Electronic supporting information

N-Protecting Group Tuning the Enantioselectivity in Strecker Reactions of Trifluoromethyl Ketimines to Synthesize Quaternary α-Trifluoromethyl Amino Nitriles by Ion Pair Catalysis

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Contents

I. General information

All solvents used in the reaction were commercial available without further purification. Purification of reaction products was carried out by flash chromatography using silica gel (300 – 400 mesh). TLC was visualized by UV fluorescence (254 nm) or $KMnO_4$, phosphomolybdic acid. The ^1H NMR spectra were recorded on a Bruker 400 or an Agilent 400 (400 MHz). All chemical shifts (δ) were given in ppm. Data were reported as follows: chemical shift, intergration, multiplicity (s = single, d = doublet, t = triplet, q = quartet, br = broad, m = multiplet) and coupling constants (Hz). ^{13}C NMR spectra were recorded on a Bruker 400 (100 MHz) or an Agilent 500 (126 MHz). ^{19}F NMR spectra were recorded on an Agilent 400 (376 MHz). ^{31}P NMR spectra were recorded on an Agilent 400 (163 MHz). High-resolution mass spectra (HRMS) were recorded on a Bruker APEXIII 7.0 Tesla ESI – FT mass spectrometer or an Agilent TOF/LC-MS 1260-6230 mass spectrometer. Melting points were determined on a SGW X-4 melting point and were uncorrected. Optical rotations were measured on an Anton Paar MCP 5500 Polarimeter at λ = 589 nm. IR spectra were recorded on a Perkin-Elmer 983G instrument. All bifunctional phosphine catalysts were synthesized according to procedures reported previously.[1,2]

II. General experimental procedure

2.1 General procedure for the preparation of ketimines

To a solution of corresponding trifluoromethyl ketone (2.0 mmol, 1.0 equiv) in toluene (5.0 mL) was added *N*-Boc-imino-(triphenyl)-phosphorane (4.0 mmol, 2.0 equiv.). The system was stirred at reflux until the completion of reaction (monitored by TLC). Then the system was cooled down to room temperature and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography to give corresponding *N*-Boc ketimines. The *N*-PMP ketimines were prepared according to the reported literature.[3,7]

2.2 General procedure for the asymmetric Strecker reaction

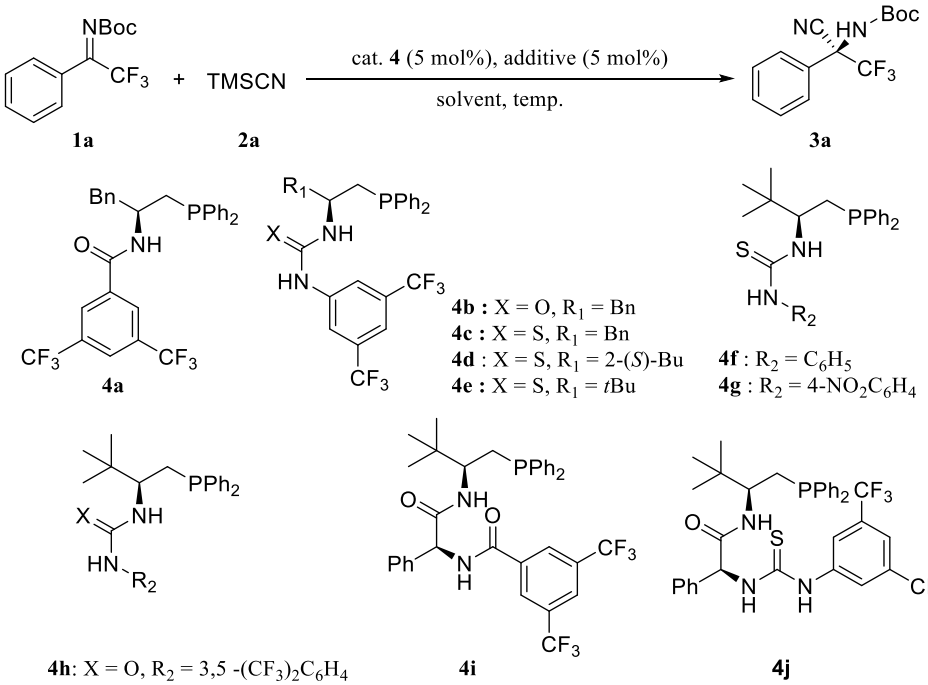
General procedure for the asymmetric Strecker reaction of *N*-PMP ketimines

To a solution of organophosphine catalyst (0.005 mmol, 5 mol%) in dichloromethane (1.0 mL) was added methyl acrylate (0.005 mmol, 5 mol%). The system was stirred at room temperature for ten minutes, then TMSCN (0.2 mmol) was added. Five minutes later the system was cooled to -20 °C and after another ten minutes corresponding ketimine (0.1 mmol) was added. After the completion of reaction (monitored by TLC) the system was allowed to warm to room temperature and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography to give the pure product.

General procedure for the asymmetric Strecker reaction of *N*-Boc ketimines

To a solution of organophosphine catalyst (0.005 mmol, 5 mol%) in dichloromethane (1.0 mL) was added methyl acrylate (0.005 mmol, 5 mol%). The system was stirred at room temperature for ten minutes and then corresponding ketimine (0.1 mmol) was added. Ten minutes later the system was cooled to -72 °C and after another ten minutes TMSCN (0.2 mmol) was added. After the completion of reaction (monitored by TLC) the system was allowed to warm to room temperature and the solvent was removed in vacuum. The residue was purified by silica gel column chromatography to give the pure product.

2.3 Optimization of the reaction conditions for the reaction of *N*-Boc ketimine[a]



Entry	Cat.	Temp./°C	Solvent	Additive	t/h	yield/%[b]	ee/%[c]
1	**4a**	20	DCM	Methyl acrylate	0.5	85	0
2	**4b**	20	DCM	Methyl acrylate	0.5	86	3
3	**4c**	20	DCM	Methyl acrylate	0.5	87	2
4	**4d**	20	DCM	Methyl acrylate	0.5	91	19
5	**4e**	20	DCM	Methyl acrylate	0.5	93	29
6	**4f**	20	DCM	Methyl acrylate	0.5	90	16
7	**4g**	20	DCM	Methyl acrylate	0.5	90	18
8	**4h**	20	DCM	Methyl acrylate	0.5	93	23
9	**4e**	0	DCM	Methyl acrylate	1	89	43
10	**4e**	-20	DCM	Methyl acrylate	1	94	60
11	**4e**	-60	DCM	Methyl acrylate	2	89	70
12	**4e**	-72	DCM	Methyl acrylate	2	91	85
13	**4e**	-72	Toluene	Methyl acrylate	2	88	46
14	**4e**	-72	Et_2O	Methyl acrylate	2	89	39
15[d]	**4e**	-72	DCM	Methyl acrylate	3	90	82
16	**4i**	-72	DCM	Methyl acrylate	3	86	35
17	**4j**	-72	DCM	Methyl acrylate	3	89	30

[a] Reaction conditions: 0.10 mmol 1'a, 0.20 mmol **2**, methyl acrylate (5 mol%), chiral phosphine (5 mol%), DCM (1.0 mL). [b] Isolated yield. [c] The ee value was determined by chiral HPLC analysis. [d] Chiral phosphine (1 mol%) was used.

2.4 Procedure for transformations of α-trifluoromethyl-α-amino nitriles

2.4.1 Procedure for the preparation of **5a**

Hydrogen chloride gas was introduced into a solution of **3'a** (15.1 mg, 0.05 mmol, 85% ee) in methanol (1.0 mL) at 0 °C until the starting material consumed. The resulting

mixture was stirred overnight and then the mixture was concentrated under reduced pressure, and saturated aqueous sodium hydrogen carbonate solution was added to adjust pH 9. The aqueous phase was extracted with dichloromethane (3 × 1.0 mL), and then the combined organic layers were washed with water and brine. Anhydrous Na_2SO_4 was added to the mixture, followed by a filtration. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give **5a** (9.0 mg) in 90% yield as colorless oil.

2.4.2 Procedure for the preparation of **5b**[4]

To a stirred solution of **3'a** (30.0 mg, 0.1 mmol, 85% ee) in acetone (2.0 mL) was added Na_2CO_3 (53.0 mg, 0.5 mmol). Then 30% H_2O_2 aq. (2.0 mL) was added dropwise to the suspension at 0 °C. The resulting mixture was stirred at room temperature overnight, then water was added and the resulting mixture was extracted with ethyl acetate (3 × 5.0 mL). The combined organic layers were washed with water and brine and dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 3/1) to give **5b** (28.0 mg) in 88% yield as colorless oil.

2.4.3 Procedure for the preparation of **5c**

To a stirred solution of **3'a** (300.2 mg, 1.0 mmol, 85% ee) and $NiCl_2$•$6H_2O$ (237.7 mg, 1.0 mmol) in methanol (18.0 mL) was added $NaBH_4$ (264.8 mg, 7.0 mmol) in portions at 0 °C over 10 minutes. The resulting mixture was stirred for 3h at 0 °C until **3'a** completely disappeared (monitored by TLC). The reaction was quenched by the addition of saturated NH_4Cl aqueous solution (2.0 mL), and the resulting mixture was stirred at room temperature until the generation of gas ceased. Anhydrous Na_2SO_4 was added to the mixture, followed by a filtration with diatomite. The filtrate was concentrated under reduced pressure and the residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1-1/1) to give **5c** (278.9 mg) in 92% yield as a white solid.

2.4.4 Procedure for the preparation of **5d**

To a stirred solution of 4-bromobenzoic acid (48.2 mg, 0.24 mmol) in CH_2Cl_2 (10.0 mL) were added HBTU (113.8 mg, 0.3 mmol) and DIPEA (51.6 mg, 0.4 mmol) successfully at 0 °C. Then **5c** (60.8 mg, 0.2 mmol, 85% ee) was added and the reaction mixture was stirred at room temperature and monitored by TLC. After 6h, the resulting solution was poured into 10.0 mL of H_2O, and extracted with dichloromethane (3 × 10.0 mL). The combined organic layers were washed with water and brine, dried over anhydrous Na_2SO_4. The filtrate was concentrated under reduced pressure, and the resulting residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 4/1) to give **5d** (89.9 mg) in 92% yield as a white solid.

2.4.5 Procedure for the preparation of **5e**

To a stirred solution of **5c** (60.8 mg, 0.2 mmol, 85% ee) in CH_2Cl_2 (5.0 mL) was added 4-nitrophenyl isothiocyanate (43.2 mg, 0.24 mmol) and the resulting mixture was stirred for 5h (monitored by TLC). Then the solvent was removed in vacuum and the

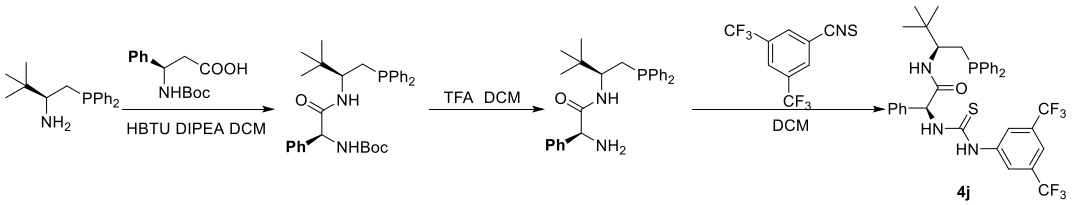
residue was purified by silica gel column chromatography (petroleum ether/ethyl acetate = 5/1) to give **5e** (91.0 mg) in 94% yield as a yellow solid.

2.4.6 Procedure for the preparation of **5f**[5]

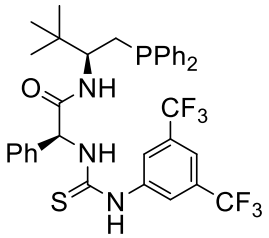
To the soulution of **5c** (30.0mg, 0.1 mmol) in toluene (1.0 mL) was added DBU (0.003 mmmol). The mixture was heated until the starting material consumed. Then it was cooled to room temperature and concentrated under reduced pressure. The residue was purified by fast silica gel column chromatography (ethyl acetate / methanol = 20/1) to afford product **5f** in 90% yield as a pale yellow solid.

2.5 Procedure for the synthesis of the bifunctional catalyst 4j

The dipeptide-based organophosphine **4i** was prepared according to the reported reference.[2]



(S)-2-(3-(3,5-bis(trifluoromethyl)phenyl)thioureido)-N-((S)-1-(diphenylphosphanyl)-3,3-dimethylbutan-2-yl)-2-phenylacetamide (4j)



4j

White solid, mp 190-192 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 9.07 (s, 1H), 8.82-8.80 (m, 1H), 7.88 (s, 2H), 7.62-7.61 (m, 2H), 7.44-7.37 (m, 5H), 7.24 (m, 5H), 7.15-7.13 (m, 6H), 6.44-6.42 (d, J=7.2Hz, 1H), 5.95-5.93 (m, 1H), 3.66-3.58 (m, 1H), 2.41-2.37 (m, 1H), 0.79 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 181.41, 172.51, 140.05, 139.21, 139.08, 136.99, 136.84, 135.49, 133.74, 133.54, 131.82, 131.64, 131.14, 130.80, 129.28, 129.23, 128.86, 128.77, 128.71, 128.45, 128.39, 128.38, 128.33, 128.17, 124.07, 121.68, 117.79, 62.17, 56.09, 35.46, 31.23, 31.09, 29.69, 26.13.; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.0; **^{31}P NMR** ($CDCl_3$, 162 MHz) δ -22.5; **IR** (Neat): 3290, 2965, 1653, 1538, 1473, 1382, 1278, 1180, 1131, 738, 695; **HRMS** (ESI): calcd for $[M+H]^+$ $(C_{35}H_{35}N_3OF_6PS)^+$ requires 690.2064; found 690.2137; $[\alpha]_D^{26.2}$ = +28.5 (c = 1.0, $CHCl_3$).

III. Experimental data

Experimental data of 3a-3n[6a,6b]

(R)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)-2-phenylpropanenitrile (3a)

White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.76-7.78 (m, 2H), 7.45-7.51 (m, 3H), 6.71 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.32 (s, 1H), 3.70 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.3, 134.6, 130.7, 129.7, 129.1, 128.0, 122.3 (q, $^1J_{CF}$ = 286.4 Hz), 120.0, 114.9, 114.5, 66.3 (q, $^2J_{CF}$ = 30.0 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.5 (s, 3F); enantiomeric excess: 91%, determined by HPLC (Chiralpak OD, hexane/i-PrOH 90/10, flow rate 0.7 mL/min; t_{major} = 8.9 min, t_{minor} = 11.0 min, λ = 254 nm); $[\alpha]_D^{28.0}$ = -68.7 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-(4-fluorophenyl)-2-((4-methoxyphenyl)amino)propanenitrile (3b)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.67-7.70 (m, 2H), 7.07-7.11 (m, 2H), 6.65 (d, *J* = 9.2 Hz, 2H), 6.53 (d, *J* = 9.2 Hz, 2H), 4.24 (s, 1H), 3.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 165.0, 163.0, 155.4, 134.3, 130.2, 130.1, 125.5, 125.4, 122.2 (q, $^1J_{CF}$ = 285.9 Hz), 120.2, 116.4, 116.3, 114.8, 114.6, 65.8 (q, $^2J_{CF}$ = 30.2 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.7 (s, 3F), -109.6 (s, 1F); enantiomeric excess: 88%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 11.9 min, t_{minor} = 13.8 min, λ = 254 nm); $[\alpha]_D^{28.3}$ = -82.9 (*c* = 1.0, $CHCl_3$).

(R)-2-(4-chlorophenyl)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)propanenitrile (3c)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62-7.64 (m, 2H), 7.36-7.39 (m, 2H), 6.65 (d, *J* = 8.8 Hz, 2 Hz), 6.52 (d, *J* = 8.8 Hz, 2H), 4.24 (s, 1H), 3.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.4, 137.1, 134.1, 129.5, 128.3, 122.1 (q, $^1J_{CF}$ = 286.6 Hz), 120.1, 114.6, 65.6 (q, $^2J_{CF}$ = 30.2 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.6 (s, 3F); enantiomeric excess: 90%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 11.8 min, t_{minor} = 13.2 min, λ = 254 nm); $[\alpha]_D^{28.5}$ = -75.5 (*c* = 1.0, $CHCl_3$).

(R)-2-(3-chlorophenyl)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)propanenitrile (3d)

White solid, mp: 78-79 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.76 (s, 1H), 7.66 (d, *J* = 8.4 Hz, 1H), 7.46-7.49 (m, 1H), 7.40 (t, *J* = 8.0 Hz, 1H), 6.72 (d, *J* = 8.8 Hz, 2H), 6.60 (d, *J* = 8.8 Hz, 2H), 4.31 (s, 1H), 3.71 (s, 3H);; **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.5, 135.4, 134.1, 131.8, 131.1, 130.4, 128.2, 126.3, 122.1 (q, $^1J_{CF}$ = 284.3 Hz), 120.1, 114.6, 66.0 (q, $^2J_{CF}$ = 29.9 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.2 (s, 3F); **IR** (Neat): 3343, 2836, 2359, 1513, 1241, 1206, 1180, 1035, 823, 788; enantiomeric excess: 89%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 5.4 min, t_{minor} = 6.0 min, λ = 254 nm); $[\alpha]_D^{25}$ = -111.7 (*c* = 1.0, $CHCl_3$).

(R)-2-(2-chlorophenyl)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)propanenitrile (3e)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.86 (d, *J* = 7.6 Hz, 1H), 7.48-7.50 (m, 1H), 7.38-7.43 (m, 1H), 7.31-7.35 (m, 1H), 6.71-6.75 (m, 2H), 6.58-6.62 (m, 2H), 4.52 (s, 1H), 3.71 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.0, 134.3, 133.5, 132.7, 131.8, 131.5, 127.5, 126.2, 122.6 (q, $^1J_{CF}$ = 285.9 Hz), 119.0, 114.6, 64.6 (q, $^2J_{CF}$ = 30.9 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -74.7 (s, 3F); **IR** (Neat): 3355, 2927, 1513, 1468, 1239, 1208, 1178, 1036, 762; **HRMS** (EI): calcd for [$C_{16}H_{12}ClF_3N_2O$] requires 340.0590; found 340.0587; enantiomeric excess: 90%, determined by

HPLC (Chiralpak AD-H, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 6.5 min, t_{minor} = 7.5 min, λ = 254 nm); $[\alpha]_D^{25}$ = -240.7 (*c* = 0.5, $CHCl_3$).

(R)-2-(4-bromophenyl)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)propanenitrile (3f)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.52-7.57 (m, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.24 (s, 1H), 3.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.4, 134.1, 132.4, 129.7, 128.8, 125.4, 122.0 (q, $^1J_{CF}$ = 286.6 Hz), 120.1, 114.6, 66.0 (q, $^2J_{CF}$ = 30.2 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.5 (s, 3F); enantiomeric excess: 90%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 12.8 min, t_{minor} = 14.0 min, λ = 254 nm); $[\alpha]_D^{28.9}$ = -60.3 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)-2-(p-tolyl)propanenitrile (3g)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.55-7.57 (m, 2H), 7.18-7.20 (m, 2H), 6.63 (d, *J* = 8.8 Hz, 2H), 6.53 d, *J* = 8.8 Hz, 2H), 4.21 (s, 1H), 3.63 (s, 3H), 2.32 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.2, 141.0, 134.7, 129.8, 127.9, 126.7, 122.4 (q, $^1J_{CF}$ = 286.3 Hz), 120.0, 115.1, 114.5, 66.2 (q, $^2J_{CF}$ = 30.1 Hz), 55.4, 21.2; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.7 (s, 3F); enantiomeric excess: 92%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 12.1 min, t_{minor} = 15.5 min, λ = 254 nm); $[\alpha]_D^{28.7}$ = -63.4 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)-2-(m-tolyl)propanenitrile (3h)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.44-7.50 (m, 2H), 7.21-7.29 (m, 2H), 6.64 (d, *J* = 8.8 Hz, 2H), 6.54 (d, *J* = 8.8 Hz, 2H), 4.21 (s, 1H), 3.63 (s, 3H), 2.33 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.2, 139.1, 134.7, 131.5, 129.6, 129.0, 128.5, 125.1, 122.3 (q, $^1J_{CF}$ = 286.4 Hz), 120.0, 115.0, 114.5, 66.4 (q, $^2J_{CF}$ = 30.1 Hz), 55.4, 21.5; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.4 (s, 3F); enantiomeric excess: 91%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 9.3 min, t_{minor} = 10.7 min, λ = 254 nm); $[\alpha]_D^{29.0}$ = -79.9 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-(4-methoxyphenyl)-2-((4-methoxyphenyl)amino)propanenitrile (3i)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 8.4 Hz, 2H), 6.88 (d, *J* = 8.8 Hz, 2H), 6.64 (d, *J* = 8.0 Hz, 2H), 6.54 (d, *J* = 8.0 Hz, 2H), 4.21 (s, 1H), 3.76 (s, 3H), 3.63 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 161.3, 155.2, 134.7, 129.4, 122.4 (q, $^1J_{CF}$ = 286.2 Hz), 121.3, 120.1, 115.1, 114.5 (2C), 65.9 (q, $^2J_{CF}$ = 30.0 Hz), 55.4 (2C); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.9 (s, 3F); enantiomeric excess: 90%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 80/20, flow rate 1.0 mL/min; t_{major} = 6.0 min, t_{minor} = 7.0 min, λ = 254 nm); $[\alpha]_D^{28.8}$ = -66.2 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)-2-(4-(trifluoromethyl)phenyl)propanenitrile (3j)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.52-7.57 (m, 4H), 6.65 (d, *J* = 8.8 Hz, 2H), 6.52 (d, *J* = 8.8 Hz, 2H), 4.24 (s, 1H), 3.64 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 155.5, 133.9, 133.7, 133.0 (q, $^2J_{CF}$ = 33.1 Hz), 128.7, 126.2 (q, $^3J_{CF}$ = 3.7 Hz), 123.5 (q, $^1J_{CF}$ = 273.2 Hz), 122.1 (q, $^1J_{CF}$ = 286.8 Hz), 120.1, 114.7, 114.4, 66.0 (q, $^2J_{CF}$ = 30.1 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -63.0 (s, 3F), -76.3 (s, 3F); enantiomeric excess: 86%, determined by HPLC (Chiralpak PC-2, hexane/i-PrOH 98/2, flow rate 0.7 mL/min; t_{major} = 10.6 min, t_{minor} = 9.6 min, λ = 254 nm); $[\alpha]_D^{29.2}$ = -74.7 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-((4-methoxyphenyl)amino)-2-(thiophen-2-yl)propanenitrile (3k)

Yellow oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.40-7.45 (m, 2H), 7.00-7.02 (m, 1H), 6.67-6.72 (m, 4H), 4.17 (s, 1H), 3.67 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 156.1, 134.2, 133.4, 130.2, 129.5, 127.2, 121.9 (q, $^1J_{CF}$ = 287.0 Hz), 121.7, 114.5, 114.3, 64.0 (q, $^2J_{CF}$ = 30.1 Hz), 55.4; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.6 (s, 3F); enantiomeric excess: 86%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 13.8 min, t_{minor} = 16.1 min, λ = 254 nm); $[\alpha]_D^{29.1}$ = -35.7 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-((4-fluorophenyl)amino)-2-phenylpropanenitrile (3l)

White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.67-7.68 (m, 2H), 7.39-7.44 (m, 3H), 6.76-6.80 (m, 2H), 6.49-6.52 (m, 2H), 4.41 (s, 1H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 158.3 (d, $^1J_{CF}$ =242 Hz), 137.3, 130.9, 129.3, 129.2, 127.9, 122.2 (q, $^1J_{CF}$ = 286.4 Hz), 119.2(d, $^3J_{CF}$ = 7.9 Hz), 115.9(d, $^2J_{CF}$ = 22.8 Hz), 114.6, 65.8 (q, $^2J_{CF}$ = 30.2 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.6 (s, 3F), -121.7 (s, 1F); enantiomeric excess: 90%, determined by HPLC (Chiralpak OJ, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 10.3 min, t_{minor} = 7.2 min, λ = 254 nm); $[\alpha]_D^{27.9}$ = -91.5 (*c* = 1.0, $CHCl_3$).

(R)-2-((4-bromophenyl)amino)-3,3,3-trifluoro-2-phenylpropanenitrile (3m)

White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64-7.66 (m, 2H), 7.40-7.44 (m, 3H), 7.17 (d, *J* = 8.8 Hz, 2H), 6.39 (d, *J* = 8.8 Hz, 2H), 4.55 (s, 1H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 140.3, 132.1, 131.0, 129.4, 128.9, 127.7, 122.1 (q, $^1J_{CF}$ = 286.6 Hz), 118.7, 114.4, 114.3, 65.2 (q, $^2J_{CF}$ = 30.5 Hz). **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.7 (s, 3F); enantiomeric excess: 82%, determined by HPLC (Chiralpak OJ, hexane/i-PrOH 95/5, flow rate 0.7 mL/min; t_{major} = 25.2 min, t_{minor} = 19.0 min, λ = 254 nm); $[\alpha]_D^{28.0}$ = -79.7 (*c* = 1.0, $CHCl_3$).

(R)-3,3,3-trifluoro-2-phenyl-2-(p-tolylamino)propanenitrile (3n)

White solid; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.68-7.69 (m, 2H), 7.39-7.40 (m, 3H), 6.87 (d, *J* = 8.4 Hz, 2H), 6.42 (d, *J* = 8.4 Hz, 2H), 4.40 (s, 1H), 2.14 (s, 3H); **^{13}C NMR** ($CDCl_3$, 126 MHz) δ 138.8, 131.3, 130.7, 129.7, 129.6, 129.2, 127.9, 122.3 (q, $^1J_{CF}$ = 286.3 Hz), 117.4, 114.8, 65.6 (q, $^2J_{CF}$ = 30.1 Hz), 20.5; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.7 (s, 3F); enantiomeric excess: 89%, determined by HPLC (Chiralpak OJ, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 9.3 min, t_{minor} = 7.0 min, λ = 254 nm); $[\alpha]_D^{28.1}$ = -106.2 (*c* = 1.0, $CHCl_3$).

Experimental data of 3'a-3'm

Tert-butyl (S)-(1-cyano-2,2,2-trifluoro-1-phenylethyl)carbamate (3'a)

White solid, mp: 81-82 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64-7.66 (m, 2H), 7.47-7.48 (m, 3H), 6.17 (br, 1H), 1.31 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.7, 130.7, 130.3, 128.9, 126.6, 121.7 (q, $^1J_{CF}$ = 284.7 Hz), 113.8, 83.2, 62.4 (q, $^2J_{CF}$ = 31.3 Hz), 27.7; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -75.7 (s, *J* = 3F); **IR** (Neat): 3244, 3147, 2980, 2933, 2855, 1717, 1492, 1454, 1370, 1250, 1192, 1156; **HRMS** (ESI): calcd for $[M-H]^-$ ($C_{14}H_{14}O_2N_2F_3$)$^-$ requires 299.1013; found 299.1005; enantiomeric excess: 85%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.6 mL/min; t_{major} = 16.1 min, t_{minor} = 11.4 min, λ = 254 nm); $[\alpha]_D^{24}$ = 35.4 (*c* = 1.0, $CHCl_3$).

Tert-butyl (S)-(1-cyano-2,2,2-trifluoro-1-(3-fluorophenyl)ethyl)carbamate (3'b)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.44-7.48 (m, 2H), 7.35-7.38 (m, 1H), 7.17-7.22 (m,

1H), 6.41 (br, 1H), 1.34 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 162.7 (d, $^1J_{CF}$ = 247.2 Hz), 152.7, 133.1, 130.6 (d, $^3J_{CF}$ = 8.2 Hz), 122.6, 122.5, 121.5 (q, $^1J_{CF}$ = 284.9 Hz), 117.5 (d, $^2J_{CF}$ = 21.0 Hz), 114.1 (d, $^2J_{CF}$ = 24.7 Hz), 113.5, 83.6, 62.0 (q, $^2J_{CF}$ = 31.0 Hz), 27.7; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.2 (s, 3F), -107.5 (s, 1F); **IR** (Neat): 3244, 3147, 2981, 1719, 1598, 1492, 1371, 1249, 1201, 1156; **HRMS** (ESI): calcd for $[M-H]^-$ $(C_{14}H_{13}O_2N_2F_4)^-$ requires 317.0919; found 317.0915; enantiomeric excess: 79%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 98/2, flow rate 0.4 mL/min; t_{major} = 36.0 min, t_{minor} = 27.3 min, λ = 254 nm); $[\alpha]_D^{25}$ = 47.6 (c = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-cyano-2,2,2-trifluoro-1-(4-fluorophenyl)ethyl)carbamate (3'c)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62-7.65 (dd, *J* = 8.4 Hz, 4.8 Hz, 2H), 7.17 (t, *J* = 8.4 Hz, 2H), 5.92 (br, 1H), 1.35 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 163.5 (d, $^1J_{CF}$ = 249.6 Hz), 152.4, 128.8 (d, $^3J_{CF}$= 8.7 Hz), 126.4, 121.6 (q, $^1J_{CF}$ = 284.4 Hz), 116.1 (d, $^2J_{CF}$ = 22.2 Hz), 113.7, 83.5, 61.9 (q, $^2J_{CF}$ = 31.0 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.1 (s, 3F), -110.2 (s, 1F); **IR** (Neat): 3246, 3148, 2981, 1719, 1605, 1512, 1395, 1371, 1251, 1191; **HRMS** (ESI): calcd for $[M-H]^-$ $(C_{14}H_{13}O_2N_2F_4)^-$ requires 317.0919; found 317.0915; enantiomeric excess: 89%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 98/2, flow rate 0.4 mL/min; t_{major} = 31.3 min, t_{minor} = 24.0 min, λ = 254 nm); $[\alpha]_D^{25}$ = 52.4 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-cyano-1-(3,5-difluorophenyl)-2,2,2-trifluoroethyl)carbamate (3'd)

White solid, mp: 96-98 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.21-7.23 (m, 2H), 6.93-6.98 (m, 1H), 6.23 (br, 1H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 163.5 (dd, $^1J_{CF}$ = 249.7 Hz, $^3J_{CF}$ = 12.4 Hz), 152.6, 134.7, 121.3 (q, $^1J_{CF}$ = 284.7 Hz), 113.1, 110.5 (d, $^2J_{CF}$ = 28.0 Hz), 110.5 (d, $^3J_{CF}$ = 11.7 Hz), 106.2 (t, $^2J_{CF}$ = 24.9 Hz), 84.0, 61.9 (q, $^2J_{CF}$ = 31.1 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -71.9 (s, 3F), -103.4 (s, 1F); **IR** (Neat): 3242, 3142, 2975, 1731, 1624, 1608, 1491, 1442, 1370, 1254, 1212, 1187, 1122; **HRMS** (ESI): calcd for $[M-H]^-$ $(C_{14}H_{12}O_2N_2F_5)^-$ requires 335.0824; found 317.0818; enantiomeric excess: 83%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.6 mL/min; t_{major} = 8.9 min, t_{minor} = 8.2 min, λ = 254 nm); $[\alpha]_D^{25}$ = 52.5 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-(2-chlorophenyl)-1-cyano-2,2,2-trifluoroethyl)carbamate (3'e)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.81-7.83 (m, 1H), 7.37-7.48 (m, 3H),5.74 (br, 1H), 1.37 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.5, 132.6, 131.4, 130.9, 127.3, 126.8, 122.1 (q, $^1J_{CF}$ = 285.9 Hz), 113.4, 83.1, 62.6 (q, $^2J_{CF}$ = 32.0 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -73.9 (s, 3F); **IR** (Neat): 3242, 3144, 2979, 1720, 1433, 1370, 1248, 1191, 1157; **HRMS** (ESI): calcd for $[M+NH_4]^+$ $(C_{14}H_{18}O_2N_3ClF_3)^+$ requires 352.1034.0623; found 352.1034; enantiomeric excess: 85%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 10.5 min, t_{minor} = 5.6 min, λ = 254 nm); $[\alpha]_D^{25}$ = 0.47 (*c* = 1.0, $CHCl_3$).

Tert-butyl (S)-(1-(3-chlorophenyl)-1-cyano-2,2,2-trifluoroethyl)carbamate (3'f)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.64 (s, 1H), 7.57 (d, *J* = 8.0 Hz, 1H), 7.40-7.49 (m, 2H),6.33 (br, 1H), 1.34 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.7, 135.1, 132.8, 130.6, 130.1, 126.8, 125.0, 121.5 (q, $^1J_{CF}$ = 284.9 Hz), 113.4, 83.7, 62.0 (q, $^2J_{CF}$ = 31.8 Hz), 27.7; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.0 (s, 3F); **IR** (Neat): 3245, 3147, 2980, 1718, 1478, 1370, 1249, 1193, 1156; **HRMS** (ESI): calcd for $[M-H]^-$ $(C_{14}H_{13}O_2N_2ClF_3)^-$ requires 333.0623; found 333.0622; enantiomeric excess: 72%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 98/2, flow rate

0.4 mL/min; t_{major} = 38.6 min, t_{minor} = 33.2 min, λ = 254 nm); $[\alpha]_D^{25}$ = 36.4 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-(4-chlorophenyl)-1-cyano-2,2,2-trifluoroethyl)carbamate (3'g)

White solid, mp: 108-110 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.59 (d, *J* = 7.6 Hz, 2H), 7.46 (d, *J* = 8.8 Hz, 2H), 6.35 (br, 1H), 1.34 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.7, 136.7, 129.1, 128.0, 121.5 (q, $^1J_{CF}$ = 284.7 Hz), 113.5, 83.6, 62.0 (q, $^2J_{CF}$ = 31.3 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.0 (s, 3F); **IR** (Neat): 3241, 3142, 2980, 1717, 1493, 1369, 1248, 1193, 1156; **HRMS** (ESI): calcd for $[M-H]^-$ ($C_{14}H_{13}O_2N_2ClF_3$)$^-$ requires 333.0623; found 333.0618; enantiomeric excess: 83%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 91/9, flow rate 0.7 mL/min; t_{major} = 6.7 min, t_{minor} = 6.2 min, λ = 214 nm); $[\alpha]_D^{25}$ = 43.3 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-(3-bromophenyl)-1-cyano-2,2,2-trifluoroethyl)carbamate (3'h)

White solid, mp: 118-120 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.79 (s, 2H), 7.62 (t, *J* = 8.0 Hz, 2H), 7.36 (t, *J* = 8.0 Hz, 1H), 6.38 (br, 1H), 1.33 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.7, 133.6, 130.4, 129.6, 125.4, 123.0, 121.4 (q, $^1J_{CF}$ = 285.0 Hz), 113.4, 83.7, 61.9 (q, $^2J_{CF}$ = 31.0 Hz), 27.7; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.1 (s, 3F); **IR** (Neat): 3245, 3147, 2980, 1719, 1476, 1370, 1249, 1193, 1156; **HRMS** (ESI): calcd for $[M-H]^-$ ($C_{14}H_{13}O_2N_2BrF_3$)$^-$ requires 377.0118; found 377.0112; enantiomeric excess: 68%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 98/2, flow rate 0.6 mL/min; t_{major} = 27.1, t_{minor} = 25.2, λ = 254 nm); $[\alpha]_D^{25}$= 25.9 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-(4-bromophenyl)-1-cyano-2,2,2-trifluoroethyl)carbamate (3'i)

White solid, mp: 102-104 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62 (d, *J* = 8.8 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 6.23 (br, 1H), 1.34 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.6, 132.2, 129.9, 128.3, 125.0, 121.5 (q, $^1J_{CF}$ = 284.4 Hz), 113.5, 83.6, 62.2 (q, $^2J_{CF}$ = 31.2 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.1 (s, 3F); **IR** (Neat): 3244, 3146, 2980, 1718, 1489, 1370, 1248, 1194, 1156, 1076; **HRMS** (ESI): calcd for $[M-H]^-$ ($C_{14}H_{13}O_2N_2BrF_3$)$^-$ requires 377.0107; found 377.0114; enantiomeric excess: 70%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 98/2, flow rate 0.4 mL/min; t_{major} = 27.8 min, t_{minor} = 23.9 min, λ = 254 nm); $[\alpha]_D^{25}$ = 33.5 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-cyano-2,2,2-trifluoro-1-(3-nitrophenyl)ethyl)carbamate (3'j)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.51 (s, 1H), 8.38 (d, *J* = 8.0 Hz, 1H), 8.05 (d, *J* = 8.0 Hz, 1H), 7.73 (t, *J* = 8.0 Hz, 1H), 6.20 (br, 1H), 1.36 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.5, 148.6, 133.1, 132.8, 130.3, 125.4, 121.8, 120.9 (q, $^1J_{CF}$ = 285.0 Hz), 113.1, 84.1, 61.9 (q, $^2J_{CF}$ = 30.6 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -72.1 (s, 3F); **IR** (Neat): 3320, 3147, 2981, 2938, 1722, 1538, 1458, 1352, 1250, 1197; **HRMS** (ESI): calcd for $[M-H]^-$ ($C_{14}H_{13}O_4N_3F_3$)$^-$ requires 344.0864; found 344.0863; enantiomeric excess: 70%, determined by HPLC (Chiralpak AS-H, hexane/i-PrOH 95/5, flow rate 0.6 mL/min; t_{major} = 17.1 min, t_{minor} = 15.6 min, λ = 254 nm); $[\alpha]_D^{25}$ = 25.4 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(1-cyano-2,2,2-trifluoro-1-(p-tolyl)ethyl)carbamate (3'k)

White solid, mp: 74-75 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.51 (d, *J* = 8.0 Hz, 2H), 7.27 (d, *J* = 8.0 Hz, 2H), 5.96 (br, 1H), 2.39 (s, 3H), 1.34 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.6, 140.6, 129.6, 127.6, 126.5, 121.8 (q, $^1J_{CF}$ = 284.2 Hz), 113.9, 83.1, 62.2 (q, $^2J_{CF}$ = 31.1 Hz), 27.8, 21.1; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -75.9 (s, 3F); **IR** (Neat): 3244, 3146, 2980, 1715, 1394, 1369, 1251,

1210, 1185, 1158; **HRMS** (ESI): calcd for $[M+NH_4]^+$ $(C_{15}H_{21}F_3N_3O_2)^+$ requires 332.1580; found 332.1581; enantiomeric excess: 84%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 5.0 min, t_{minor} = 4.6 min, λ = 254 nm); $[\alpha]_D^{25}$ = 25.4 (*c* = 1.0, $CHCl_3$).

Tert-butyl (S)-(1-cyano-2,2,2-trifluoro-1-(thiophen-2-yl)ethyl)carbamate (3'l)

White solid; mp: 61-62 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.43-7.45 (m, 2H), 7.06-7.08 (m, 1H), 6.56 (br, 1H), 1.38 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 152.9, 134.2, 129.3, 128.2, 127.2, 111.4 (q, $^1J_{CF}$ = 284.9 Hz), 113.2, 83.6, 59.2 (q, $^2J_{CF}$ = 32.8 Hz), 27.8; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.3 (s, 3F); **IR** (Neat): 3146, 2981, 2359, 1716, 1370, 1251, 1216, 1188,1157; **HRMS** (ESI): calcd for $[M+NH_4]^+$ $(C_{12}H_{17}F_3N_3O_2S)^+$ requires 324.0988; found 324.0988; enantiomeric excess: 77%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.8 mL/min; t_{major} = 12.7 min, t_{minor} = 10.0 min, λ = 220 nm); $[\alpha]_D^{25}$ = 14.2 (*c* = 1.0, $CHCl_3$).

Benzyl (S)-(1-cyano-2,2,2-trifluoro-1-phenylethyl)carbamate (3'm)

White solid, mp: 91-92 °C; 88% yield; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.62-7.60 (m, 2H), 7.48-7.40 (m, 3H), 7.30-7.19 (m, 5H), 6.29 (br, 1H), 5.12-5.03 (m, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 153.6, 134.8, 130.6, 129.9, 129.1, 128.6, 128.3, 126.7, 121.8 (q, $^1J_{CF}$ = 284.5 Hz), 113.5, 68.4, 62.4 (q, $^2J_{CF}$ = 31.2 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -100.4 (s, 3F); **IR** (Neat): 3301, 3035, 1724, 1525, 1454, 1258, 1005, 742; **HRMS** (ESI): calcd for $[M+Na]^+$ $(C_{17}H_{13}F_3N_2O_2Na)^+$ requires 357.0821; found 357.0824; enantiomeric excess: 49%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 9.0 min, t_{minor} = 7.0 min, λ = 254 nm); $[\alpha]_D^{25}$ = 25.1 (*c* = 1.0, $CHCl_3$).

Experimental data of 5a-5f

(S)-2-amino-3,3,3-trifluoro-2-phenylpropanenitrile (5a)[6a]

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.78 (d, *J* = 8.0 Hz, 2H), 7.45-7.52 (m, 3H), 2.31 (br, 2H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 131.0, 130.8, 129.0, 127.2, 122.5 (q, $^1J_{CF}$ = 283.0 Hz), 117.9, 61.2 (q, $^2J_{CF}$ = 31.6 Hz); **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -78.5 (s, 3F); **HRMS** (ESI): calcd for $[M+H]^+$ $(C_9H_8F_3N_2)^+$ requires 201.0634 ; found 201.0635 ; enantiomeric excess: 85%, determined by HPLC (Chiralpak AD-H, hexane/i-PrOH 95/5, flow rate 0.8 mL/min; t_{major} = 12.3 min, t_{minor} = 11.6. min, λ = 220 nm); $[\alpha]_D^{25}$ = 0.20 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(3-amino-1,1,1-trifluoro-3-oxo-2-phenylpropan-2-yl)carbamate (5b)

Colorless oil; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.39-7.49 (m, 5H), 6.30 (br, 1H), 5.88 (br, 2H), 1.32 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 167.7, 153.2, 132.9, 129.1, 128.8, 127.0, 123.9 (q, $^1J_{CF}$ = 285.9 Hz), 81.0, 67.9 (q, $^2J_{CF}$ = 27.5 Hz), 28.0; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -70.5 (s, 3F); **IR** (Neat): 3354, 2980, 1698, 1600, 1480, 1425, 1369, 1255, 1161, 1052; **HRMS** (ESI): calcd for $[M+H]^+$ $(C_{14}H_{18}O_3N_2F_3)^+$ requires 319.1264; found 319.1267; enantiomeric excess: 85%, determined by HPLC (Chiralpak PC-2, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 13.5 min, t_{minor} = 9.4 min, λ = 220 nm); $[\alpha]_D^{25}$ = 30.7 (*c* = 0.5, $CHCl_3$).

Tert-butyl (S)-(3-amino-1,1,1-trifluoro-2-phenylpropan-2-yl)carbamate (5c)

White solid, mp: 70-71 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 7.31-7.45 (m, 5H), 5.71 (br, 1H), 3.64 (d, *J* = 13.6 Hz 1H), 3.27 (d, *J* = 13.2 Hz, 1H), 1.39 (s, 11H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 154.0,

136.1, 128.5, 128.3, 126.3, 126.0 (q, $^{1}J_{CF}$ = 285.6 Hz), 80.5, 65.1 (q, $^{2}J_{CF}$ = 25.0 Hz), 46.7, 28.1; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -70.7 (s, 3F); enantiomeric excess: 85%, determined by HPLC (Chiralpak IC, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 7.7 min, t_{minor} = 8.5 min, λ = 254 nm); $[\alpha]_D^{25}$ = 20.8 (*c* = 1.0, $CHCl_3$).

Tert-butyl (S)-(3-(4-bromobenzamido)-1,1,1-trifluoro-2-phenylpropan-2-yl)carbamate (5d)

White solid, mp: 48-49 °C; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.11 (br, 1H), 7.42-7.51 (m, 6H), 7.31-7.38 (m, 3H), 5.86 (br, 1H), 4.79 (br, 1H), 3.94 (d, *J* = 14.0 Hz, 1H), 1.46 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 166.6, 155.4, 133.0, 132.7, 131.6, 129.0, 128.6, 128.5, 127.2, 126.1, 124.9 (q, $^{1}J_{CF}$ = 284.2 Hz), 81.7, 65.8 (q, $^{2}J_{CF}$ = 25.6 Hz), 43.8, 28.2; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -76.2 (s, 3F); **IR** (Neat): 3300, 2978, 1713, 1651 1591, 1258, 1157, 1011 843; **HRMS** (ESI): calcd for $[M+H]^+$ $(C_{21}H_{23}BrF_3N_2O_3)^+$ requires 487.0839; found 487.0843; enantiomeric excess: 85%, determined by HPLC (Chiralpak PC-2, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 8.6 min, t_{minor} = 6.7 min, λ = 254 nm); $[\alpha]_D^{25}$ = -57.9 (*c* = 1.0, $CHCl_3$).

Tert-butyl (S)-(1,1,1-trifluoro-3-(3-(4-nitrophenyl)thioureido)-2-phenylpropan-2-yl)carbamate (5e)

Yellow solid, mp: 72-74 °C ; **^{1}H NMR** ($CDCl_3$, 400 MHz) δ 8.89 (br, 1H), 8.61 (br, 1H), 7.97 (d, *J* = 8.0 Hz, 2H), 7.44-7.48 (m, 5H), 6.73 (br, 2H), 5.64 (br, 1H), 5.42 (br, 1H), 3.96 (d, *J* = 12.4 Hz, 1H), 1.31 (s, 9H); **^{13}C NMR** ($CDCl_3$, 100 MHz) δ 179.8, 155.5, 144.4, 142.3, 132.2, 129.4, 128.7, 127.7, 125.0, 124.6 (q, $^{1}J_{CF}$ = 284.4 Hz), 123.0, 82.4, 66.1 (q, $^{2}J_{CF}$ = 21.1 Hz), 49.6, 27.9; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -77.6 (s, 3F); **IR** (Neat): 3280, 2979, 1712, 1596, 1344, 1260, 1015, 853, 703; **HRMS** (ESI): calcd for $[M-H]^-$ $(C_{21}H_{24}F_3N_4O_4S)^+$ requires 485.1466; found 485.1465; enantiomeric excess: 86%, determined by HPLC (Chiralpak ADH, hexane/i-PrOH 90/10, flow rate 1.0 mL/min; t_{major} = 23.8 min, t_{minor} = 30.2 min, λ = 254 nm); $[\alpha]_D^{25}$ = 13.1 (*c* = 1.0, $CHCl_3$).

(S)-4-phenyl-4-(trifluoromethyl)imidazolidin-2-one (5f)[5,6b]

White solid; **^{1}H NMR** (DMSO-d_6, 400 MHz) δ 8.31 (br, 1H), 7.42-7.53 (m, 5H), 6.79 (br, 1H), 4.03 (d, *J* = 10.4 Hz, 1H), 3.68 (d, *J* = 11.2 Hz, 1H); **^{13}C NMR** (DMSO-d_6, 100 MHz) δ 161.6, 137.5, 129.2, 128.9, 127.2, 126.3 (q, $^{1}J_{CF}$ = 284.2 Hz), 64.8 (q, $^{2}J_{CF}$ = 28.0 Hz), 48.0; **^{19}F NMR** ($CDCl_3$, 376 MHz) δ -74.8 (s, 3F); enantiomeric excess: 88%, determined by HPLC (Chiralpak OD-H, hexane/i-PrOH 85/15, flow rate 1.0 mL/min; t_{major} = 6.2 min, t_{minor} = 6.9 min, λ = 254 nm).

IV. References

1 H. Xiao, Z. Chai, C.-W. Zheng, Y.-Q. Yang, W. Liu, J.-K. Zhang and G. Zhao, *Angew. Chem. Int. Ed.*, 2010, **49**, 4467.

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3 Y.-L. Liu, X.-P. Yin and J. Zhou, *Chin. J. Chem.*, 2018, **36**, 321.

4 P. V. Balaji, L. Brewitz, N. Kumagai and M. Shibasaki, *Angew. Chem. Int. Ed.*, 2019, **58**, 2644.

5 I. V. Kutovaya, O. I. Shmatova, V. M. Tkachuk, N. V. Melnichenko, M. V. Vovk and V. G. Nenajdenko, *Eur. J. Org. Chem.*, 2015, 6749.

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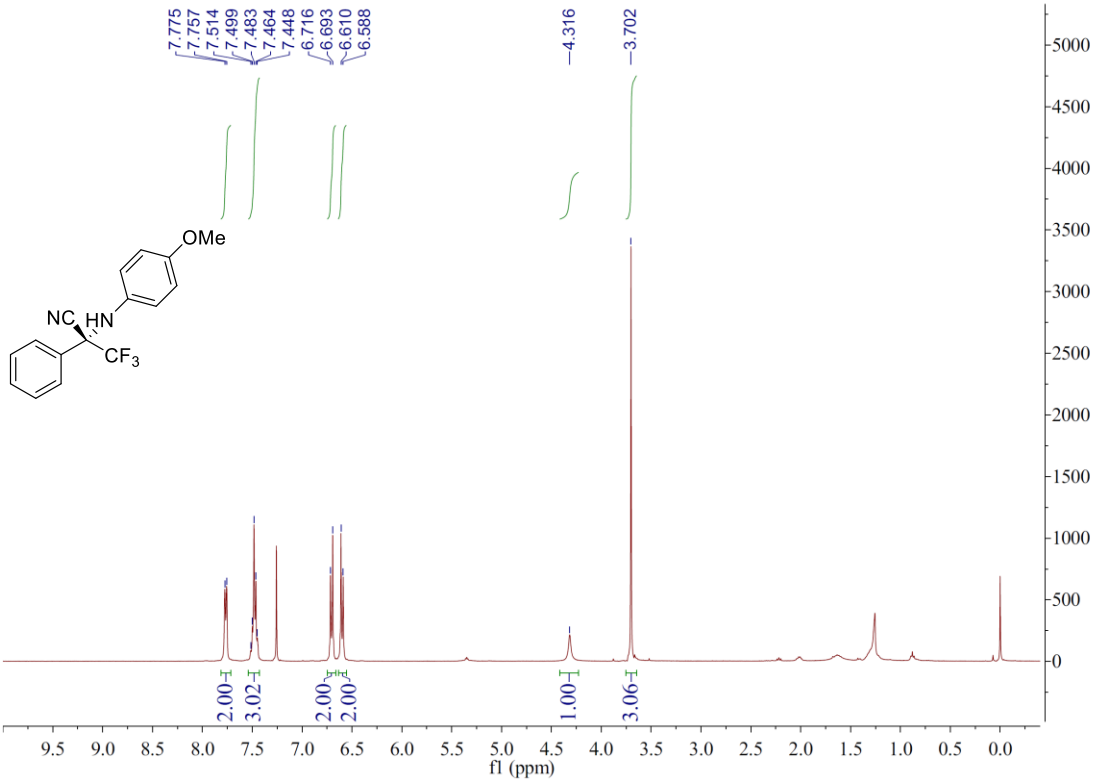
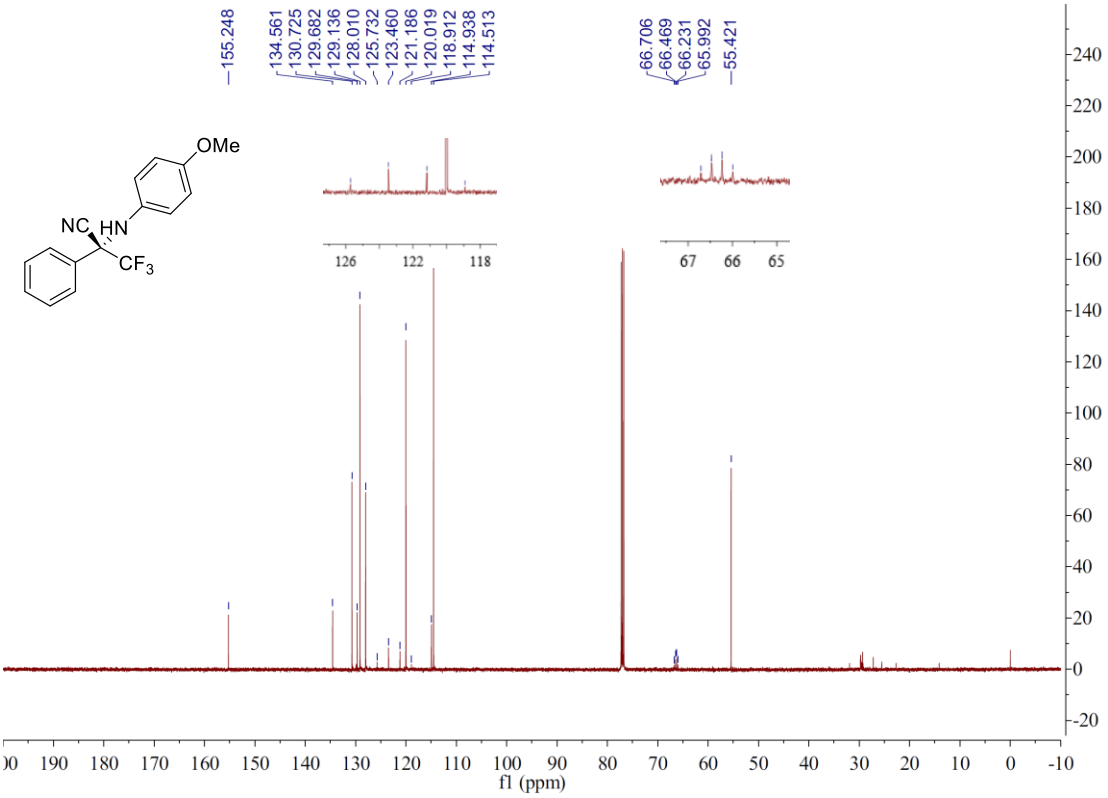
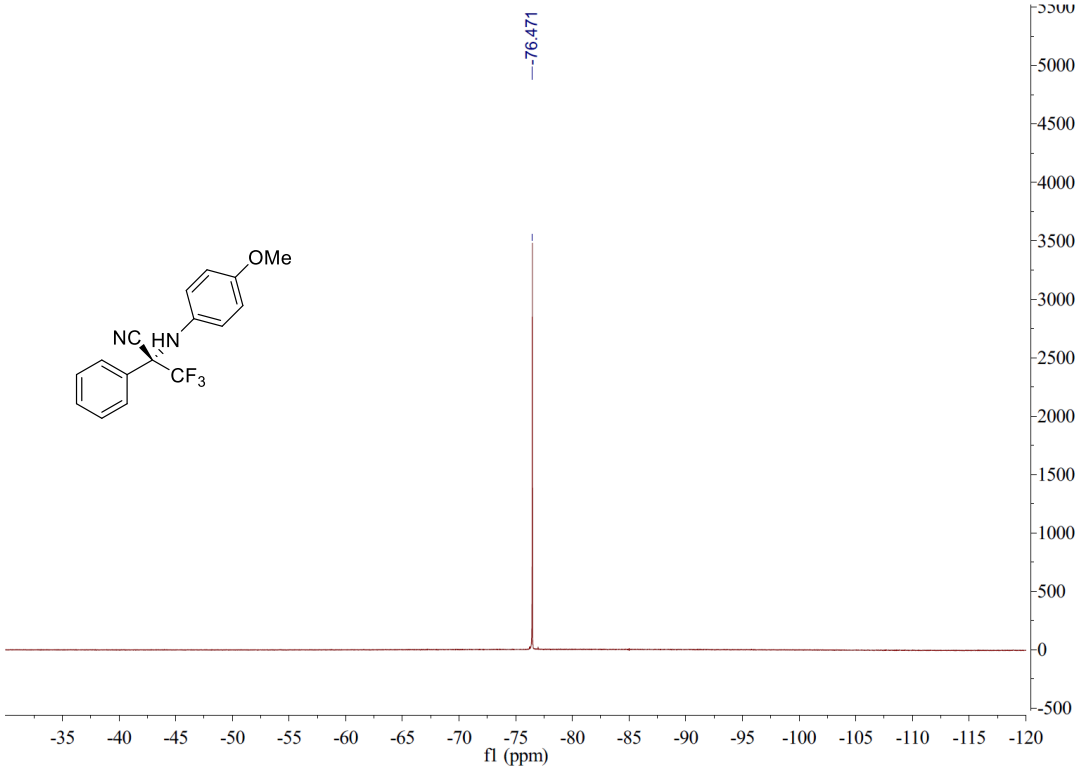
7 (*a*) Fetyukhin et al, *Journal of Organic Chemistry USSR* (English Translation), *1977*, **13**, 244; *Zhurnal Organicheskoi Khimii*, 1977, **13**, 271; (*b*) N. V. Mel'nichenko and M. V. Vovk, *Russian Journal of Organic Chemistry*, 2008, **44**, 149.

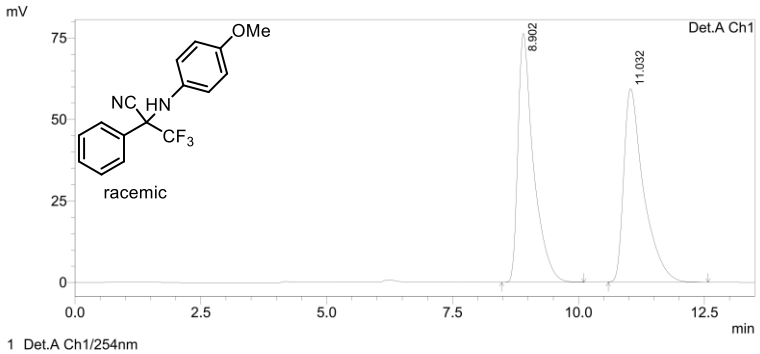
V. Copies of NMR and HPLC spectra

Copies of NMR and HPLC spectra for 3a-3n







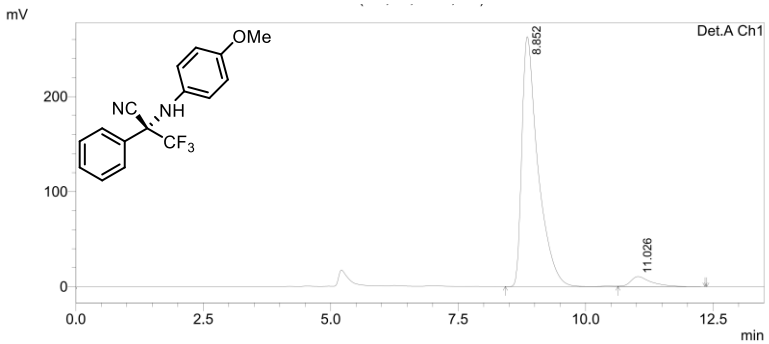


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.902	1640839	76376	50.113	56.234
2	11.032	1633441	59443	49.887	43.766
Total		3274280	135820	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
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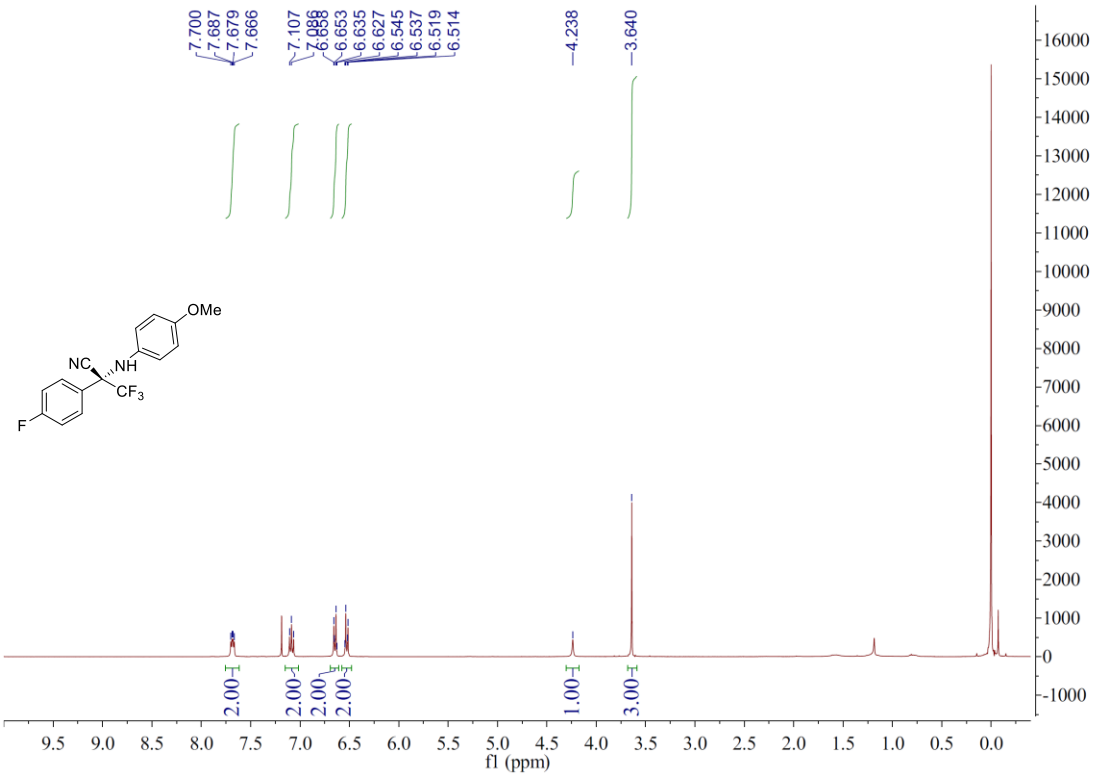
Total		6091151	273395	100.000	100.000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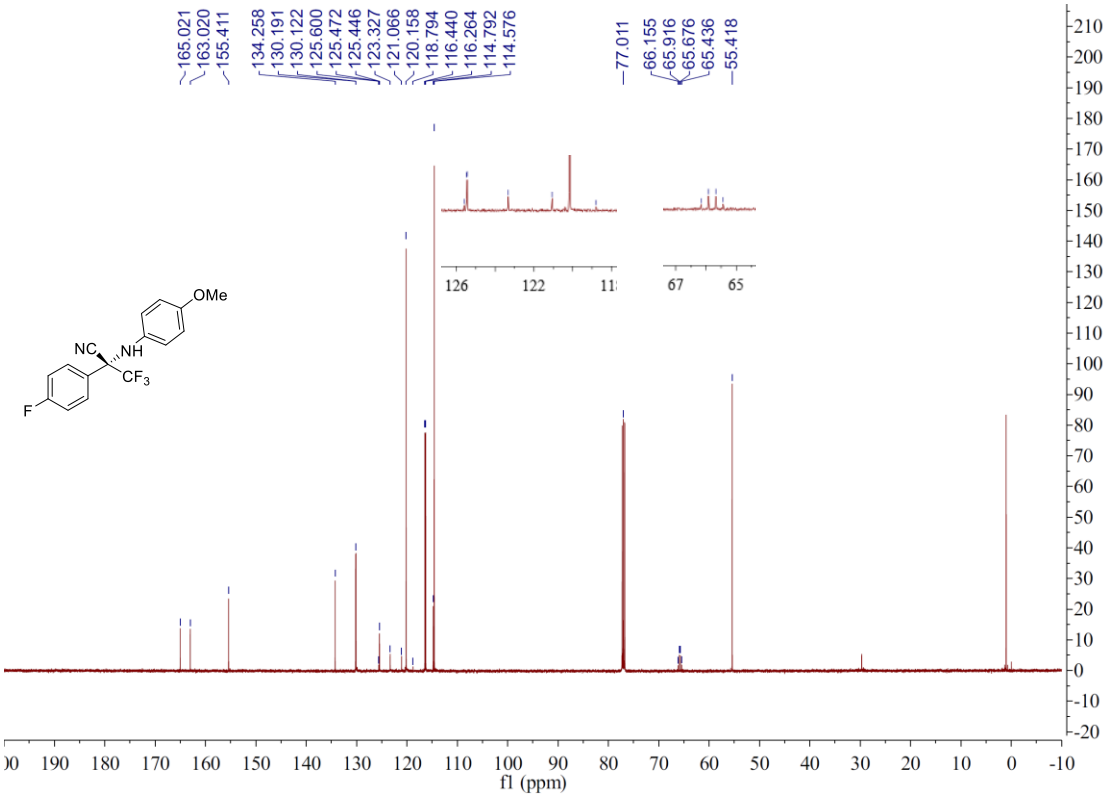
7.679
7.666
7.107
6.653
6.635
6.627
6.545
6.537
6.519
6.514
4.238
3.640
OMe
NC
NH
CF3
F
2.00
2.00
2.00
2.00
1.00
3.00
fl (ppm)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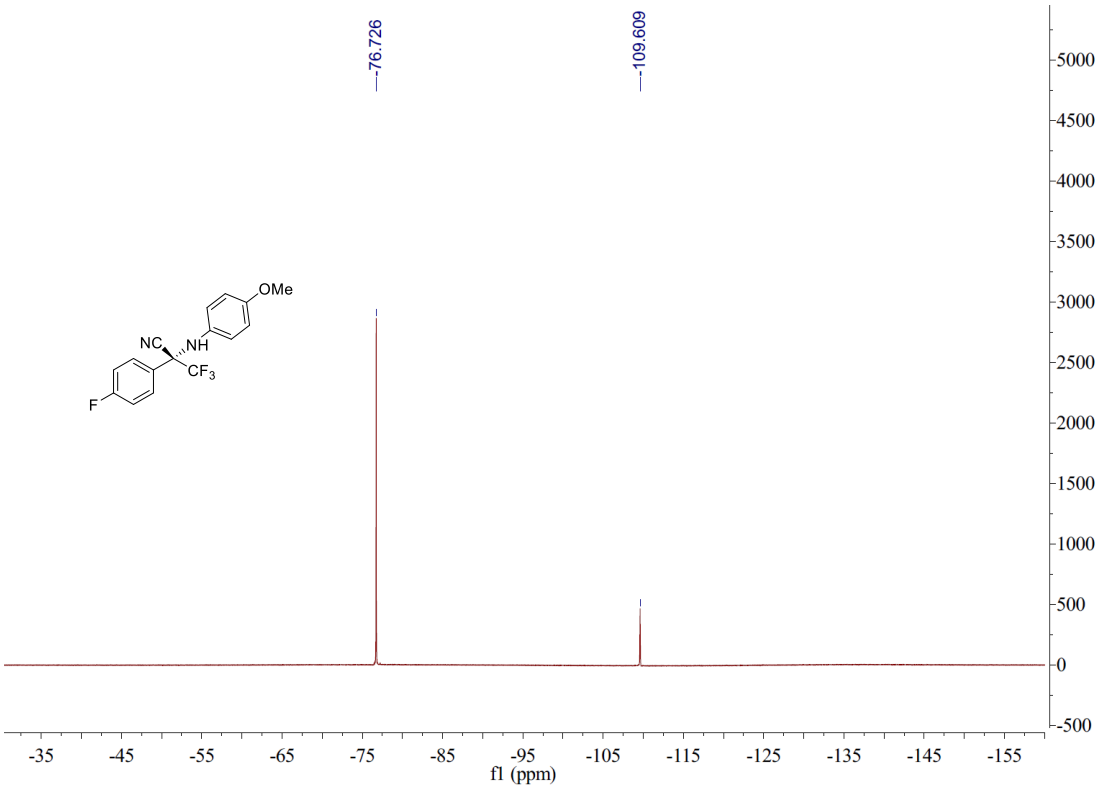
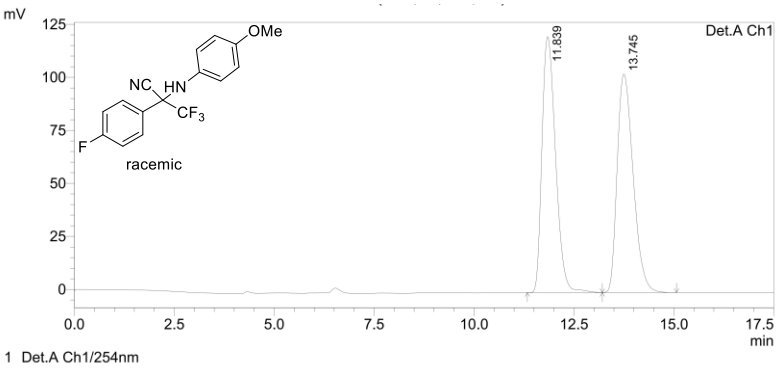
134.258
130.191
130.122
125.600
125.472
125.446
123.327
121.066
120.158
118.794
116.440
116.264
114.792
114.576
77.011
66.155
65.916
65.676
65.436
55.418
126
122
67
65
OMe
NC
NH
CF3
F
fl (ppm)



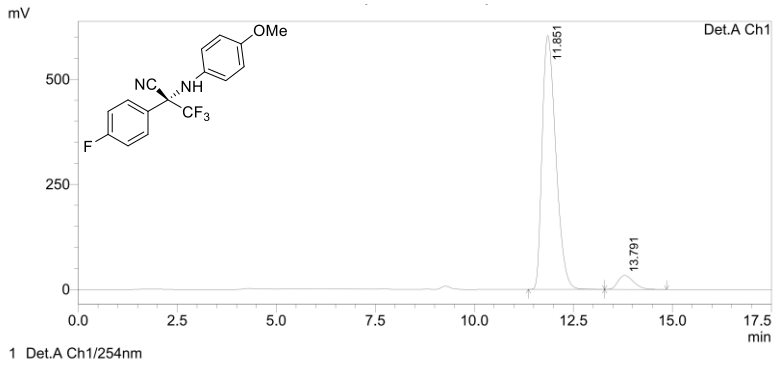


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.839	2858688	120701	49.942	53.947
2	13.745	2865352	103040	50.058	46.053
Total		5724040	223741	100.000	100.000



1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

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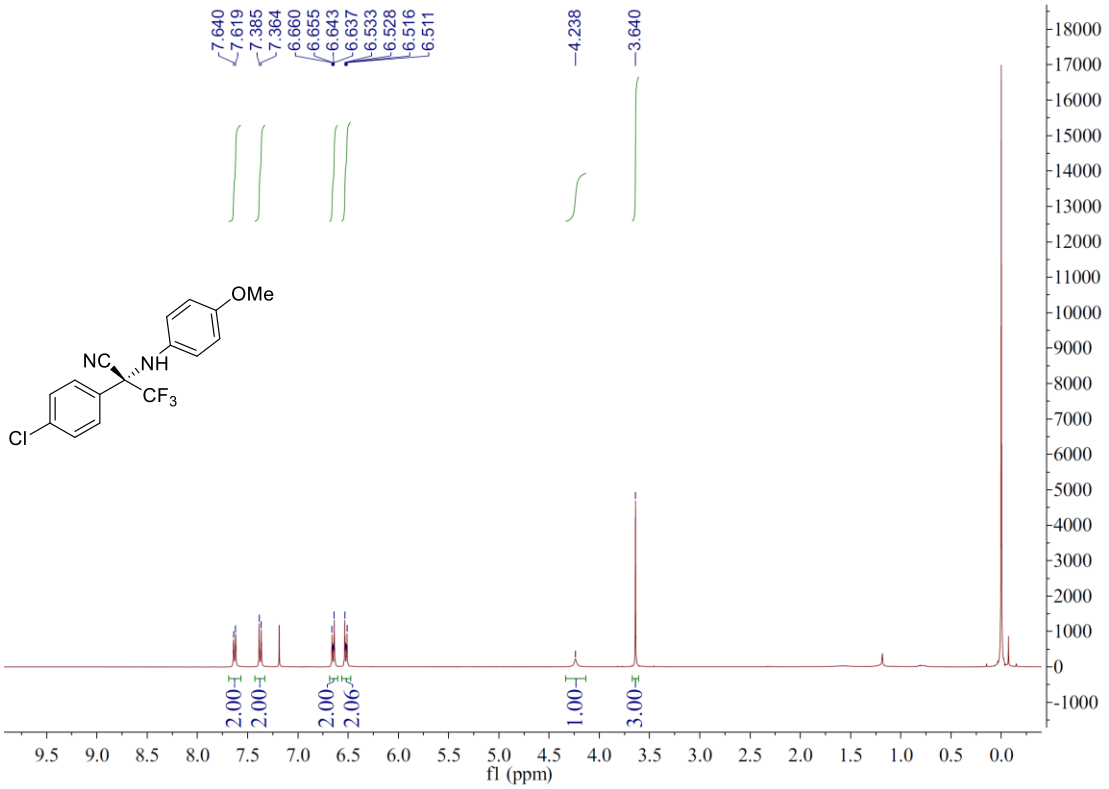
2	13.791	909326	33050	5.901	5.187
Total		15408923	637182	100.000	100.000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7.385
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6.528
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6.511
4.238
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NC
NH
CF3
Cl
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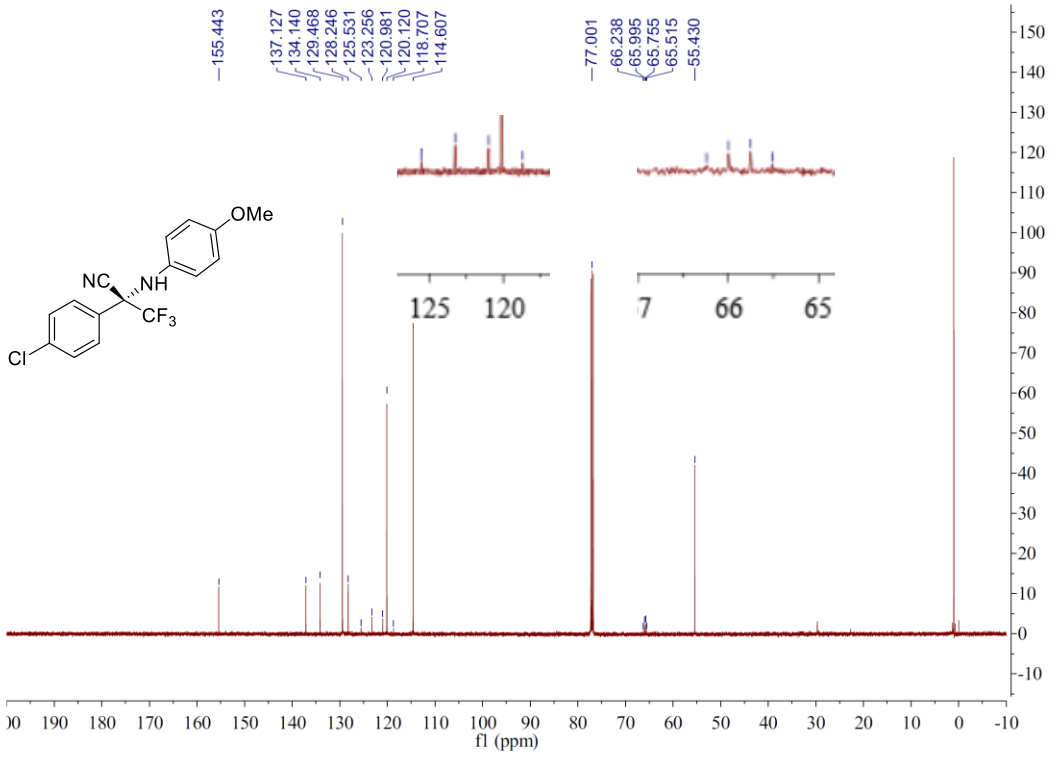
2.00
2.00
2.06
1.00
3.00
fl (ppm)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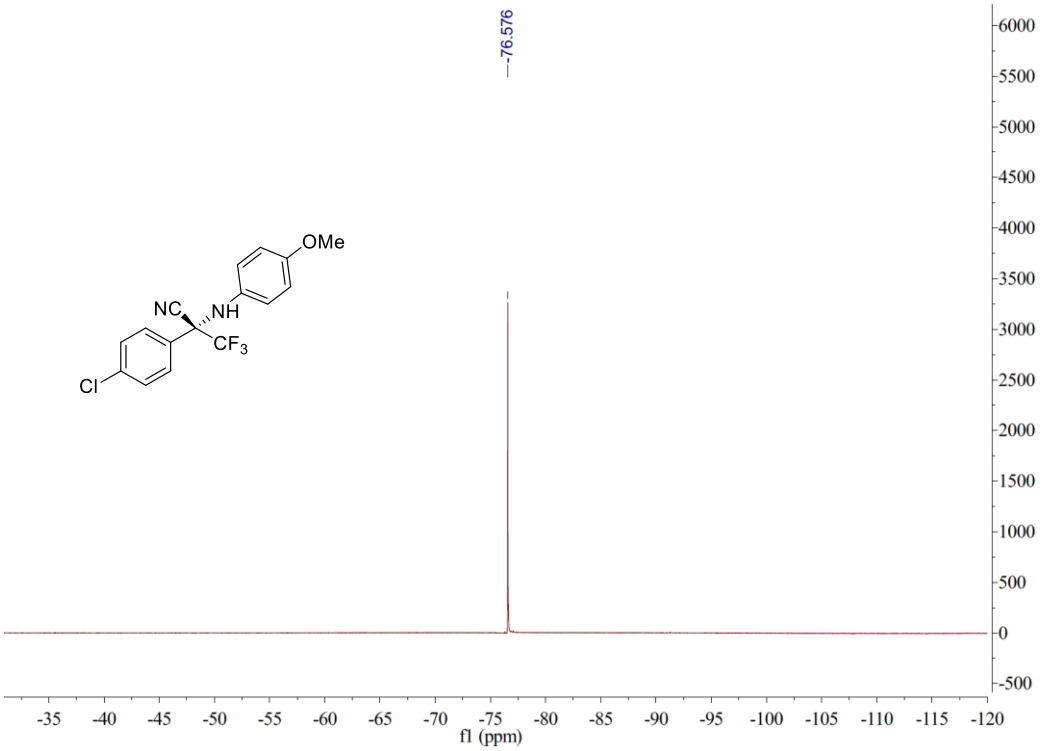
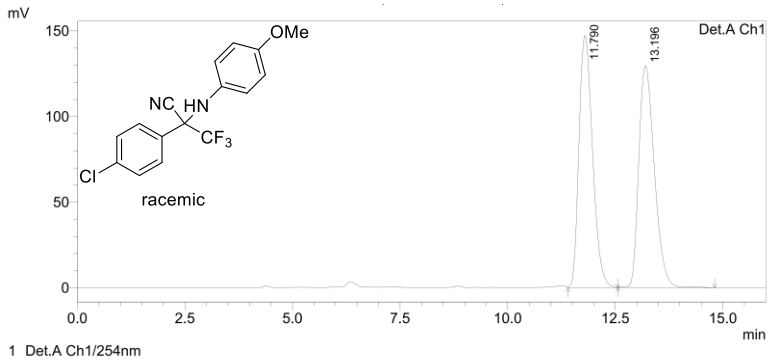
CF3
Cl
125
120
7
66
65
fl (ppm)

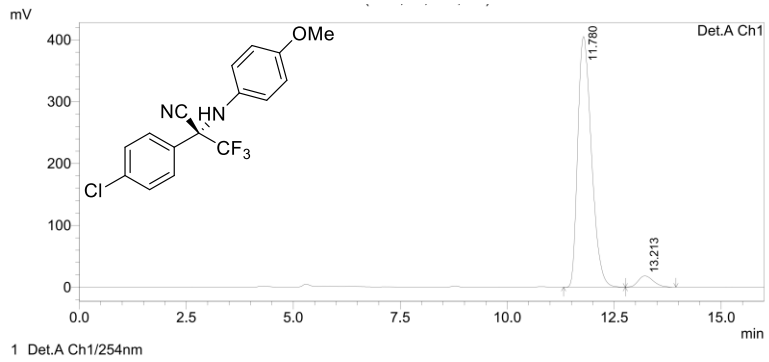




PeakTable

Detector A Ch1 254nm

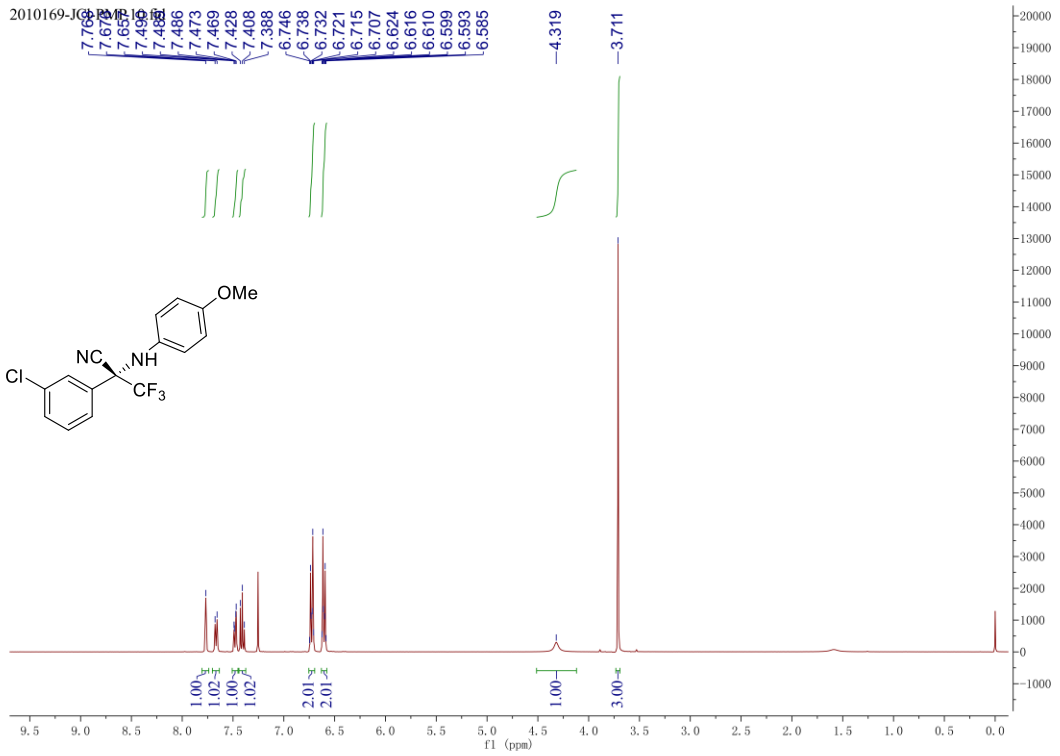
Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.790	3240784	147474	49.737	53.195
2	13.196	3275056	129757	50.263	46.805
Total		6515840	277231	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.780	9046621	405320	95.249	95.699
2	13.213	451249	18218	4.751	4.301
Total		9497870	423538	100.000	100.000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7.495
7.488
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7.428
7.408
7.388
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6.738
6.732
6.721
6.715
6.707
6.624
6.616
6.610
6.599
6.593
6.585
4.319
3.711
OMe
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NH
Cl
CF3
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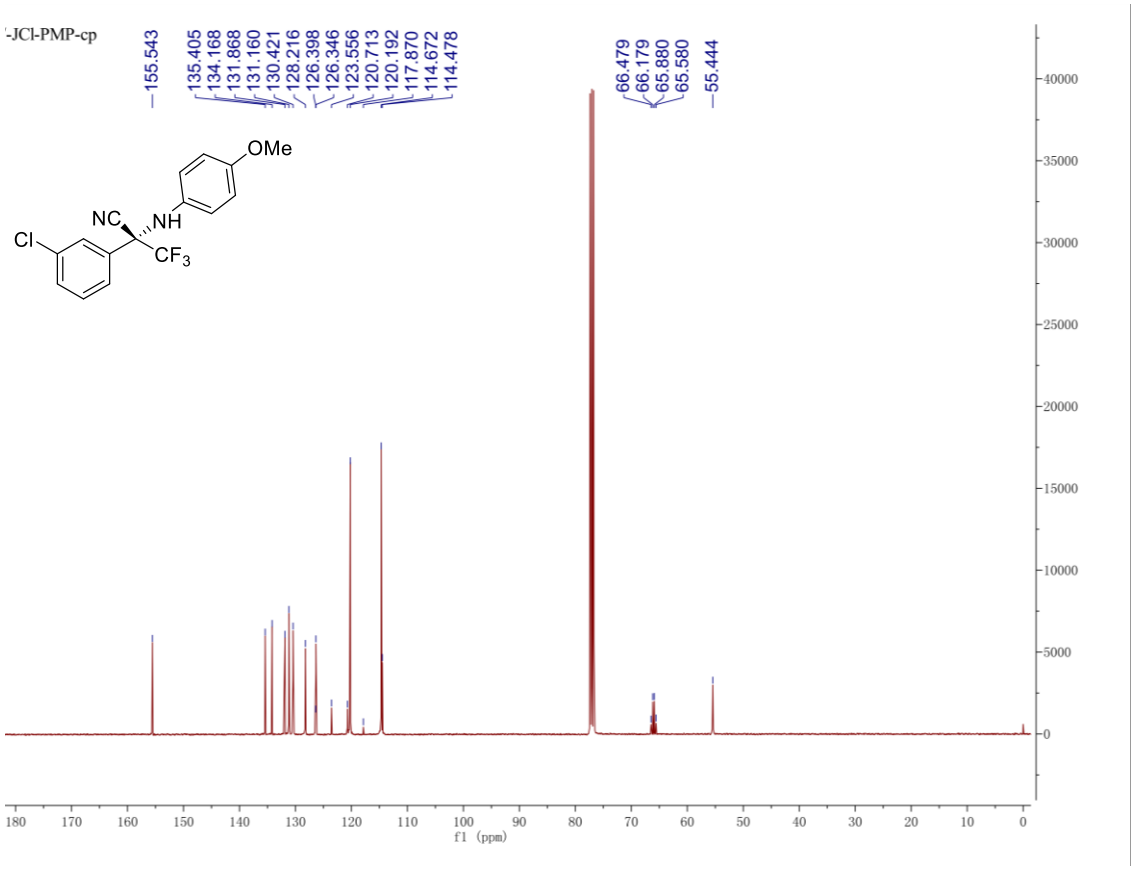
1.00
1.02
2.01
2.01
1.00
3.00
f1 (ppm)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120.713
120.192
117.870
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66.479
66.179
65.880
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OMe
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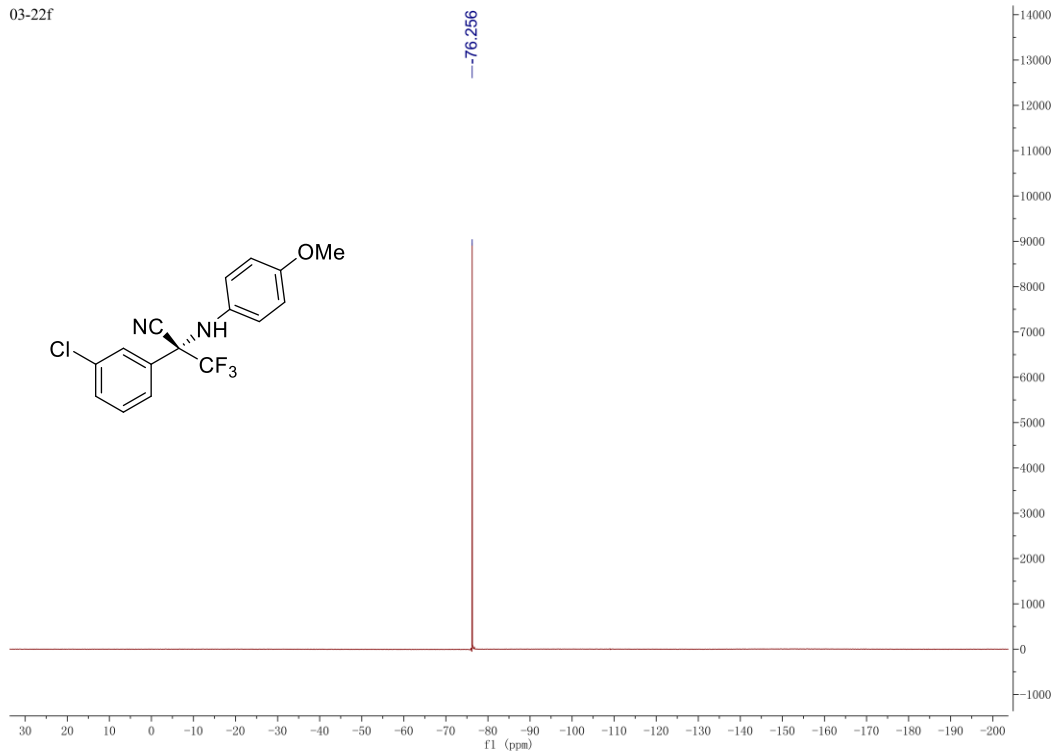
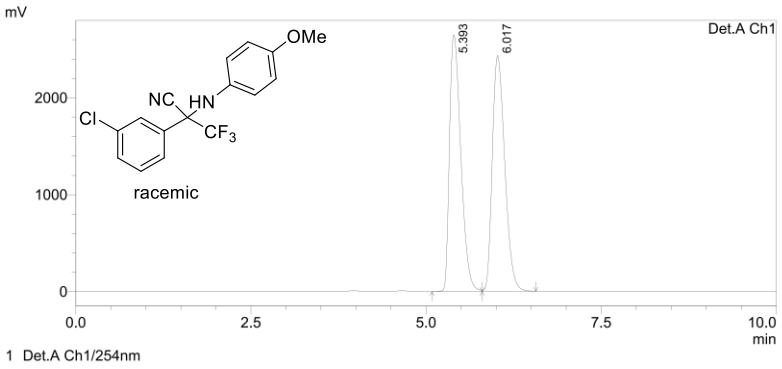
NH
Cl
CF3
f1 (ppm)

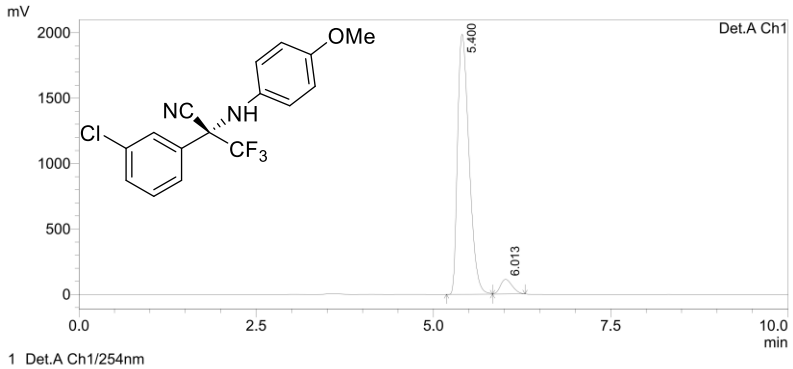




PeakTable

Detector A Ch1 254nm

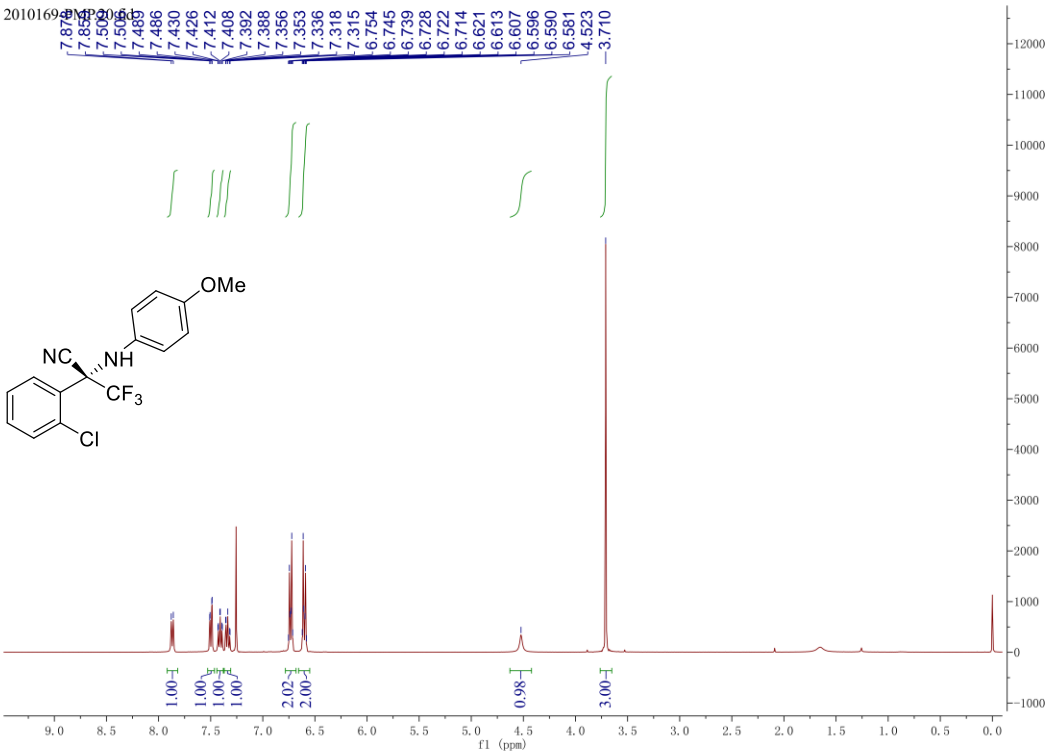
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.393	29846374	2650647	49.692	52.148
2	6.017	30215811	2432307	50.308	47.852
Total		60062184	5082954	100.000	100.000



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.400	22296505	1986464	94.450	94.638
2	6.013	1310269	112540	5.550	5.362
Total		23606774	2099004	100.000	100.000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7.503
7.489
7.486
7.430
7.426
7.412
7.408
7.392
7.388
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7.318
7.315
6.754
6.745
6.739
6.728
6.722
6.714
6.621
6.613
6.607
6.596
6.590
6.581
4.523
3.710
OMe
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NH
CF3
Cl
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1.00
1.00
1.00
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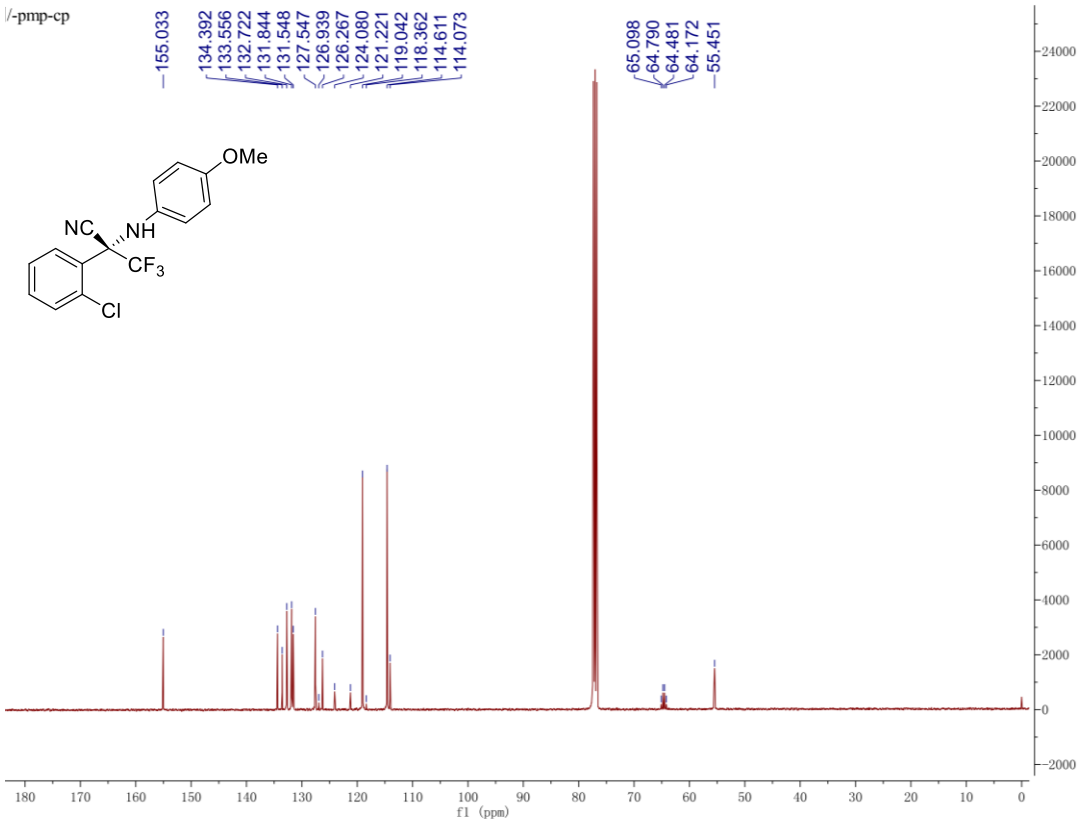
2.00
0.98
3.00
f1 (ppm)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119.042
118.362
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OMe
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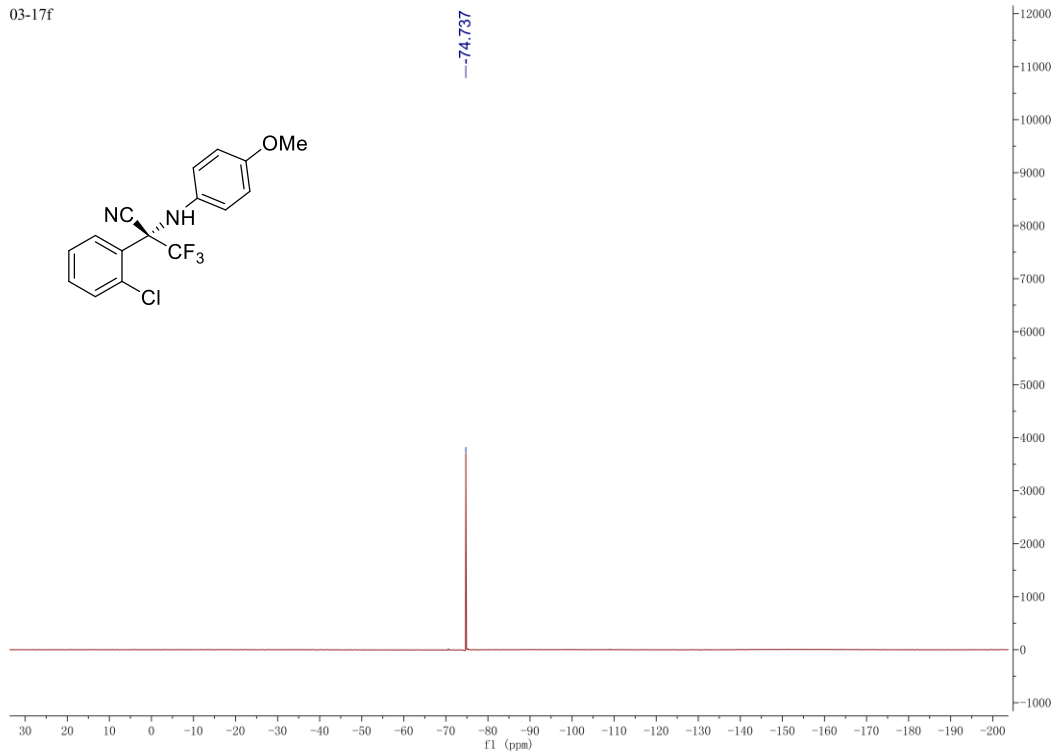
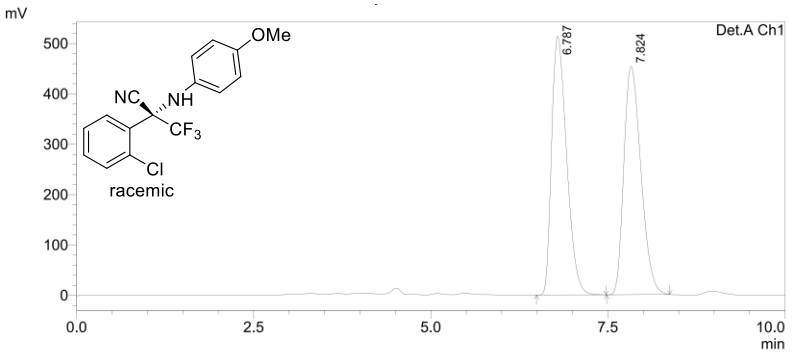
NH
CF3
Cl
f1 (ppm)



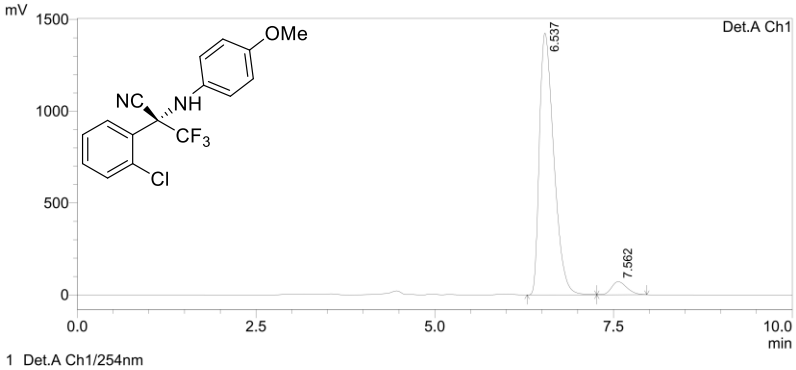


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.787	7591456	513917	49.924	53.141
2	7.824	7614598	453165	50.076	46.859
Total		15206054	967082	100.000	100.000

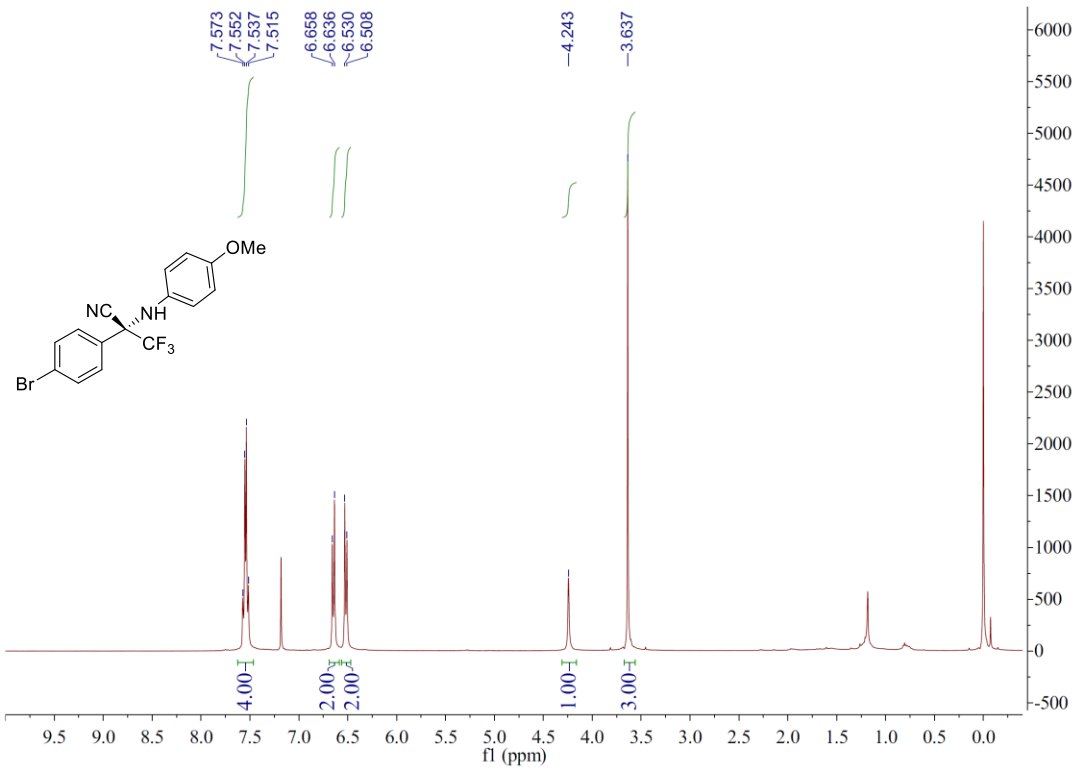


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.537	20024440	1426112	94.921	95.244
2	7.562	1071540	71207	5.079	4.756
Total		21095980	1497318	100.000	100.000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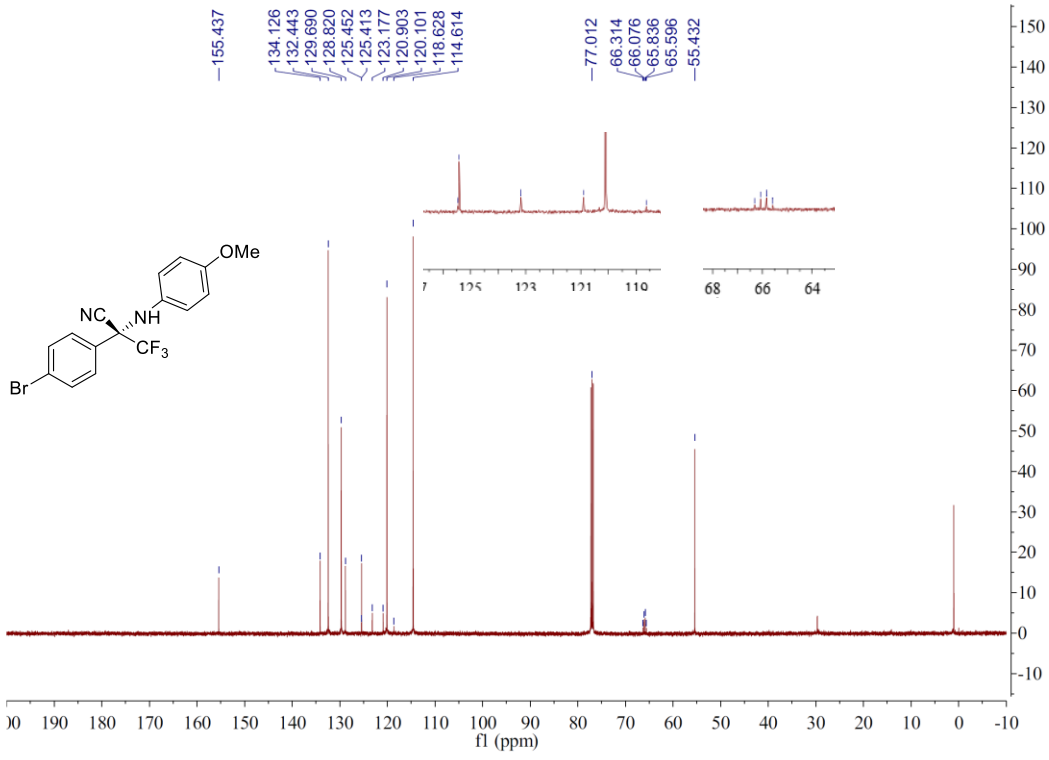
7.537
7.515
6.658
6.636
6.530
6.508
4.243
3.637
OMe
NC
NH
CF3
Br
4.00
2.00
2.00
1.00
3.00
fl (ppm)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125.413
123.177
120.903
120.101
118.628
114.614
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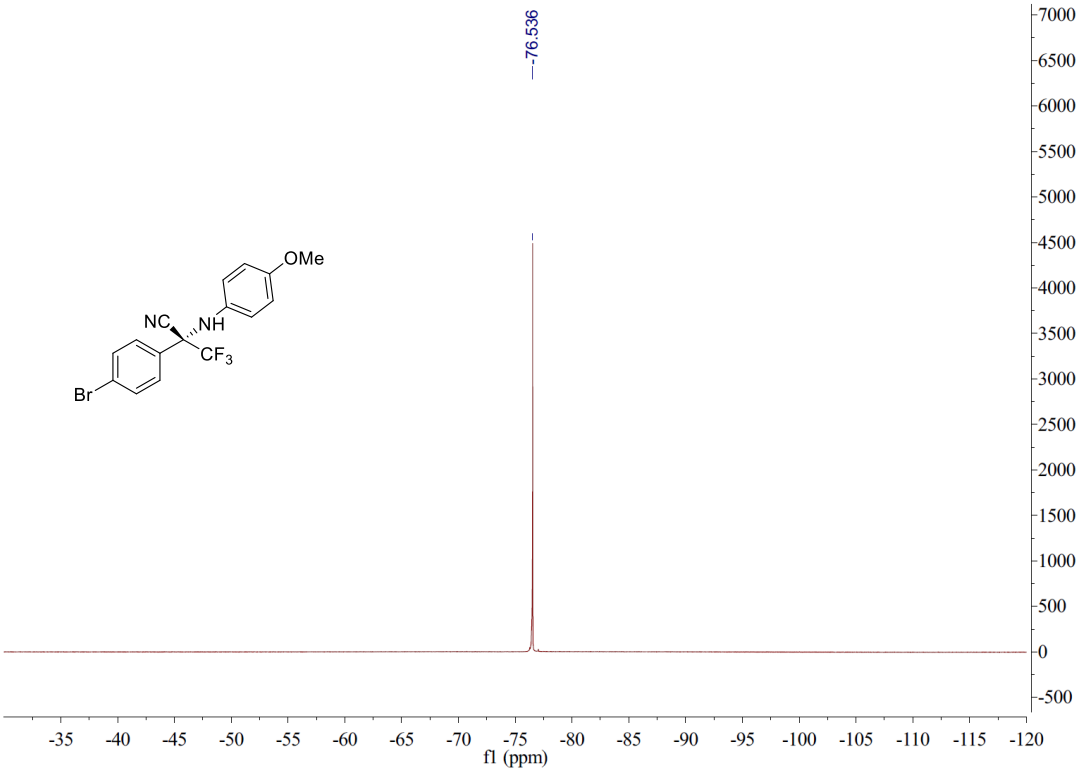
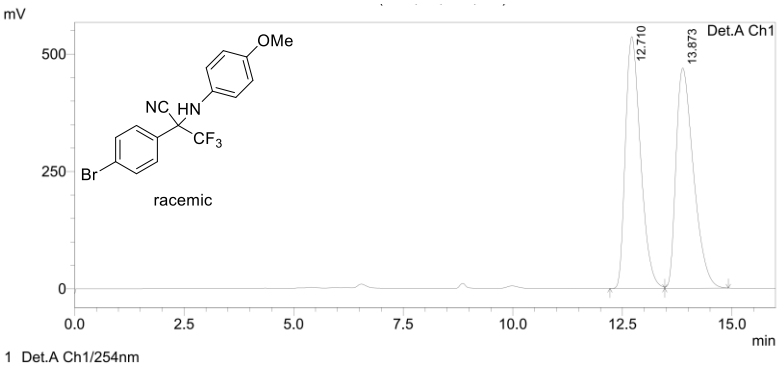
66.314
66.076
65.836
65.596
55.432
OMe
NC
NH
CF3
Br
fl (ppm)





PeakTable

Detector A Ch1 254nm

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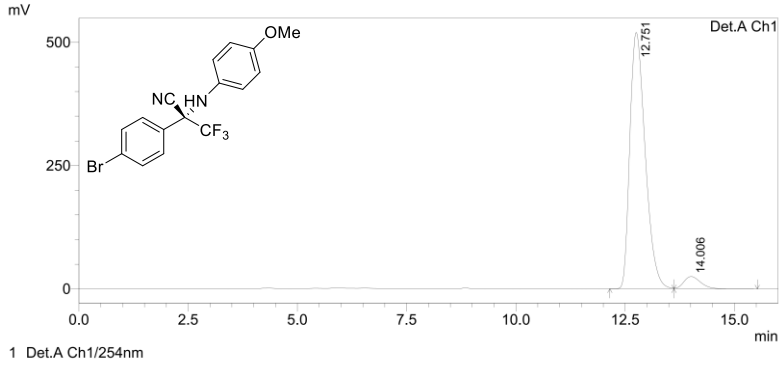
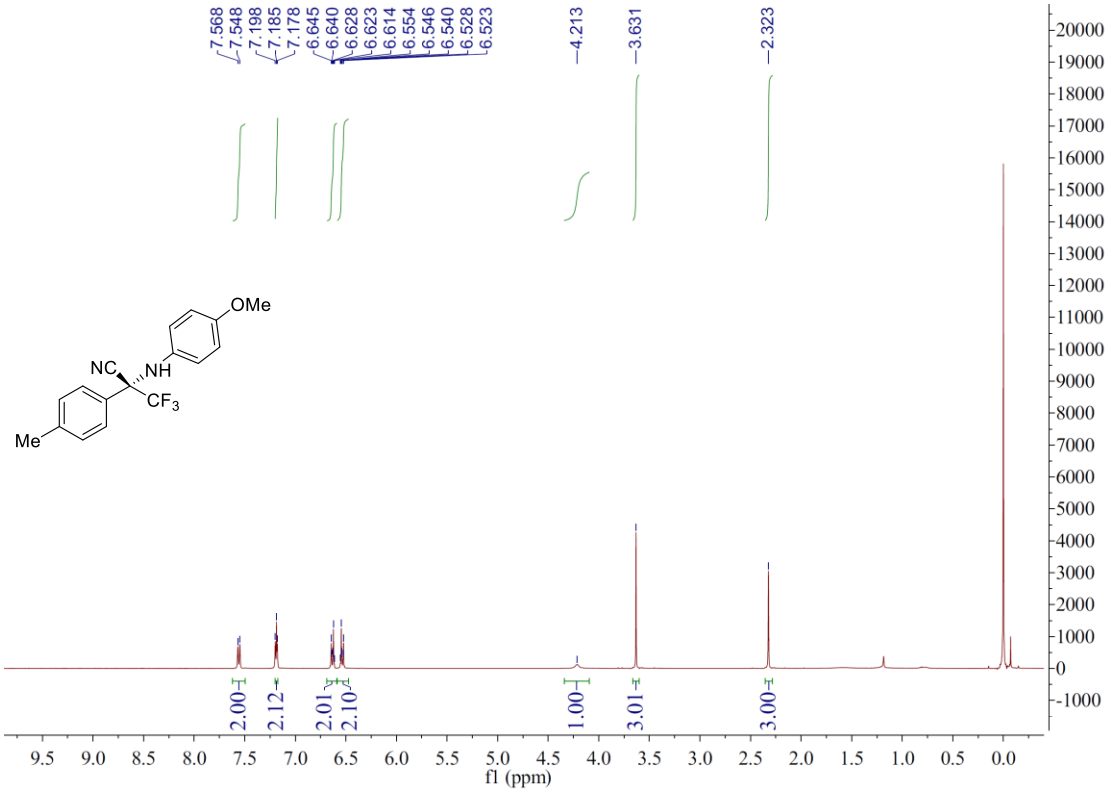
1	12.710	12880066	536272	49.702	53.345
2	13.873	13034602	469011	50.298	46.655
Total		25914668	1005283	100.000	100.000

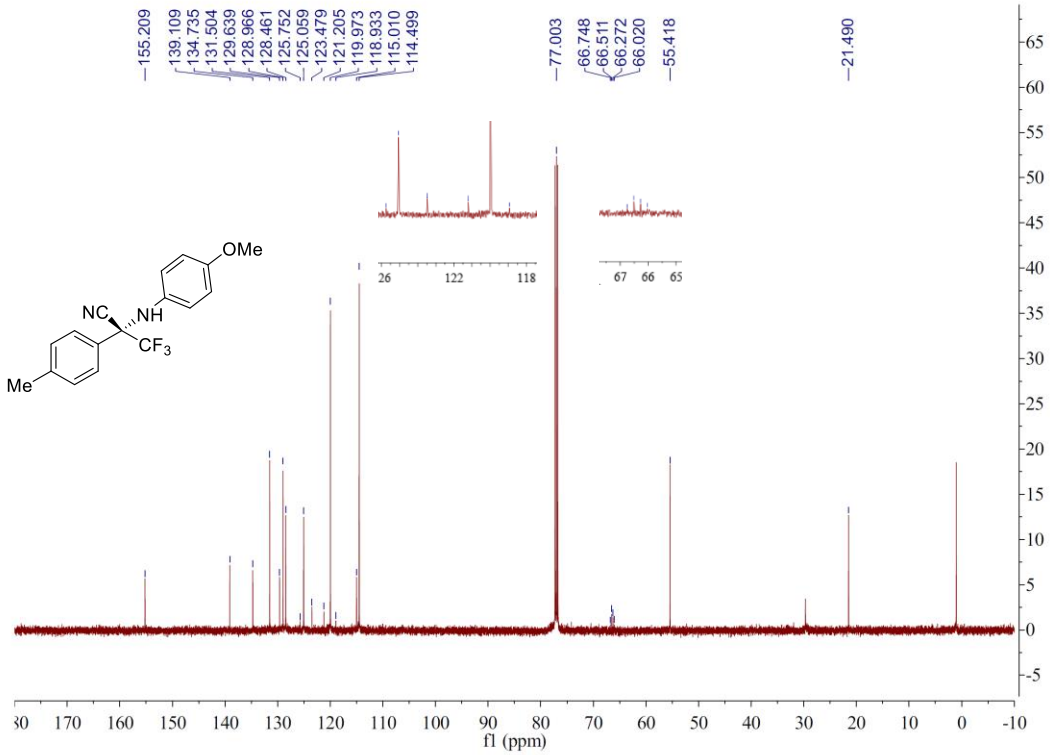


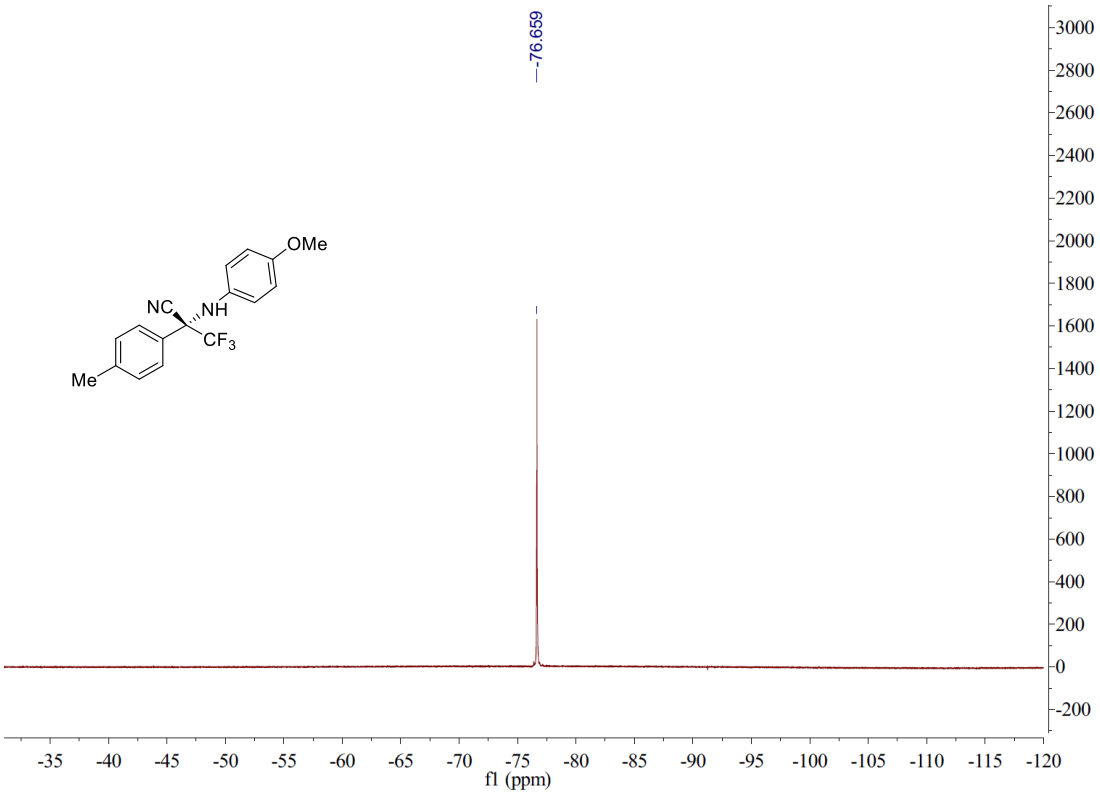
PeakTable

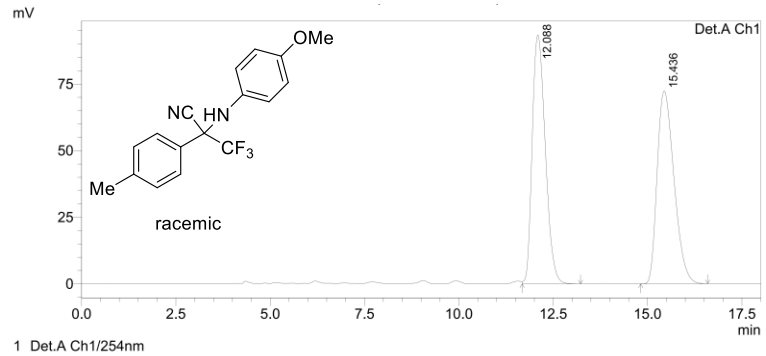
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.751	12739425	519876	94.961	95.408
2	14.006	675980	25021	5.039	4.592
Total		13415405	544896	100.000	100.000


7.568
7.548
7.198
7.185
7.178
6.645
6.640
6.628
6.623
6.614
6.554
6.546
6.540
6.528
6.523
4.213
3.631
2.323
OMe
NC
NH
CF3
Me
2.00
2.12
2.01
2.10
1.00
3.01
3.00
f1 (ppm)


155.209
139.109
134.735
131.504
129.639
128.966
128.461
125.752
125.059
123.479
121.205
119.973
118.933
115.010
114.499
77.003
66.748
66.511
66.272
66.020
55.418
21.490
OMe
NC
NH
CF3
Me
f1 (ppm)



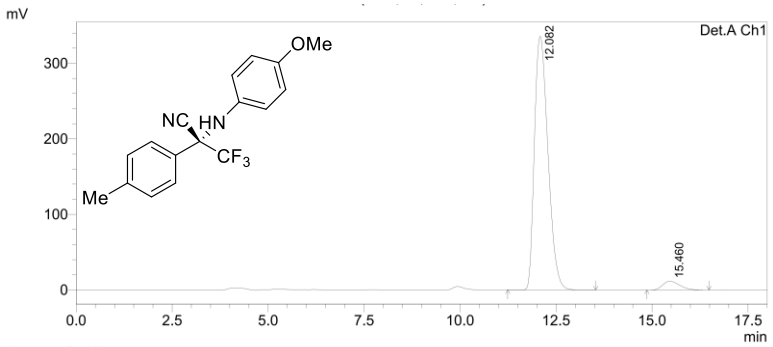


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.088	2255617	93437	50.047	56.353
2	15.436	2251376	72370	49.953	43.647
Total		4506994	165806	100.000	100.000

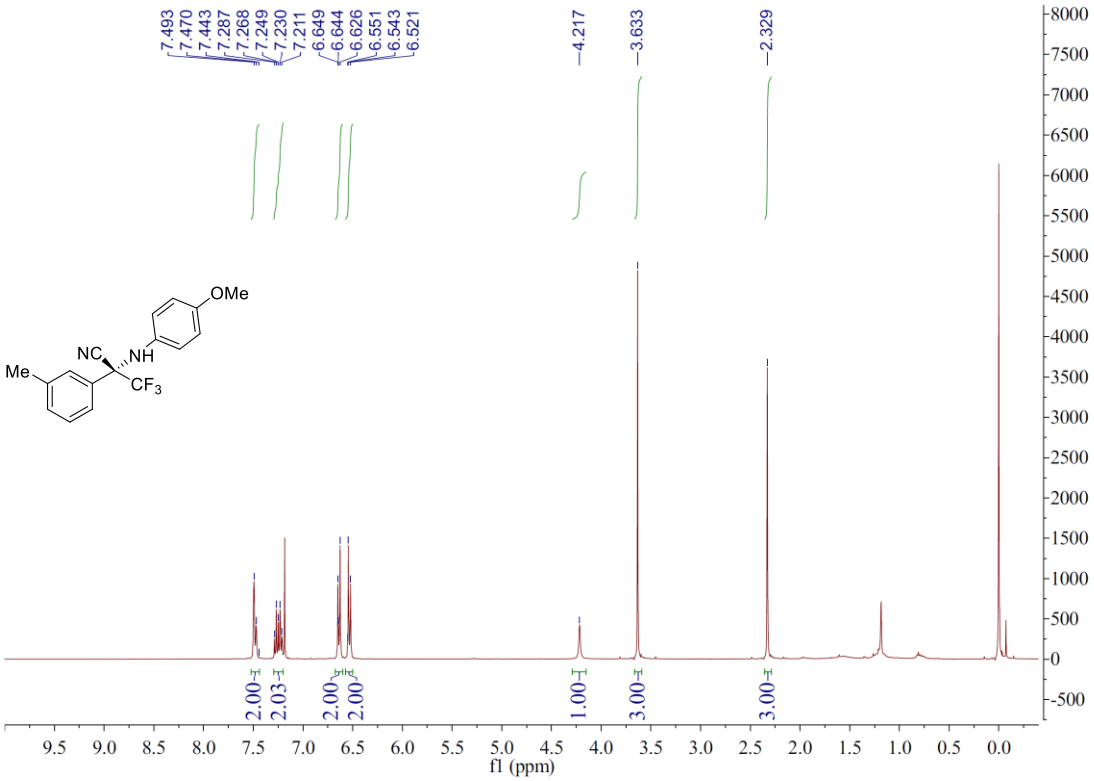


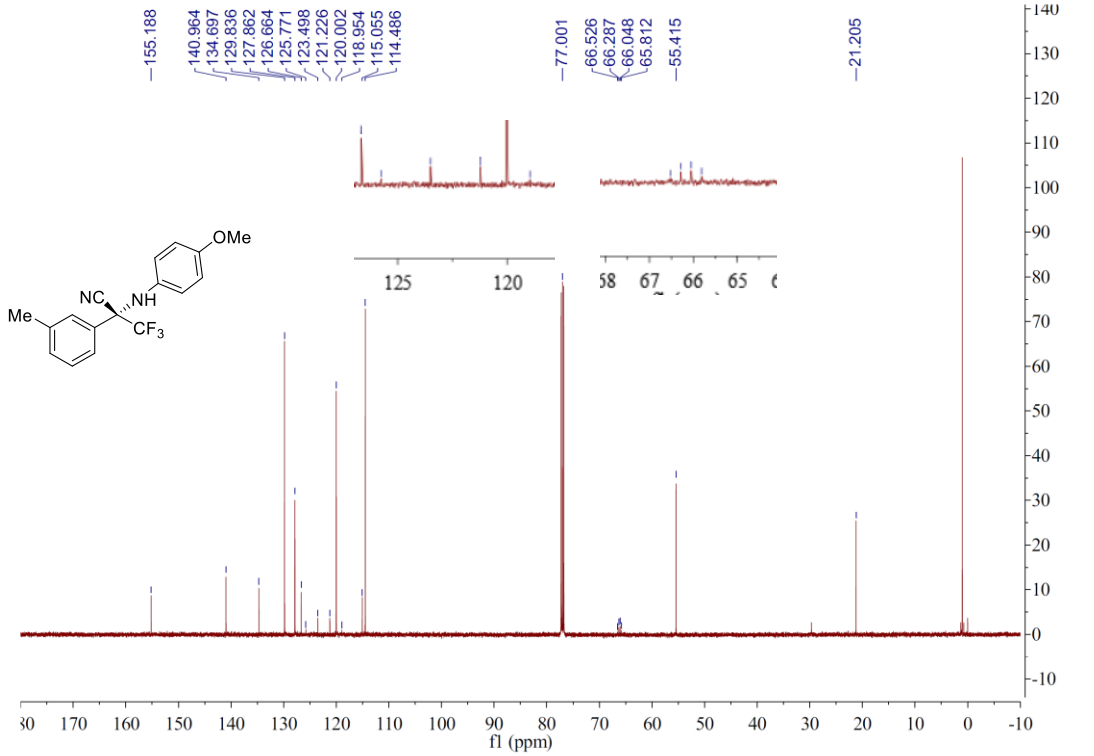
1 Det.A Ch1/254nm

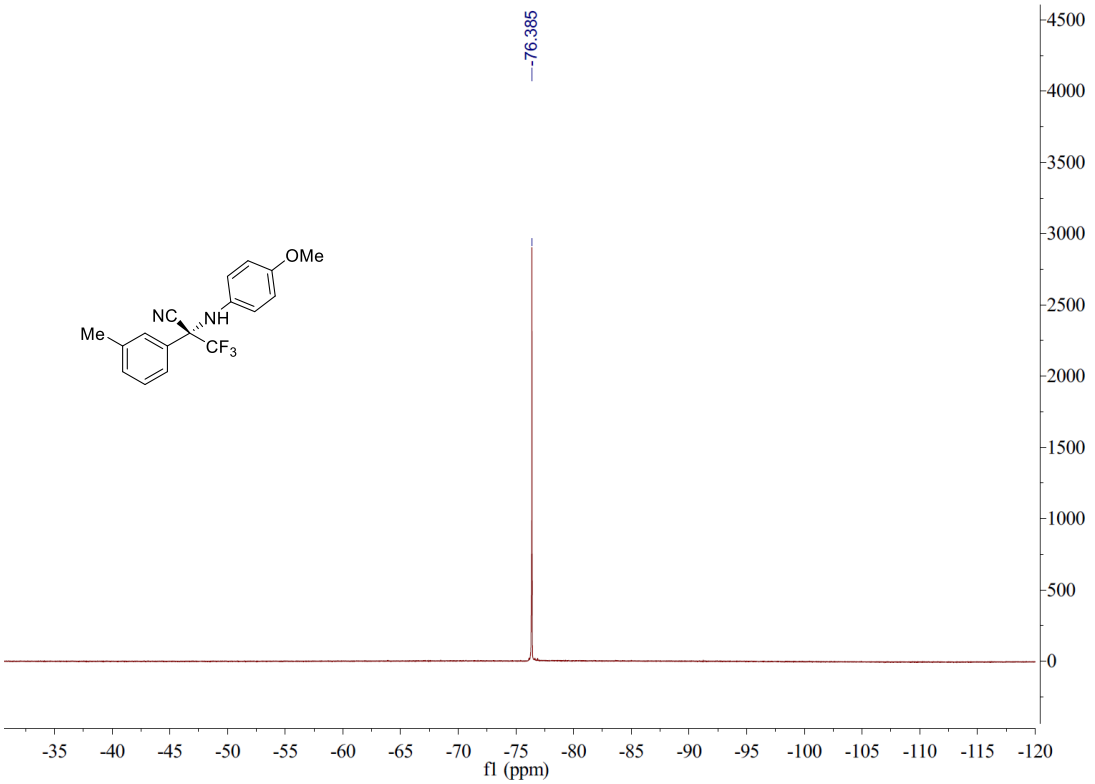
PeakTable

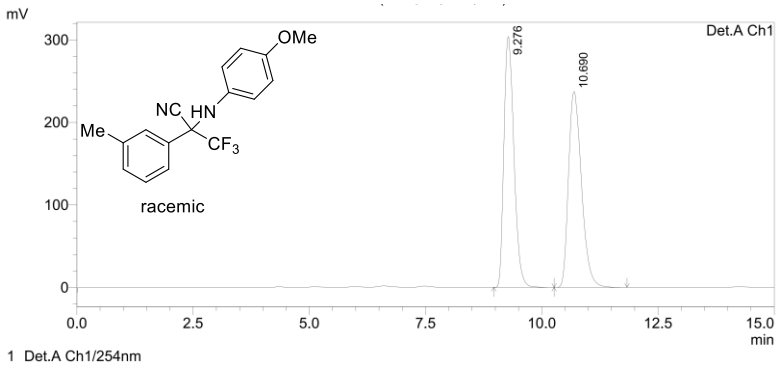
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	12.082	8227729	335850	95.838	96.673
2	15.460	357297	11559	4.162	3.327
Total		8585026	347409	100.000	100.000


7.493
7.470
7.443
7.287
7.268
7.249
7.230
7.211
6.649
6.644
6.626
6.551
6.543
6.521
4.217
3.633
2.329
OMe
NC
NH
Me
CF3
2.00
2.03
2.00
2.00
1.00
3.00
3.00
fl (ppm)


155.188
140.964
134.697
129.836
127.862
126.664
125.771
123.498
121.226
120.002
118.954
115.055
114.486
77.001
66.526
66.287
66.048
65.812
55.415
21.205
OMe
NC
NH
Me
CF3
125
120
fl (ppm)

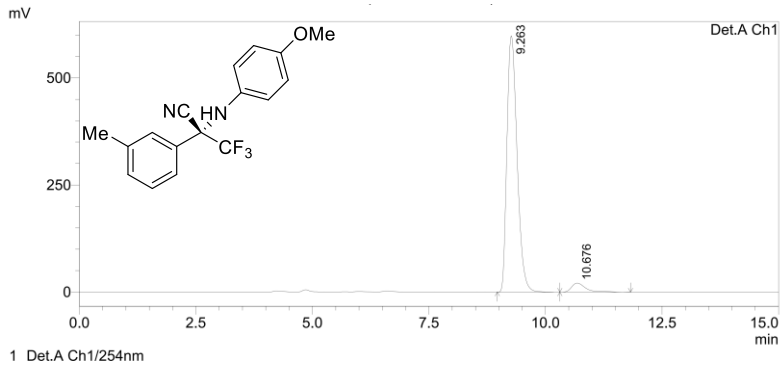




PeakTable

Detector A Ch1 254nm

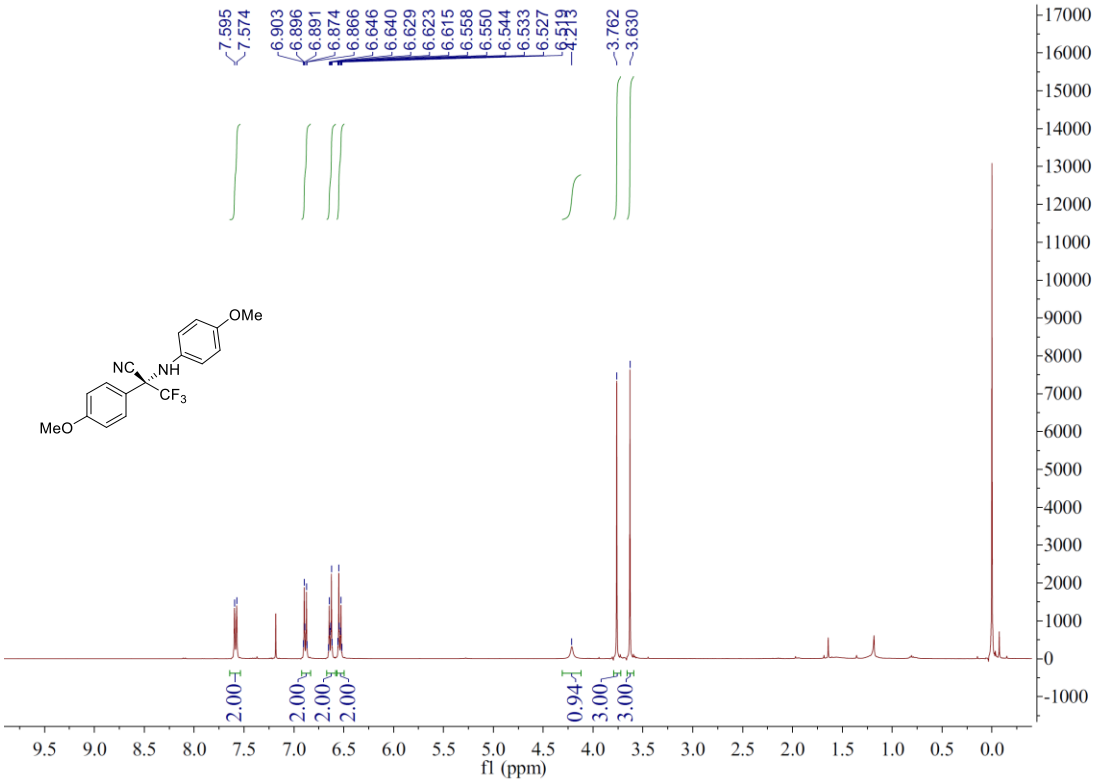
Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.276	4569402	303896	49.698	56.158
2	10.690	4624961	237244	50.302	43.842
Total		9194363	541140	100.000	100.000

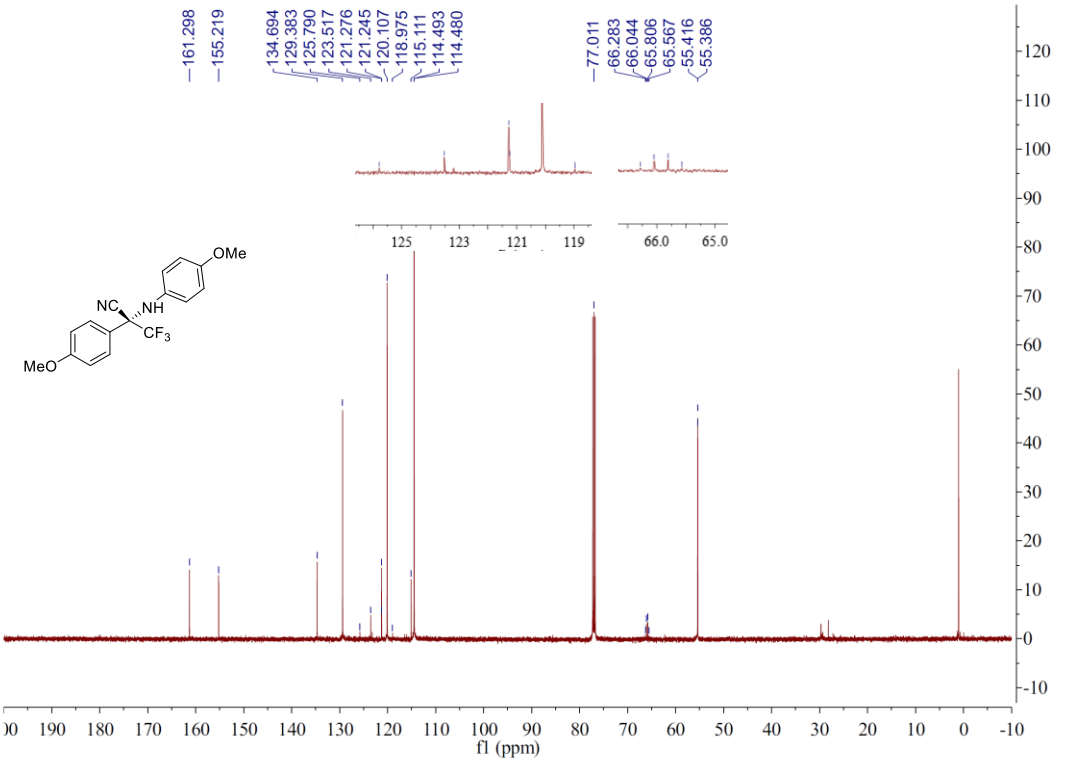


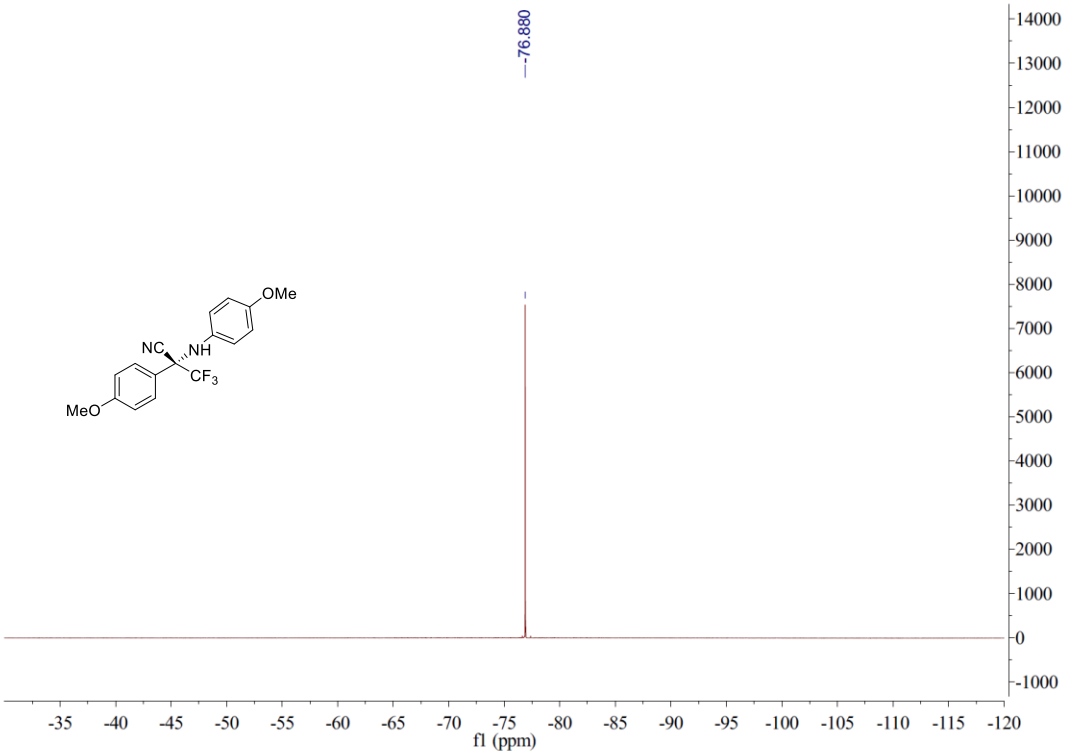
PeakTable

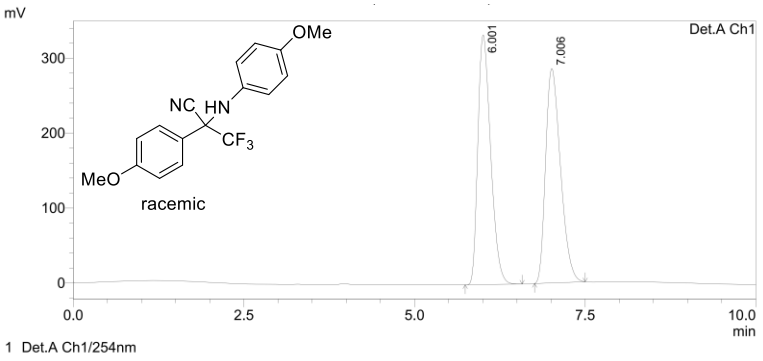
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.263	9101589	598514	95.392	96.622
2	10.676	439695	20924	4.608	3.378
Total		9541284	619437	100.000	100.000


7.595
7.574
6.903
6.896
6.891
6.874
6.866
6.646
6.640
6.629
6.623
6.615
6.558
6.550
6.544
6.533
6.527
6.519
4.213
3.762
3.630
OMe
NC
NH
CF3
MeO
2.00
2.00
2.00
2.00
0.94
3.00
3.00
fl (ppm)


161.298
155.219
134.694
129.383
125.790
123.517
121.276
121.245
120.107
118.975
115.111
114.493
114.480
77.011
66.283
66.044
65.806
65.567
55.416
55.386
OMe
NC
NH
CF3
MeO
fl (ppm)



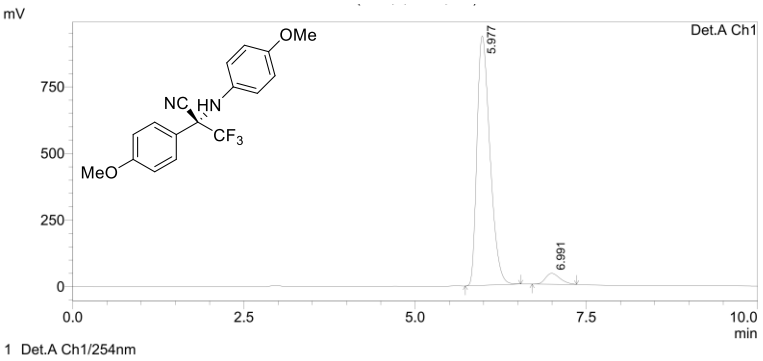


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.001	4334083	333015	49.977	53.786
2	7.006	4338000	286132	50.023	46.214
Total		8672083	619147	100.000	100.000

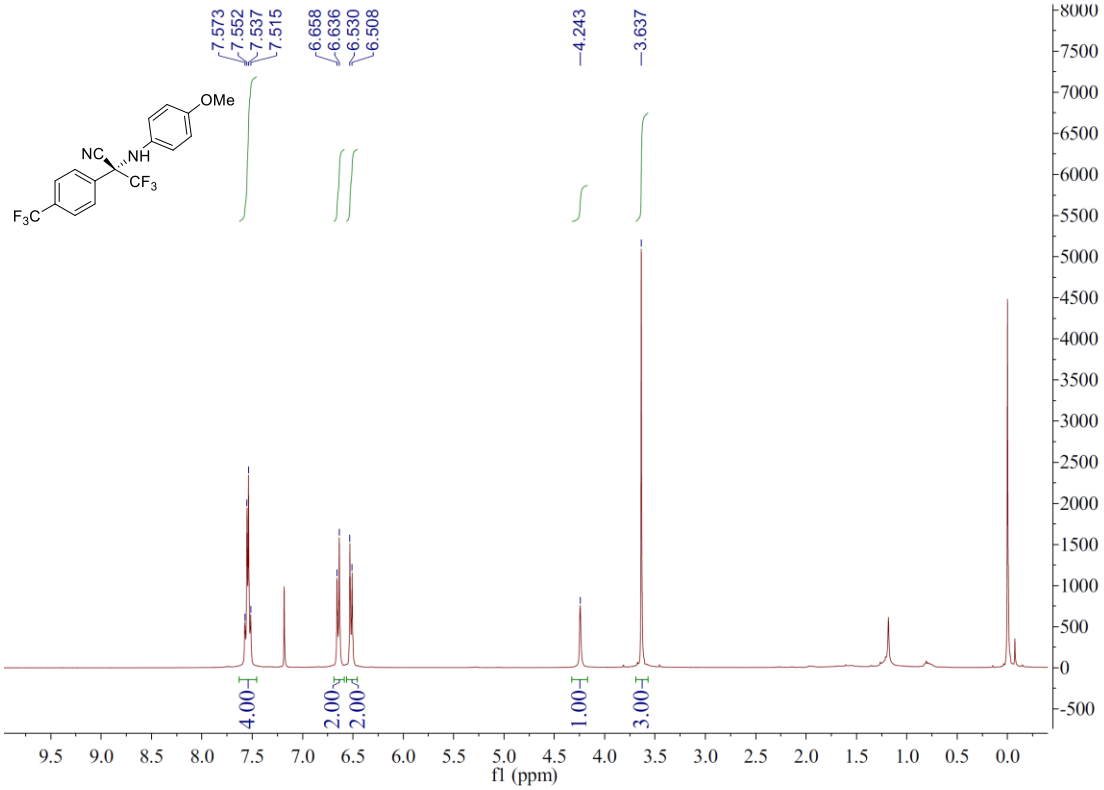


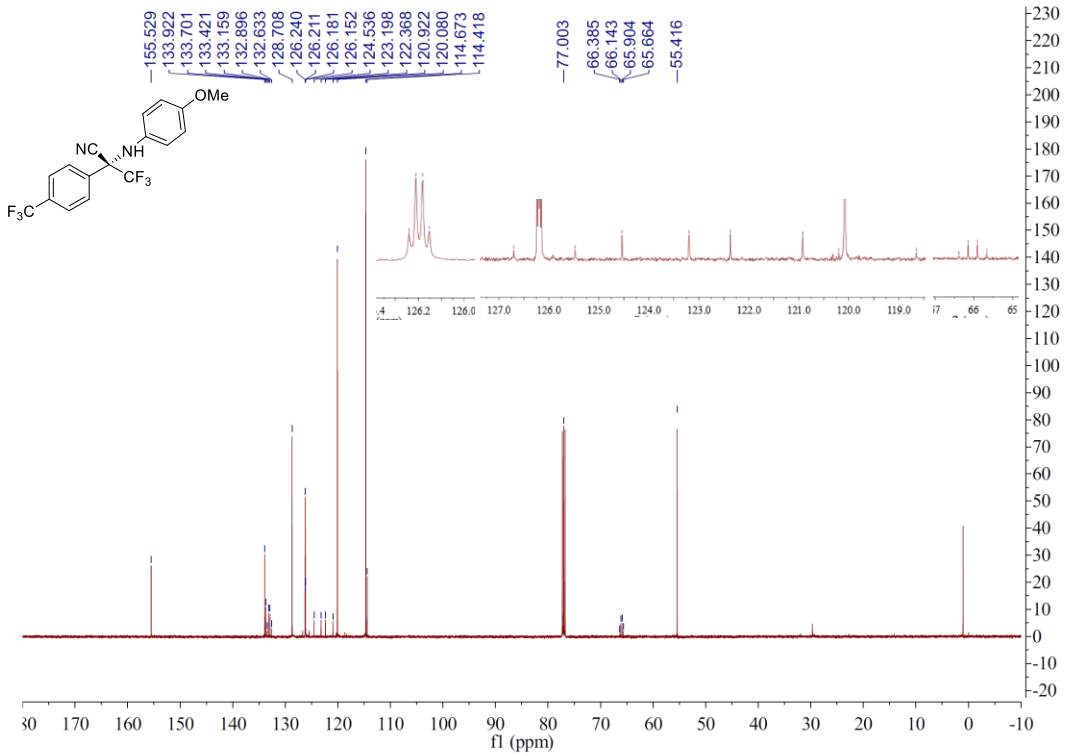
1 Det.A Ch1/254nm

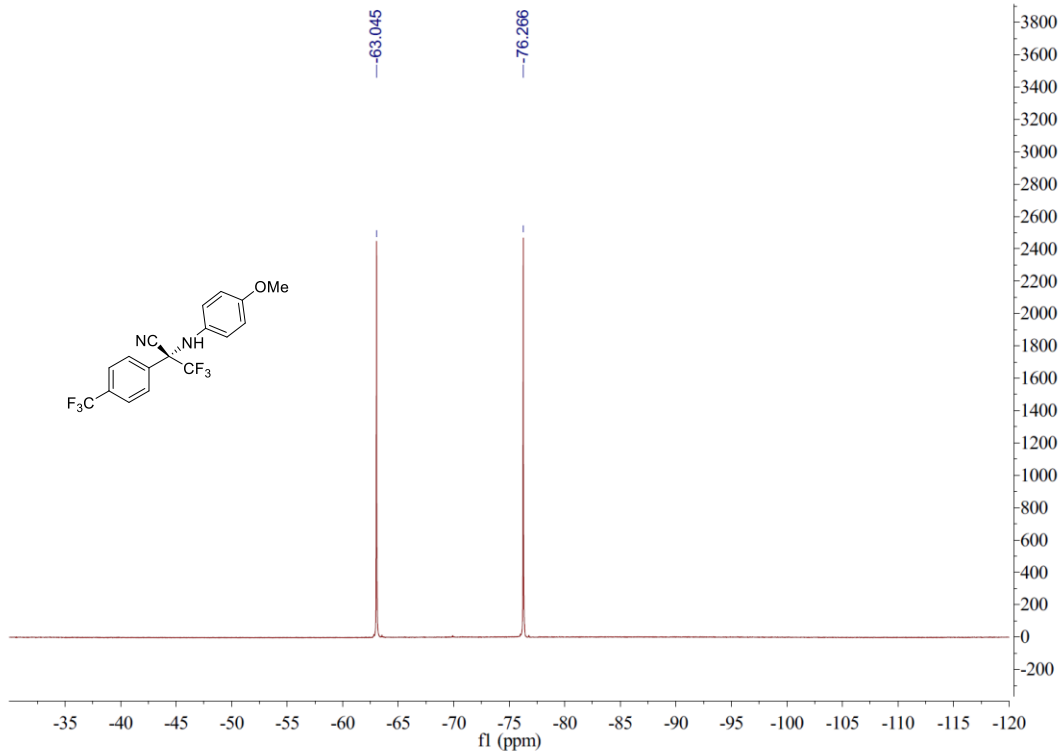
PeakTable

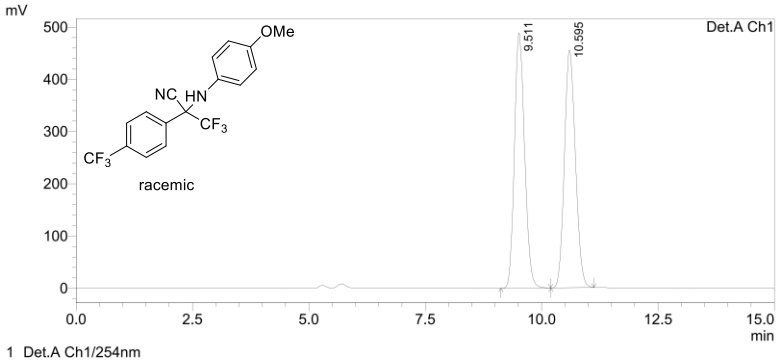
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.977	12319889	935441	95.376	95.827
2	6.991	597334	40738	4.624	4.173
Total		12917223	976179	100.000	100.000


7.573
7.552
7.537
7.515
6.658
6.636
6.530
6.508
4.243
3.637
OMe
NC
NH
CF3
F3C
4.00
2.00
2.00
1.00
3.00
fl (ppm)


155.529
133.922
133.701
133.421
133.159
132.896
132.633
128.708
126.240
126.211
126.181
126.152
124.536
123.198
122.368
120.922
120.080
114.673
114.418
77.003
66.385
66.143
65.904
65.664
55.416
OMe
NC
NH
CF3
F3C
fl (ppm)



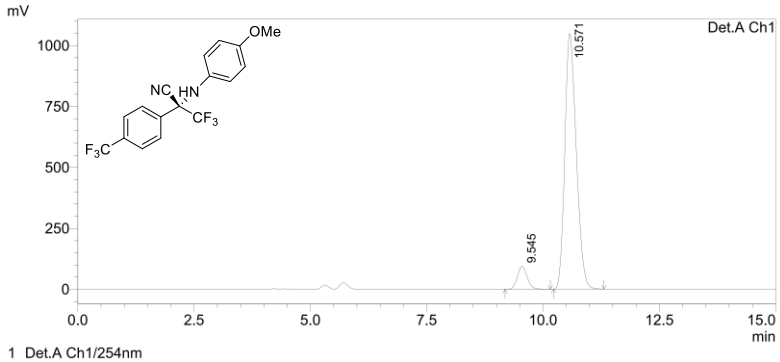


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.511	7417456	488545	49.775	51.766
2	10.595	7484436	455209	50.225	48.234
Total		14901892	943754	100.000	100.000

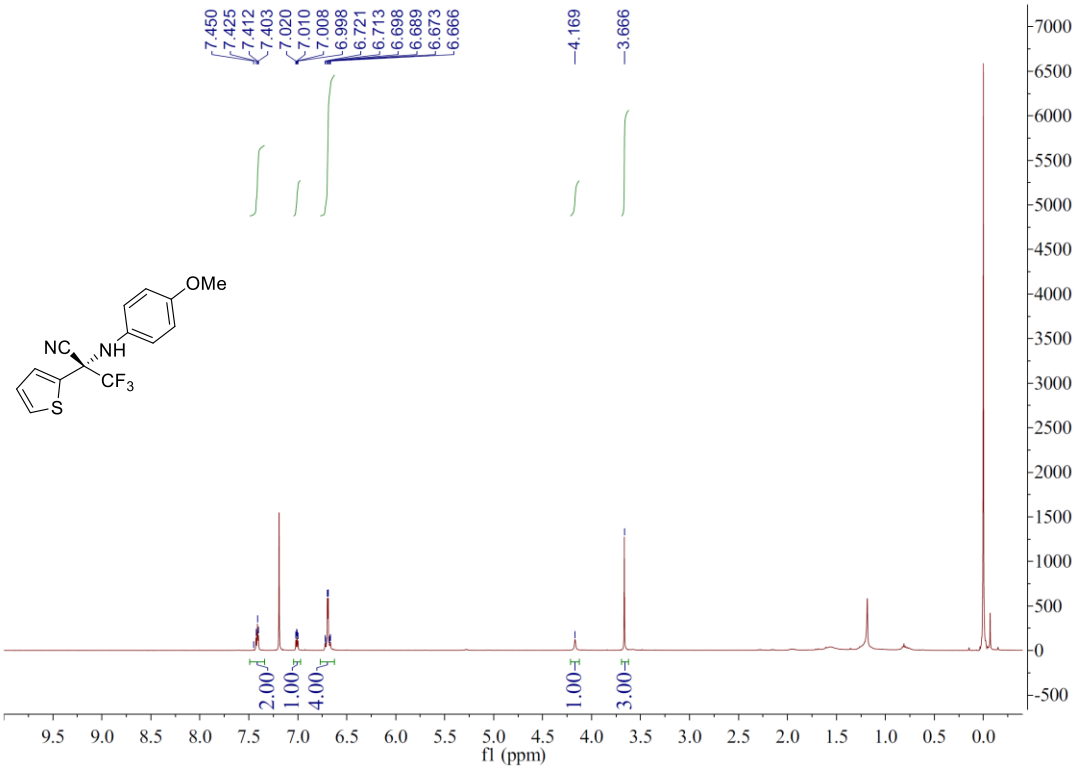


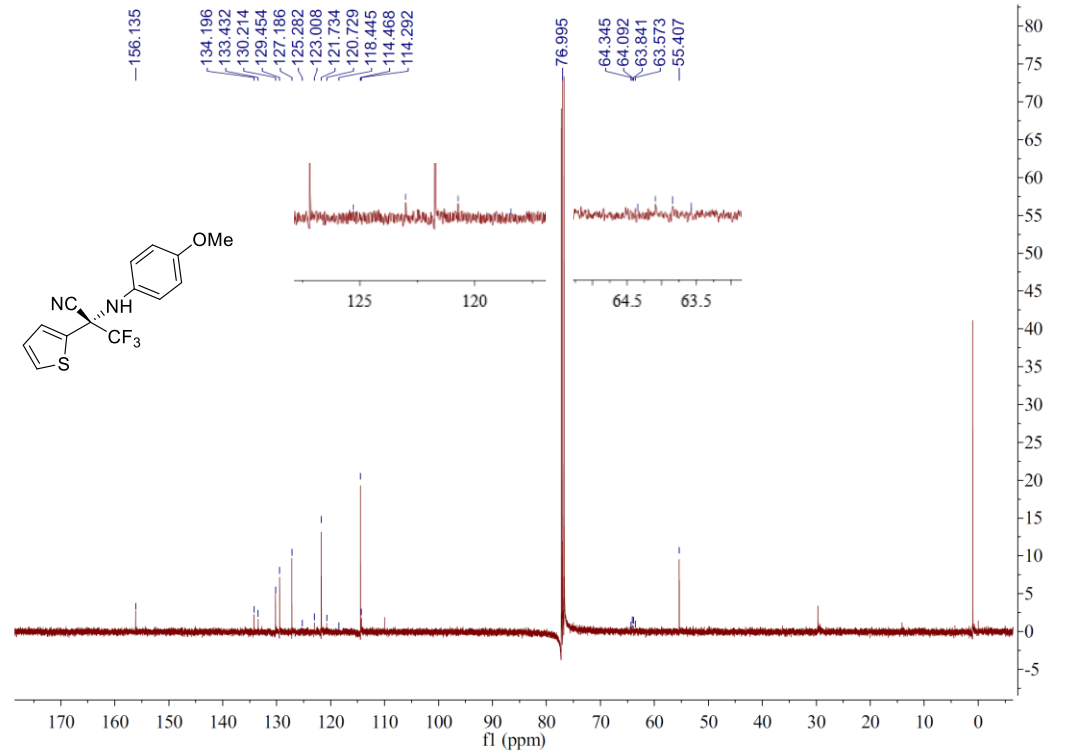
1 Det.A Ch1/254nm

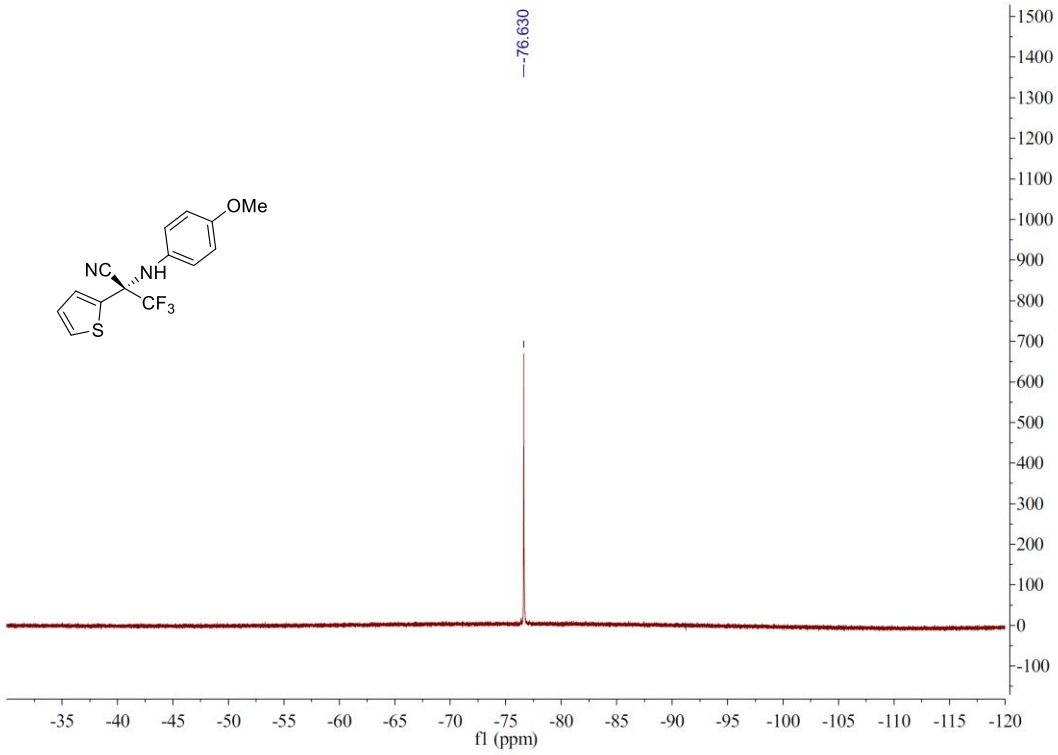
PeakTable

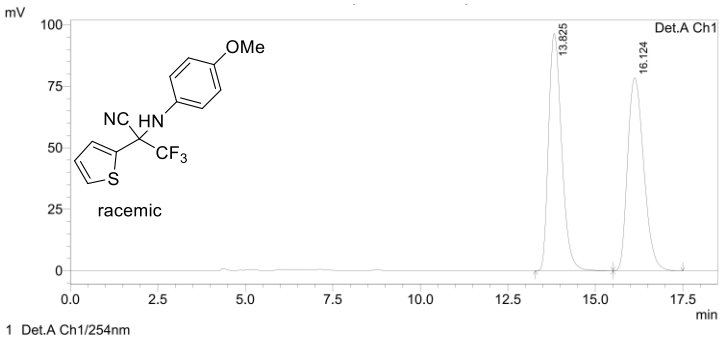
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.545	1390496	94677	7.205	8.280
2	10.571	17908298	1048827	92.795	91.720
Total		19298794	1143504	100.000	100.000


7.450
7.425
7.412
7.403
7.020
7.010
7.008
6.998
6.721
6.713
6.698
6.689
6.673
6.666
4.169
3.666
OMe
NC
NH
CF3
S
2.00
1.00
4.00
1.00
3.00
f1 (ppm)


156.135
134.196
133.432
130.214
129.454
127.186
125.282
123.008
121.734
120.729
118.445
114.468
114.292
76.995
64.345
64.092
63.841
63.573
55.407
OMe
NC
NH
CF3
S
125
120
64.5
63.5
f1 (ppm)



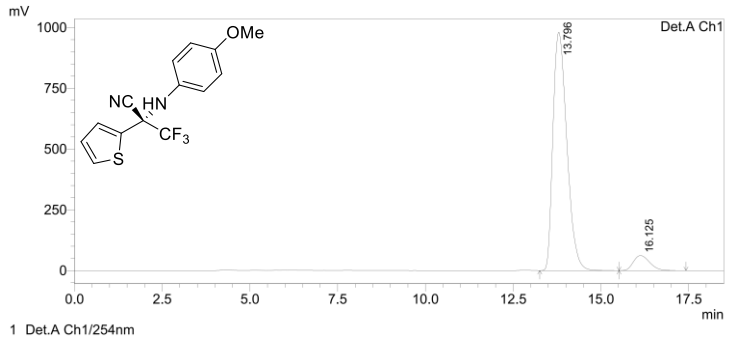


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.825	2506689	96429	49.894	55.153
2	16.124	2517294	78409	50.106	44.847
Total		5023983	174839	100.000	100.000

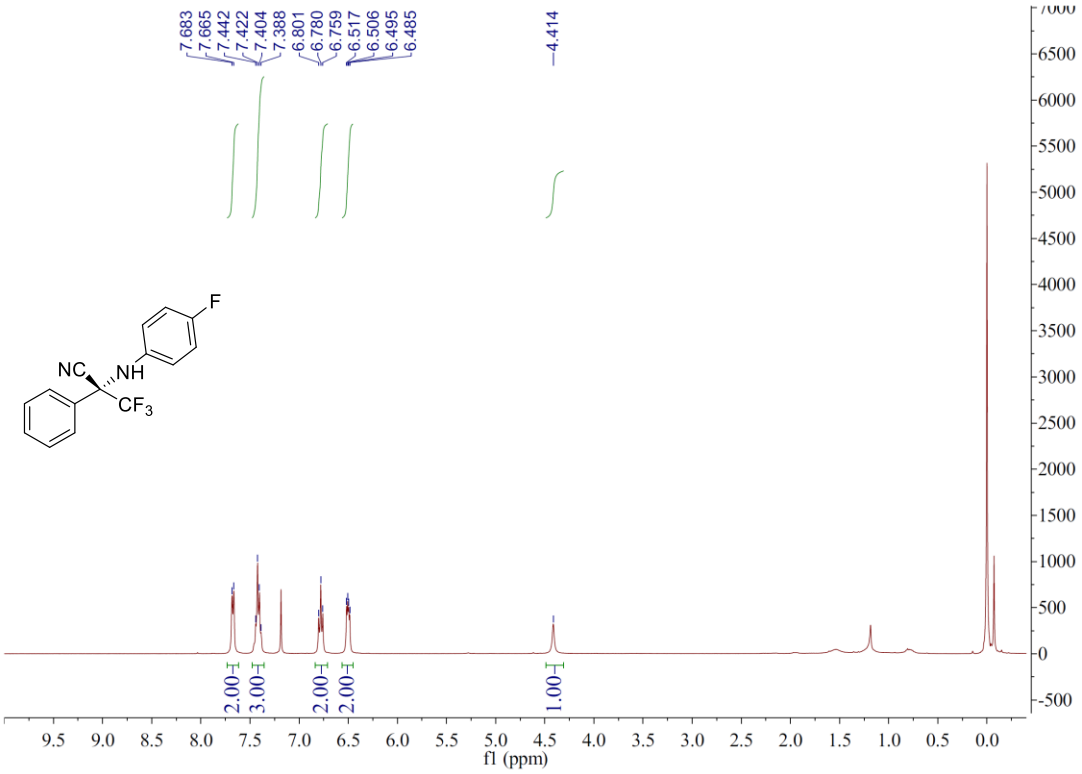


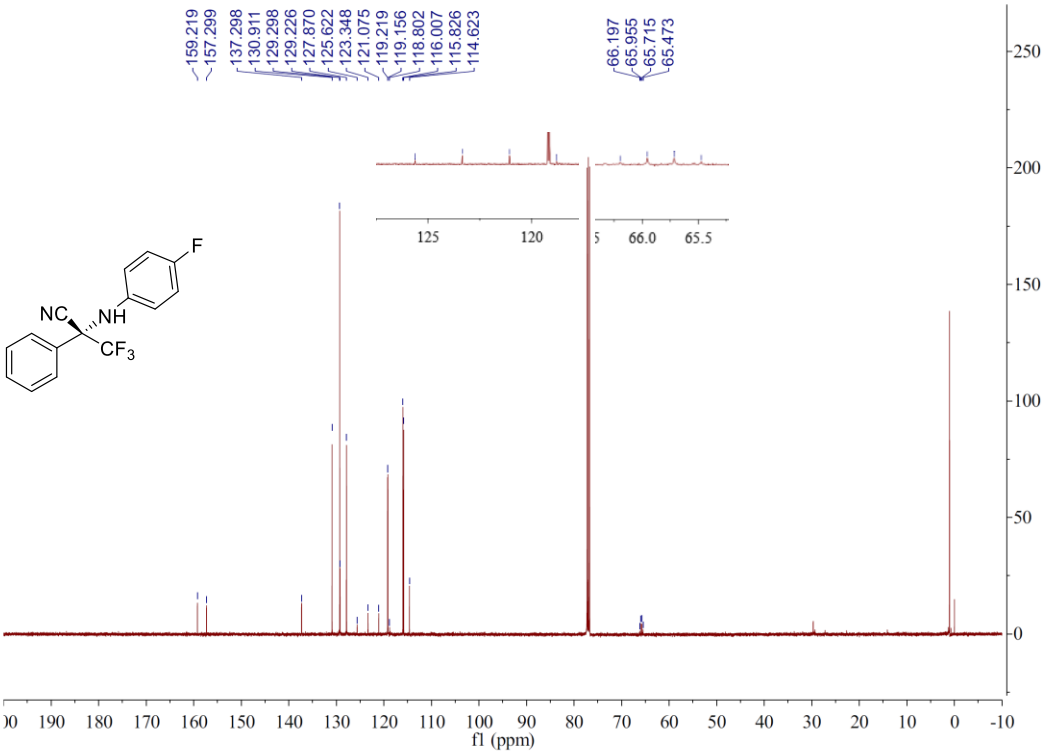
1 Det.A Ch1/254nm

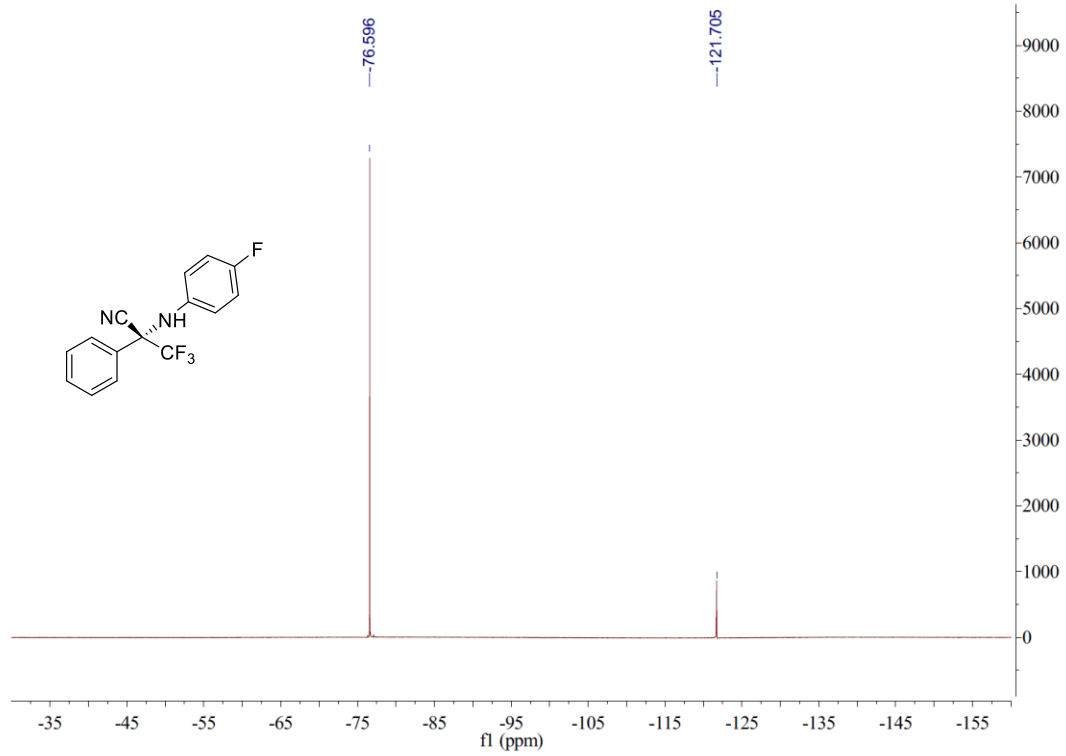
PeakTable

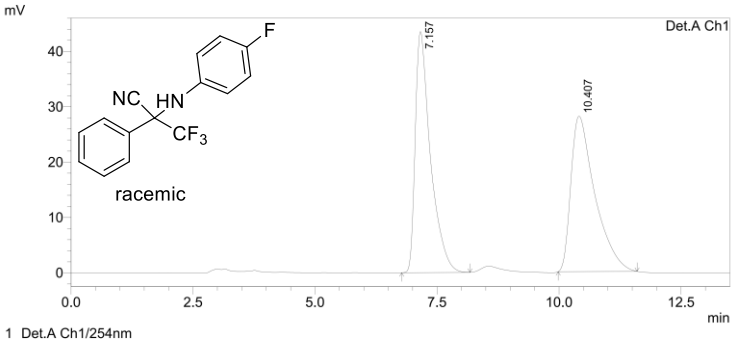
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	13.796	27021081	980862	93.176	94.094
2	16.125	1978838	61562	6.824	5.906
Total		28999919	1042424	100.000	100.000


7.683
7.665
7.442
7.422
7.404
7.388
6.801
6.780
6.759
6.517
6.506
6.495
6.485
4.414
F
NC
NH
CF3
2.00
3.00
2.00
2.00
1.00
fl (ppm)


159.219
157.299
137.298
130.911
129.298
129.226
127.870
125.622
123.348
121.075
119.219
119.156
118.802
116.007
115.826
114.623
66.197
65.955
65.715
65.473
F
NC
NH
CF3
125
120
66.0
65.5
fl (ppm)

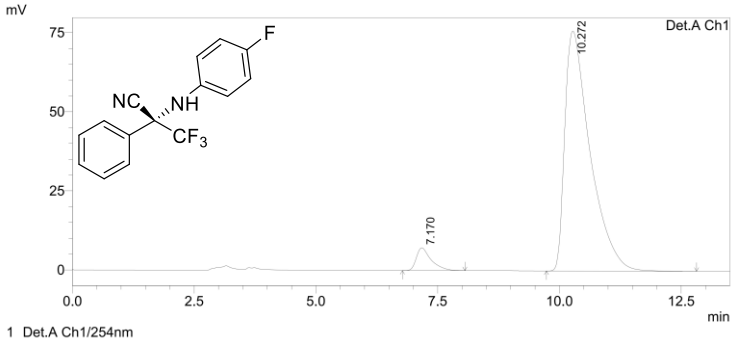




PeakTable

Detector A Ch1 254nm

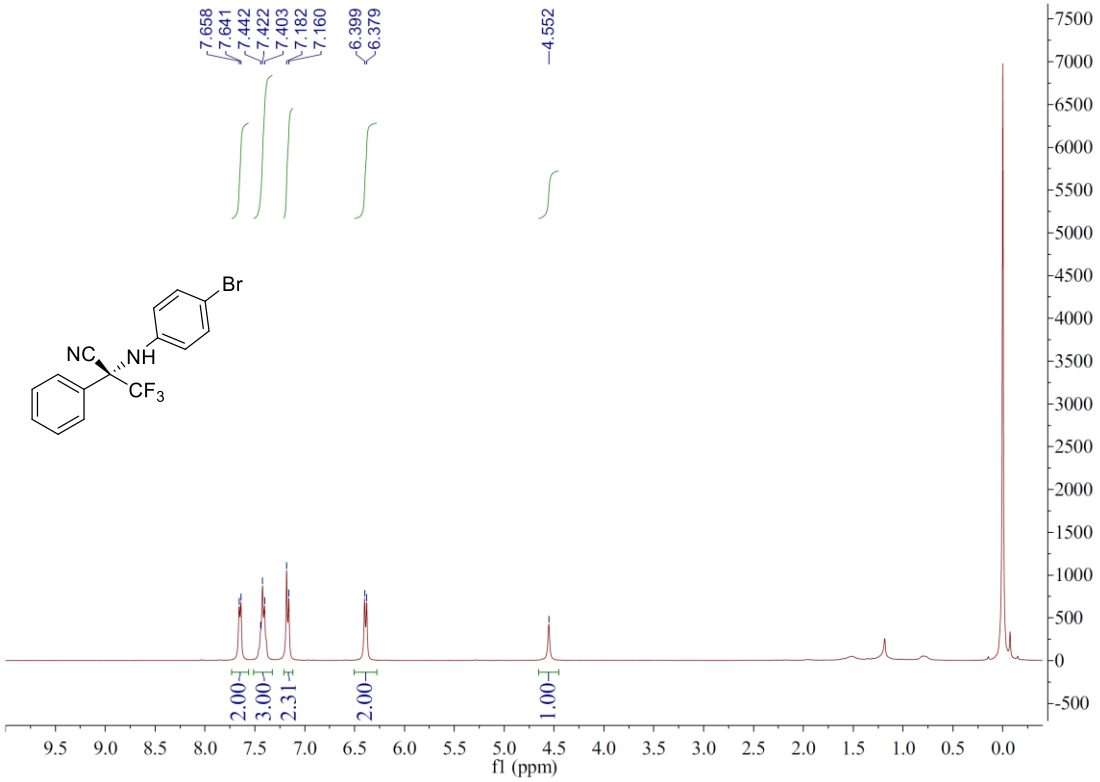
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.157	944140	43542	49.578	60.802
2	10.407	960208	28070	50.422	39.198
Total		1904349	71612	100.000	100.000

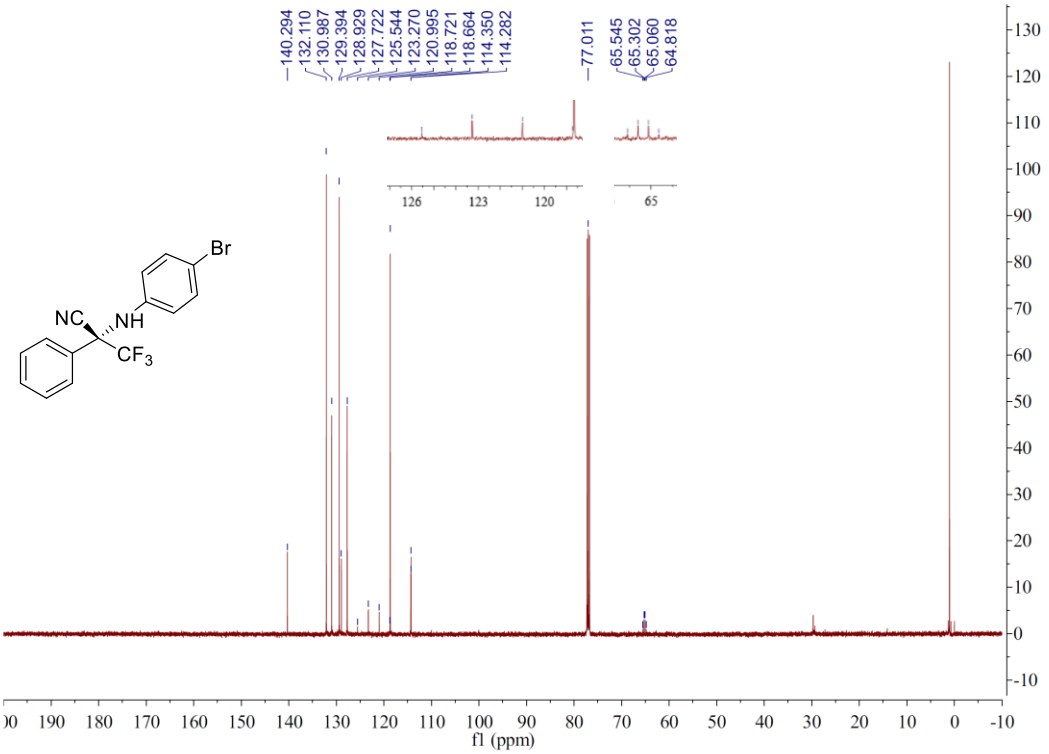


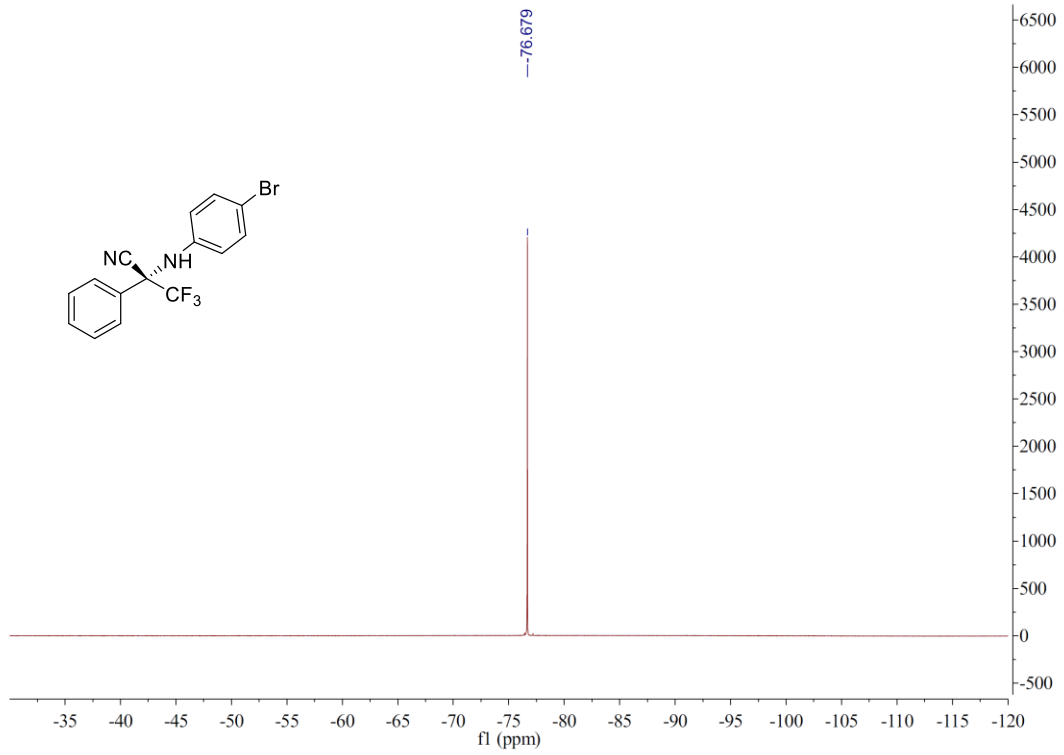
PeakTable

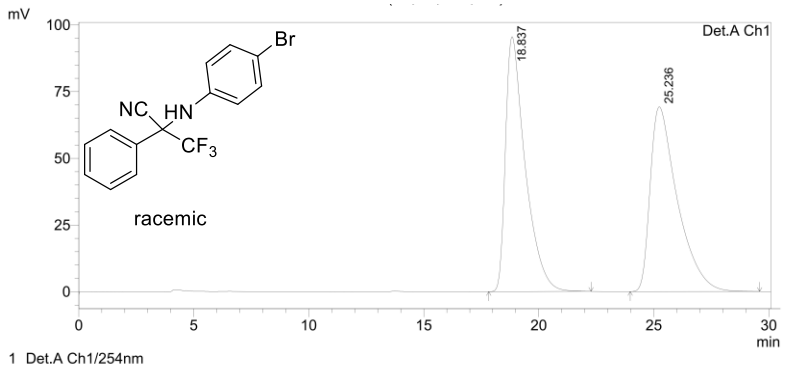
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.170	151659	7200	5.240	8.671
2	10.272	2742313	75836	94.760	91.329
Total		2893972	83036	100.000	100.000


7.658
7.641
7.442
7.422
7.403
7.182
7.160
6.399
6.379
4.552
Br
NC
NH
CF3
2.00
3.00
2.31
2.00
1.00
f1 (ppm)


140.294
132.110
130.987
129.394
128.929
127.722
125.544
123.270
120.995
118.721
118.664
114.350
114.282
77.011
65.545
65.302
65.060
64.818
126
123
120
65
Br
NC
NH
CF3
f1 (ppm)



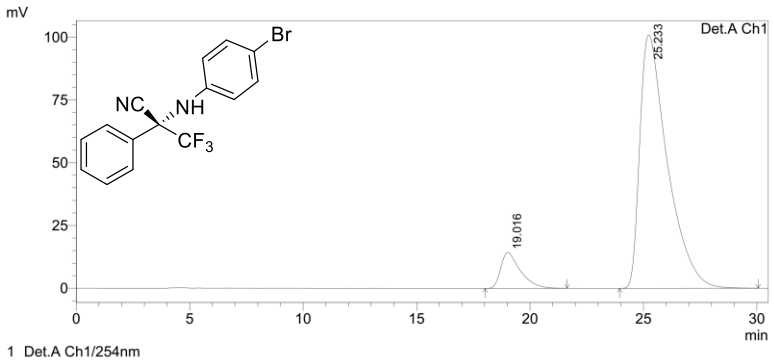


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	18.837	5684862	95514	49.972	57.981
2	25.236	5691280	69218	50.028	42.019
Total		11376142	164731	100.000	100.000

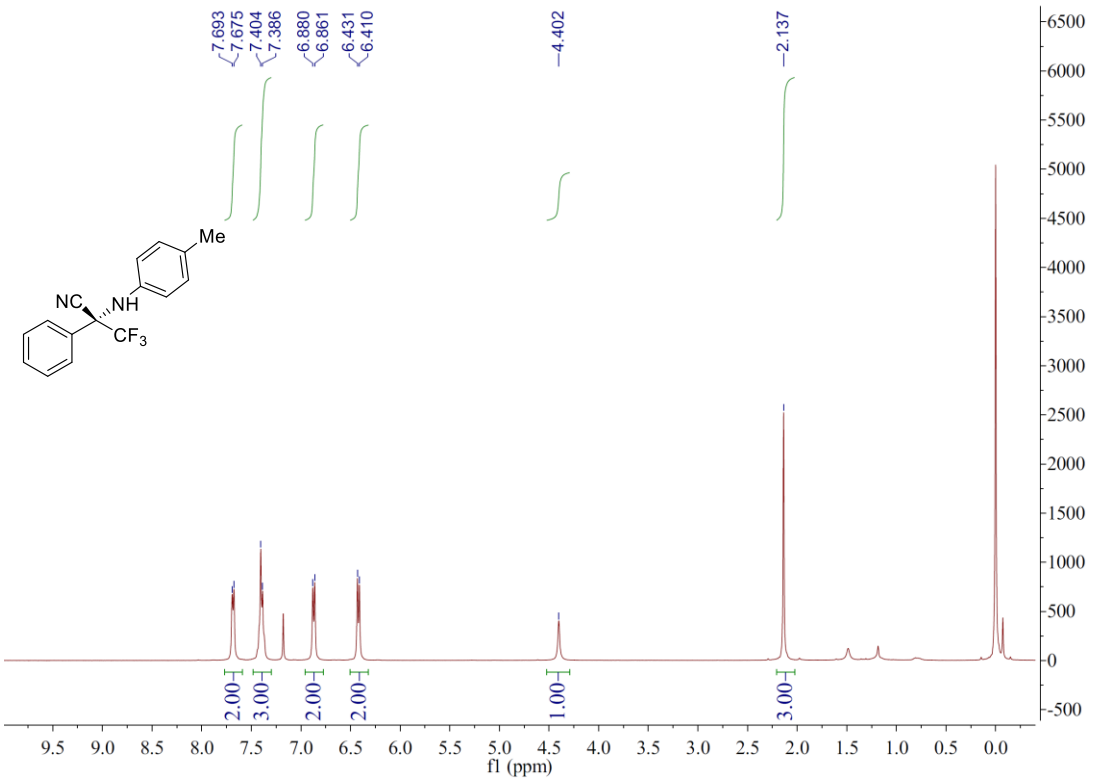


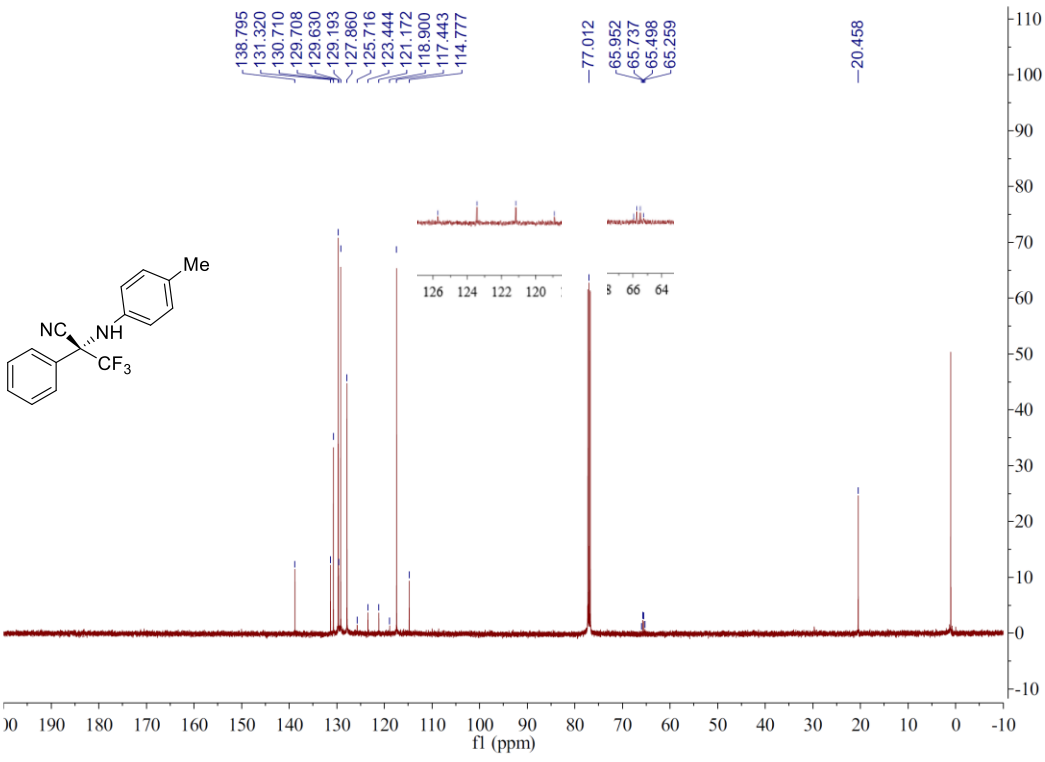
1 Det.A Ch1/254nm

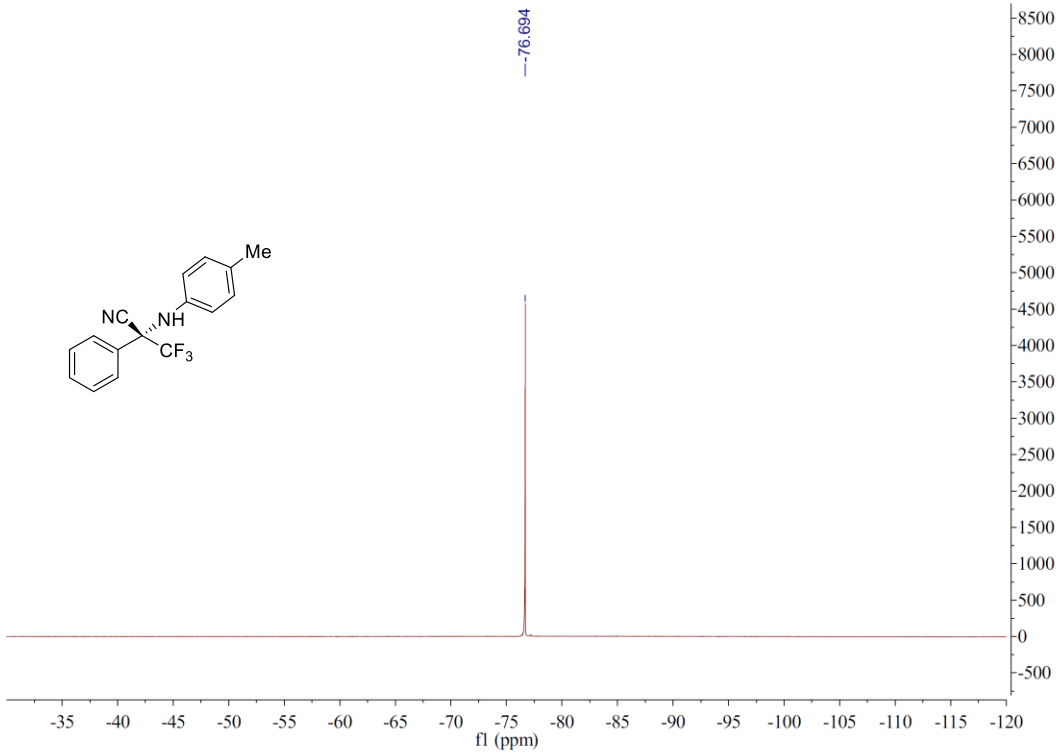
PeakTable

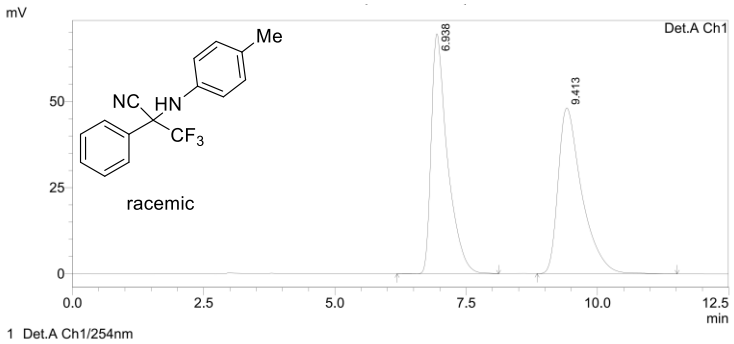
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	19.016	859340	14318	9.154	12.414
2	25.233	8528152	101013	90.846	87.586
Total		9387493	115331	100.000	100.000


7.693
7.675
7.404
7.386
6.880
6.861
6.431
6.410
4.402
2.137
Me
NC
NH
CF3
2.00
3.00
2.00
2.00
1.00
3.00
f1 (ppm)


138.795
131.320
130.710
129.708
129.630
129.193
127.860
125.716
123.444
121.172
118.900
117.443
114.777
77.012
65.952
65.737
65.498
65.259
20.458
Me
NC
NH
CF3
f1 (ppm)

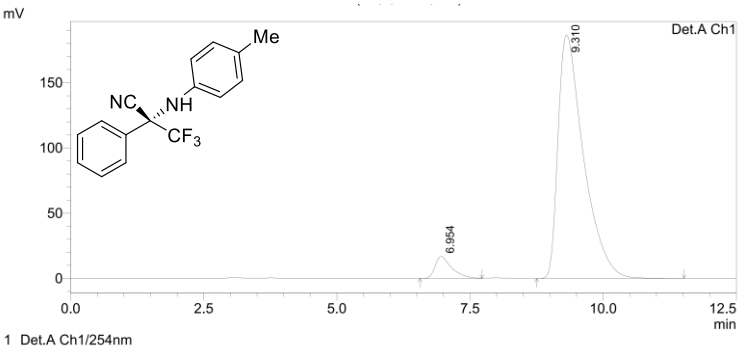




PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.938	1505337	69618	49.935	59.156
2	9.413	1509241	48067	50.065	40.844
Total		3014578	117685	100.000	100.000

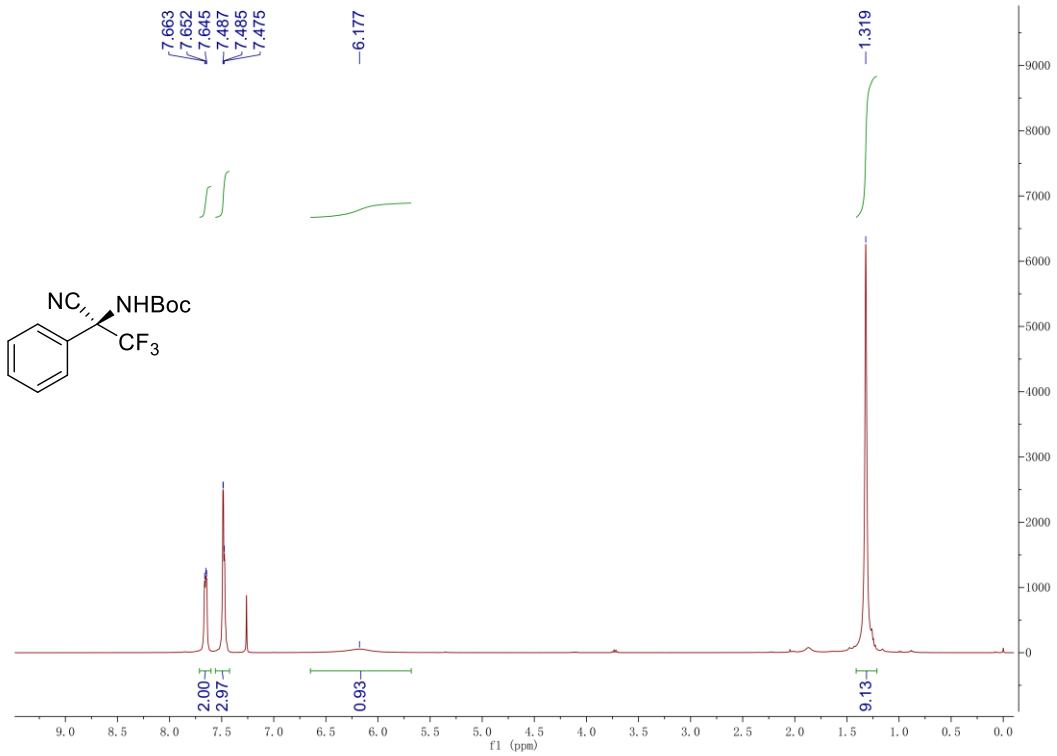


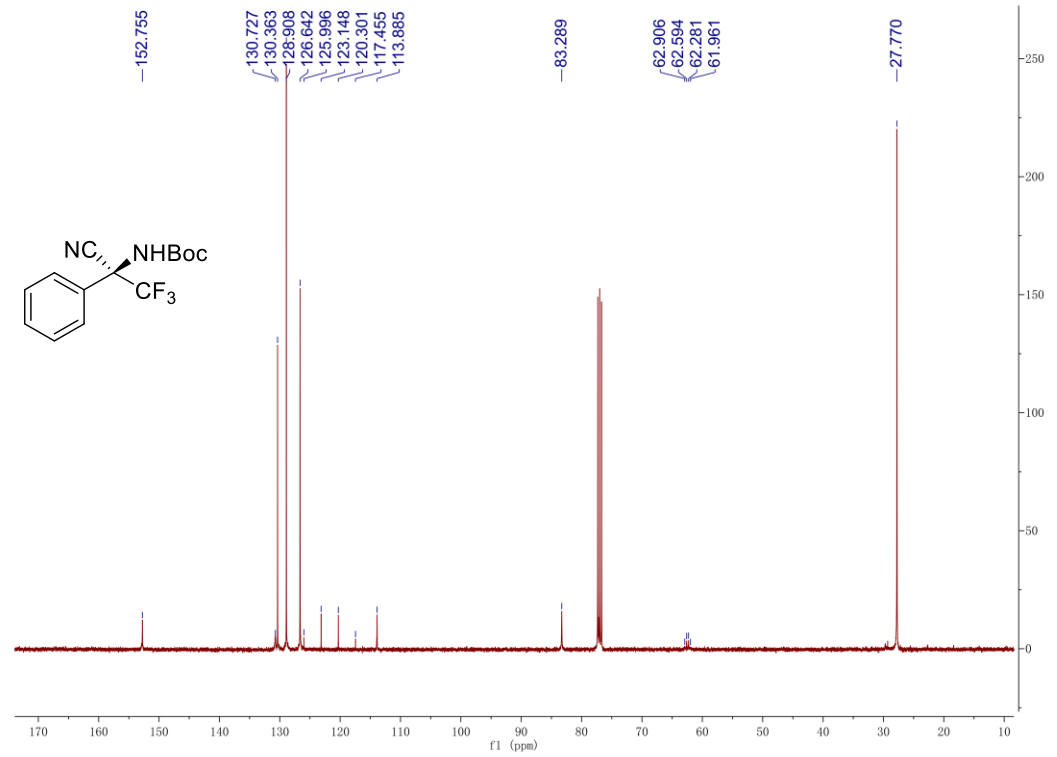
PeakTable

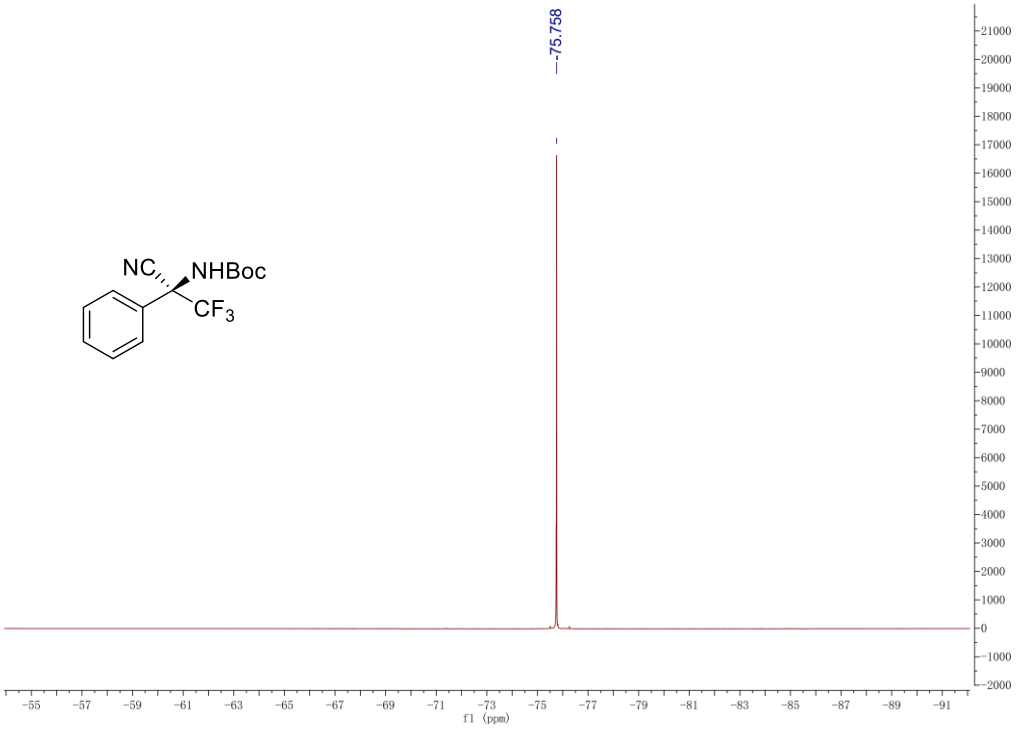
Detector A Ch1 254nm

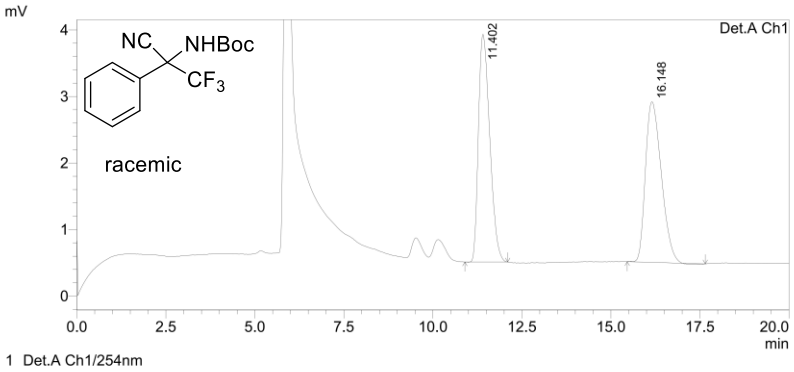
Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.954	363581	16839	5.525	8.282
2	9.310	6217539	186492	94.475	91.718
Total		6581120	203331	100.000	100.000

Copies of NMR and HPLC spectra for 3'a-3'm







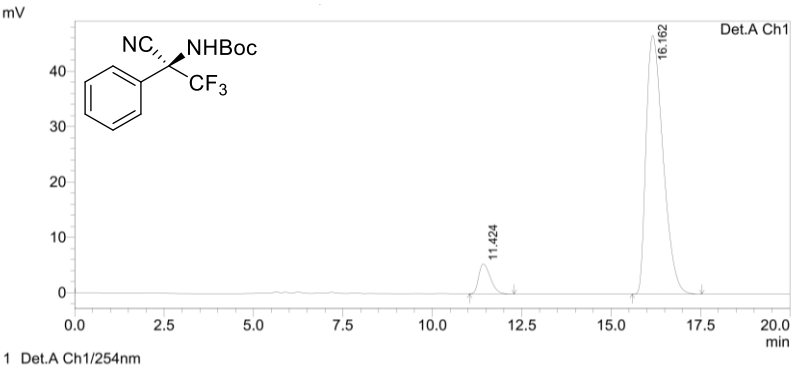


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.402	75836	3422	50.406	58.644
2	16.148	74616	2413	49.594	41.356
Total		150452	5835	100.000	100.000

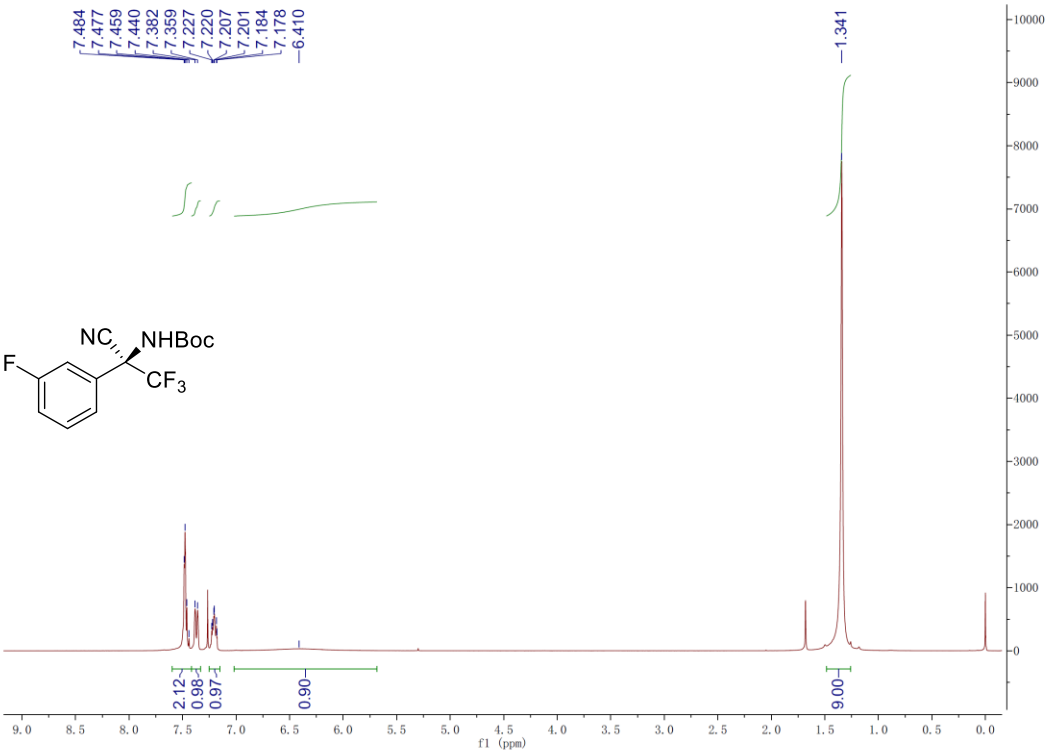


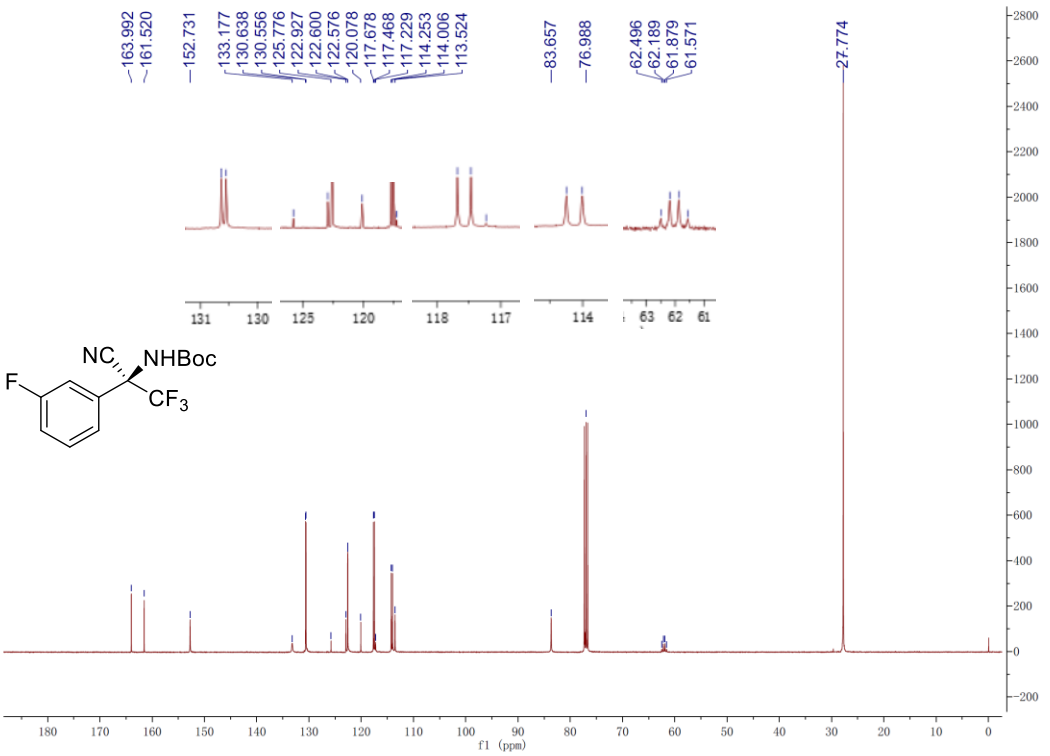
1 Det.A Ch1/254nm

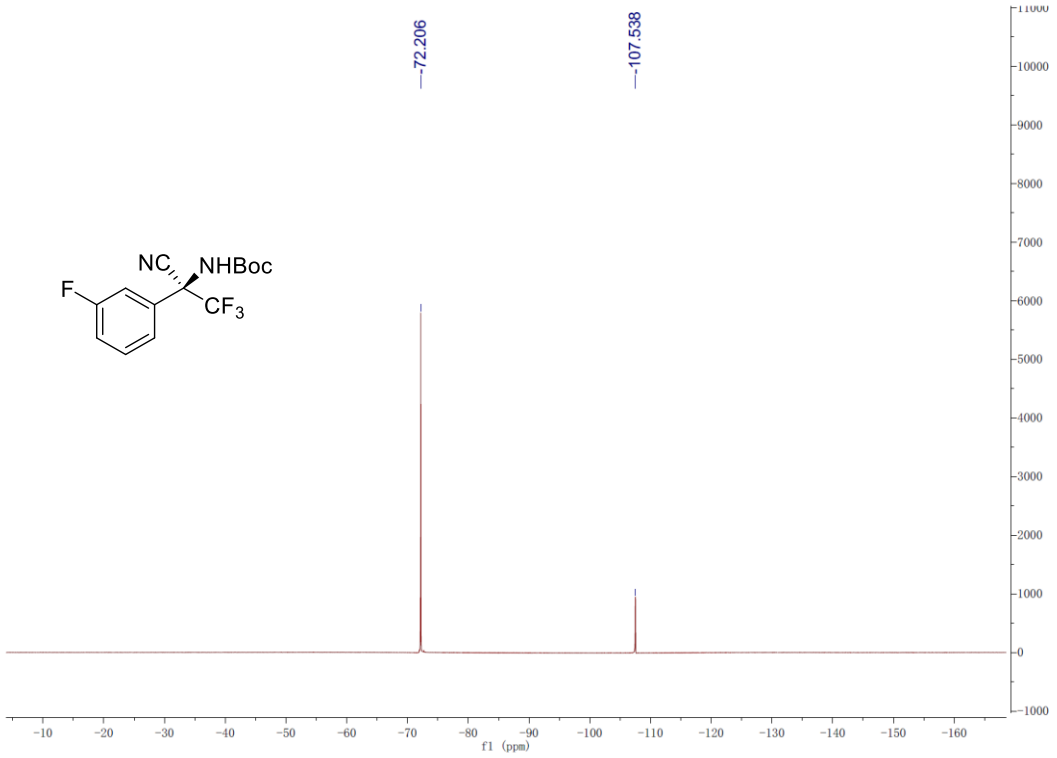
PeakTable

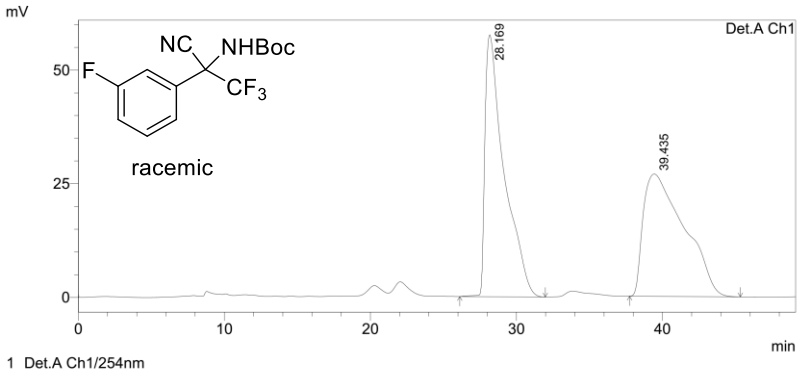
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.424	122320	5407	7.341	10.374
2	16.162	1543906	46719	92.659	89.626
Total		1666226	52127	100.000	100.000


7.484
7.477
7.459
7.440
7.382
7.359
7.227
7.220
7.207
7.201
7.184
7.178
6.410
1.341
NC
NHBoc
F
CF3
2.12
0.98
0.97
0.90
9.00
f1 (ppm)


163.992
161.520
152.731
133.177
130.638
130.556
125.776
122.927
122.600
122.576
120.078
117.678
117.468
117.229
114.253
114.006
113.524
83.657
76.988
62.496
62.189
61.879
61.571
27.774
NC
NHBoc
F
CF3
f1 (ppm)



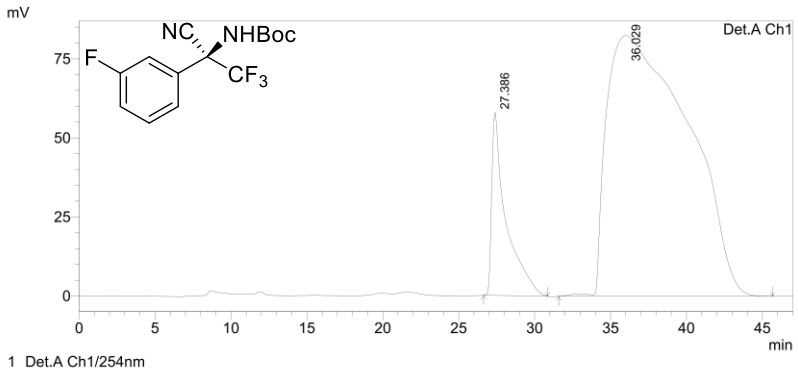


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	28.169	5256870	57601	49.964	68.169
2	39.435	5264340	26896	50.036	31.831
Total		10521210	84497	100.000	100.000

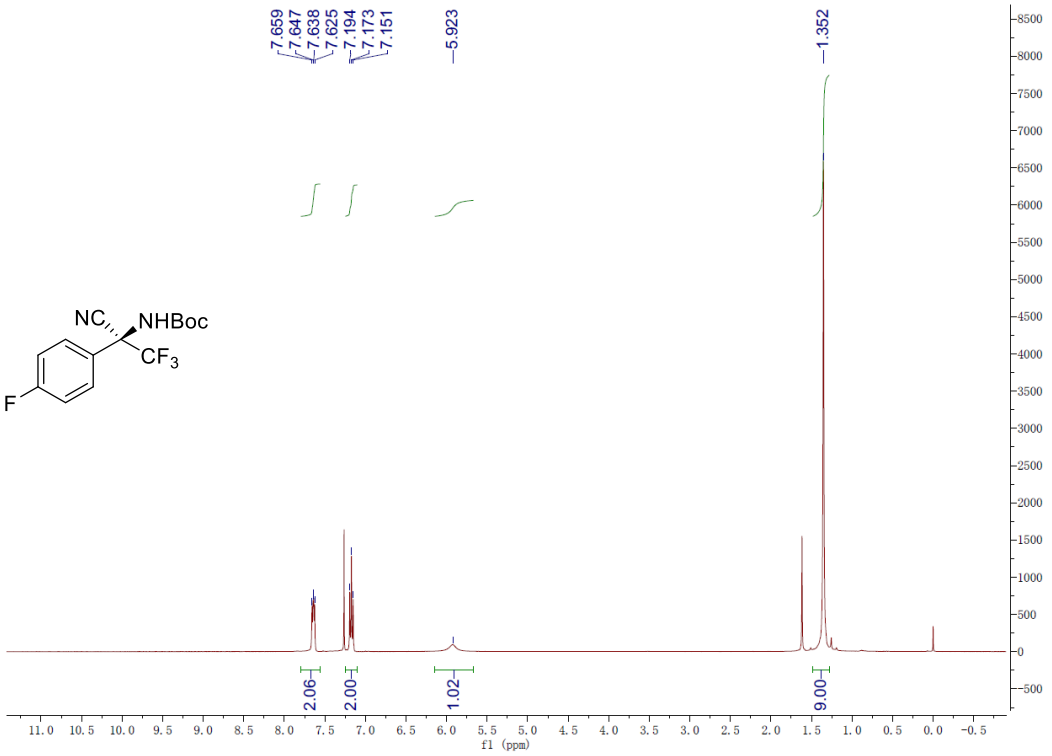


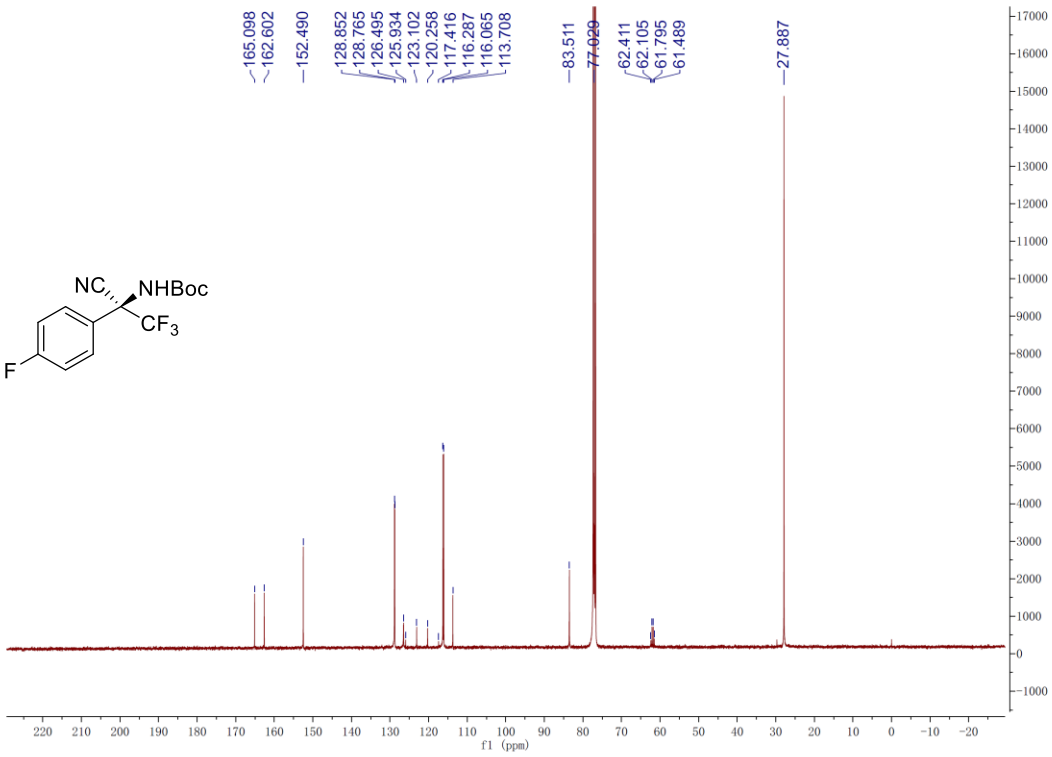
1 Det.A Ch1/254nm

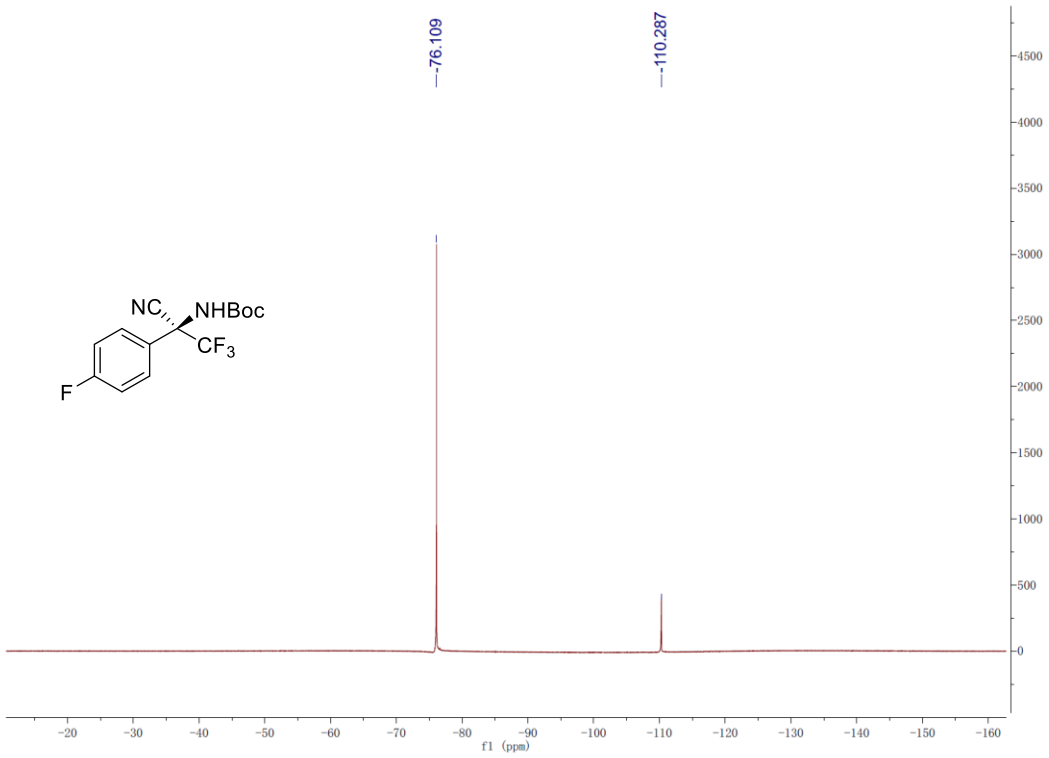
PeakTable

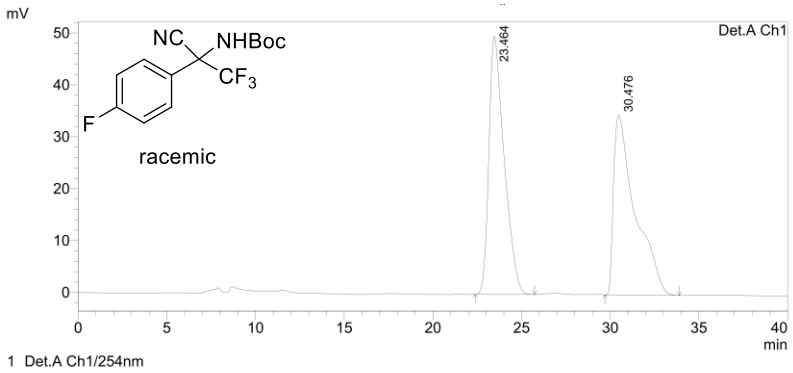
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	27.386	3804323	57773	11.035	41.218
2	36.029	30671670	82392	88.965	58.782
Total		34475993	140165	100.000	100.000


7.659
7.647
7.638
7.625
7.194
7.173
7.151
5.923
1.352
NC
NHBoc
CF3
F
2.06
2.00
1.02
9.00
f1 (ppm)


165.098
162.602
152.490
128.852
128.765
126.495
125.934
123.102
120.258
117.416
116.287
116.065
113.708
83.511
77.029
62.411
62.105
61.795
61.489
27.887
NC
NHBoc
CF3
F
f1 (ppm)

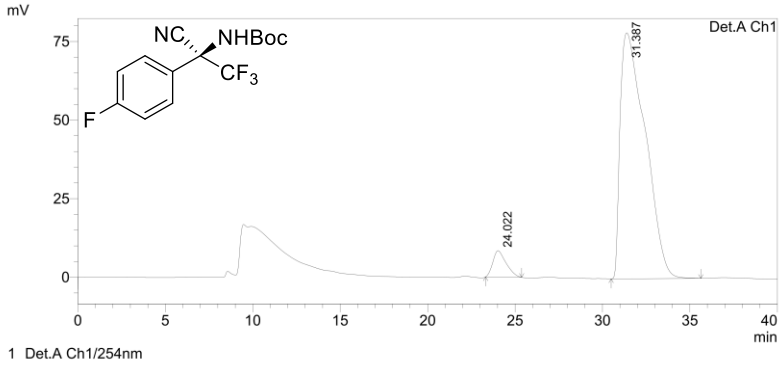




PeakTable

Detector A Ch1 254nm

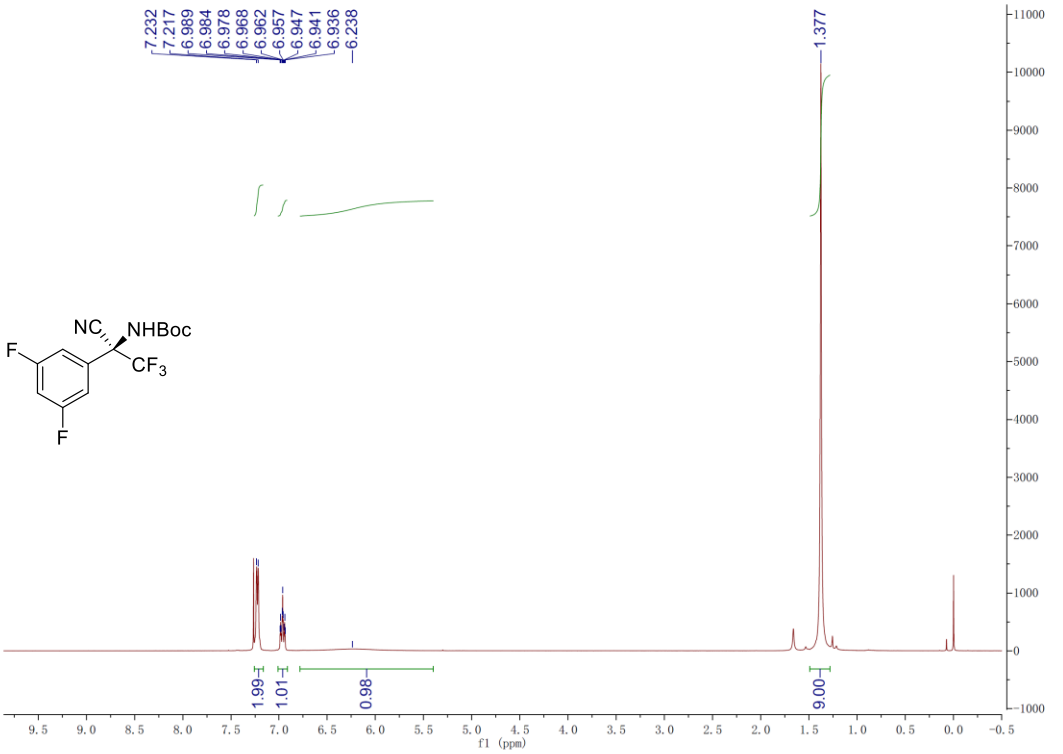
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.464	2969201	49678	50.259	58.953
2	30.476	2938619	34589	49.741	41.047
Total		5907821	84267	100.000	100.000

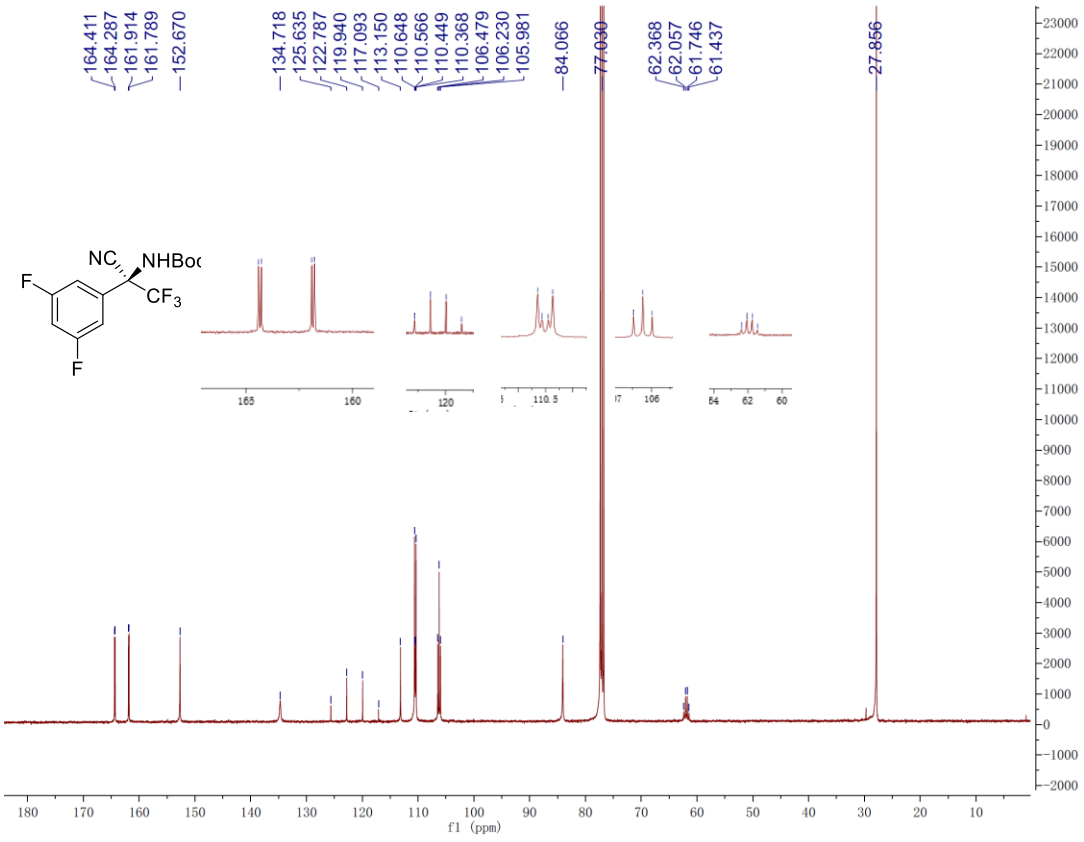


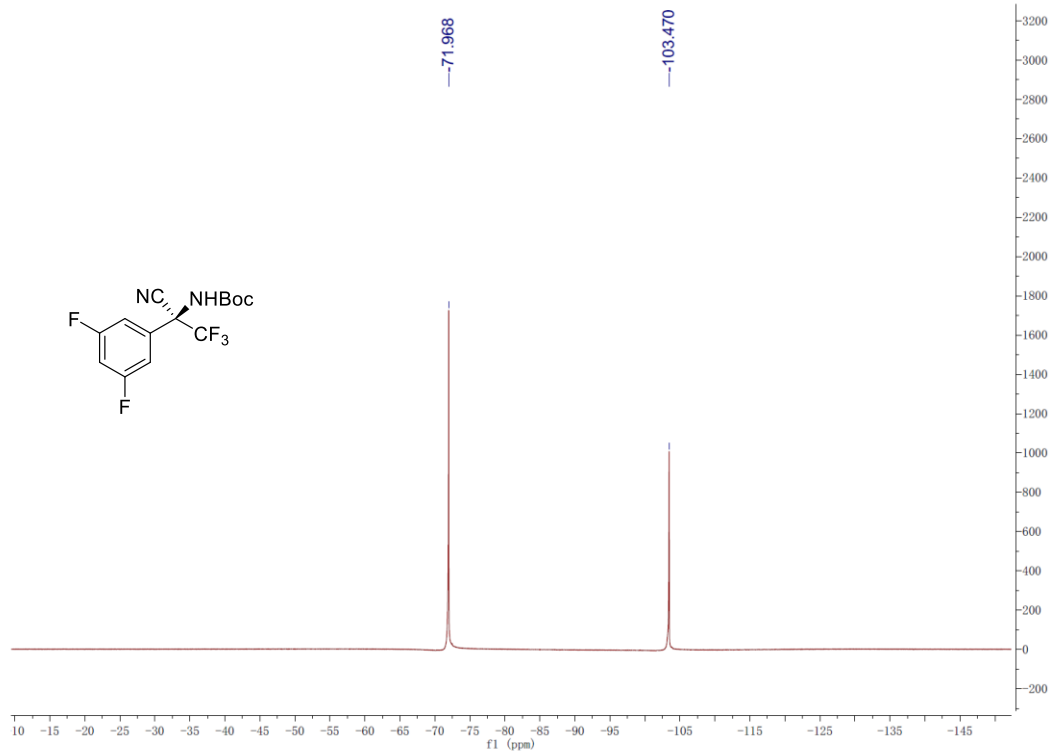
PeakTable

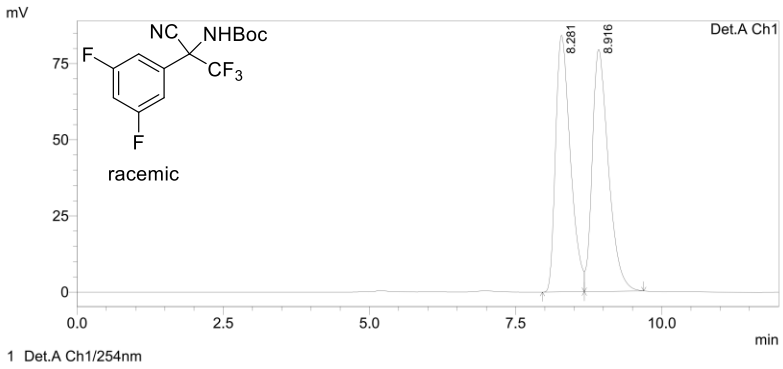
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	24.022	440700	8385	5.335	9.678
2	31.387	7820426	78252	94.665	90.322
Total		8261127	86636	100.000	100.000


7.232
7.217
6.989
6.984
6.978
6.968
6.962
6.957
6.947
6.941
6.936
6.238
1.377
NC
NHBoc
F
CF3
F
1.99
1.01
0.98
9.00
f1 (ppm)


164.411
164.287
161.914
161.789
152.670
134.718
125.635
122.787
119.940
117.093
113.150
110.648
110.566
110.449
110.368
106.479
106.230
105.981
84.066
77.030
62.368
62.057
61.746
61.437
27.856
NC
NHBoc
F
CF3
F
f1 (ppm)

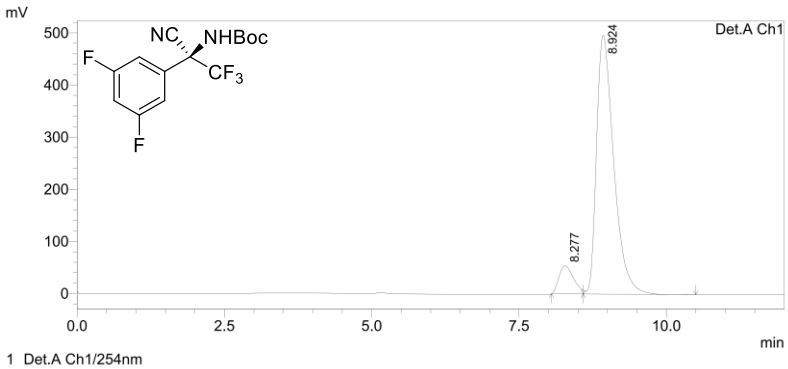




PeakTable

Detector A Ch1 254nm

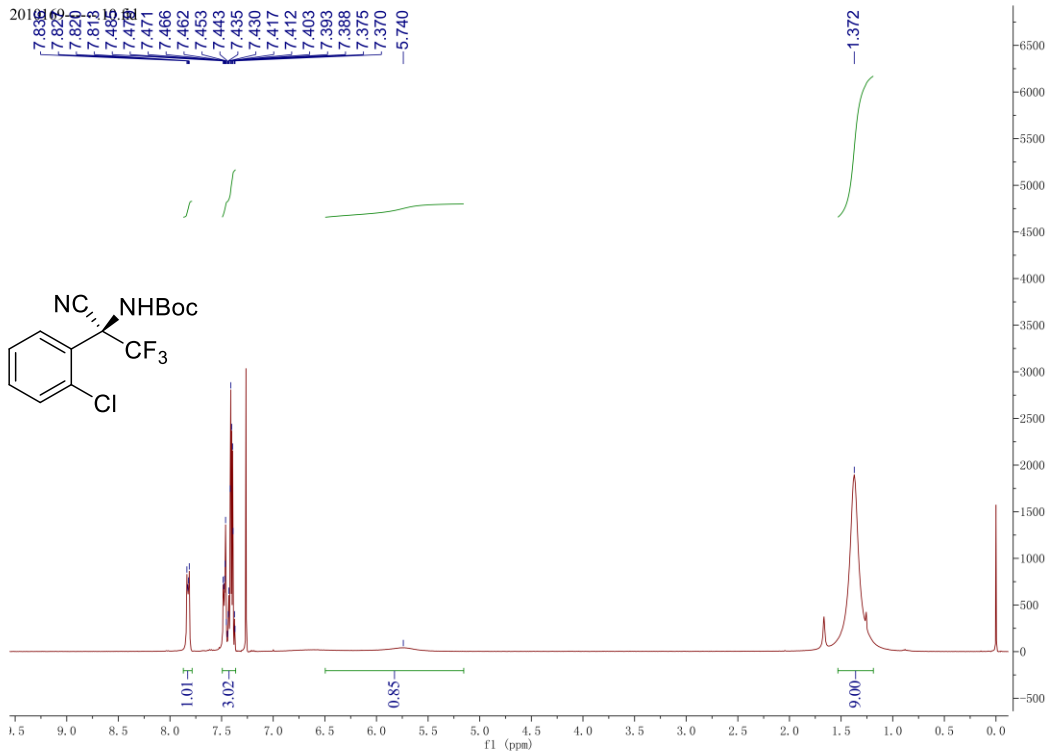
Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.281	1479171	84252	49.110	51.472
2	8.916	1532811	79433	50.890	48.528
Total		3011982	163685	100.000	100.000

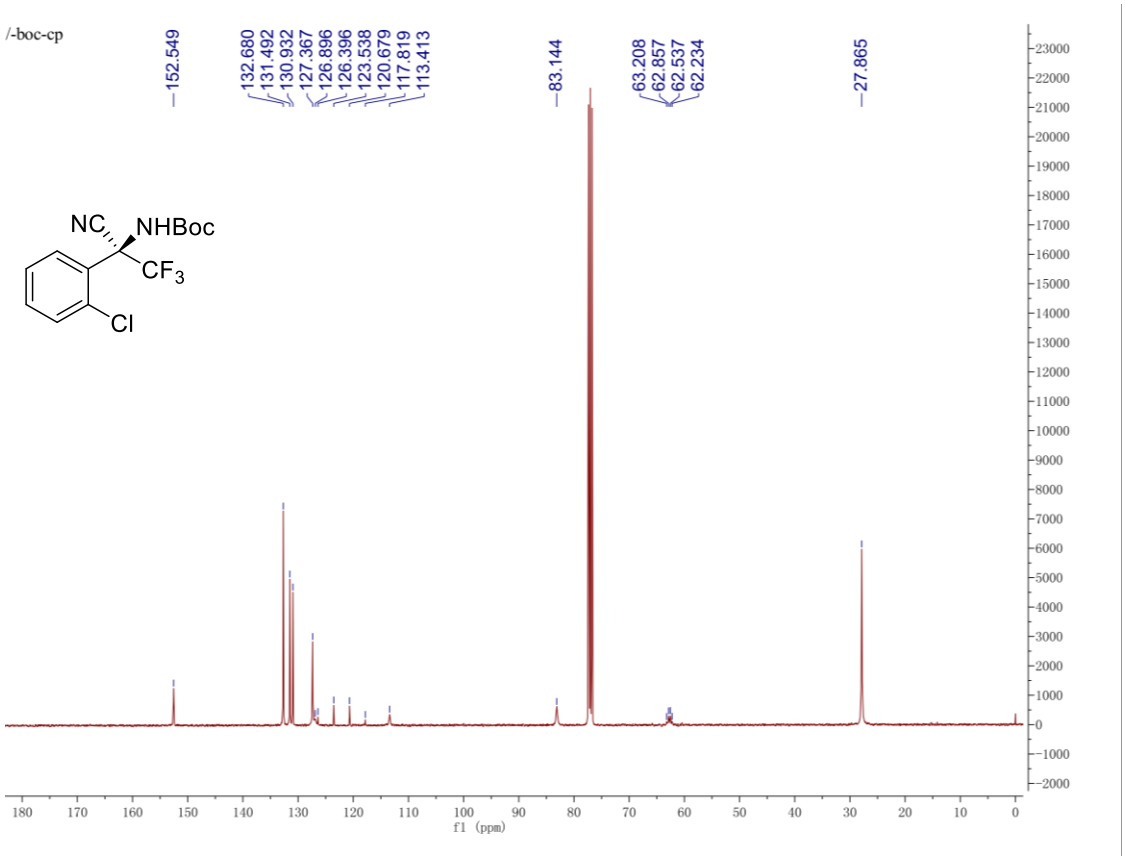


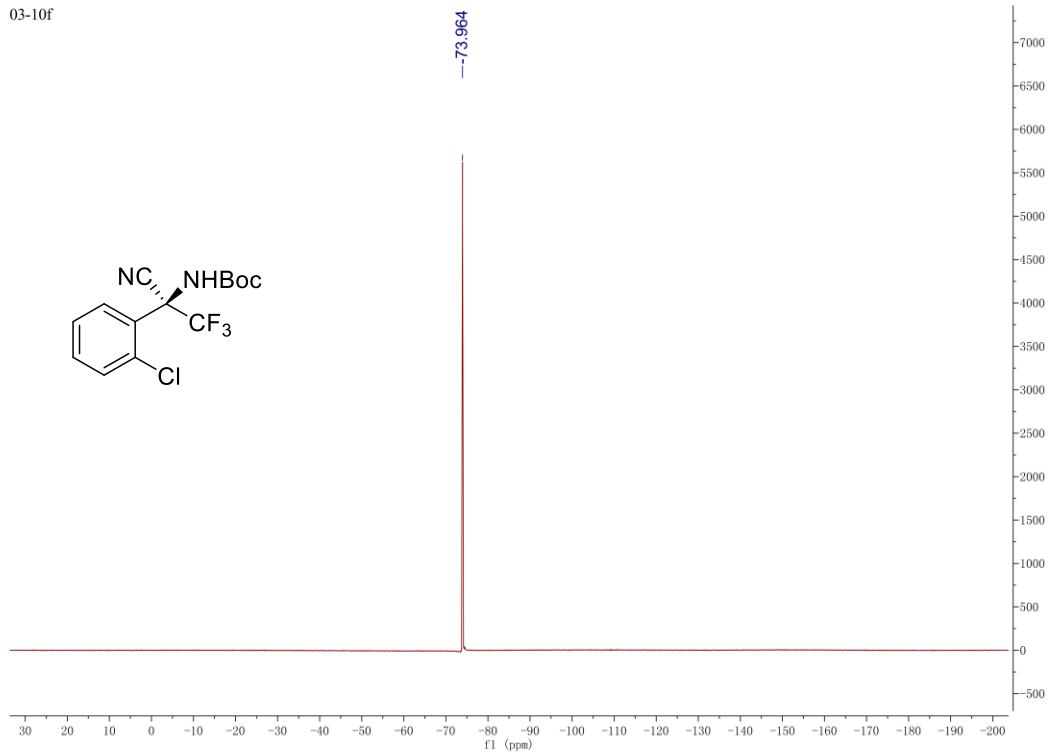
PeakTable

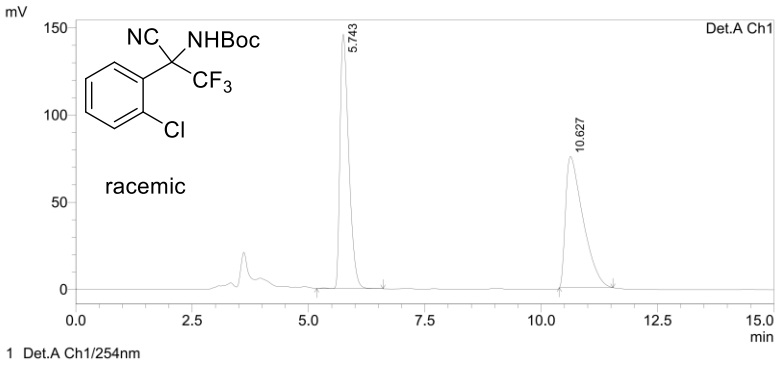
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	8.277	933576	54205	8.477	9.845
2	8.924	10078868	496386	91.523	90.155
Total		11012444	550591	100.000	100.000


7.836
7.822
7.820
7.813
7.485
7.478
7.471
7.466
7.462
7.453
7.443
7.435
7.430
7.417
7.412
7.403
7.393
7.388
7.375
7.370
5.740
1.372
NC
NHBoc
CF3
Cl
1.01
3.02
0.85
9.00
f1 (ppm)


/-boc-cp
152.549
132.680
131.492
130.932
127.367
126.896
126.396
123.538
120.679
117.819
113.413
83.144
63.208
62.857
62.537
62.234
27.865
NC
NHBoc
CF3
Cl
f1 (ppm)

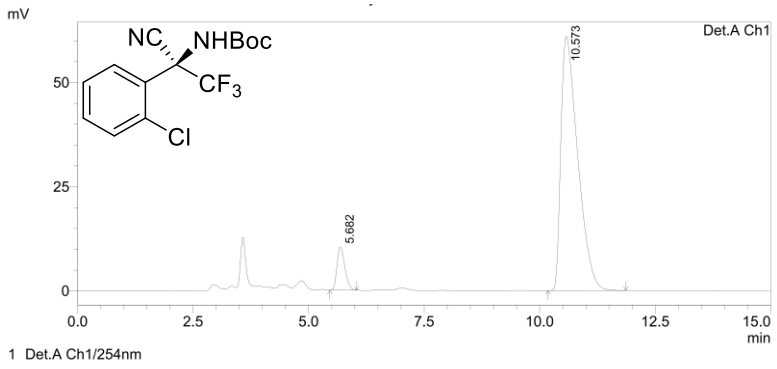




PeakTable

Detector A Ch1 254nm

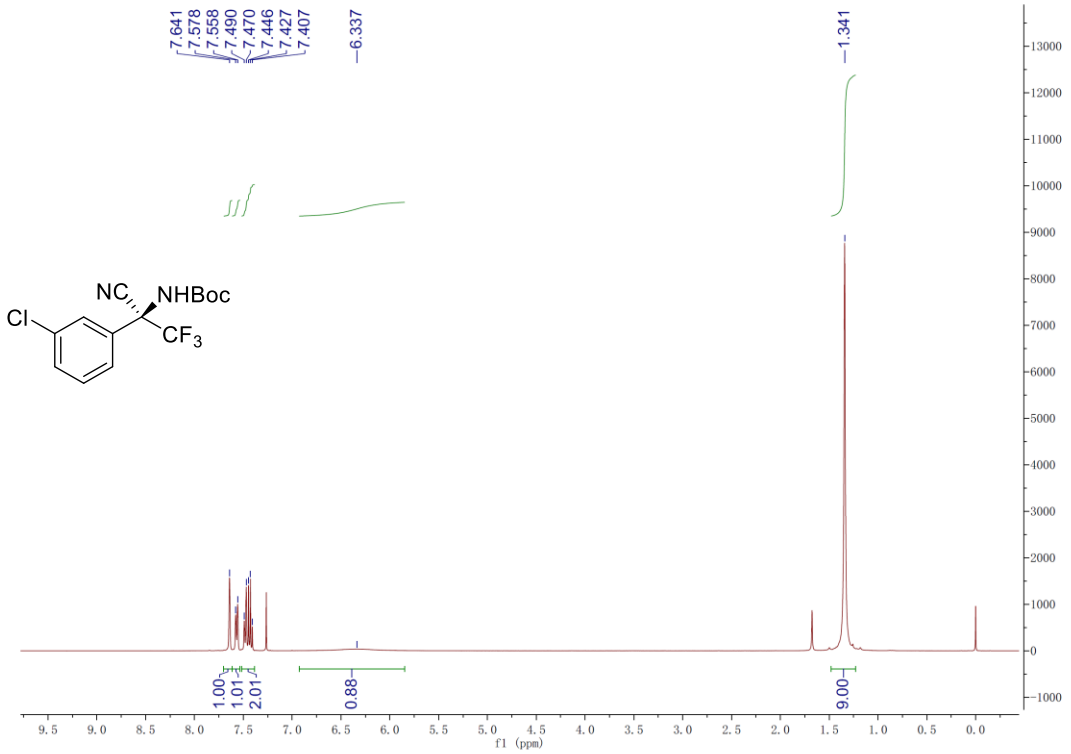
Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.743	1912930	145744	49.325	65.936
2	10.627	1965297	75295	50.675	34.064
Total		3878227	221039	100.000	100.000

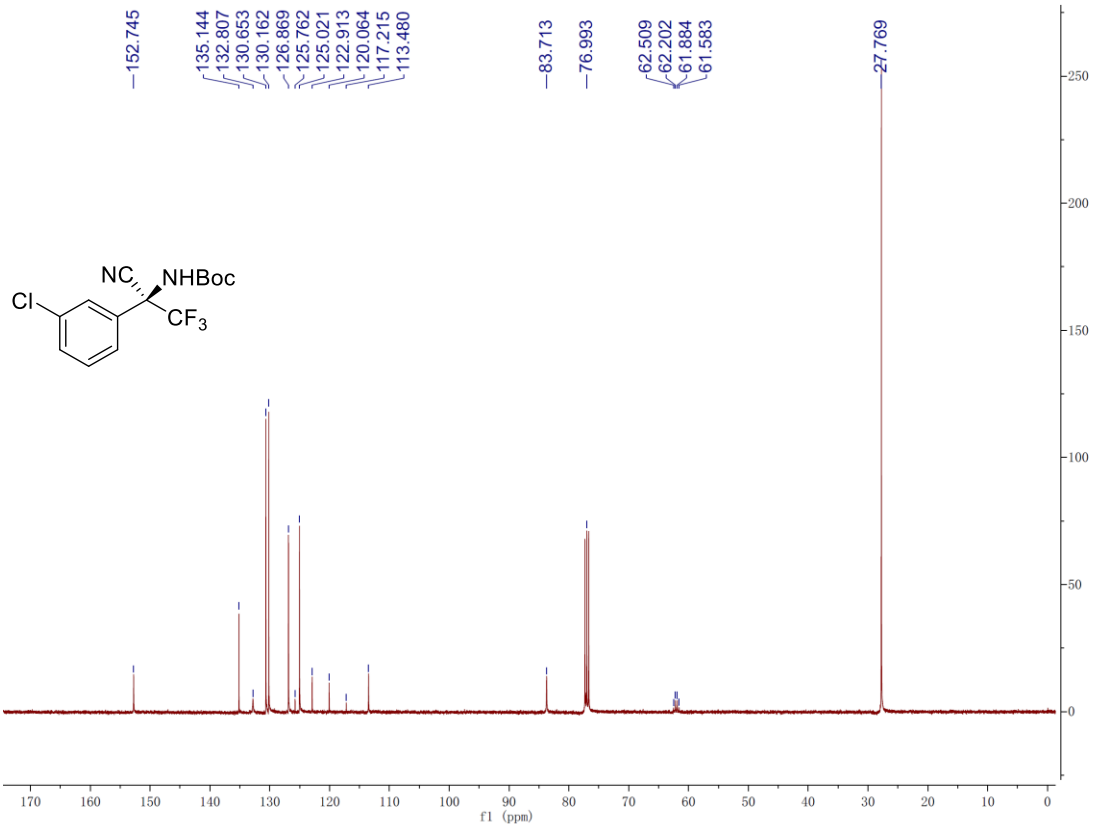


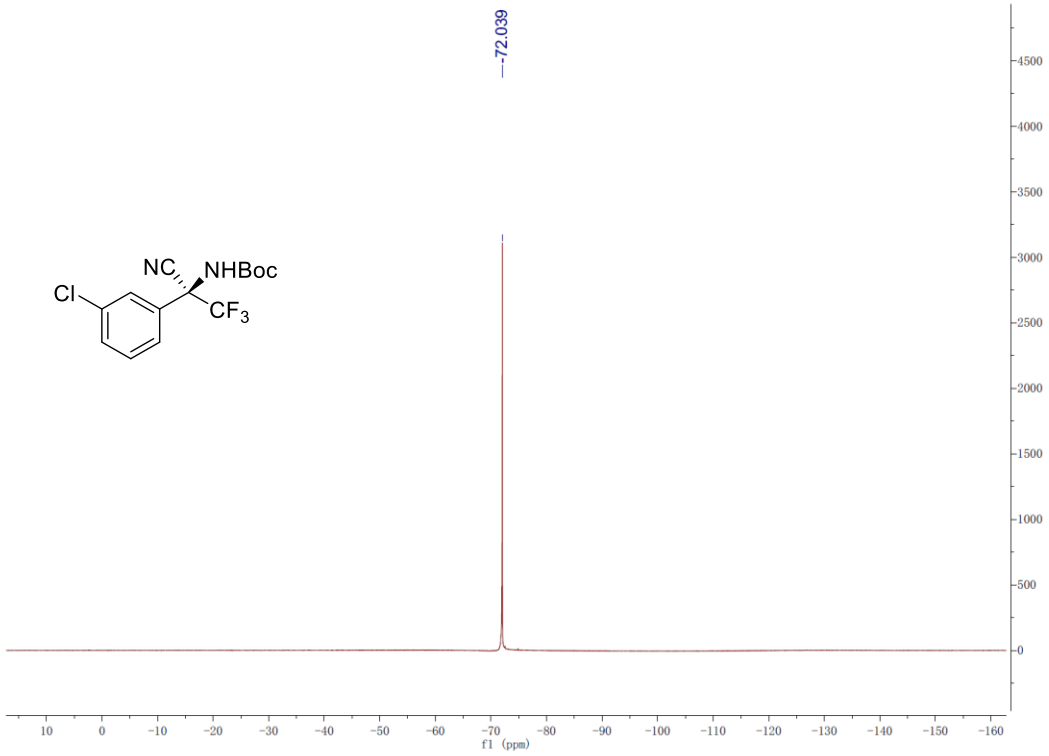
PeakTable

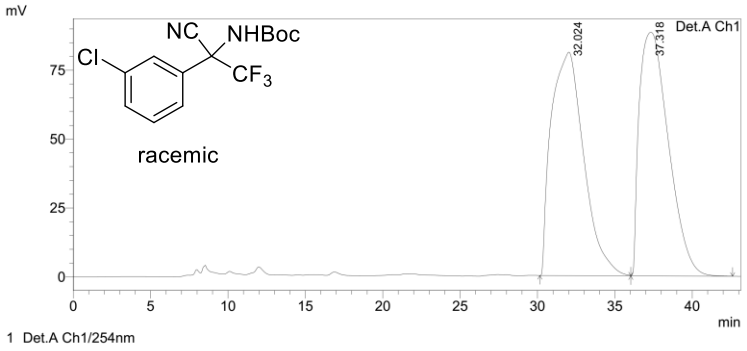
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	5.682	122731	10354	7.367	14.513
2	10.573	1543324	60988	92.633	85.487
Total		1666055	71342	100.000	100.000


7.641
7.578
7.558
7.490
7.470
7.446
7.427
7.407
6.337
1.341
NC
NHBoc
Cl
CF3
1.00
1.01
2.01
0.88
9.00
f1 (ppm)


152.745
135.144
132.807
130.653
130.162
126.869
125.762
125.021
122.913
120.064
117.215
113.480
83.713
76.993
62.509
62.202
61.884
61.583
27.769
NC
NHBoc
Cl
CF3
f1 (ppm)



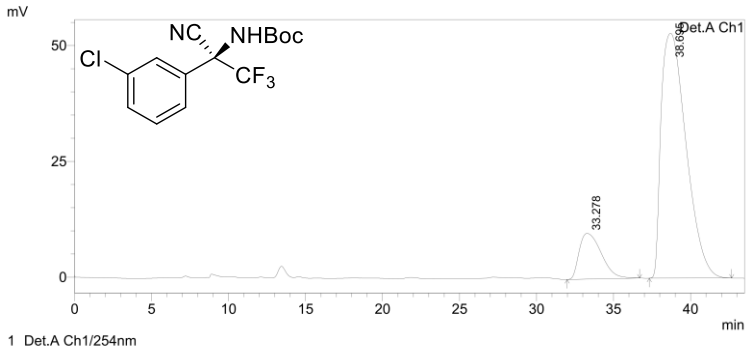


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	32.024	11848979	81108	50.542	47.845
2	37.318	11594683	88414	49.458	52.155
Total		23443662	169522	100.000	100.000

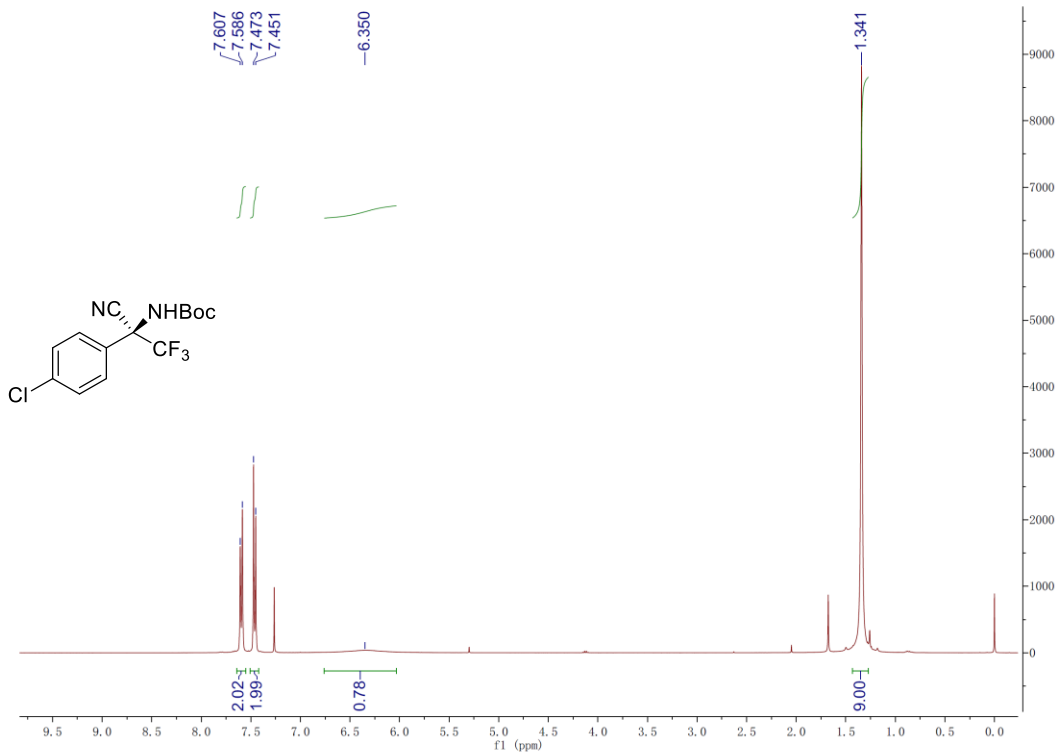


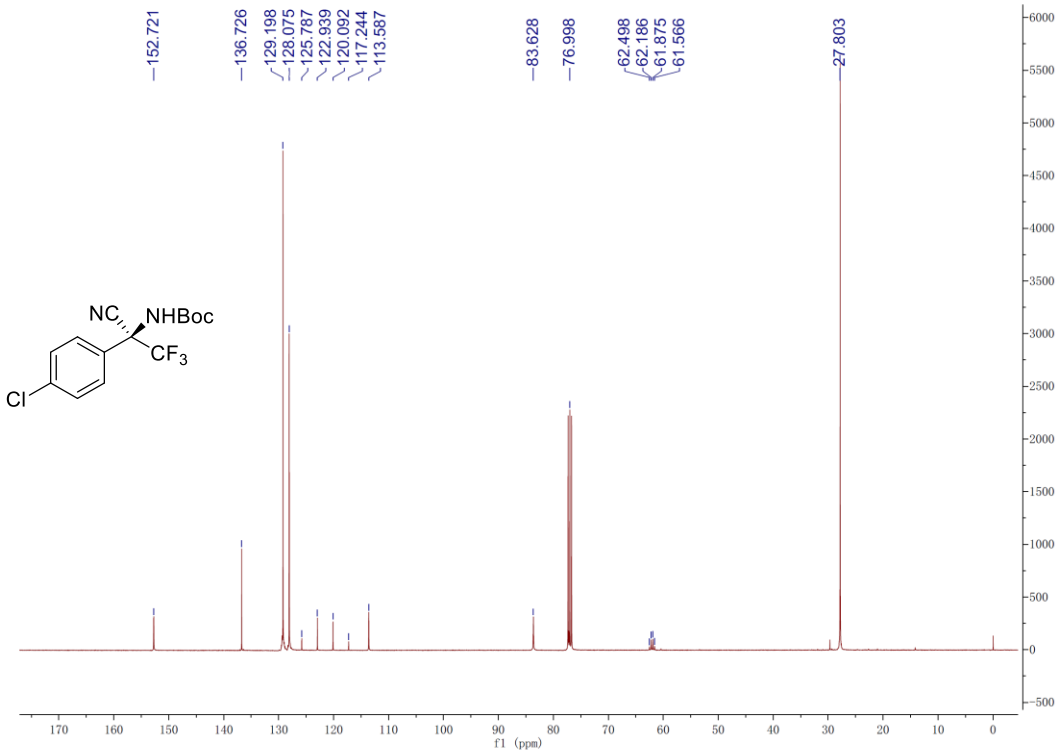
1 Det.A Ch1/254nm

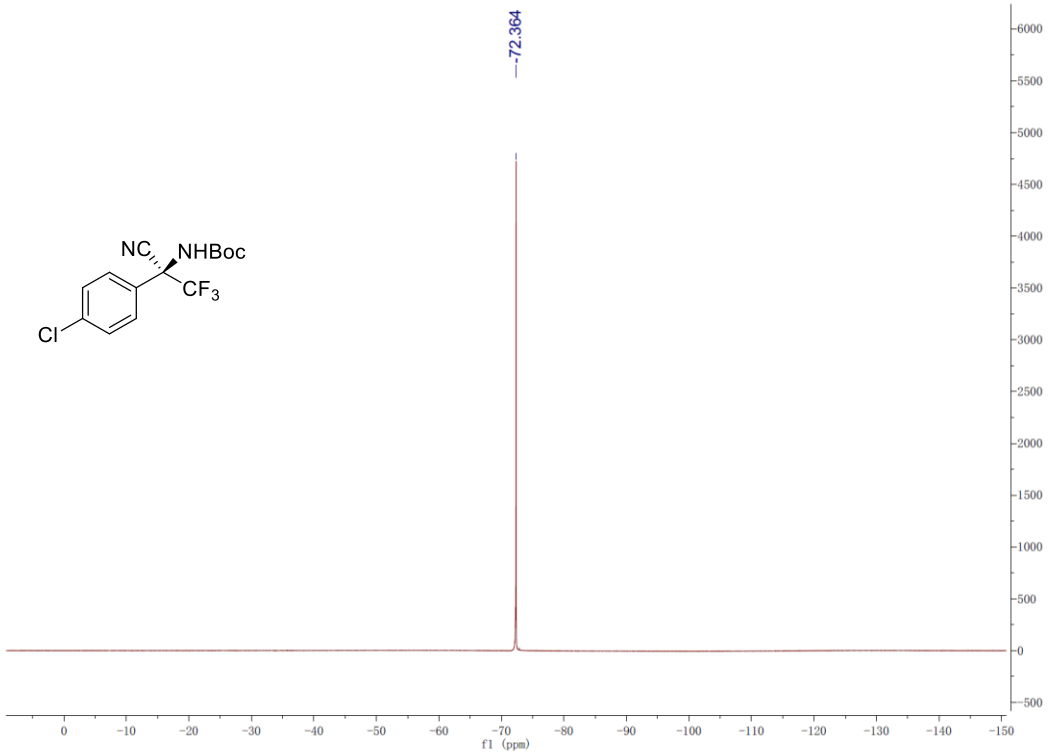
PeakTable

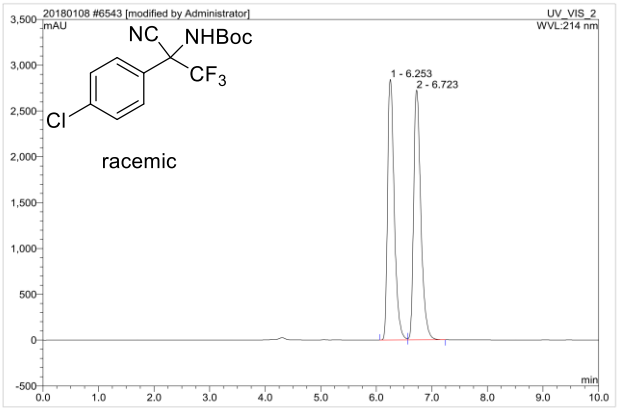
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	33.278	984057	9872	14.175	15.738
2	38.695	5958203	52854	85.825	84.262
Total		6942259	62726	100.000	100.000

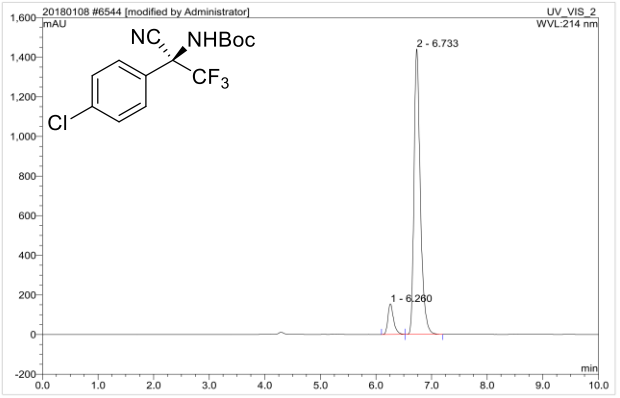

7.607
7.586
7.473
7.451
6.350
1.341
NC
NHBoc
CF3
Cl
2.02
1.99
0.78
9.00
f1 (ppm)


152.721
136.726
129.198
128.075
125.787
122.939
120.092
117.244
113.587
83.628
76.998
62.498
62.186
61.875
61.566
27.803
NC
NHBoc
CF3
Cl
f1 (ppm)

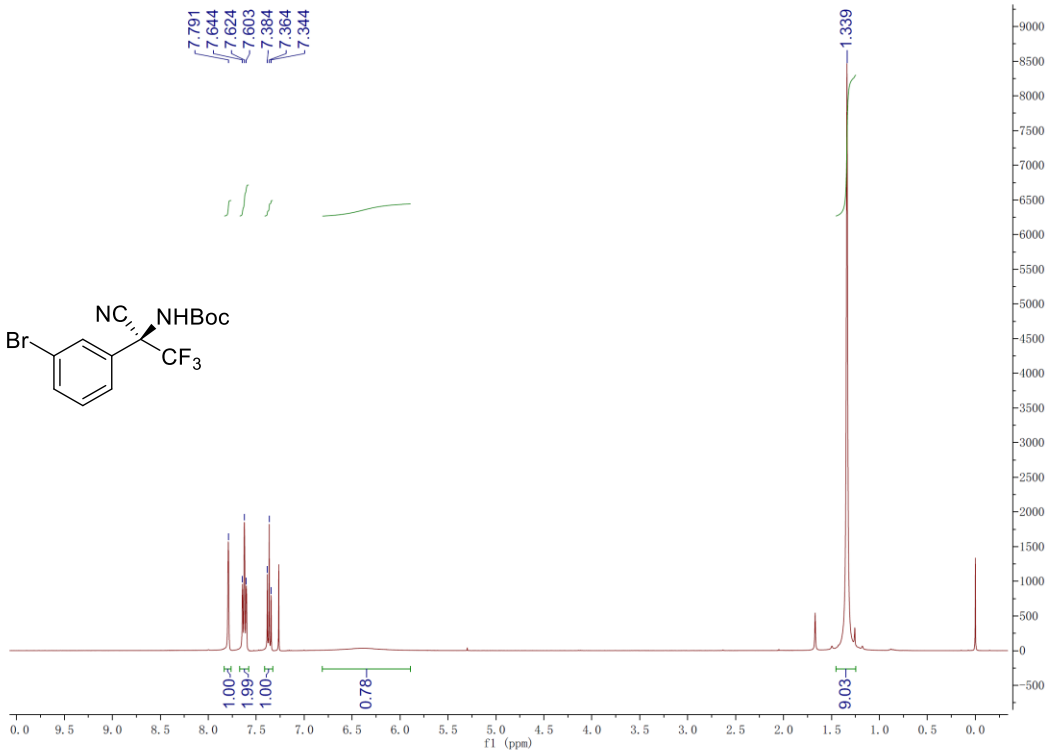


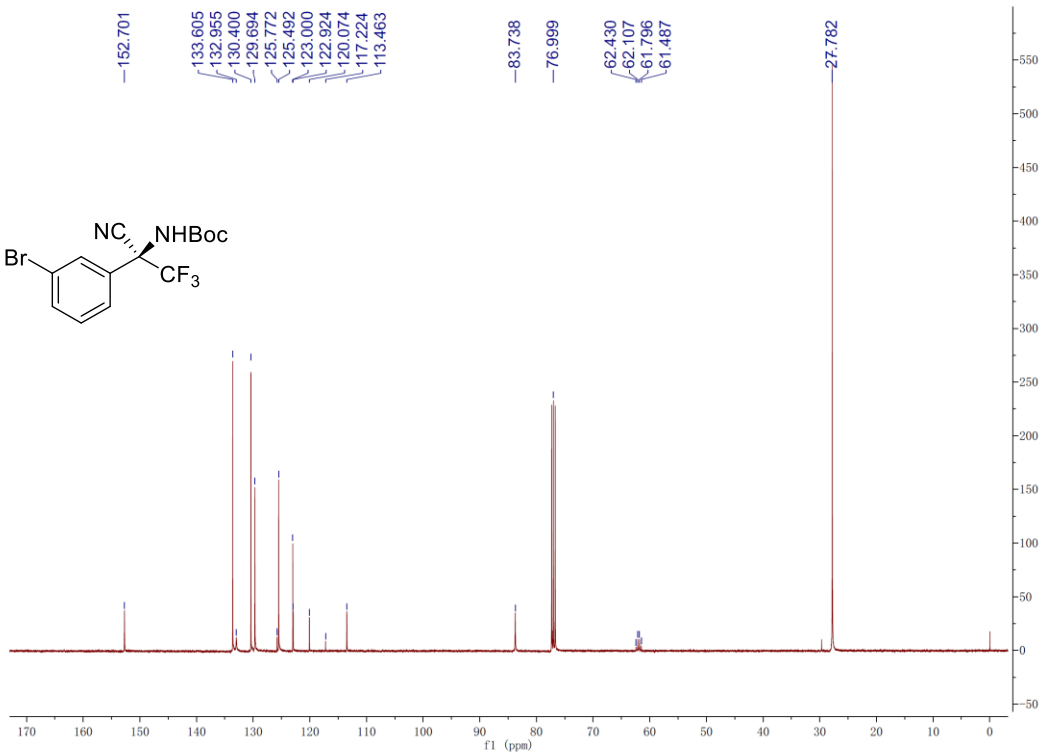


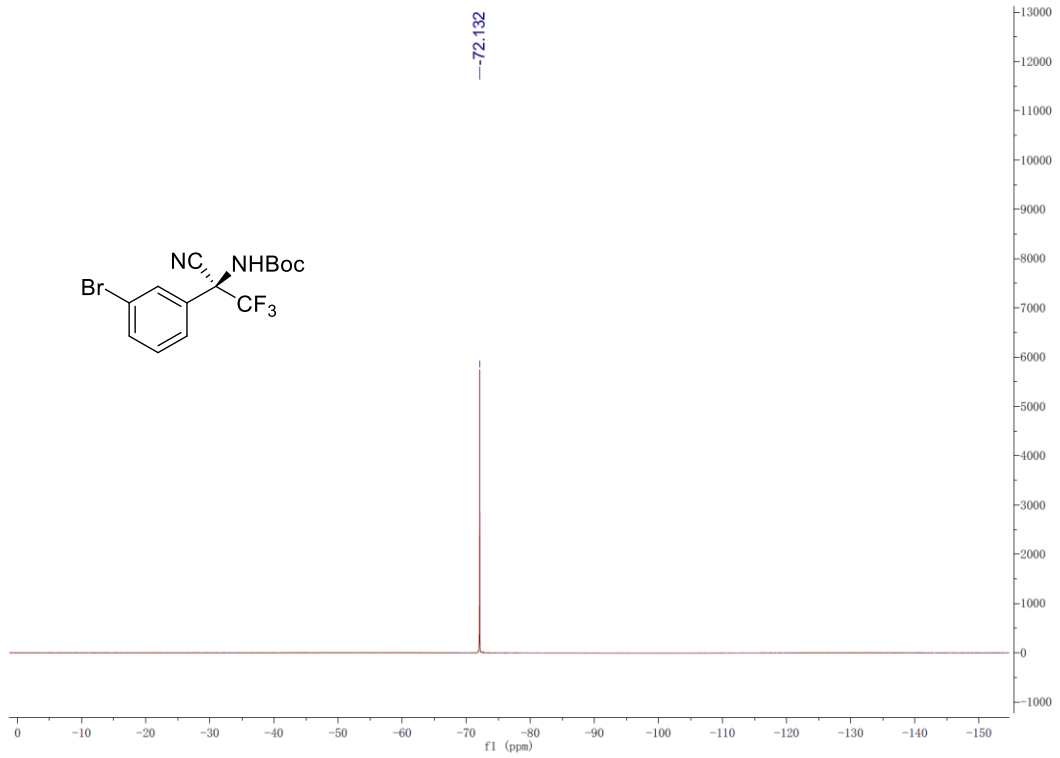
No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.25	n.a.	2844.704	397.448	49.31	n.a.	BM
2	6.72	n.a.	2726.574	408.540	50.69	n.a.	MB
Total:			5571.278	805.988	100.00	0.000	

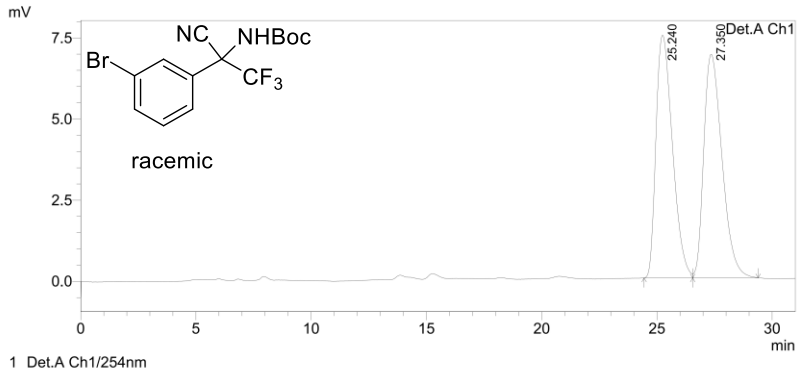


No.	Ret.Time min	Peak Name	Height mAU	Area mAU*min	Rel.Area %	Amount	Type
1	6.26	n.a.	154.471	18.074	8.71	n.a.	BMb*
2	6.73	n.a.	1441.387	189.329	91.29	n.a.	bMB*
Total:			1595.858	207.403	100.00	0.000	


7.791
7.644
7.624
7.603
7.384
7.364
7.344
1.339
NC
NHBoc
Br
CF3
1.00
1.99
1.00
0.78
9.03
f1 (ppm)


152.701
133.605
132.955
130.400
129.694
125.772
125.492
123.000
122.924
120.074
117.224
113.463
83.738
76.999
62.430
62.107
61.796
61.487
27.782
NC
NHBoc
Br
CF3
f1 (ppm)



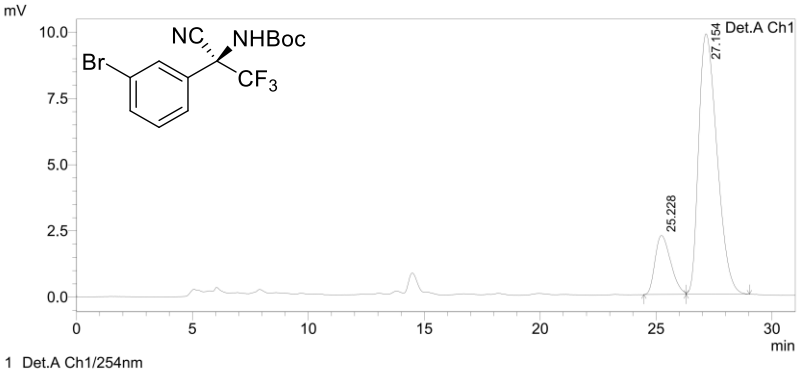


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.240	371787	7482	49.453	52.048
2	27.350	380018	6893	50.547	47.952
Total		751805	14376	100.000	100.000

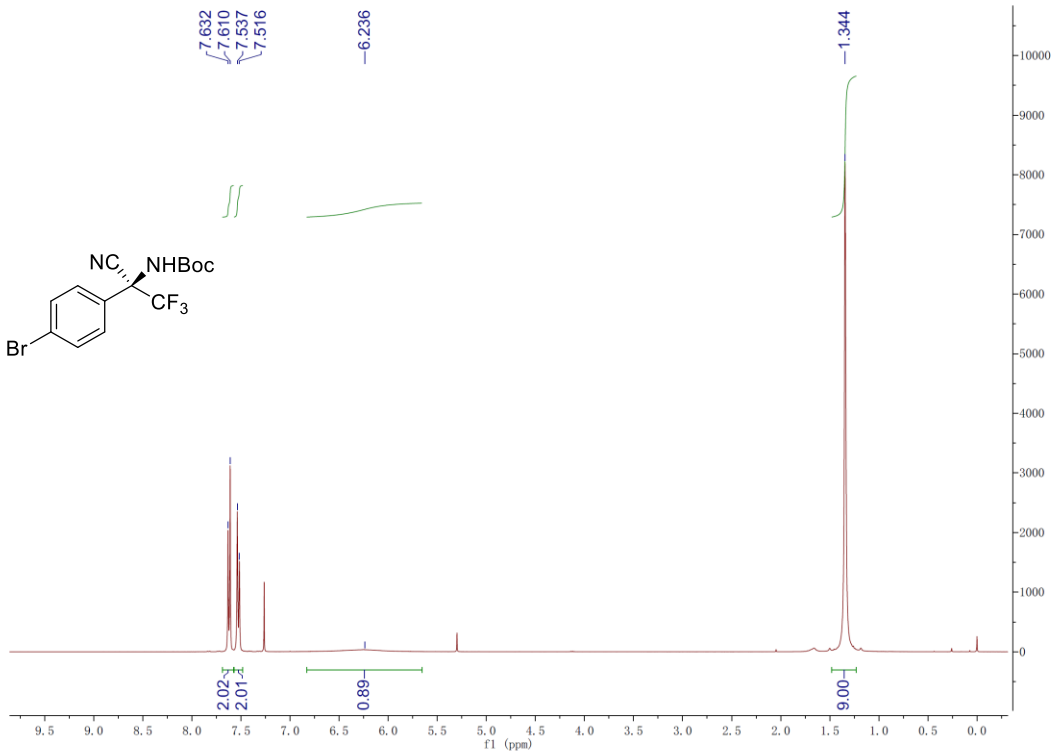


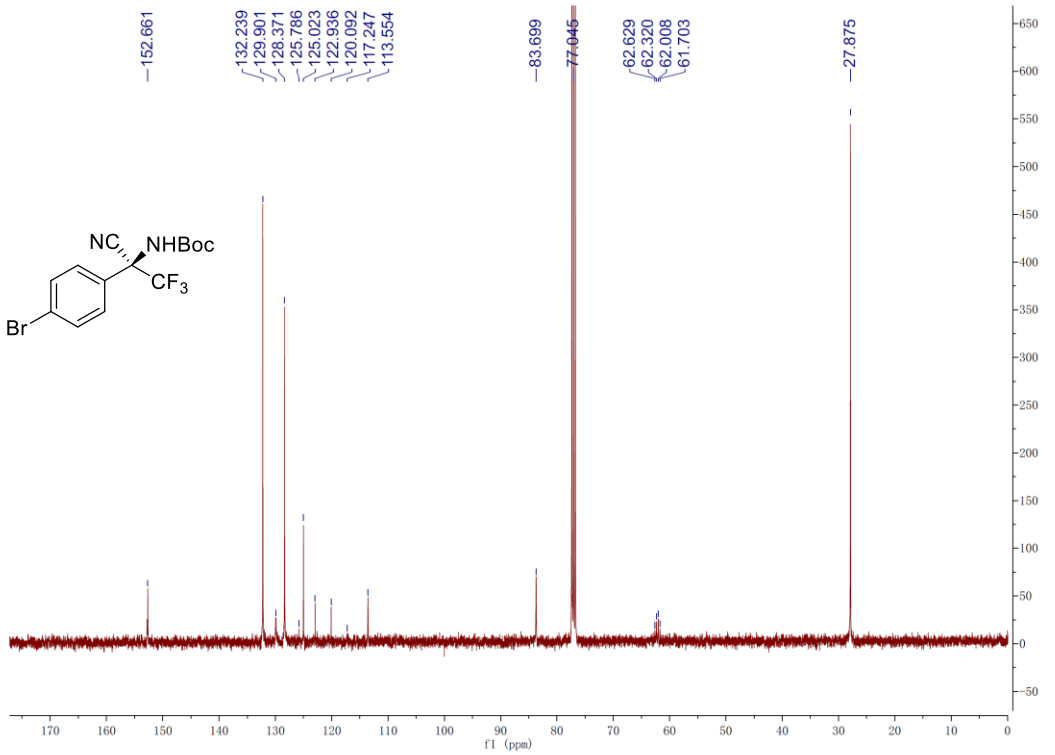
1 Det.A Ch1/254nm

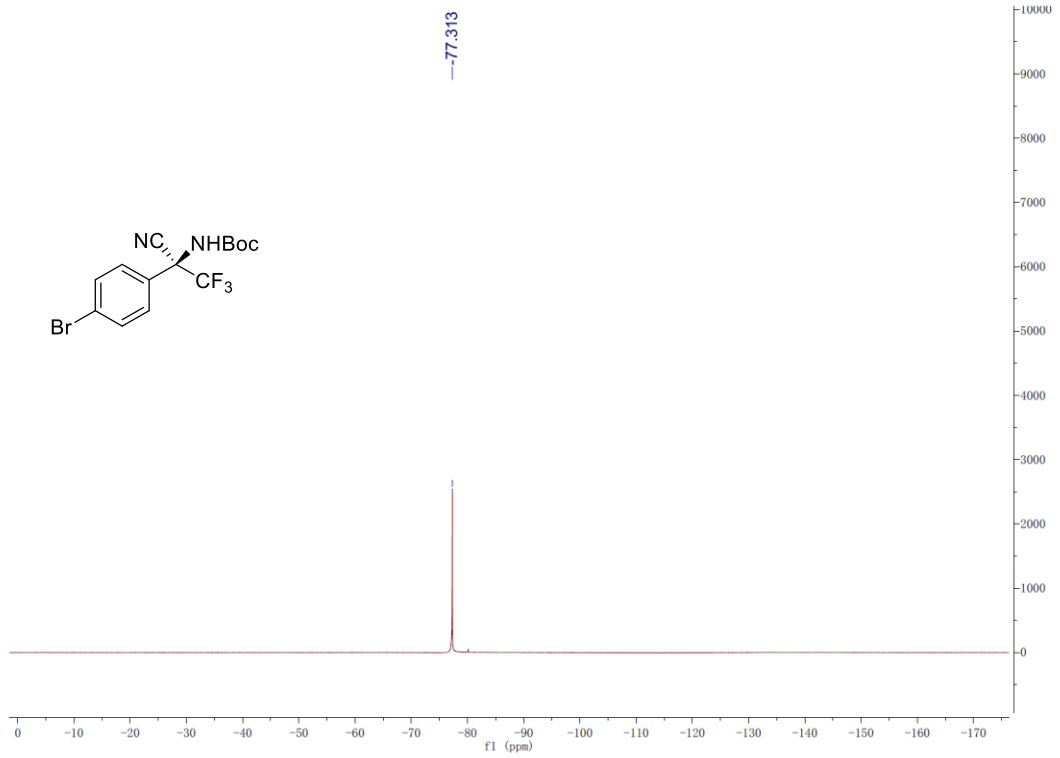
PeakTable

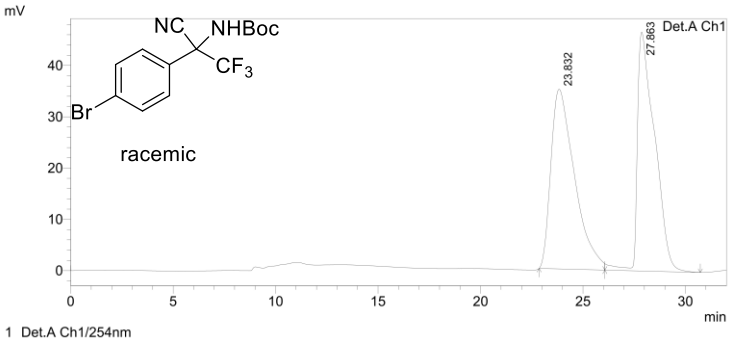
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	25.228	104230	2226	16.113	18.450
2	27.154	542641	9839	83.887	81.550
Total		646870	12064	100.000	100.000


7.632
7.610
7.537
7.516
6.236
1.344
NC
NHBoc
CF3
Br
2.02
2.01
0.89
9.00
f1 (ppm)


152.661
132.239
129.901
128.371
125.786
125.023
122.936
120.092
117.247
113.554
83.699
77.045
62.629
62.320
62.008
61.703
27.875
NC
NHBoc
CF3
Br
f1 (ppm)



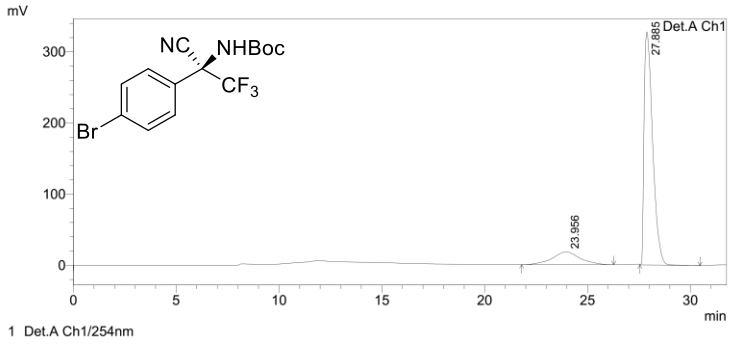


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.832	2810148	35043	50.614	42.923
2	27.863	2741990	46599	49.386	57.077
Total		5552138	81641	100.000	100.000

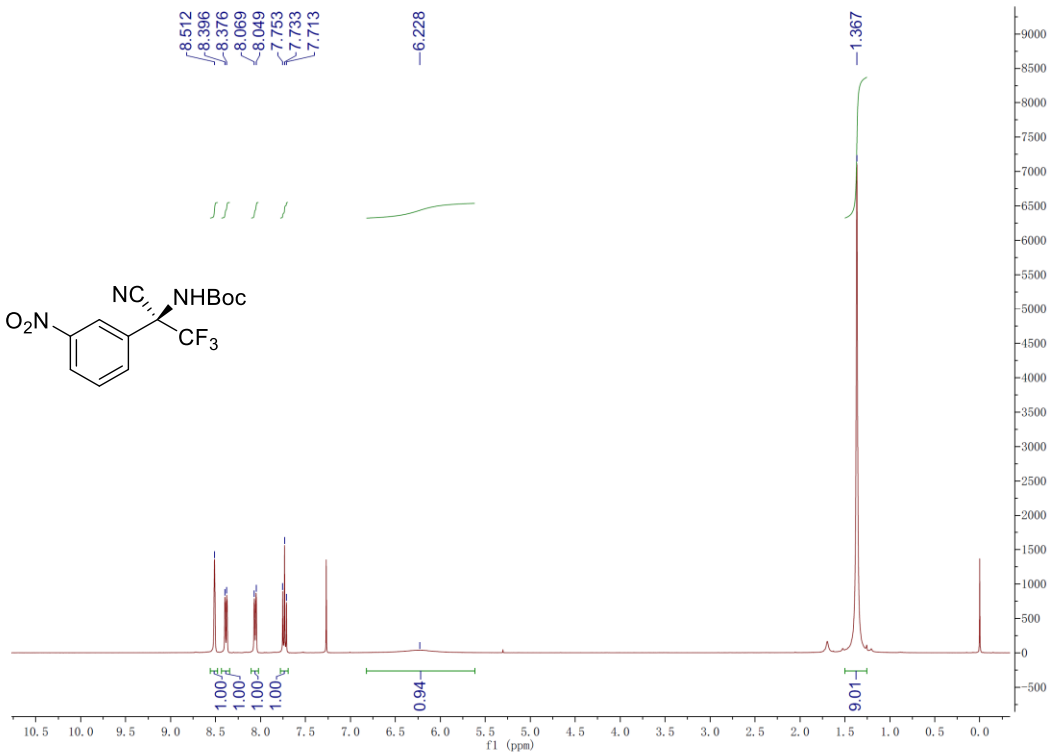


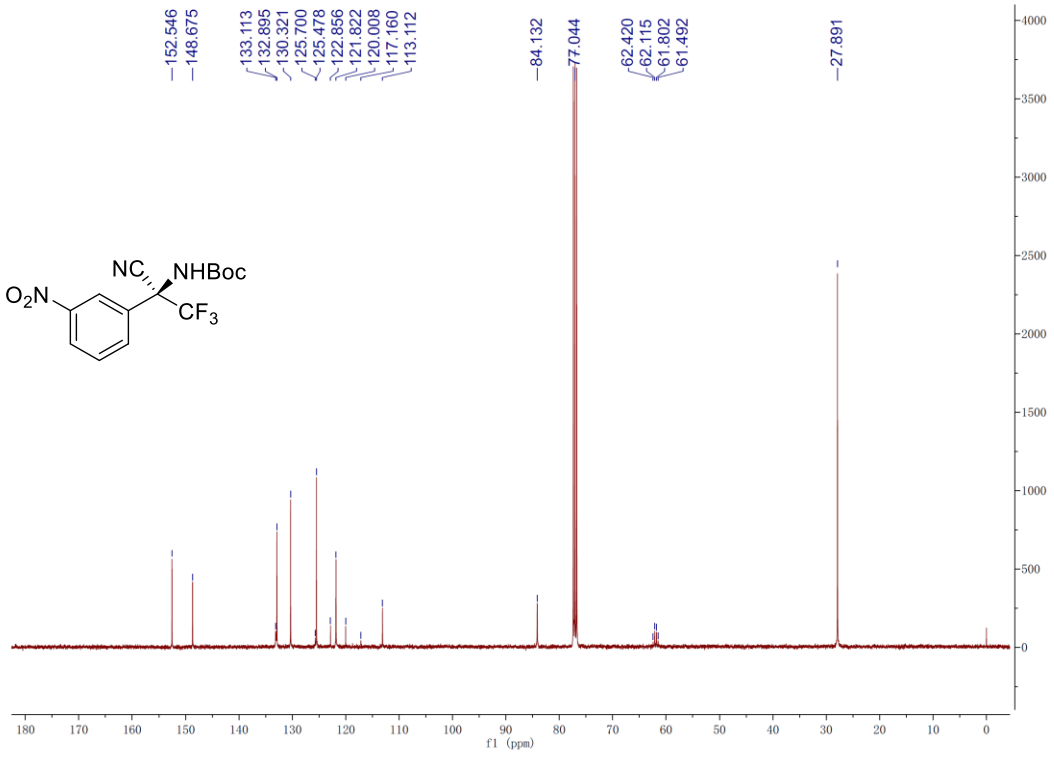
1 Det.A Ch1/254nm

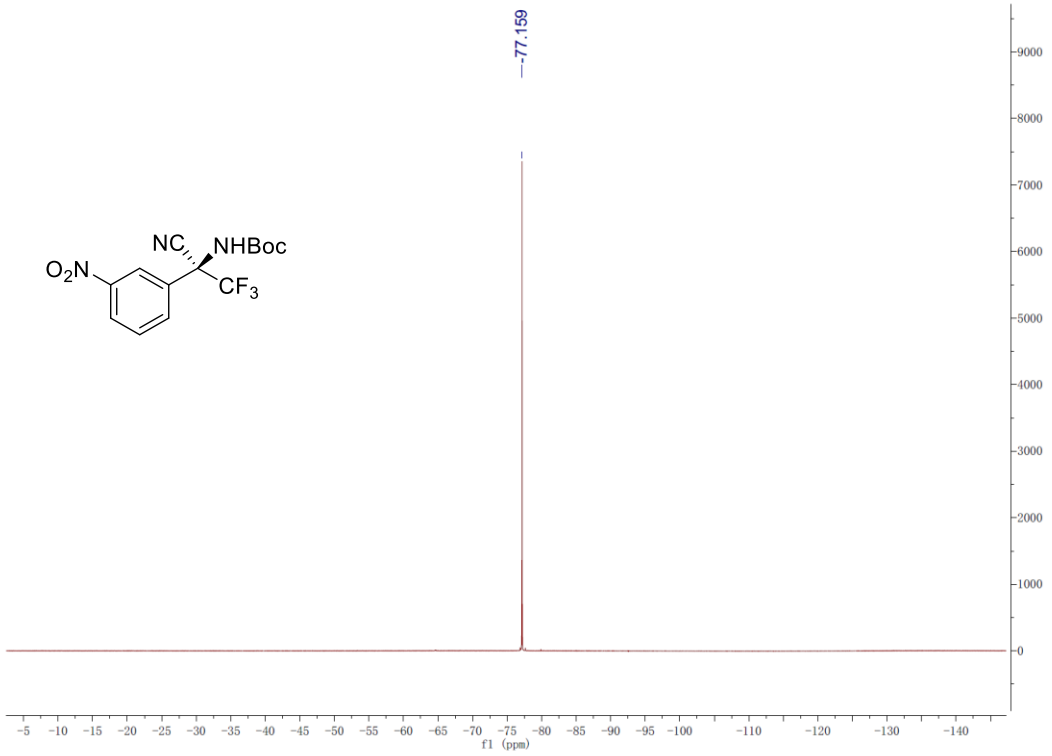
PeakTable

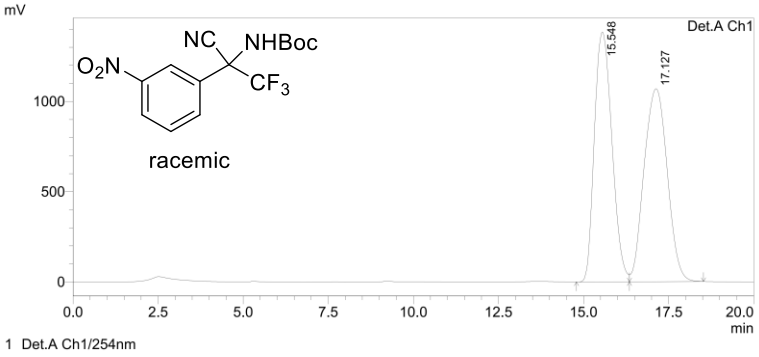
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.956	1682653	18113	15.091	5.239
2	27.885	9467668	327596	84.909	94.761
Total		11150321	345709	100.000	100.000


8.512
8.396
8.376
8.069
8.049
7.753
7.733
7.713
6.228
1.367
NC
NHBoc
O2N
CF3
1.00
1.00
1.00
1.00
0.94
9.01
f1 (ppm)


152.546
148.675
133.113
132.895
130.321
125.700
125.478
122.856
121.822
120.008
117.160
113.112
84.132
77.044
62.420
62.115
61.802
61.492
27.891
NC
NHBoc
O2N
CF3
f1 (ppm)



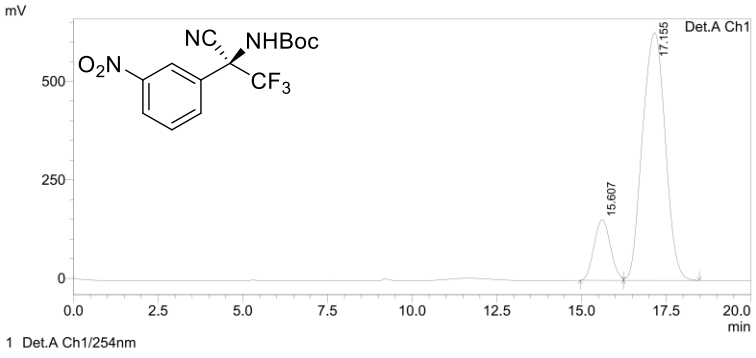


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.548	49836195	1384486	49.541	56.422
2	17.127	50760596	1069339	50.459	43.578
Total		100596791	2453825	100.000	100.000

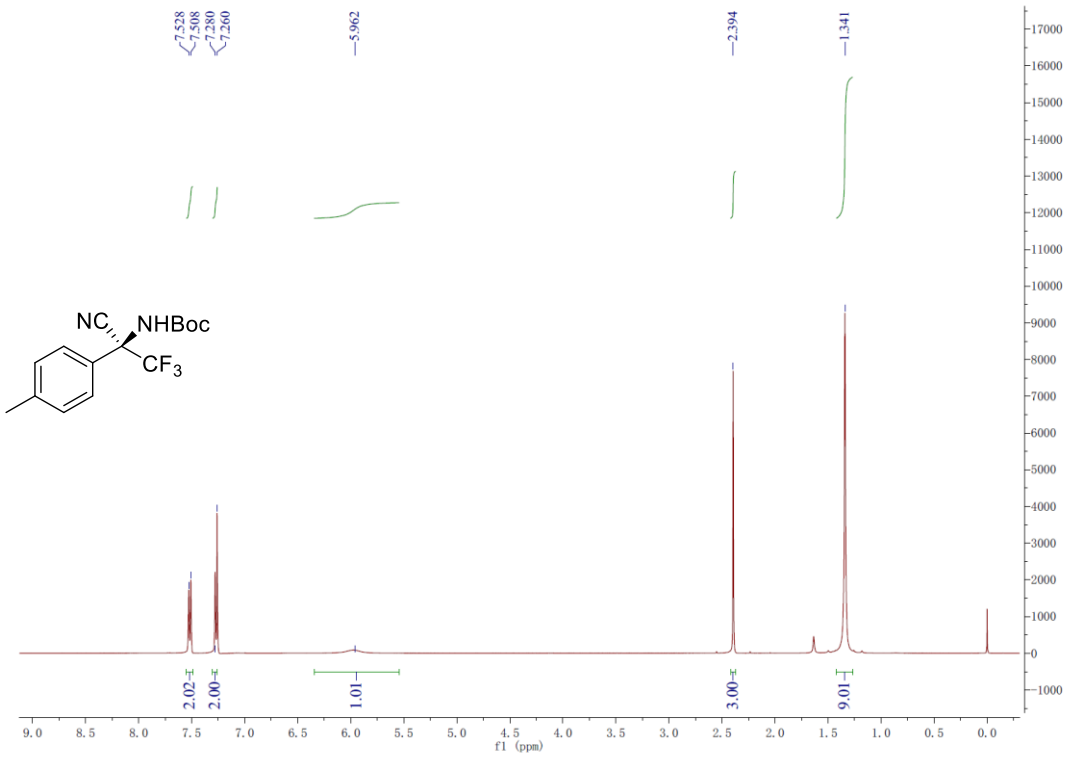


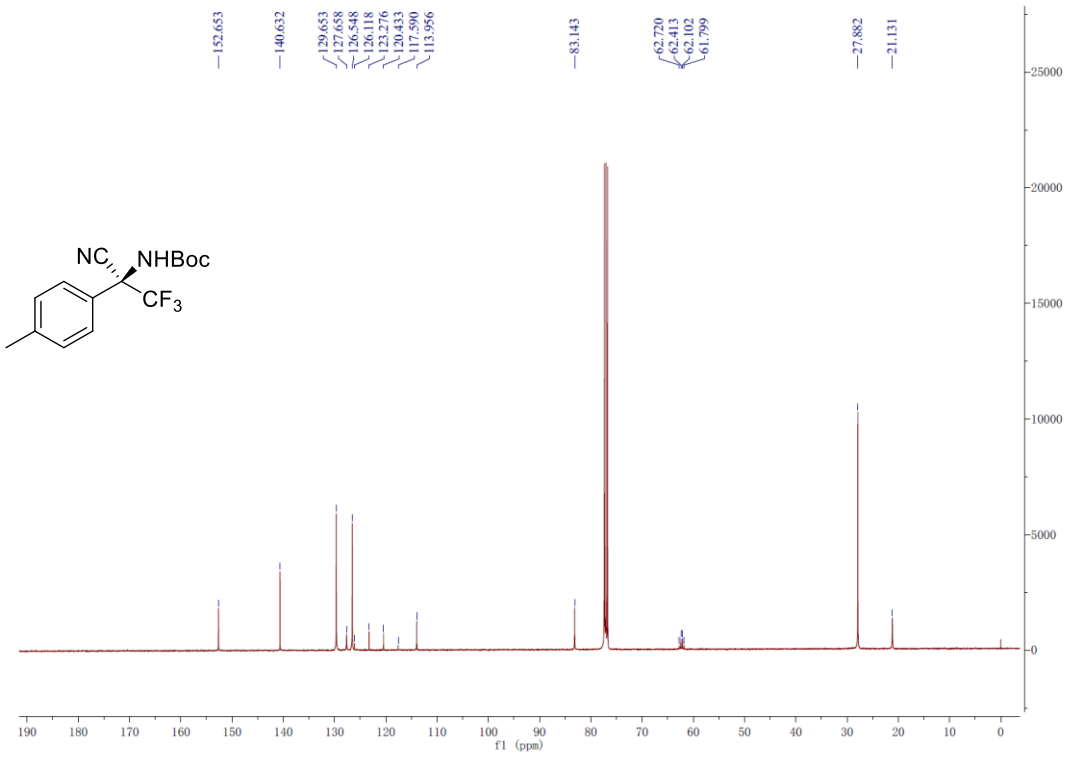
1 Det.A Ch1/254nm

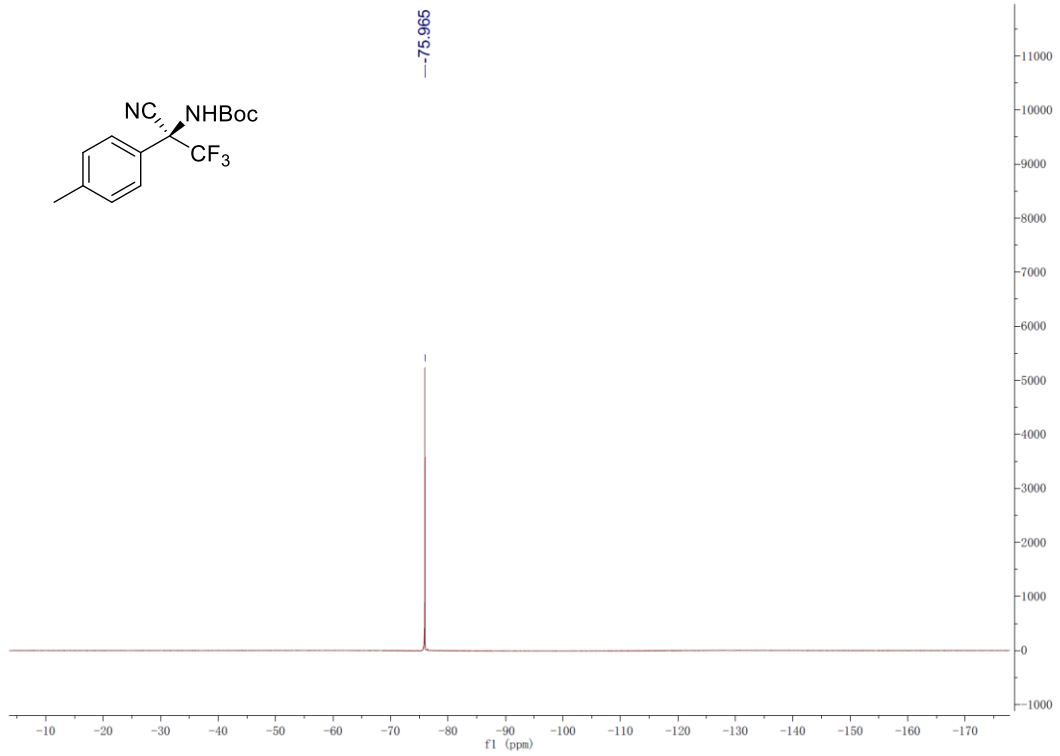
PeakTable

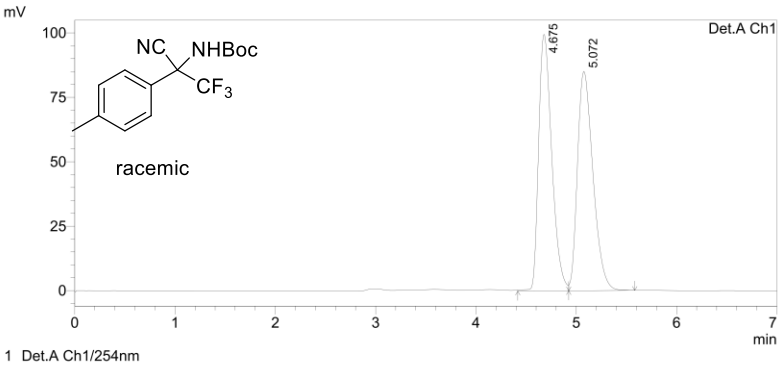
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	15.607	5159651	153472	14.932	19.620
2	17.155	29394668	628742	85.068	80.380
Total		34554319	782214	100.000	100.000


7.528
7.508
7.280
7.260
5.962
2.394
1.341
NC
NHBoc
CF3
2.02
2.00
1.01
3.00
9.01
f1 (ppm)


152.653
140.632
129.653
127.658
126.548
126.118
123.276
120.433
117.590
113.956
83.143
62.720
62.413
62.102
61.799
27.882
21.131
NC
NHBoc
CF3
f1 (ppm)

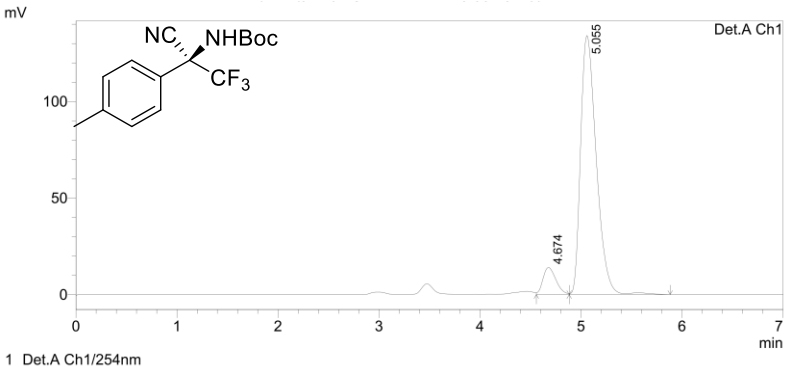




PeakTable

Detector A Ch1 254nm

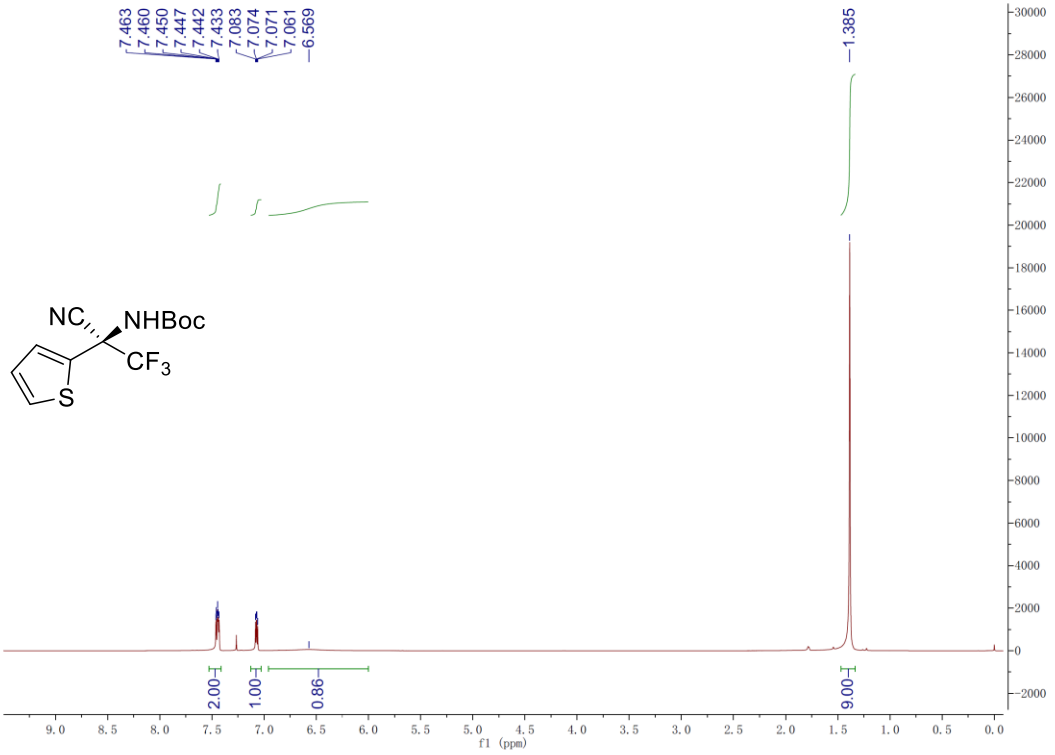
Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.675	907044	99442	49.763	53.879
2	5.072	915695	85122	50.237	46.121
Total		1822740	184564	100.000	100.000

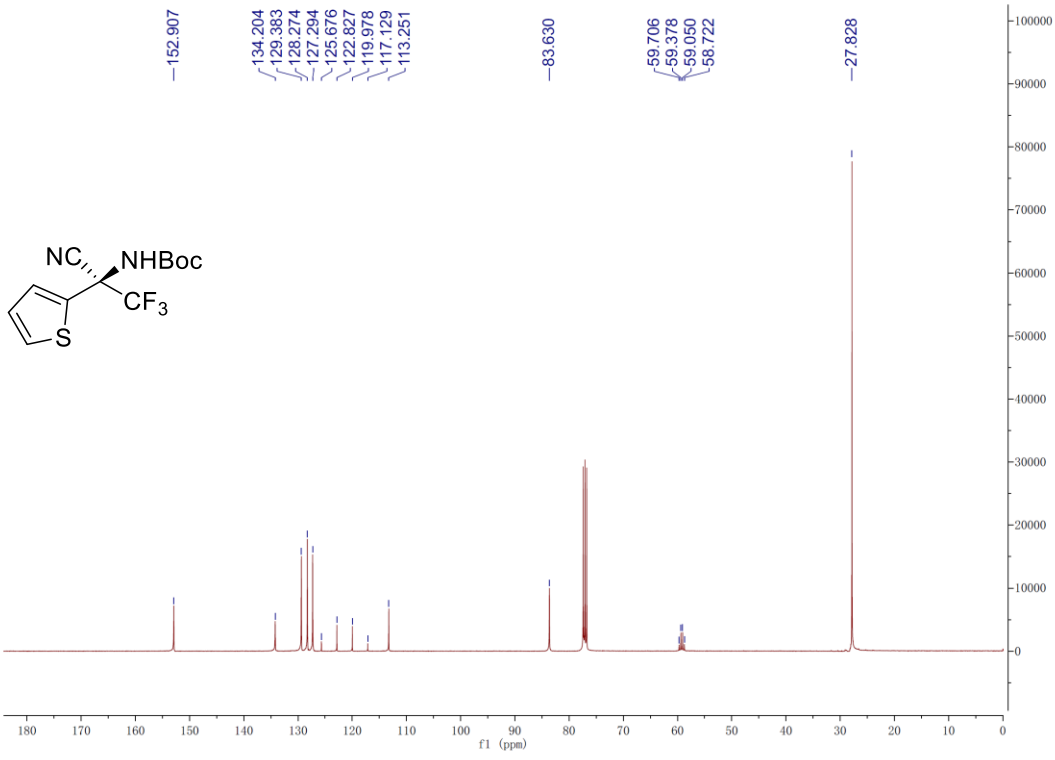


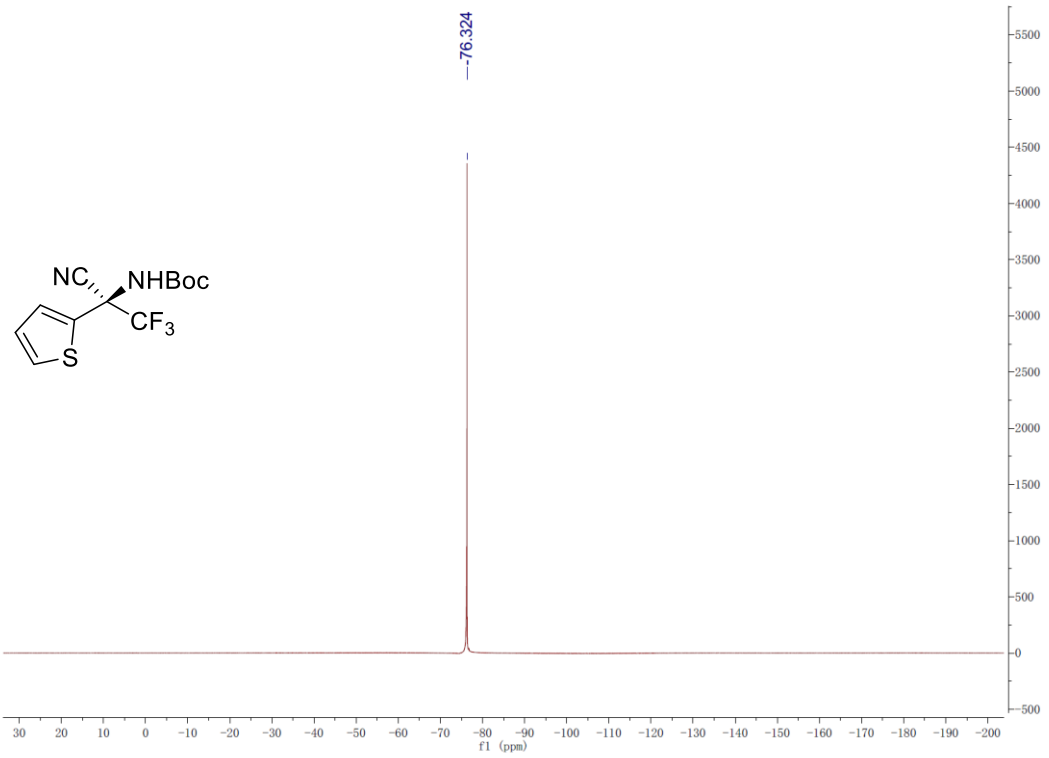
PeakTable

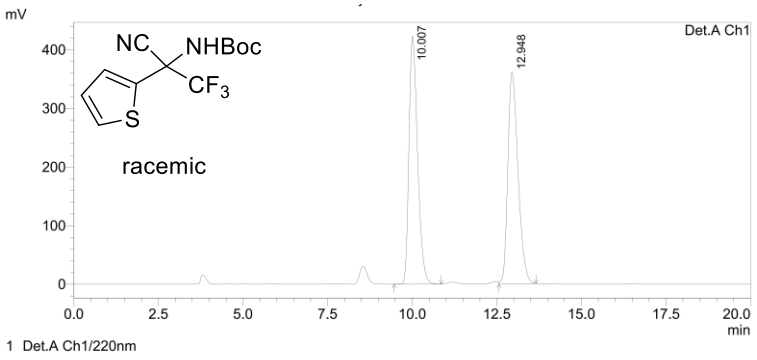
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	4.674	125300	14016	8.006	9.463
2	5.055	1439864	134099	91.994	90.537
Total		1565164	148115	100.000	100.000


7.463
7.460
7.450
7.447
7.442
7.433
7.083
7.074
7.071
7.061
6.569
1.385
NC
NHBoc
CF3
S
2.00
1.00
0.86
9.00
f1 (ppm)


152.907
134.204
129.383
128.274
127.294
125.676
122.827
119.978
117.129
113.251
83.630
59.706
59.378
59.050
58.722
27.828
NC
NHBoc
CF3
S
f1 (ppm)

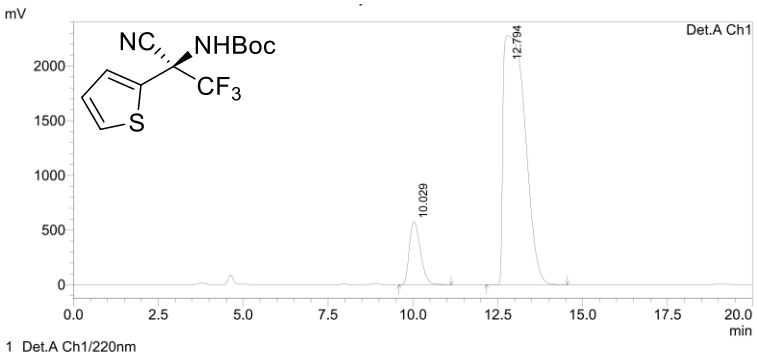




PeakTable

Detector A Ch1 220nm

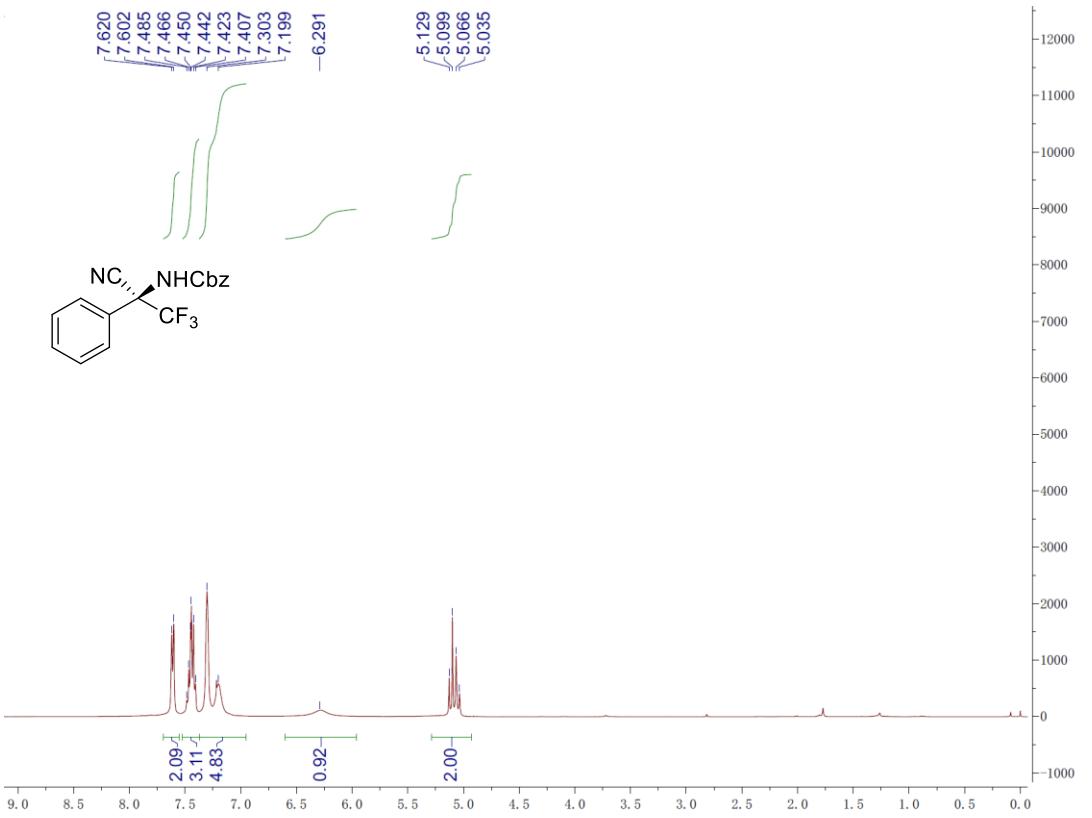
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.007	7486355	423183	49.789	54.000
2	12.948	7549700	360488	50.211	46.000
Total		15036055	783671	100.000	100.000

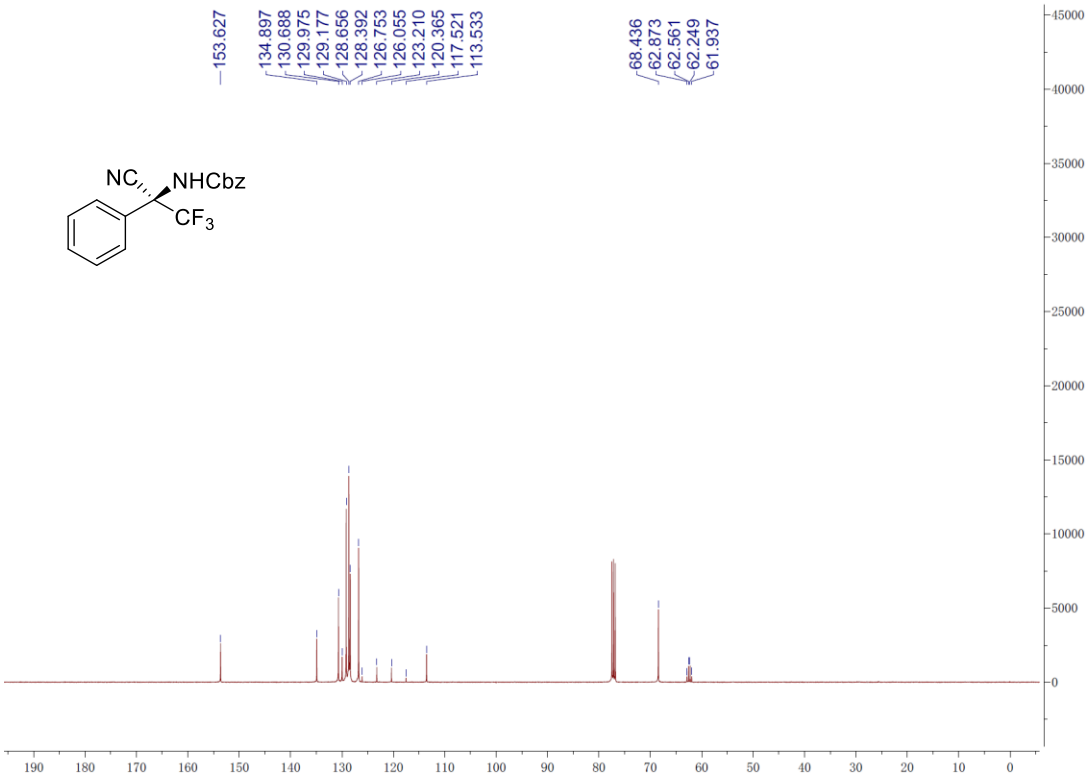


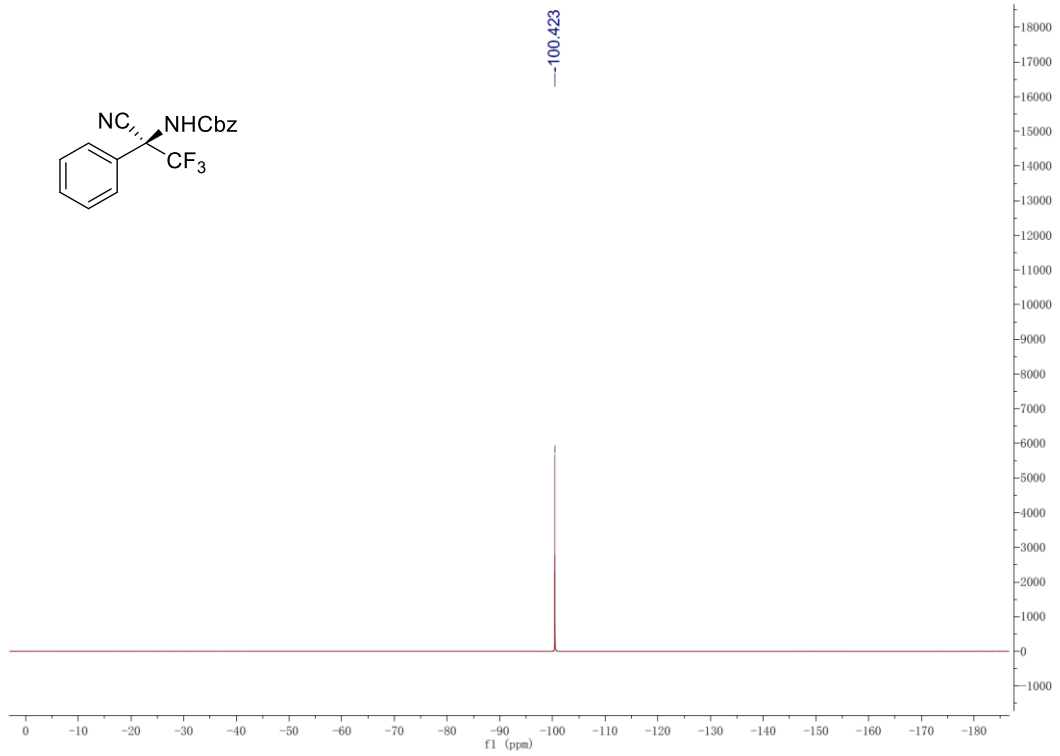
PeakTable

Detector A Ch1 220nm

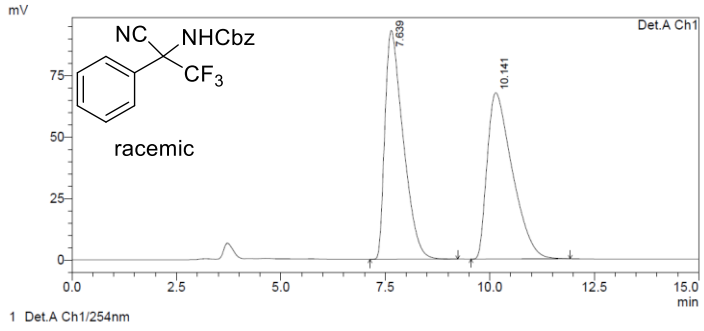
Peak#	Ret. Time	Area	Height	Area %	Height %
1	10.029	13124581	577375	11.385	20.230
2	12.794	102153772	2276748	88.615	79.770
Total		115278352	2854123	100.000	100.000


7.620
7.602
7.485
7.466
7.450
7.442
7.423
7.407
7.303
7.199
6.291
5.129
5.099
5.066
5.035
NC
NHCbz
CF3
2.09
3.11
4.83
0.92
2.00


153.627
134.897
130.688
129.975
129.177
128.656
128.392
126.753
126.055
123.210
120.365
117.521
113.533
68.436
62.873
62.561
62.249
61.937
NC
NHCbz
CF3



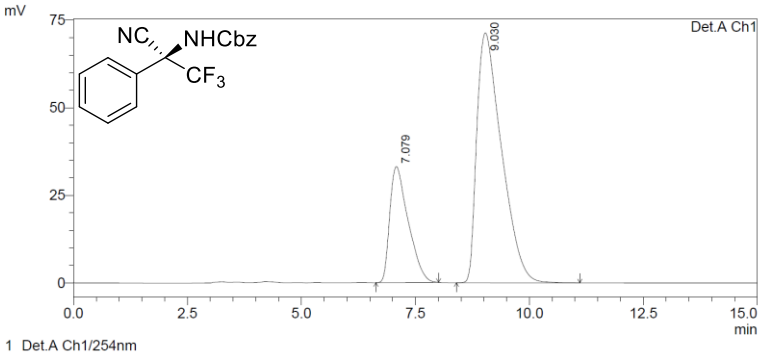
ee



PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.639	2828525	93104	49.928	57.917
2	10.141	2836710	67650	50.072	42.083
Total		5665235	160754	100.000	100.000

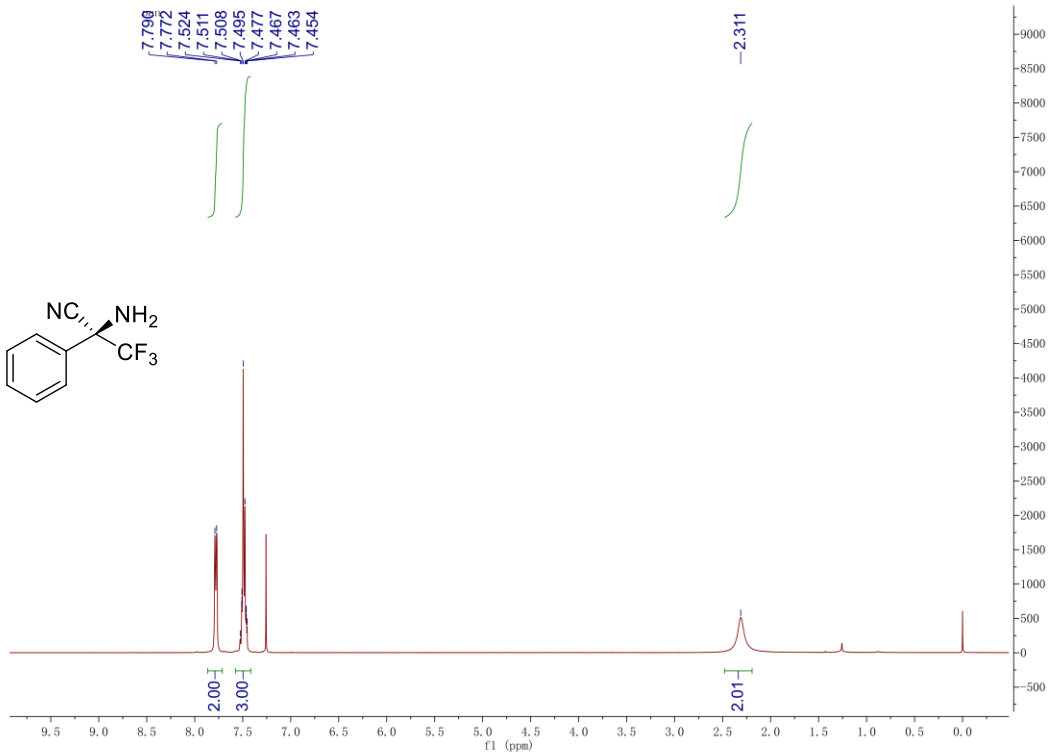


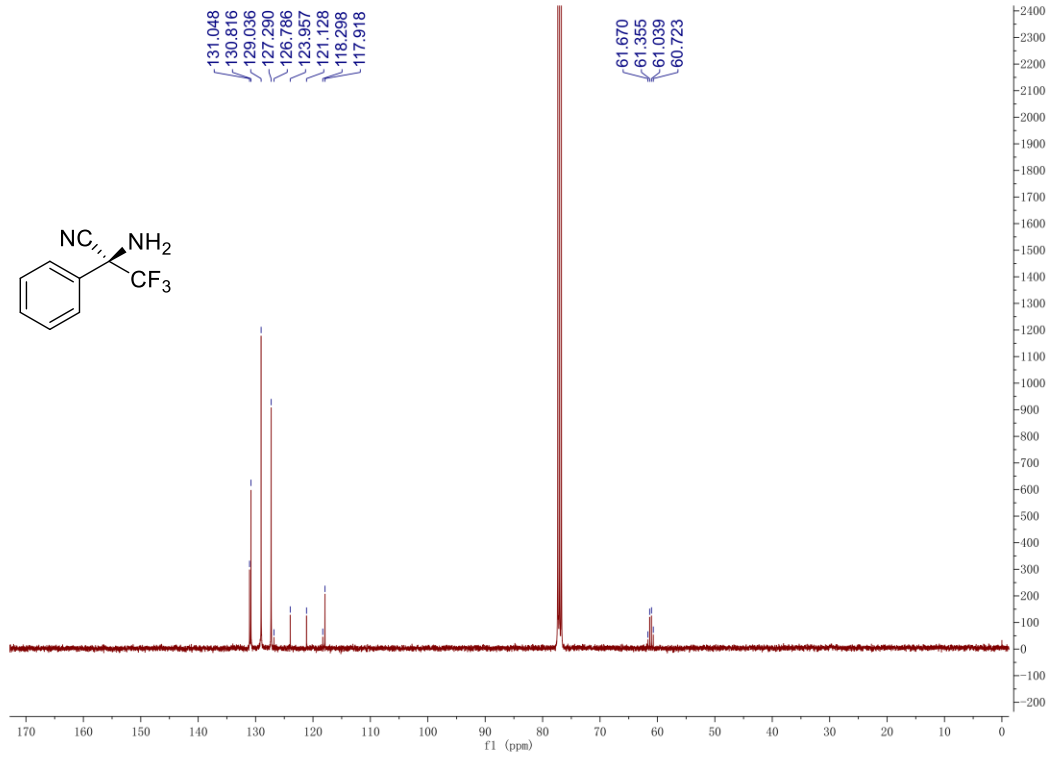
PeakTable

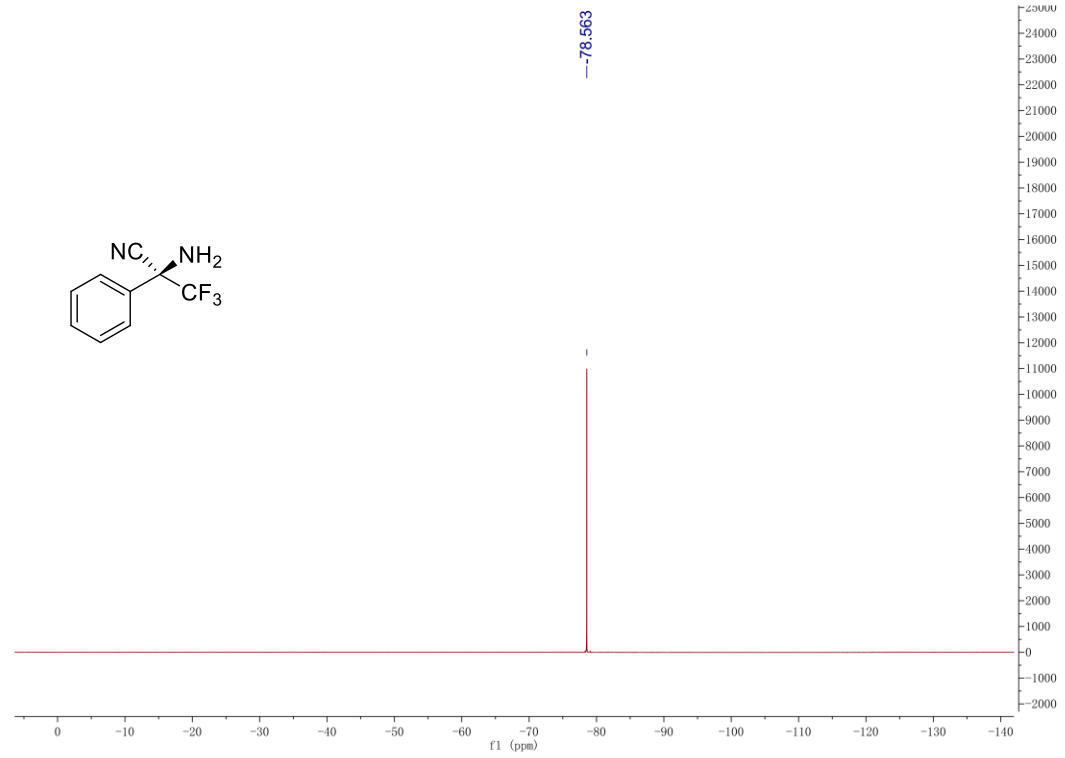
Detector A Ch1 254nm

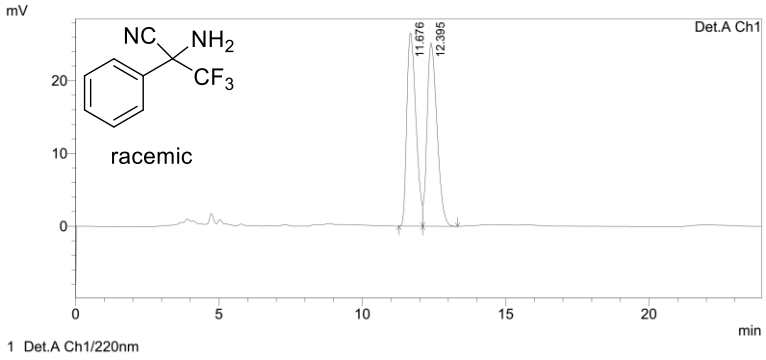
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.079	932218	33136	25.695	31.711
2	9.030	2695840	71358	74.305	68.289
Total		3628058	104495	100.000	100.000

Copies of NMR and HPLC spectra for 5a-5f







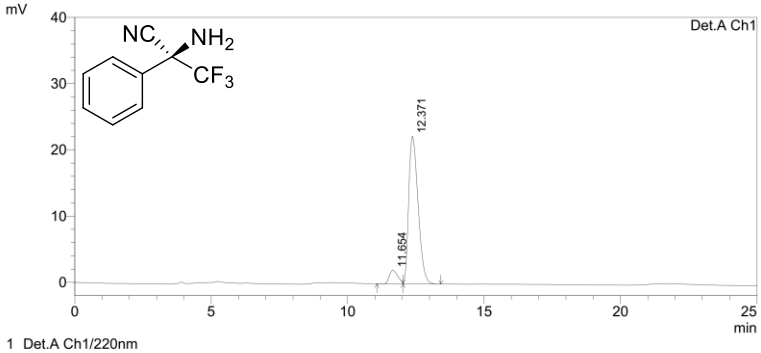


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.676	590196	26563	49.251	51.346
2	12.395	608146	25170	50.749	48.654
Total		1198342	51732	100.000	100.000

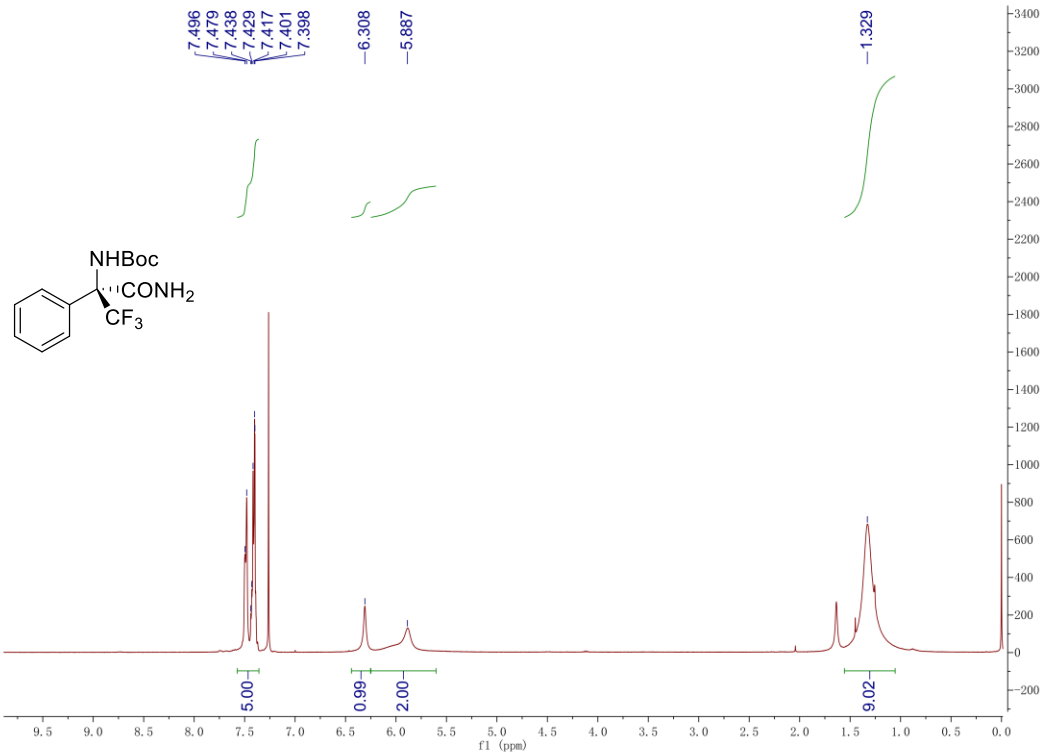


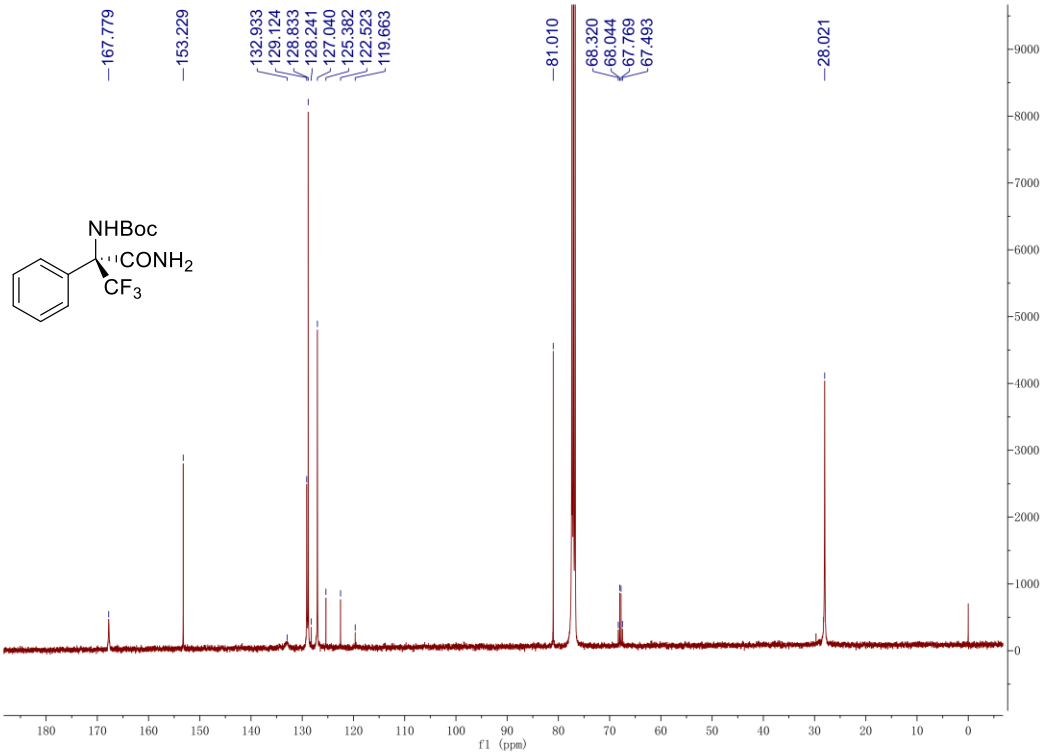
1 Det.A Ch1/220nm

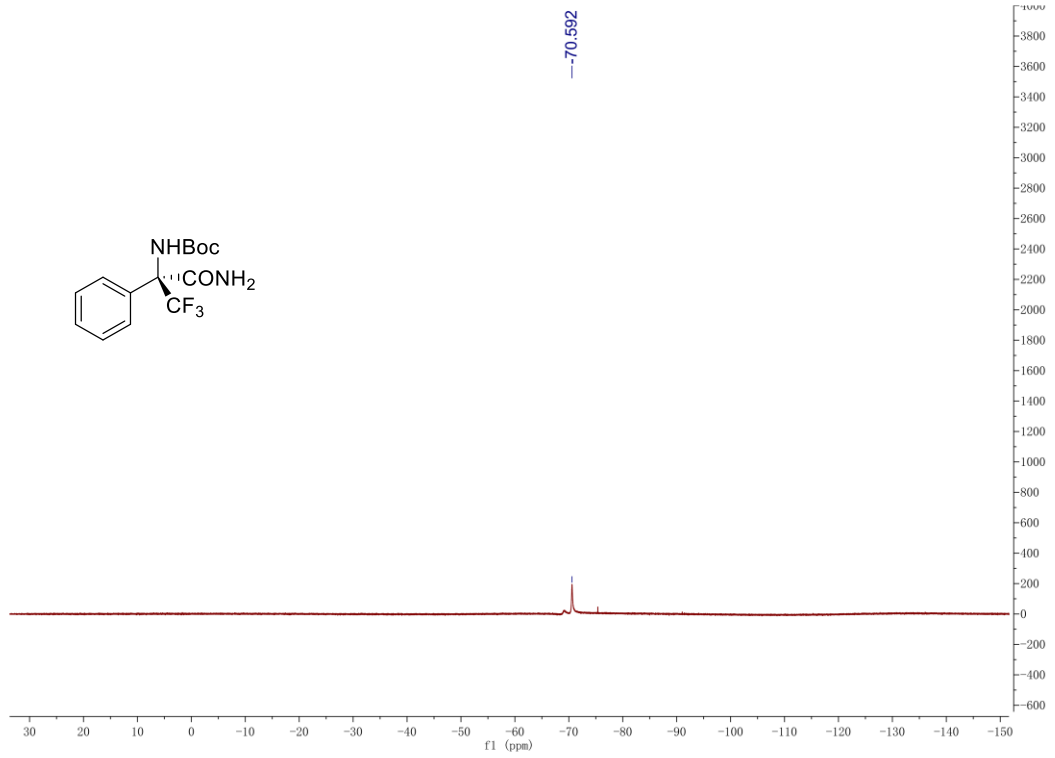
PeakTable

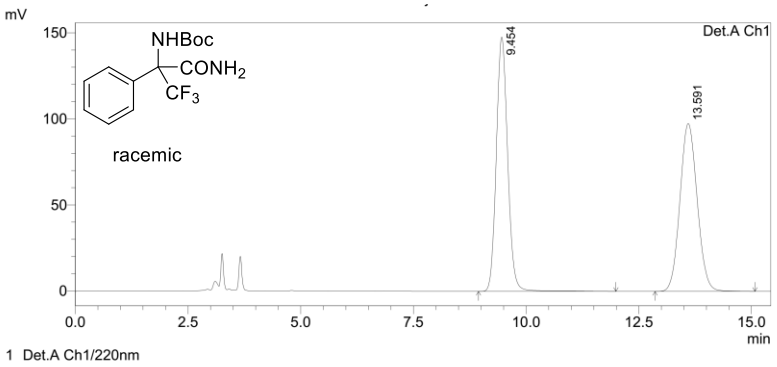
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	11.654	43659	2040	7.556	8.376
2	12.371	534179	22314	92.444	91.624
Total		577838	24354	100.000	100.000


7.496
7.479
7.438
7.429
7.417
7.401
7.398
6.308
5.887
1.329
NHBoc
CONH2
CF3
5.00
0.99
2.00
9.02
f1 (ppm)


167.779
153.229
132.933
129.124
128.833
128.241
127.040
125.382
122.523
119.663
81.010
68.320
68.044
67.769
67.493
28.021
NHBoc
CONH2
CF3
f1 (ppm)



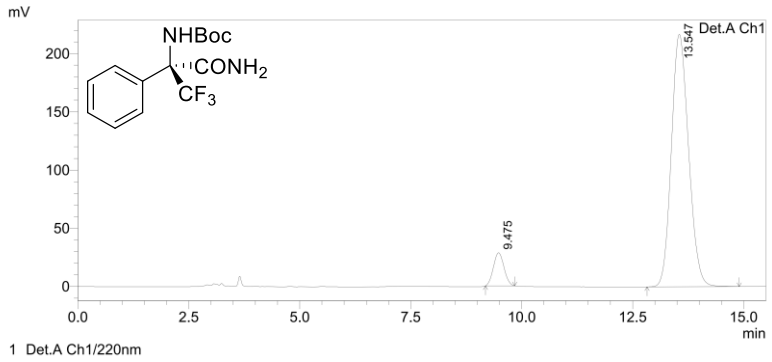


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.454	2597590	147805	50.048	60.250
2	13.591	2592658	97516	49.952	39.750
Total		5190249	245320	100.000	100.000

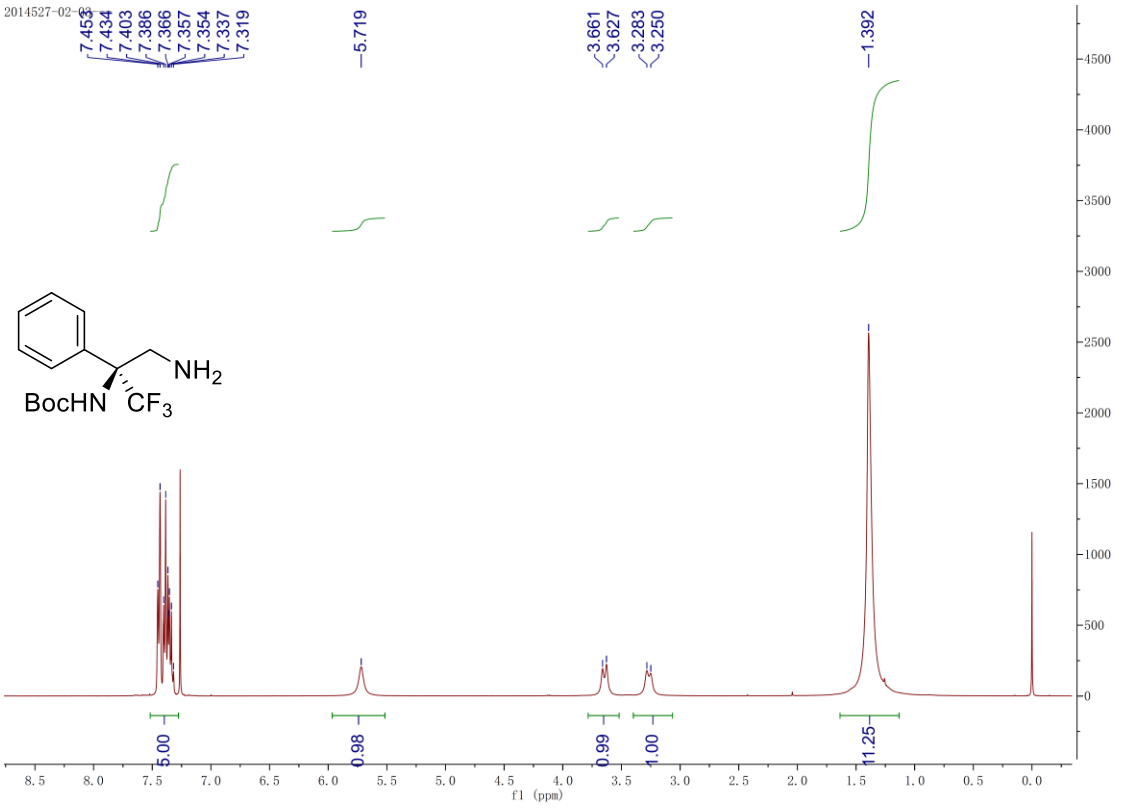


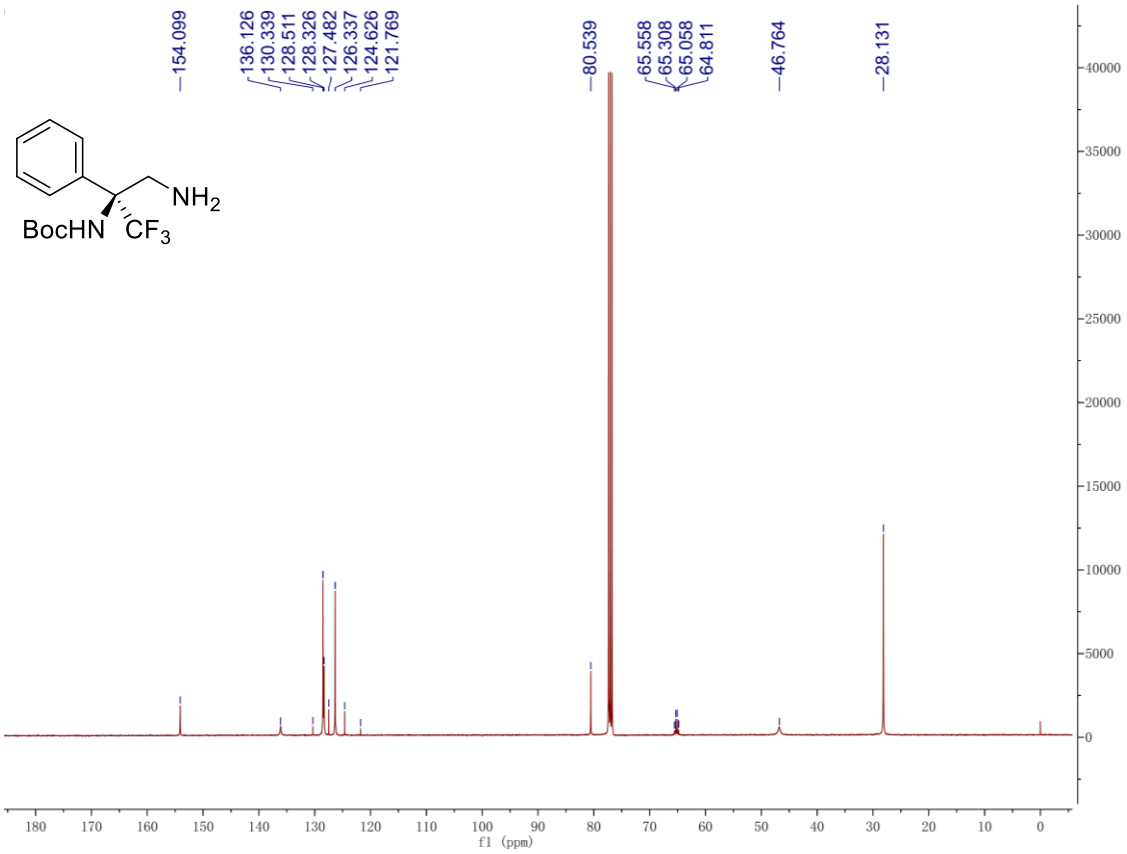
1 Det.A Ch1/220nm

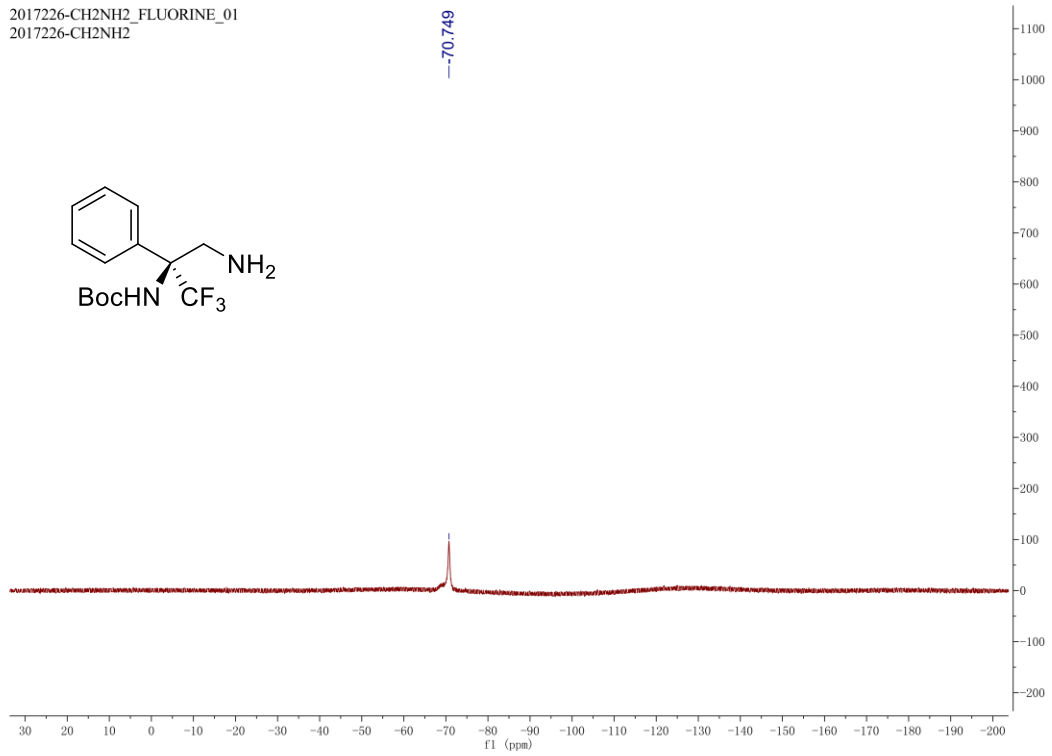
PeakTable

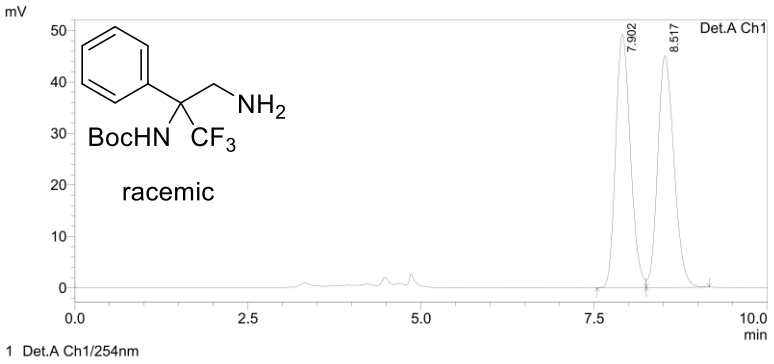
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	9.475	470381	28371	7.458	11.568
2	13.547	5836663	216892	92.542	88.432
Total		6307044	245263	100.000	100.000


2014527-02-03
7.453
7.434
7.403
7.386
7.366
7.357
7.354
7.337
7.319
5.719
3.661
3.627
3.283
3.250
1.392
NH2
BocHN
CF3
5.00
0.98
0.99
1.00
11.25
f1 (ppm)


154.099
136.126
130.339
128.511
128.326
127.482
126.337
124.626
121.769
80.539
65.558
65.308
65.058
64.811
46.764
28.131
NH2
BocHN
CF3
f1 (ppm)

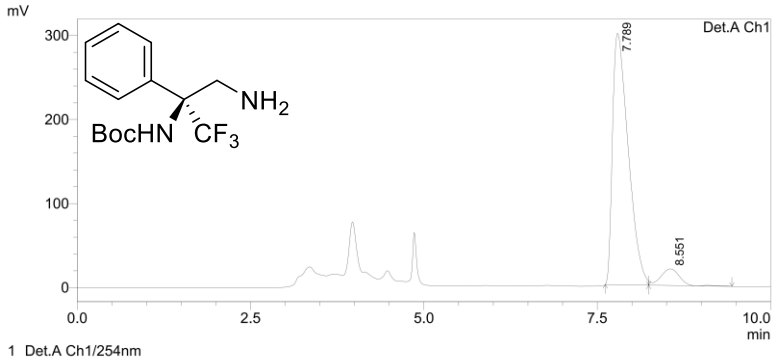




PeakTable

Detector A Ch1 254nm

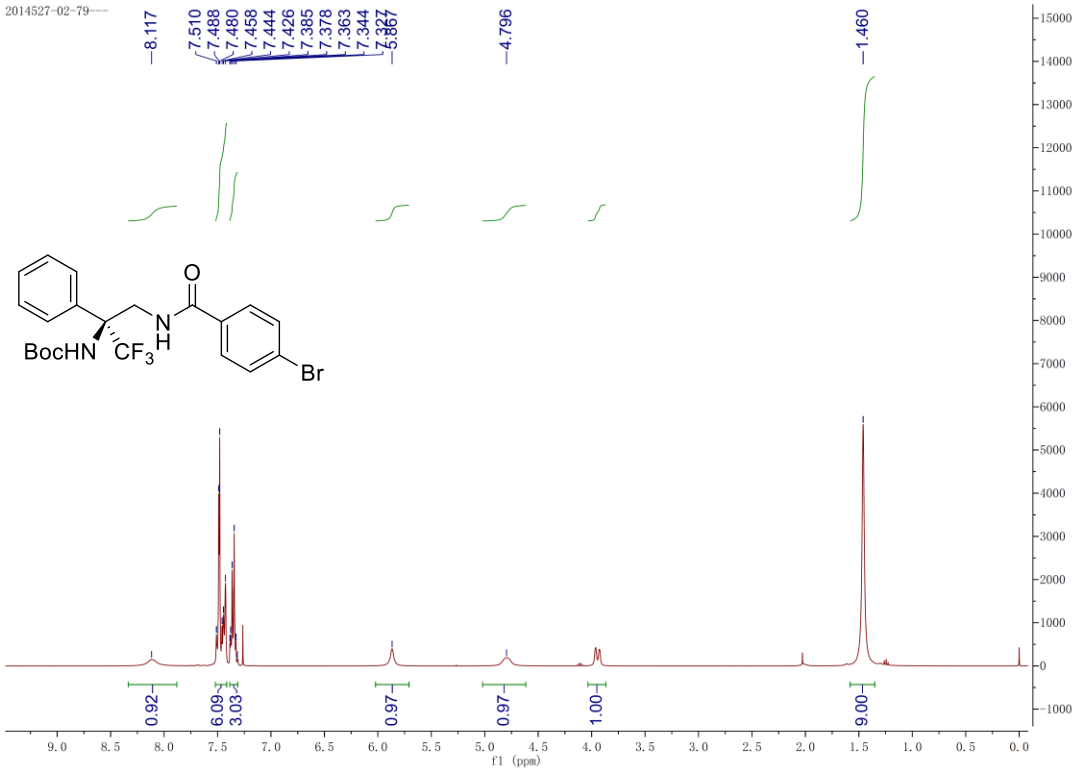
Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.902	726903	49250	49.712	52.241
2	8.517	735324	45025	50.288	47.759
Total		1462227	94275	100.000	100.000

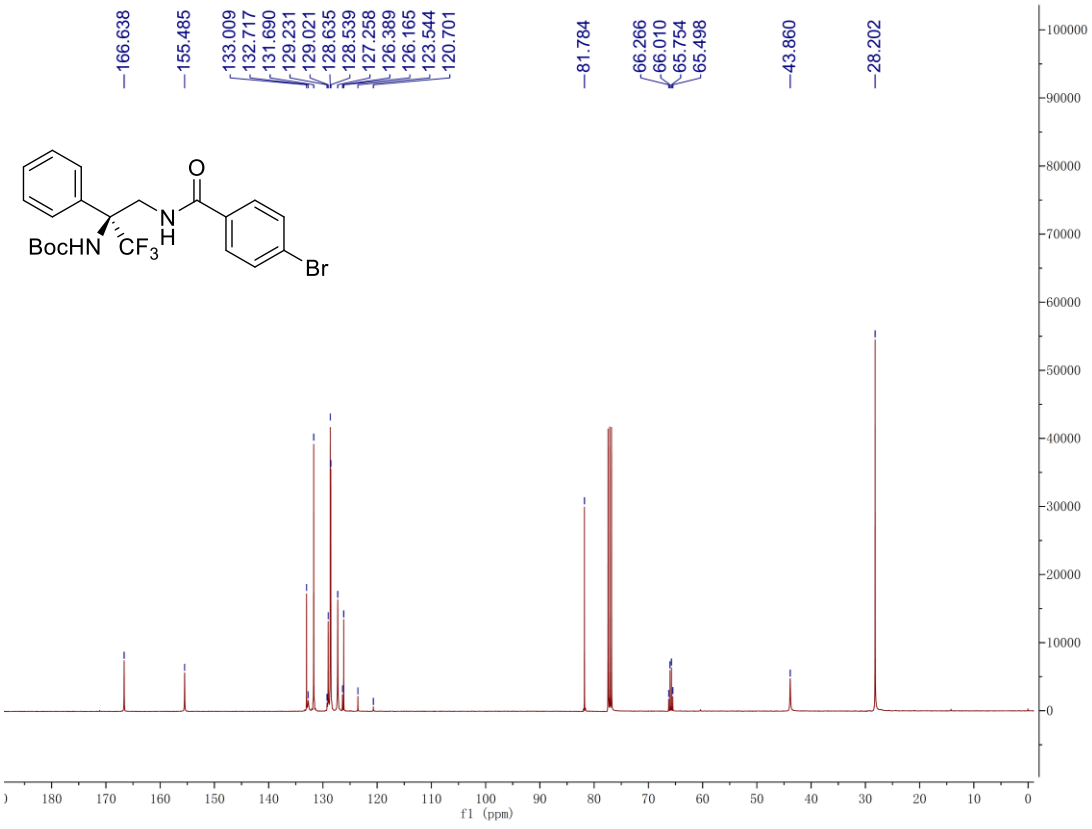


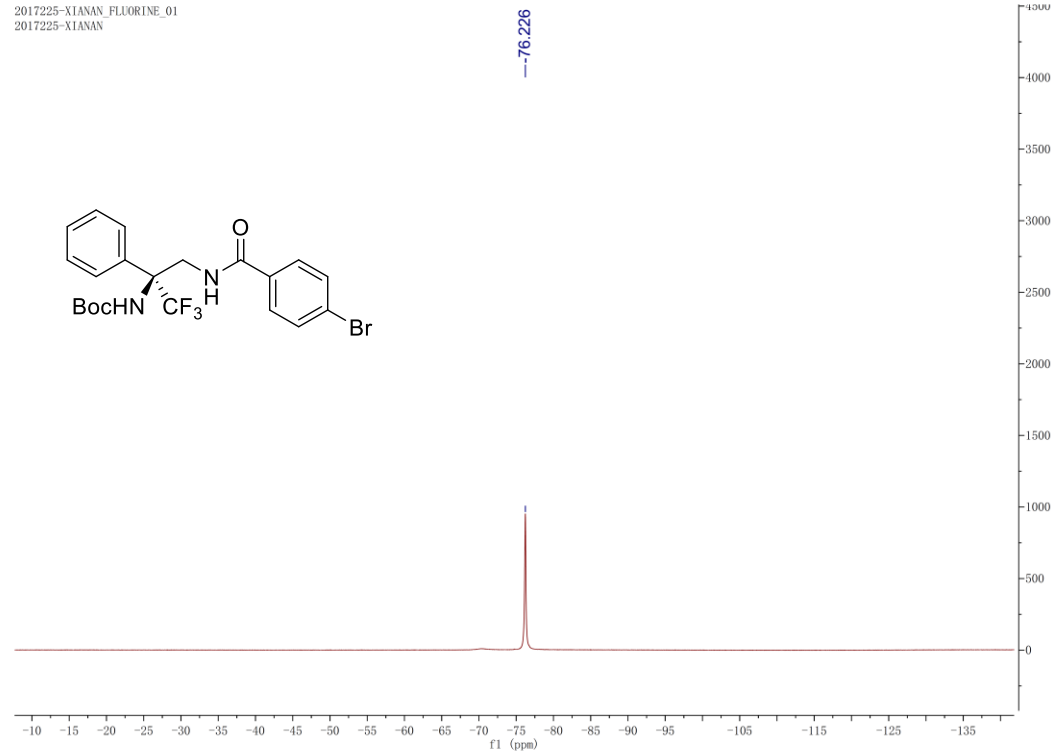
PeakTable

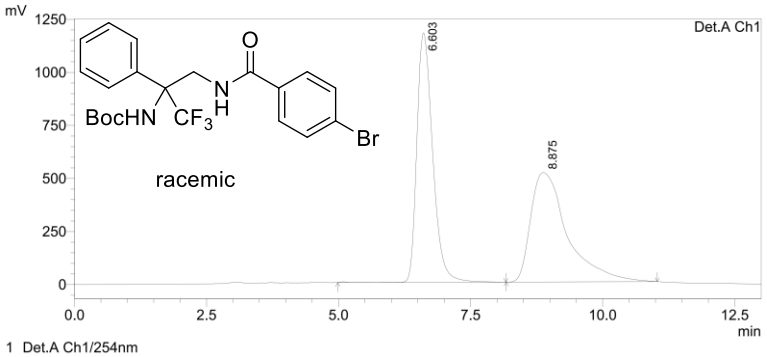
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	7.789	4703628	299095	92.558	93.827
2	8.551	378214	19679	7.442	6.173
Total		5081842	318774	100.000	100.000


2014527-02-79---
8.117
7.510
7.488
7.480
7.458
7.444
7.426
7.385
7.378
7.363
7.344
5.367
4.796
1.460
BocHN
CF3
N
H
O
Br
0.92
6.09
3.03
0.97
0.97
1.00
9.00
f1 (ppm)


166.638
155.485
133.009
132.717
131.690
129.231
129.021
128.635
128.539
127.258
126.389
126.165
123.544
120.701
81.784
66.266
66.010
65.754
65.498
43.860
28.202
BocHN
CF3
N
H
O
Br
f1 (ppm)



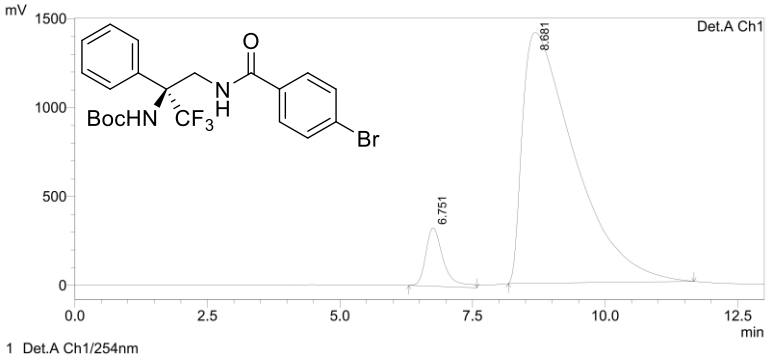


1 Det.A Ch1/254nm

PeakTable

Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.603	24556553	1176033	49.646	69.510
2	8.875	24906577	515866	50.354	30.490
Total		49463130	1691899	100.000	100.000

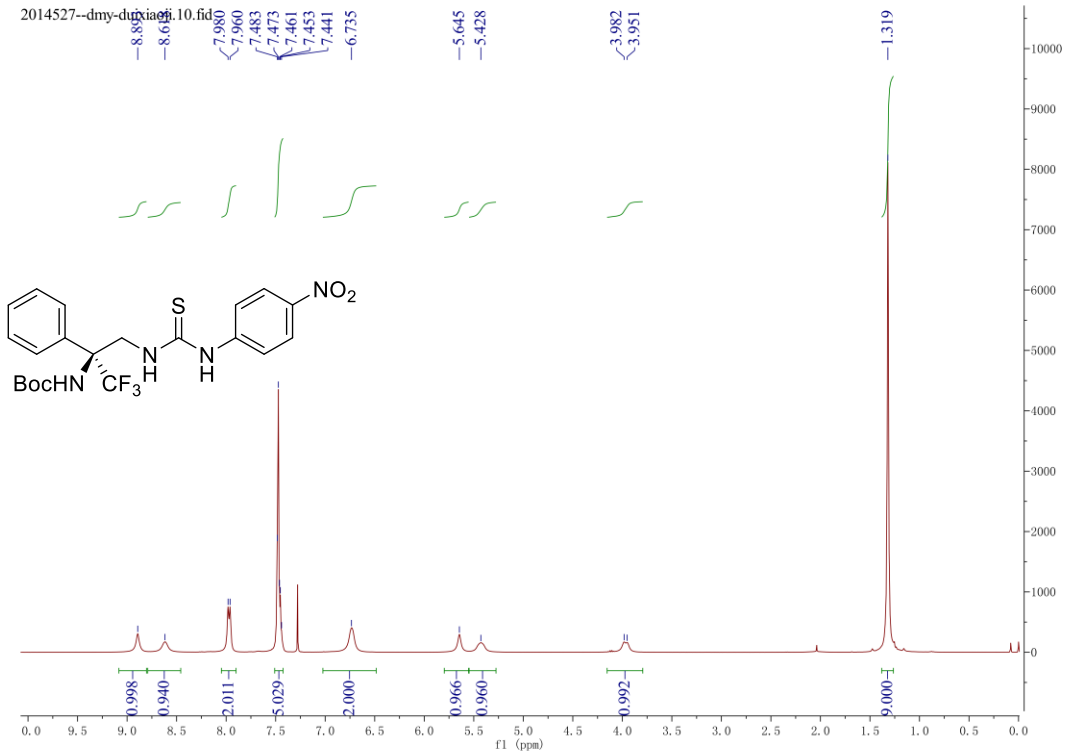


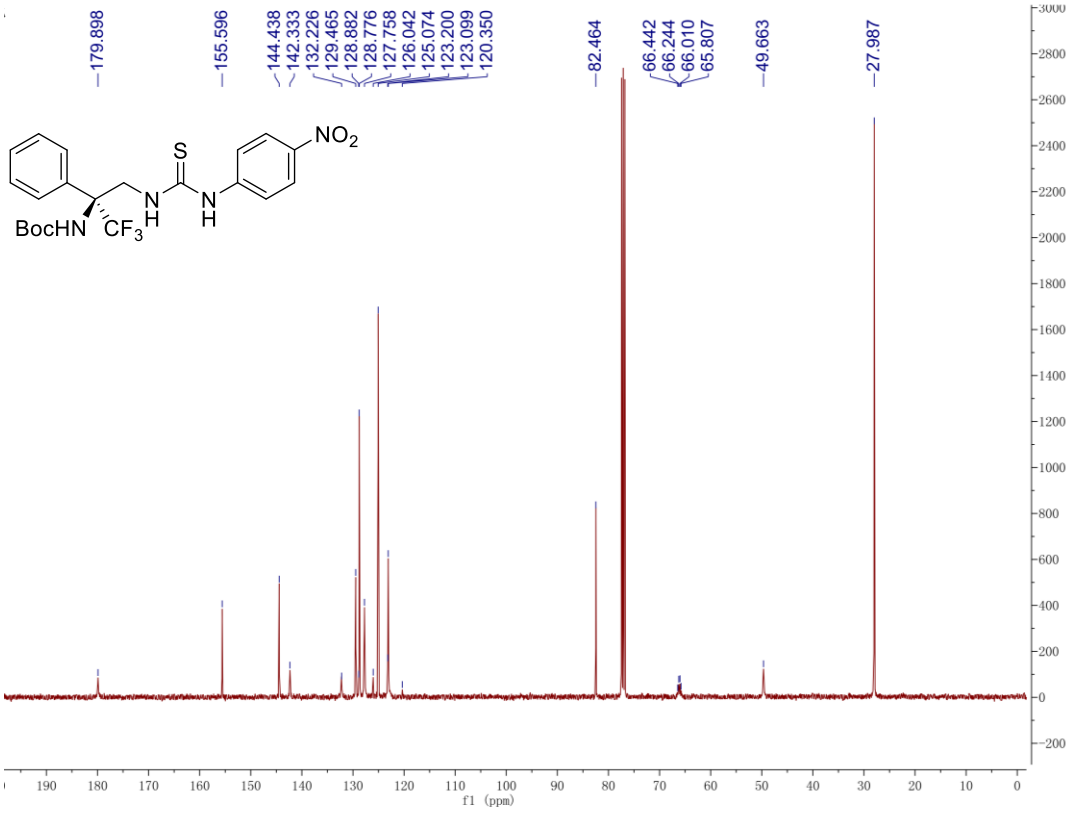
1 Det.A Ch1/254nm

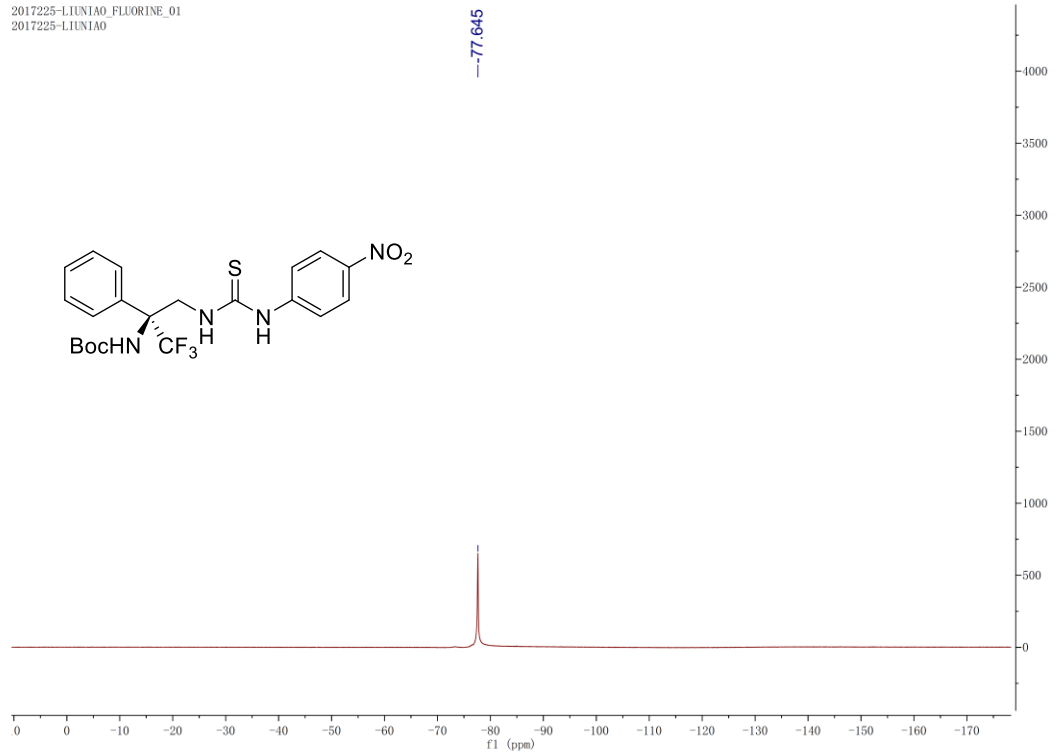
PeakTable

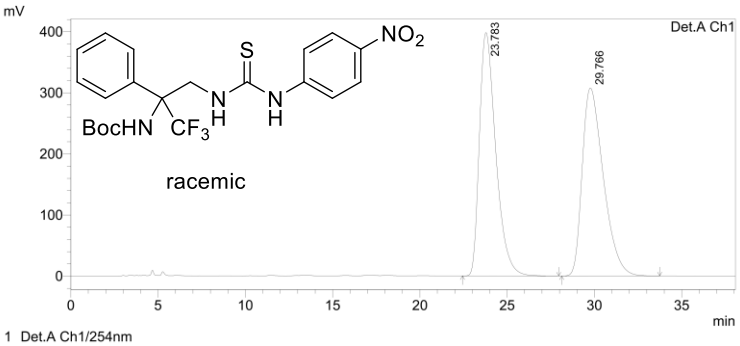
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.751	7568486	328220	7.255	18.874
2	8.681	96756331	1410833	92.745	81.126
Total		104324817	1739053	100.000	100.000


2014527--dmy-duixiaoji.10.fid
8.895
8.612
7.980
7.960
7.483
7.473
7.461
7.453
7.441
6.735
5.645
5.428
3.982
3.951
1.319
NO2
S
N
H
N
H
BocHN
CF3
0.998
0.940
2.011
5.029
2.000
0.966
0.960
0.992
9.000
f1 (ppm)


179.898
155.596
144.438
142.333
132.226
129.465
128.882
128.776
127.758
126.042
125.074
123.200
123.099
120.350
82.464
66.442
66.244
66.010
65.807
49.663
27.987
NO2
S
N
H
N
H
BocHN
CF3
f1 (ppm)

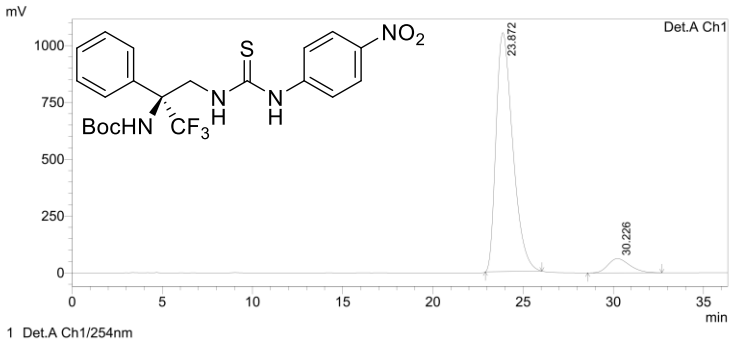




PeakTable

Detector A Ch1 254nm

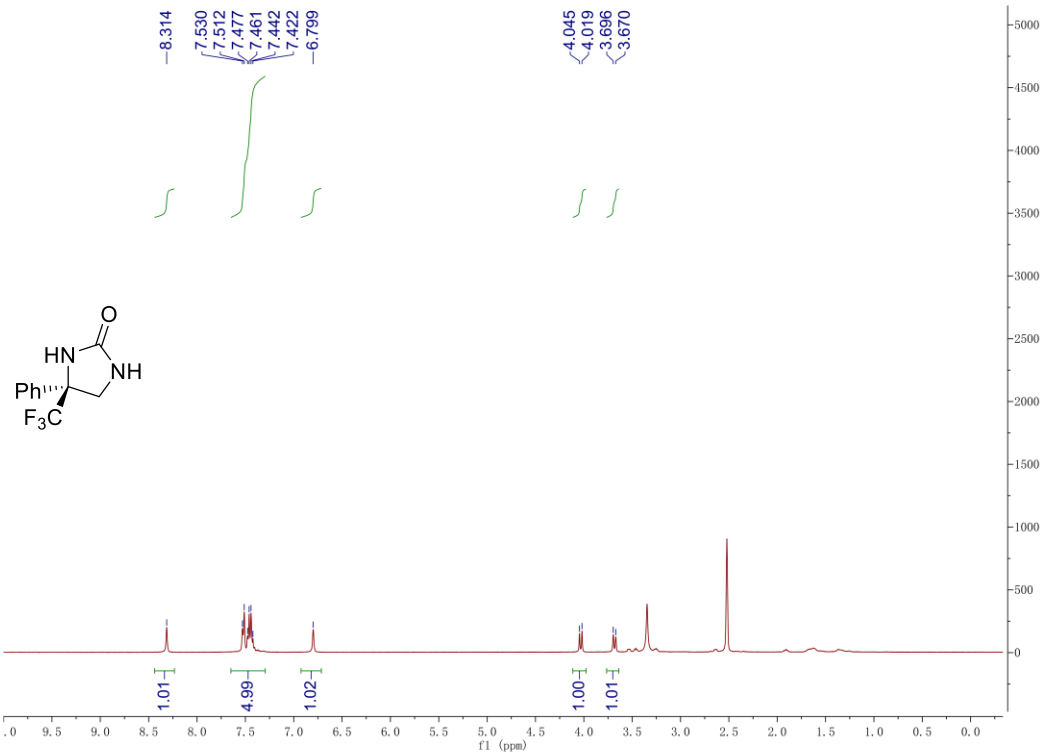
Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.783	25979287	398267	50.068	56.416
2	29.766	25909195	307674	49.932	43.584
Total		51888482	705941	100.000	100.000

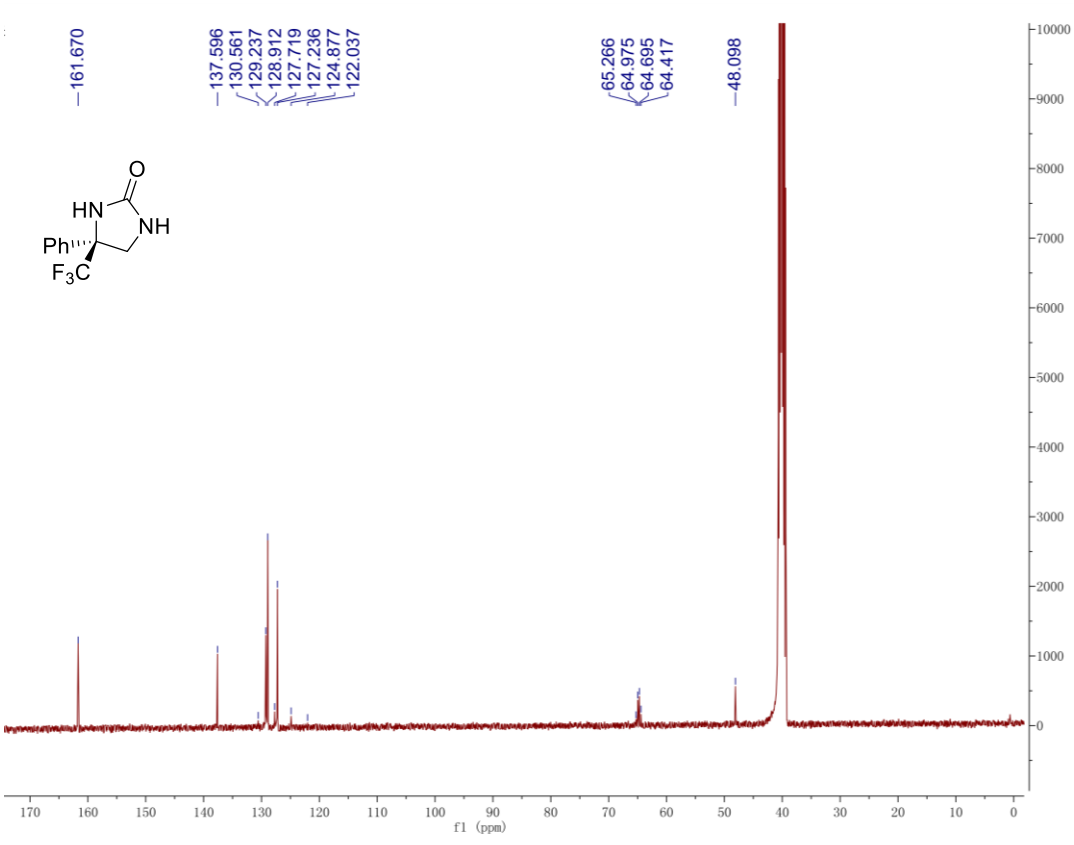


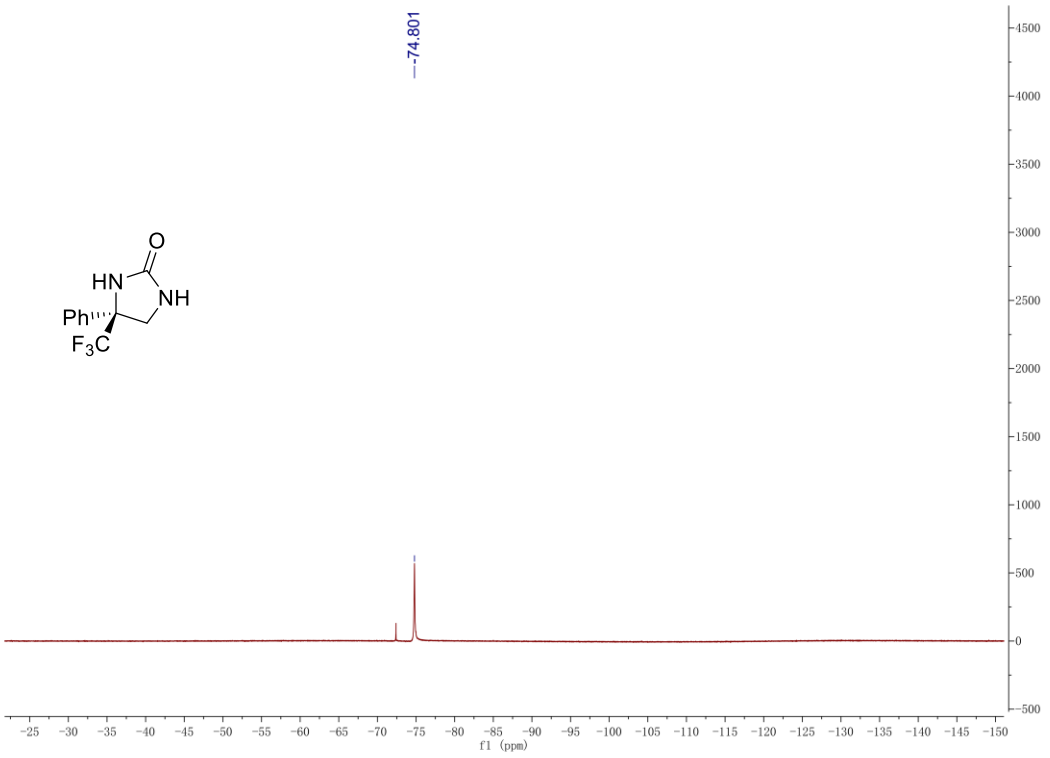
PeakTable

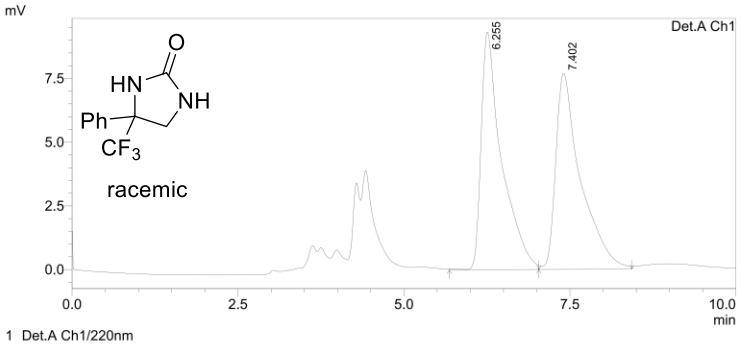
Detector A Ch1 254nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	23.872	67918212	1051086	92.854	94.390
2	30.226	5227166	62467	7.146	5.610
Total		73145378	1113553	100.000	100.000


8.314
7.530
7.512
7.477
7.461
7.442
7.422
6.799
4.045
4.019
3.696
3.670
HN
NH
Ph
F3C
O
1.01
4.99
1.02
1.00
1.01
f1 (ppm)


161.670
137.596
130.561
129.237
128.912
127.719
127.236
124.877
122.037
65.266
64.975
64.695
64.417
48.098
HN
NH
Ph
F3C
O
f1 (ppm)



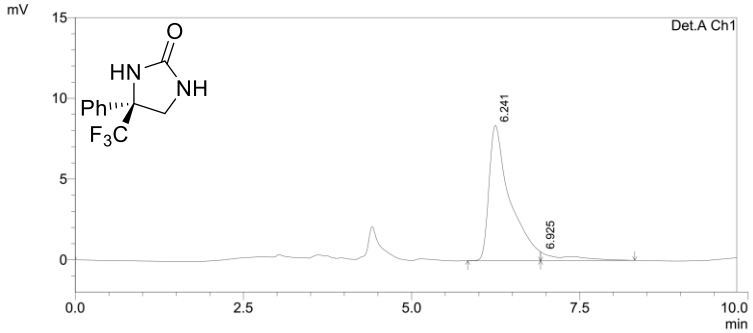


1 Det.A Ch1/220nm

PeakTable

Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.255	200620	9329	49.998	54.791
2	7.402	200635	7698	50.002	45.209
Total		401256	17027	100.000	100.000

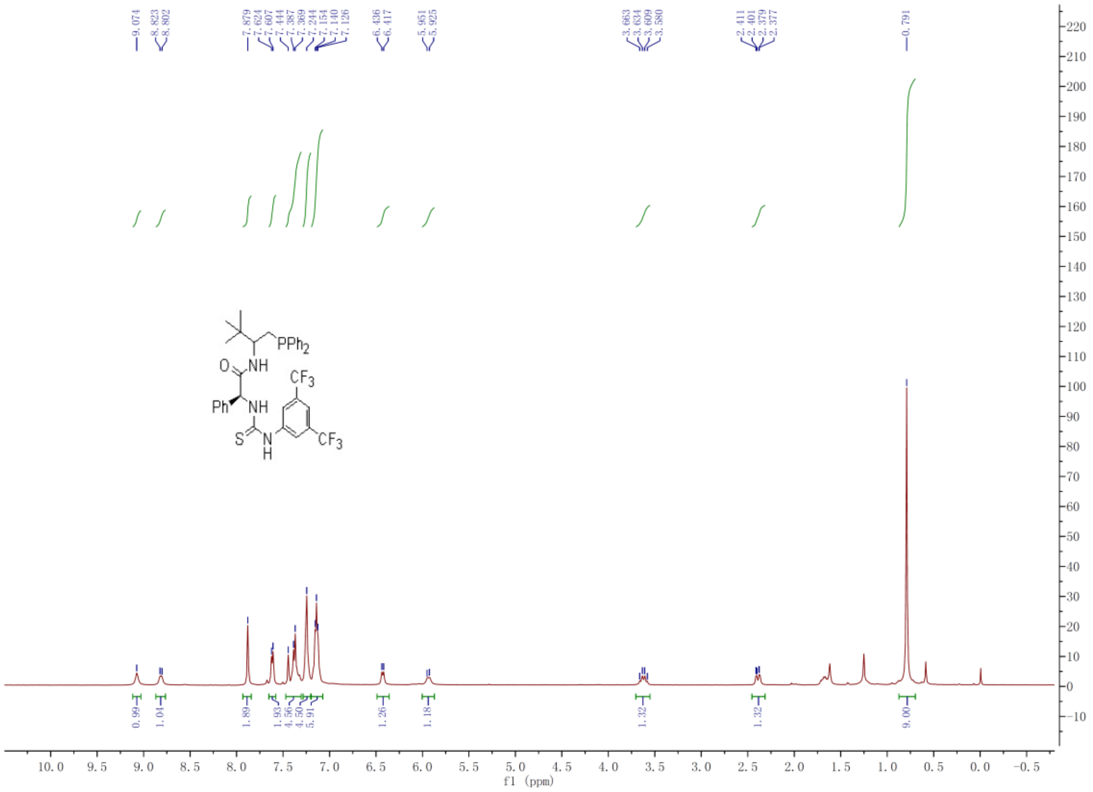


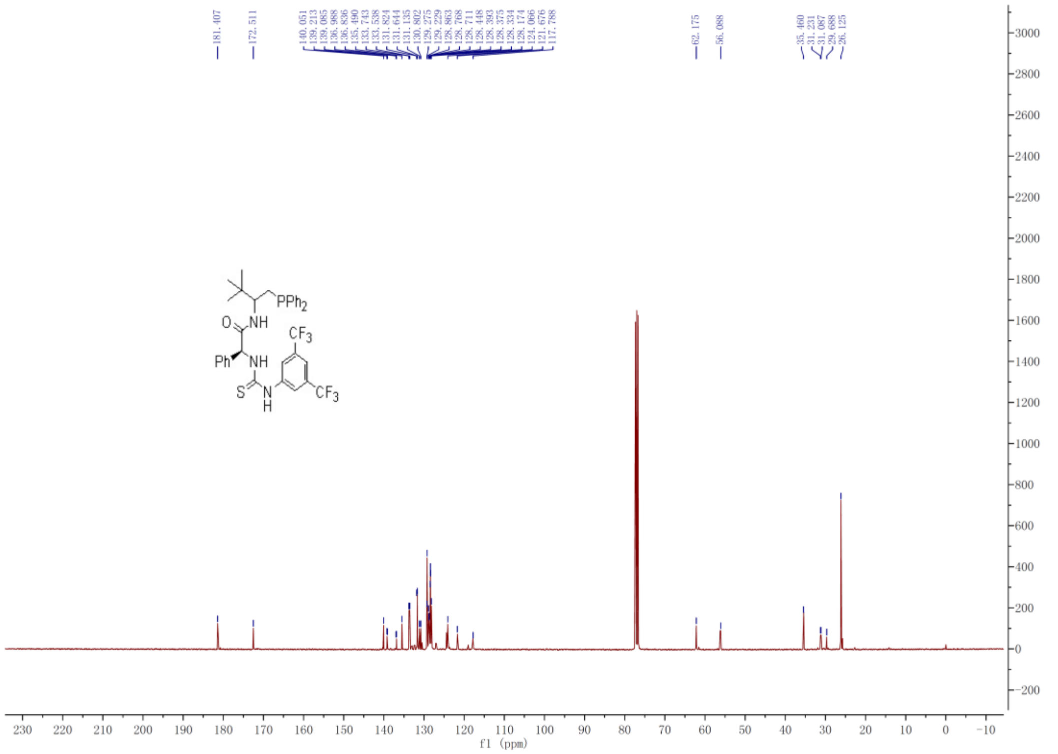
1 Det.A Ch1/220nm

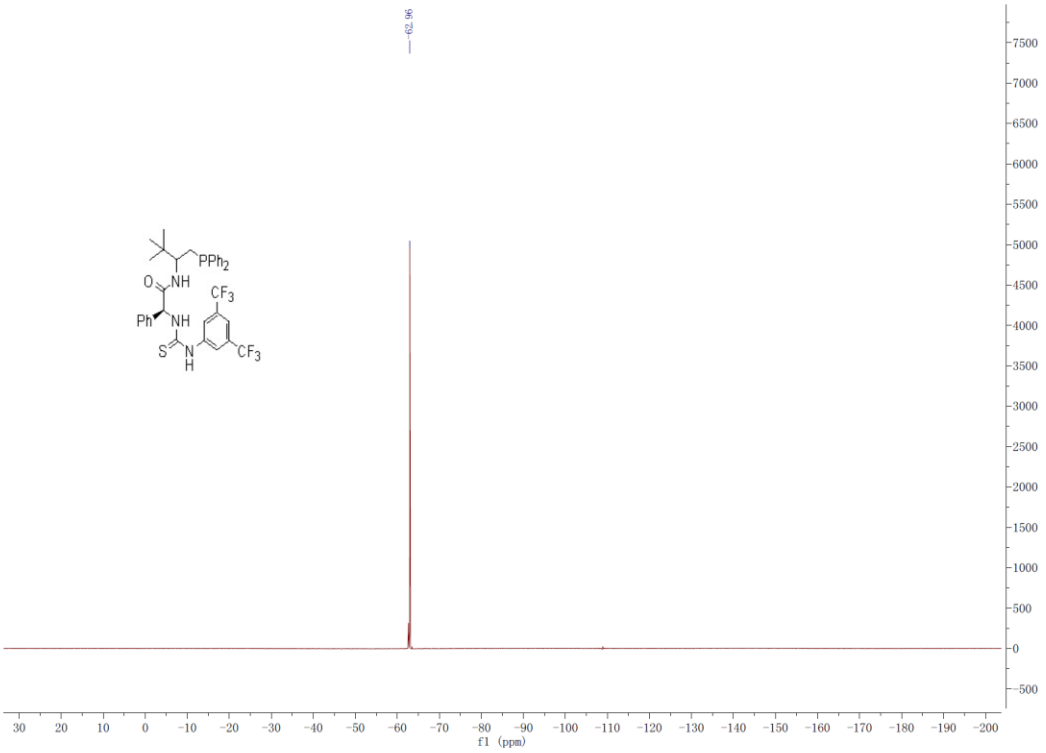
PeakTable

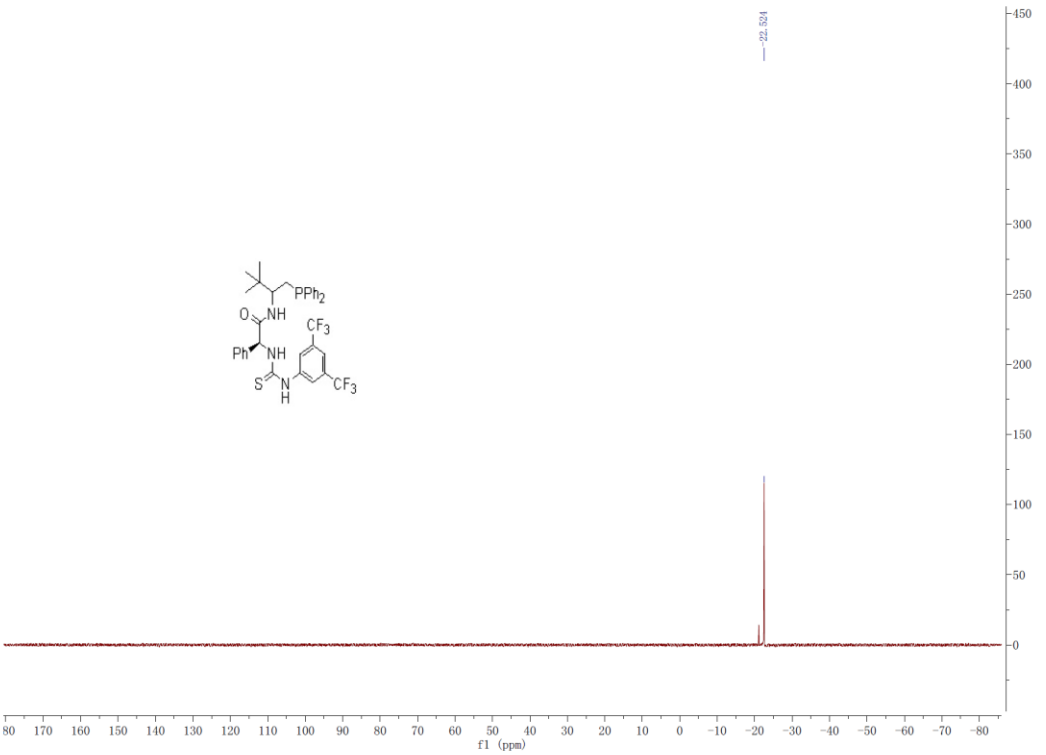
Detector A Ch1 220nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	6.241	181967	8389	94.160	94.166
2	6.925	11286	520	5.840	5.834
Total		193254	8908	100.000	100.000

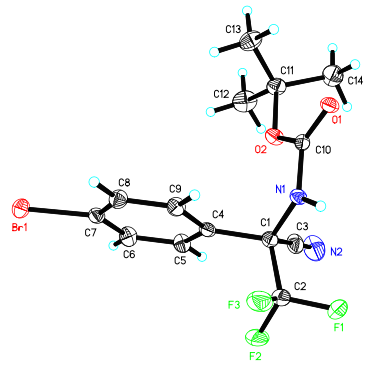

PPh2
O
NH
CF3
Ph
NH
S
N
H
CF3
f1 (ppm)


PPh2
O
NH
CF3
Ph
NH
S
N
H
CF3
f1 (ppm)


-62.96
PPh2
O
NH
Ph
NH
S
N
H
CF3
CF3
f1 (ppm)


-22.524
PPh2
O
NH
Ph
NH
S
N
H
CF3
CF3
f1 (ppm)

VI. Crystal structure data for 3’i



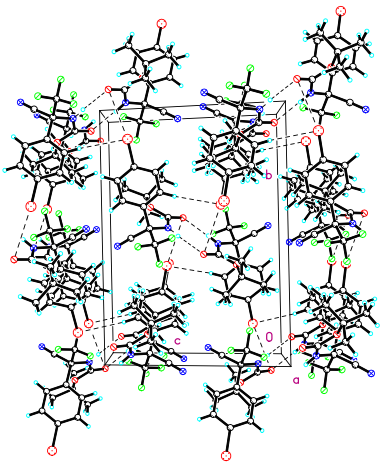


Table 1. Crystal data and structure refinement for mo_d8v19305_0m.

Identification code	mo_d8v19305_0m	
Empirical formula	C14 H14 Br F3 N2 O2	
Formula weight	379.18	
Temperature	193(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 9.2263(4) Å	α= 90°.
	b = 15.7424(7) Å	β= 108.325(2)°.
	c = 11.8768(6) Å	γ = 90°.
Volume	1637.56(13) $Å^3$	
Z	4	
Density (calculated)	1.538 Mg/m^3	
Absorption coefficient	2.547 mm^{-1}	
F(000)	760	
Crystal size	0.170 x 0.150 x 0.120 mm^3	
Theta range for data collection	2.588 to 25.998°.	
Index ranges	-11<=h<=11, -19<=k<=19, -12<=l<=14	
Reflections collected	16250	
Independent reflections	3207 [R(int) = 0.0356]	
Completeness to theta = 25.242°	99.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7456 and 0.4692	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3207 / 0 / 207	
Goodness-of-fit on F^2	1.040	
Final R indices [I>2sigma(I)]	R1 = 0.0291, wR2 = 0.0706	
R indices (all data)	R1 = 0.0389, wR2 = 0.0753	
Extinction coefficient	0.0023(7)	
Largest diff. peak and hole	0.521 and -0.344 $e.Å^{-3}$	

Table 2. Atomic coordinates (x 10^4) and equivalent isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v19305_0m. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
Br(1)	11226(1)	8777(1)	8432(1)	38(1)
F(1)	8340(2)	3917(1)	6905(2)	60(1)
F(2)	10260(2)	4619(1)	8014(2)	59(1)
F(3)	9302(2)	4932(1)	6168(2)	53(1)
O(1)	4050(2)	5749(1)	5563(1)	30(1)
O(2)	5422(2)	6197(1)	7403(1)	31(1)
N(1)	6500(2)	5346(1)	6412(2)	26(1)
N(2)	7320(3)	4646(2)	9273(2)	63(1)
C(1)	7867(2)	5323(1)	7424(2)	29(1)
C(2)	8958(3)	4691(2)	7115(3)	43(1)
C(3)	7550(3)	4955(2)	8494(2)	41(1)
C(4)	8654(2)	6194(1)	7707(2)	26(1)
C(5)	9432(3)	6436(2)	8854(2)	34(1)
C(6)	10186(3)	7211(2)	9081(2)	36(1)
C(7)	10140(2)	7733(1)	8146(2)	29(1)
C(8)	9347(3)	7511(1)	6996(2)	34(1)
C(9)	8608(2)	6736(2)	6781(2)	32(1)
C(10)	5216(2)	5770(1)	6405(2)	25(1)
C(11)	4143(3)	6661(2)	7639(2)	34(1)
C(12)	4901(3)	7011(2)	8865(2)	54(1)
C(13)	3612(3)	7369(2)	6743(2)	46(1)
C(14)	2889(3)	6033(2)	7628(3)	52(1)

Table 3. Bond lengths [Å] and angles [°] for mo_d8v19305_0m.

Br(1)-C(7)	1.899(2)
F(1)-C(2)	1.335(3)
F(2)-C(2)	1.338(3)
F(3)-C(2)	1.317(3)
O(1)-C(10)	1.218(2)
O(2)-C(10)	1.324(3)
O(2)-C(11)	1.488(3)
N(1)-C(10)	1.357(3)
N(1)-C(1)	1.444(3)
N(1)-H(1)	0.84(2)
N(2)-C(3)	1.123(3)
C(1)-C(3)	1.507(3)
C(1)-C(4)	1.538(3)
C(1)-C(2)	1.539(3)
C(4)-C(5)	1.379(3)
C(4)-C(9)	1.382(3)
C(5)-C(6)	1.388(3)
C(5)-H(5)	0.9500
C(6)-C(7)	1.371(3)
C(6)-H(6)	0.9500
C(7)-C(8)	1.376(3)
C(8)-C(9)	1.382(3)
C(8)-H(8)	0.9500
C(9)-H(9)	0.9500
C(11)-C(12)	1.508(4)
C(11)-C(13)	1.511(4)
C(11)-C(14)	1.519(3)
C(12)-H(12A)	0.9800
C(12)-H(12B)	0.9800
C(12)-H(12C)	0.9800
C(13)-H(13A)	0.9800
C(13)-H(13B)	0.9800
C(13)-H(13C)	0.9800
C(14)-H(14A)	0.9800
C(14)-H(14B)	0.9800
C(14)-H(14C)	0.9800

C(10)-O(2)-C(11)	121.31(17)
C(10)-N(1)-C(1)	123.38(19)
C(10)-N(1)-H(1)	115.5(17)
C(1)-N(1)-H(1)	119.8(17)
N(1)-C(1)-C(3)	111.12(18)
N(1)-C(1)-C(4)	112.88(18)
C(3)-C(1)-C(4)	111.26(19)
N(1)-C(1)-C(2)	106.44(19)
C(3)-C(1)-C(2)	105.5(2)
C(4)-C(1)-C(2)	109.24(17)
F(3)-C(2)-F(1)	107.9(2)
F(3)-C(2)-F(2)	107.9(2)
F(1)-C(2)-F(2)	107.2(2)
F(3)-C(2)-C(1)	111.6(2)
F(1)-C(2)-C(1)	111.2(2)
F(2)-C(2)-C(1)	110.7(2)
N(2)-C(3)-C(1)	177.0(3)
C(5)-C(4)-C(9)	119.5(2)
C(5)-C(4)-C(1)	121.7(2)
C(9)-C(4)-C(1)	118.8(2)
C(4)-C(5)-C(6)	120.5(2)
C(4)-C(5)-H(5)	119.7
C(6)-C(5)-H(5)	119.7
C(7)-C(6)-C(5)	118.9(2)
C(7)-C(6)-H(6)	120.6
C(5)-C(6)-H(6)	120.6
C(6)-C(7)-C(8)	121.6(2)
C(6)-C(7)-Br(1)	119.58(17)
C(8)-C(7)-Br(1)	118.84(17)
C(7)-C(8)-C(9)	119.0(2)
C(7)-C(8)-H(8)	120.5
C(9)-C(8)-H(8)	120.5
C(8)-C(9)-C(4)	120.5(2)
C(8)-C(9)-H(9)	119.7
C(4)-C(9)-H(9)	119.7
O(1)-C(10)-O(2)	126.13(19)
O(1)-C(10)-N(1)	122.5(2)
O(2)-C(10)-N(1)	111.40(18)

O(2)-C(11)-C(12)	101.98(18)
O(2)-C(11)-C(13)	109.32(18)
C(12)-C(11)-C(13)	111.1(2)
O(2)-C(11)-C(14)	108.98(18)
C(12)-C(11)-C(14)	111.5(2)
C(13)-C(11)-C(14)	113.3(2)
C(11)-C(12)-H(12A)	109.5
C(11)-C(12)-H(12B)	109.5
H(12A)-C(12)-H(12B)	109.5
C(11)-C(12)-H(12C)	109.5
H(12A)-C(12)-H(12C)	109.5
H(12B)-C(12)-H(12C)	109.5
C(11)-C(13)-H(13A)	109.5
C(11)-C(13)-H(13B)	109.5
H(13A)-C(13)-H(13B)	109.5
C(11)-C(13)-H(13C)	109.5
H(13A)-C(13)-H(13C)	109.5
H(13B)-C(13)-H(13C)	109.5
C(11)-C(14)-H(14A)	109.5
C(11)-C(14)-H(14B)	109.5
H(14A)-C(14)-H(14B)	109.5
C(11)-C(14)-H(14C)	109.5
H(14A)-C(14)-H(14C)	109.5
H(14B)-C(14)-H(14C)	109.5

Symmetry transformations used to generate equivalent atoms:

Table 4. Anisotropic displacement parameters ($Å^2 x\ 10^3$) for mo_d8v19305_0m. The anisotropic displacement factor exponent takes the form: $-2\pi^2[\ h^2\ a^{*2}U^{11} + ...\ \ + 2\ h\ k\ a^*\ b^*\ U^{12}\ ]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
Br(1)	40(1)	28(1)	46(1)	-9(1)	10(1)	-3(1)
F(1)	44(1)	28(1)	92(1)	-9(1)	2(1)	5(1)
F(2)	32(1)	49(1)	78(1)	-5(1)	-9(1)	13(1)
F(3)	42(1)	56(1)	64(1)	-12(1)	22(1)	9(1)
O(1)	22(1)	33(1)	31(1)	-6(1)	2(1)	4(1)
O(2)	26(1)	40(1)	28(1)	-8(1)	8(1)	2(1)
N(1)	22(1)	29(1)	26(1)	-6(1)	5(1)	1(1)
N(2)	60(2)	70(2)	50(2)	19(1)	4(1)	-14(1)
C(1)	25(1)	29(1)	30(1)	1(1)	2(1)	0(1)
C(2)	29(1)	34(1)	59(2)	-5(1)	1(1)	4(1)
C(3)	35(1)	39(1)	38(2)	9(1)	-3(1)	-7(1)
C(4)	20(1)	29(1)	29(1)	-1(1)	6(1)	2(1)
C(5)	34(1)	38(1)	27(1)	2(1)	7(1)	-4(1)
C(6)	38(1)	41(1)	26(1)	-8(1)	7(1)	-5(1)
C(7)	24(1)	27(1)	36(1)	-7(1)	9(1)	1(1)
C(8)	35(1)	32(1)	31(1)	1(1)	7(1)	0(1)
C(9)	32(1)	33(1)	26(1)	-2(1)	1(1)	-2(1)
C(10)	25(1)	23(1)	28(1)	-1(1)	9(1)	-1(1)
C(11)	35(1)	38(1)	35(1)	-6(1)	18(1)	6(1)
C(12)	66(2)	61(2)	37(2)	-12(1)	20(1)	11(2)
C(13)	57(2)	38(1)	44(2)	-4(1)	20(1)	11(1)
C(14)	44(2)	51(2)	73(2)	-4(1)	38(2)	0(1)

Table 5. Hydrogen coordinates (x 10^4) and isotropic displacement parameters ($Å^2$x 10^3) for mo_d8v19305_0m.

	x	y	z	U(eq)
H(1)	6400(30)	5006(16)	5850(20)	32(7)
H(5)	9451	6069	9494	41
H(6)	10726	7376	9871	43
H(8)	9309	7885	6360	40
H(9)	8063	6575	5990	39
H(12A)	5252	6541	9425	81
H(12B)	4167	7358	9107	81
H(12C)	5776	7363	8861	81
H(13A)	4492	7709	6721	68
H(13B)	2885	7730	6970	68
H(13C)	3113	7125	5957	68
H(14A)	2408	5827	6817	78
H(14B)	2122	6314	7911	78
H(14C)	3329	5553	8148	78

Table 6. Torsion angles [°] for mo_d8v19305_0m.

C(10)-N(1)-C(1)-C(3)	58.8(3)
C(10)-N(1)-C(1)-C(4)	-67.0(3)
C(10)-N(1)-C(1)-C(2)	173.1(2)
N(1)-C(1)-C(2)-F(3)	60.5(2)
C(3)-C(1)-C(2)-F(3)	178.61(19)
C(4)-C(1)-C(2)-F(3)	-61.7(3)
N(1)-C(1)-C(2)-F(1)	-60.1(3)
C(3)-C(1)-C(2)-F(1)	58.1(3)
C(4)-C(1)-C(2)-F(1)	177.8(2)
N(1)-C(1)-C(2)-F(2)	-179.23(19)
C(3)-C(1)-C(2)-F(2)	-61.1(2)
C(4)-C(1)-C(2)-F(2)	58.6(3)
N(1)-C(1)-C(4)-C(5)	147.1(2)
C(3)-C(1)-C(4)-C(5)	21.4(3)
C(2)-C(1)-C(4)-C(5)	-94.7(3)
N(1)-C(1)-C(4)-C(9)	-34.5(3)
C(3)-C(1)-C(4)-C(9)	-160.19(19)
C(2)-C(1)-C(4)-C(9)	83.7(2)
C(9)-C(4)-C(5)-C(6)	-1.1(3)
C(1)-C(4)-C(5)-C(6)	177.3(2)
C(4)-C(5)-C(6)-C(7)	0.3(3)
C(5)-C(6)-C(7)-C(8)	1.0(3)
C(5)-C(6)-C(7)-Br(1)	-177.73(17)
C(6)-C(7)-C(8)-C(9)	-1.3(3)
Br(1)-C(7)-C(8)-C(9)	177.40(17)
C(7)-C(8)-C(9)-C(4)	0.4(3)
C(5)-C(4)-C(9)-C(8)	0.8(3)
C(1)-C(4)-C(9)-C(8)	-177.7(2)
C(11)-O(2)-C(10)-O(1)	5.1(3)
C(11)-O(2)-C(10)-N(1)	-175.52(17)
C(1)-N(1)-C(10)-O(1)	-176.48(19)
C(1)-N(1)-C(10)-O(2)	4.1(3)
C(10)-O(2)-C(11)-C(12)	178.2(2)
C(10)-O(2)-C(11)-C(13)	-64.1(3)
C(10)-O(2)-C(11)-C(14)	60.2(3)

Symmetry transformations used to generate equivalent atoms:

Table 7. Hydrogen bonds for mo_d8v19305_0m [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
C(14)-H(14A)...O(1)	0.98	2.44	3.002(3)	116.1
C(13)-H(13C)...O(1)	0.98	2.43	2.997(3)	116.3
C(13)-H(13B)...Br(1)#1	0.98	3.12	4.070(3)	163.2
N(1)-H(1)...O(1)#2	0.84(2)	1.99(3)	2.826(2)	174(2)

Symmetry transformations used to generate equivalent atoms:

#1 x-1,y,z #2 -x+1,-y+1,-z+1