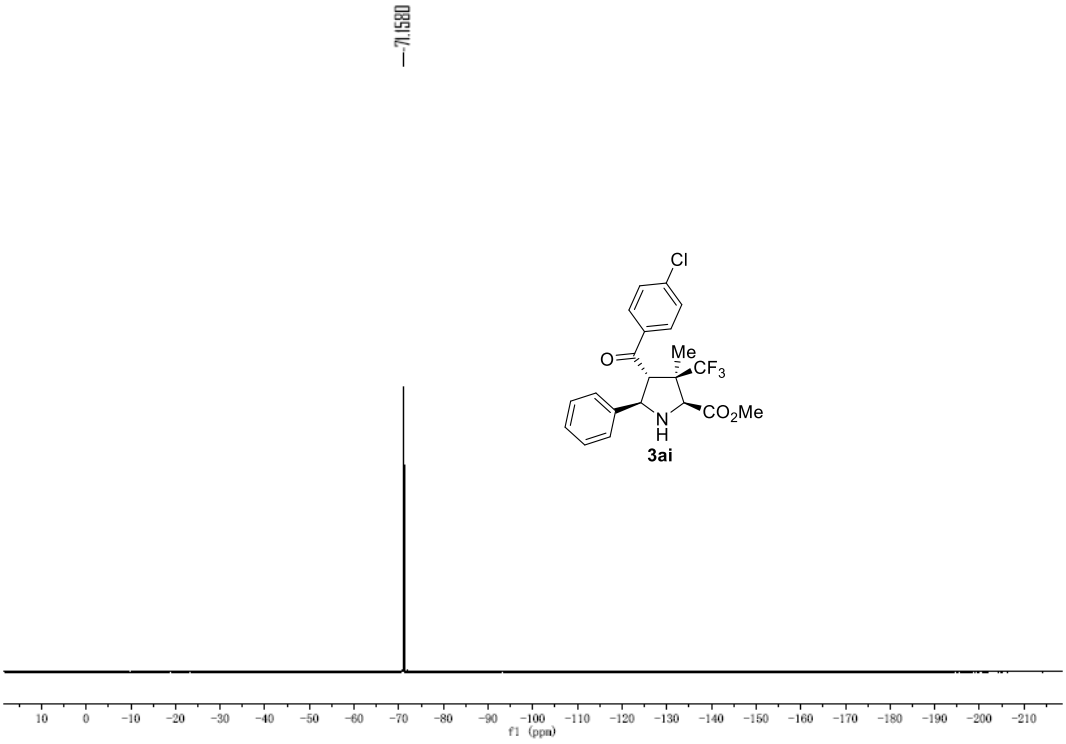
4.01
3.02
1.00
1.00
1.01
3.01
1.00
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)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Me
CF3
CO2Me
N
H
3ai
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0
-10
-20
-30
-40
-50
-60
-70
-80
-90
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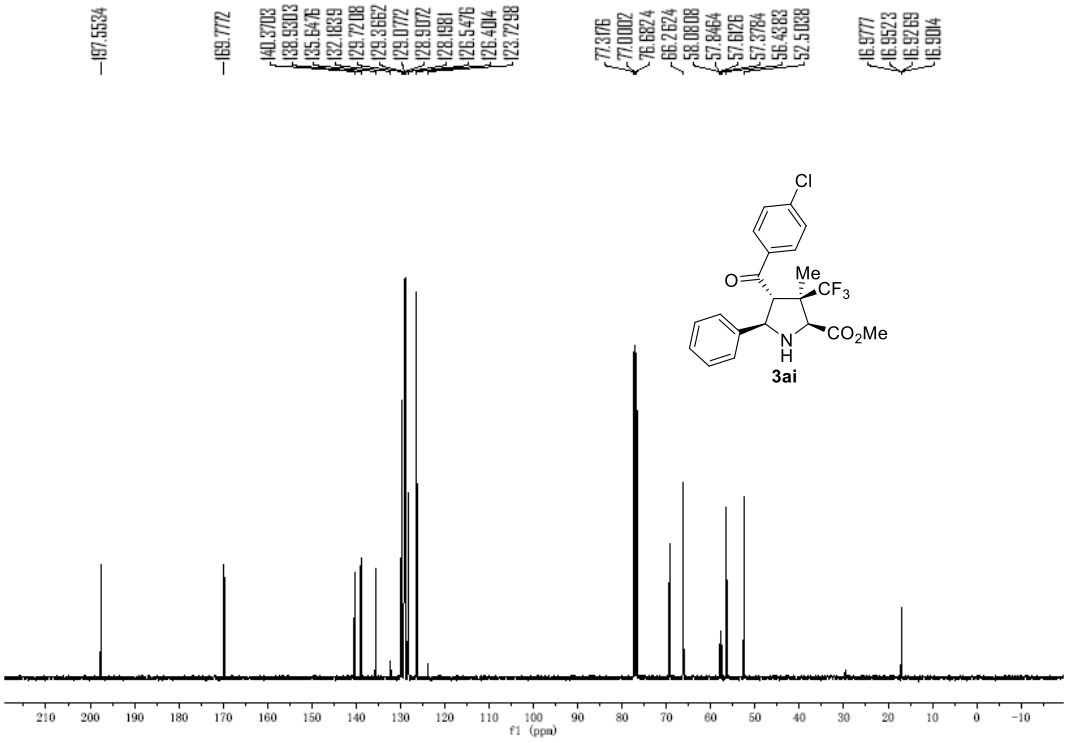
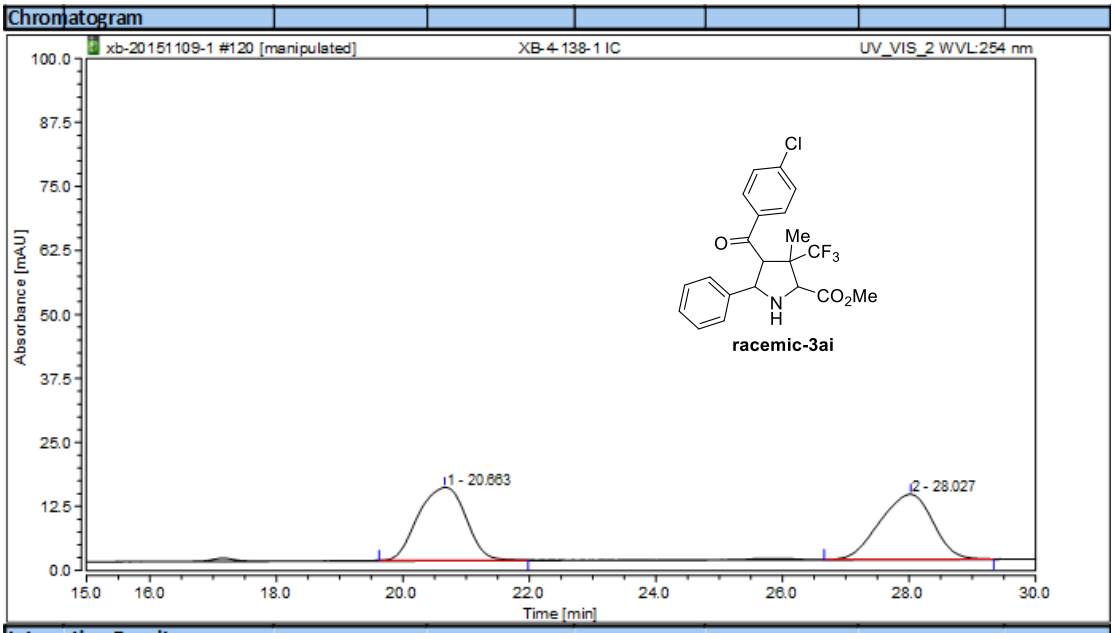
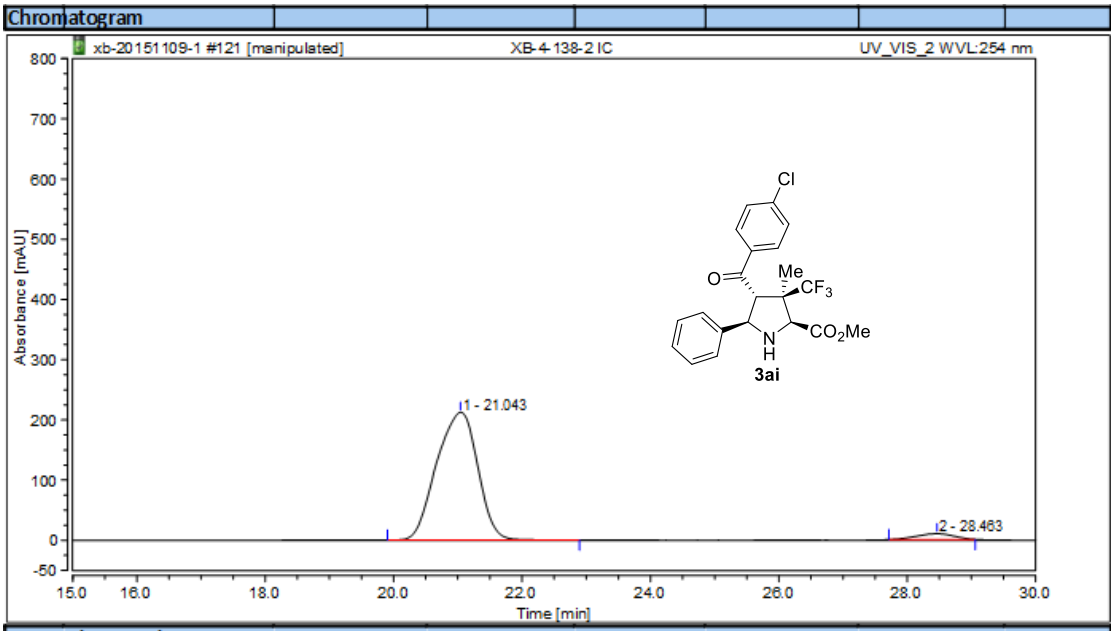
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)





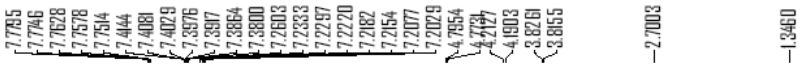
Integration Results

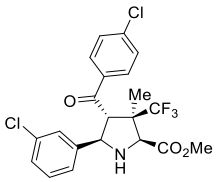
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		20.663	12.402	14.244	50.20	52.87	n.a.
2		28.027	12.303	12.696	49.80	47.13	n.a.
Total:			24.705	26.941	100.00	100.00	

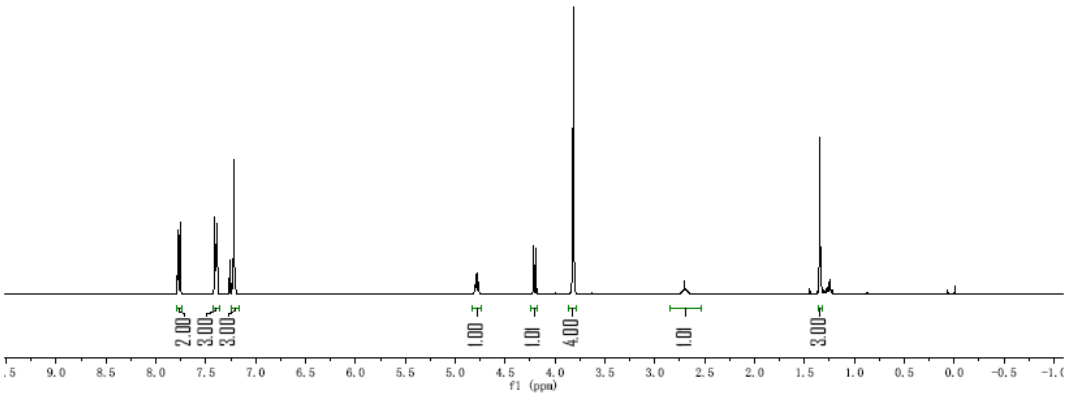


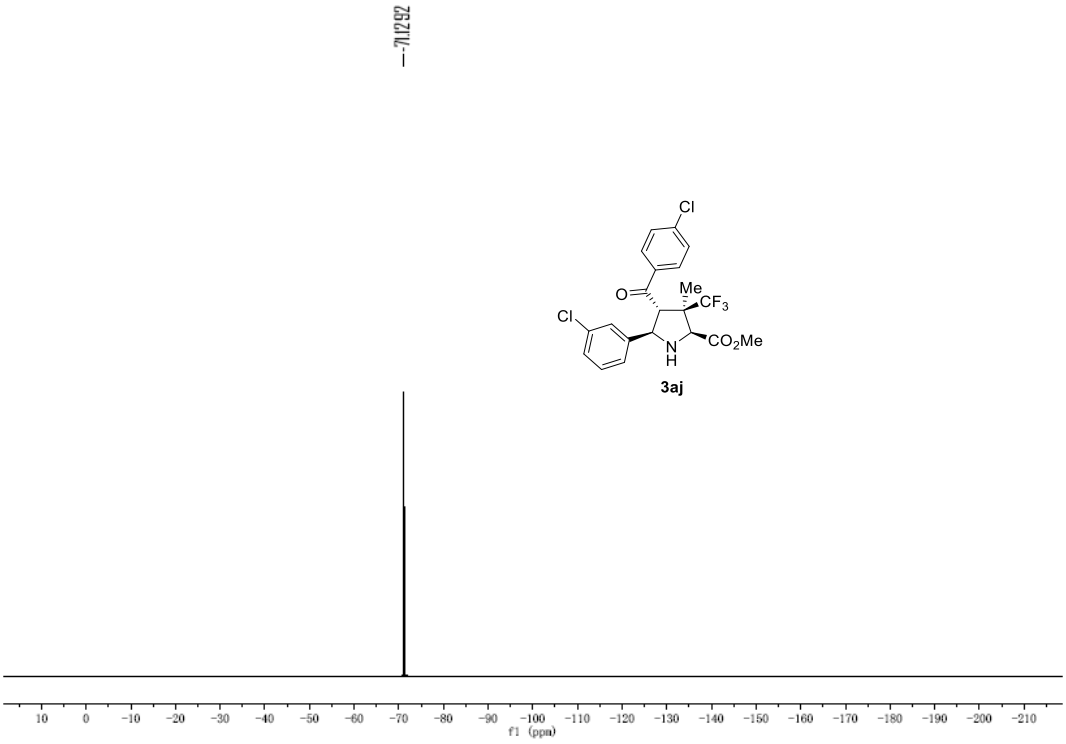
Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		21.043	157.634	212.324	95.99	95.60	n.a.
2		28.463	6.584	9.767	4.01	4.40	n.a.
Total:			164.218	222.091	100.00	100.00	





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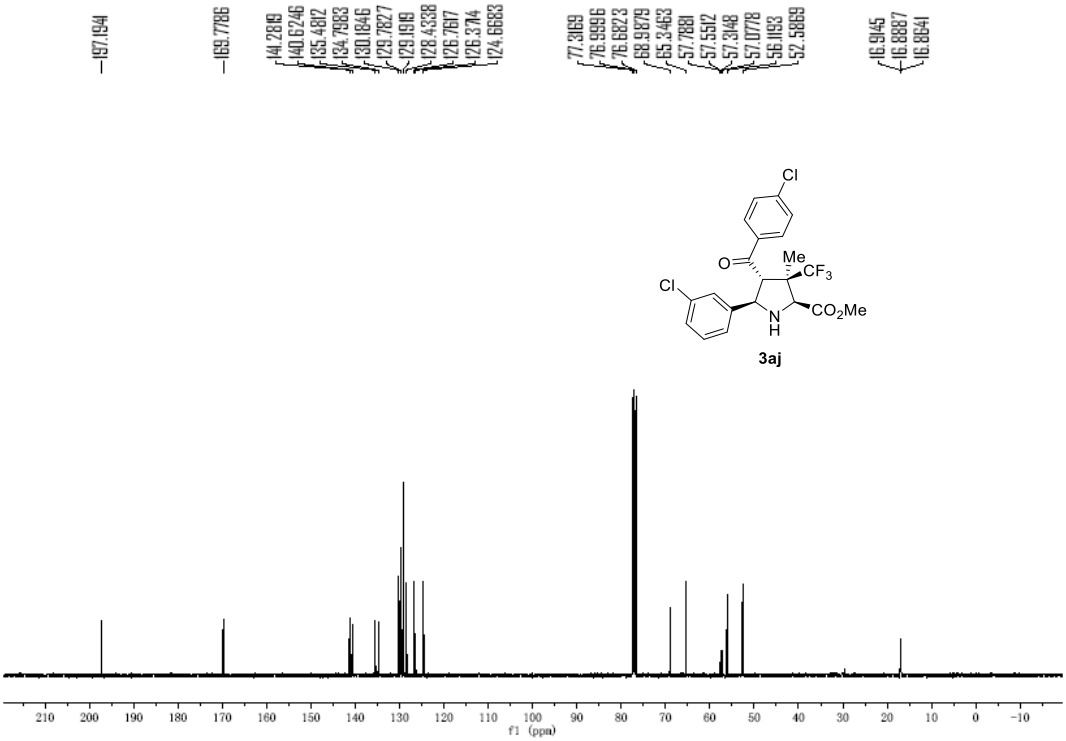
O
Me
CF3
Cl
N
H
CO2Me
3aj
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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16.8887
16.8641
Cl
O
Me
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3aj
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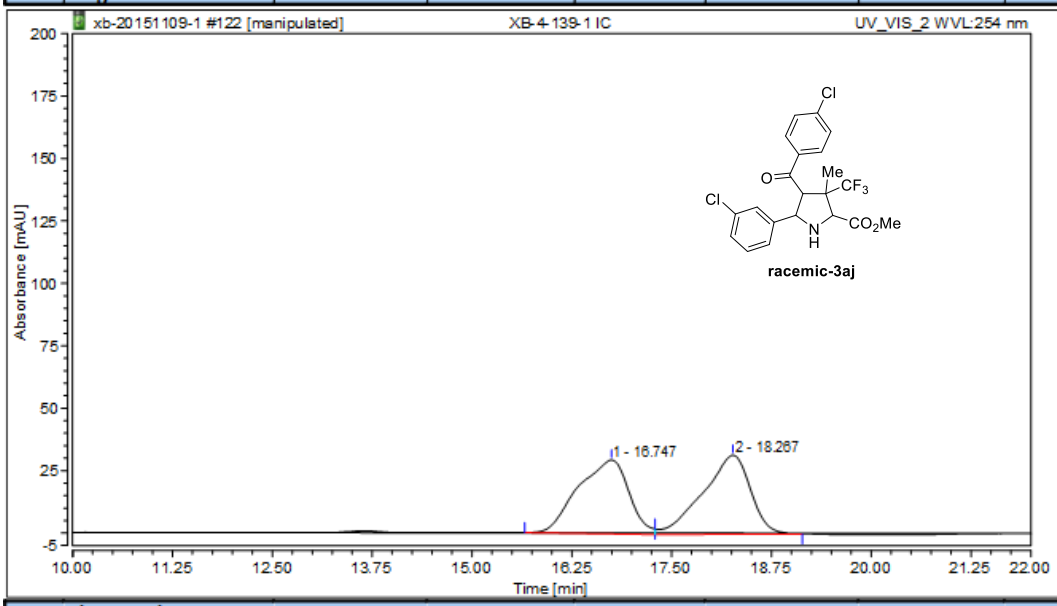
f1 (ppm)

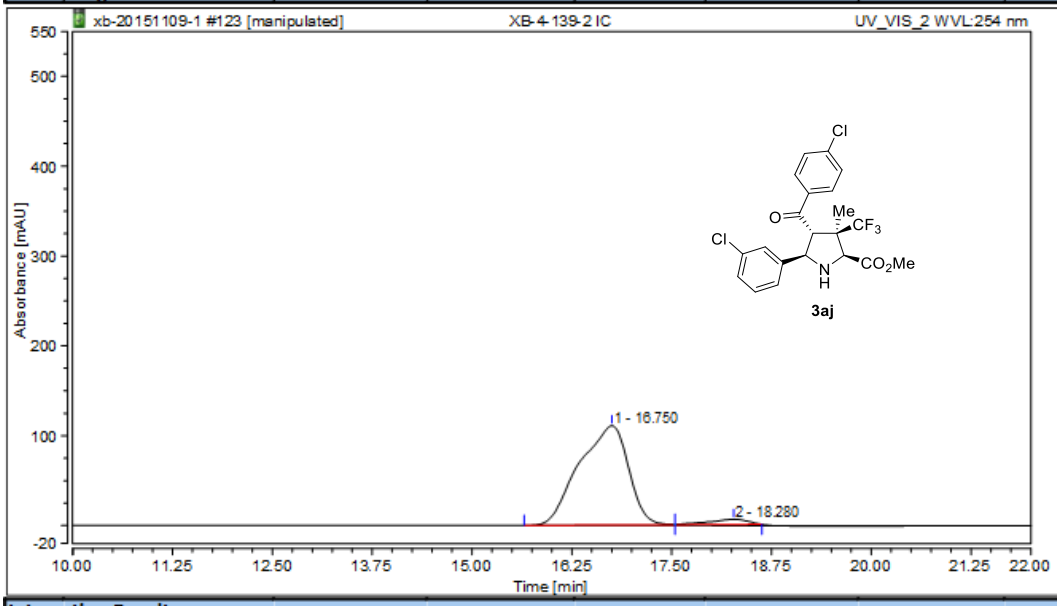
Chromatogram



Integration Results

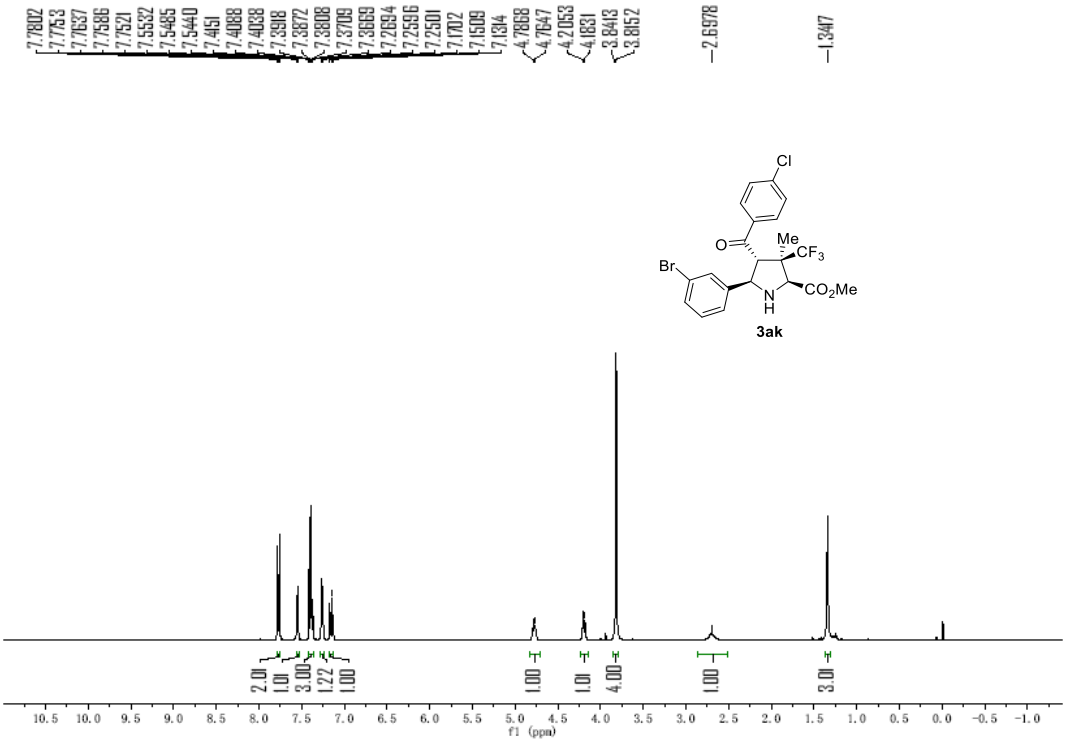
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		16.747	21.772	29.551	49.90	48.32	n.a.
2		18.267	21.863	31.610	50.10	51.68	n.a.
Total:			43.635	61.161	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		16.750	79.041	110.496	96.04	95.05	n.a.
2		18.280	3.260	5.750	3.96	4.95	n.a.
Total:			82.302	116.246	100.00	100.00	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CF3
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3ak
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1.01
3.00
1.22
1.00
1.00
1.01
4.00
1.00
3.01
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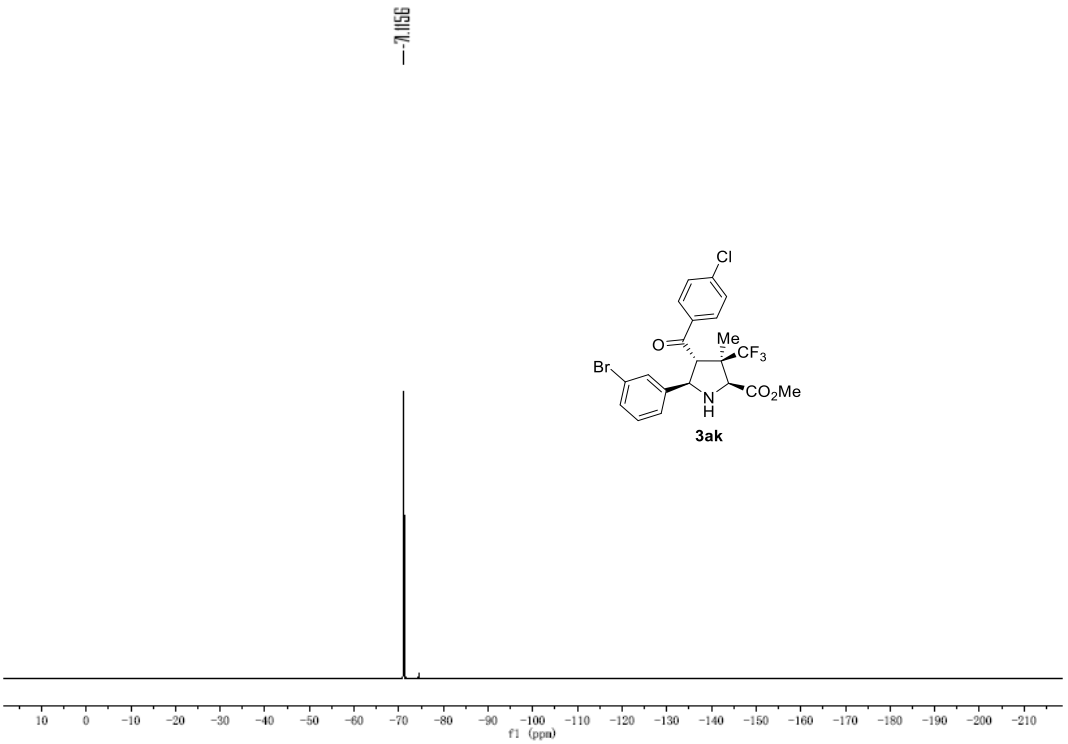
f1 (ppm)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Br
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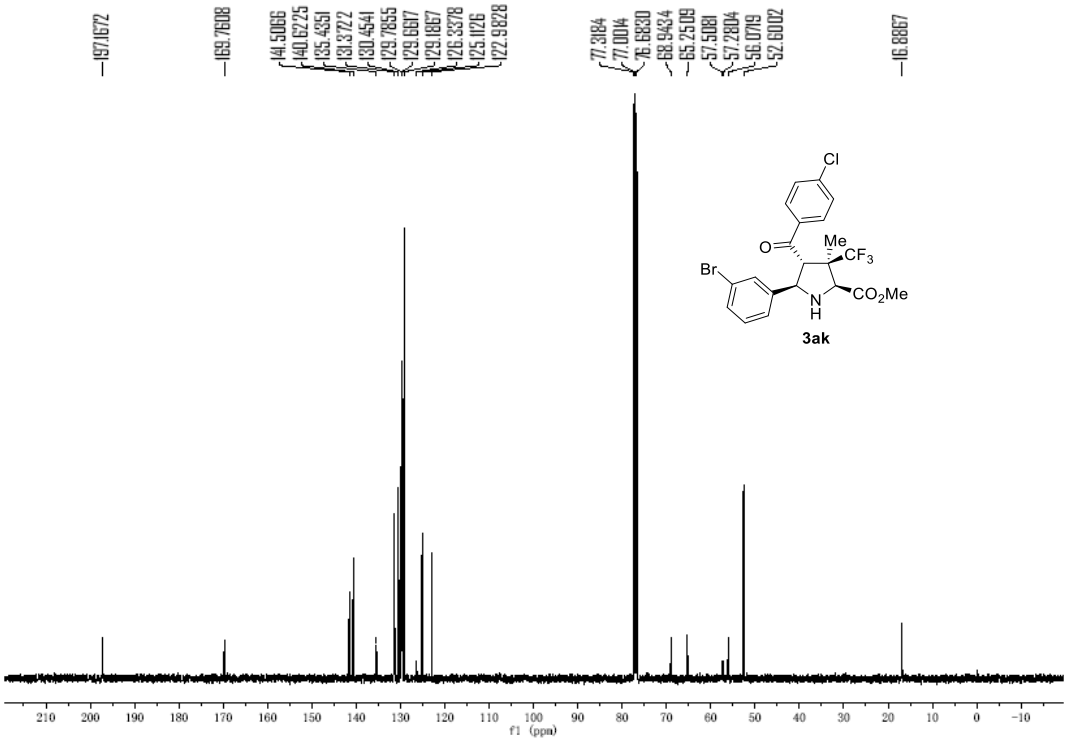
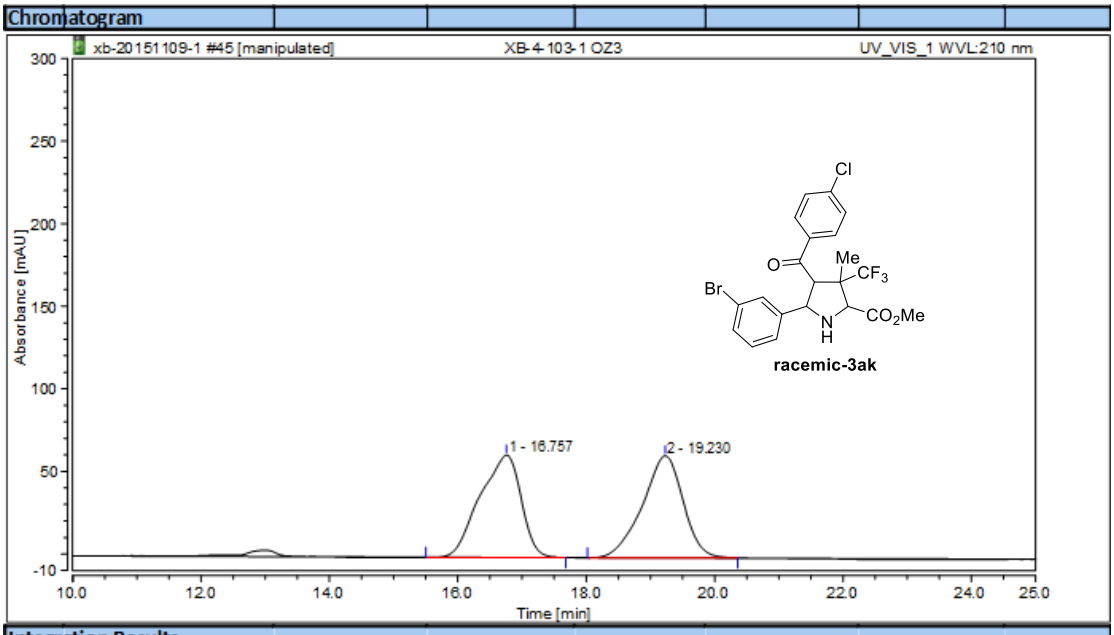
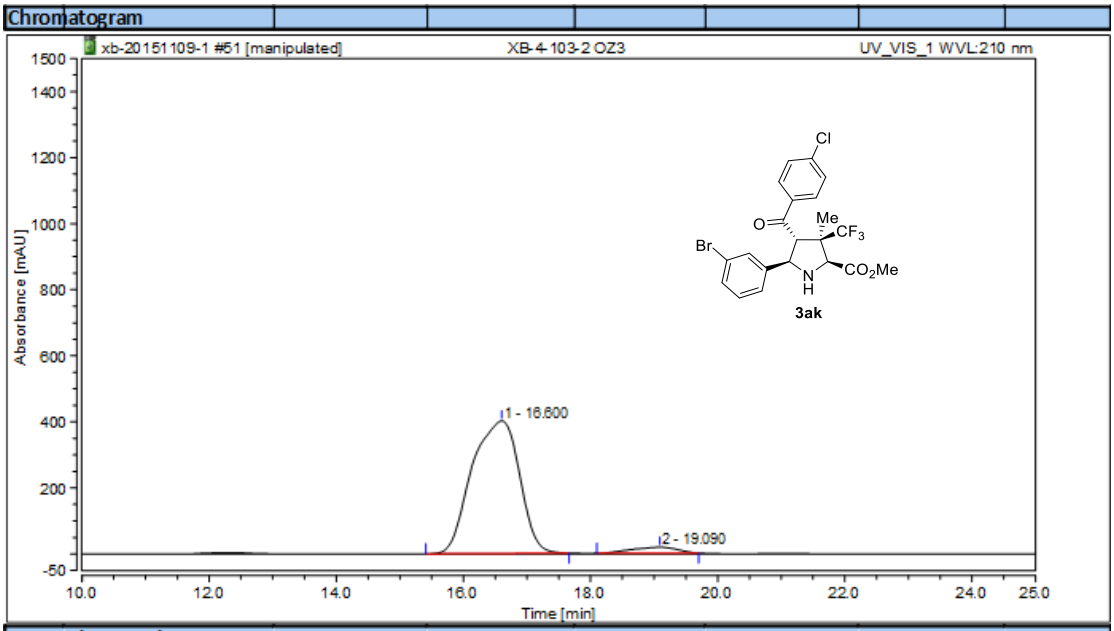
3ak
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)





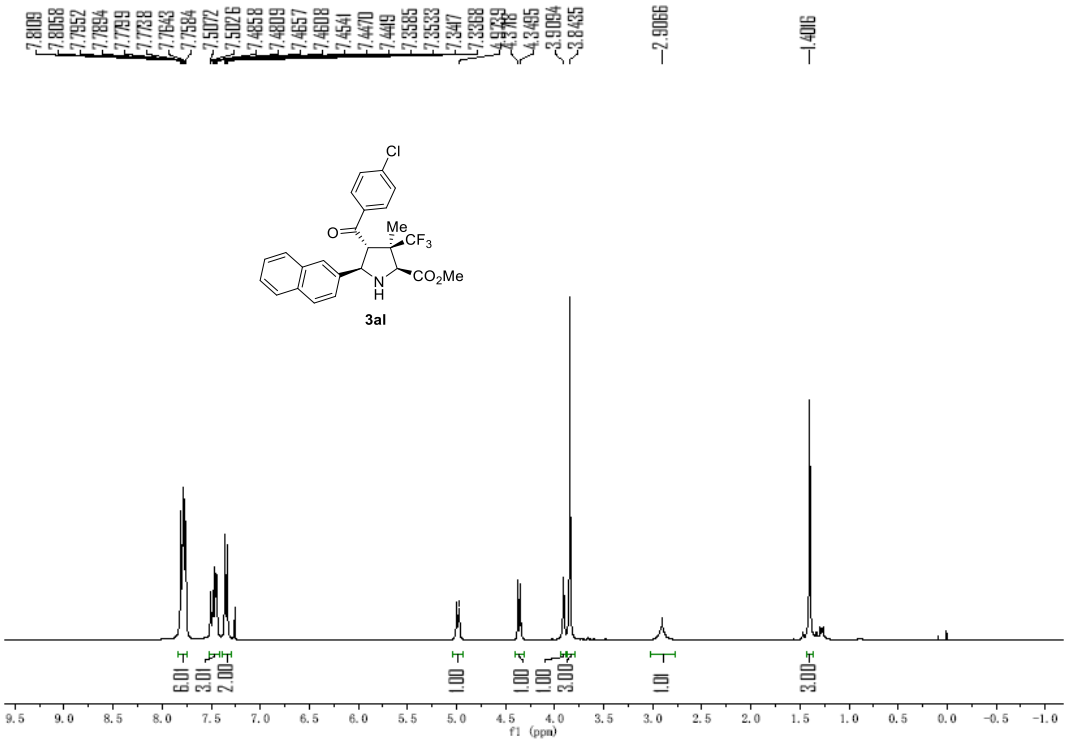
Integration Results

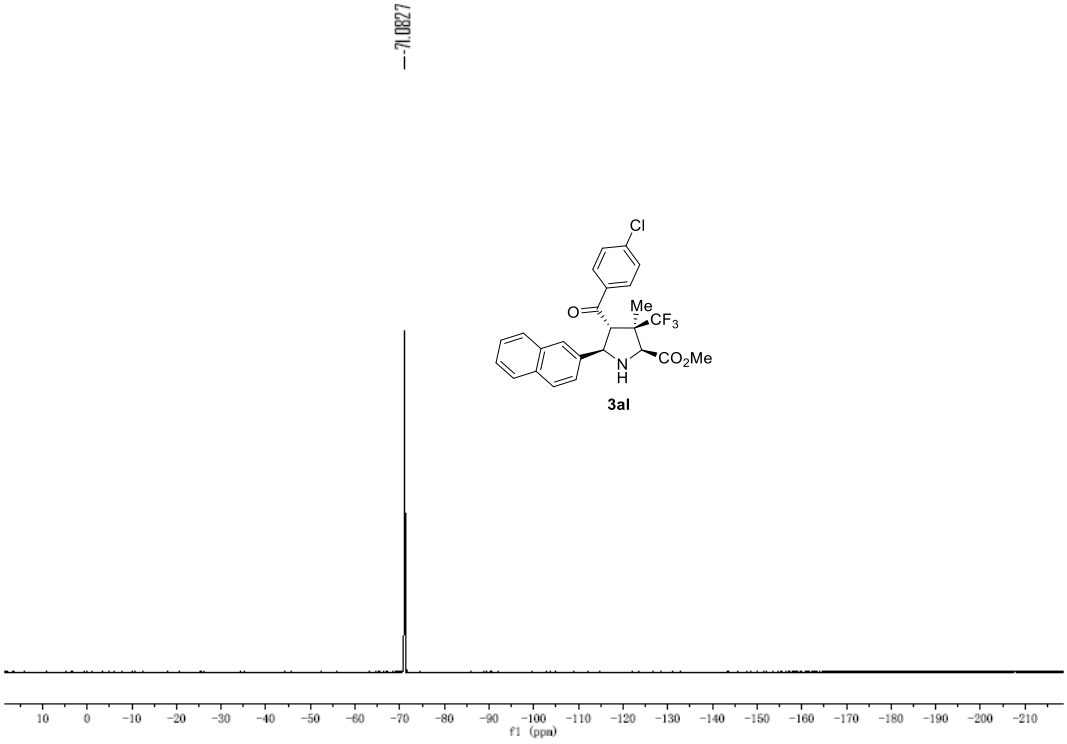
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		16.757	46.055	61.979	50.31	50.09	n.a.
2		19.230	45.481	61.751	49.69	49.91	n.a.
Total:			91.536	123.730	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		16.600	348.167	401.477	95.79	95.70	n.a.
2		19.090	15.302	18.025	4.21	4.30	n.a.
Total:			363.468	419.501	100.00	100.00	

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Me
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CO2Me
N
H
3al
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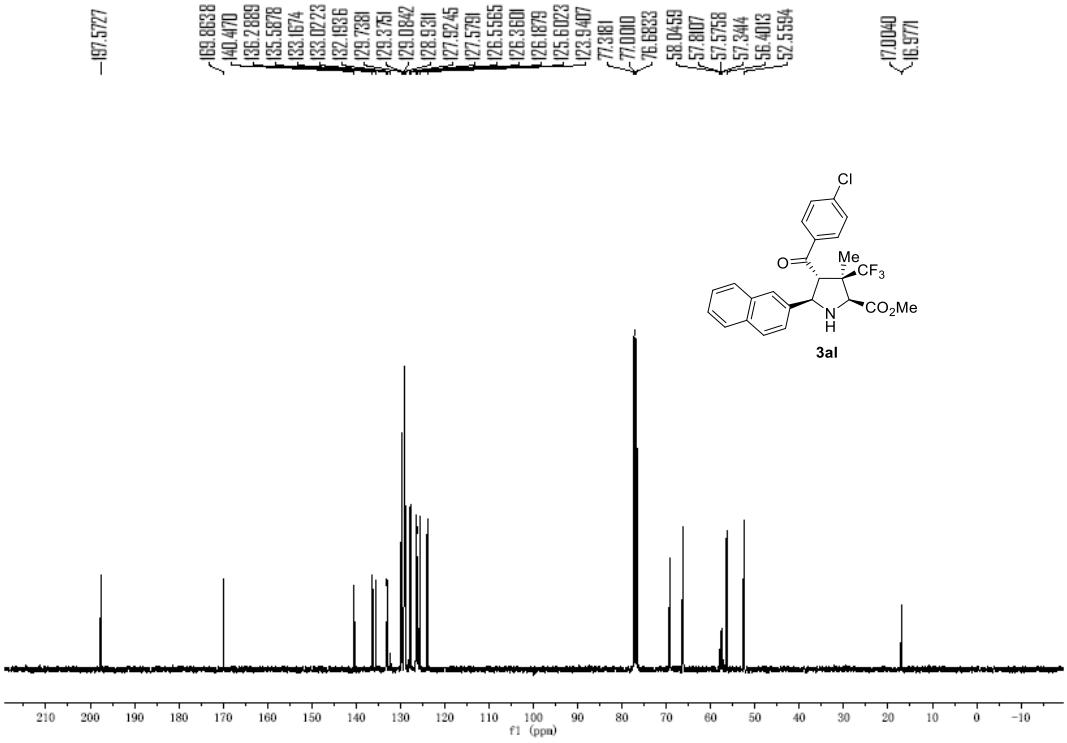
f1 (ppm)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Cl
O
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3al
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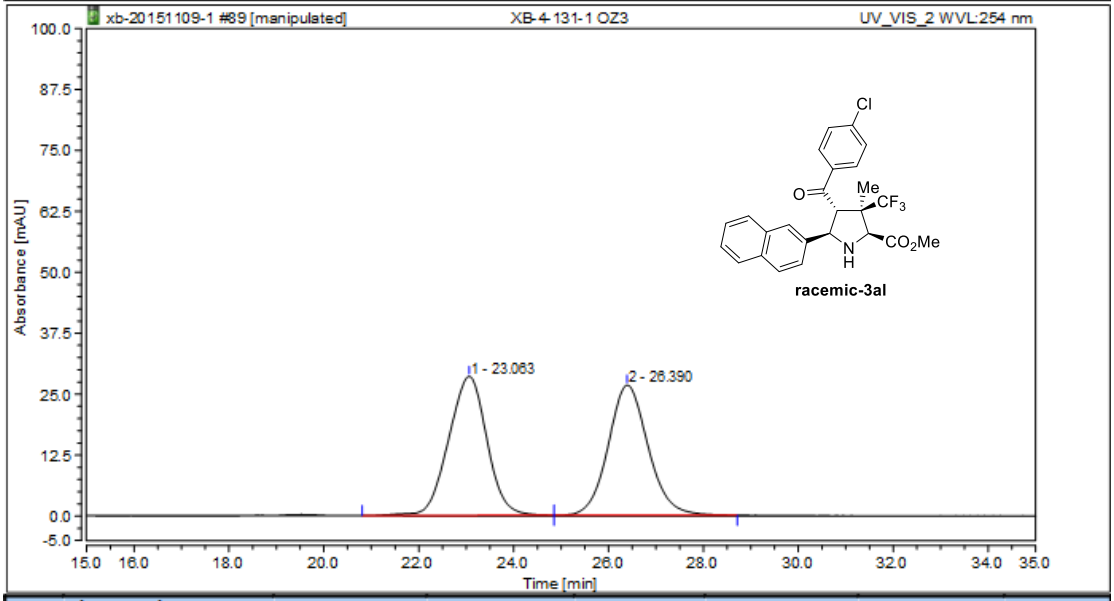
f1 (ppm)

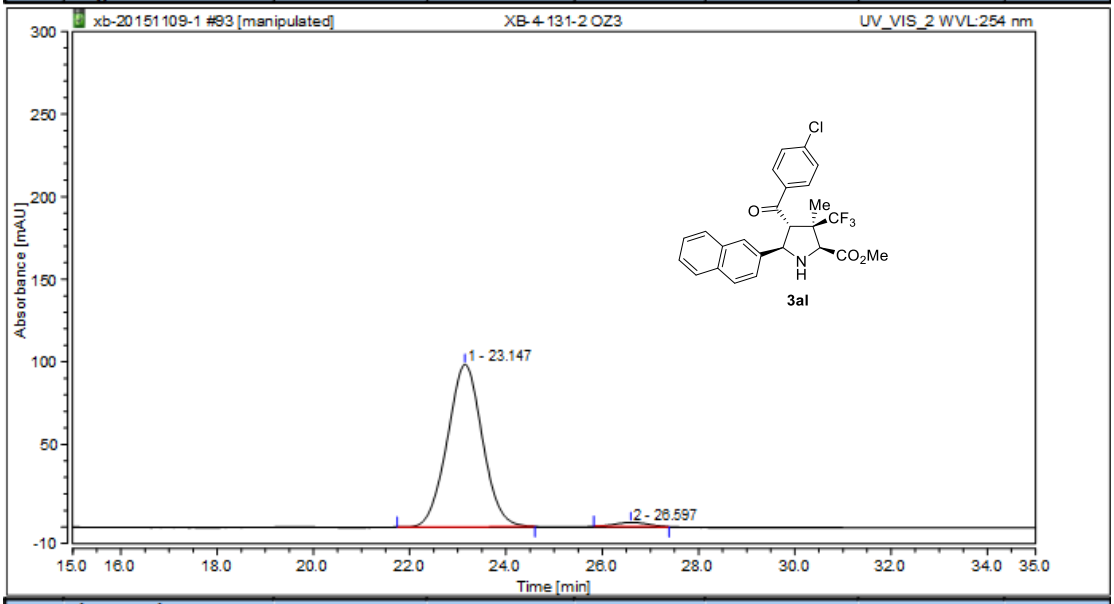
Chromatogram



Integration Results

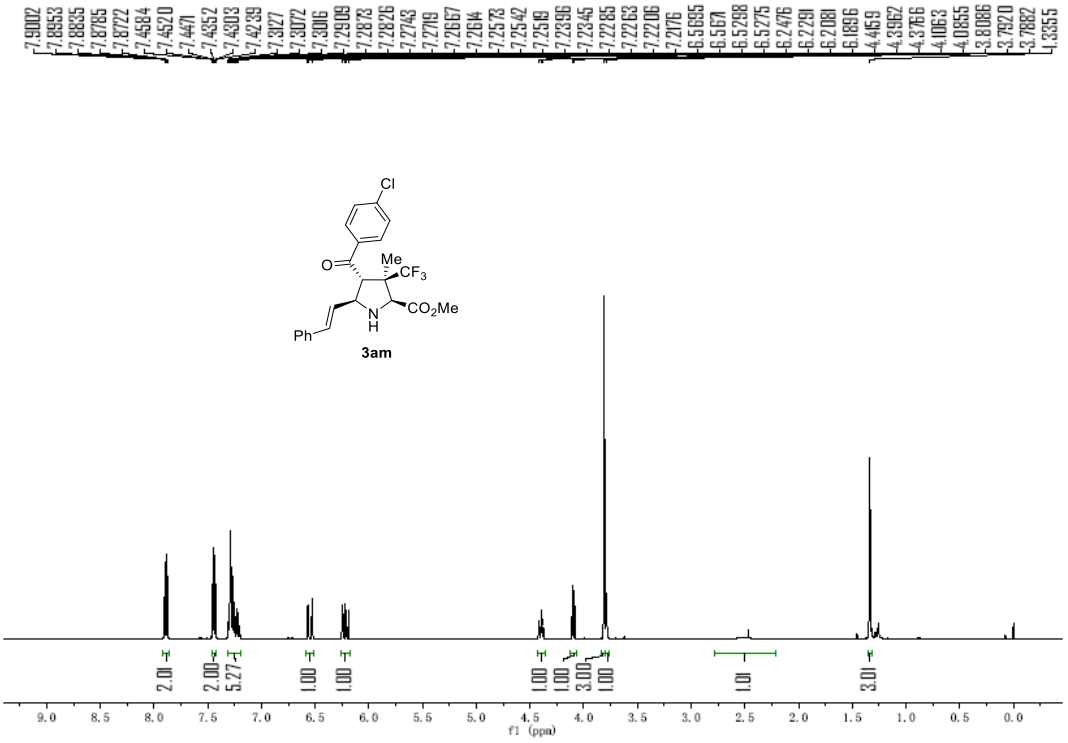
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		23.063	26.675	28.495	50.67	51.65	n.a.
2		26.390	25.968	26.673	49.33	48.35	n.a.
Total:			52.643	55.169	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		23.147	83.027	98.393	97.64	97.51	n.a.
2		26.597	2.010	2.514	2.36	2.49	n.a.
Total:			85.037	100.907	100.00	100.00	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7.2345
7.2285
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O
Me
CF3
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N
H
Ph
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5.5
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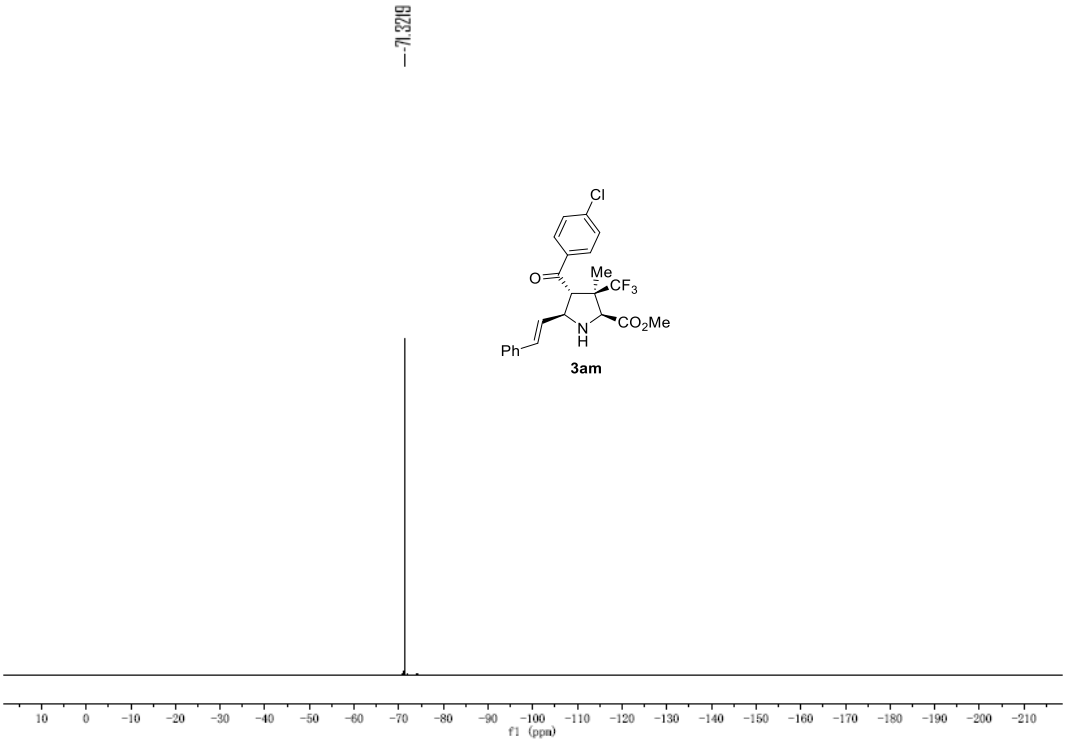
0.0
f1 (ppm)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N
H
Ph
3am
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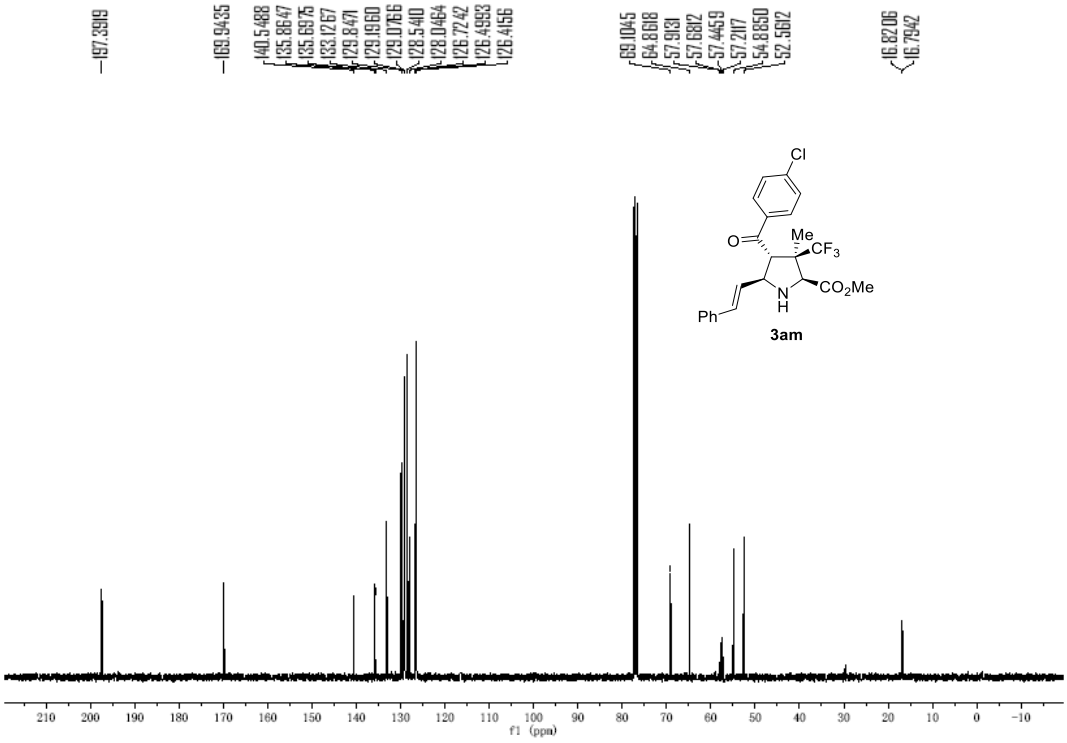
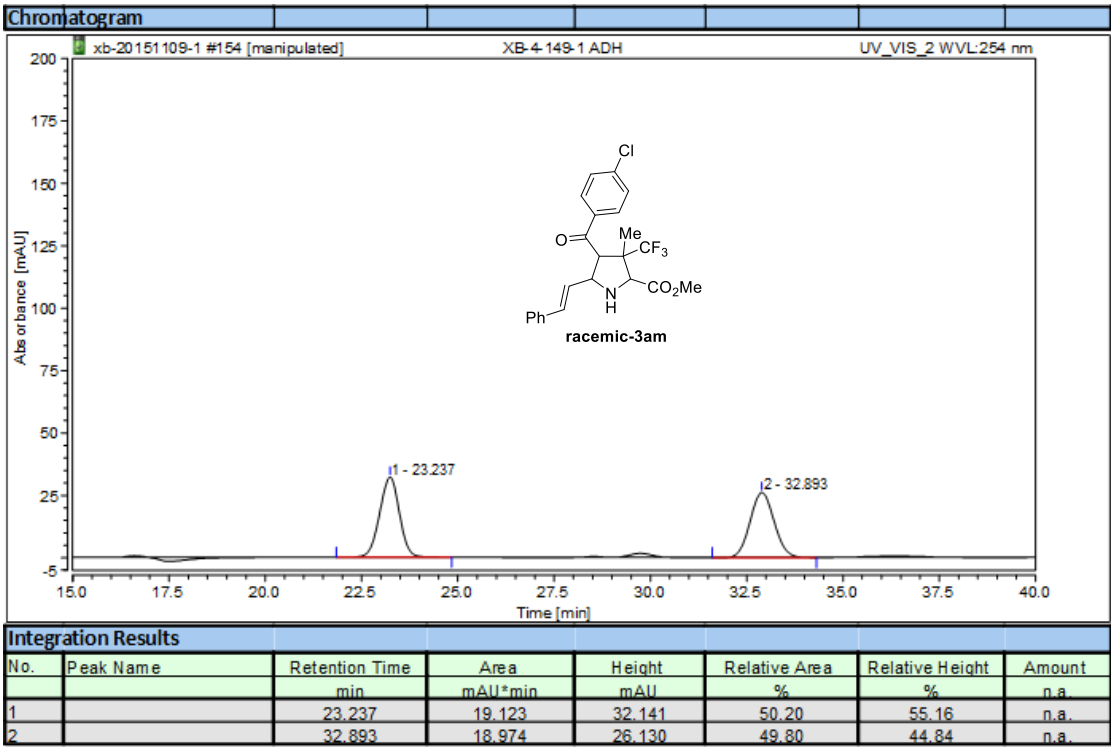
-10
-20
-30
-40
-50
-60
-70
-80
-90
-100
-110
-120
-130
-140
-150
-160
-170
-180
-190
-200
-210
f1 (ppm)

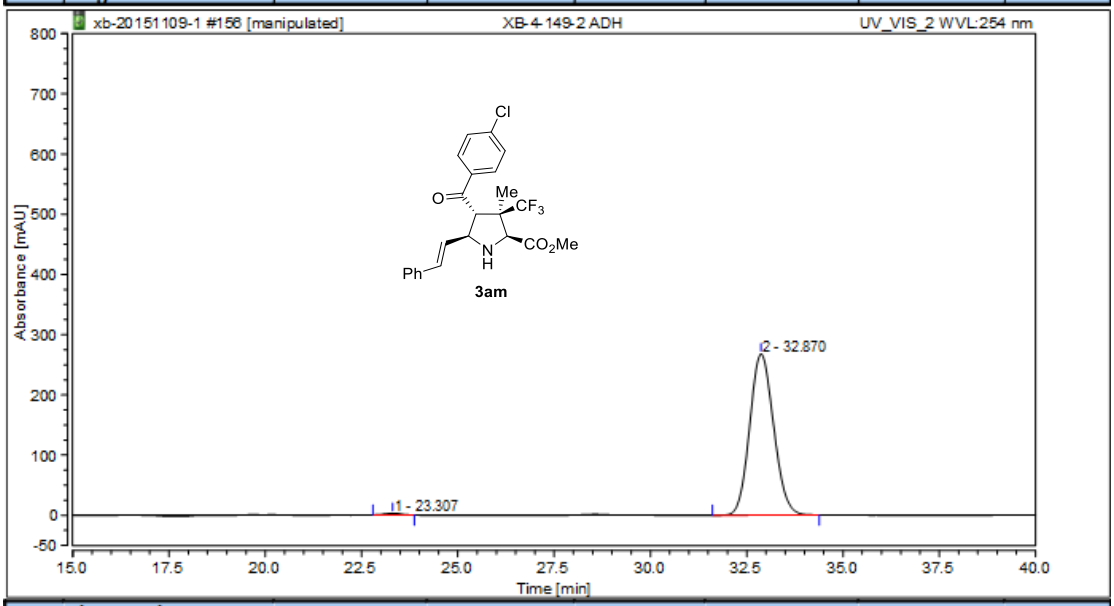




Integration Results

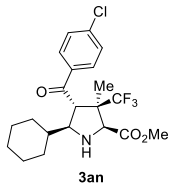
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		23.237	19.123	32.141	50.20	55.16	n.a.
2		32.893	18.974	26.130	49.80	44.84	n.a.

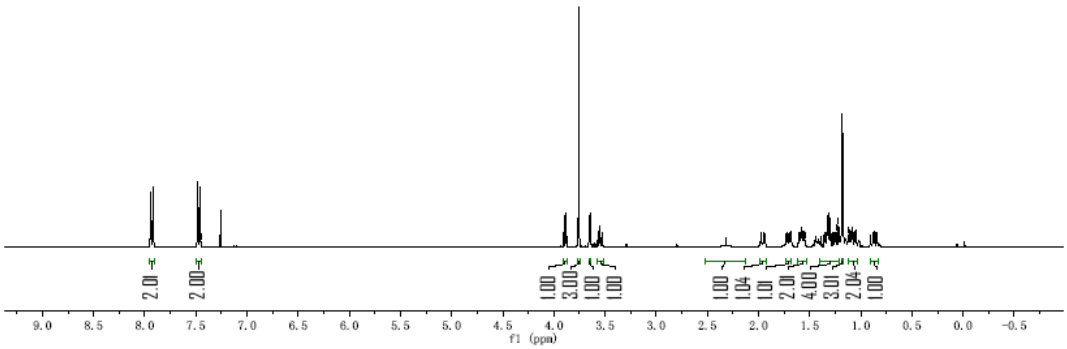
Chromatogram

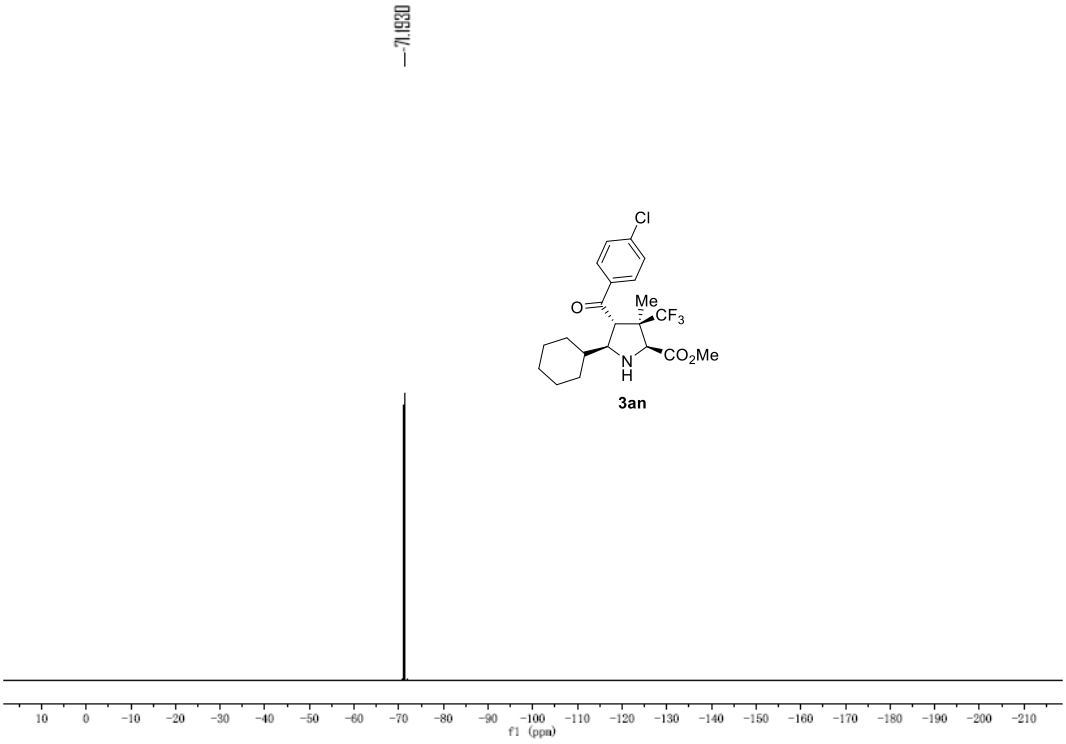


Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		23.307	1.549	3.035	0.80	1.12	n.a.
2		32.870	193.104	267.856	99.20	98.88	n.a.
Total:			194.653	270.891	100.00	100.00	



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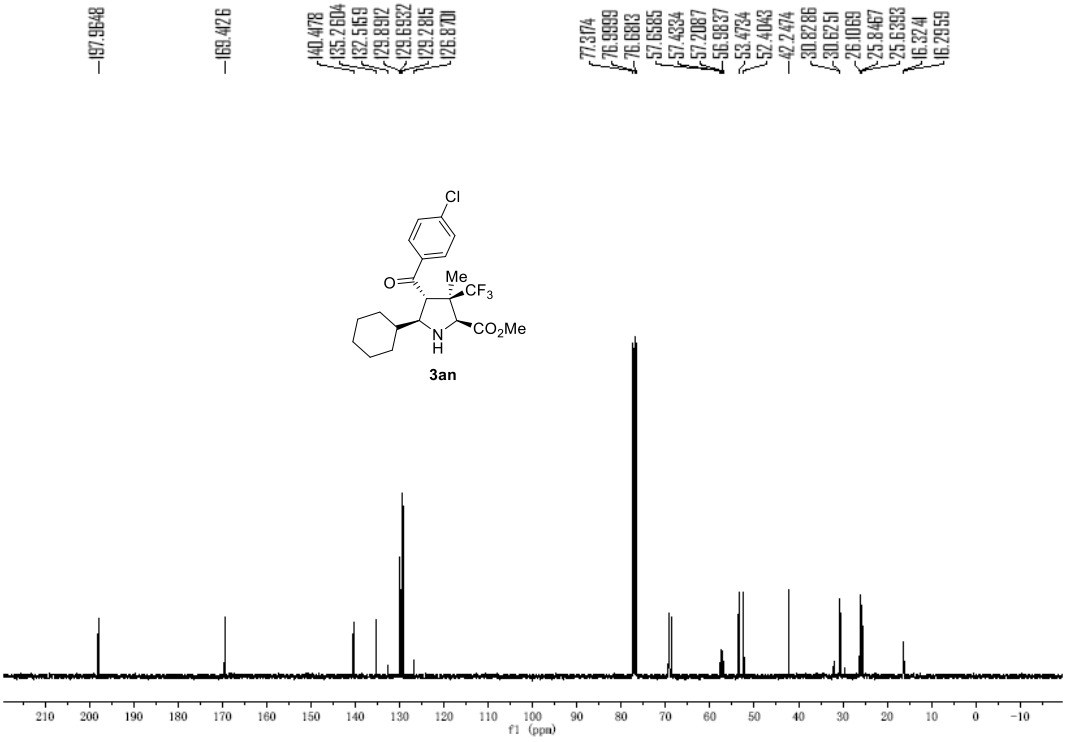
f1 (ppm)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16.5244
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Cl
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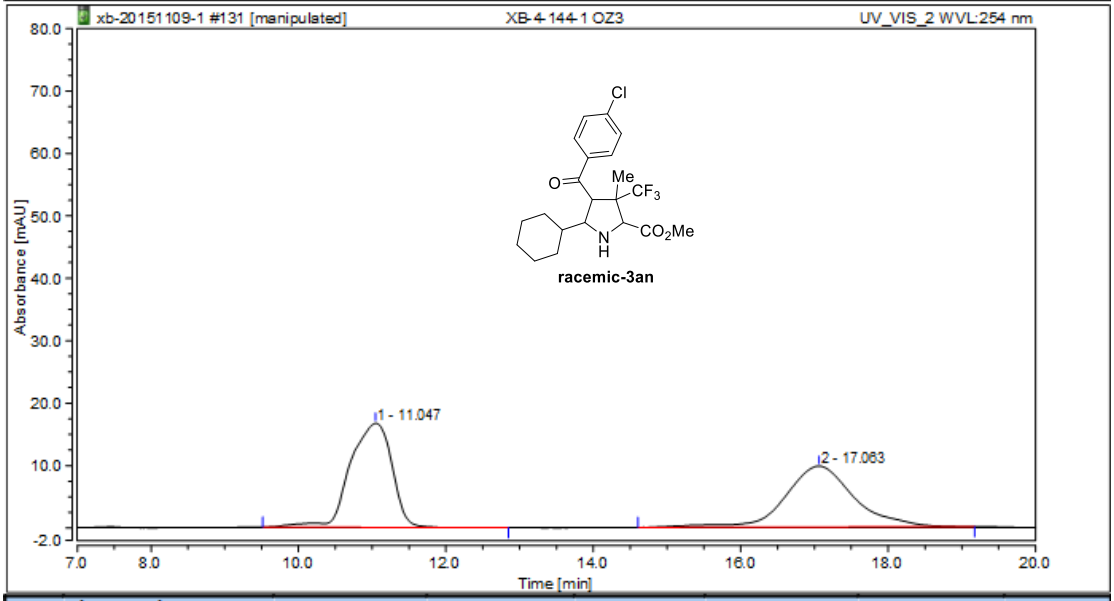
N
H
3an
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

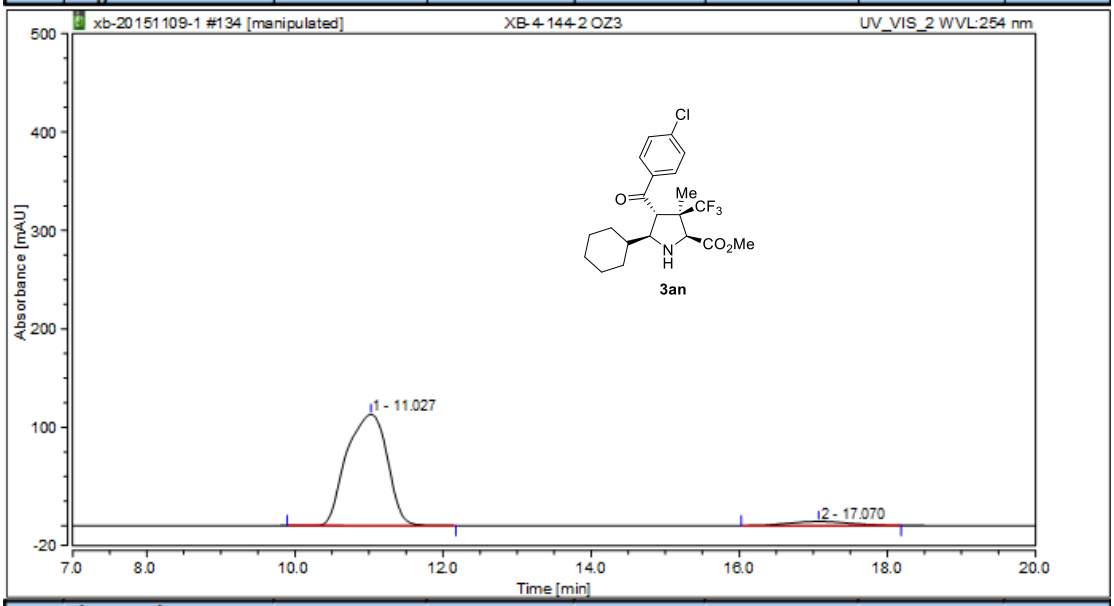
Chromatogram



Integration Results

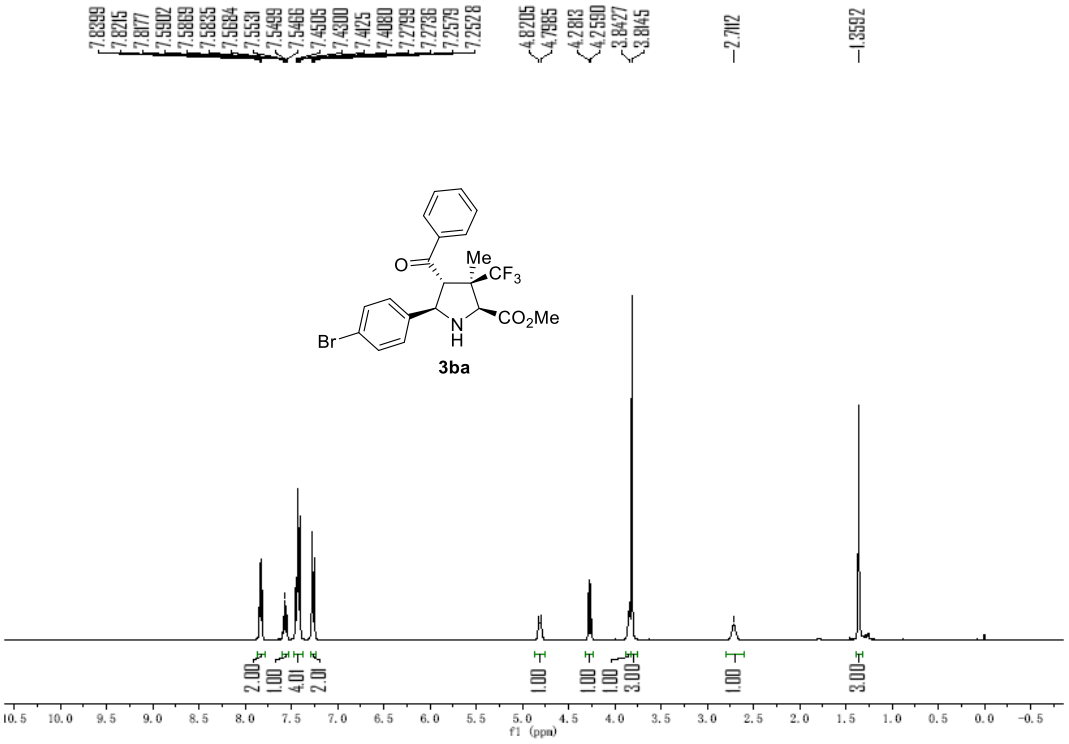
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.047	10.922	16.668	50.91	63.11	n.a.
2		17.063	10.530	9.741	49.09	36.89	n.a.
Total:			21.452	26.410	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.027	71.849	112.953	94.74	96.40	n.a.
2		17.070	3.989	4.215	5.26	3.60	n.a.
Total:			75.838	117.169	100.00	100.00	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4.7985
4.2813
4.2590
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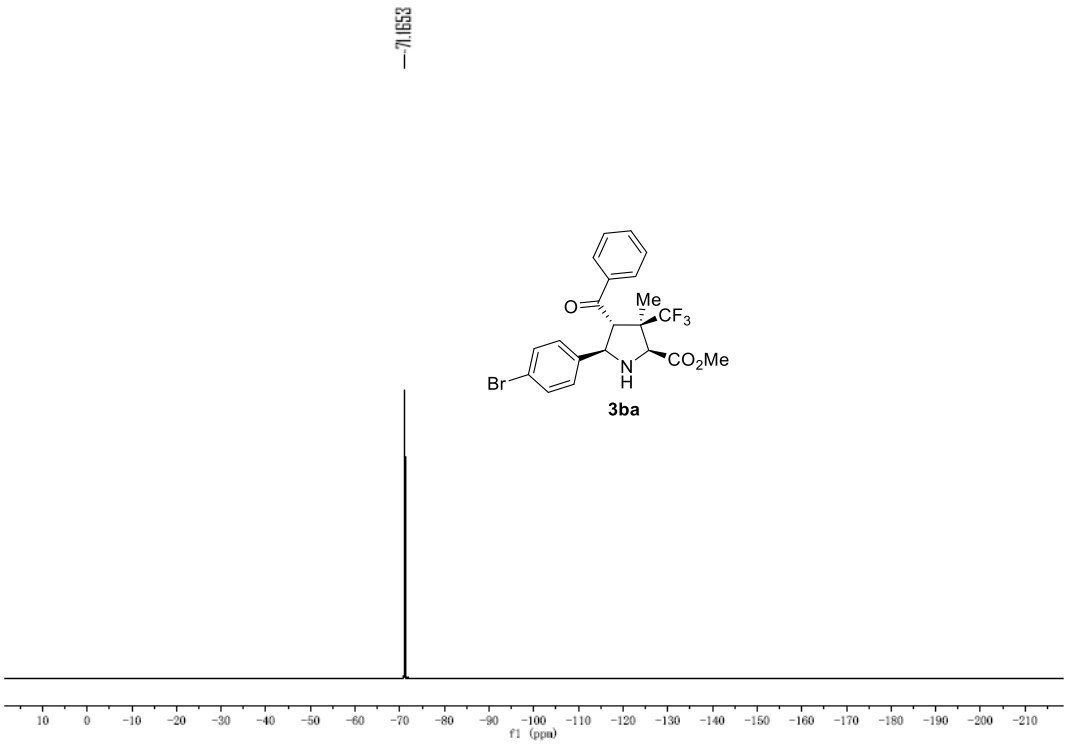
3.8445
2.7112
1.3592
Me
CF3
O
CO2Me
N
H
Br
3ba
2.00
1.00
4.01
2.01
1.00
1.00
1.00
3.00
1.00
3.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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O
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N
H
Br
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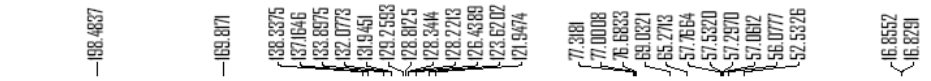
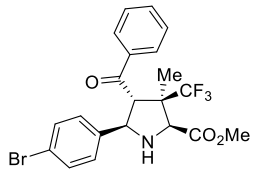
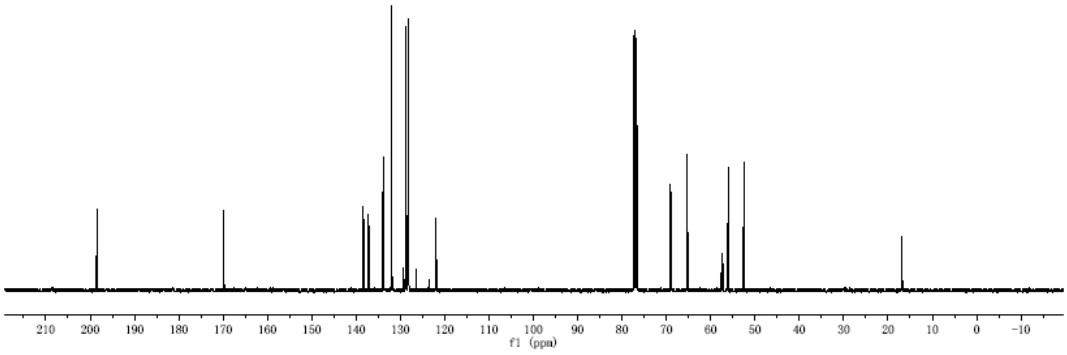
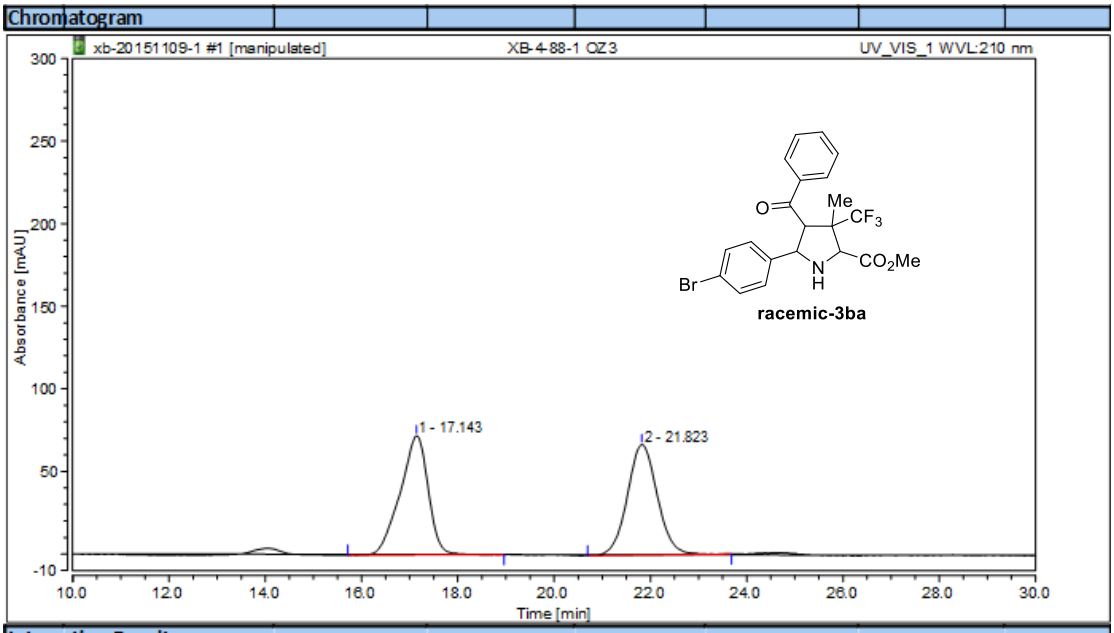
f1 (ppm)





3ba

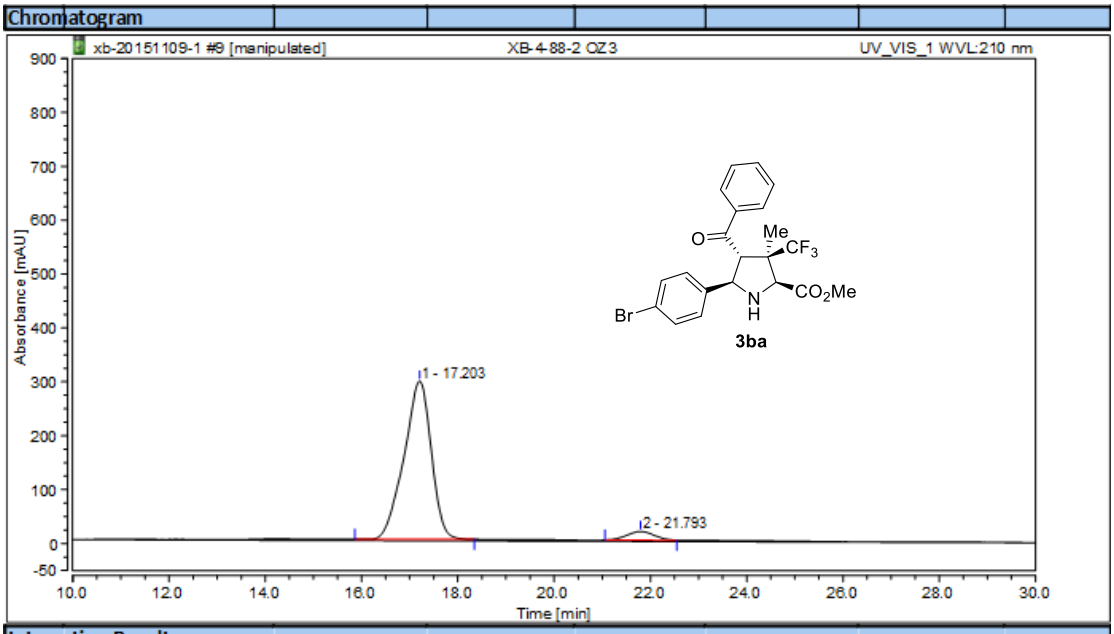




racemic-3ba

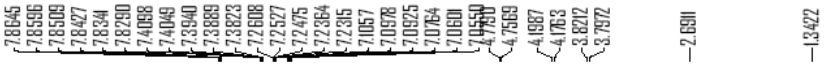
Integration Results

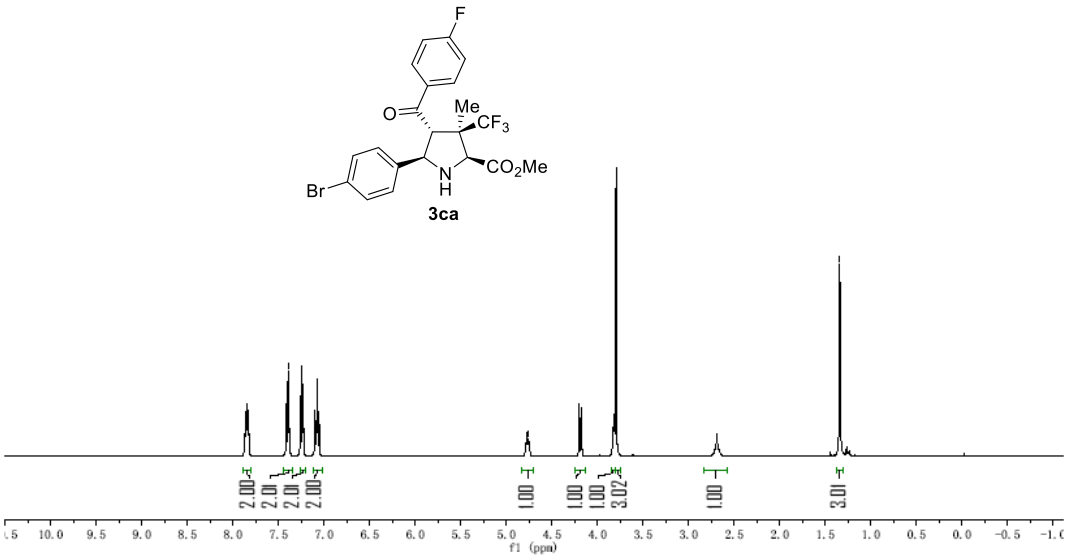
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		17.143	48.588	72.160	50.12	51.85	n.a.
2		21.823	48.364	67.004	49.88	48.15	n.a.
Total:			96.951	139.164	100.00	100.00	

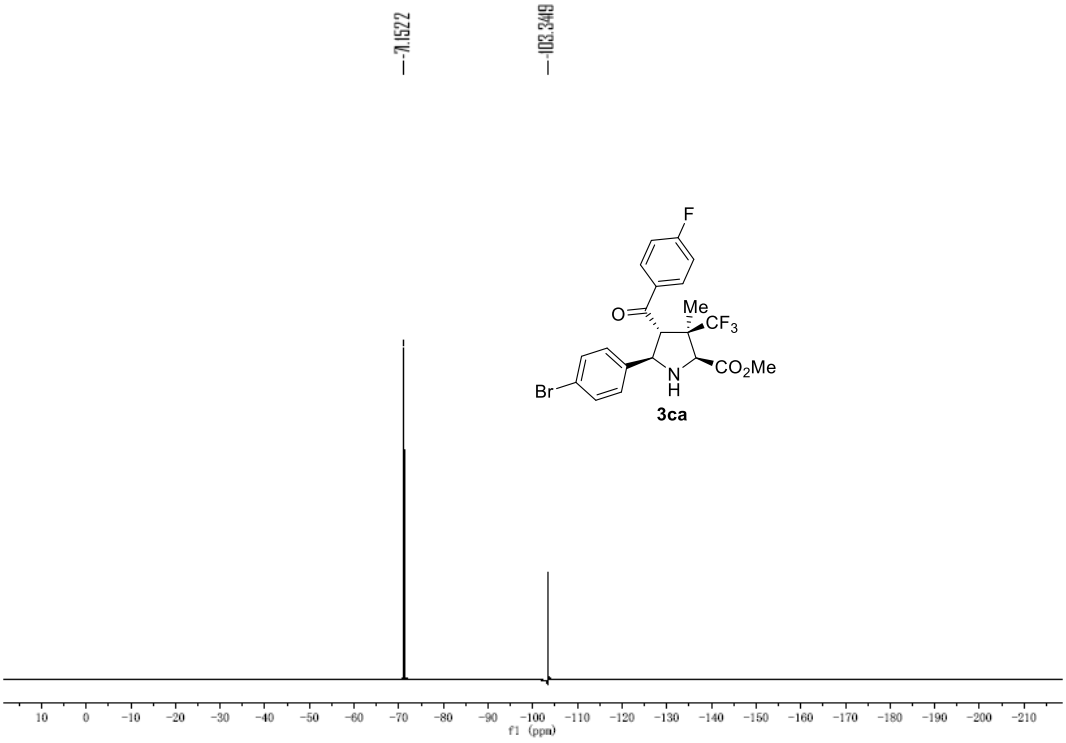


Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		17.203	192.357	294.057	94.79	94.84	n.a.
2		21.793	10.582	15.996	5.21	5.16	n.a.
Total:			202.939	310.053	100.00	100.00	



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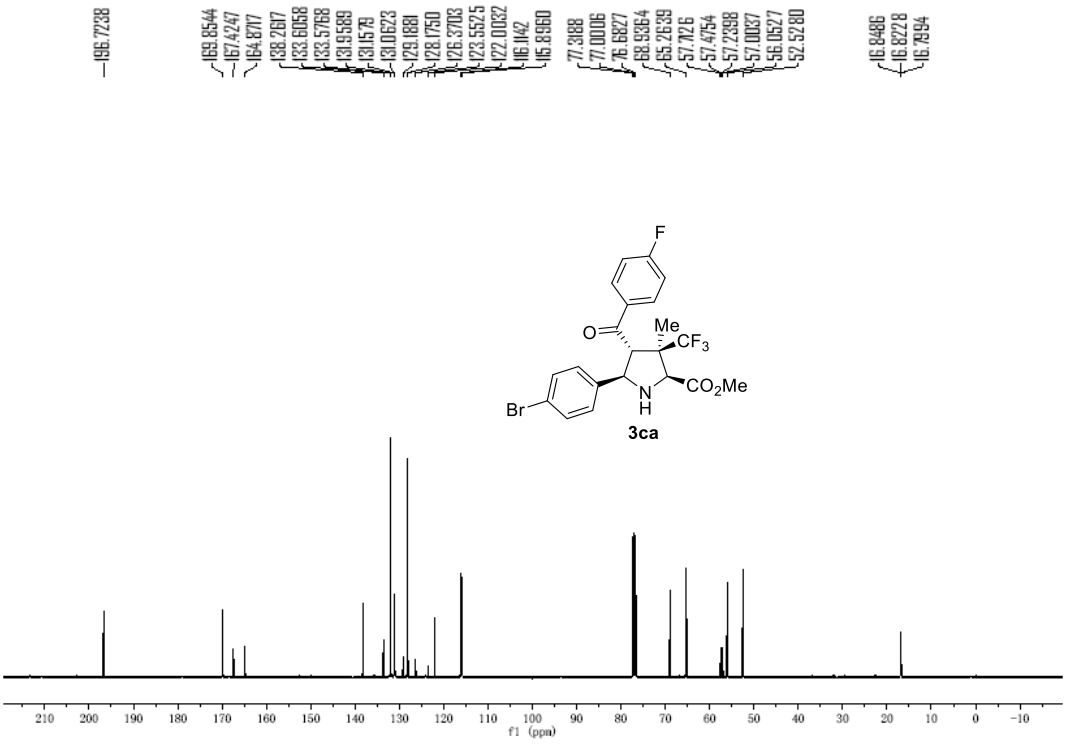
f1 (ppm)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F
O
Me
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H
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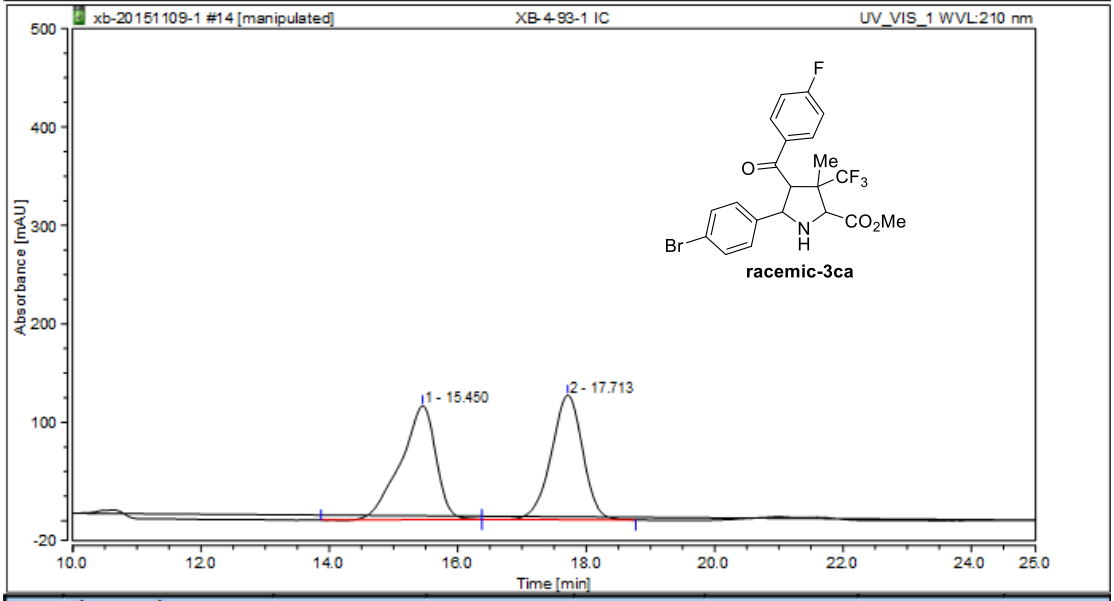
3ca
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

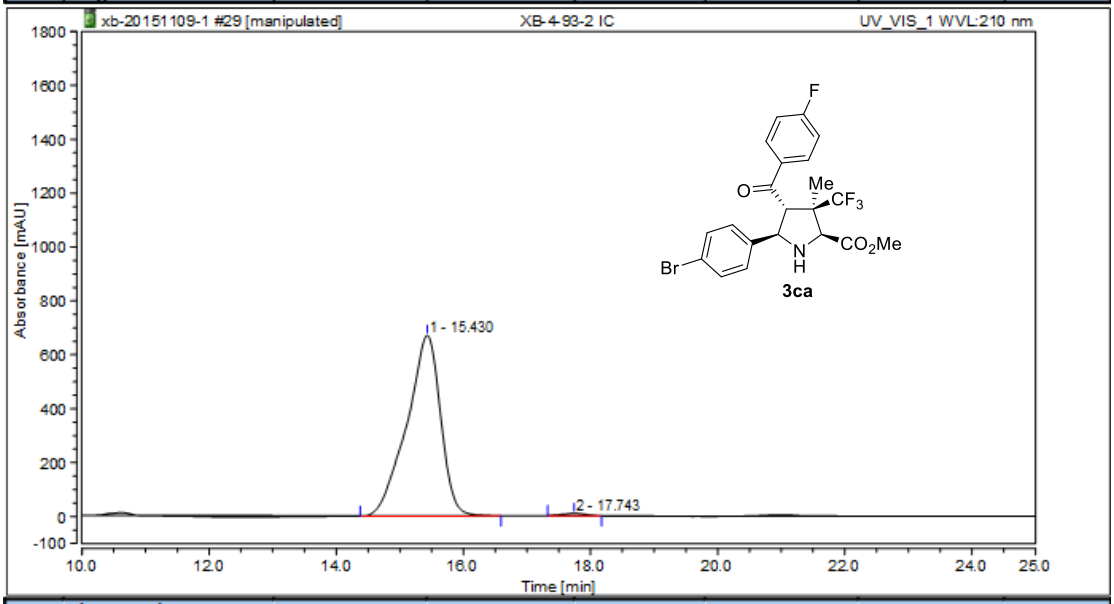
Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		15.450	73.730	115.661	50.72	47.81	n.a.
2		17.713	71.623	126.281	49.28	52.19	n.a.
Total:			145.354	241.942	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		15.430	413.428	670.428	99.08	98.76	n.a.
2		17.743	3.823	8.408	0.92	1.24	n.a.
Total:			417.251	678.837	100.00	100.00	


7.6731
7.6685
7.6566
7.6516
7.5581
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7.5352
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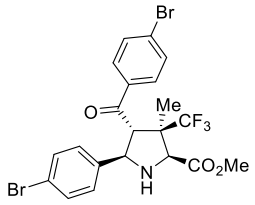
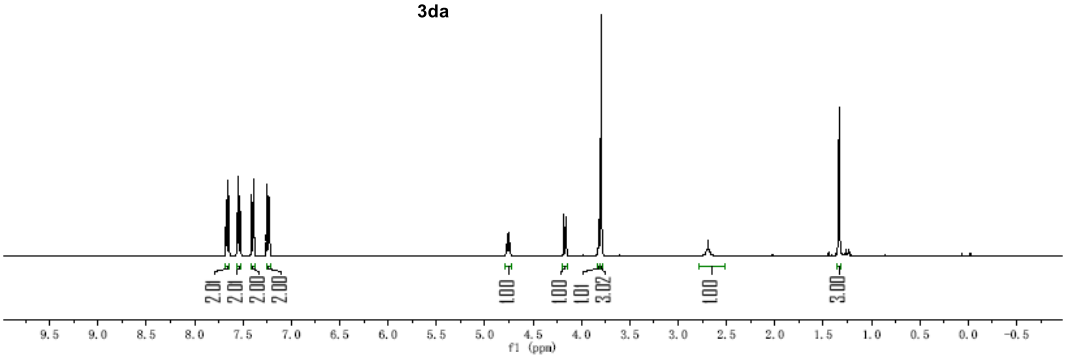

Br
O
Me
CF3
CO2Me
N
H
Br

3da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3.00
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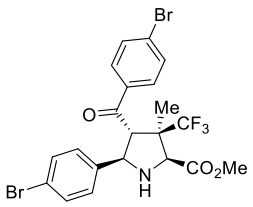
f1 (ppm)


-71.1210


Br
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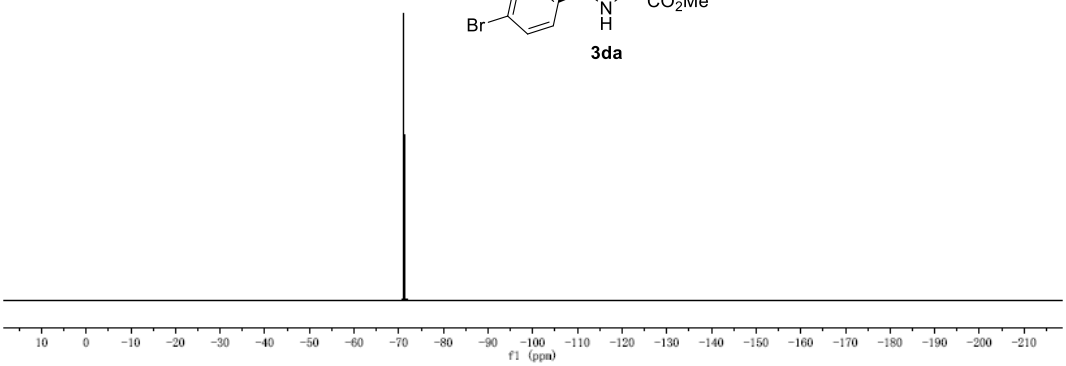
Br

3da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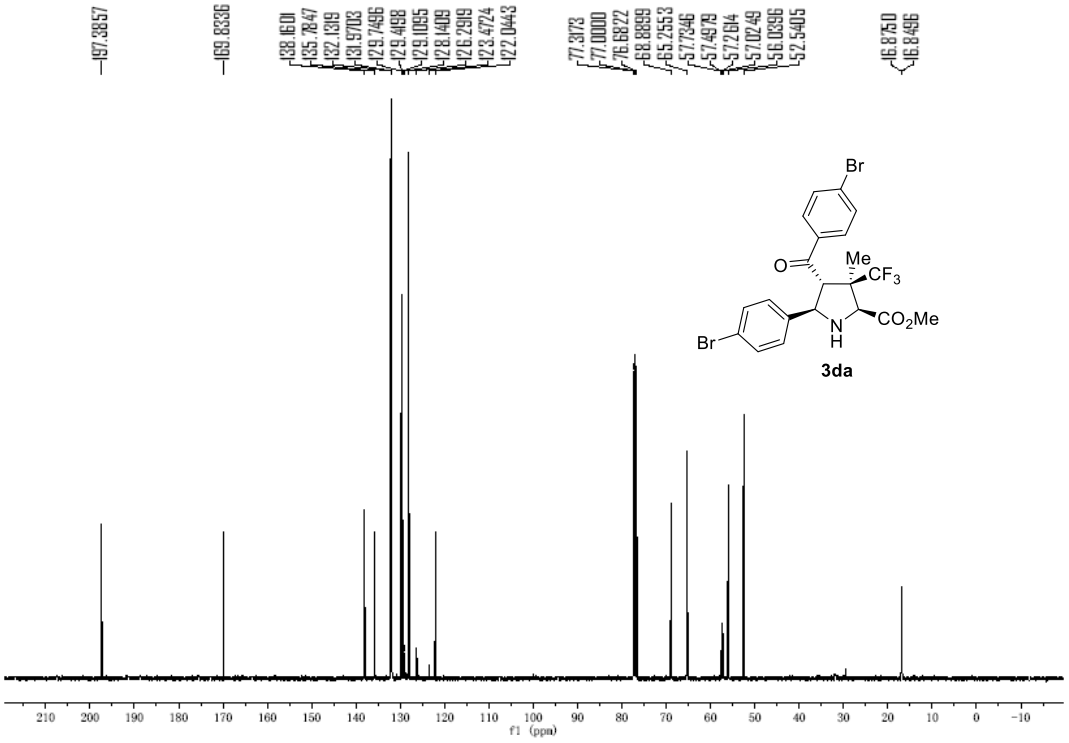
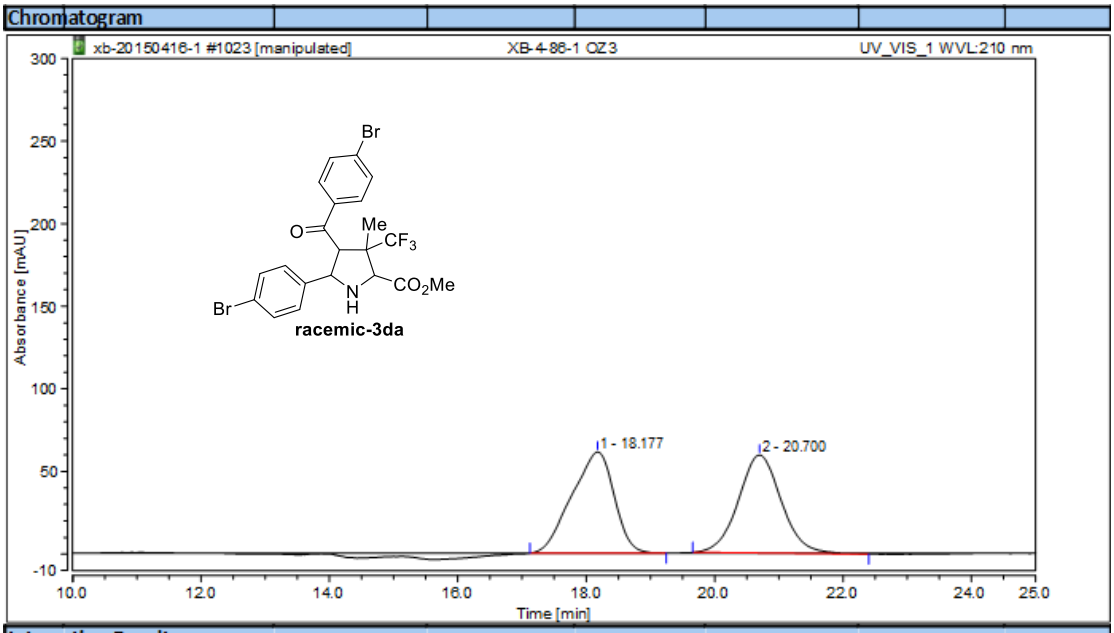
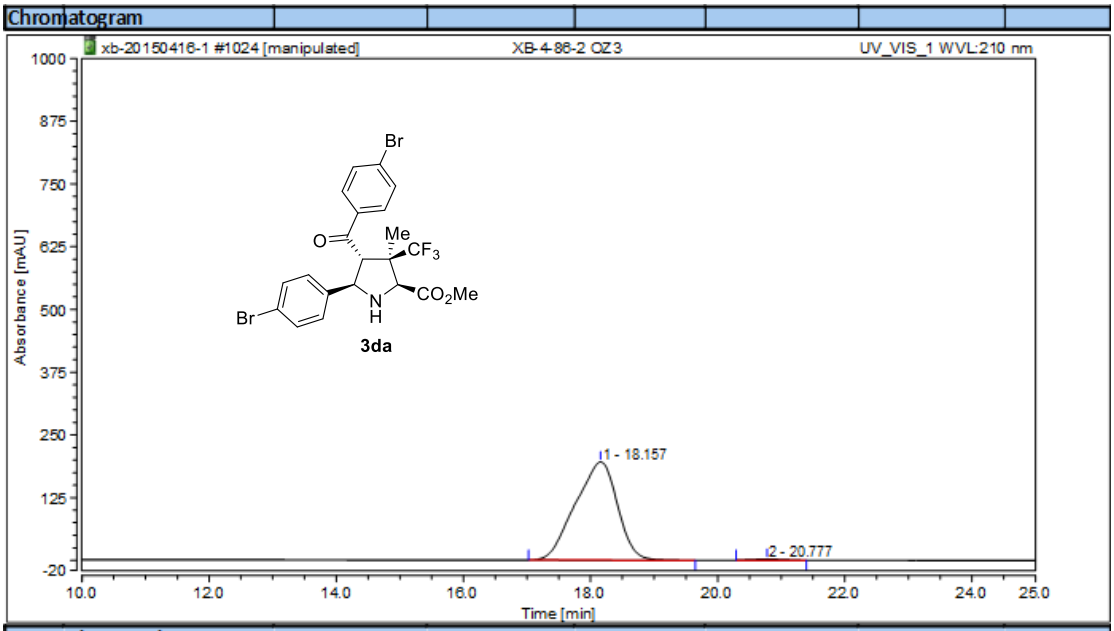
f1 (ppm)





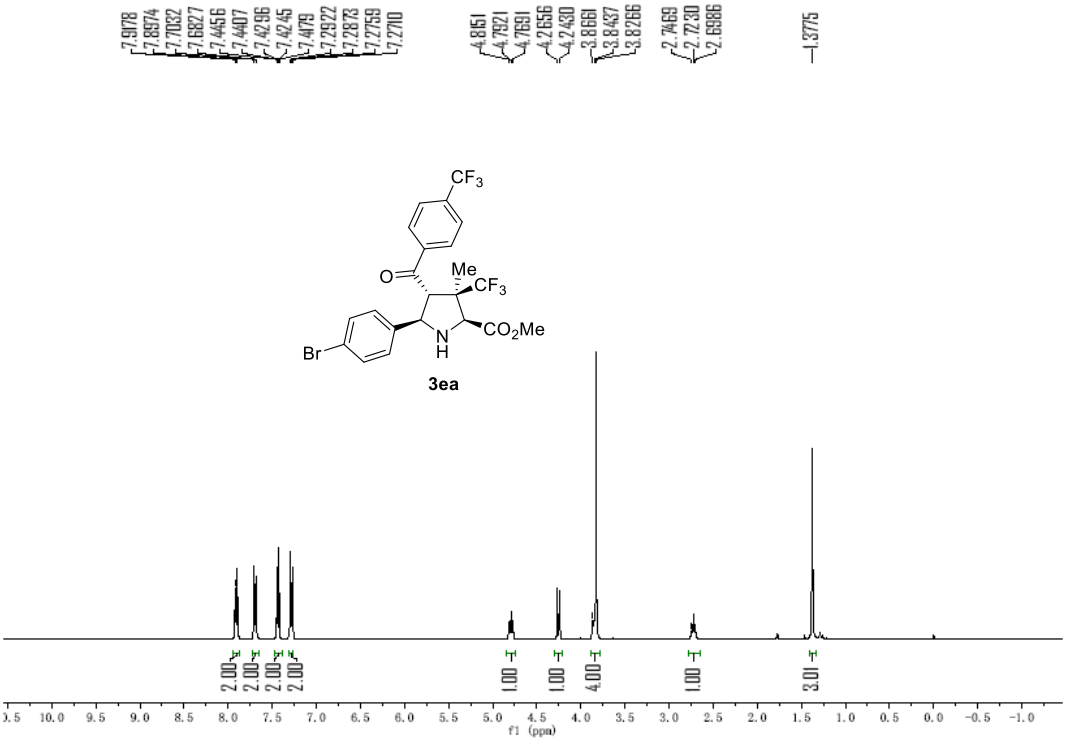
Integration Results

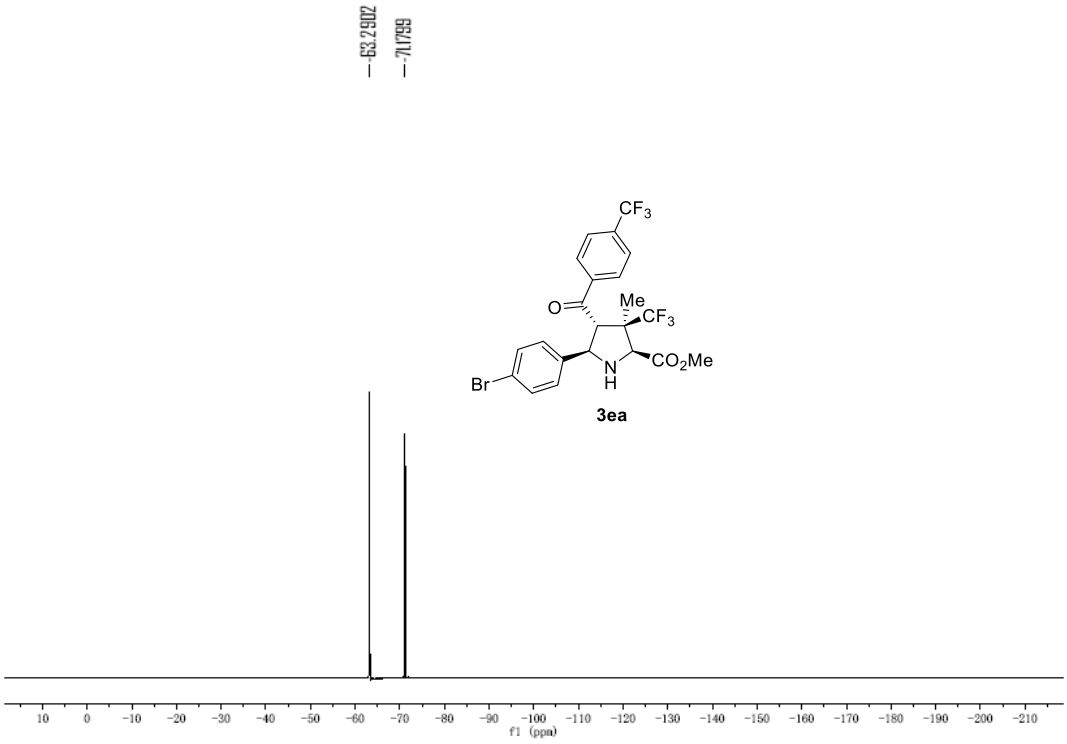
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		18.177	46.896	61.277	50.50	50.81	n.a.
2		20.700	45.976	59.332	49.50	49.19	n.a.
Total:			92.872	120.610	100.00	100.00	



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		18.157	150.281	195.779	99.20	98.94	n.a.
2		20.777	1.206	2.094	0.80	1.06	n.a.
Total:			151.487	197.872	100.00	100.00	

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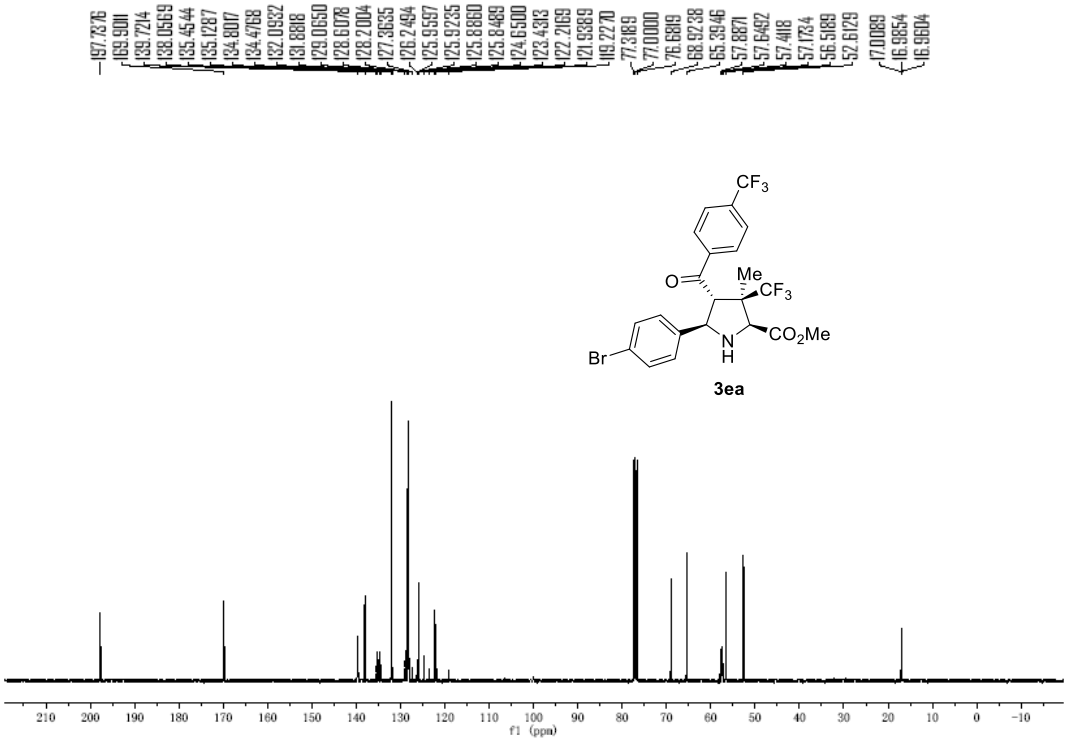
O
Me
CF3
CO2Me
N
H
Br
3ea
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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128.2004
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125.9235
125.8860
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124.6500
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77.0000
76.6849
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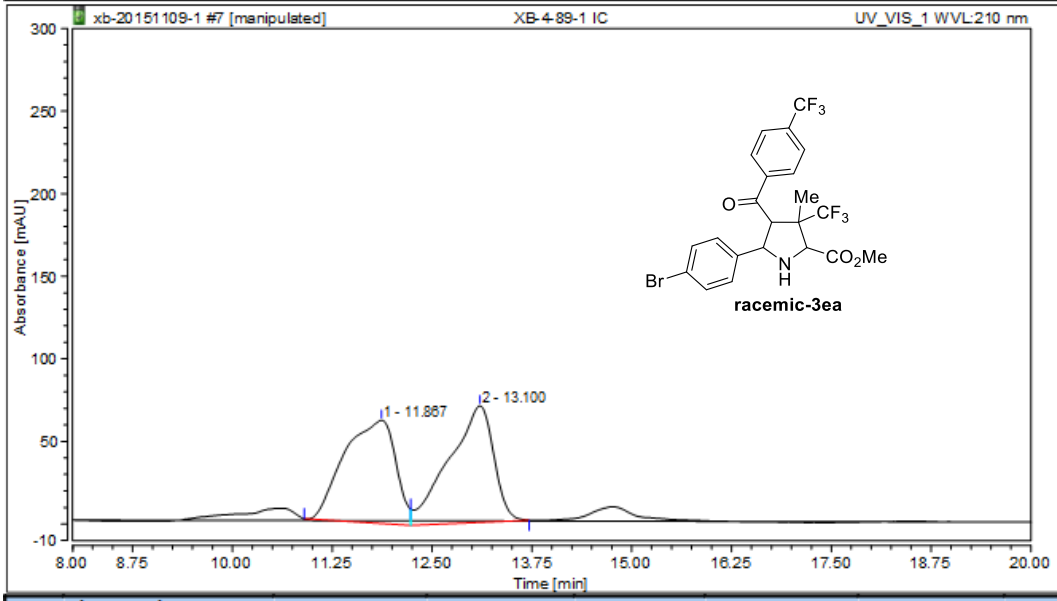
57.8871
57.6492
57.4118
57.1734
56.5169
52.6129
17.0089
16.9854
16.9604
CF3
O
Me
CF3
CO2Me
N
H
Br
3ea
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

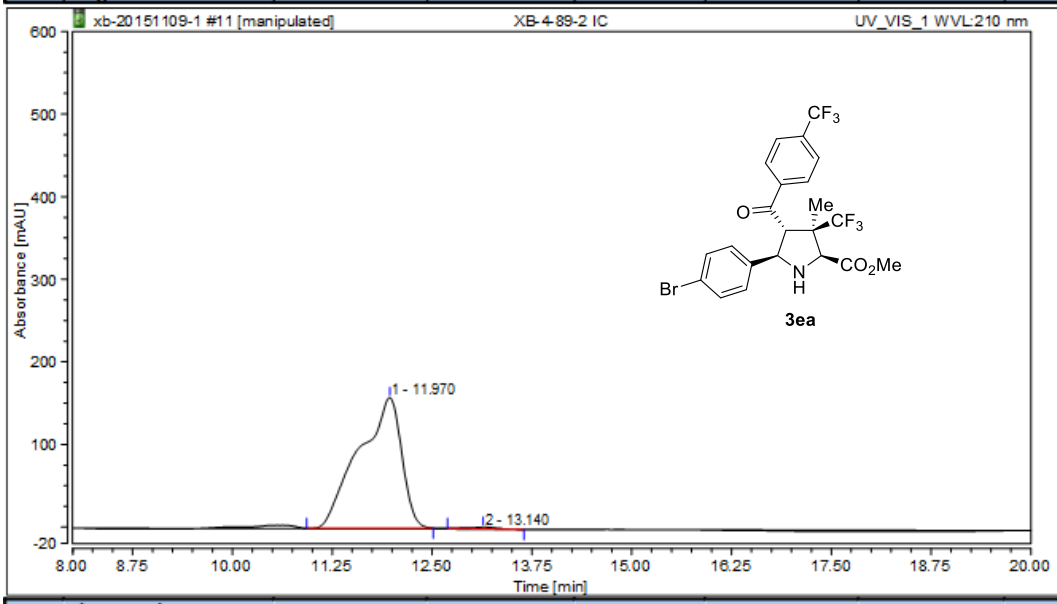
Chromatogram



Integration Results

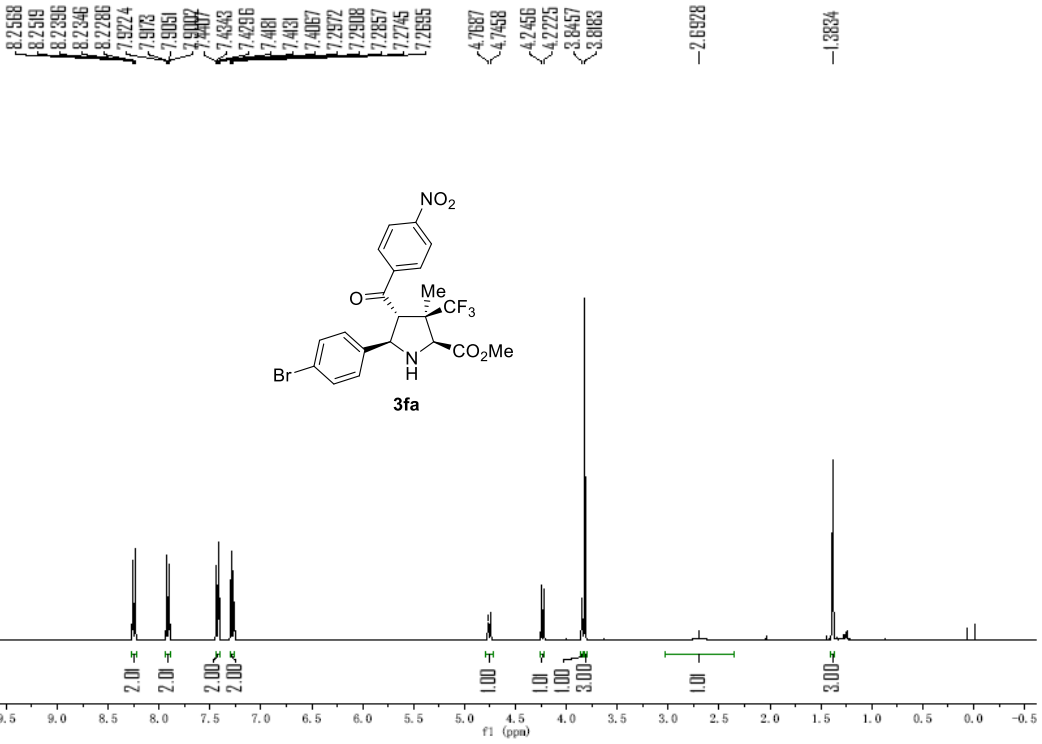
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.867	46.376	62.520	50.33	46.96	n.a.
2		13.100	45.760	70.605	49.67	53.04	n.a.
Total:			92.136	133.124	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.970	97.891	158.198	99.05	98.65	n.a.
2		13.140	0.934	2.163	0.95	1.35	n.a.
Total:			98.825	160.361	100.00	100.00	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7.4296
7.4181
7.4131
7.4067
7.2972
7.2908
7.2657
7.2745
7.2695
4.7687
4.7458
4.2456
4.2225
3.8457
3.8183
2.6928
1.3834
NO2
O
Me
CF3
CO2Me
N
H
Br
3fa
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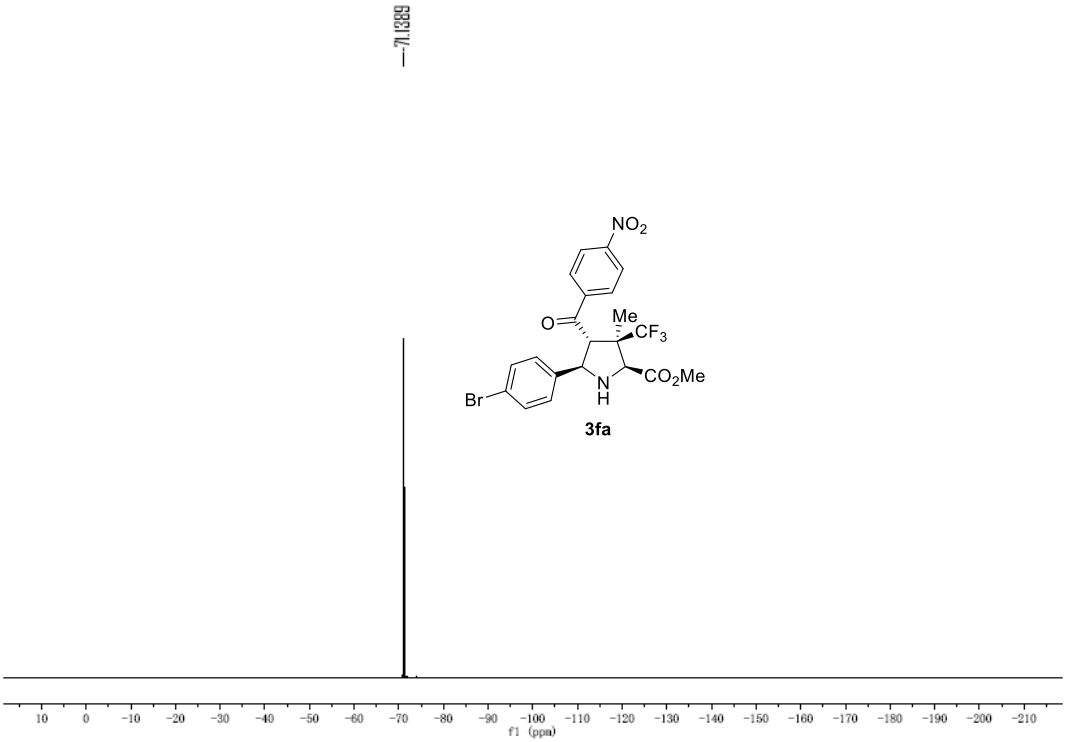
2.01
2.00
2.00
1.00
1.01
1.00
3.00
1.01
3.00
f1 (ppm)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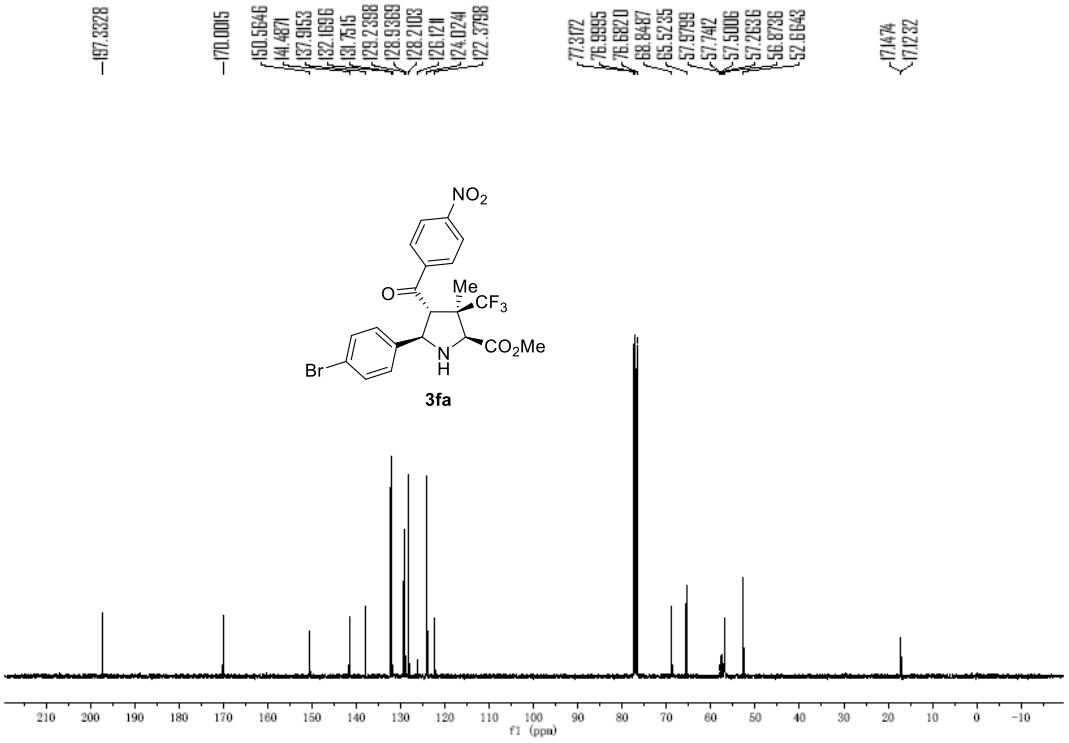
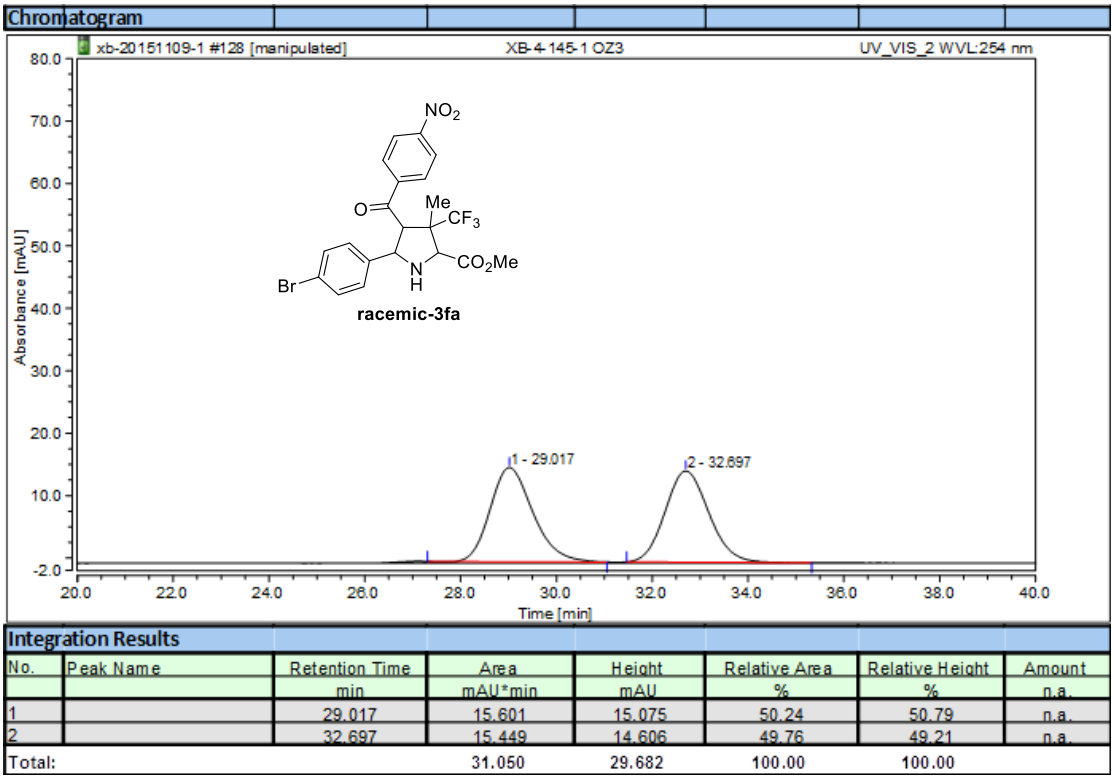
O
Me
CF3
CO2Me
N
H
Br
3fa
f1 (ppm)

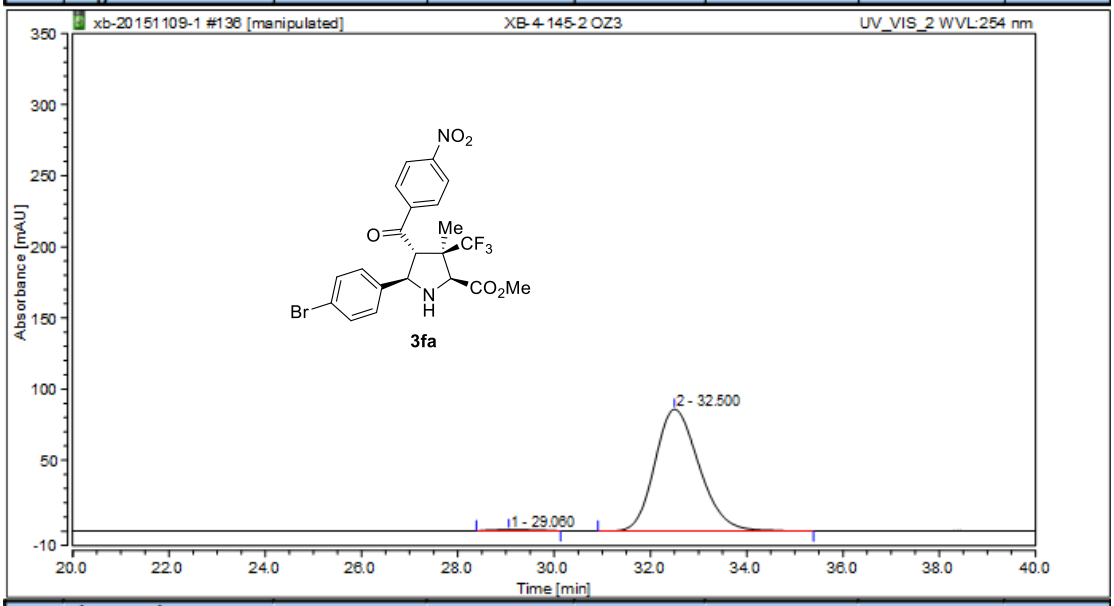




Integration Results

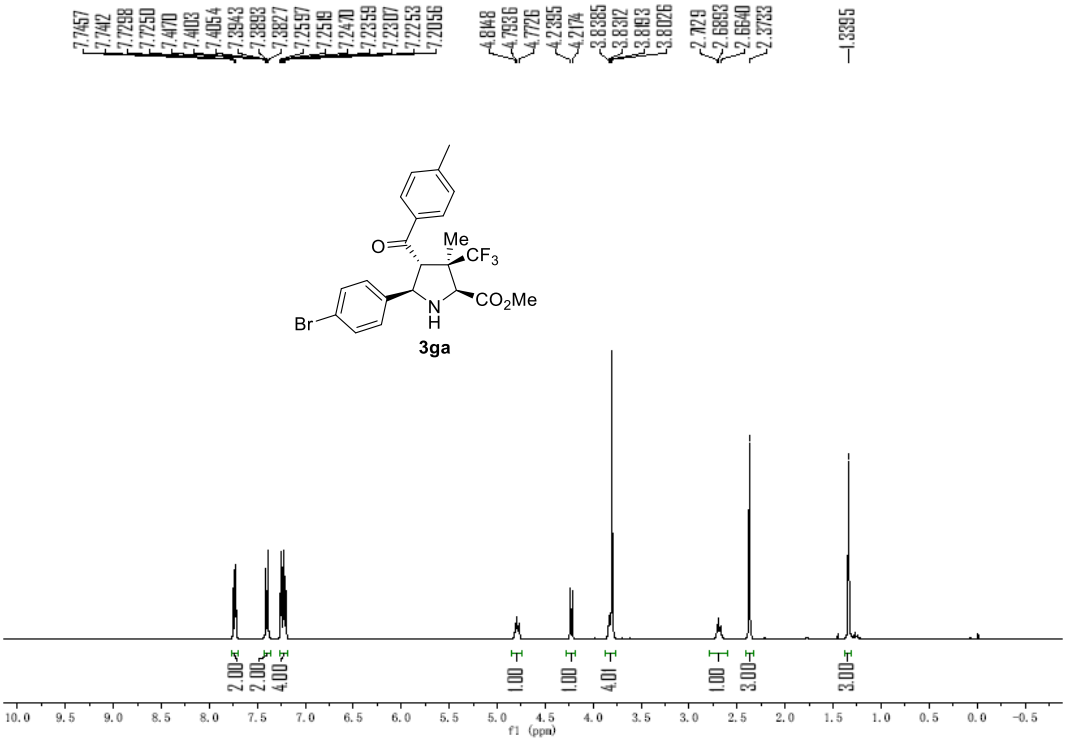
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		29.017	15.601	15.075	50.24	50.79	n.a.
2		32.697	15.449	14.606	49.76	49.21	n.a.
Total:			31.050	29.682	100.00	100.00	

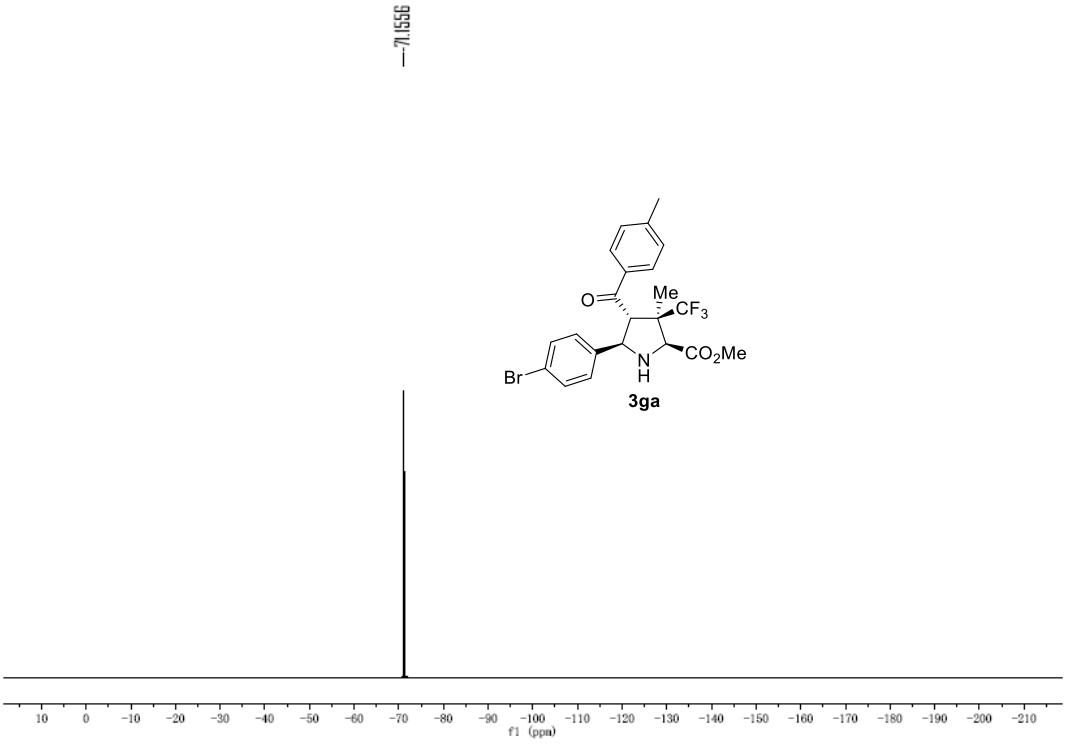
Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		29.060	0.800	0.840	0.87	0.97	n.a.
2		32.500	91.485	85.701	99.13	99.03	n.a.
Total:			92.285	86.541	100.00	100.00	

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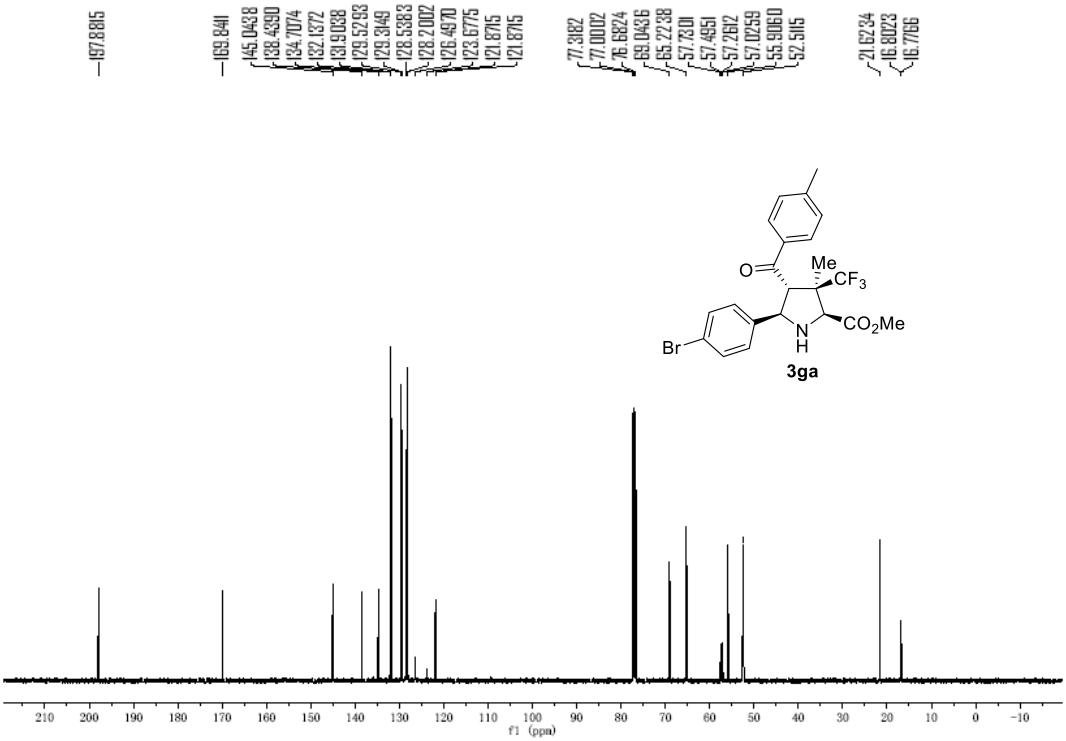
CO2Me
N
H
Br
3ga
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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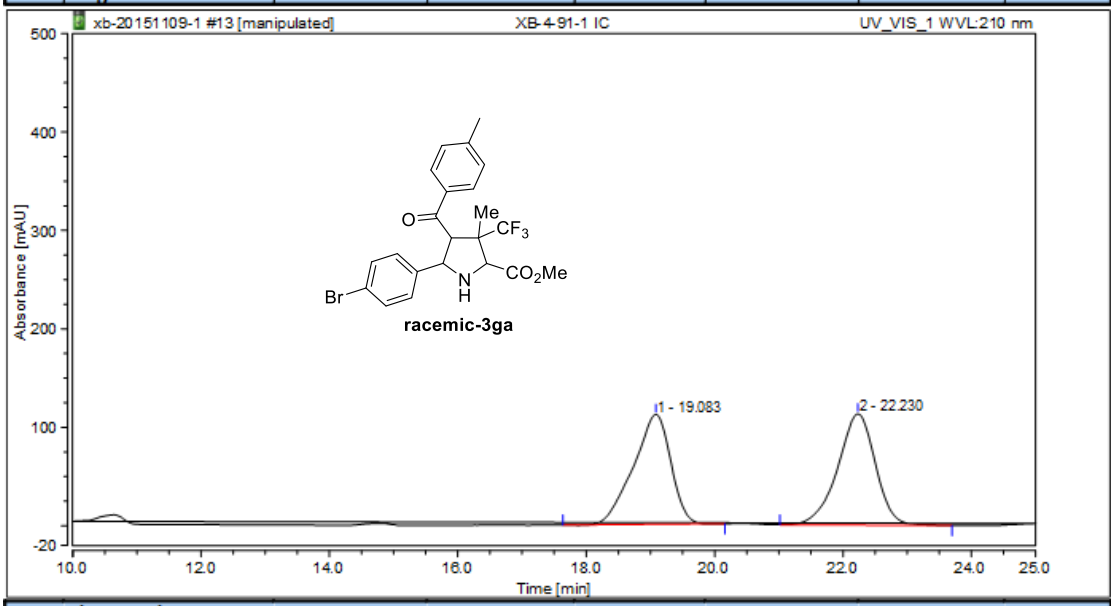
128.2002
126.4970
123.6775
121.8715
121.8715
77.3182
77.0002
76.6824
69.0436
65.2238
57.7310
57.4951
57.2612
57.0259
55.9060
52.5115
21.6234
16.8023
16.7766
Me
CF3
O
CO2Me
N
H
Br
3ga
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

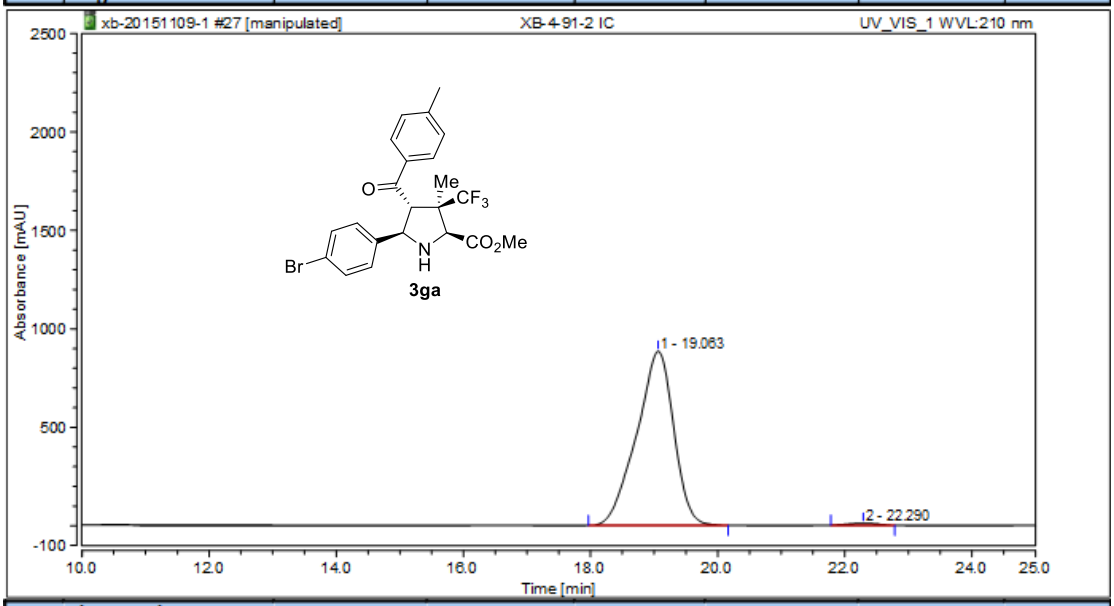
Chromatogram



Integration Results

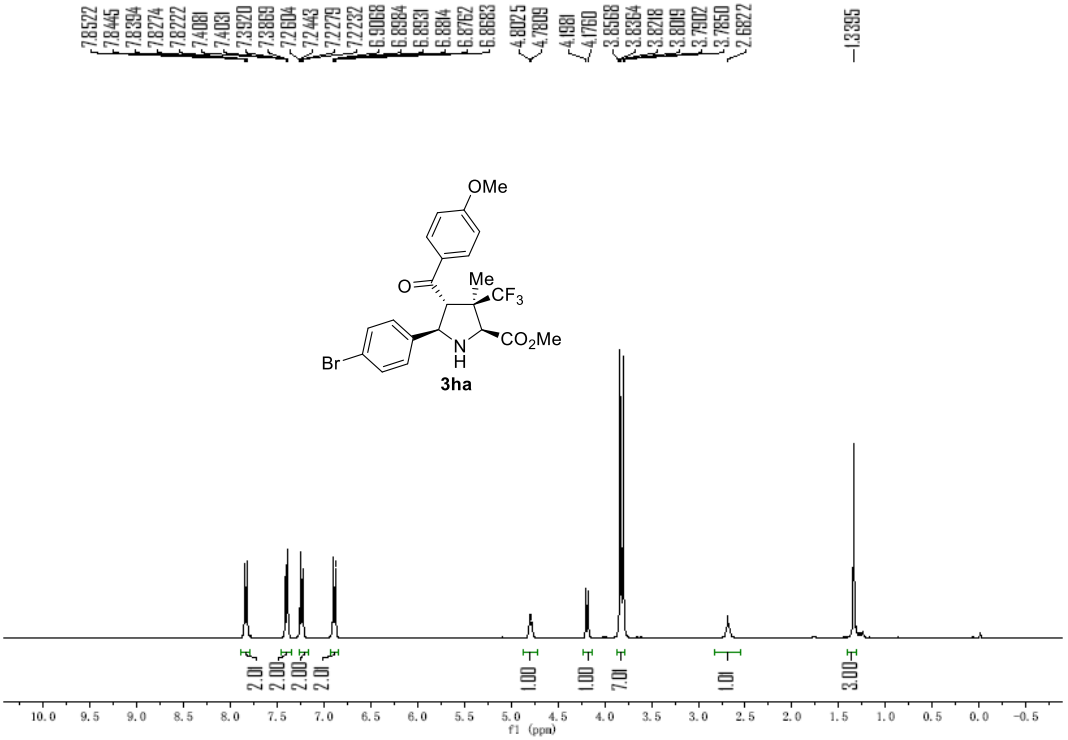
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		19.083	75.239	111.559	49.37	49.69	n.a.
2		22.230	77.166	112.946	50.63	50.31	n.a.
Total:			152.405	224.505	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		19.063	599.101	885.395	99.07	98.83	n.a.
2		22.290	5.619	10.510	0.93	1.17	n.a.
Total:			604.720	895.905	100.00	100.00	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7.8274
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7.4031
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7.2604
7.2443
7.2279
7.2232
6.9066
6.8984
6.8931
6.8814
6.8762
6.8683
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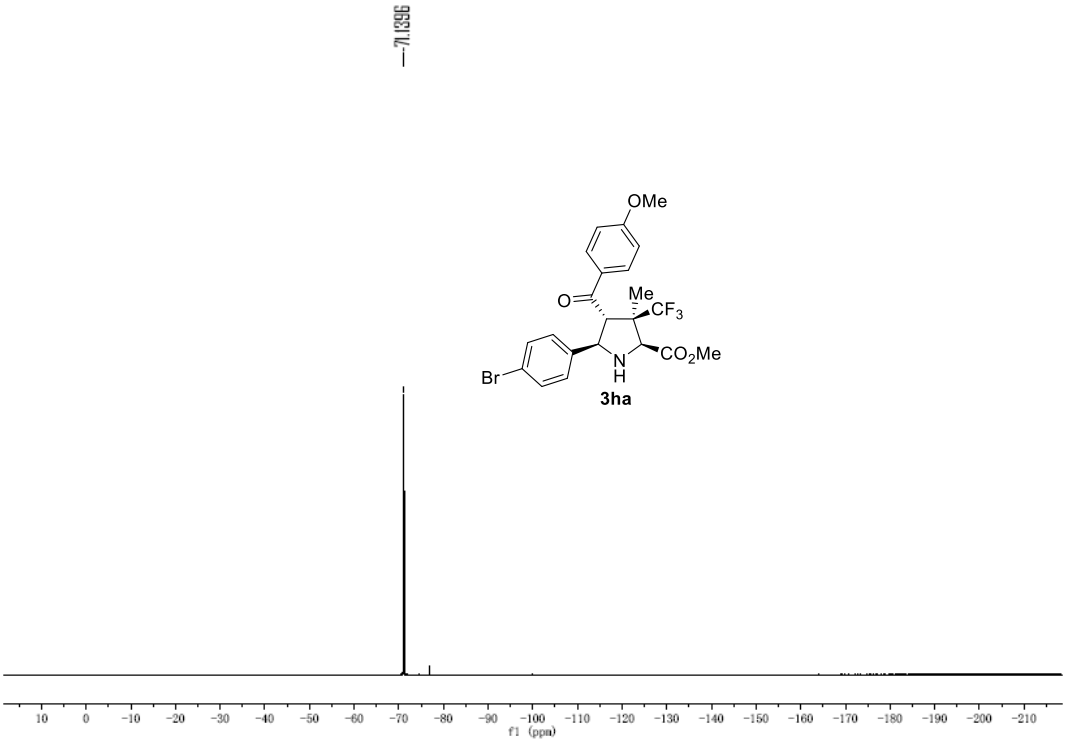
4.1760
3.8568
3.8364
3.8218
3.8019
3.7902
3.7850
2.6822
1.3395
OMe
O
Me
CF3
CO2Me
N
H
Br
3ha
2.01
2.00
2.00
2.01
1.00
1.00
7.01
1.01
3.00
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)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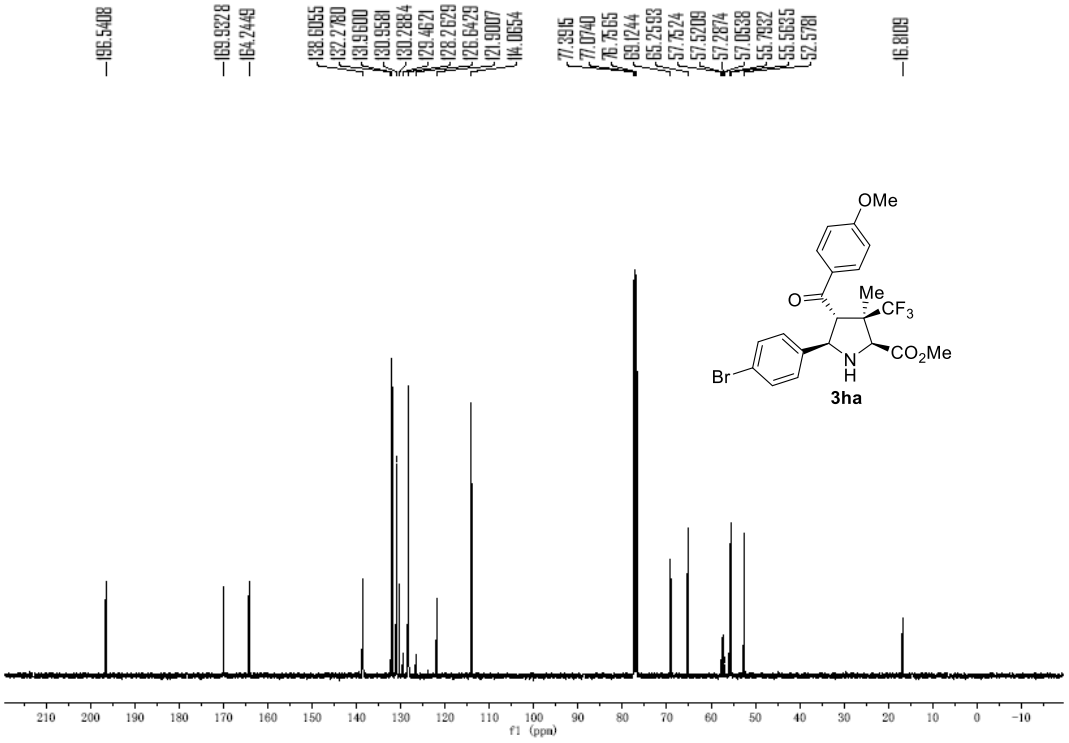
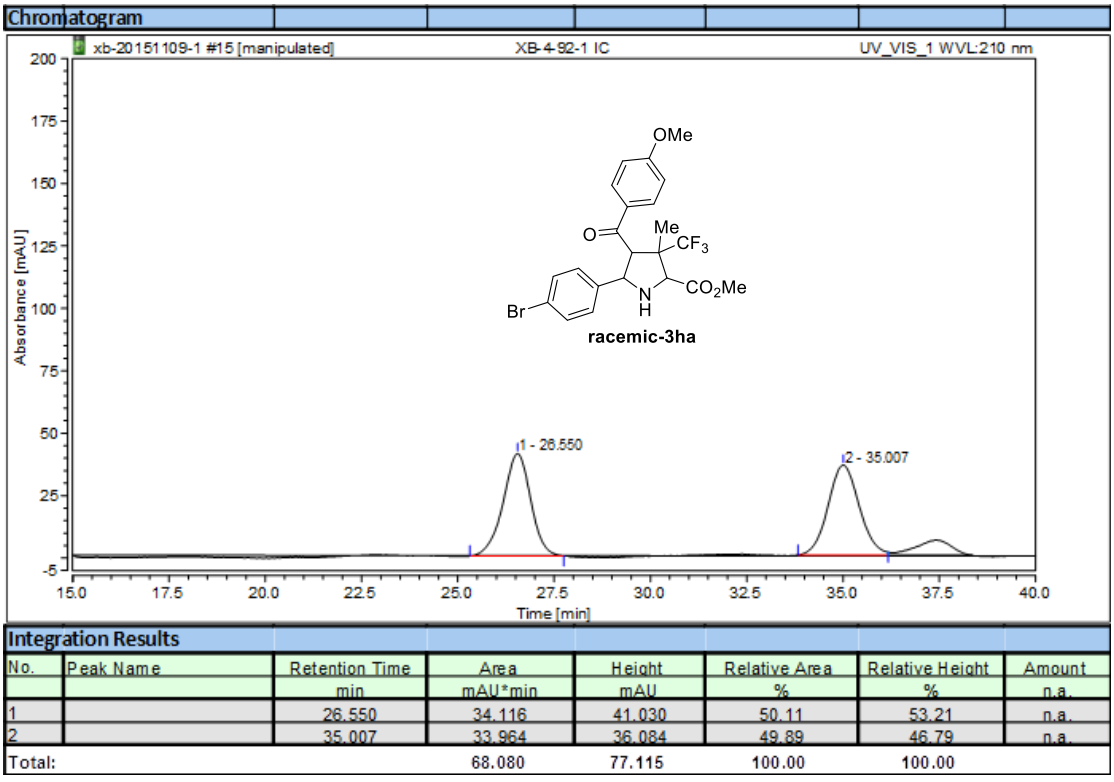
Me
CF3
CO2Me
N
H
Br
3ha
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)

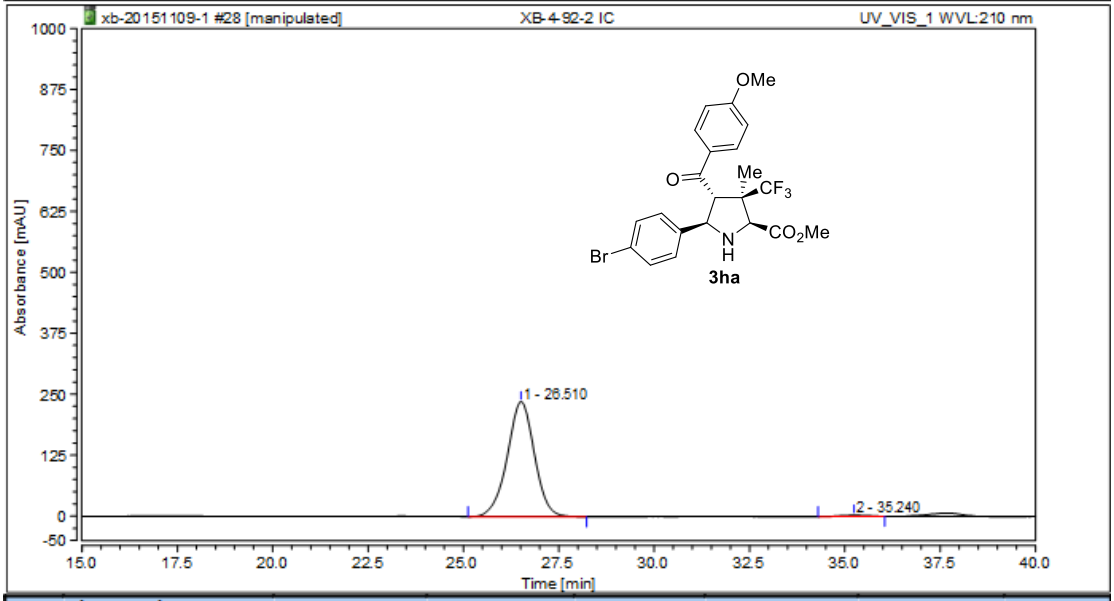




Integration Results

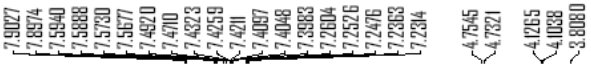
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		26.550	34.116	41.030	50.11	53.21	n.a.
2		35.007	33.964	36.084	49.89	46.79	n.a.
Total:			68.080	77.115	100.00	100.00	

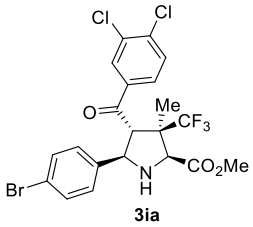
Chromatogram

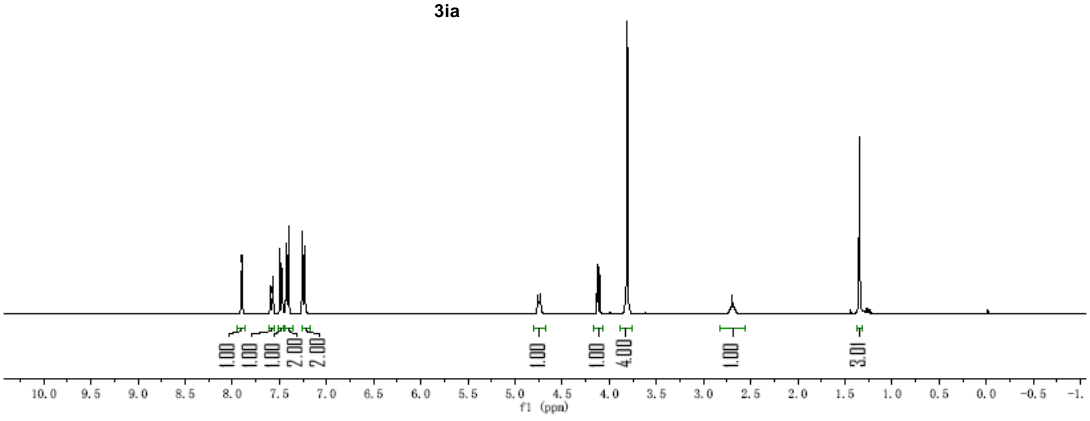


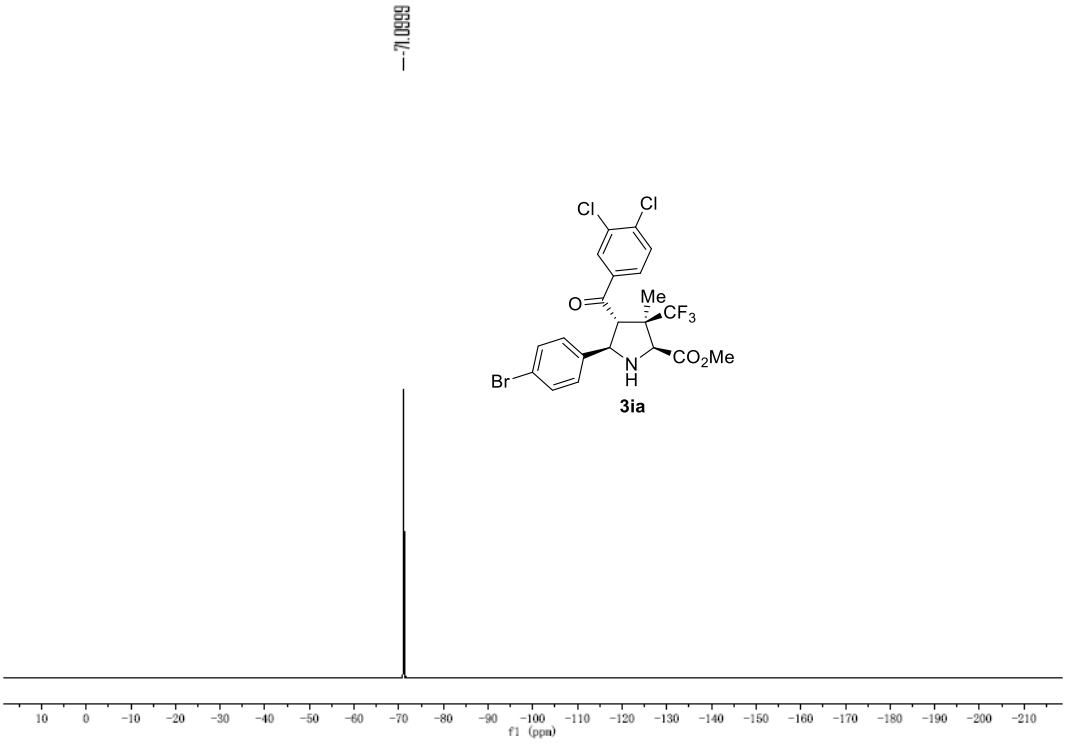
Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		26.510	195.171	235.865	98.89	98.95	n.a.
2		35.240	2.196	2.506	1.11	1.05	n.a.
Total:			197.367	238.371	100.00	100.00	





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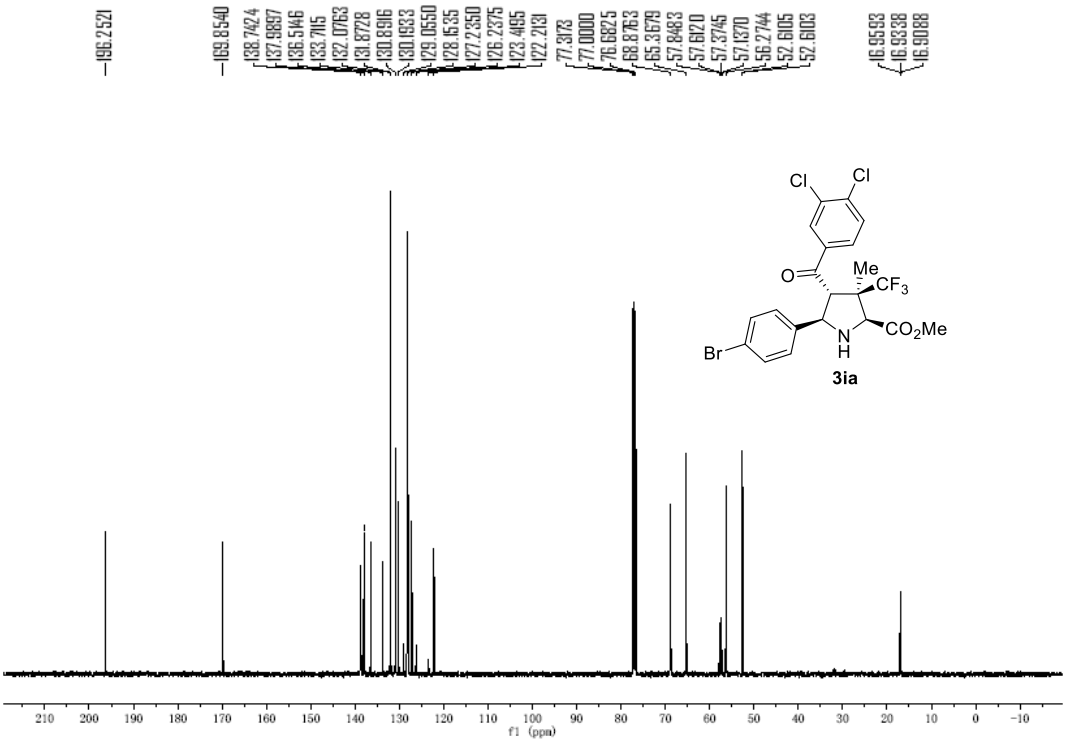
Cl
O
Me
CF3
CO2Me
N
H
Br
3ia
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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56.2744
52.6105
52.6103
16.9593
16.9338
16.9088
Cl
Cl
O
Me
CF3
CO2Me
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H
Br
3ia
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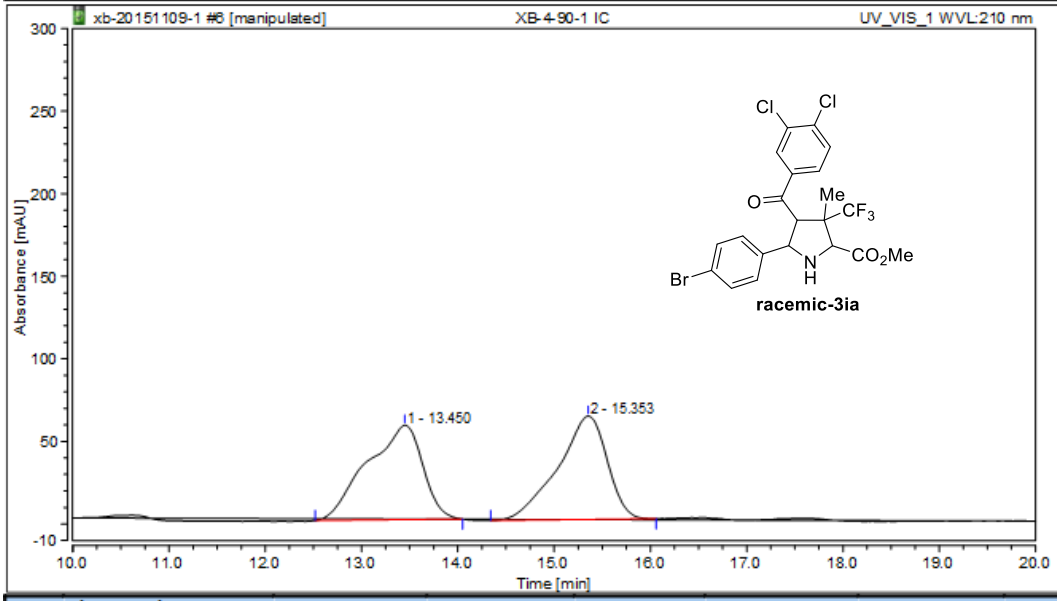
f1 (ppm)

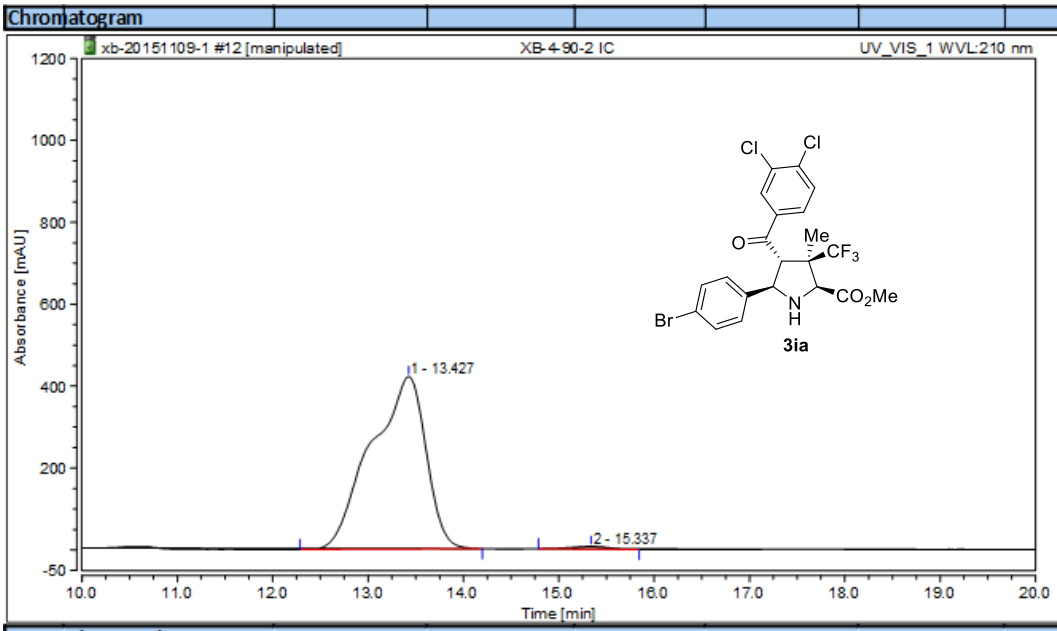
Chromatogram



Integration Results

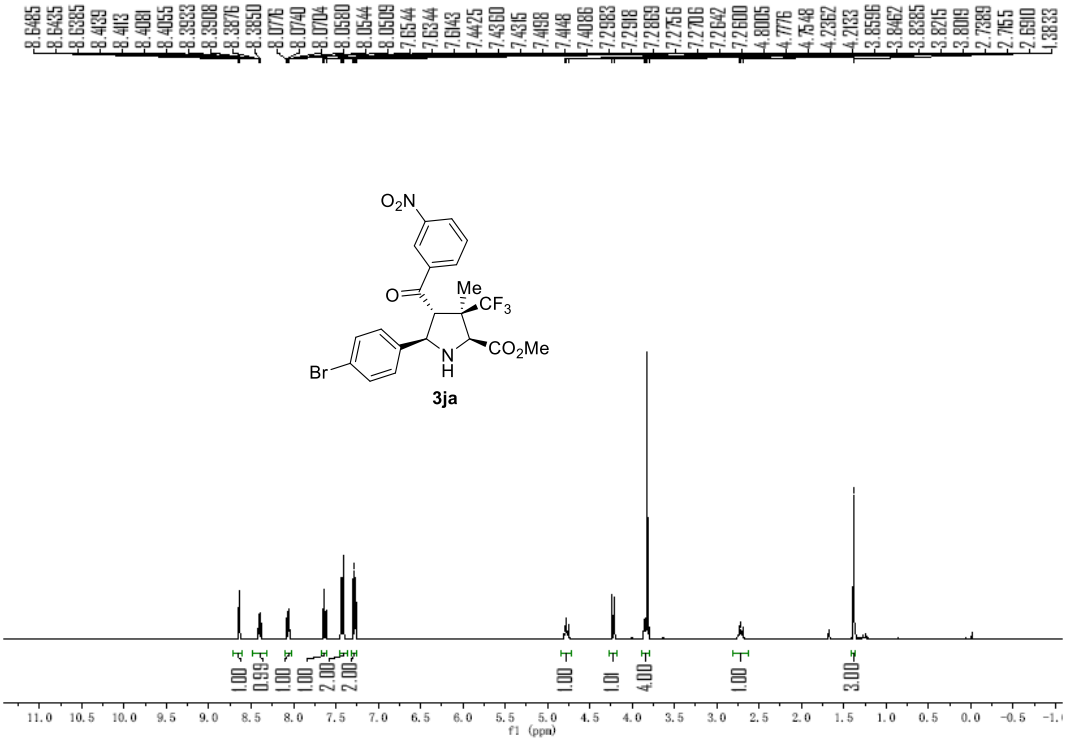
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		13.450	38.376	57.196	50.78	47.76	n.a.
2		15.353	37.194	62.555	49.22	52.24	n.a.
Total:			75.570	119.750	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		13.427	280.395	421.253	98.91	98.48	n.a.
2		15.337	3.093	6.495	1.09	1.52	n.a.
Total:			283.488	427.747	100.00	100.00	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4.2123
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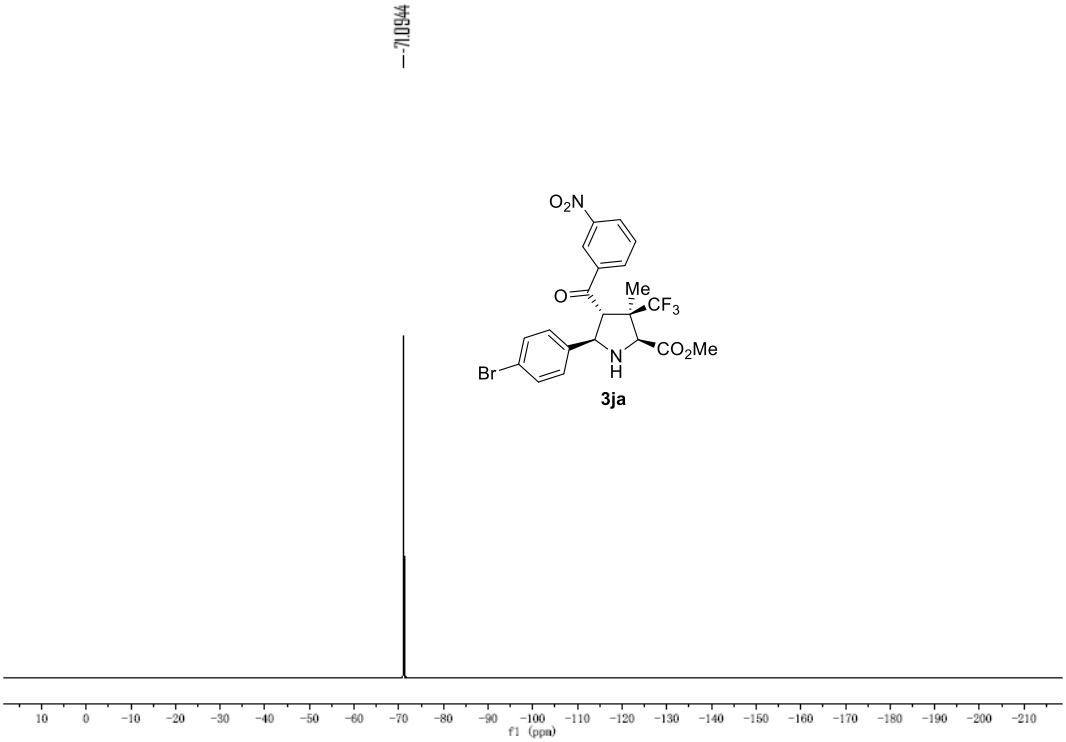
3.8385
3.8215
3.8009
2.7383
2.7165
2.6910
1.3853
O2N
O
Me
CF3
CO2Me
N
H
Br
3ja
1.00
0.99
1.00
1.00
2.00
2.00
1.00
1.01
4.00
1.00
3.00
f1 (ppm)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CF3
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H
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3ja
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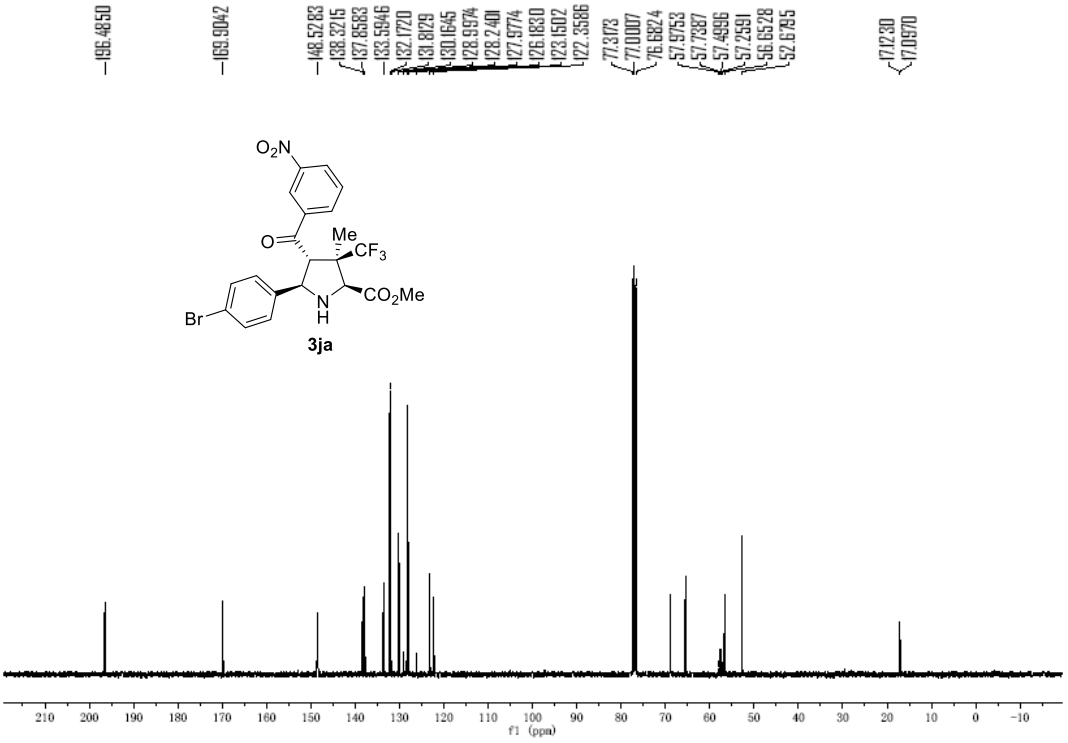
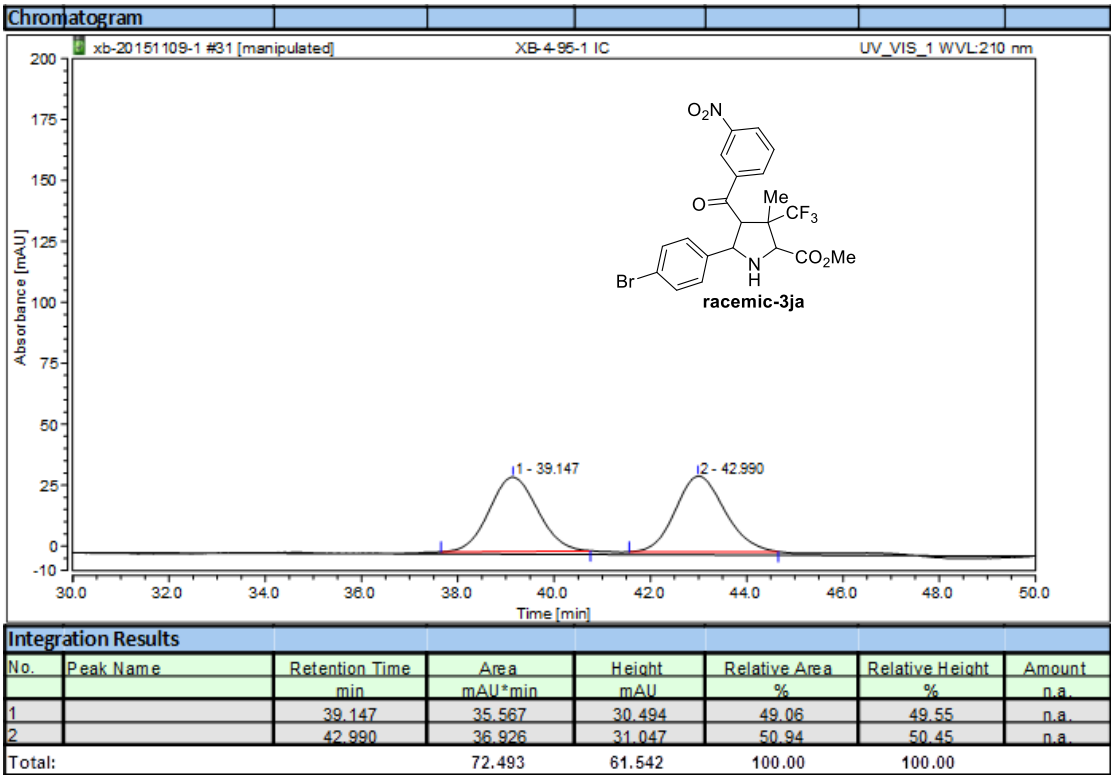
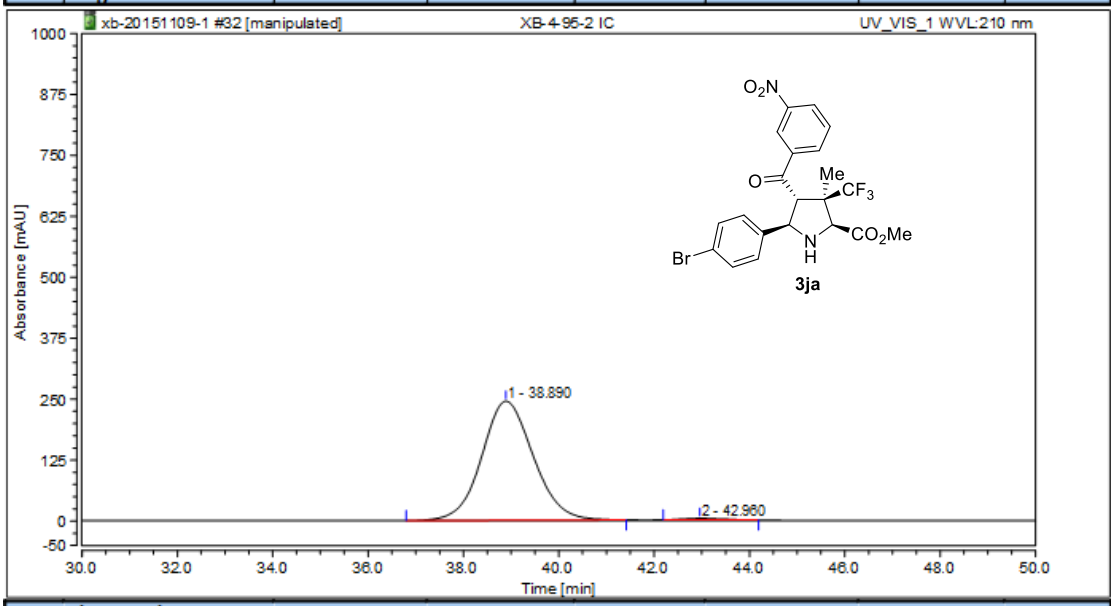




Integration Results

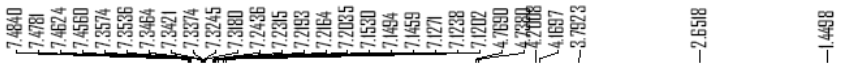
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		39.147	35.567	30.494	49.06	49.55	n.a.
2		42.990	36.926	31.047	50.94	50.45	n.a.
Total:			72.493	61.542	100.00	100.00	

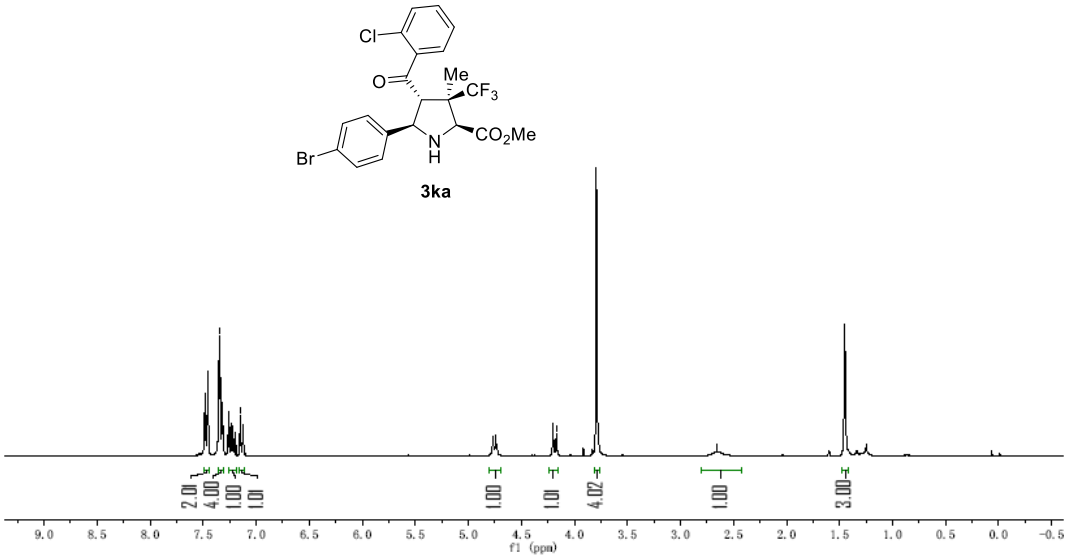
Chromatogram

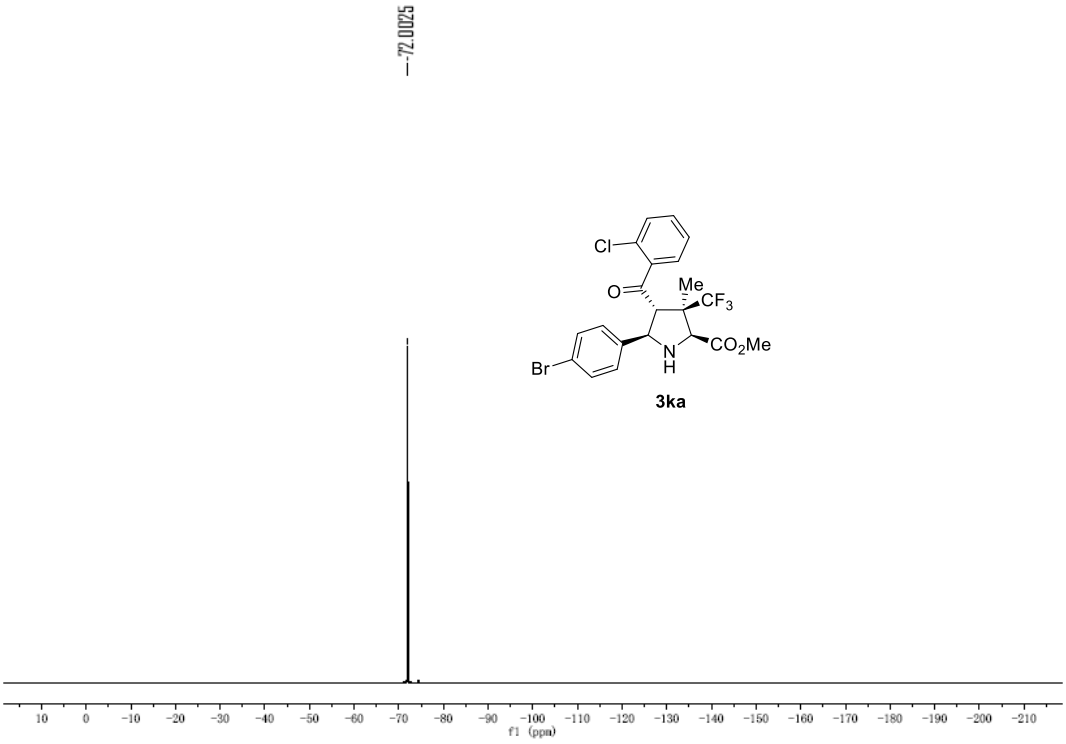


Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		38.890	306.142	244.177	98.99	98.78	n.a.
2		42.960	3.139	3.014	1.01	1.22	n.a.
Total:			309.281	247.191	100.00	100.00	



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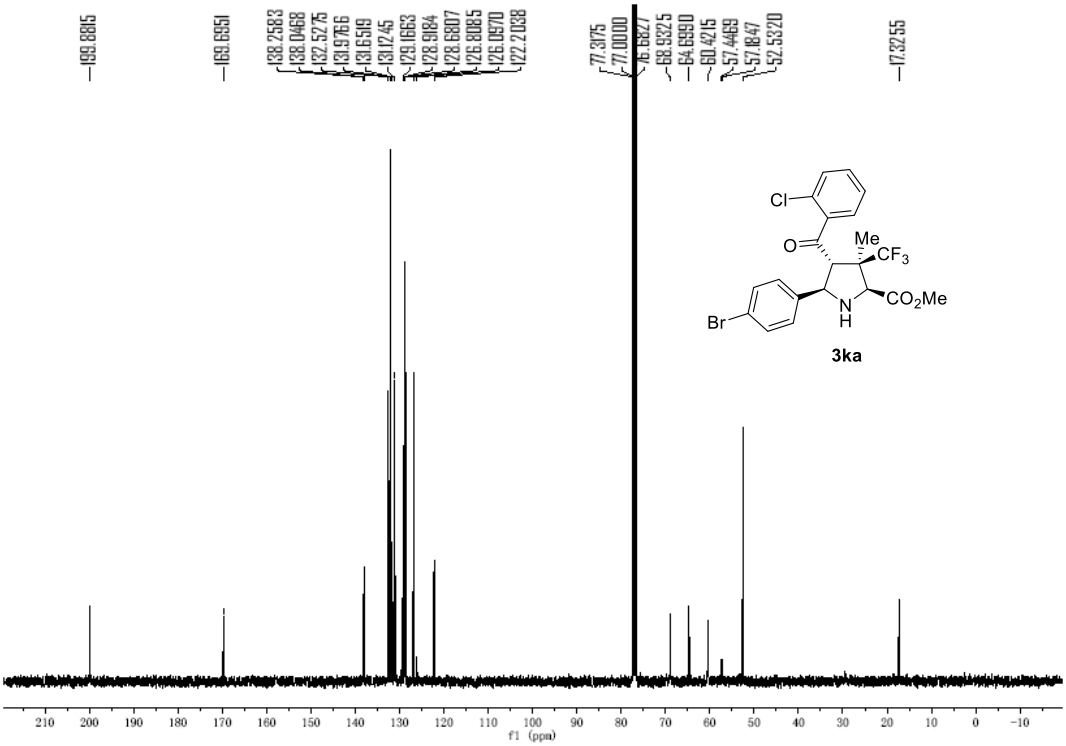
f1 (ppm)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64.6590
60.4215
57.4469
57.1847
52.5320
17.3255
Cl
O
Me
CF3
CO2Me
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H
Br
3ka
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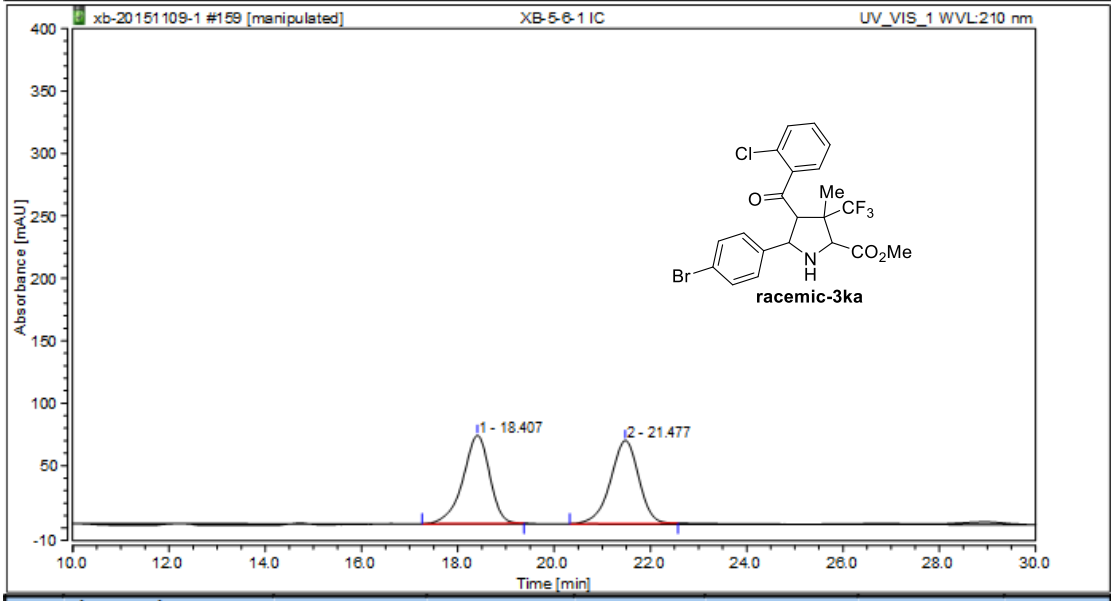
f1 (ppm)

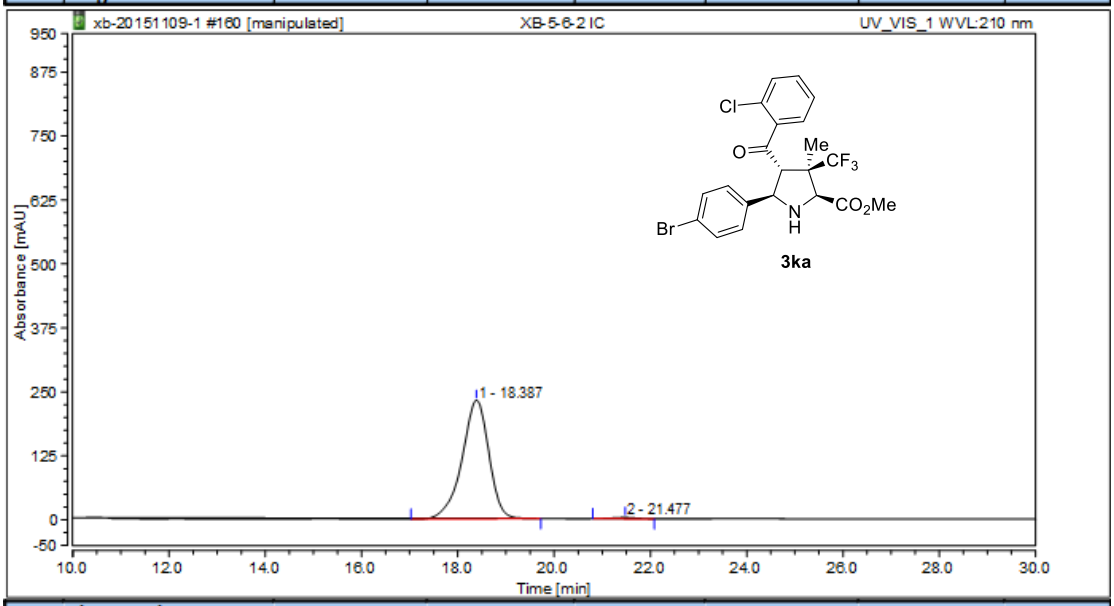
Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		18.407	45.349	70.558	50.24	51.51	n.a.
2		21.477	44.923	66.427	49.76	48.49	n.a.
Total:			90.272	136.985	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		18.387	150.128	231.542	98.90	98.81	n.a.
2		21.477	1.676	2.787	1.10	1.19	n.a.
Total:			151.804	234.329	100.00	100.00	


7.7446
7.7357
7.7280
7.7230
7.7166
7.417
7.4049
7.4001
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7.3839
7.3802
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7.3537
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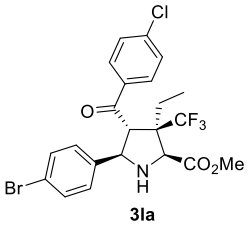
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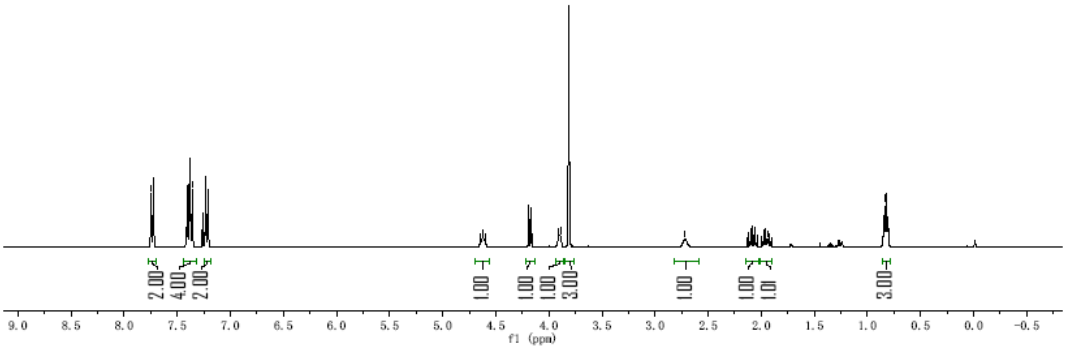
N
H
Br

3la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2.00
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1.00
1.00
3.00
1.00
1.00
1.01
3.00
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f1 (ppm)


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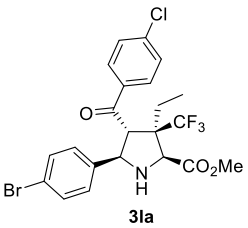
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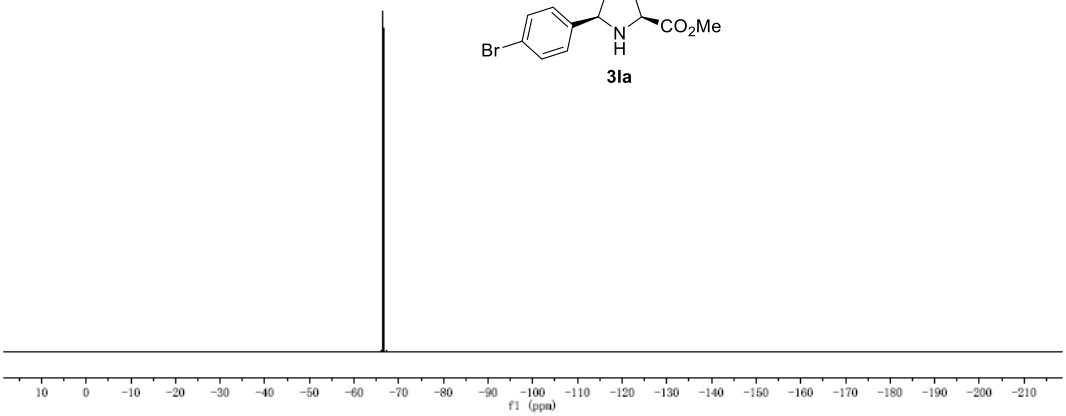
CO2Me
N
H
Br

3la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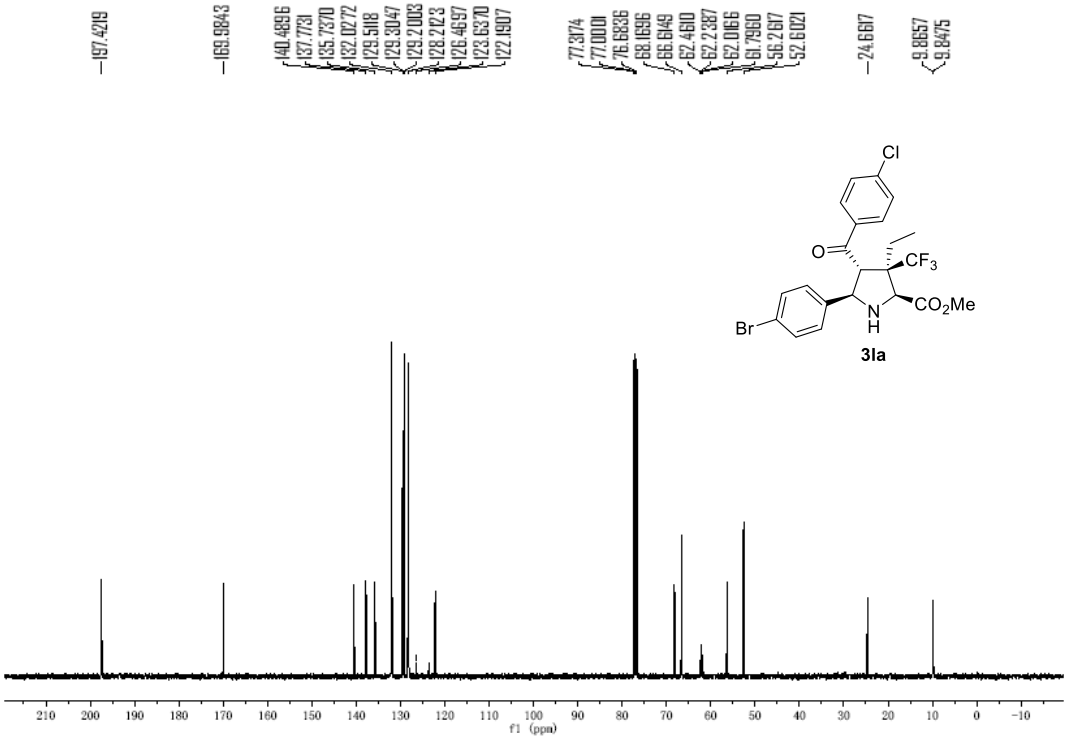
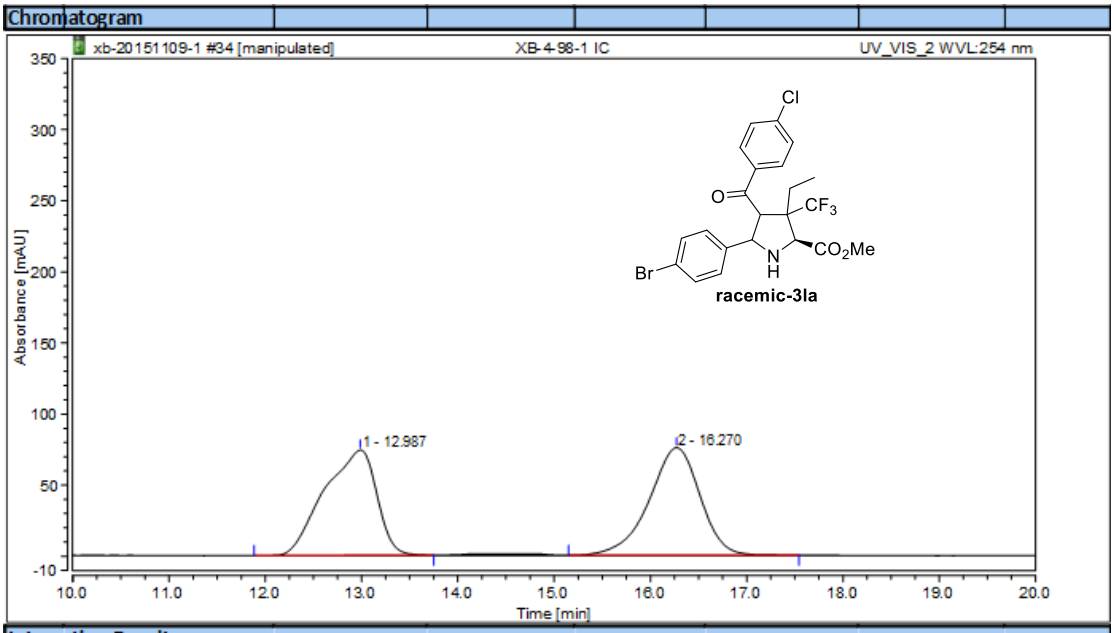
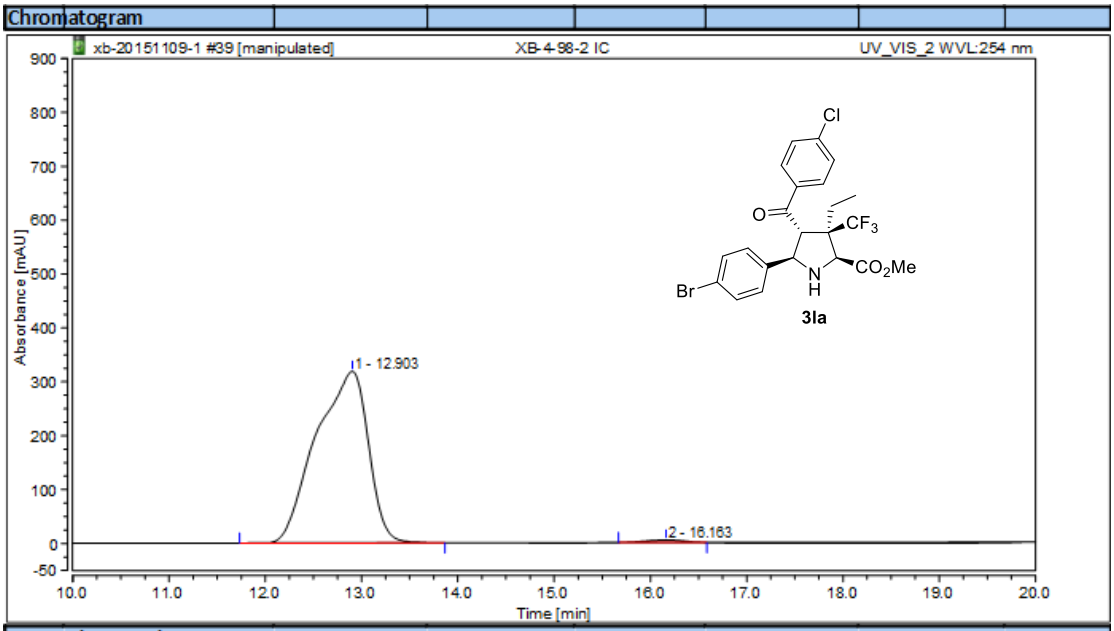
f1 (ppm)





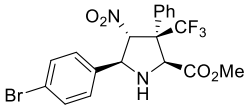
Integration Results

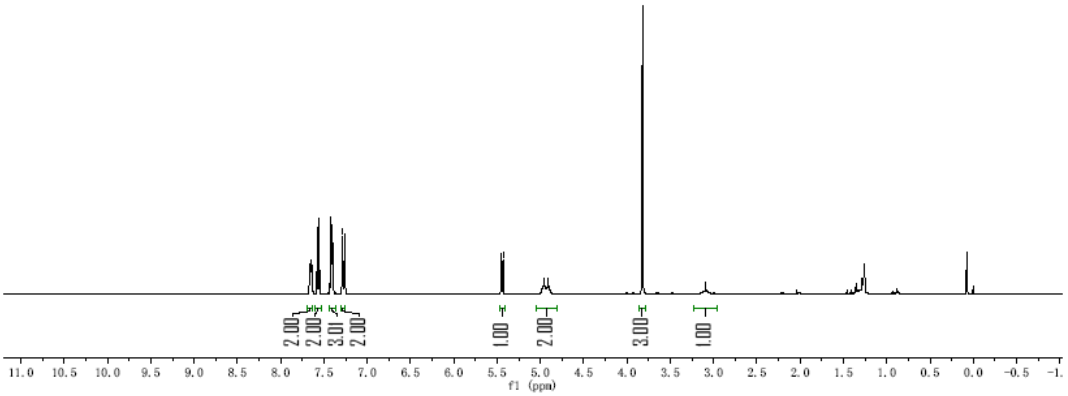
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		12.987	46.767	74.088	50.15	49.50	n.a.
2		16.270	46.479	75.597	49.85	50.50	n.a.
Total:			93.246	149.685	100.00	100.00	

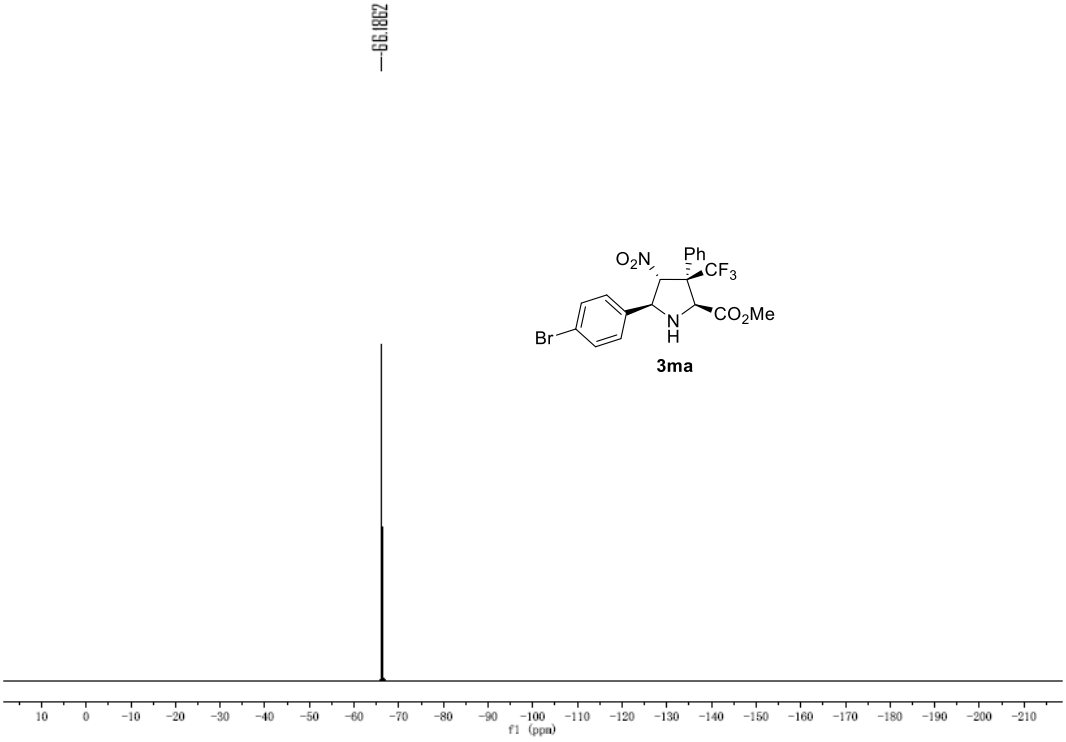


Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		12.903	200.137	318.362	98.84	98.51	n.a.
2		16.163	2.344	4.827	1.16	1.49	n.a.
Total:			202.481	323.189	100.00	100.00	



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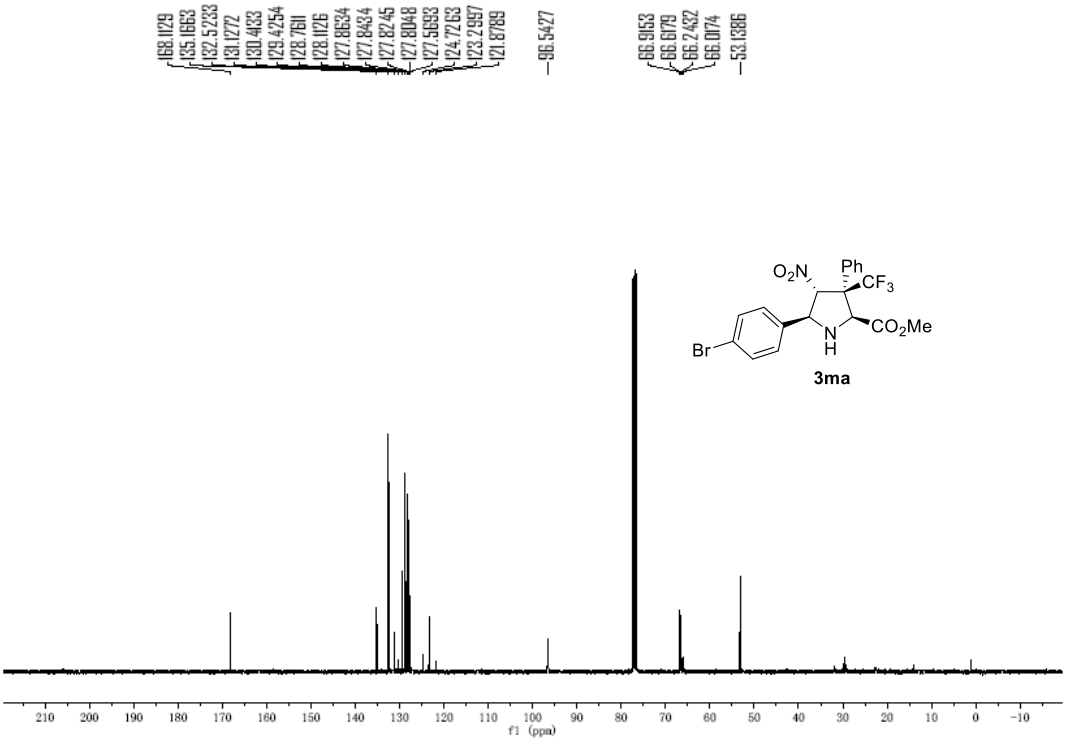
f1 (ppm)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66.0074
53.1386
O2N
Ph
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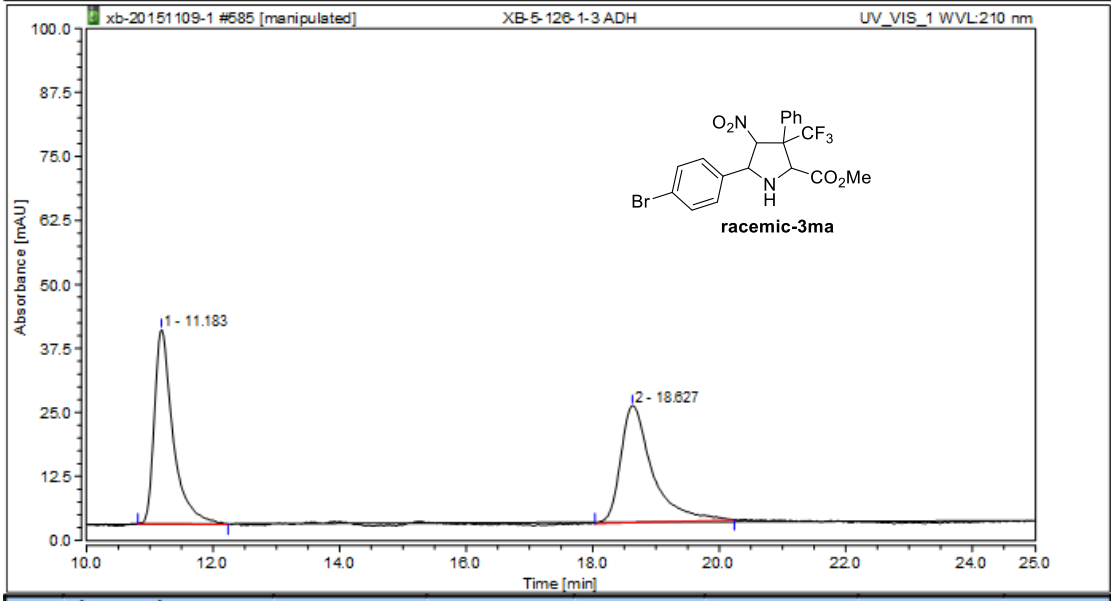
H
Br
3ma
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

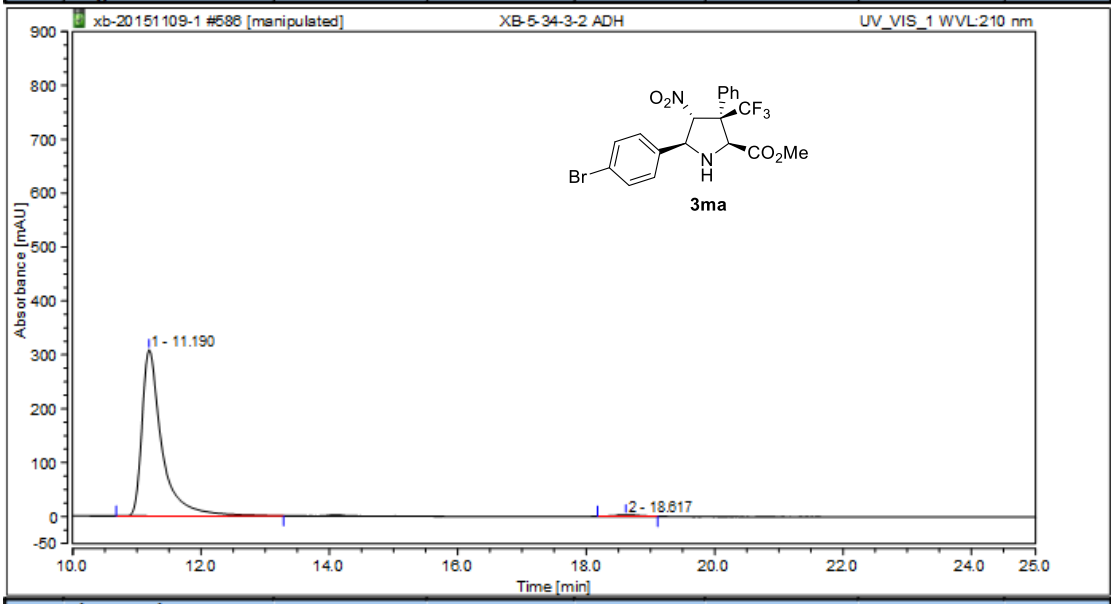
Chromatogram



Integration Results

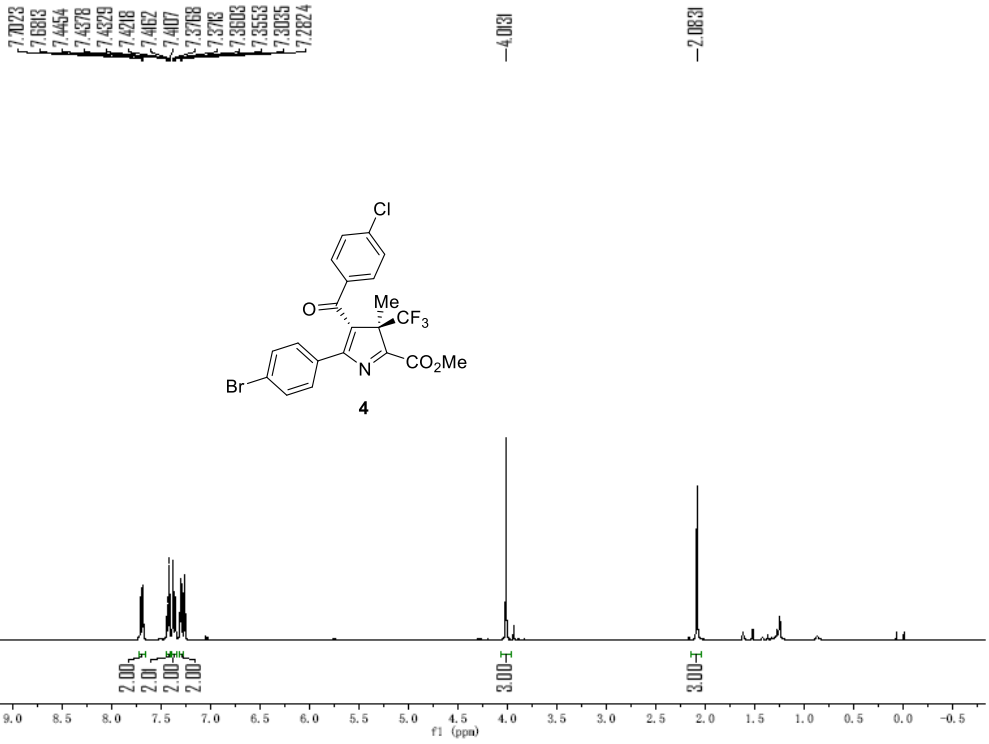
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.183	13.033	38.025	49.45	62.43	n.a.
2		18.627	13.321	22.884	50.55	37.57	n.a.
Total:			26.354	60.909	100.00	100.00	

Chromatogram



Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		11.190	111.038	308.620	98.91	99.12	n.a.
2		18.617	1.227	2.742	1.09	0.88	n.a.
Total:			112.265	311.362	100.00	100.00	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Cl
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Br
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2.01
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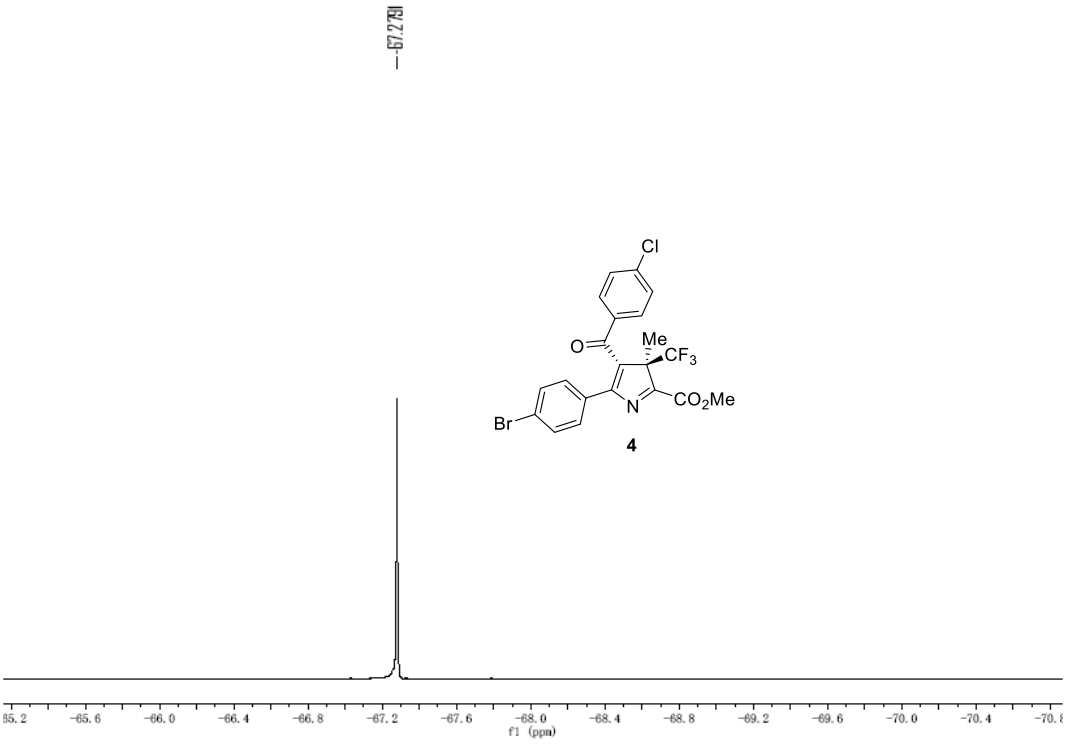
2.00
3.00
3.00
f1 (ppm)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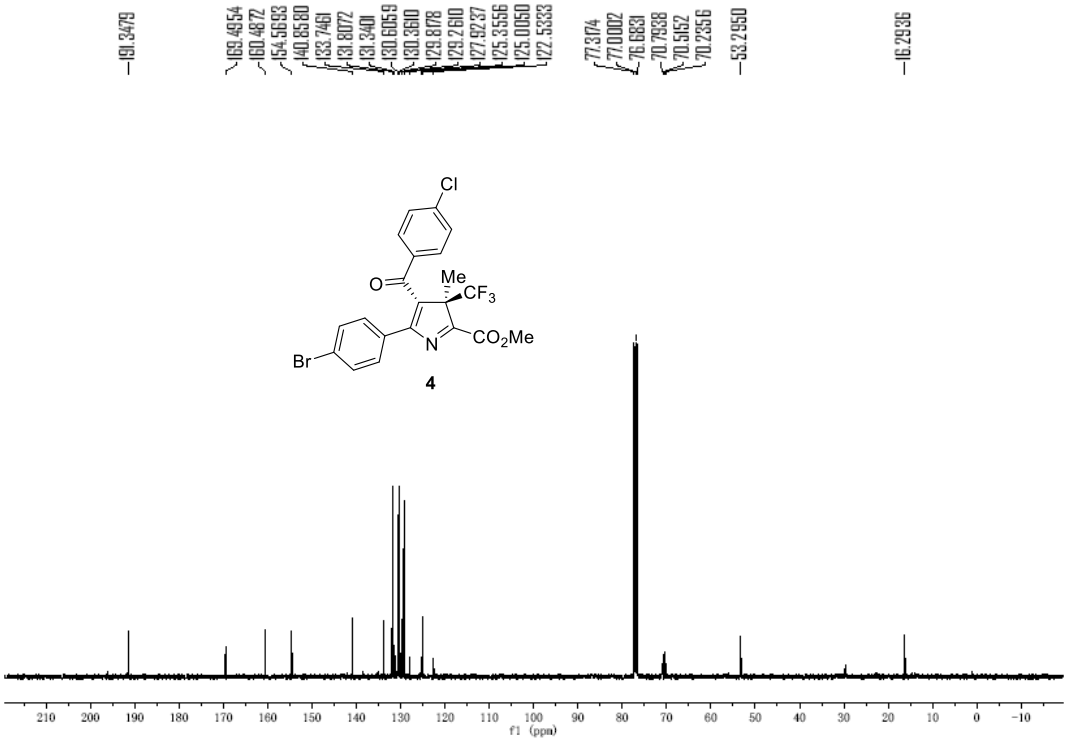
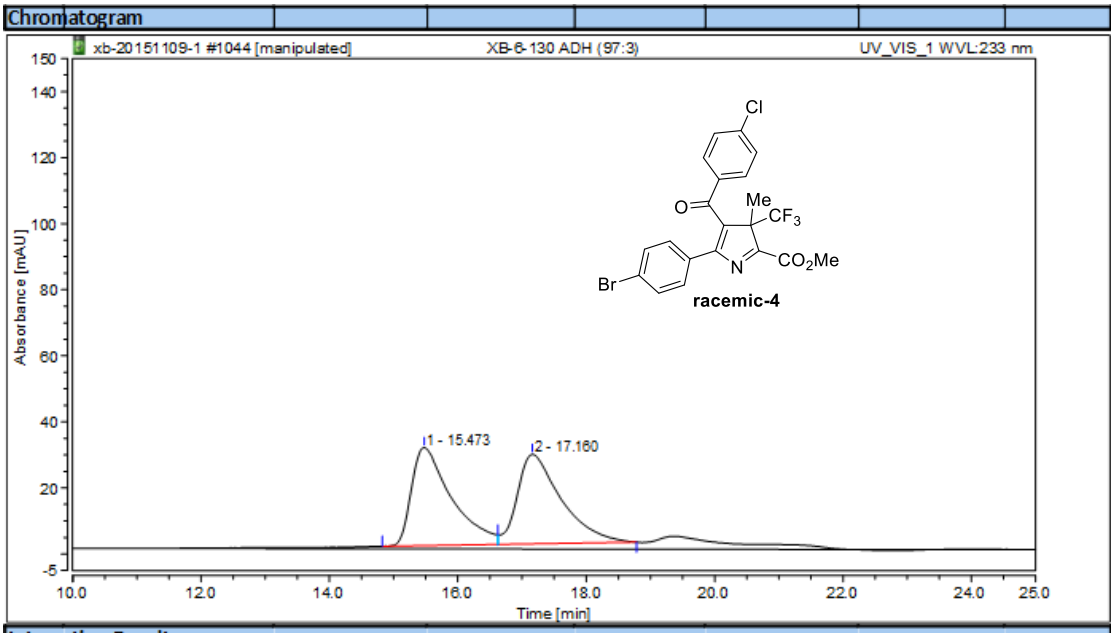
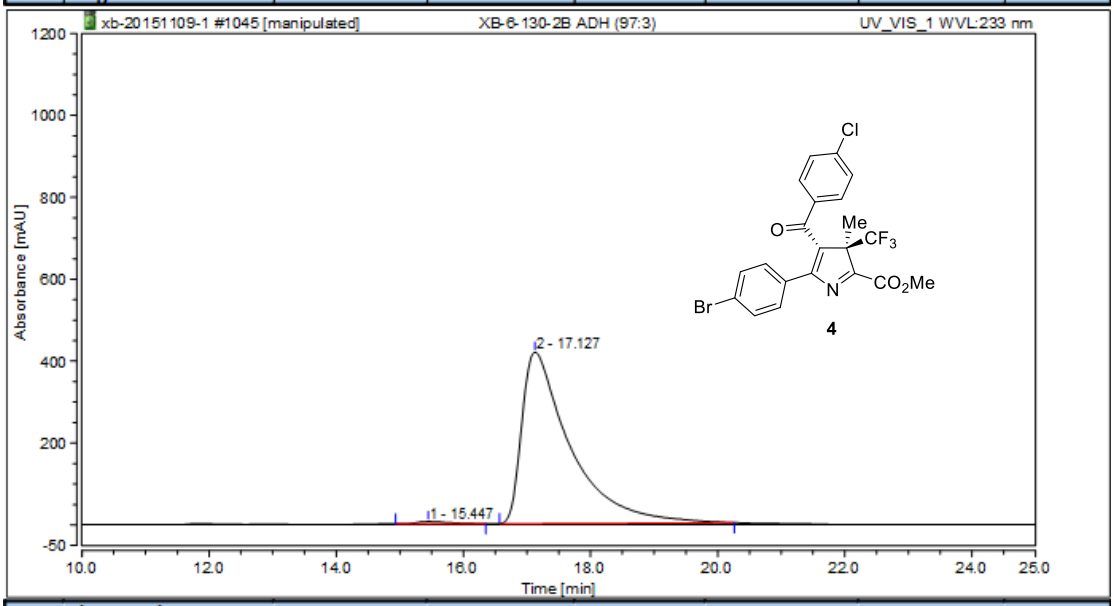




Integration Results

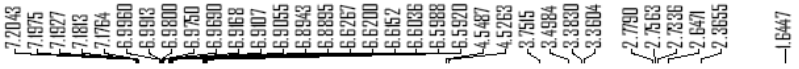
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		15.473	21.313	29.651	49.84	52.26	n.a.
2		17.160	21.454	27.087	50.16	47.74	n.a.
Total:			42.767	56.738	100.00	100.00	

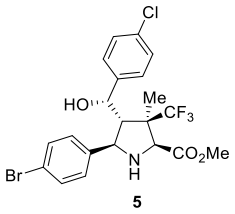
Chromatogram

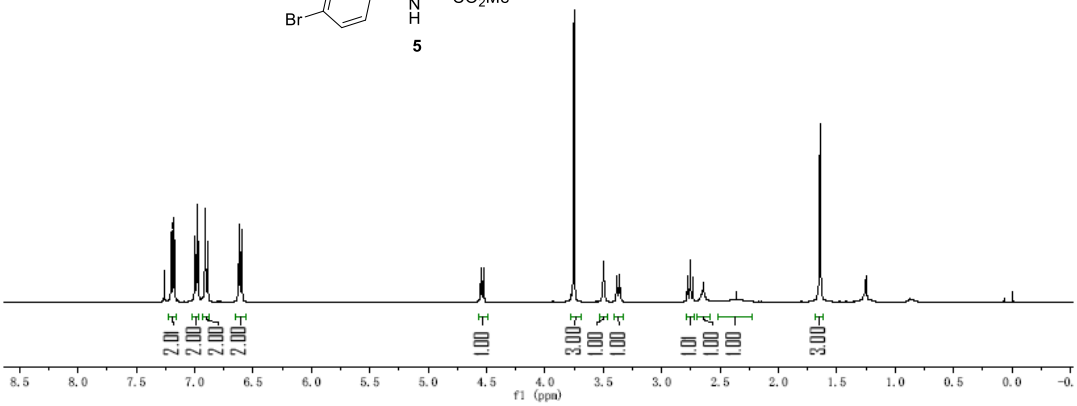


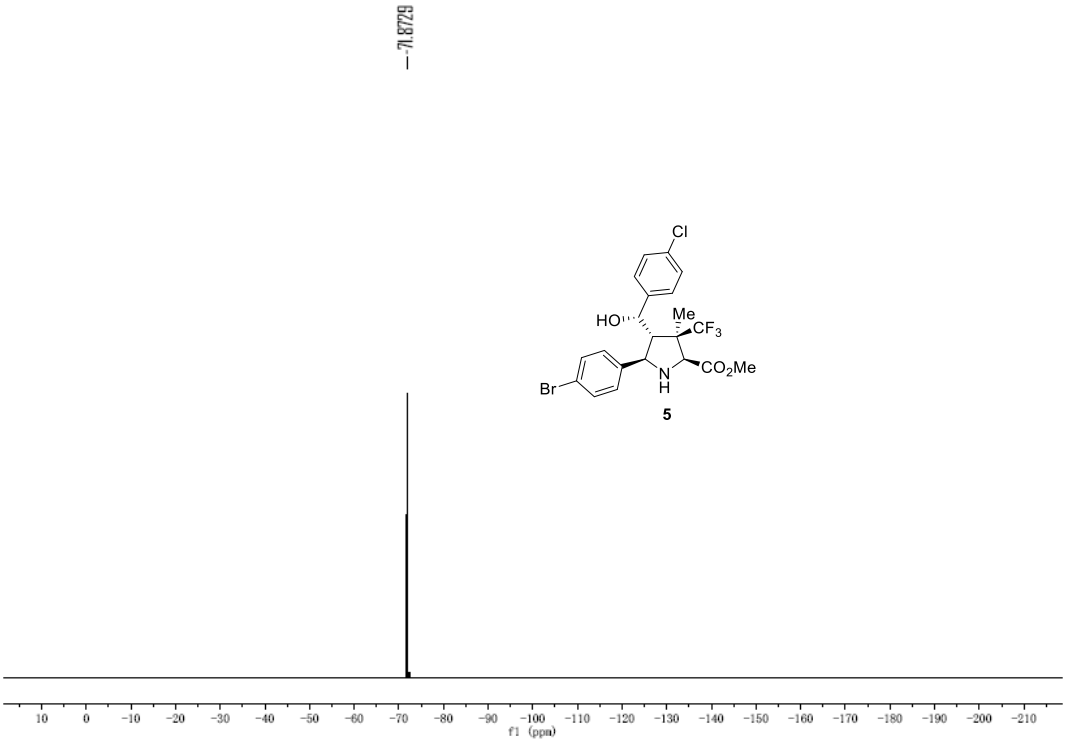
Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		15.447	3.672	6.012	0.98	1.42	n.a.
2		17.127	369.601	418.314	99.02	98.58	n.a.
Total:			373.272	424.326	100.00	100.00	





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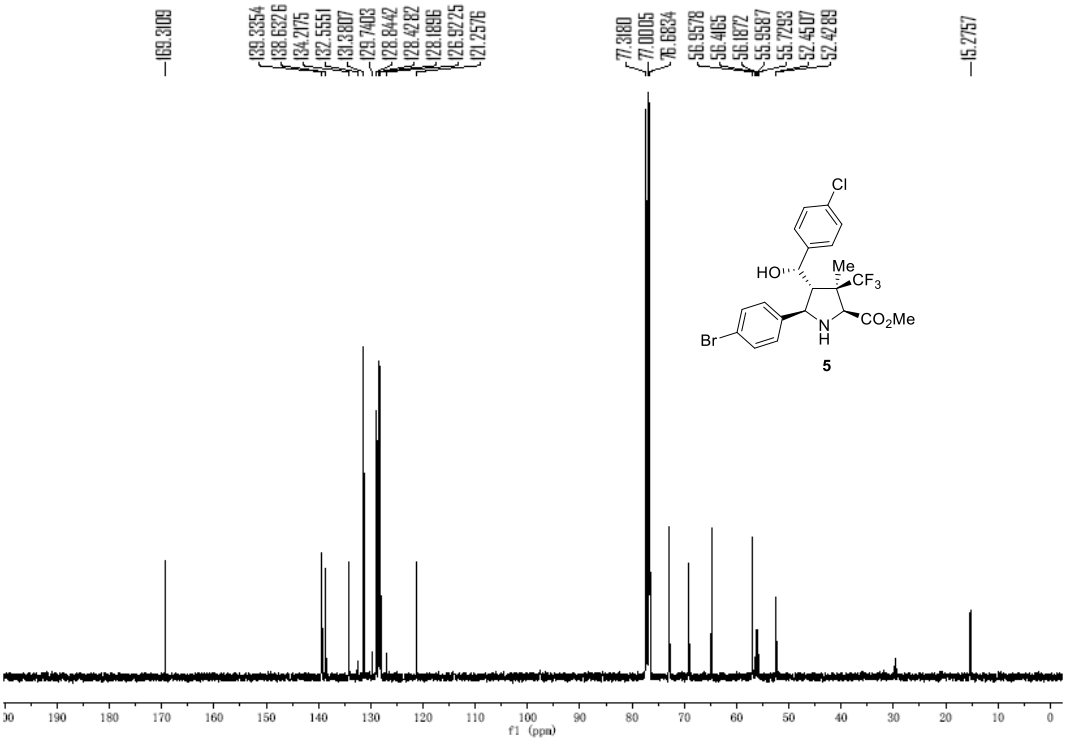
f1 (ppm)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55.9587
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52.4289
15.2757
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CF3
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H
Br
5
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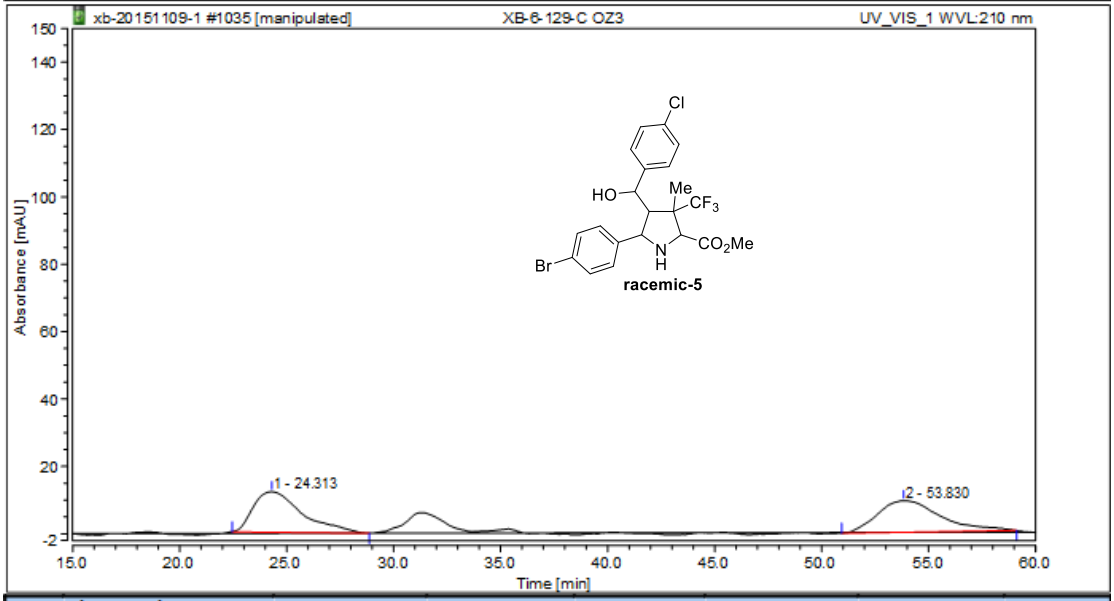
f1 (ppm)

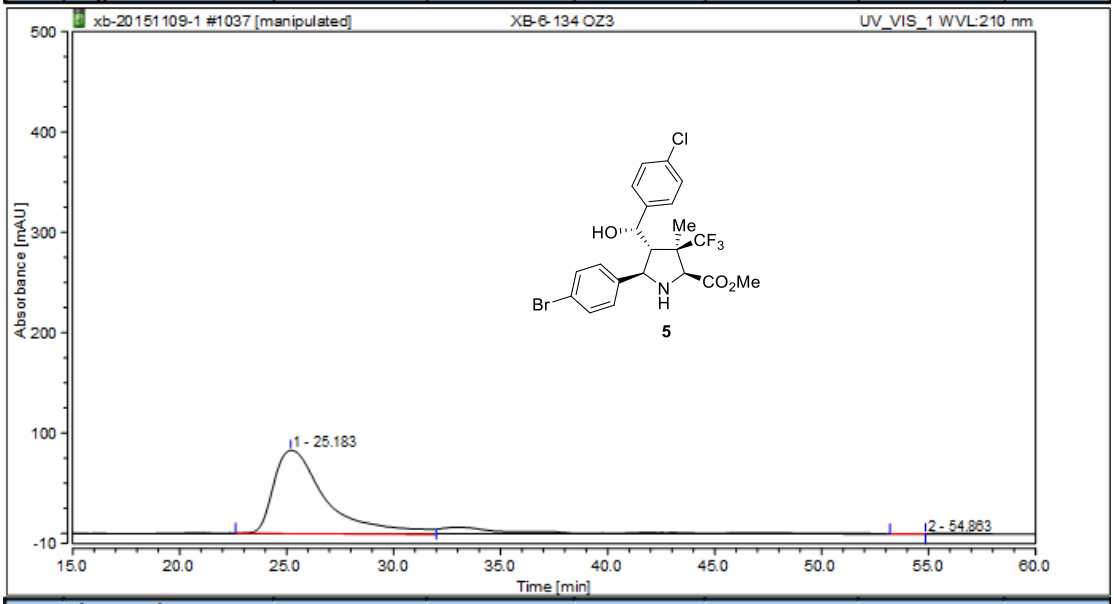
Chromatogram



Integration Results

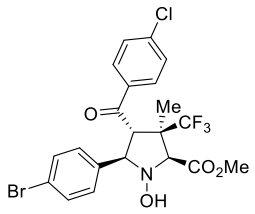
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		24.313	31.826	12.055	49.87	56.15	n.a.
2		53.830	31.996	9.415	50.13	43.85	n.a.
Total:			63.822	21.470	100.00	100.00	

Chromatogram

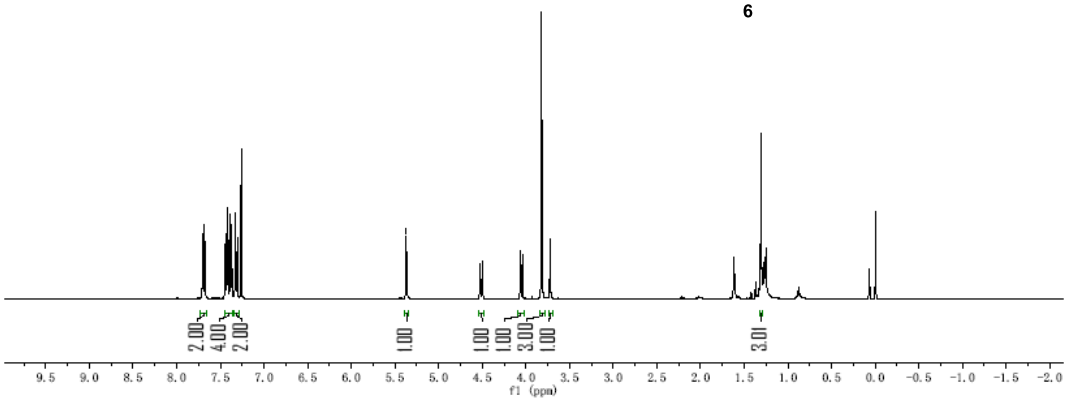


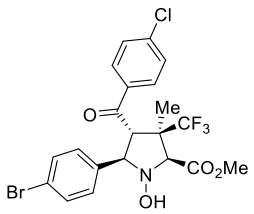
Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		25.183	235.181	82.872	99.79	100.00	n.a.
2		54.863	0.489	0.000	0.21	0.00	n.a.
Total:			235.670	82.872	100.00	100.00	


Cl
O
Me
CF3
CO2Me
N
OH
Br

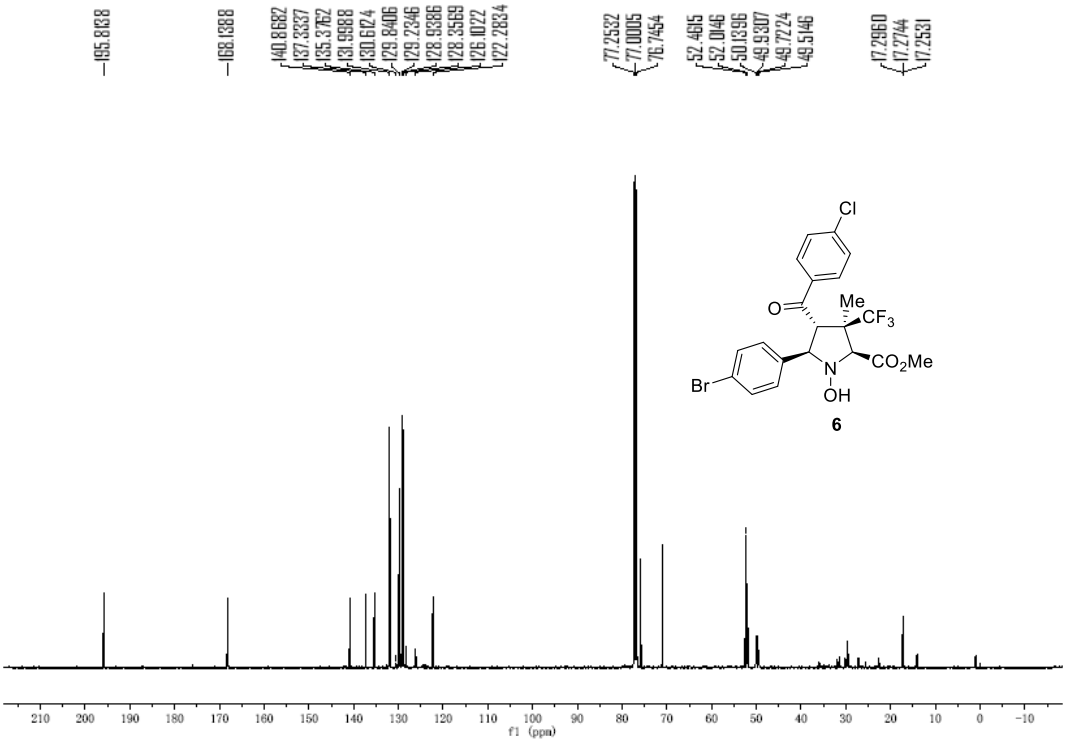
6

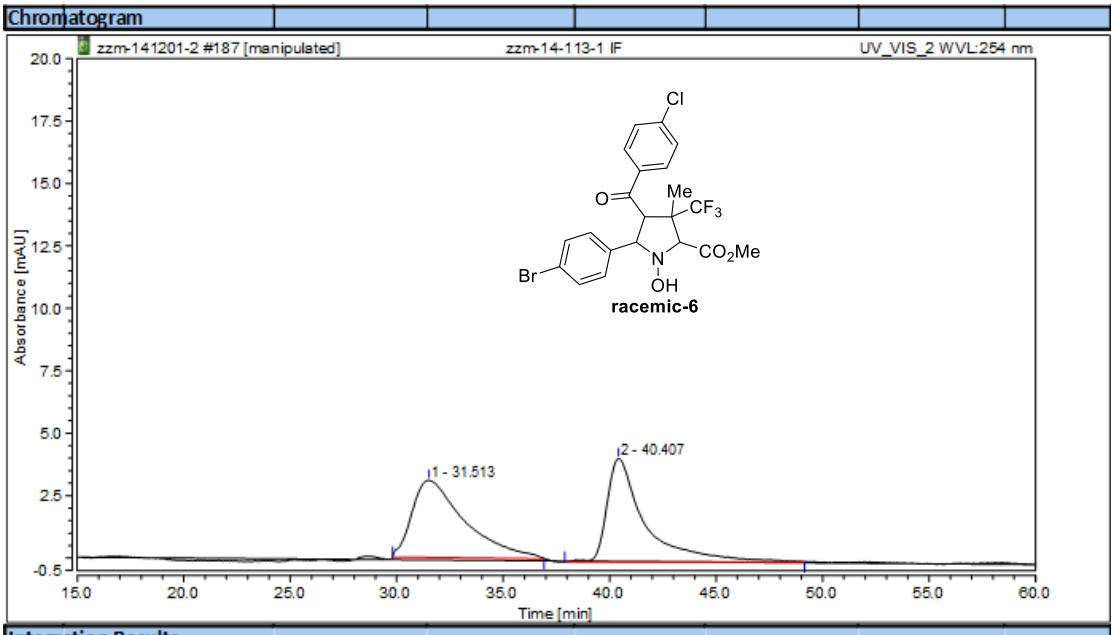

2.00
4.00
2.00
1.00
1.00
1.00
3.00
1.00
3.01
f1 (ppm)


Cl
O
Me
CF3
CO2Me
N
OH
Br

6

f1 (ppm)

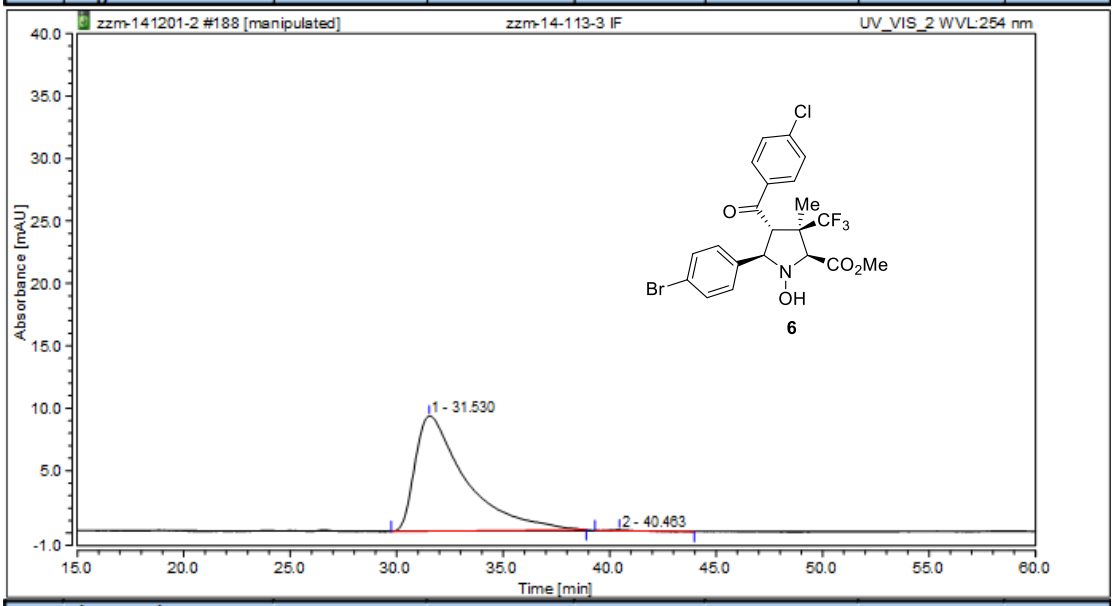




Integration Results

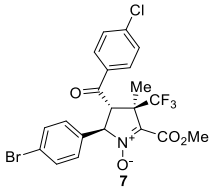
No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		31.513	8.795	3.089	50.69	42.73	n.a.
2		40.407	8.556	4.140	49.31	57.27	n.a.
Total:			17.352	7.229	100.00	100.00	

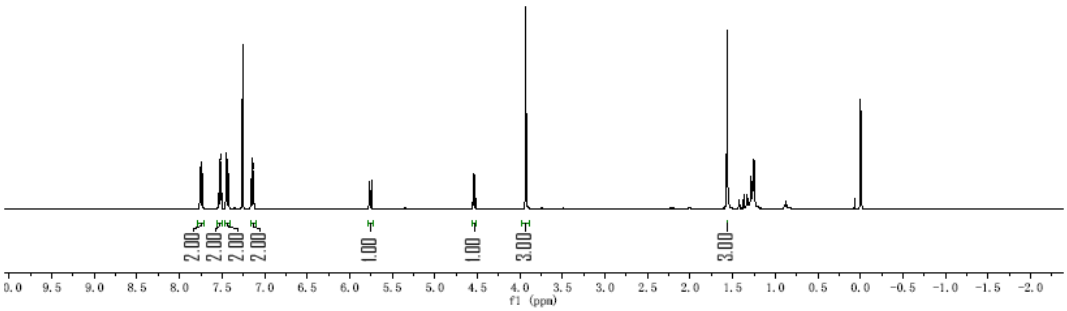
Chromatogram

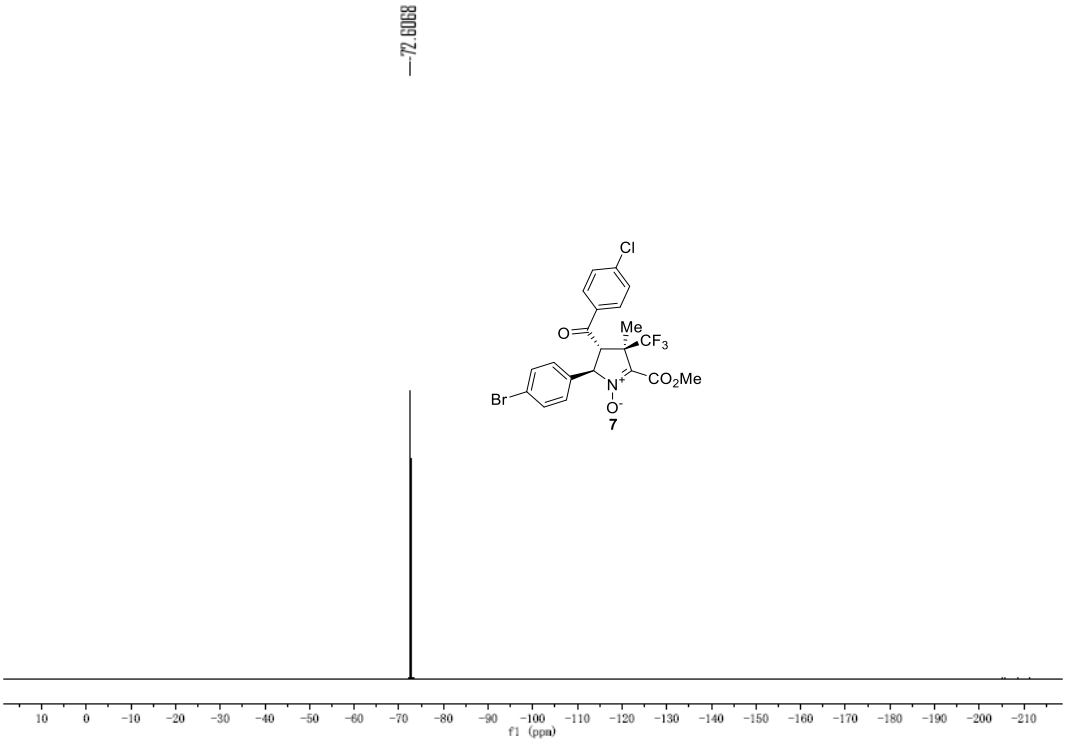


Integration Results

No.	Peak Name	Retention Time	Area	Height	Relative Area	Relative Height	Amount
		min	mAU*min	mAU	%	%	n.a.
1		31.530	25.310	9.225	99.60	98.98	n.a.
2		40.463	0.101	0.095	0.40	1.02	n.a.
Total:			25.410	9.319	100.00	100.00	



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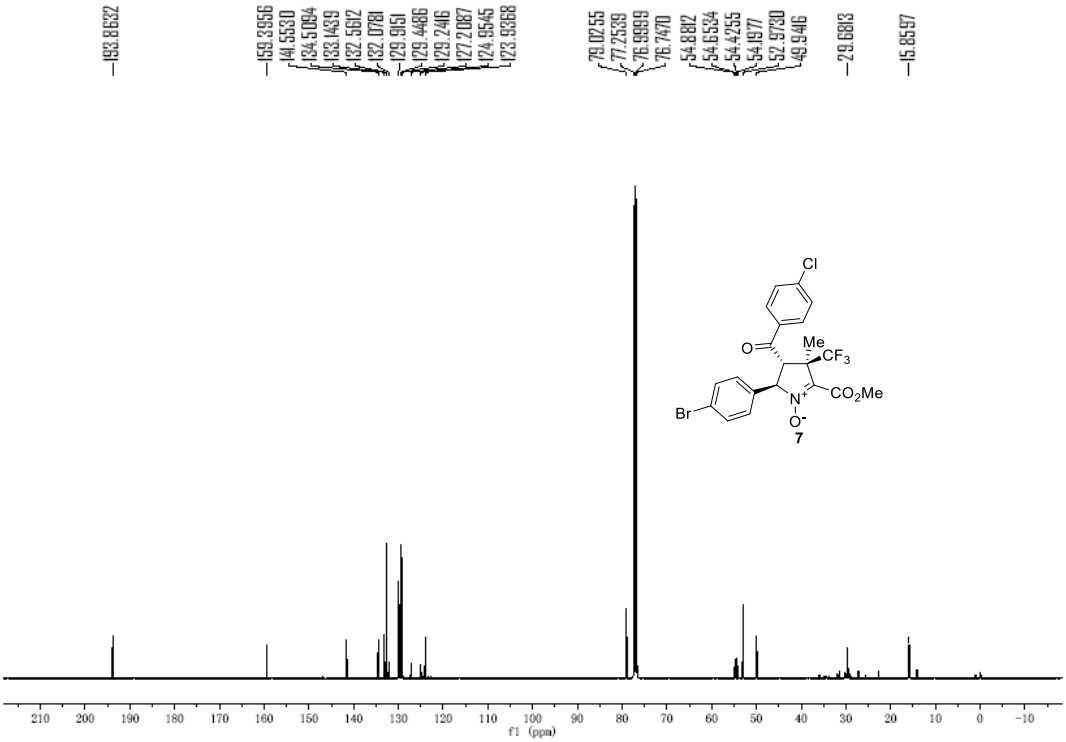
Cl
O
Me
CF3
CO2Me
N+
O-
Br
7
10 0 -10 -20 -30 -40 -50 -60 -70 -80 -90 -100 -110 -120 -130 -140 -150 -160 -170 -180 -190 -200 -210
f1 (ppm)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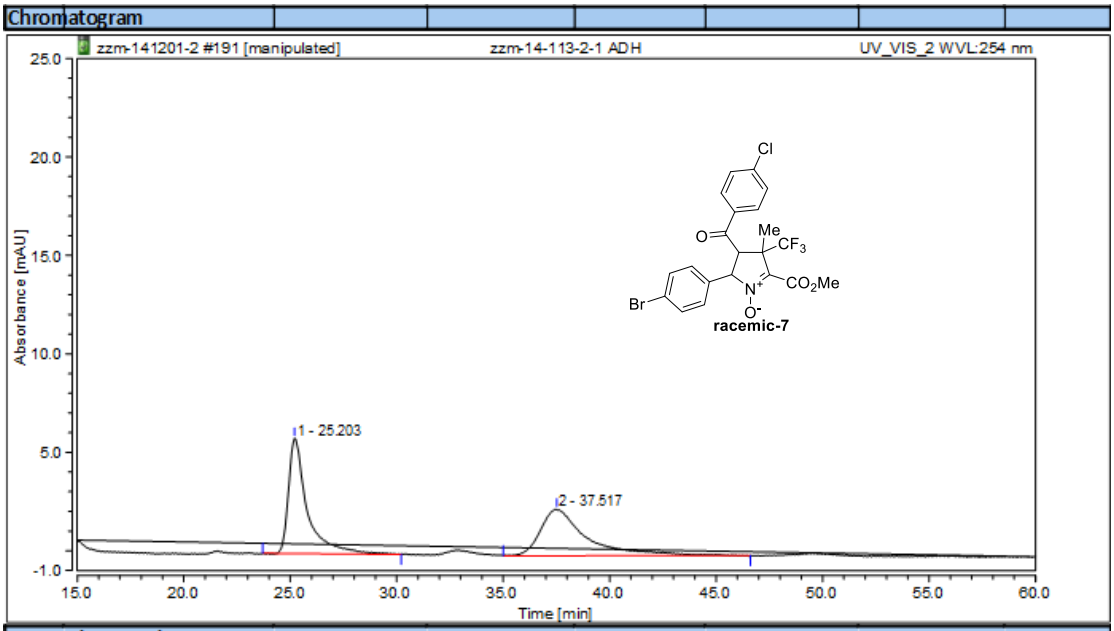
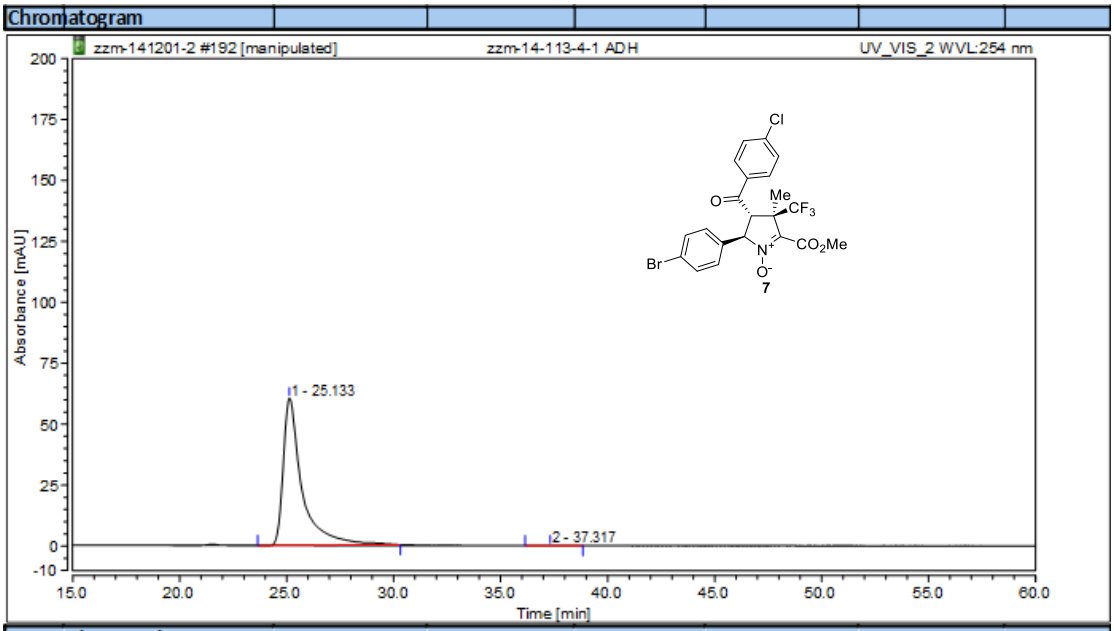
159.3956
141.5530
134.5094
133.1439
132.5612
132.0781
129.9151
129.4486
129.2246
127.2087
124.9545
123.9368
79.0255
77.2539
76.9899
76.7470
54.8812
54.6534
54.4255
54.1977
52.9730
49.9446
29.6813
15.8597
Cl
O
Me
CF3
CO2Me
N+
O-
Br
7
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 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		25.203	5.987	5.868	50.42	71.18	n.a.
2		37.517	5.887	2.376	49.58	28.82	n.a.
Total:			11.874	8.244	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		25.133	61.459	60.457	99.94	99.90	n.a.
2		37.317	0.035	0.062	0.06	0.10	n.a.
Total:			61.495	60.519	100.00	100.00	

7. References

(1) (a) H. Kawai, S. Okusu, E. Tokunaga, H. Sato, M. Shiro, N. Shibata, *Angew. Chem. Int. Ed.* **2012**, *51*, 4959−4962. (b) H. Kawai, Z. Yuan, T. Kitayama, E. Tokunaga,

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(2) (a) S. Cabrera, R. G. Arrayás, J. C. Carretero, *J. Am. Chem. Soc*, **2005**, *127*, 16394−16395. (b) C. Nájera, M. de Gracia Retamosa, J. M. Sansano, *Org. Lett.* **2007**, *9*, 4025−4028. (c) A. López-Pérez, J. Adrio, J. C. Carretero, *J. Am. Chem. Soc*, **2008**, *130*, 10084−10085.

(3) J.-R. Gao, H. Wu, B. Xiang, W.-B. Yu, L. Han, Y.-X. Jia, *J. Am. Chem. Soc*, **2013**, *135*, 2983−2986.