Supporting Information

for

Chiral Aldehyde Catalysis Enables Direct Asymmetric α–Substitution Reaction of *N*-Unprotected Amino Acids with Halohydrocarbons

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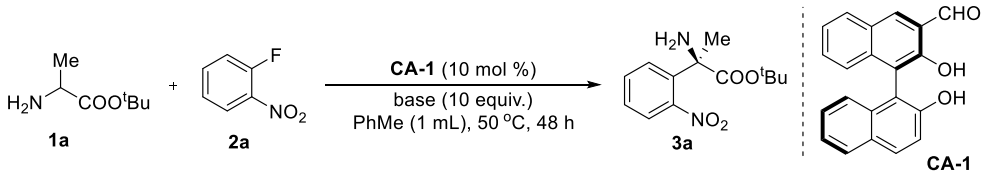
1. General data

All non-aqueous reactions were carried out in a flame-dried glassware under nitrogen atmosphere or in a nitrogen-filled glove box unless otherwise noted. Solvents for reactions were dried appropriately before use: toluene, THF and Et_2O were dried by refluxing with sodium and benzophenone as indicator, CH_2Cl_2 and $CHCl_3$ were dried by refluxing with CaH_2. Reagents were purchased from Aladdin, Adamas-beta®, Sigma-Aldrich, TCI, Bide or Alfa Aesar and used as received unless otherwise stated. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker Avance 600 MHz or 400 MHz spectrometer. Chemical shifts (δ) are reported in ppm from tetramethylsilane (TMS) with the solvent resonance as the internal standard. Proton signal multiplicities are given as s(singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad) or a combination of them. *J*-values are in Hz. HRMS (ESI-Q-TOF) spectra were recorded on Bruker Impact-II mass spectrometer. Enantiomer ratios were determined by HPLC (Chiralpak AD-H, IC, OD-H, IG, IA, IH columns were purchased from Daicel Chemical Industries, LTD). Optical rotations were determined at λ = 589 nm (sodium D line) by using a Rudolph-API automatic polarimeter. Amino acid esters[1] , chiral aldehydes catalysts[2] and allylic chloride[3,4,5] were prepared according to literature procedures. The racemic samples were prepared by running reactions with a racemic catalyst.

2. Reaction condition optimization

2.1 Reaction condition optimization for the asymmetric α–arylation

Table S1: Base screening[a]

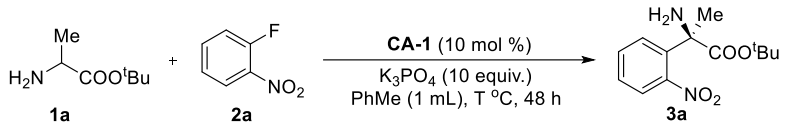


entry	base	time (h)	yield (%)[b]	ee (%)[c]
1	TMG[d]	48	N.R.[e]	N.D.[f]
2	DBU[g]	48	N.R.	N.D.
3	Et_3N	48	N.R.	N.D.
4	CH_3OK	48	N.R.	N.D.
5	CsOH	48	N.R.	N.D.
6	Cs_2CO_3	48	25	>99
7	K_2CO_3	48	Trace	N.D.
8	$LiOH·H_2O$	48	N.R.	N.D.

9	KF	48	N.R.	N.D.
10	KOH	48	N.R.	N.D.
11	Na_2CO_3	48	N.R.	N.D.
12	K_3PO_4	48	31	>99

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.10 mmol), **4a**(0.01 mmol) and base (1.0 mmol) in toluene (1.0 mL) at 50 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] 1,1,3,3-tetramethylguanidine. [e] N.R. = No reaction. [f] N.D. = Not determined. [g] 1,8-Diazabicyclo[5.4.0]undec-7-ene.

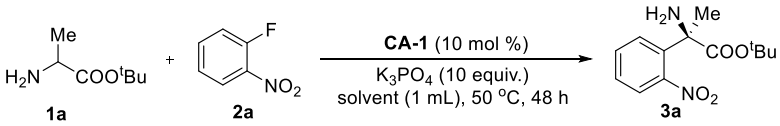
Table S2: Reaction temperature screening[a]



entry	T (°C)	time (h)	yield (%)[b]	ee (%)[c]
1	30	48	23	>99
2	40	48	26	>99
3	50	48	31	>99
4	80	48	16	>99
5	100	48	trace	N.D.[d]
6	120	48	trace	N.D.

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.10 mmol), **4a**(0.01 mmol) and K_3PO_4 (1.0 mmol) in toluene (1.0 mL) at T °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not determined.

Table S3: Solvent screening[a]

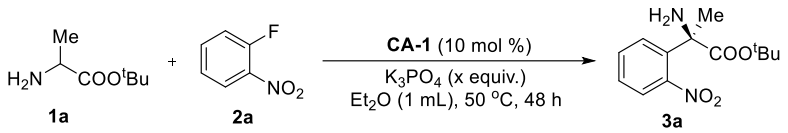


entry	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	mesitylene	48	28	>99
2	C_6F_6	48	32	>99
3	$CHCl_3$	48	29	>99
4	PhF	48	19	>99
5	PhCl	48	16	>99
6	CH_3OH	48	N.R.[e]	N.D.[d]
7	DMF	48	trace	N.D.
8	CH_3CN	48	N.R.	N.D.
9	CH_2Cl_2	48	59	>99
10	CCl_4	48	37	>99
11	EA	48	N.R.	N.D.
12	CH_2Cl_2:PhMe=1:4	48	36	>99
13	Et_2O	48	86	>99
14	THF	48	21	>99
15	$^nBu_2O$	48	48	>99
16	1,2-dimethoxyethane	48	N.R.	N.D.

17	1,4-dioxane	48	N.R.	N.D.

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.10 mmol), **4a**(0.01 mmol) and K_3PO_4 (1.0 mmol) in solvent (1.0 mL) at 50 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not determined. [e] N.R. = No reaction.

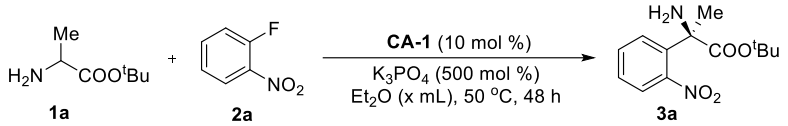
Table S4: Base equivalents screening[a]



entry	x	time (h)	yield (%)[b]	ee (%)[c]
1	1	48	65	>99
2	2	48	73	>99
3	3	48	81	>99
4	5	48	86	>99
5	10	48	86	>99
6	15	48	78	>99

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.10 mmol), **4a**(0.01 mmol) and K_3PO_4 (x equiv.) in Et_2O (1.0 mL) at 50 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table S5: Reaction concentration screening[a]

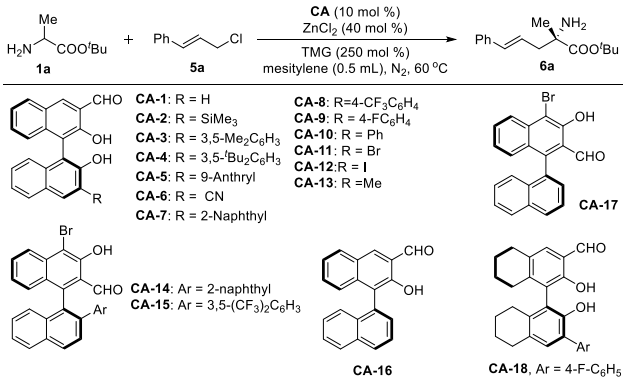


entry	x	time (h)	yield (%)[b]	ee (%)[c]
1	0.5	48	78	>99
2	1	48	86	>99
3	1.5	48	84	>99
4	2	48	79	>99
5	3	48	74	>99
6	4	48	68	>99

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.10 mmol), **4a**(0.01 mmol) and K_3PO_4 (0.50 mmol) in Et_2O (x mL) at 50 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

2.2 Reaction condition optimization for the asymmetric α–allylation

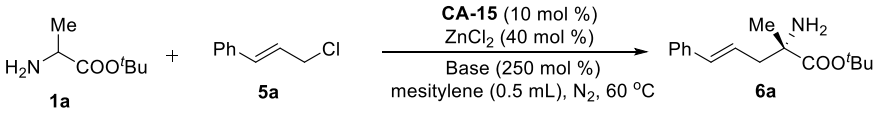
Table S6: Chiral aldehyde screening



entry	CA	time (h)	yield (%)[b]	ee (%)[c]
1	**CA-1**	8	89	16
2	**CA-2**	8	96	30
3	**CA-3**	8	85	18
4	**CA-4**	8	81	4
5	**CA-5**	8.5	98	30
6	**CA-6**	8	62	78
7	**CA-7**	8	N.R.[d]	N.D.[e]
8	**CA-8**	8	86	12
9	**CA-9**	8	88	16
10	**CA-10**	8	22	52
11	**CA-11**	8	8	22
12	**CA-12**	8	19	26
13	**CA-13**	7	99	22
14	**CA-14**	8	49	84
15	**CA-15**	8	61	94
16	**CA-16**	8	39	4
17	**CA-17**	8	49	58
18	**CA-18**	8	38	24

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in mesitylene (0.5 mL) at 60 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.R. = No reaction. [e] N.D. = Not determined.

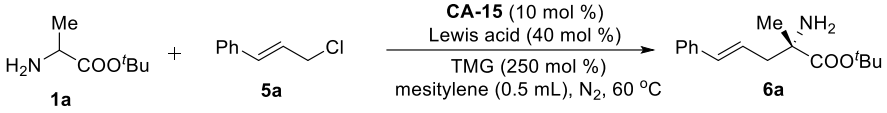
Table S7: Base screening[a]



entry	base	time (h)	yield (%)[b]	ee (%)[c]
1	TMG	8	49	94
2	2-^{t}BuTMG[d]	9	trace	N.D.[e]
3	metformin	8	49	98
4	DBN[f]	8.5	15	66
5	ectoine	8	22	70
6	TBD[g]	9	20	94
7	Cs_2CO_3	11	trace	N.D.
8	^{t}BuOK	10	trace	N.D.
9	DBU	9	10	70
10	TMEDA[h]	10	N.R.[i]	N.D.
11	quinuclidine	9	N.R.	N.D.
12		8.5	22	70

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), base (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in mesitylene (0.5 mL) at 60 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] 2-tertbutyl-1,1,3,3-tetramethylguanidine. [e] N.D. = Not determined. [f] 1,5-diazabicyclo [4.3.0] non-5-ene. [g] 1,5,7-Triazabicyclo[4.4.0]dec-5-ene. [h] N,N,N,N′-tetramethylethylenediamine. [i] N.R. = No Reaction.

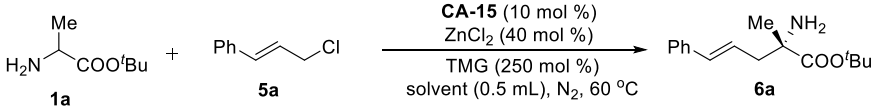
Table S8: Lewis acid screening[a]



entry	Lewis acid	time (h)	yield (%)[b]	ee (%)[c]
1	$ZnCl_2$	8	49	94
2	$Ni(acac)_2$	8	trace	N.D.[d]
3	$Cu(OTf)_2$	8	N.R.[e]	N.D.
4	$MgCl_2$	8	9	62
5	$FeCl_3$	8	34	88
6	ZnF_2	8	42	94
7	$ZnBr_2$	8	35	94
8	$Zn(OTf)_2$	8.5	24	94
9	$Zn(OAc)_2$	8.5	12	94
10	$Zn(BF_4)_2 \cdot xH_2O$	8	22	94
11	$Zn(ClO_4)_2 \cdot 6H_2O$	8	21	92
12	benzoic acid	9	N.R.	N.D.
13	dipicolinic acid	9	N.R.	N.D.

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and Lewis acid (0.08 mmol) in mesitylene (0.5 mL) at 60 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not determined. [e] N.R. = No reaction.

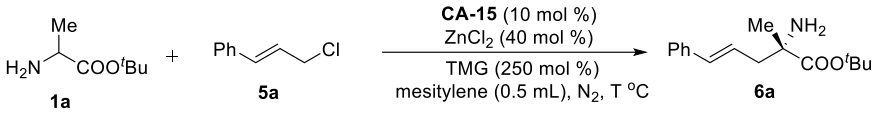
Table S9: Solvent screening



entry	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	mesitylene	12	61	94
2	toluene	8	35	94
3	$PhCF_3$	12	13	85
4	*p*-xylene	8	10	94
5	*m*-xylene	8	22	98
6	*o*-xylene	8.5	28	94
7	THF	8	52	90
8	dioxane	8	12	96
9	DME	8	40	78
10	PhC_2H_5	8	17	96
11	DCE	8.5	15	98
12	CH_3CN	4.5	trace	N.D.[d]
13	C_2H_5OH	9.5	29	96
14	EA	8	17	96
15	chlorobenzene	8	17	99
16	cyclohexane	10.5	37	94
17	n-heptane	11	49	94
18	methylcyclohexane	11	36	92

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in solvent (0.5 mL) at 60 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not determined.

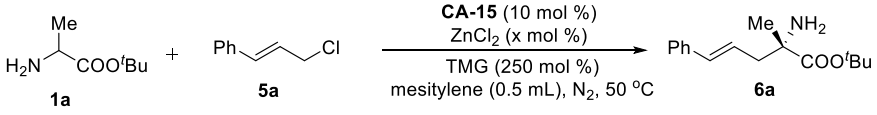
Table S10: Reaction temperature screening[a]



entry	T (ºC)	time (h)	yield (%)[b]	ee (%)[c]
1	30	40	N.R.[d]	N.D.[e]
2	40	40	46	95
3	50	24	65	94
4	60	24	61	94
5	70	24	58	93
6	80	24	39	92

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in mesitylene (0.5 mL) at T ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.R. = No Reaction. [e] N.D. = Not Determined.

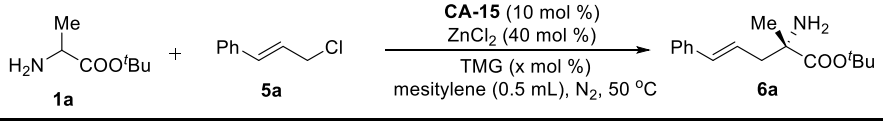
Table S11: Lewis acid equivalents screening[a]



entry	x	time (h)	yield (%)[b]	ee (%)[c]
1	20	24	62	94
2	40	24	65	94
3	60	24	64	94
4	80	24	61	94
5	100	24	62	94

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (x mol %) in mesitylene (0.5 mL) at 50 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

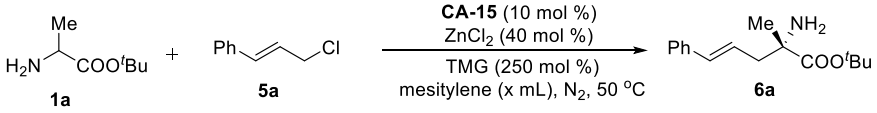
Table S12: Base equivalents screening[a]



entry	x	time (h)	yield (%)[b]	ee (%)[c]
1	150	24	44	94
2	200	24	56	94
3	250	24	65	94
4	400	24	49	89
5	600	24	46	88
6	800	24	38	88

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (x mol %), and $ZnCl_2$ (0.08 mmol) in mesitylene (0.5 mL) at 50 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

Table S13: Reactant concentration screening[a]

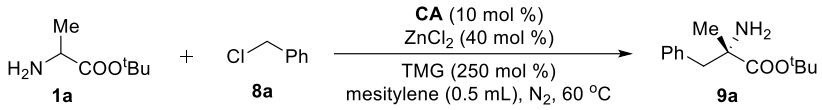


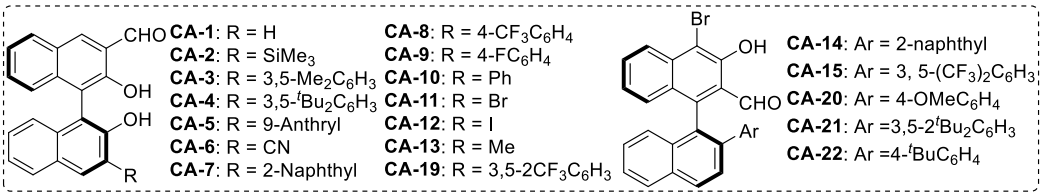
entry	x	time (h)	yield (%)[b]	ee (%)[c]
1	0.5	24	65	94
2	0.4	24	70	94
3	0.3	24	59	94
4	0.2	24	39	93
5	0.4	48	73	94

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **5a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in mesitylene (x mL) at 50 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

2.3 Reaction optimization for the asymmetric α–benzylation

Table S14: Chiral aldehyde screening[a]



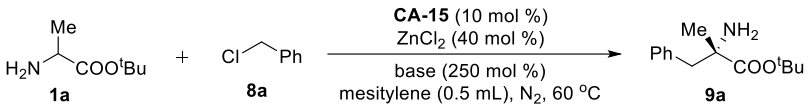


entry	CA	time (h)	yield (%)[b]	ee (%)[c]
1	**CA-1**	12	15	5
2	**CA-2**	12	68	25
3	**CA-3**	12	85	18
4	**CA-4**	12	57	0
5	**CA-5**	11.5	57	47
6	**CA-6**	12	18	78
7	**CA-7**	12	34	46
8	**CA-8**	11.5	55	12
9	**CA-9**	12.5	75	17
10	**CA-10**	12	22	48
11	**CA-11**	13.5	trace	N.D.[d]
12	**CA-12**	11.5	6	22
13	**CA-13**	12	48	14
14	**CA-14**	12	23	83
15	**CA-15**	11	20	88
16	**CA-20**	8	20	88
17	**CA-21**	8	10	90
18	**CA-22**	8	14	86

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **8a** (0.20 mmol), **CA** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in mesitylene (0.5 mL) at 60 ºC. [b] Isolated yield. [c] Determined by chiral HPLC

analysis. [d] N.D. = Not determined.

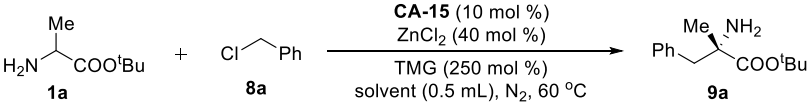
Table S15: Base screening[a]



entry	base	time (h)	yield (%)[b]	ee (%)[c]
1	TMG	12	34	86
2	metformin	13.5	trace	N.D.[d]
3	DBN[e]	11.5	trace	N.D.
4	TDMAIP[f]	11.5	trace	N.D.
5	TBD	12	trace	N.D.
6	Cs_2CO_3	12	trace	N.D.
7	^{t}BuOK	10.5	N.R.[g]	N.D.
8	MTBD[h]	10	11	78
9	DBU	13	18	77
10	MTMG	12	trace	N.D.
11	TEA	7.5	N.R.	N.D.
12	TMEDA[i]	7.5	N.R.	N.D.
13		11.5	trace	N.D.

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **8a** (0.20 mmol), **CA-15** (0.02 mmol), base (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in mesitylene (0.5 mL) at 60 ºC. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not Determined. [e] 1,5-diazabicyclo [4.3.0] non-5-ene. [f] Iminotris(dimethylamino)phosphorane. [g] N.R. = No Reaction. [h] 7-Methyl-1,5,7-triazabicyclo[4.4.0]decene-5. [i] N,N,N,N′-tetramethylethylenediamine.

Table S16: Solvent screening[a]

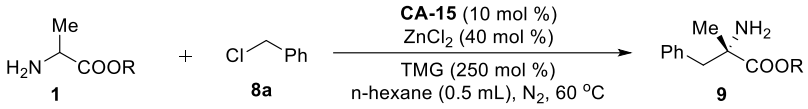


entry	solvent	time (h)	yield (%)[b]	ee (%)[c]
1	mesitylene	11	20	88
2	toluene	12	34	86
3	$PhCF_3$	12	13	85
4	*p*-xylene	12	15	86
5	*m*-xylene	12	trace	N.D.[d]
6	*o*-xylene	13.5	33	85
7	THF	12.5	45	78
8	dioxane	12	trace	N.D.
9	DME	12	trace	N.D.
10	PhC_2H_5	12.5	34	75
11	DCE	12.5	trace	N.D.
12	CH_3CN	12	15	82
13	C_2H_5OH	12	trace	N.D.
14	EA	12.5	30	74
15	chlorobenzene	12.5	16	75

16	cyclohexane	12.5	55	86
17	octane	12	48	90
18	methylcyclohexane	10.5	52	91
19	*n*-hexane	13.5	60	90
20	*n*-heptane	11.5	52	89
21	2,2,4-trimethylpentane	11.5	45	90

[a] Unless noted otherwise, reactions were performed with **1a** (0.30 mmol), **8a** (0.20 mmol), **CA-15** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in solvent (0.5 mL) at 60 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not determined.

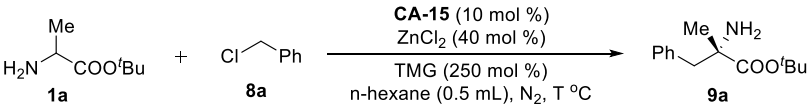
Table S17: Alkoxyl group screening[a]



entry	R	time (h)	yield (%)[b]	ee (%)[c]
1	^{t}Bu	13.5	60	90
2	Me	11	trace	N.D.[d]
3	Et	11	trace	N.D.
4	^{i}Pr	11	22	89
5	Bn	11	trace	N.D.
6	CF_3	10.5	N.R.[e]	N.D.

[a] Unless noted otherwise, reactions were performed with **1** (0.30 mmol), **8a** (0.20 mmol), **CA-15** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in ^{n}Hexane (0.5 mL) at 60 °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis. [d] N.D. = Not determined. [e] N.R. = No reaction.

Table S18: Reaction temperature screening

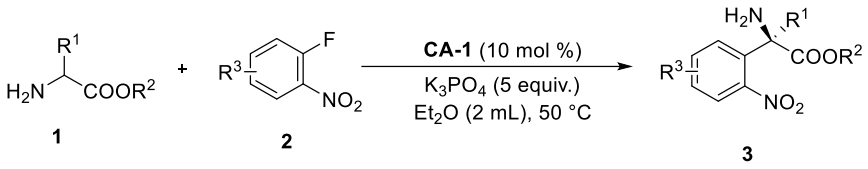


entry	T (°C)	time (h)	yield (%)[b]	ee (%)[c]
1	50	24	67	90
2	50	48	71	90
3	60	13.5	60	90
4	60	24	61	89
5	60	48	58	88
6	80	24	55	83

[a] Unless noted otherwise, reactions were performed with **1** (0.30 mmol), **8a** (0.20 mmol), **CA-15** (0.02 mmol), TMG (0.50 mmol), and $ZnCl_2$ (0.08 mmol) in ^{n}Hexane (0.5 mL) at T °C. [b] Isolated yield. [c] Determined by chiral HPLC analysis.

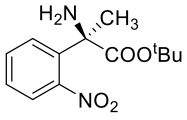
3. General procedures for the catalytic asymmetric reactions

3.1 General procedure for the asymmetric α–arylation

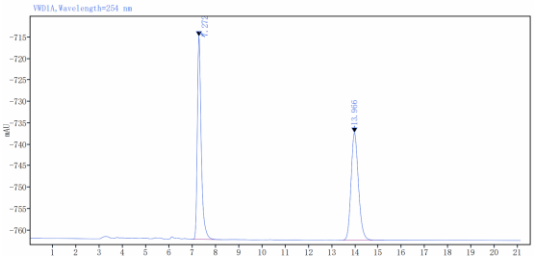


Chiral aldehyde catalyst (6.3 mg, 0.02 mmol), amino acid ester (0.4 mmol), Et_2O (2 mL) and K_3PO_4 (212 mg, 1 mmol) were successively added to a 10 mL reaction tube with stirring magneton. The mixture was stirred at room temperature for 10 minutes, then nitrobenzene derivative **2** (0.2 mmol) was added. The reaction system was sealed and continuously stirred at 50 °C. After the reaction completed (detected by TLC), the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3).

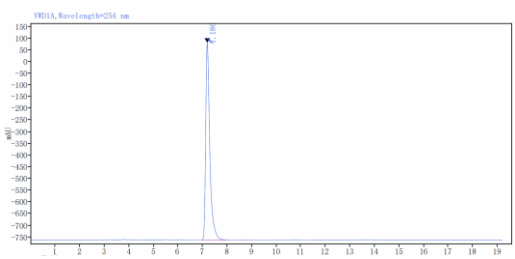
***tert*-Butyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate (3a):**



A pale yellow oil (45.8 mg, 86%); R_f= 0.30 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.186 min; $[\alpha]_D^{25}$ = -58.93 (c = 0.67, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 6.0 Hz, 1H), 7.87 (d, *J* = 6.0 Hz, 1H), 7.60 (t, *J* = 6.0 Hz , 1H), 7.42 (t, *J* = 6.0 Hz, 1H), 2.02 (s, 2H), 1.77 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.81, 148.84, 138.88, 132.82, 128.45, 128.03, 124.95, 82.10, 60.27, 27.87, 27.59. **HRMS(ESI)** m/z: $[M+H]^+$ calculated for $C_{14}H_{21}N_2O_4^+$ 267.1334; found 267.1349.

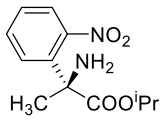


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.272	BB	1.2767	552.2866	47.3565	49.8839
	13.966	BB	1.9200	554.8573	25.0522	50.1161



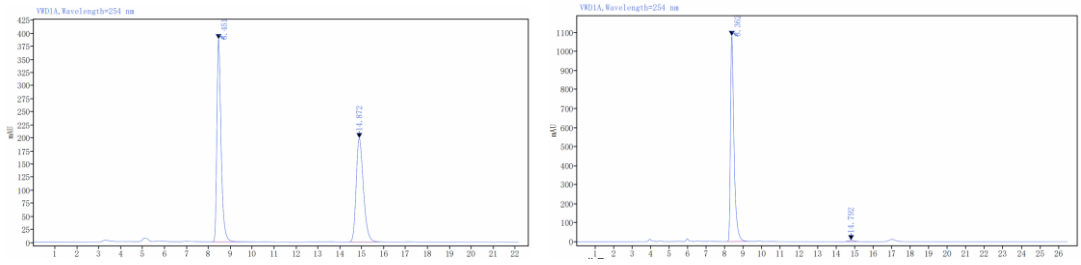
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.186	BB	2.1667	9775.4456	841.3780	100.0000

Isopropyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate (3b):



A pale yellow oil (36.4 mg, 72%); R_f= 0.38 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 98% by HPLC analysis on Daicel

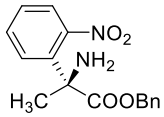
Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 8.362 min, t_R(minor) 14.792 min; $[\alpha]_D^{25}$ = -65.85 (c = 0.33, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 6.0 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 1H), 7.62 (t, *J* = 9.0 Hz, 1H), 7.43 (t, *J* = 9.0 Hz, 1H), 4.99 – 5.05 (m, 1H), 2.09 (s, 2H), 1.79 (s, 3H), 1.18 – 1.21 (m, 6H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.26, 148.66, 138.69, 132.97, 128.40, 128.21, 125.12, 69.33, 59.85, 27.80, 21.43, 21.39. **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{11}H_{17}N_2O_4^+$ 253.1183; found 253.1189.



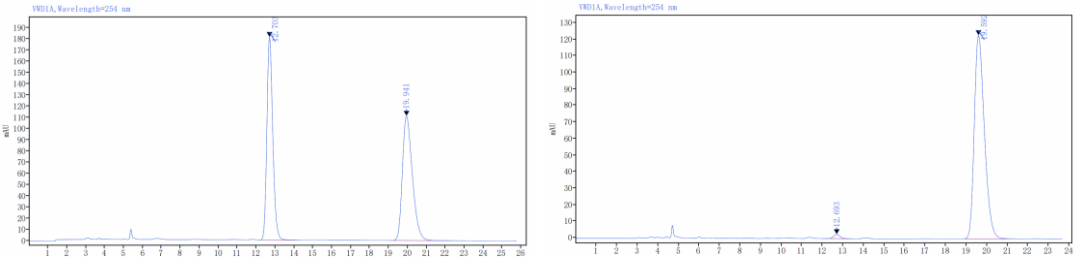
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.451	BB	1.9867	5176.7590	386.9539	53.3143
2	14.872	BB	2.3950	4533.1328	198.0241	46.6857

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.362	BB	1.2491	14387.2298	1079.3140	98.9594
2	14.792	BB	1.6183	151.2838	6.4442	1.0406

Benzyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate (3c):



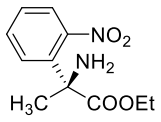
A pale yellow oil (35.5 mg, 59%); R_f = 0.29 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 19.592 min, t_R(minor) 12.693 min; $[\alpha]_D^{25}$ = -77.13 (c = 0.36, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 12.0 Hz, 1H), 7.88 (d, *J* = 6.0 Hz, 1H), 7.60 (t, *J* = 9.0 Hz, 1H), 7.43 (t, *J* = 9.0 Hz, 1H), 7.34 – 7.24 (m, 5H), 5.12 (s, 2H), 1.99 (s, 2H), 1.80 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.64, 148.69, 138.50, 135.49, 133.04, 128.53, 128.40, 128.36, 128.32, 125.15, 67.28, 59.94, 27.79; HRMS(ESI) m/z: $[M+H]^+$ Calculated for $C_{16}H_{17}N_2O_4^+$ 301.1183; found 301.1189.



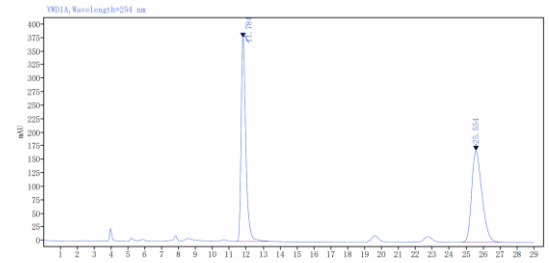
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.703	BB	2.3333	3905.2670	181.0444	49.0182
2	19.941	BB	3.1700	4061.7138	111.1564	50.9818

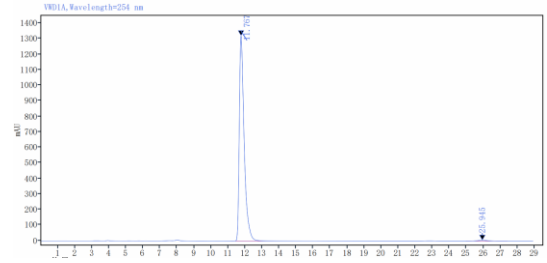
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.693	BB	1.4500	55.8742	2.5297	1.3145
2	19.592	BB	3.0067	4194.5798	122.7623	98.6855

Ethyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate (3d):



A pale yellow oil (39.1 mg, 82%); R_f = 0.29 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 98% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 11.767 min, t_R(minor) 25.945 min; $[\alpha]_D^{25}$ = -105.0 (c = 0.30, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (d, *J* = 6.0 Hz, 1H), 7.89 (d, *J* = 6.0 Hz, 1H), 7.62 (t, *J* = 6.0 Hz , 1H), 7.44 (t, *J* = 6.0 Hz, 1H), 4.18 – 4.14 (m, 2H), 2.13 (s, 2H), 1.81 (s, 3H), 1.22 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** 174.70, 148.70, 138.45, 133.00, 128.40, 128.32, 125.09, 61.64, 59.79, 27.77, 13.89; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{11}H_{15}N_2O_4^+$ 239.1026; found 239.1038.

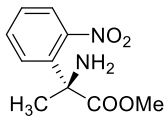




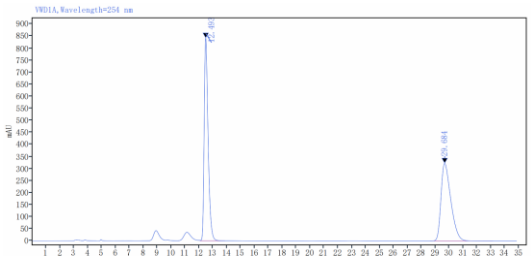
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.784	BB	2.2567	7239.8510	375.9946	50.3076
	25.554	BB	3.6267	7151.3175	168.7961	49.6924

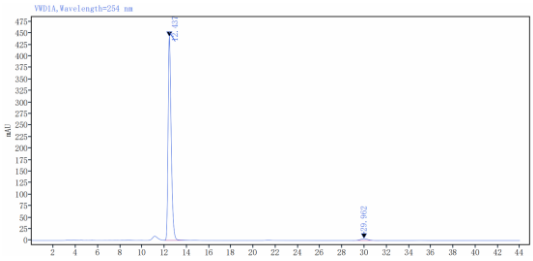
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.767	BB	4.0700	26333.5436	1321.4667	99.2166
	25.945	BB	2.4417	207.9375	4.9166	0.7834

Methyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate (3e):



A pale yellow oil (26.2 mg, 52%); R_f = 0.26 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 12.437 min, t_R(minor) 29.962 min; $[\alpha]_D^{25}$ = -85.43 (c = 0.30, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.93 (d, *J* = 6.0 Hz, 1H), 7.88 (d, *J* = 6.0 Hz, 1H), 7.62 (t, *J* = 9.0 Hz, 1H), 7.45 (t, *J* = 9.0 Hz, 1H), 3.70 (s, 3H), 1.97 (s, 2H), 1.80 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.31, 148.71, 138.49, 132.99, 128.35, 128.27, 125.09, 59.75, 52.42, 27.86; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{10}H_{13}N_2O_4^+$ 225.0870; found 225.0878.

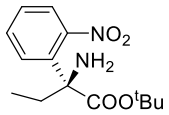




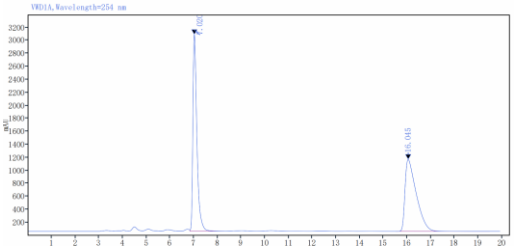
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.493	VB	1.8037	16474.6703	841.0386	51.1513
	29.684	BB	4.5250	15733.0823	321.9173	48.8487

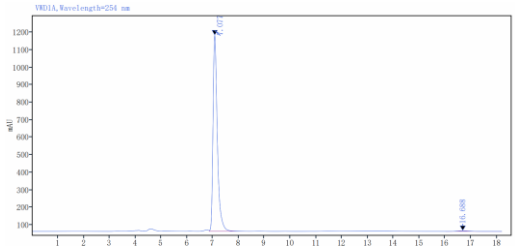
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.437	VB	2.2537	8610.1116	441.9469	97.9992
	29.962	BB	2.4100	175.7885	3.8661	2.0008

***tert*-Butyl (*S*)-2-amino-2-(2-nitrophenyl)butanoate (3f):**



A pale yellow oil (48.7 mg, 87%); R_f = 0.31 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 98% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.077 min; $[\alpha]_D^{25}$ = -38.53 (c = 0.78, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.77 (m, 2H), 7.57 (t, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 2.23 – 2.29 (m, 1H), 2.13 – 2.60 (m, 1H), 2.08 (s, 2H), 1.42 (s, 9 H), 0.90 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.92, 149.79, 136.97, 132.09, 129.25, 127.96, 124.95, 82.28, 63.29, 32.00, 27.69, 8.23; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{21}N_2O_4^+$ 281.1496; found 281.1501.

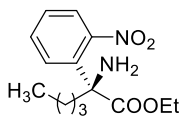




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.020	VB	1.4479	35689.9874	3024.2858	49.5529
	16.045	BB	3.9533	36334.0373	1106.0608	50.4471

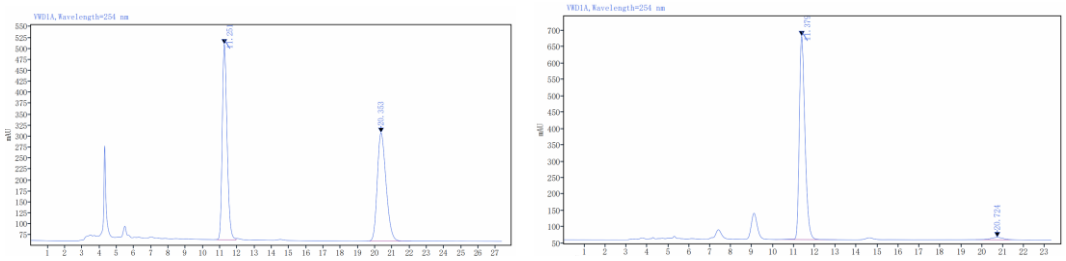
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.077	VB	1.6070	13063.0818	1119.9107	99.1922
	16.688	BBA	2.1767	106.3798	3.6638	0.8078

Ethyl (*S*)-2-amino-2-(2-nitrophenyl)butanoate (3g):



A pale yellow oil (33.3 mg, 54%); R_f = 0.49 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 11.379 min, t_R(minor) 20.724 min; $[\alpha]_D^{25}$ = -6.18 (c = 0.36, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.80 (m, 2H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.42 (t, *J* = 6.0 Hz, 1H), 4.21 – 4.12 (m, 2H), 2.22 – 2.11 (m, 2H), 1.97 (s, 2H), 1.36 – 1.26 (m, 2H), 1.22 (t, *J* = 6.0 Hz, 3H), 1.17 – 1.10 (m, 1H), 0.89 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.17,

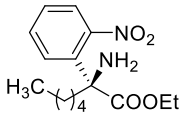
149.53, 137.01, 132.29, 129.07, 128.17, 125.01, 62.60, 61.50, 38.88, 25.94, 22.89, 13.94, 13.85. **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{21}N_2O_4^+$ 281.1496; found 281.1502.



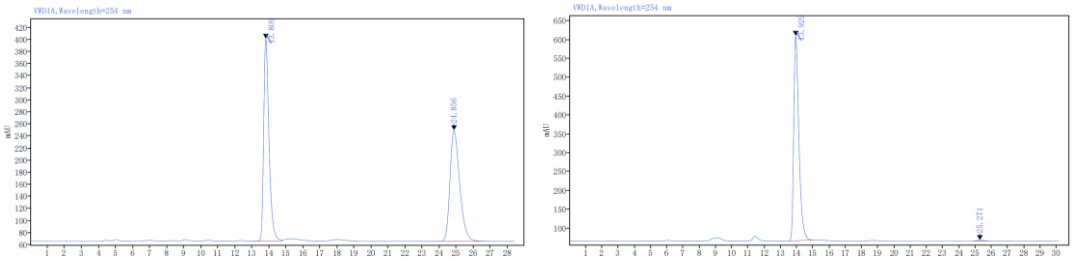
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.251	BV	1.2957	8668.1270	445.5077	49.8777
	20.353	BB	2.5967	8710.6382	246.5980	50.1223

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.379	BB	2.9600	11698.5125	621.6781	97.5436
	20.724	BB	2.6000	294.6036	7.0823	2.4564

Ethyl (*S*)-2-amino-2-(2-nitrophenyl)butanoate (3h):



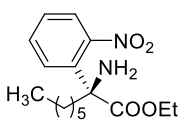
A pale yellow oil (41.2 mg, 64%); R_f = 0.48 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 13.929 min, t_R(minor) 25.271 min; $[\alpha]_D^{25}$ = -13.13 (c = 0.72, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.83 – 7.79 (m, 2H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.42 (t, *J* = 6.0 Hz, 1H), 4.16 (m, 2H), 2.22 – 2.09 (m, 2H), 2.06 (s, 2H), 1.30 (m, 5H), 1.21 (t, *J* = 9.0 Hz, 3H), 1.16 (m, 1H), 0.89 – 0.83 (m, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.18, 149.55, 137.09, 132.24, 129.05, 128.13, 124.98, 62.64, 61.46, 39.13, 31.96, 23.42, 22.37, 13.92, 13.86. **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{15}H_{23}N_2O_4^+$ 295.1652; found 295.1674.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.809	BV	1.6997	7257.5436	334.8495	50.0570
	24.856	BB	3.8733	7241.0190	183.6259	49.9430

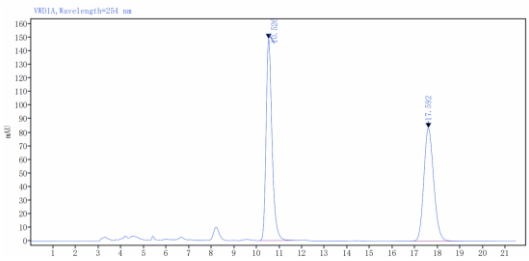
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.929	BB	1.5583	11905.1486	542.9634	99.3998
	25.271	BB	2.7467	71.8839	1.7647	0.6002

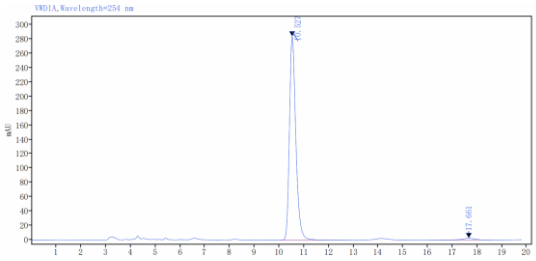
Ethyl (*S*)-2-amino-2-(2-nitrophenyl)butanoate (3i):



A pale yellow oil (43.9 mg, 65%); R_f = 0.48 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30

°C), UV 254 nm, t_R(major) 10.527 min, t_R(minor) 17.661min; $[\alpha]_D^{25}$ = -6.56 (c = 0.43, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.81 (m, 2H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.42 (t, *J* = 6.0 Hz, 1H), 4.22 – 4.10 (m, 2H), 2.16 (m, 2H), 1.99 (s, 2H), 1.34 – 1.19 (m, 11H), 0.86 (t, *J* = 6.8 Hz, 3H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.19, 149.55, 137.08, 132.25, 129.05, 128.14, 125.01, 62.65, 61.49, 39.19, 31.56, 29.46, 23.74, 22.50, 13.94, 13.93; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{25}N_2O_4^+$ 309.1809; found 309.1824.

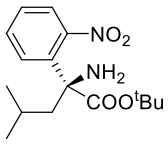




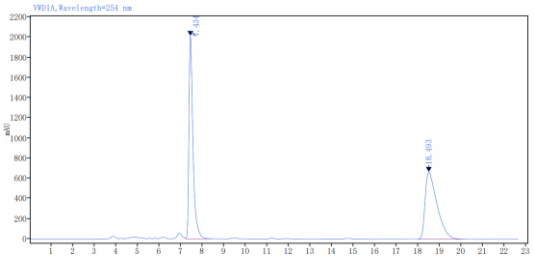
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	10.526	BB	1.7067	2719.4055	148.8595	51.8046
	17.592	BB	2.3733	2529.9450	83.3962	48.1954

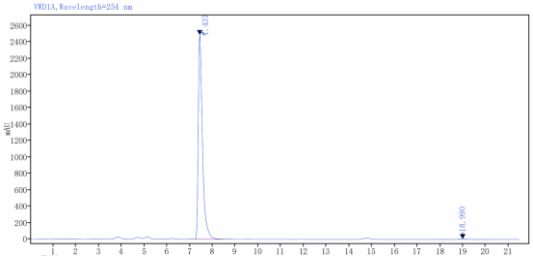
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	10.527	BB	2.8467	5062.0305	283.2790	98.3188
	17.661	BB	2.4917	86.5581	2.3926	1.6812

***tert*-Butyl (*S*)-2-amino-4-methyl-2-(2-nitrophenyl)pentanoate (3j):**



White solid (47.1 mg, 84%); m.p. = 82-84 °C ; R_f = 0.41 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.437 min, t_R(minor) 18.990 min; $[\alpha]_D^{25}$ = -39.58 (c = 0.32, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.97 (d, *J* = 6.0 Hz, 1H), 7.80 (d, *J* = 6.0 Hz, 1H), 7.56 (t, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 2.17 (dd, *J* = 18.0, 6.0 Hz, 1H), 2.04 (dd, *J* = 18.0, 6.0 Hz, 1H), 1.86 (s, 2H), 1.72 – 1.65 (m, 1H), 1.41 (s, 9H), 0.95 (d, *J* = 6.0 Hz, 3H), 0.70 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.24, 149.42, 137.82, 131.98, 129.29, 127.90, 124.87, 82.08, 63.50, 46.92, 27.68, 24.81, 24.38, 23.91; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{25}N_2O_4^+$ 309.1809; found 309.1812.

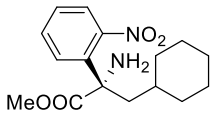




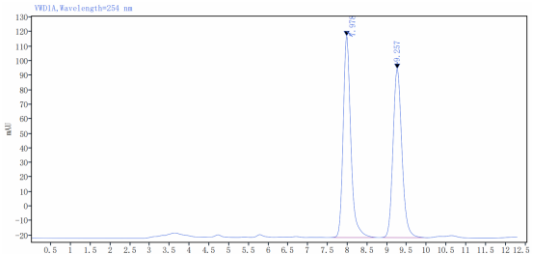
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.434	VB	1.3465	26026.7568	2010.0685	50.6475
	18.493	BB	3.4567	25361.2462	664.7665	49.3525

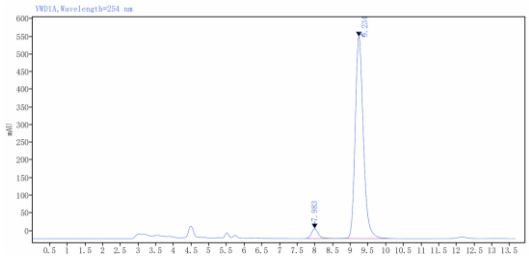
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.437	VB	1.9991	31987.6405	2481.2305	99.7228
	18.990	BB	2.1917	88.9280	2.5982	0.2772

Methyl (*S*)-2-amino-3-cyclohexyl-2-(2-nitrophenyl)propanoate (3k):



A pale yellow oil (31.1 mg, 51%); R_f = 0.42 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 9.234 min, t_R(minor) 7.983 min; $[\alpha]_D^{25}$ = 8.05 (c = 0.29, $CHCl_3$);**^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 6.0 Hz, 1H), 7.80 (d, *J* = 6.0 Hz, 1H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.48(t, *J* = 6.0 Hz, 1H), 3.68 (s, 3H), 2.12 – 2.05 (m, 2H), 1.86 (s, 2H), 1.70 – 1.62 (m, 2H), 1.56 – 1.52 (m, 2H), 1.37 – 1.27 (m, 2H), 1.21– 0.97 (m, 4H), 0.91 – 0.85 (m, 1H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.86, 149.43, 137.40, 132.33, 128.93, 128.30, 125.09, 62.67, 52.28, 46.15, 35.22, 35.01, 33.11, 26.37, 26.21, 26.10; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{23}N_2O_4^+$ 307.1652; found 307.1666.

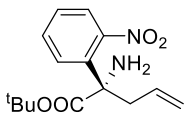




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.978	BB	1.3000	1886.0549	138.5718	50.9512
	9.257	BB	1.2400	1815.6331	116.0901	49.0488

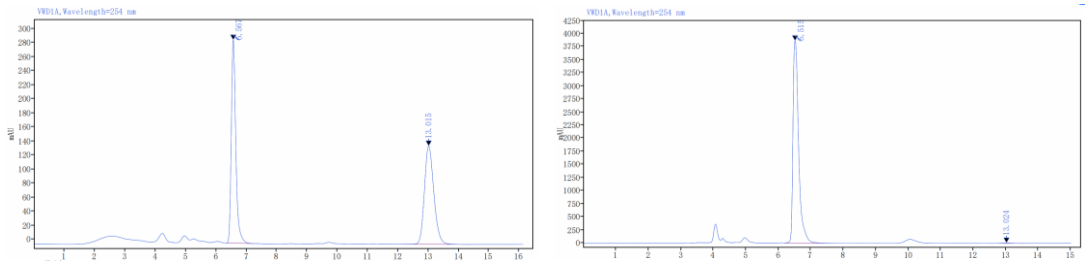
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.983	BB	0.9417	374.4790	27.4447	3.9482
	9.234	BB	2.0600	9110.2755	570.7746	96.0518

***tert*-Butyl (*S*)-2-amino-2-(2-nitrophenyl)pent-4-enoate (3l):**



A pale yellow oil (48.4 mg, 83%); R_f = 0.42 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 6.515 min, t_R(minor) 13.024 min; $[\alpha]_D^{25}$ = -78.53 (c = 0.29, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.81 – 7.78 (m, 2H), 7.56 (t, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 5.69 – 5.70 (m, 1H), 5.16 – 5.12 (m, 2H), 2.98 – 2.89 (m, 2H), 1.96 (s, 2H), 1.42 (s, 9H) ; **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.54, 149.58, 137.32, 132.27, 132.04, 129.16, 128.05, 124.91, 119.86, 82.48, 62.47, 43.70, 27.71; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{15}H_{21}N_2O_4^+$ 293.1496; found

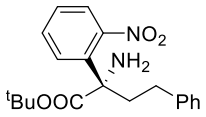
293.1510.



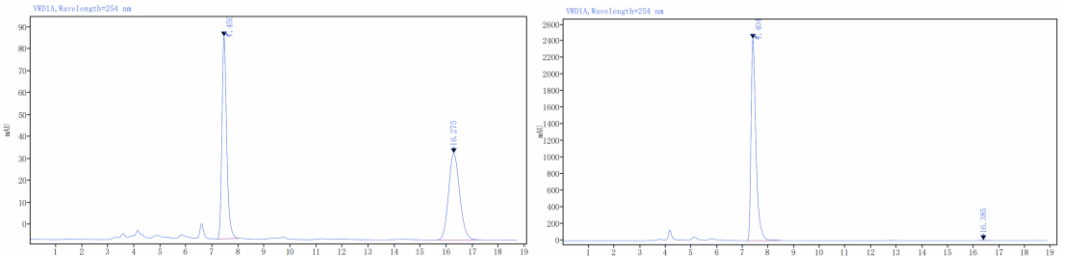
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.567	BB	0.9209	2975.8424	288.7805	49.7414
	13.015	BB	2.3300	3006.7884	139.8386	50.2586

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.515	VB	1.7799	46655.2956	3867.2612	99.7177
	13.024	BB	1.0933	132.0697	5.7722	0.2823

***tert*-Butyl (*S*)-2-amino-2-(2-nitrophenyl)-4-phenylbutanoate (3m):**



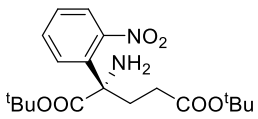
A pale yellow oil (71.4 mg, 89%); R_f = 0.46 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.404 min, t_R(minor) 16.385 min; $[\alpha]_D^{25}$ = -36.27 (c = 0.82, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.88 (d, *J* = 12.0 Hz, 1H), 7.83 (d, *J* = 12.0 Hz, 1H), 7.58 (t, *J* = 12.0 Hz, 1H), 7.42 (t, *J* = 9.0 Hz, 1H), 7.27 (t, *J* = 6.0 Hz, 2H), 7.17 (m, 3H), 2.72 – 2.61 (m, 1H), 2.53 – 2.43 (m, 3H), 2.16 (s, 2H), 1.45 (s, 9H). **^{13}C NMR (151 MHz, $CDCl_3$)** δ172.86, 149.62, 141.41, 136.96, 132.27, 129.16, 128.52, 128.29, 128.17, 126.07, 125.07, 82.53, 63.09, 40.89, 30.38, 27.74; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{25}N_2O_4^+$ 357.1809; found 357.1822.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.450	BB	0.9117	1170.7961	92.1296	50.0737
	16.275	BB	2.2850	1167.3494	39.4247	49.9263

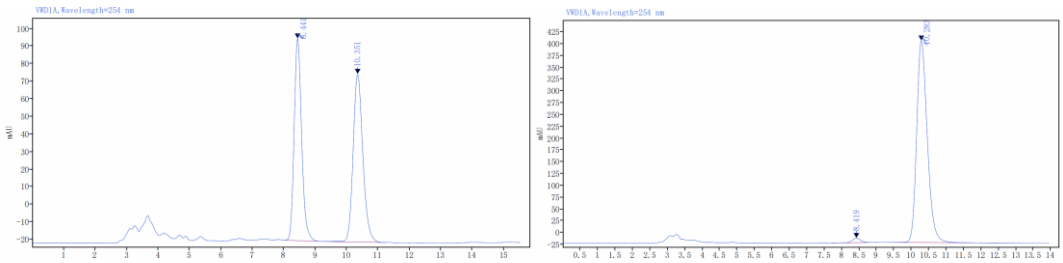
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.404	BB	1.7817	32413.8058	2431.1400	99.8243
	16.385	BB	1.2800	57.0490	1.9548	0.1757

Di-*tert*-butyl (*S*)-2-amino-2-(2-nitrophenyl)pentanedioate (3n):



A pale yellow oil (48.4 mg, 64%); R_f= 0.47 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 10.283 min, t_R(minor) 8.419 min; $[\alpha]_D^{25}$ = -75.11 (c = 0.29, $CHCl_3$); **^{1}H**

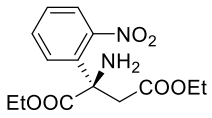
NMR (600 MHz, $CDCl_3$) δ 7.93 (d, *J* = 6.0 Hz, 1H), 7.86 (d, *J* = 6.0 Hz, 1H), 7.59 (t, *J* = 6.0 Hz, 1H), 7.42 (t, *J* = 6.0 Hz, 1H), 2.51 (t, *J* = 6.0 Hz, 2H), 2.26 – 2.33 (m, 1H), 2.11 – 2.15 (m, 1H), 1.80 (s, 2H), 1.42 (s, 9H), 1.41 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.64, 172.46, 149.37, 136.74, 132.42, 129.20, 128.19, 125.16, 82.44, 80.46, 62.68, 33.35, 30.41, 28.06, 27.65; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated. for $C_{19}H_{29}N_2O_6^+$ 381.2020; found 381.2031.



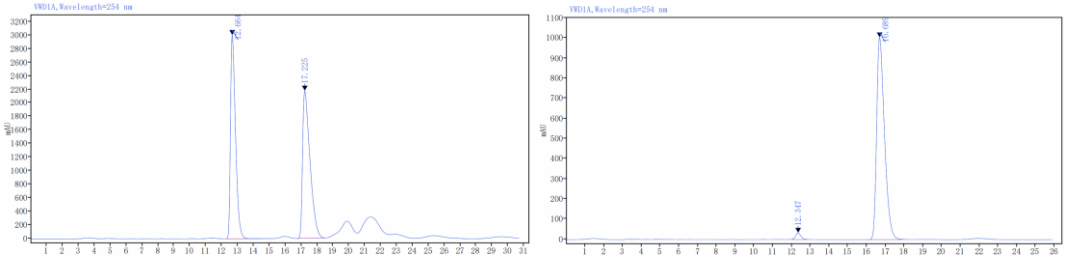
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.441	BB	1.1633	1906.6976	114.8743	48.1712
	10.351	BB	1.9100	2051.4683	95.5246	51.8288

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.419	BB	1.1417	159.3015	9.4793	1.7274
	10.283	BBA	3.1733	9062.8924	427.5883	98.2726

Diethyl (*R*)-2-amino-2-(2-nitrophenyl)succinate (3o):



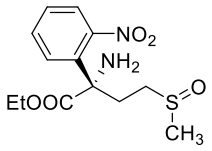
A pale yellow oil (32.2 mg, 52%); R_f = 0.42 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 16.689 min, t_R(minor) 12.347 min; $[\alpha]_D^{25}$ = -57.86 (c = 0.58, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 6.0 Hz, 1H), 7.77 (d, *J* = 6.0 Hz, 1H), 7.58 (t, *J* = 9.0 Hz, 1H), 7.45 (t, *J* = 9.0 Hz, 1H), 4.19 (q, *J* = 6.0 Hz, 2H), 4.11 (q, *J* = 6.0 Hz, 2H), 3.25 (d, *J* = 18.0 Hz, 1H), 3.12 (d, *J* = 18.0 Hz, 1H), 2.61 (s, 2H), 1.25 – 1.20 (m, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.73, 170.80, 149.24, 136.29, 132.22, 128.80, 128.77, 124.94, 62.20, 61.95, 60.75, 42.76, 14.03, 13.84; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{19}N_2O_6^+$ 311.1238; found 311.1248.



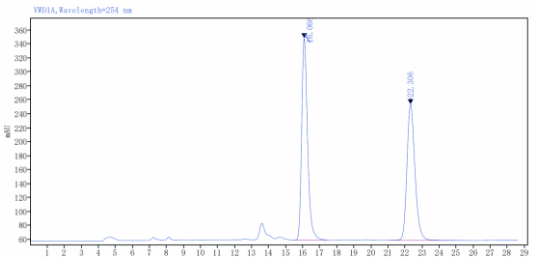
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.664	BB	2.3317	65794.4445	2997.1415	48.3356
	17.225	BB	1.7646	70325.7028	2172.0285	51.6644

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.347	BB	1.8233	640.0913	32.3327	2.1559
	16.689	BB	2.3383	29050.3166	1003.7082	97.8441

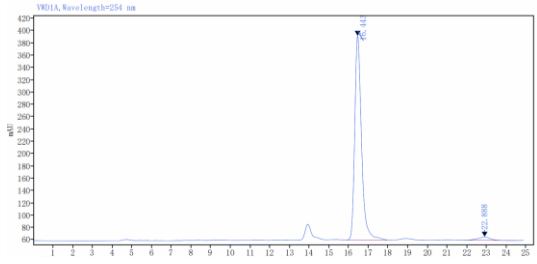
Ethyl (2*S*, 5*R*)-2-amino-4-(methylsulfinyl)-2-(2-nitrophenyl)butanoate (3p):



A pale yellow oil (42.3 mg, 67%); R_f = 0.46 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 16.443 min, t_R(minor) 22.888 min; $[\alpha]_D^{25}$ = -54.76 (c = 0.45, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.92 (d, *J* = 6.0 Hz, 1H), 7.87 (d, *J* = 6.0 Hz, 1H), 7.62 (t, *J* = 6.0 Hz, 1H), 7.46 (t, *J* = 9.0 Hz, 1H), 4.17 (q, *J* = 6.0 Hz, 2H), 2.55 – 2.48 (m, 3H), 2.30 – 2.26 (m, 1H), 2.08 (s, 3H), 1.61 (s, 2H), 1.22 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.59, 149.21, 136.29, 132.59, 128.99, 128.51, 125.28, 62.59, 61.71, 38.49, 28.68, 15.55, 13.92; **HRMS(ESI)** m/z: $[M+Na]^+$ Calculated for $C_{13}H_{19}N_2O_5SNa^+$ 315.1009; found 315.1010.

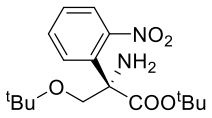


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	16.066	BB	2.2100	6927.4854	288.8164	52.1471
	22.306	BB	5.4033	6357.0148	194.6055	47.8529

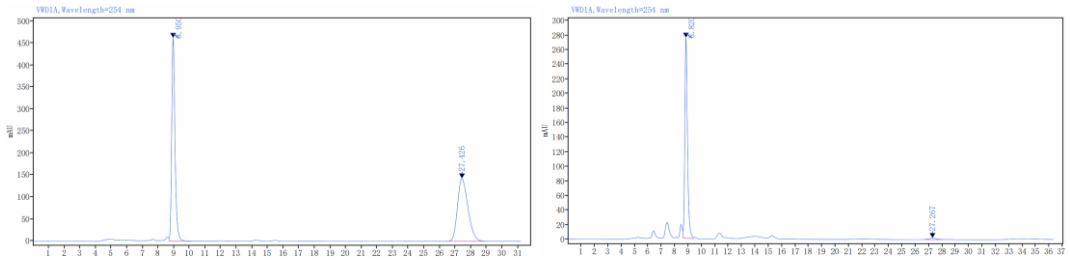


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	16.443	BB	2.3667	7918.7158	331.3081	97.0451
	22.888	BB	2.5867	241.1116	5.4840	2.9549

***tert*-Butyl (*S*)-2-amino-3-(*tert*-butoxy)-2-(2-nitrophenyl)propanoate (3q):**



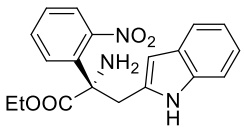
A pale yellow oil (33.4 mg, 49%); R_f = 0.48 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 8.820 min, t_R(minor) 27.267 min; $[\alpha]_D^{25}$ = -58.86 (c = 0.25, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.67 – 7.69 (m, 2H), 7.51 (t, *J* = 6.0 Hz, 1H), 7.38 (t, *J* = 6.0 Hz, 1H), 3.92 (d, *J* = 6.0 Hz, 1H), 3.83 (d, *J* = 6.0 Hz, 1H), 2.01 (s, 2H), 1.44 (s, 9H), 1.18 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 171.79, 150.11, 135.95, 131.55, 129.47, 128.06, 124.69, 82.39, 73.66, 67.09, 63.85, 27.81, 27.45; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{17}H_{27}N_2O_5^+$ 339.1914; found 339.1914.



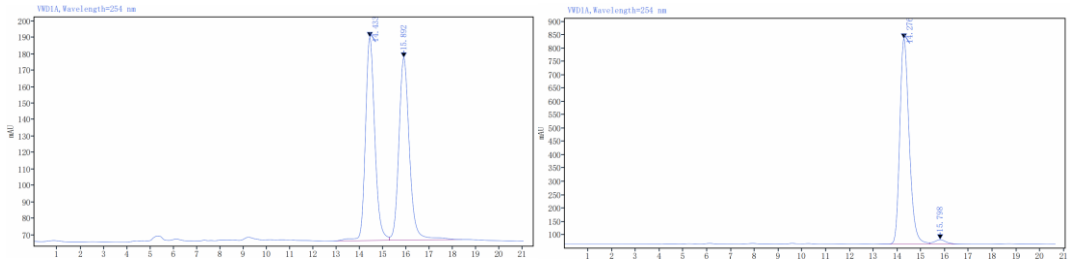
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.950	VB	1.4172	6716.3997	461.1876	50.4290
	27.426	BB	3.4150	6602.1297	142.2216	49.5710

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.820	VV	0.7906	3815.9814	274.9332	98.0152
	27.267	BB	1.8517	77.2739	1.7902	1.9848

Ethyl (*S*)-2-amino-3-(1*H*-indol-2-yl)-2-(2-nitrophenyl)propanoate(3r):



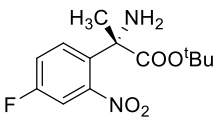
A pale yellow oil (28.9 mg, 41%); m.p. = 95-97 ºC, R_f = 0.49 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 14.276 min, t_R(minor) 15.798 min; $[\alpha]_D^{25}$ = -24.15 (c = 0.43, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.04 (s, 1H), 7.70 (d, *J* = 6.0 Hz, 1H), 7.64 (d, *J* = 6.0 Hz, 1H), 7.36 – 7.28 (m, 3H), 7.22 (d, *J* = 6.0 Hz, 1H), 7.06 (t, *J* = 9.0 Hz, 1H), 6.95 (t, *J* = 6.0 Hz, 1H), 6.83 (s, 1H), 4.04 – 3.97 (m, 2H), 3.65 (dd, *J* = 24.0, 12.0 Hz, 2H), 1.94 (s, 2H), 1.05 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.78, 149.54, 137.46, 135.85, 131.90, 129.32, 128.52, 128.20, 124.75, 124.09, 122.02, 119.62, 118.90, 110.98, 109.61, 63.72, 61.63, 34.77, 13.79; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{20}N_3O_4^+$354.1448; found 354.1469.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	14.433	BV	2.3929	3447.2162	123.4065	49.7154
	15.892	VB	3.1254	3486.6907	110.7714	50.2846

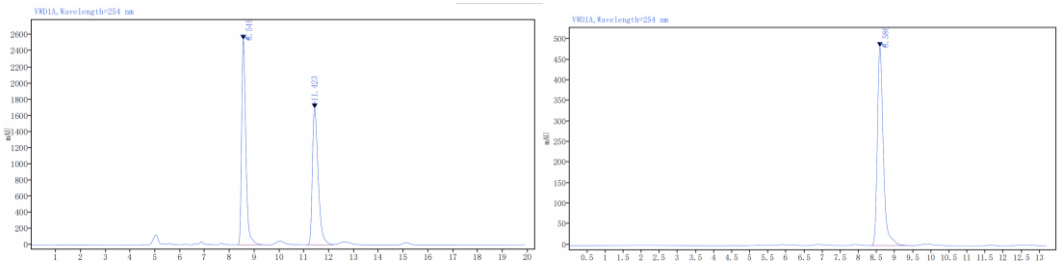
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	14.276	BV	2.3343	21051.8048	768.8665	97.5397
	15.798	VB	1.7107	531.0118	16.0761	2.4603

***tert*-Butyl (*S*)-2-amino-2-(4-fluoro-2-nitrophenyl)propanoate (3s):**



A pale yellow oil (52.1 mg, 91%); R_f = 0.36 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0

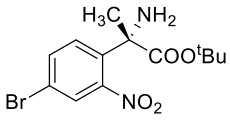
mL/min, T = 30 ºC), UV 254 nm, t_R(major) 8.586 min; $[\alpha]_D^{25}$ = -77.35 (c = 0.75, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.94 (dd, *J* = 12.0, 6.0 Hz, 1H), 7.59 (dd, *J* = 8.3, 2.8 Hz, 1H), 7.34 – 7.26 (m, 1H), 2.06 (s, 2H), 1.75 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.44, 161.81, 160.15, 149.24, 134.88, 130.42, 130.37, 119.75, 119.61, 112.59, 112.41, 82.34, 60.03, 27.86, 27.56; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{13}H_{18}FN_2O_4^+$ 285.1245; found 285.1259.



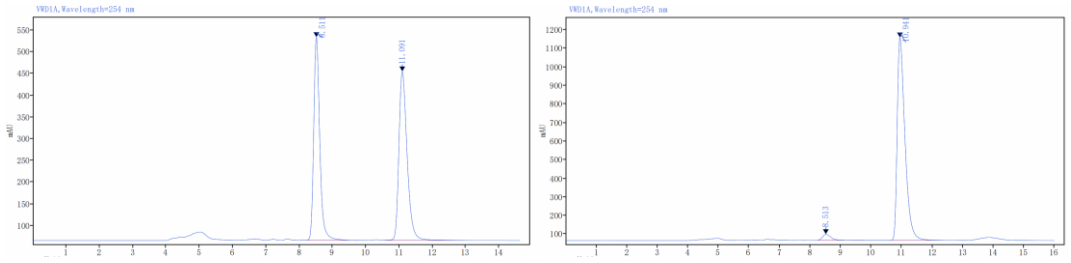
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.549	BB	1.3316	29662.1185	2535.0039	51.9384
	11.423	VV	1.1336	27448.1222	1684.9988	48.0616

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.586	VB	1.2035	5545.4669	482.6208	100.0000

***tert*-Butyl (*S*)-2-amino-2-(4-bromo-2-nitrophenyl)propanoate (3t):**



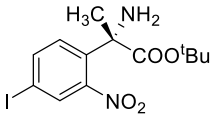
A pale yellow oil (48.7 mg, 71%); R_f = 0.38 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 10.941 min, t_R(minor) 8.513 min; $[\alpha]_D^{25}$ = -81.92 (c = 0.78, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.98 (s, 1H), 7.82 (d, *J* = 12.0 Hz, 1H), 7.70 (d, *J* = 12.0 Hz, 1H), 1.98 (s, 2H), 1.74 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.23, 149.29, 138.13, 135.66, 130.15, 127.75, 121.11, 82.42, 60.16, 27.76, 27.58; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{13}H_{18}BrN_2O_4^+$ 345.0444; found 345.0458.



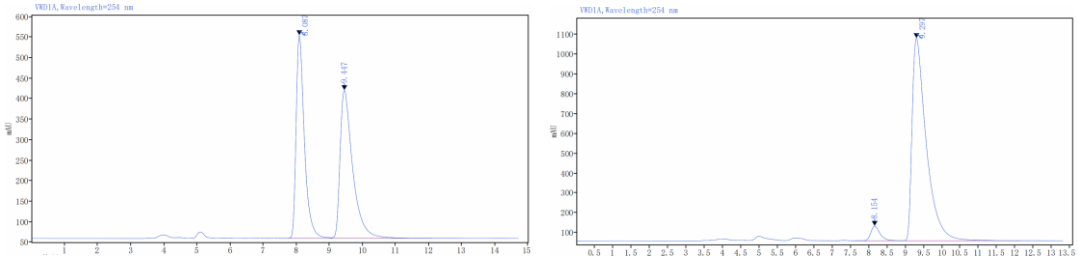
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.511	VB	1.5739	5880.3604	466.7264	46.9799
	11.091	VB	2.6965	6636.3869	388.2168	53.0201

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.513	BB	1.6033	604.5258	31.1387	3.0565
	10.941	BB	1.9625	19173.6460	1090.1798	96.9435

***tert*-Butyl (*S*)-2-amino-2-(4-iodo-2-nitrophenyl)propanoate (3u):**



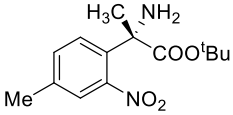
A pale yellow oil (43.3 mg, 55%); R_f = 0.38 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak ID column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 9.297 min, t_R(minor) 8.154 min; $[\alpha]_D^{25}$ = -51.67 (c = 0.33, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.14 (s, 1H), 7.89 (d, *J* = 6.0 Hz, 1H), 7.66 (d, *J* = 6.0 Hz, 1H), 2.02 (s, 2H), 1.73 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.22, 149.18, 141.67, 138.77, 133.35, 130.25, 91.62, 82.44, 60.20, 27.71, 27.59; **HRMS(ESI)** m/z: $[M+Na]^+$ Calculated for $C_{13}H_{17}IN_2NaO_4^+$ 415.0125; found 415.0123.



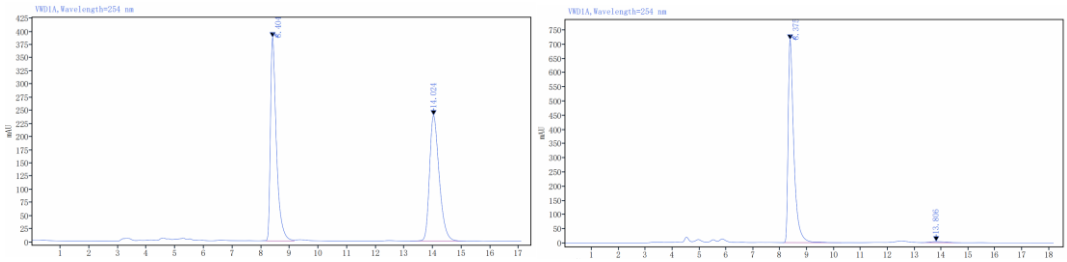
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.087	BV	1.3217	8594.9445	494.5145	47.3661
2	9.447	VB	3.0333	9550.8279	360.5925	52.6339

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.154	BV	1.3488	1300.7925	73.4194	4.5140
2	9.297	VB	3.2229	27516.1343	1018.8825	95.4860

***tert*-Butyl (*S*)-2-amino-2-(4-methyl-2-nitrophenyl)propanoate (3v):**

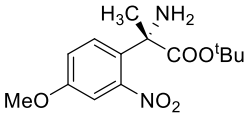


A pale yellow oil (38.6 mg, 69%); R_f = 0.26 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 8.375 min, t_R(minor) 13.806 min; $[\alpha]_D^{25}$ = -27.6 (c = 0.51, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.75 (d, *J* =6.0 Hz, 1H), 7.68 (s, 1H), 7.39 (d, *J* = 12.0 Hz, 1H), 2.41 (s, 3H), 1.97 (s, 2H), 1.74 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.03, 148.62, 138.44, 135.86, 133.52, 128.29, 125.35, 81.99, 60.04, 27.86, 27.59, 20.53; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{21}N_2O_4^+$ 281.1496; found 281.1495.

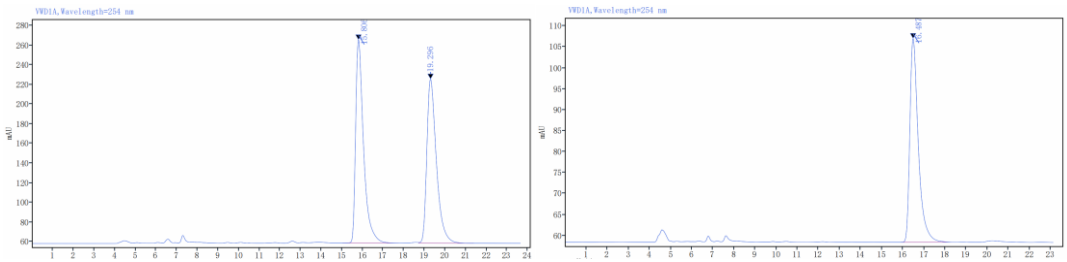


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.404	BV	1.2208	5592.0718	386.0433	49.9962		8.375	BB	2.1733	10494.6017	713.3597	98.5177
	14.024	BB	1.9467	5592.9119	238.2571	50.0038		13.806	BB	1.4833	157.9042	3.6360	1.4823

***tert*-Butyl (*S*)-2-amino-2-(4-methoxy-2-nitrophenyl)propanoate (3w):**

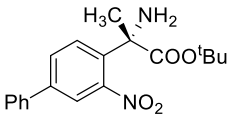


A pale yellow oil (45.6 mg, 77%); R_f = 0.27 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 16.487 min; $[\alpha]_D^{25}$ = -30.6 (c = 0.25, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 12.0 Hz, 1H), 7.38 (s, 1H), 7.10 (d, *J* = 6.0 Hz, 1H), 3.86 (s, 3H), 2.19 (s, 2H), 1.74 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.09, 158.80, 149.32, 130.63, 129.51, 118.70, 110.10, 82.00, 59.87, 55.79, 27.90, 27.60; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{21}N_2O_5^+$ 297.1445; found 297.1447.

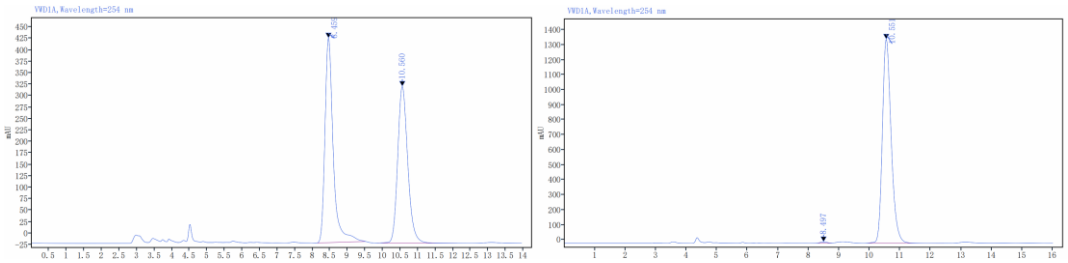


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	15.806	BB	2.7200	5504.6620	206.6404	50.6407		16.487	BB	2.4750	1356.0870	48.5729	100.0000
	19.296	VB	2.6575	5365.3823	166.8838	49.3593							

***tert*-Butyl (*S*)-2-amino-2-(3-nitro-[1,1'-biphenyl]-4-yl)propanoate (3x):**



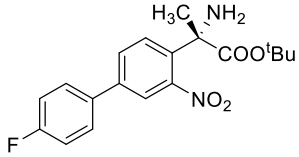
A pale yellow oil (47.2 mg, 69%); R_f = 0.38 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 99% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 10.551 min, t_R(minor) 8.497 min; $[\alpha]_D^{25}$ = -31.17 (c = 0.80, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.09 (s, 1H), 7.96 (d, *J* = 12.0 Hz, 1H), 7.81 (d, *J* = 6.0 Hz, 1H), 7.61 (d, *J* = 6.0 Hz, 2H), 7.49 – 7.40 (m, 3H), 2.04 (s, 2H), 1.80 (s, 3H), 1.43 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.85, 149.20, 141.38, 138.22, 137.49, 130.97, 129.10, 129.01, 128.45, 126.99, 123.35, 82.19, 60.20, 27.90, 27.64; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{23}N_2O_4^+$ 343.1652 ; found 343.1652.



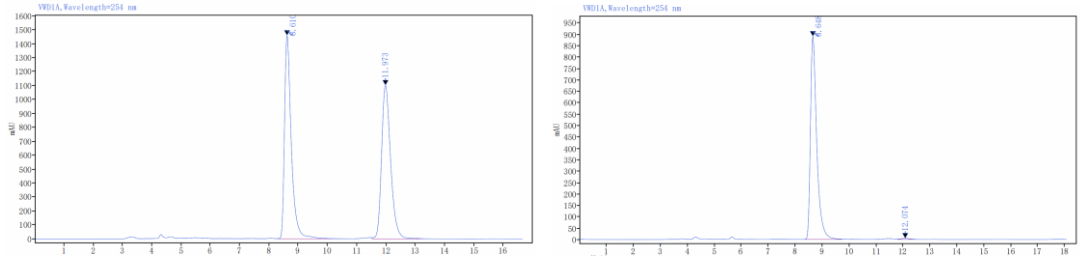
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.459	BM m	0.2457	7292.7703	446.1755	51.7795
	10.560	BB	2.2800	6791.5159	341.8489	48.2205

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.497	BV	0.7141	119.8623	7.8416	0.4395
	10.551	VB	2.6373	27153.4995	1358.0694	99.5605

***tert*-Butyl (*S*)-2-amino-2-(4'-fluoro-3-nitro-[1,1'-biphenyl]-4-yl)propanoate (3y):**



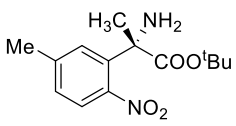
A pale yellow oil (42.8 mg, 60%); R_f = 0.38 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 98% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 8.648 min, t_R(minor) 12.074 min; $[\alpha]_D^{25}$ = -40.20 (c = 0.60, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (s, 1H), 7.96 (d, *J* = 6.0 Hz, 1H), 7.75 (d, *J* = 6.0 Hz, 1H), 7.59 – 7.56 (m, 2H), 7.17 (t, *J* = 9.0 Hz, 2H), 2.08 (s, 2H), 1.80 (s, 3H), 1.43 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.69, 163.93, 162.29, 149.20, 140.40, 137.36, 134.32, 130.84, 129.17, 128.74, 128.69, 123.18, 116.17, 116.02, 82.31, 60.18, 27.80, 27.62; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{22}FN_2O_4^+$ 361.1558; found 361.1557.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.610	VB	2.5372	23551.4873	1457.5365	49.9339
	11.973	VB	3.4971	23613.8432	1100.3359	50.0661

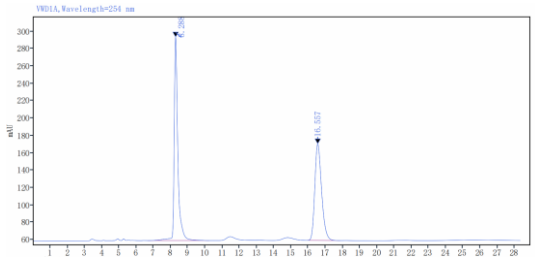
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.648	BV	1.4972	14472.4951	889.4304	99.1824
	12.074	VB	1.0740	119.3003	4.9362	0.8176

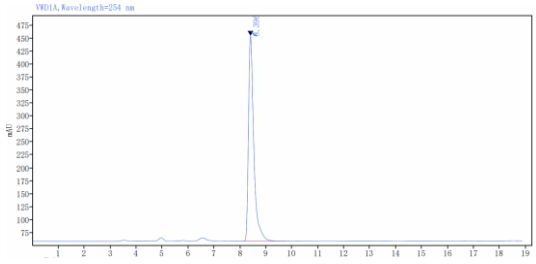
***tert*-Butyl (*S*)-2-amino-2-(5-methyl-2-nitrophenyl)propanoate (3z):**



A pale yellow oil (38.6 mg, 69%); R_f = 0.26 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 8.396 min; $[\alpha]_D^{25}$ = -11.95 (c = 0.66, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.82 (d, *J* = 6.0 Hz, 1H), 7.70 (s, 1H), 7.20 (d, *J* = 12.0 Hz, 1H), 2.45 (s, 3H),

2.06 (s, 2H), 1.75 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.97, 146.50, 144.09, 138.75, 128.95, 128.46, 125.28, 81.99, 60.26, 27.61, 27.59, 21.64; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{21}N_2O_4^+$ 281.1496; found 281.1496.

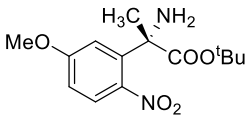




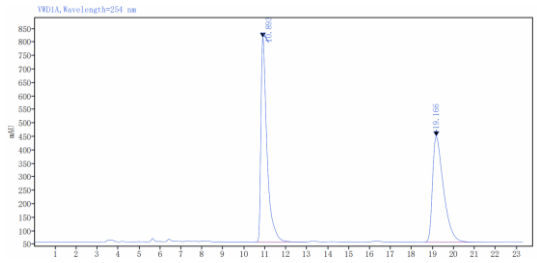
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.288	BB	3.5683	3449.4843	234.2910	53.0214
2	16.557	BB	1.9233	3056.3538	111.1442	46.9786

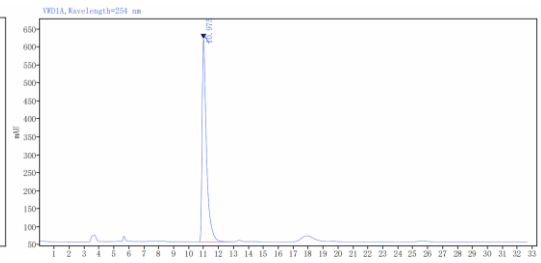
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.396	BB	1.6767	5615.2964	395.2744	100.0000

***tert*-Butyl (*S*)-2-amino-2-(5-methoxy-2-nitrophenyl)propanoate (3aa):**



A pale yellow oil (34.9 mg, 59%); R_f = 0.27 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 10.975 min; $[\alpha]_D^{25}$ = -31.47 (c = 0.62, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.03 (d, *J* = 12.0 Hz, 1H), 7.48 (s, 1H), 6.85 (d, *J* = 12.0 Hz, 1H), 3.91 (s, 3H), 2.09 (s, 2H), 1.74 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.70, 163.35, 142.04, 141.61, 127.97, 114.38, 111.85, 81.87, 60.53, 55.79, 27.60, 27.21; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{21}N_2O_5^+$ 297.1445; found 297.1445.

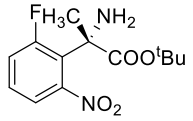




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.893	BB	2.4083	15202.9004	756.8794	51.7809
2	19.166	BB	3.8133	14157.1406	390.9754	48.2191

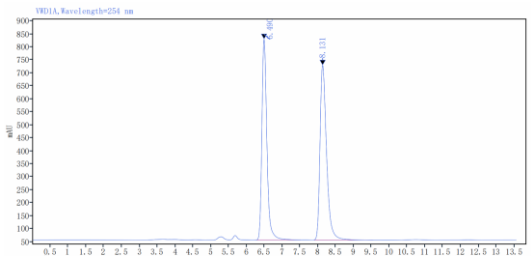
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.975	BB	2.4261	11434.1551	563.4794	100.0000

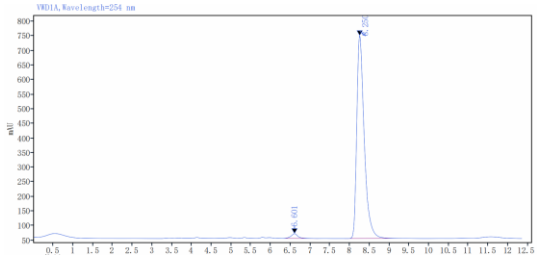
***tert*-Butyl (*S*)-2-amino-2-(2-fluoro-6-nitrophenyl)propanoate (3ab):**



A pale yellow oil (36.9 mg, 65%); R_f = 0.62 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min,

T = 30 °C), UV 254 nm, t_R(major) 8.250 min, t_R(minor) 6.601 min; $[\alpha]_D^{25}$ = 85.05 (c = 0.66, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.35 (m, 1H), 7.30 – 7.25 (m, 1H), 7.23 – 7.17 (m, 1H), 1.86 (s, 2H), 1.76 (d, *J* = 6.0 Hz, 3H), 1.44 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.00, 161.16, 159.50, 151.06, 128.90, 128.84, 126.14, 126.03, 119.76, 119.74, 118.75, 118.59, 82.09, 59.74, 27.59, 26.03, 25.99; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{13}H_{18}FN_2O_4^+$ 285.1245; found 285.1247.

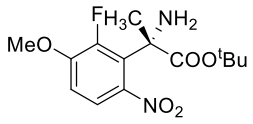




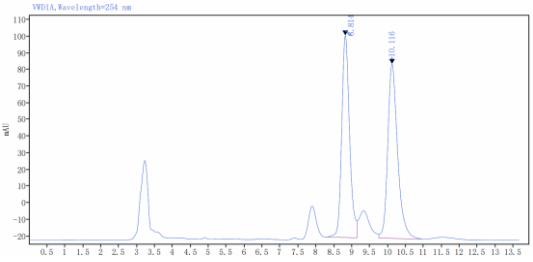
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.490	BB	1.3000	7570.6034	773.5950	46.7879
2	8.131	BB	1.6879	8610.0730	673.1867	53.2121

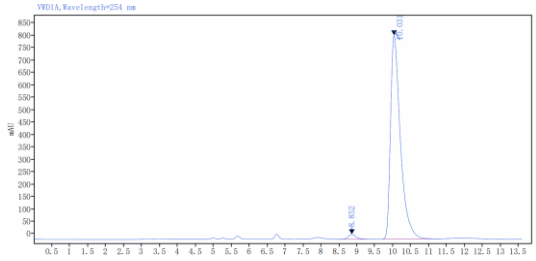
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.601	VB	0.9071	209.1208	16.4376	2.2462
2	8.250	BB	1.4528	9100.8487	695.2932	97.7538

***tert*-Butyl (*S*)-2-amino-2-(2-fluoro-3-methoxy-6-nitrophenyl)propanoate (3ac):**



White solid (35.8 mg, 57%); m.p. = 81-82 °C; R_f = 0.27 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 10.031 min, t_R(minor) 8.852 min; $[\alpha]_D^{25}$ = 116.16 (c = 0.30, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.44 (d, *J* = 6.0 Hz, 1H), 6.90 (t, *J* = 9.0 Hz, 1H), 3.94 (s, 3H), 1.89 (s, 2H), 1.82 (d, *J* = 6.0 Hz, 3H), 1.44 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.96, 168.25, 154.38, 135.47, 131.26, 125.17, 124.24, 123.42, 119.20, 117.46, 116.46, 79.63, 61.78, 59.82, 30.96, 28.44, 24.11, 23.97, 14.05; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}FN_2O_5^+$ 315.1351; found 315.1352.

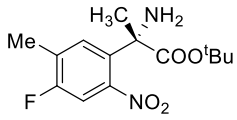




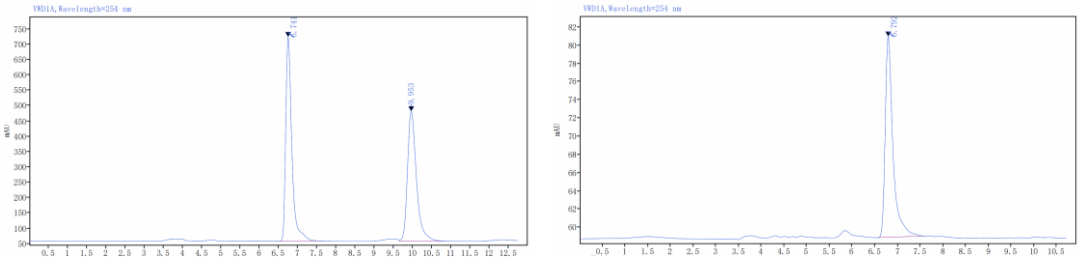
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.814	BV	0.8695	1843.2860	121.1615	48.0142
2	10.116	VB	1.2610	1995.7593	104.6251	51.9858

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.852	BB	0.9358	292.4944	19.0899	1.8388
2	10.031	BB	1.6443	15614.6763	820.5803	98.1612

***tert*-Butyl (*S*)-2-amino-2-(4-fluoro-5-methyl-2-nitrophenyl)propanoate (3ad):**



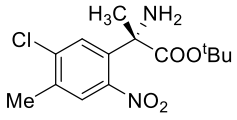
White solid (43.5 mg, 73%); m.p. = 85-87 °C; R_f = 0.42 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be >99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.792 min; $[\alpha]_D^{25}$ = -39.38 (c = 0.77, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.77 (d, *J* = 6.0 Hz, 1H), 7.60 (d, *J* = 12.0 Hz, 1H), 2.36 (s, 3H), 2.12 (s, 2H), 1.74 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.68, 160.02, 158.37, 146.90, 146.85, 134.66, 134.63, 131.45, 131.42, 130.83, 130.72, 112.38, 112.20, 82.15, 60.03, 27.65, 27.56, 14.81, 14.79.; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}FN_2O_4^+$ 299.1402; found 299.1405.



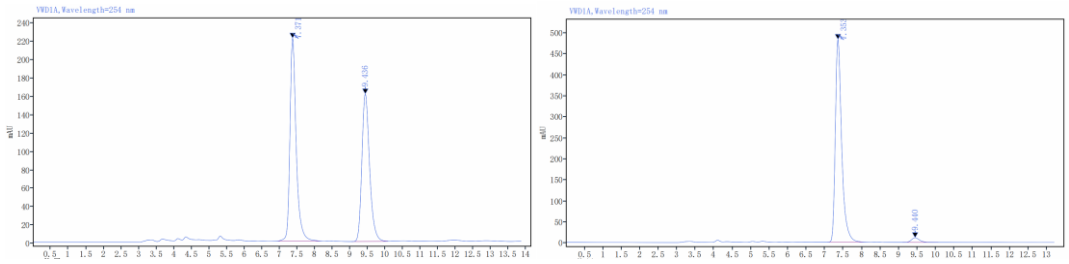
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.741	BB	1.3167	7368.7933	664.2735	51.8851
	9.953	VB	1.9054	6833.3547	422.2931	48.1149

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.792	BB	1.0417	262.7770	22.0293	100.0000

***tert*-Butyl (*S*)-2-amino-2-(5-chloro-4-methyl-2-nitrophenyl)propanoate (3ae):**



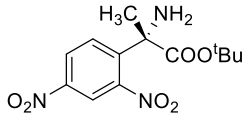
White solid (34.6 mg, 55%); m.p. = 89-90 °C; R_f = 0.58 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.353 min, t_R(minor) 9.440 min; $[\alpha]_D^{25}$ = -44.03 (c = 0.54, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (s, 1H), 7.79 (s, 1H), 2.42 (s, 3H), 2.19 (s, 2H), 1.74 (s, 3H), 1.40 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.32, 146.63, 139.48, 138.04, 136.50, 129.21, 127.20, 82.33, 60.03, 27.58, 27.48, 19.43; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}ClN_2O_4^+$ 315.1106; found 315.1109.



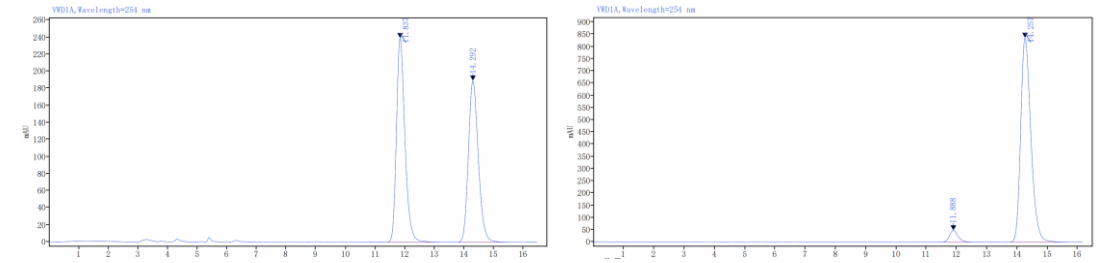
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.371	BB	1.5492	2720.4121	220.2715	52.7120
	9.436	BV	1.0270	2440.4830	160.1728	47.2880

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.353	VB	1.1592	5755.5910	482.2172	97.1974
	9.440	BB	0.9700	165.9576	10.8930	2.8026

***tert*-Butyl (*S*)-2-amino-2-(2,4-dinitrophenyl)propanoate (3af):**



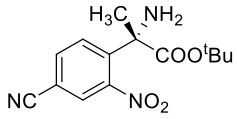
A pale yellow oil (33.0 mg, 50%); R_f = 0.62 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 14.257 min, t_R(minor) 11.888 min; $[\alpha]_D^{25}$ = -130.02 (c = 0.37, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.67 (d, *J* = 2.4 Hz, 1H), 8.41 (dd, *J* = 6.0, 2.4 Hz, 1H), 8.22 (d, *J* = 12.0 Hz, 1H), 1.97 (s, 2H), 1.81 (s, 3H), 1.42 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.45, 149.05, 146.93, 145.99, 130.36, 126.67, 120.30, 83.08, 60.64, 27.85, 27.62; **HRMS(ESI)** m/z: $[M+Na]^+$ Calculated for $C_{13}H_{17}N_3NaO_6^+$ 334.1010; found 334.1011.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.837	BB	2.6183	4756.4868	238.9976	52.0594
	14.292	BB	2.1917	4380.1667	189.1064	47.9406

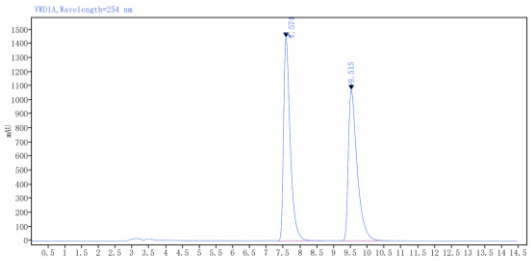
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.888	BB	2.0367	944.4390	47.4247	4.6108
	14.257	BBA	2.5333	19538.9641	835.5250	95.3892

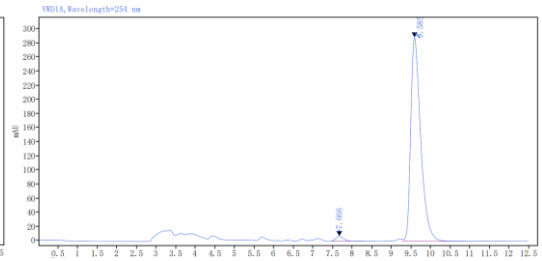
***tert*-Butyl (*S*)-2-amino-2-(4-cyano-2-nitrophenyl)propanoate (3ag):**



White solid (39.1 mg, 63%); m.p. = 78-79 °C; R_f = 0.26 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 9.585 min, t_R(minor) 7.666 min; $[\alpha]_D^{25}$ = -178.52 (c = 0.72, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.15 – 8.12 (m, 2H), 7.86 (d, *J* = 12.0 Hz, 1H), 2.02 (s, 2H), 1.78 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.52,

149.08, 144.36, 135.54, 130.03, 128.31, 116.39, 112.52, 82.90, 60.52, 27.71, 27.56; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{18}N_3O_4^+$ 292.1292; found 292.1294.

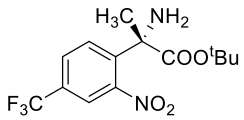




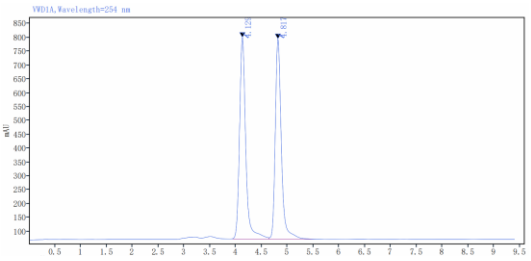
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.574	BB	1.3639	19845.8646	1441.5398	50.4400
	9.515	BB	1.5261	19499.6151	1069.2173	49.5600

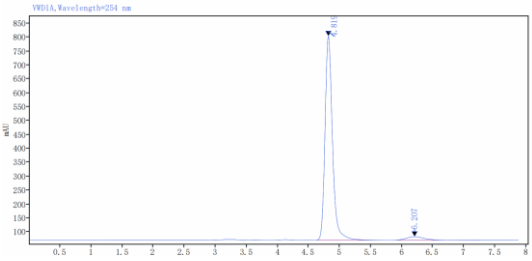
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.666	BB	0.8889	95.3911	6.8158	1.8397
	9.585	VB	1.5964	5089.6235	288.4410	98.1603

***tert*-Butyl (*S*)-2-amino-2-(2-nitro-4-(trifluoromethyl)phenyl)propanoate (3ah):**



A pale yellow oil (59.4 mg, 85%); R_f = 0.63 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.819 min, t_R(minor) 6.207 min; $[\alpha]_D^{25}$ = -113.01 (c = 0.50, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.13 (d, *J* = 12.0 Hz, 1H), 8.11 (s, 1H), 7.84 (d, *J* = 12.0 Hz, 1H), 2.07 (s, 2H), 1.79 (s, 3H), 1.42 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.91, 148.91, 143.04, 131.10, 130.87, 130.64, 129.68, 129.16, 129.14, 129.12, 129.09, 125.51, 123.71, 122.18, 122.15, 122.12, 122.10, 121.90, 82.67, 60.41, 27.78, 27.57; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{18}F_3N_2O_4^+$ 335.1213; found 335.1215.

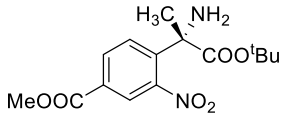




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.129	BV	0.7560	6093.7444	727.5999	50.8625
	4.817	VV	0.9090	5887.0736	722.8791	49.1375

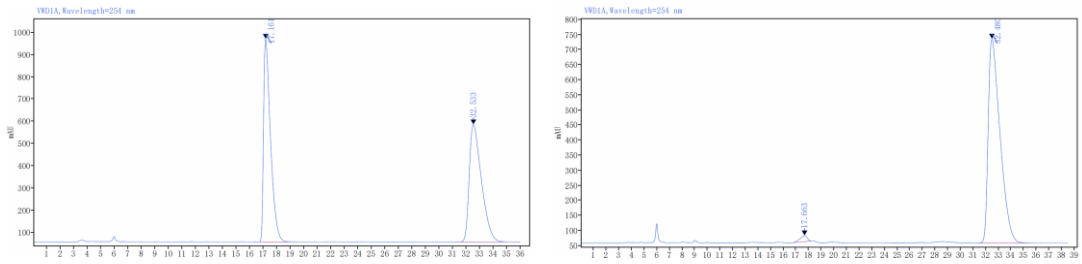
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.819	VB	1.1903	6089.9878	733.1863	96.1672
	6.207	BB	1.4600	242.7169	12.3837	3.8328

Methyl (*S*)-4-(2-amino-1-(*tert*-butoxy)-1-oxopropan-2-yl)-3-nitrobenzoate (3ai):



A pale yellow oil (46.8 mg, 69%); R_f = 0.45 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol =

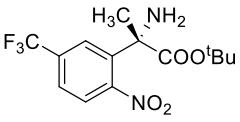
70/30, flow rate 1 mL/min, T = 30 °C), UV 254 nm, t_R(major) 32.480 min, t_R(minor) 17.663 min; $[\alpha]_D^{25}$ = -82.76 (c = 0.71, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.47 (s, 1H), 8.22 (d, *J* = 6.0 Hz, 1H), 8.02 (d, *J* = 6.0 Hz, 1H), 3.96 (s, 3H), 2.04 (s, 2H), 1.78 (s, 3H), 1.41 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 173.16, 164.87, 148.93, 143.58, 133.30, 130.43, 129.02, 126.03, 82.54, 60.47, 52.64, 27.86, 27.62; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{15}H_{21}N_2O_6^+$ 325.1394; found 325.1395.



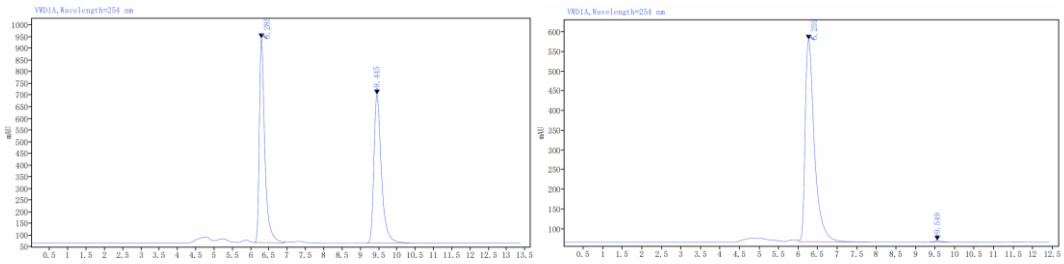
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	17.161	BB	4.5650	32653.3798	911.2702	49.8018
	32.533	BBA	4.8033	32913.3250	526.5886	50.1982

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	17.663	BB	1.5780	786.9834	19.8185	1.7603
	32.480	BB	5.3833	43919.8110	676.1935	98.2397

***tert*-Butyl (*S*)-2-amino-2-(2-nitro-5-(trifluoromethyl)phenyl)propanoate (3aj):**



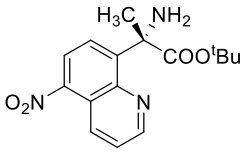
A pale yellow oil (52.1 mg, 74%); R_f = 0.73 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 99% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.259 min, t_R(minor) 9.549 min; $[\alpha]_D^{25}$ = -92.15 (c = 0.45, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.26 (s, 1H), 7.93 (d, *J* = 6.0 Hz, 1H), 7.69 (d, *J* = 12.0 Hz, 1H), 2.06 (s, 2H), 1.80 (s, 3H), 1.42 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.88, 150.82, 140.35, 134.58, 134.36, 134.14, 133.92, 126.19, 126.17, 126.14, 126.12, 125.36, 125.26, 125.24, 125.21, 125.19, 123.97, 122.17, 82.68, 60.37, 27.77, 27.55; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{18}F_3N_2O_4^+$ 335.1213; found 335.1215.



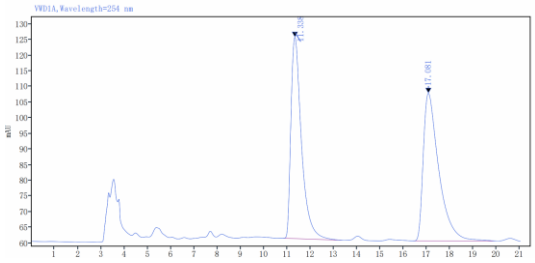
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.285	BV	0.8377	9101.3733	874.8949	49.9942
	9.445	BB	2.1067	9103.4686	636.1602	50.0058

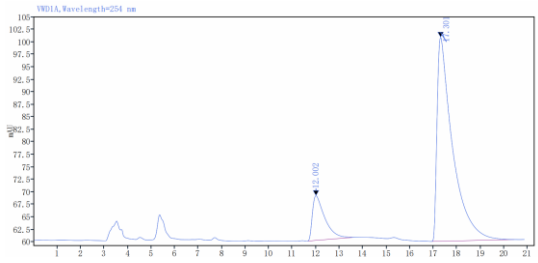
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.259	VB	1.8098	8476.8187	513.1982	99.3418
	9.549	BB	1.4200	56.1666	3.4080	0.6582

***tert*-Butyl (*S*)-2-amino-2-(5-nitroquinolin-8-yl)propanoate (3ak):**



White solid (39.2 mg, 62%); m.p. = 88-89 ºC; R_f = 0.28 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 70% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 17.301 min, t_R(minor) 12.002 min; $[\alpha]_D^{25}$ = -8.99 (c = 0.46, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 9.04 (d, *J* = 6.0 Hz, 1H), 8.95 (d, *J* = 6.0 Hz, 1H), 8.38 (d, *J* = 6.0 Hz, 1H), 7.98 (d, *J* = 12.0 Hz, 1H), 7.62 (dd, *J* = 12.0, 6.0 Hz 1H), 2.40 (s, 2H), 1.83 (s, 3H), 1.25 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.21, 150.34, 149.54, 145.59, 144.76, 132.39, 124.55, 124.05, 123.43, 121.24, 80.71, 60.10, 27.63, 25.63; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{20}N_3O_4^+$ 318.1448; found 318.1449.

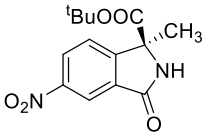




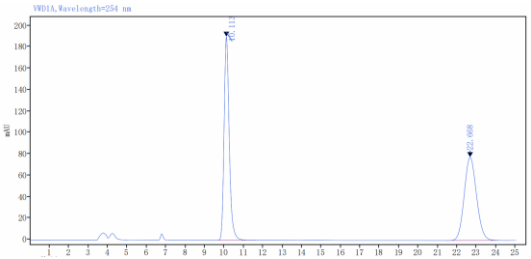
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	11.338	BB	2.5333	2031.3182	64.4242	48.1401
2	17.081	BB	3.6433	2188.2779	47.2373	51.8599

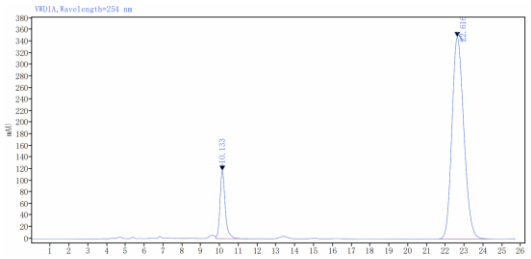
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.002	BB	1.9783	327.3358	8.9329	14.9145
2	17.301	BB	3.5133	1867.4167	40.7966	85.0855

***tert*-Butyl (*S*)-1-methyl-5-nitro-3-oxoisoindoline-1-carboxylate (3al):**



White solid (37.4 mg, 64%); m.p. = 124-126 ºC; R_f = 0.27 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 75% by HPLC aalysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 22.616 min, t_R(minor) 10.133 min; $[\alpha]_D^{25}$ = -9.97 (c = 0.49, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.65 (d, *J* = 6.0 Hz, 1H), 8.48 (m, 1H), 7.85 (d, *J* = 12.0 Hz, 1H), 7.38 (s, 1H), 1.84 (s, 3H), 1.47 (s, 9H); **^{13}C NMR (101 MHz, $CDCl_3$)** δ 168.63, 167.22, 152.01, 149.08, 132.58, 127.25, 124.51, 119.49, 84.21, 65.45, 27.78, 25.53; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{17}N_2O_5^+$ 293.1132; found 293.1131.

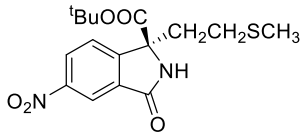




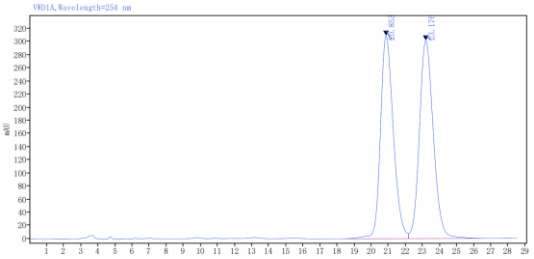
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.113	BB	1.9683	3508.4671	190.2345	50.6366
2	22.668	BB	3.2617	3420.2546	77.7864	49.3634

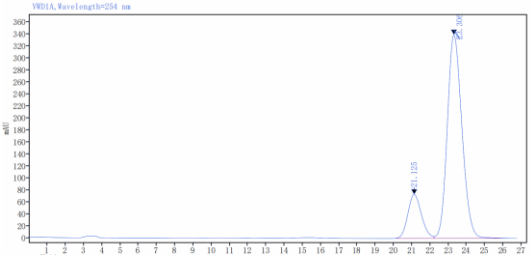
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.133	VB	1.7132	2242.3090	116.9036	12.7701
2	22.616	BB	3.4650	15316.7735	347.9157	87.2299

***tert*-Butyl (*S*)-1-(2-(methylthio)ethyl)-5-nitro-3-oxoisoindoline-1-carboxylate (3am):**



A pale yellow oil (41.0 mg, 58%); R_f = 0.34 (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 67% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 °C), UV 254 nm, t_R(major) 23.316 min, t_R(minor) 20.853 min; $[\alpha]_D^{25}$ = 2.64 (c = 0.32, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.65 (s, 1H), 8.48 (d, *J* = 6.0 Hz, 1H), 7.85 (d, *J* = 6.0 Hz, 1H), 7.48 (s, 1H), 2.67 – 2.62 (m, 1H), 2.55 – 2.50 (m, 1H), 2.37 – 2.33 (m, 1H), 2.24 – 2.19 (m, 1H), 2.08 (s, 3H), 1.48 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 167.81, 167.46, 150.46, 149.28, 132.84, 127.34, 124.44, 119.60, 84.64, 68.58, 37.81, 28.82, 27.82, 15.63; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{20}N_2NaO_5S^+$ 375.0985; found 375.0986.

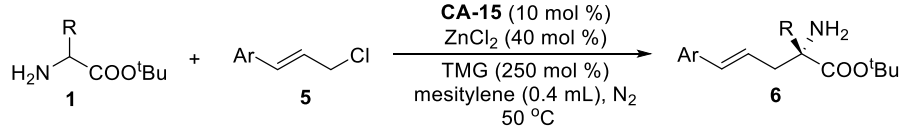




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	20.853	BV	4.0735	16127.2476	308.7899	48.6241
2	23.176	VB	4.7532	17039.9619	301.4502	51.3759

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	21.125	BV	2.2738	3809.3154	73.1804	16.7129
2	23.306	VBA	4.2562	18983.3662	339.3966	83.2871

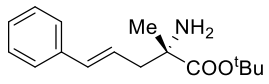
3.2 General procedure for the asymmetric α–allylation



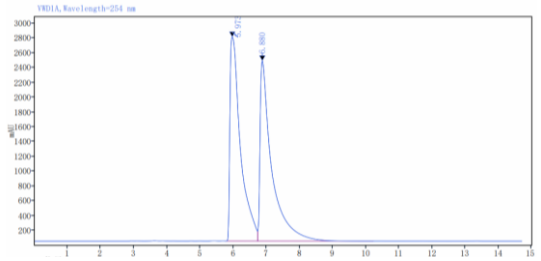
Under nitrogen atmosphere, amino acid ester **1** (0.30 mmol), allylic chloride derivative **5** (0.20 mmol), chiral aldehyde **CA-15** (11.8 mg, 0.02 mmol), $ZnCl_2$ (10.9 mg, 0.08 mmol), TMG (57.5 mg,

0.50 mmol) and super dry mesitylene (0.4 ml) were added to a 10 mL vial. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed (detected by TLC), the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3).

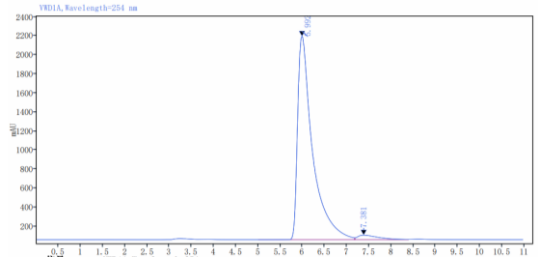
***tert*-Butyl (*S, E*)-2-amino-2-methyl-5-phenylpent-4-enoate (6a)** [3]**:**



Colorless oil (38.7 mg, 74%); R_f = 0.33 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IA column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.992 min, t_R(minor) 7.381 min; $[\alpha]_D^{20}$ = -10.83 (c = 0.74, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 6.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.20 (t, *J* = 9.0 Hz, 1H), 6.47 (d, *J* = 18.0 Hz, 1H), 6.16 – 6.11 (m, 1H), 2.64 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.39(dd, *J* = 13.6, 8.3 Hz, 1H), 1.67 (s, 2H), 1.47 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.37, 137.27, 133.95, 128.49, 127.28, 126.15, 124.82, 80.92, 58.09, 44.55, 28.03, 26.42.

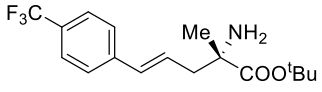


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.973	VV	0.9723	60748.0606	2752.0737	50.4644
	6.880	VB	3.4938	59629.9047	2430.7847	49.5356



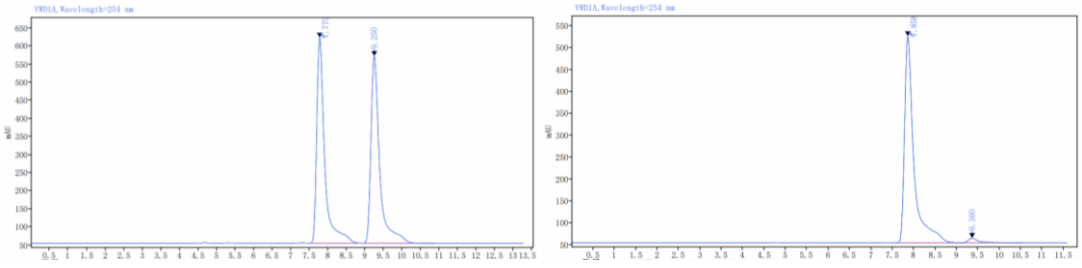
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.992	BV	2.1763	50143.3855	2137.0863	96.9955
	7.381	VV	1.2113	1553.2055	47.3853	3.0045

***tert*-Butyl (*S, E*)-2-amino-2-methyl-5-(4-(trifluoromethyl)phenyl)pent-4-enoate(6b)** [3]**:**



Colorless oil (44.8 mg, 68%); R_f = 0.44 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.858 min, t_R(minor) 9.360 min; $[\alpha]_D^{20}$ = -6.56 (c = 0.78, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 (s, 1H), 7.50 (d, *J* = 6.0 Hz, 1H), 7.46 (d, *J* = 6.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 6.51 (d, *J* = 18.0 Hz, 1H), 6.27 – 6.22 (m, 1H), 2.65 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.44 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.78 (s, 2H), 1.47 (s, 9H), 1.35 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.13, 138.01, 132.50, 131.12, 130.90, 129.24, 128.94, 127.09, 125.01, 123.85, 123.83, 123.80,

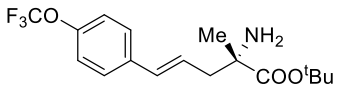
123.78, 123.21, 122.83, 122.81, 122.78, 122.75, 81.14, 58.09, 44.38, 27.99, 26.30.



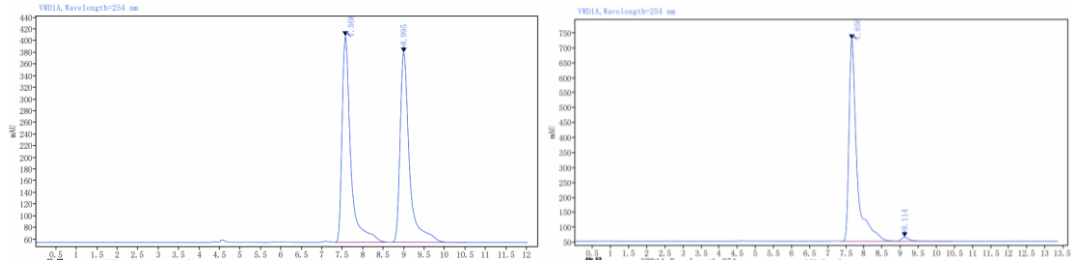
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.779	VB	1.4361	8518.3866	567.9994	50.0255
	9.250	BB	1.9461	8509.6909	517.0084	49.9745

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.858	VV	1.5284	7220.1320	471.6990	97.5496
	9.360	VB	1.4456	181.3691	10.3101	2.4504

***tert*-Butyl (*S, E*)-2-amino-2-methyl-5-(4-(trifluoromethoxy)phenyl)pent-4-enoate (6c):**



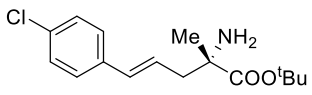
Colorless oil (37.3 mg, 54%); R_f = 0.47 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.565 min, t_R(minor) 9.114 min; $[\alpha]_D^{20}$ = -6.69 (c = 0.61, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 (s, 1H), 7.50 (d, *J* = 6.0 Hz, 1H), 7.46 (d, *J* = 12.0 Hz, 1H), 7.40 (t, *J* = 9.0 Hz 1H), 6.50 (d, *J* = 12.0 Hz, 1H), 6.26 – 6.21 (m, 1H), 2.65 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.43 (dd, *J* = 18.0, 12.0 Hz, 1H), 1.71 (s, 2H), 1.47 (s, 9H), 1.35 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.18, 138.01, 132.49, 131.12, 130.91, 129.24, 128.94, 127.11, 123.84, 123.81, 122.81, 122.78, 81.13, 77.19, 76.98, 76.77, 58.08, 44.40, 28.00, 26.33; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{17}H_{22}F_3NO_3^+$346.1625 ; found 346.1776.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.568	VB	1.3828	5193.5328	352.6162	50.0284
	8.995	BB	1.8433	5187.6296	324.5486	49.9716

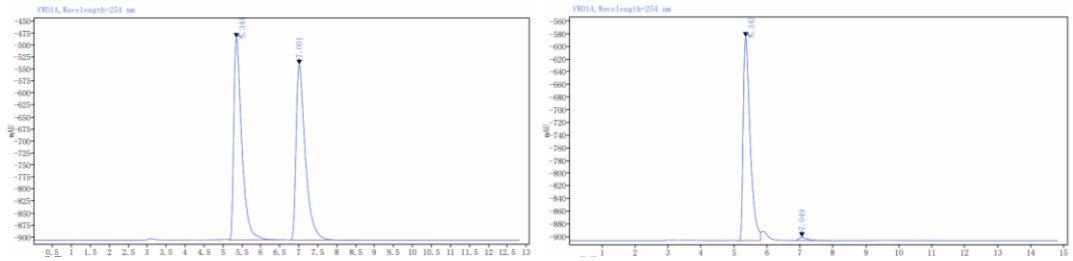
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.656	VV	1.4971	10294.2744	673.8683	97.8563
	9.114	VB	1.5438	225.5153	13.1346	2.1437

***tert*-Butyl (*S, E*)-2-amino-5-(4-chlorophenyl)-2-methylpent-4-enoate (6d)** [3]**:**



Colorless oil (35.4 mg, 60%); R_f= 0.39 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T

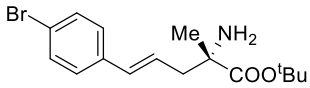
= 30 ºC), UV 254 nm, t_R(major) 5.345 min, t_R(minor) 7.049 min; $[\alpha]_D^{20}$ = -10.68 (c = 0.70, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.17 (s, 4H), 6.35 (d, *J* = 18.0 Hz, 1H), 6.07 – 6.02 (m, 1H), 2.55 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.31 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.69 (s, 2H), 1.39 (s, 9H), 1.26 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.23, 135.74, 132.91, 132.66, 128.65, 127.33, 125.62, 81.01, 58.07, 44.46, 28.01, 26.35.



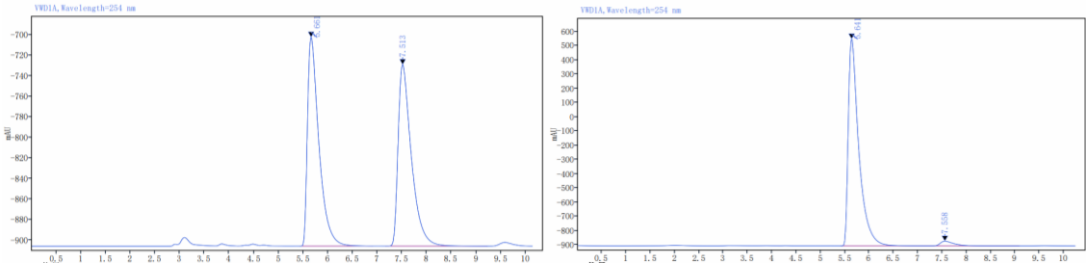
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.344	VB	1.3120	6135.5051	419.9301	49.8871
2	7.001	BB	1.8048	6163.2674	364.6493	50.1129

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.345	VV	0.6810	4713.3059	320.7555	98.1367
2	7.049	BB	1.1367	89.4900	4.9288	1.8633

***tert*-Butyl (*S, E*)-2-amino-5-(4-bromophenyl)-2-methylpent-4-enoate (6e):**



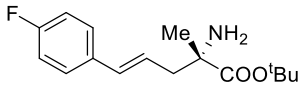
Colorless oil (40.7 mg, 51%); R_f= 0.34 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 5.641 min, t_R(minor) 7.558 min; $[\alpha]_D^{20}$ = -10.3 (c = 0.38, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 (d, *J* = 6.0 Hz, 2H), 7.19 (d, *J* = 6.0 Hz, 2H), 6.40 (d, *J* = 18.0 Hz, 1H), 6.16 – 6.11 (m, 1H), 2.62 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.38 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.74 (s, 2H), 1.46 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.22, 136.18, 132.72, 131.61, 127.67, 125.77, 121.02, 81.04, 58.07, 44.47, 28.02, 26.35; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{22}BrNO_2^+$ 340.0907; found 340.0908.



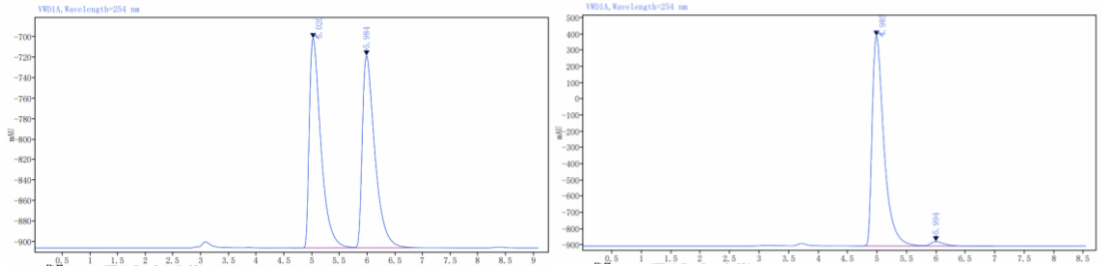
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.661	BB	1.4817	3273.7459	203.5210	49.8728
2	7.513	BB	2.0700	3290.4444	176.8166	50.1272

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.641	BB	1.7917	21887.3245	1454.2273	97.1900
2	7.558	BB	1.8767	632.8192	33.0343	2.8100

***tert*-Butyl (*S, E*)-2-amino-5-(4-fluorophenyl)-2-methylpent-4-enoate (6f)** [3]**:**



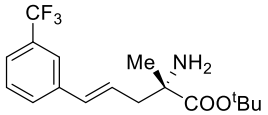
Colorless oil (39.6 mg, 71%); R_f= 0.51 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.985 min, t_R(minor) 5.994 min; $[\alpha]_D^{20}$ = -8.64 (c = 0.61, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.29 – 7.27 (m, 2H), 6.97 (t, *J* = 9.0 Hz, 2H), 6.44 (d, *J* = 18.0 Hz, 1H), 6.08 – 6.03 (m, 1H), 2.62 (dd, *J* = 18.0, 12.0 Hz, 1H), 2.38 (dd, *J* = 18.0, 12.0 Hz, 1H), 1.73 (s, 2H), 1.47 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.30, 162.99, 161.35, 133.43, 133.41, 132.71, 127.61, 127.56, 124.56, 115.43, 115.29, 80.96, 58.53, 44.44, 28.44, 26.36.



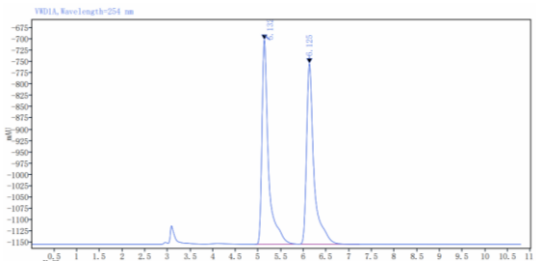
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.020	BV	1.1425	2959.4289	204.4150	50.0563
	5.984	VB	1.4025	2952.7688	187.3814	49.9437

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.985	BV	1.1288	18024.5355	1293.0875	97.5878
	5.994	VB	1.1744	445.5366	26.8412	2.4122

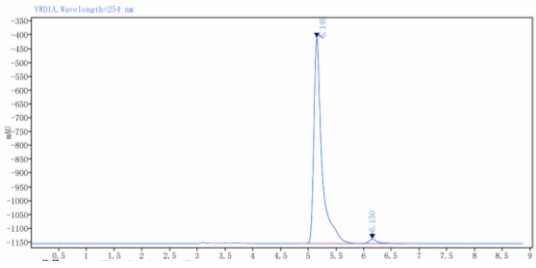
***tert*-Butyl (*S, E*)-2-amino-2-methyl-5-(3-(trifluoromethyl)phenyl)pent-4-enoate (6g):**



Colorless oil (45.3 mg, 69%); R_f= 0.39 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 5.149 min, t_R(minor) 6.150 min; $[\alpha]_D^{20}$ = -8.96 (c = 0.80, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.56 (s, 1H), 7.49 (d, *J* = 12.0 Hz, 1H), 7.46 (d, *J* = 12.0 Hz, 1H), 7.40 (t, *J* = 6.0 Hz, 1H), 6.50 (d, *J* = 12.0 Hz, 1H), 6.26 – 6.21 (m, 1H), 2.65 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.42 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.68 (s, 2H), 1.47 (s, 9H), 1.35 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.19, 138.02, 132.48, 131.13, 130.91, 129.24, 128.94, 127.13, 123.84, 123.81, 123.78, 122.83, 122.81, 122.78, 122.76, 81.12, 58.08, 44.41, 28.00, 26.33; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{17}H_{22}F_3NO_2^+$ 330.1675; found 330.1673.

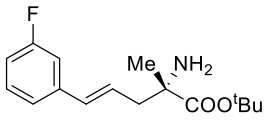


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.132	BB	0.9733	4568.9246	452.5829	49.9963
	6.125	BB	1.3333	4569.5968	399.9406	50.0037

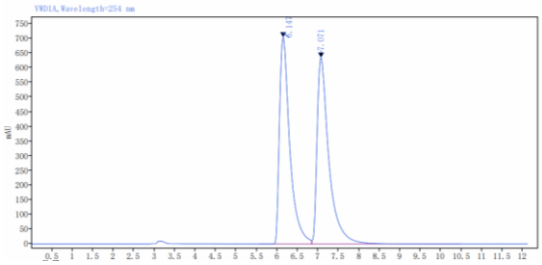


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.149	VV	1.0081	7538.8944	743.8283	97.7303
	6.150	VB	0.7550	175.0849	15.6170	2.2697

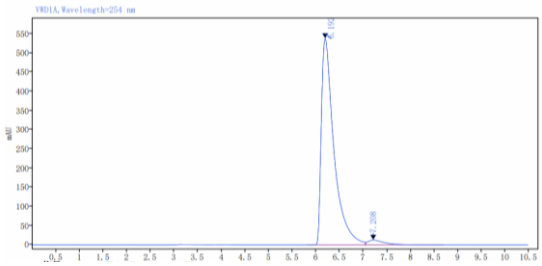
***tert*-Butyl (*S, E*)-2-amino-5-(3-fluorophenyl)-2-methylpent-4-enoate (6h)** [3]**:**



Colorless oil (37.2 mg, 67%); R_f= 0.44 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 6.192 min, t_R(minor) 7.208 min; $[\alpha]_D^{20}$ = -8.88 (c = 0.53, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.26 – 7.22 (m, 1H), 7.09 (d, *J* = 6.0 Hz, 1H), 7.02 (d, *J* = 12.0 Hz, 1H), 6.90 (t, *J* = 9.0 Hz, 1H), 6.44 (d, *J* = 12.0 Hz, 1H), 6.19 – 6.13 (m, 1H), 2.63 (dd, *J* = 18.0, 12.0 Hz, 1H), 2. 40 (dd, *J* = 18.0, 12.0 Hz, 1H), 1.65 (s, 2H), 1.47 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.24, 163.94, 162.32, 139.63, 139.58, 132.83, 132.81, 129.94, 129.89, 126.40, 122.01, 121.99, 114.14, 113.99, 112.66, 112.52, 81.05, 58.07, 44.40, 28.02, 26.38.

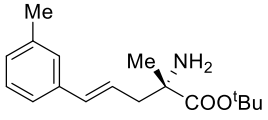


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.147	BV	1.2786	12397.1632	703.3873	49.4071
	7.071	VB	3.6481	12694.7264	633.9018	50.5929



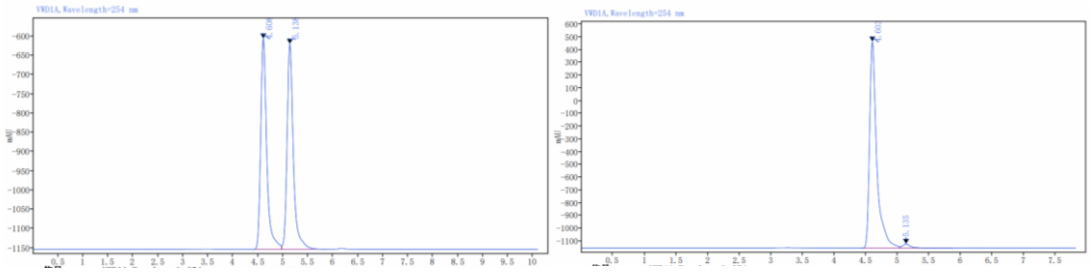
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.192	BV	1.2302	9930.3187	537.8134	97.0454
	7.208	VB	1.6482	302.3345	12.3605	2.9546

***tert*-Butyl (*S, E*)-2-amino-2-methyl-5-(*m*-tolyl)pent-4-enoate (6i):**



Colorless oil (33.6 mg, 61%); R_f= 0.28 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.603 min, t_R(minor) 5.135 min; $[\alpha]_D^{20}$ = -10.06 (c = 0.66, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.18 (t, *J* = 9.0 Hz, 1H), 7.13 (t, *J* = 6.0 Hz, 2H), 7.03 (d, *J* = 6.0 Hz, 1H), 6.45 (d, *J* = 18.0 Hz, 1H), 6.15 – 6.10 (m, 1H), 2.63 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.38 (dd, *J*

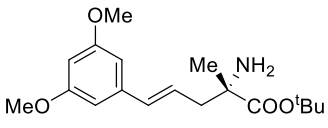
= 12.0, 6.0 Hz, 1H), 2.32 (s, 3H), 1.71 (s, 2H), 1.47 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.38, 138.02, 137.21, 134.05, 128.39, 128.08, 126.90, 124.54, 123.31, 80.92, 58.09, 44.53, 28.03, 26.40, 21.32; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{17}H_{25}NO_2^+$ 276.1958; found 276.1953.



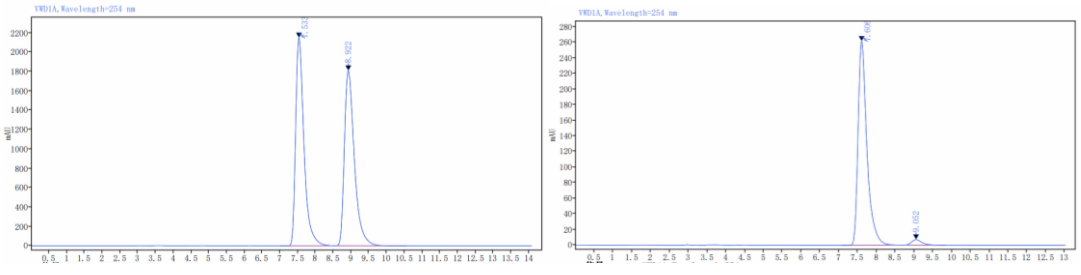
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.608	BV	0.5732	4600.1008	546.5921	49.7018
	5.138	VB	0.9085	4655.2994	532.9103	50.2982

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.603	BV	0.6136	12824.3822	1615.7847	97.7983
	5.135	VB	0.8363	288.7154	30.8769	2.2017

***tert*-Butyl (*S, E*)-2-amino-5-(3,5-dimethoxyphenyl)-2-methylpent-4-enoate (6j):**



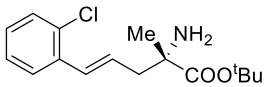
Colorless oil (34.7 mg, 54%); R_f = 0.28 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 92/8, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 7.606 min, t_R(minor) 9.052 min; $[\alpha]_D^{20}$ = -14.25 (c = 0.55, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 6.49 (d, *J* = 2.3 Hz, 2H), 6.40 (d, *J* = 18.0 Hz, 1H), 6.35 (s, 1H), 6.15 – 6.11 (m, 1H), 3.78 (s, 6H), 2.63 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.39 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.69 (s, 2H), 1.47 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.30, 160.94, 139.29, 133.92, 125.36, 104.39, 99.67, 80.98, 58.09, 55.29, 44.43, 28.02, 26.39; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{27}NO_4^+$ 322.2013; found 322.2005.



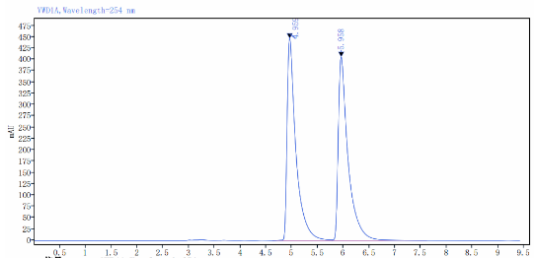
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.533	BB	1.5547	35097.3259	2146.4652	49.9039
	8.922	BB	2.0153	35232.4798	1806.9215	50.0961

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.606	BB	1.6239	4284.7416	261.9502	97.0098
	9.052	BB	1.1400	132.0735	6.9946	2.9902

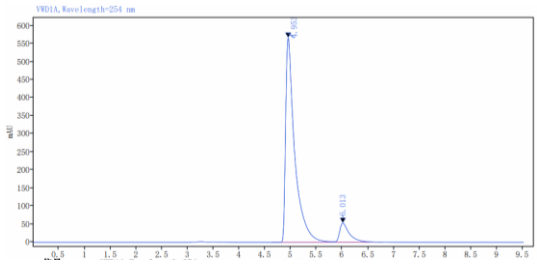
***tert*-Butyl (*S, E*)-2-amino-5-(2-chlorophenyl)-2-methylpent-4-enoate (6k):**



Colorless oil (43.2 mg, 73%); R_f= 0.44 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 82% by HPLC analysis on Daicel Chirapak IB column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.953 min, t_R(minor) 6.013 min; $[\alpha]_D^{20}$ = -8.04 (c = 0.79, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.48 (d, *J* = 6.0 Hz, 1H), 7.33 (d, *J* = 6.0 Hz, 1H), 7.20 – 7.14 (m, 2H), 6.85 (d, *J* = 18.0 Hz, 1H), 6.17 – 6.12 (m, 1H), 2.67 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.45 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.68 (s, 2H), 1.47 (s, 9H), 1.35 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.24, 135.37, 132.74, 130.10, 129.63, 128.29, 127.86, 126.84, 126.76, 81.07, 58.05, 44.62, 28.02, 26.42; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{22}ClNO_2^+$ 296.1412; found 296.1413.

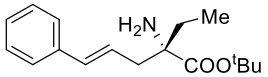


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.959	VV	1.1627	5347.6930	446.7169	49.8755
	5.958	VB	1.8345	5374.3912	405.7339	50.1245

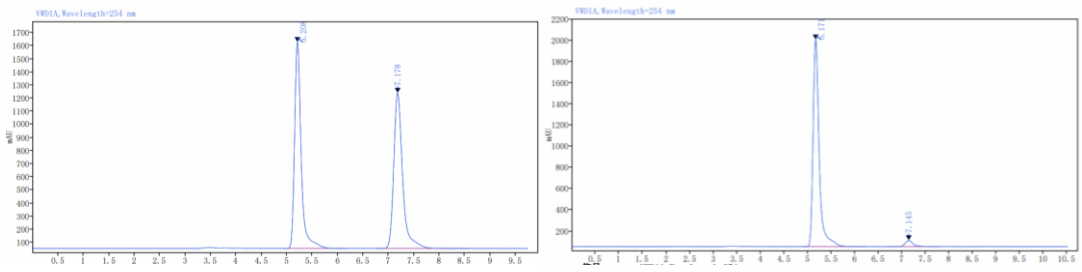


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.953	BV	1.1982	6931.1493	566.6859	90.8423
	6.013	VB	0.9401	698.7187	52.9051	9.1577

***tert*-Butyl (*S, E*)-2-amino-2-ethyl-5-phenylpent-4-enoate (6l)** [3]**:**



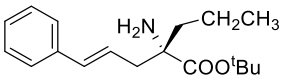
Colorless oil (31.4 mg, 57%); R_f= 0.51 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 5.171 min, t_R(minor) 7.145 min; $[\alpha]_D^{20}$ = -16.51 (c = 0.22, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 6.0 Hz, 2H), 7.29 (t, *J* = 9.0 Hz, 2H), 7.21 (t, *J* = 6.0 Hz, 1H), 6.49 (d, *J* = 18.0 Hz, 1H), 6.15 – 6.10 (m, 1H), 2.68 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.36 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.86 – 1.79 (m, 1H), 1.67 (s, 2H), 1.61 – 1.55 (m, 1H), 1.48 (s, 9H), 0.90 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.83, 137.25, 133.97, 128.50, 127.27, 126.15, 124.72, 80.97, 61.52, 43.39, 32.95, 28.09, 8.14.



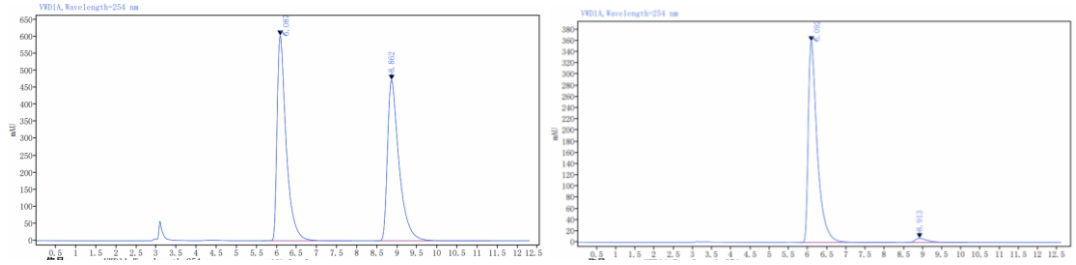
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.208	BB	1.2417	14216.0029	1571.9572	49.7117
	7.178	BB	1.8267	14380.9062	1184.3790	50.2883

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.171	BB	1.3492	17587.2488	1950.4628	96.2354
	7.145	BB	1.1167	687.9854	57.2995	3.7646

***tert*-Butyl (*S, E*)-2-amino-5-phenyl-2-propylpent-4-enoate (6m):**



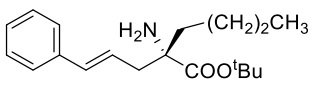
Colorless oil (28.4 mg, 49%); R_f = 0.64 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 6.092 min, t_R(minor) 8.913 min; $[\alpha]_D^{20}$ = -15.29 (c = 0.51, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 6.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.21 (t, *J* = 6.0 Hz, 1H), 6.48 (d, *J* = 18.0 Hz, 1H), 6.14 – 6.09 (m, 1H), 2.67 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.37 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.77 – 1.72 (m, 1H), 1.63 (s, 2H), 1.56 – 1.51 (m, 1H), 1.47 (s, 9H), 1.44 – 1.37 (m, 1H), 1.25 – 1.19 (m, 1H), 0.93 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.96, 137.25, 134.00, 128.50, 127.28, 126.16, 124.66, 80.97, 61.23, 43.75, 42.49, 28.09, 17.21, 14.44; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{27}NO_2^+$ 290.2115; found 290.2117.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.087	BB	2.2400	9456.8480	601.8007	50.0375
	8.862	BB	2.8750	9442.6570	471.8479	49.9625

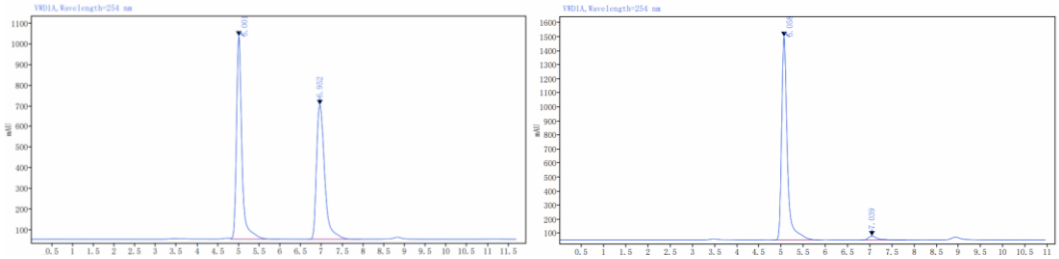
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.092	BB	2.4933	5848.3653	358.5941	97.3169
	8.913	BB	1.6300	161.2414	7.1114	2.6831

***tert*-Butyl (*S, E*)-2-amino-2-cinnamylhexanoate (6n)** [3]**:**



Colorless oil (41.5 mg, 68%); R_f = 0.72 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 5.058 min, t_R(minor) 7.039 min; $[\alpha]_D^{20}$ = -13.35 (c = 0.69, $CHCl_3$);

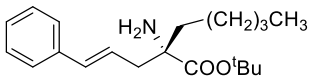
^{1}H NMR (600 MHz, $CDCl_3$) δ 7.33 (d, *J* = 6.0 Hz, 2H), 7.30 – 7.26 (m, 2H), 7.21 (t, *J* = 9.0 Hz, 1H), 6.48 (d, *J* = 12.0 Hz, 1H), 6.14 – 6.09 (m, 1H), 2.67 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.37 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.80 – 1.75 (m, 1H), 1.67 (s, 2H), 1.58 – 52 (m, 1H), 1.48 (s, 9H), 1.41 – 1.29 (m, 3H), 1.18 – 1.14 (m, 1H), 0.91 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.97, 137.25, 134.00, 128.49, 127.27, 126.15, 124.67, 80.94, 61.21, 43.77, 39.83, 28.09, 26.04, 22.97, 13.90.



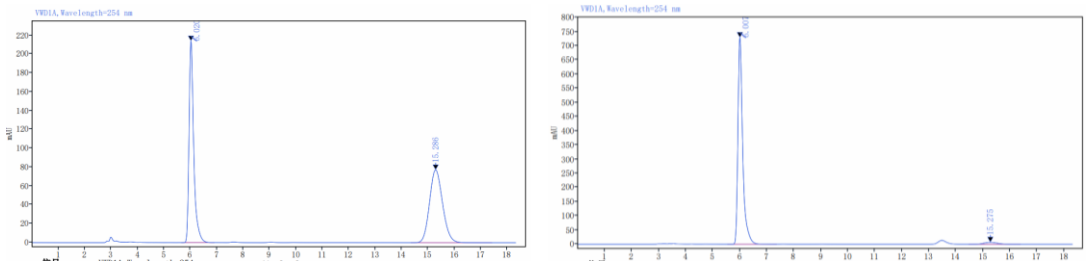
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.001	VB	1.1741	8948.0149	983.4792	50.2340
	6.952	BB	1.2808	8864.6432	650.5425	49.7660

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.058	VV	1.0281	12975.5386	1444.8752	97.2016
	7.039	BB	1.0109	373.5653	26.5902	2.7984

***tert*-Butyl (*S, E*)-2-amino-2-cinnamylheptanoate (6o):**



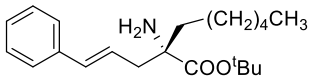
Colorless oil (28.2 mg, 43%); R_f= 0.69 (petroleum ether/ ethyl acetate = 3:1).; the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.007 min, t_R(minor) 15.275 min; $[\alpha]_D^{20}$ = -13.5 (c = 0.45, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 6.0 Hz, 2H), 7.29 – 7.26 (m, 2H), 7.20 (t, *J* = 6.0 Hz, 1H), 6.47 (d, *J* = 18.0 Hz, 1H), 6.14 – 6.09 (m, 1H), 2.67 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.36 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.78 – 1.74 (m, 1H), 1.67 (s, 2H), 1.56 – 1.51 (m, 1H), 1.47 (s, 9H), 1.42 – 1.36 (m, 1H), 1.34 – 1.26 (m, 4H), 1.23 – 1.16 (m, 1H), 0.89 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.97, 137.27, 133.99, 128.48, 127.26, 126.15, 124.67, 80.94, 61.25, 43.77, 40.12, 32.09, 28.09, 23.49, 22.42, 13.89; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{31}NO_2^+$ 318.2428; found 318.2424.



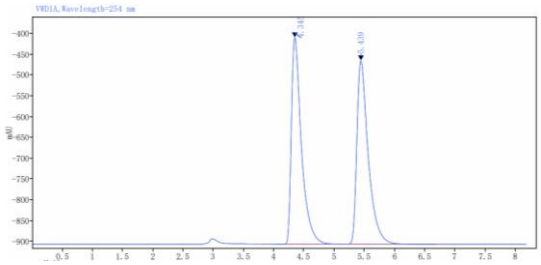
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.020	BB	1.2500	2652.5662	214.3539	49.9881
	15.286	BB	3.0767	2653.8247	77.3951	50.0119

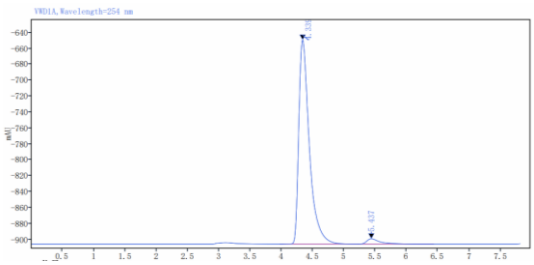
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.007	BB	1.8258	9036.1141	729.1401	97.3859
	15.275	BB	1.9133	242.5510	7.1045	2.6141

***tert*-Butyl (*S, E*)-2-amino-2-cinnamyloctanoate (6p):**



Colorless oil (34.3 mg, 50%); R_f= 0.64 (petroleum ether/ ethyl acetate = 4:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.339 min, t_R(minor) 5.437 min; $[\alpha]_D^{20}$= -17.3 (c = 0.21, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 (d, *J* = 6.0 Hz, 2H), δ 7.30 – 7.26 (m, 2H),7.20 (t, *J* = 12.0 Hz, 1H), 6.48 (d, *J* = 18.0 Hz, 1H), 6.14 – 6.09 (m, 1H), 2.67 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.37 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.79 – 1.74 (m, 1H), 1.65 (s, 2H), 1.56 – 1.51 (m, 1H), 1.47 (s, 9H), 1.40 – 1.35 (m, 1H), 1.33 – 1.26 (m, 6H), 1.20 – 1.14 (m, 1H), 0.89 – 0.87 (m, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.98, 137.25, 134.00, 128.49, 127.28, 126.16, 124.65, 80.95, 61.25, 43.77, 40.17, 31.63, 29.55, 28.09, 23.79, 22.50, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{33}NO_2^+$ 332.2584; found 332.2583.

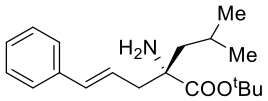




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.345	BB	1.0662	5737.2919	496.1821	49.9667
	5.439	BB	1.5905	5744.9416	440.7816	50.0333

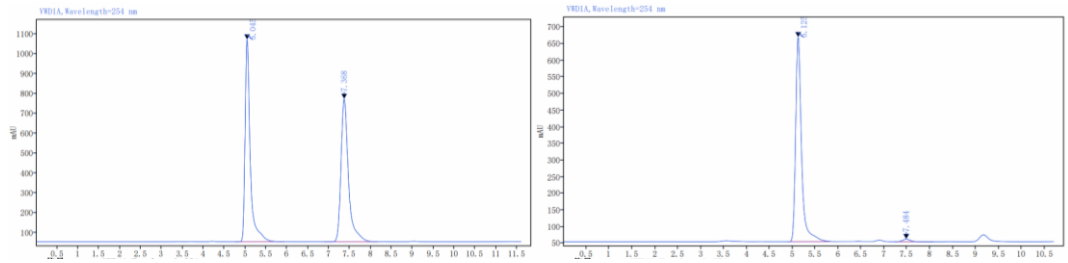
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.339	BV	1.2550	3014.6336	256.6383	96.7698
	5.437	VB	1.2083	100.6278	6.7121	3.2302

***tert*-Butyl (*S, E*)-2-amino-2-isobutyl-5-phenylpent-4-enoate (6q):**



Colorless oil (26.5 mg, 44%); R_f= 0.69 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 5.125 min, t_R(minor) 7.484 min; $[\alpha]_D^{20}$= -29.9 (c = 0.38, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.32 (d, *J* = 6.0 Hz, 2 H), 7.30 – 7.26 (m, 2H), 7.20 (t, *J* = 9.0 Hz, 1H), 6.47 (d, *J* = 12.0 Hz, 1H), 6.12 – 6.06 (m, 1H), 2.66 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.34 (dd, *J* = 12.0, 6.0 Hz, 1H), 1.80 – 1.76 (m, 2H), 1.69 (s, 2H), 1.55 – 1.52 (m, 1H), 1.48 (s, 9H), 0.97 (d, *J* = 12.0 Hz, 3H), 0.91 (d, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.43, 137.23, 134.17,

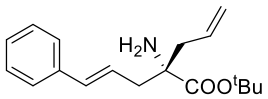
128.50, 127.29, 126.17, 124.41, 81.08, 61.02, 48.45, 45.30, 28.07, 24.65, 24.48, 23.46; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{29}NO_2^+$ 304.2271; found 304.2268.



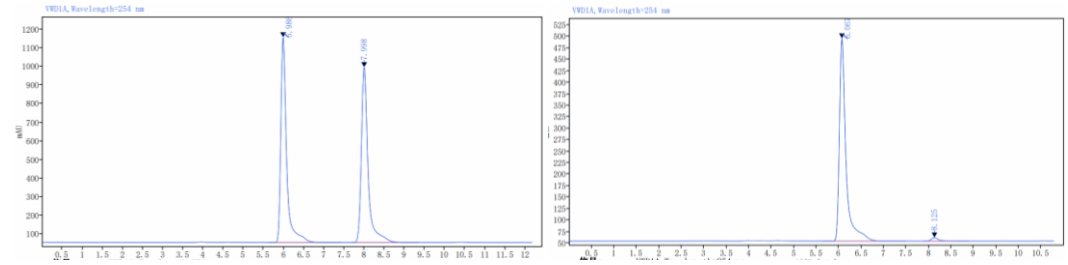
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.045	BB	1.1800	8769.7709	1015.8075	49.4933
	7.368	BV	1.2667	8949.3420	717.5975	50.5067

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.125	BB	1.0770	5532.6469	614.6690	98.3530
	7.484	BB	0.8550	92.6492	7.6602	1.6470

***tert*-Butyl (*S, E*)-2-allyl-2-amino-5-phenylpent-4-enoate (6r)** [3]**:**



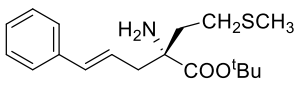
Colorless oil (27.3 mg, 48%); R_f = 0.53 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.067 min, t_R(minor) 8.125 min; $[\alpha]_D^{20}$ = 2.63 (c = 0.30, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 – 7.27 (m, 4H), 7.20 (t, *J* = 9.0 Hz, 1H), 6.49 (d, *J* = 18.0 Hz, 1H), 6.15 – 6.10 (m, 1H), 5.78 – 5.71 (m, 1H), 5.16 (t, *J* = 10.0 Hz, 2H), 2.68 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.59 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.38 (dd, *J* = 18.0, 12.0 Hz, 1H), 2.28 (dd, *J* = 18.0, 12.0 Hz, 1H), 1.71 (s, 2H), 1.47 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.33, 137.20, 134.13, 132.77, 128.50, 127.32, 126.17, 124.35, 119.22, 81.22, 60.76, 44.29, 43.58, 28.10.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.986	VB	1.7938	11096.0710	1103.1560	50.2617
	7.998	BB	1.6606	10980.5257	941.9023	49.7383

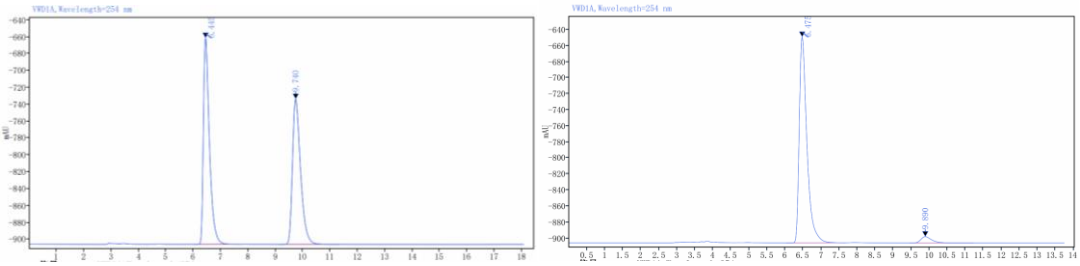
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.067	BB	1.8533	4548.0259	441.3258	98.0326
	8.125	BB	1.0250	91.2736	7.4355	1.9674

***tert*-Butyl (*R, E*)-2-amino-2-(2-(methylthio)ethyl)-5-phenylpent-4-enoate (6s)** [3]**:**



Colorless oil (33.2 mg, 52%); R_f = 0.53 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T

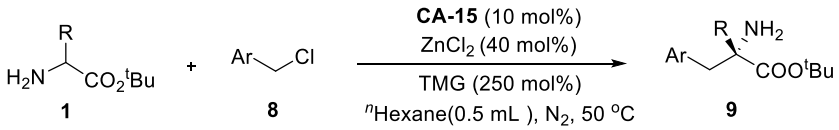
= 30 °C), UV 254 nm, t_R(major) 6.475 min, t_R(minor) 9.890 min; $[\alpha]_D^{20}$ = -2.73 (c = 0.46, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.33 – 7.28 (m, 4H), 7.21 (t, *J* = 6.0 Hz, 1H), 6.48 (d, *J* = 18.0 Hz, 1H), 6.12 – 6.07 (m, 1H), 2.67 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.58 (dd, *J* = 12.0, 6.0 Hz, 1H), 2.45 – 2.38 (m, 2H), 2.11 (s, 3H), 2.09 – 2.06 (m, 1H), 1.88 – 1.83 (m, 1H), 1.67 (s, 3H), 1.48 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.15, 137.06, 134.45, 128.53, 127.42, 126.18, 123.95, 81.46, 61.10, 43.77, 39.61, 28.86, 28.08, 15.56.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.445	BB	1.7033	3747.8737	244.3000	51.4955
	9.740	BB	2.2050	3530.1928	172.0637	48.5045

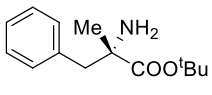
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.475	BB	1.6433	3815.3660	256.7280	95.9451
	9.890	BB	1.7733	161.2480	7.8042	4.0549

3.3 General procedure for the asymmetric α–benzylation



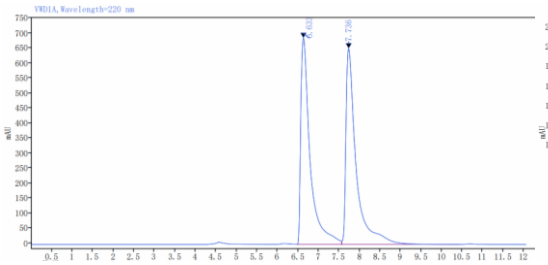
Under nitrogen atmosphere, amino acid ester **1** (0.30 mmol), benzylic chloride derivative **8** (0.20 mmol), chiral aldehyde **CA-15** (11.8 mg, 0.02 mmol), $ZnCl_2$ (10.9 mg, 0.08 mmol), TMG (57.5 mg, 0.50 mmol) and n-hexane (0.5 ml) were added to a 10 mL vial. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed (detected by TLC), the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =300/100/4).

***tert*-Butyl (*S*)-2-amino-2-methyl-3-phenylpropanoate (9a):**

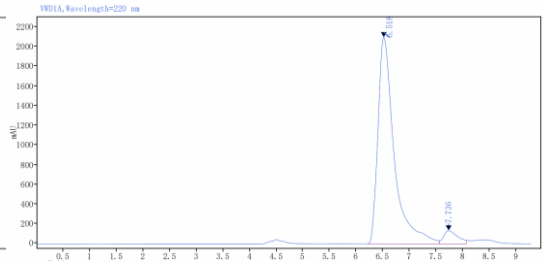


Colorless oil (33.4 mg, 71%); R_f = 0.6 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak OJ-H column (hexane/isopropanol = 98/2, flow rate 0.8 mL/min, T = 30 °C), UV 220 nm, t_R(major) 6.518 min, t_R(minor) 7.736 min; $[\alpha]_D^{25}$ = -12.96 (c = 0.58, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.27 (t, *J* = 6.0 Hz, 2H), 7.22 (t, *J* = 6.0 Hz, 3H), 3.10 (d, *J* = 12.0 Hz, 1H), 2.78

(d, J = 12.0 Hz, 1H), 1.58 (s, 2H), 1.45 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.28, 136.92, 130.22, 128.12, 126.74, 81.04, 58.74, 46.50, 27.99, 26.99; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{22}NO_2^+$ 236.1645; found 236.1642.

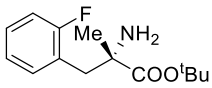


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.633	VV	1.0999	10869.2821	687.5171	48.9347
	7.736	VB	2.8759	11342.5376	652.6602	51.0653

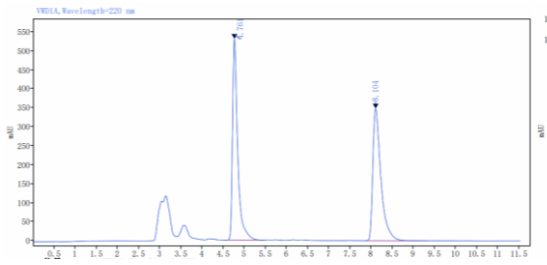


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.518	BV	1.3870	44363.1279	2096.2537	94.7318
	7.736	VM m	0.2727	2467.1012	134.0870	5.2682

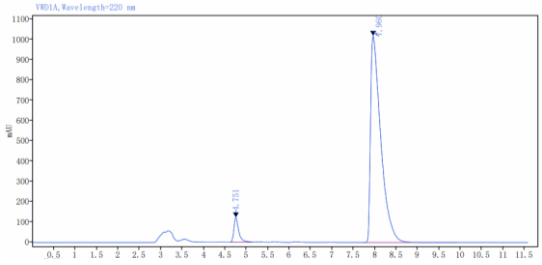
***tert*-Butyl (*S*)-2-amino-3-(2-fluorophenyl)-2-methylpropanoate (9b):**



Colorless oil (35.7 mg, 66%); R_f = 0.49 (petroleum ether/ ethyl acetate = 4:1); the enantiomeric excess was determined to be 89% by HPLC analysis on Daicel Chirapak IF column (hexane/isopropanol = 80/20, flow rate 1 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 7.960 min, t_R(minor) 4.751 min; $[\alpha]_D^{25}$ = -5.64 (c = 0.39, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.26 – 7.20 (m, 2H), 7.07 – 7.01 (m, 2H), 3.05 (d, J = 12.0 Hz, 1H), 2.95 (d, J = 18.0 Hz, 1H), 1.69 (s, 2H), 1.45 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.89, 162.36, 160.73, 132.54, 132.51, 128.54, 128.49, 123.97, 123.86, 123.69, 123.67, 115.38, 115.23, 81.19, 58.72, 39.11, 27.89, 26.26; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}FNO_2^+$ 254.1551; found 254.1548.

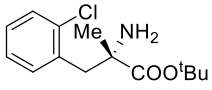


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.761	BB	0.9267	4532.8091	529.1050	49.4719
	8.104	BB	1.4867	4629.5765	347.2247	50.5281



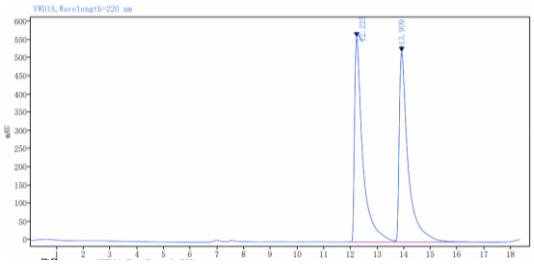
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.751	BV	0.5906	970.1320	121.0729	5.4321
	7.960	BB	2.1950	16889.2317	1016.4231	94.5679

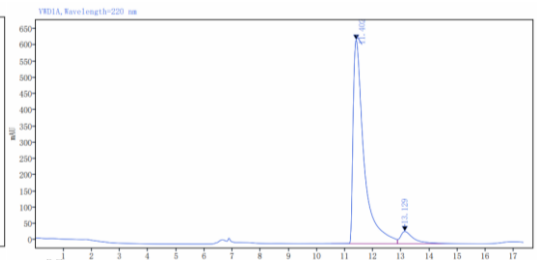
***tert*-Butyl (*S*)-2-amino-3-(2-chlorophenyl)-2-methylpropanoate (9c):**



Colorless oil (29.2 mg, 54%); R_f = 0.56 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 86% by HPLC analysis on

Daicel Chirapak OJ-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 11.402 min, t_R(minor) 13.129 min; $[\alpha]_D^{25}$ = -6.61 (c = 0.22, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.37 – 7.36 (m, 1H), 7.32 – 7.31 (m, 1H), 7.19 – 7.15 (m, 2H), 3.15 (t, *J* = 15.0 Hz, 2H), 1.70 (s, 2H), 1.47 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.98, 135.28, 135.01, 132.00, 129.69, 128.04, 126.40, 81.23, 59.30, 42.37, 27.93, 26.35; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}ClNO_2^+$ 270.1255; found 270.1245.

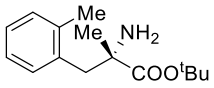




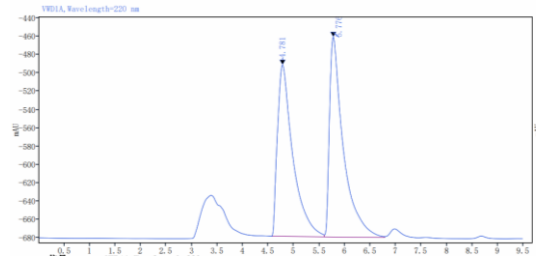
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.225	BV	2.3894	12018.9446	562.4213	49.7574
	13.909	VB	3.9439	12136.1293	521.9907	50.2426

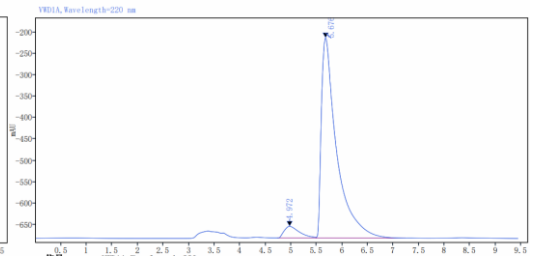
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.402	BV	2.3545	16751.2423	626.6725	93.1098
	13.129	VB	2.7155	1239.6045	37.5010	6.8902

***tert*-Butyl (*S*)-2-amino-2-methyl-3-(*o*-tolyl)propanoate (9d)** [7]**:**



Colorless oil (29.9 mg, 60%); R_f = 0.56 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 89% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 80/20, flow rate 1 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 5.676 min, t_R(minor) 4.972 min; $[\alpha]_D^{25}$ = -8.66 (c = 0.46, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.19 (d, *J* = 12.0 Hz, 1H), 7.15 (d, *J* = 6.0 Hz, 1H), 7.13 – 7.08 (m, 2H), 3.06 (d, *J* = 12.0 Hz, 1H), 2.94 (d, *J* = 12.0 Hz, 1H), 2.37 (s, 3H), 1.54 (s, 2H), 1.46 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.72, 137.47, 135.47, 130.49, 130.39, 126.65, 125.56, 81.02, 59.43, 42.19, 27.94, 27.04, 20.36.

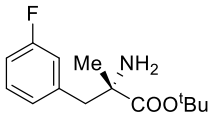




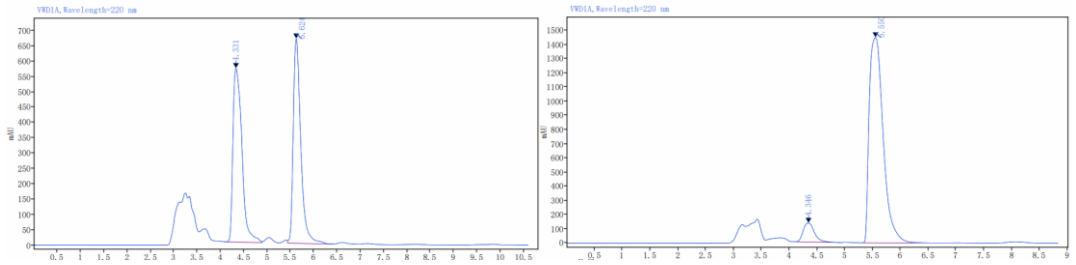
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.781	BV	1.0398	3934.9869	187.3900	48.8432
	5.776	VV	1.1817	4121.3865	218.4706	51.1568

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.972	BV	0.7643	560.2734	27.1176	5.4416
	5.676	VB	1.7507	9735.8266	466.9107	94.5584

***tert*-Butyl (*S*)-2-amino-3-(3-fluorophenyl)-2-methylpropanoate (9e):**



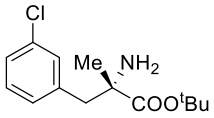
Colorless oil (31.8 mg, 63%); R_f = 0.44 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 86% by HPLC analysis on Daicel Chirapak IF column (hexane/isopropanol = 80/20, flow rate 1 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 5.550 min, t_R(minor) 4.346 min; $[\alpha]_D^{25}$ = -7.41 (c = 0.38, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.27 – 7.21 (m, 1H), 7.01 (d, *J* = 6.0 Hz, 1H), 6.96 – 6.92 (m, 2H), 3.09 (d, *J* = 12.0 Hz, 1H), 2.78 (d, *J* = 18.0 Hz, 1H), 1.70 (s, 2H), 1.46 (s, 9H), 1.35 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.93, 163.45, 161.83, 139.44, 139.39, 129.53, 129.48, 125.91, 125.89, 117.13, 113.74, 113.60, 81.37, 58.77, 46.10, 27.97, 26.91; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}FNO_2H^+$ 254.1551; found 254.1547.



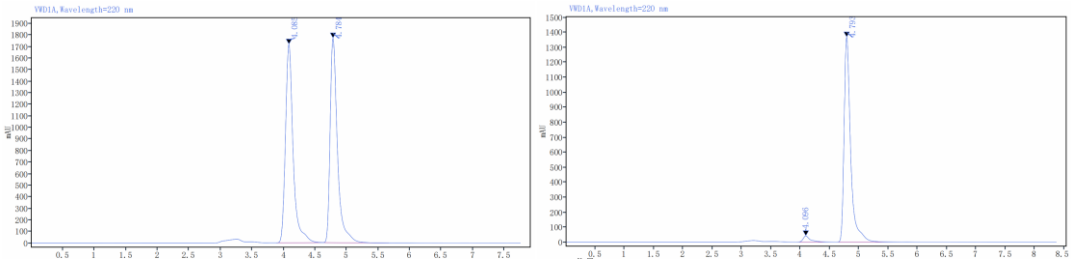
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.331	BV	0.7990	7587.2897	566.1825	50.3201
	5.624	VB	0.9472	7490.7598	666.7213	49.6799

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.346	BB	0.8273	1871.3379	132.6176	6.9183
	5.550	BB	1.2926	25177.5916	1446.0737	93.0817

***tert*-Butyl (*S*)-2-amino-3-(3-chlorophenyl)-2-methylpropanoate (9f):**

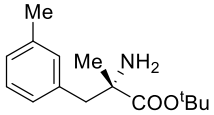


Colorless oil (40.1 mg, 74%); R_f = 0.56 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IF column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 4.793 min, t_R(minor) 4.096 min; $[\alpha]_D^{25}$ = -6.61 (c = 0.22, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.26 – 7.19 (m, 3H), 7.12 (d, *J* = 6.0 Hz, 1H), 3.07 (d, *J* = 12.0 Hz, 1H), 2.75 (d, *J* = 18.0 Hz, 1H), 1.58 (s, 2H), 1.46 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.98, 139.02, 133.98, 130.26, 129.32, 128.38, 126.94, 81.38, 58.74, 46.10, 27.98, 26.98; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{14}H_{20}ClNO_2^+$ 270.1255; found 270.1256.

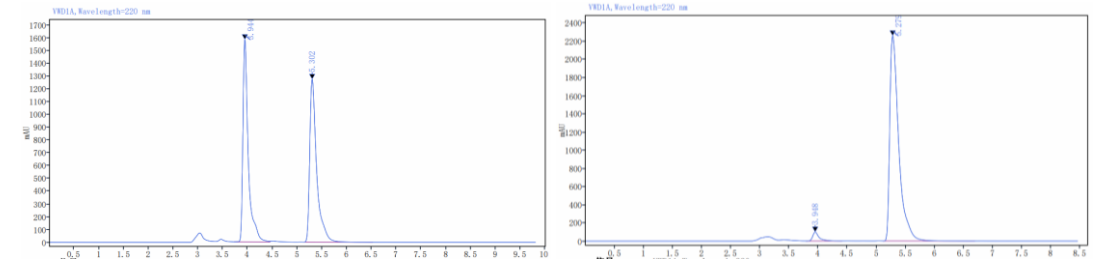


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.085	VB	0.7347	14495.5603	1715.7342	50.3146		4.096	VB	0.6826	343.2081	40.6132	3.1283
	4.784	BB	1.0444	14314.2768	1768.2509	49.6854		4.793	BV	1.1108	10627.9725	1366.6341	96.8717

***tert*-Butyl (*S*)-2-amino-2-methyl-3-(*m*-tolyl)propanoate (9g):**

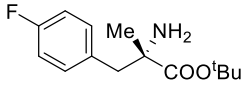


Colorless oil (39.8 mg, 80%); R_f = 0.49 (petroleum ether/ ethyl acetate = 4:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IF column (hexane/isopropanol = 70/30, flow rate 1 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 5.279 min, t_R(minor) 3.948 min; $[\alpha]_D^{25}$ = -7.56 (c = 0.52, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.16 (t, *J* = 6.0 Hz, 1H), 7.04 – 7.01 (m, 3H), 3.09 (d, *J* = 18.0 Hz, 1H), 2.73 (d, *J* = 12.0 Hz, 1H), 2.31 (s, 3H), 1.71 (s, 2H), 1.46 (s, 9H), 1.35 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.26, 137.65, 136.74, 130.95, 128.05, 127.51, 127.21, 81.06, 58.79, 46.36, 28.00, 27.05, 21.29; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{15}H_{23}NO_2^+$ 250.1802; found 250.1796.



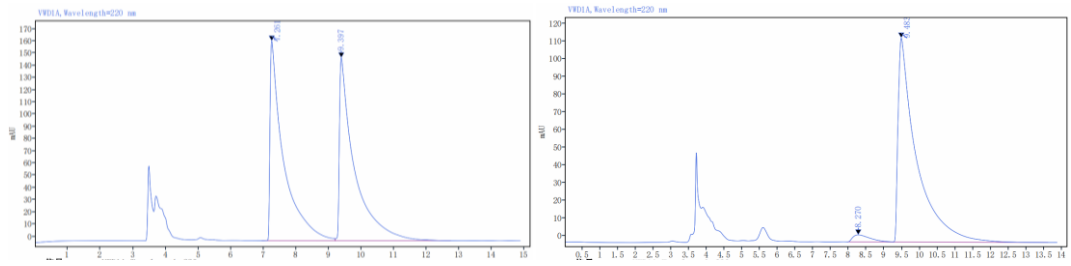
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	3.944	BV	0.7250	12004.8701	1583.8802	49.0742		3.948	VV	0.6179	769.8121	99.1303	3.0749
	5.302	VB	1.3991	12457.8142	1274.9678	50.9258		5.279	VB	1.5764	24265.6786	2259.3166	96.9251

***tert*-Butyl (*S*)-2-amino-3-(4-fluorophenyl)-2-methylpropanoate (9h)** [7]**:**



Colorless oil (29.4 mg, 58%); R_f = 0.39 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 95/5, flow rate 1 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 9.483 min, t_R(minor) 8.270 min; $[\alpha]_D^{25}$ = -5.52 (c = 0.72, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.19 (t, *J* = 6.0 Hz, 2H), 6.96 (t, *J* = 9.0 Hz, 1H), 3.07 (d, *J* = 12.0 Hz, 1H), 2.75 (d, *J* = 18.0 Hz, 1H), 1.71 (s, 2H), 1.45 (s, 9H), 1.34 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.15,

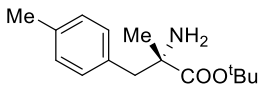
162.78, 161.15, 132.64, 132.62, 131.66, 131.61, 114.97, 114.83, 81.17, 58.71, 45.58, 27.98, 26.85.



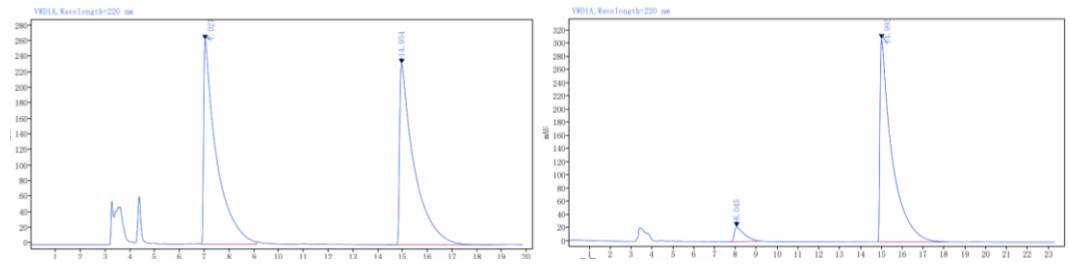
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.261	BV	2.2536	4687.8381	163.5356	49.6319
2	9.397	VB	3.5497	4757.3708	149.8298	50.3681

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.270	BV	1.3019	135.0608	3.9660	3.1622
2	9.483	VB	4.3647	4136.0261	115.2528	96.8378

***tert*-Butyl (*S*)-2-amino-2-methyl-3-(*p*-tolyl)propanoate (9i)** [7]**:**



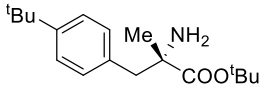
Colorless oil (37.4 mg, 75%); R_f= 0.53 (petroleum ether/ ethyl acetate = 3:1); The enantiomeric excess was determined to be 89% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 220 nm, t_R(major) 14.995 min, t_R(minor) 8.045 min; $[\alpha]_D^{25}$= -16.58 (c = 0.71, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.11 – 7.07 (m, 4H), 3.07 (d, *J* = 18.0 Hz, 1H), 2.73 (d, *J* = 12.0 Hz, 1H), 2.31 (s, 3H), 1.58 (s, 2H), 1.46 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.39, 136.26, 133.74, 130.07, 128.84, 80.99, 58.75, 46.01, 28.01, 26.95, 20.97.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.027	VV	2.2218	9384.6007	262.8221	49.9048
2	14.954	BB	4.3300	9420.3931	232.5488	50.0952

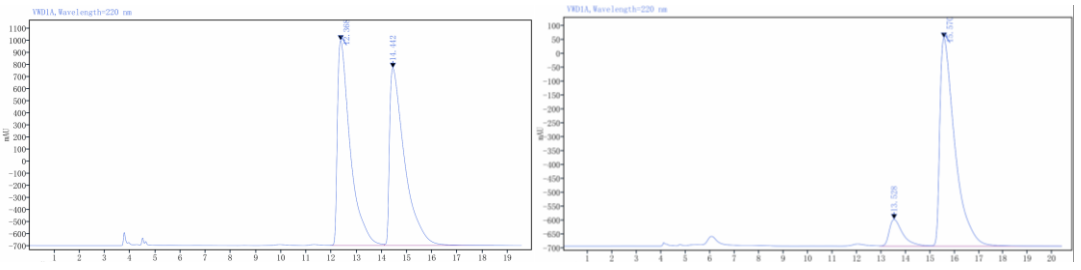
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.045	BM m	0.4762	716.1154	21.5191	5.5378
2	14.995	BB	4.1167	12215.2237	307.9258	94.4622

***tert*-Butyl (*S*)-2-amino-3-(4-(*tert*-butyl)phenyl)-2-methylpropanoate (9j)** [7]**:**



Colorless oil (34.4 mg, 59%); R_f= 0.21 (petroleum ether/ ethyl acetate = 4:1); the enantiomeric excess was determined to be 79% by HPLC analysis on Daicel Chirapak IF column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C), UV 220 nm, t_R(major) 15.570 min, t_R(minor) 13.528 min; $[\alpha]_D^{25}$ = -9.03 (c = 0.74, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 (t, *J* = 12.0 Hz, 2H), δ 7.15 (d, *J* = 6.0 Hz, 2H), 3.08 (d, *J* = 12.0 Hz, 1H), 2.75 (d, *J* = 12.0 Hz, 1H), 1.70 (s, 2H), 1.46 (s, 9H), 1.35 (s, 3H), 1.30 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.27, 149.62, 133.65, 129.89, 125.07, 81.09, 58.83, 45.84, 34.38, 31.34,

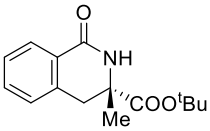
28.00, 26.89.



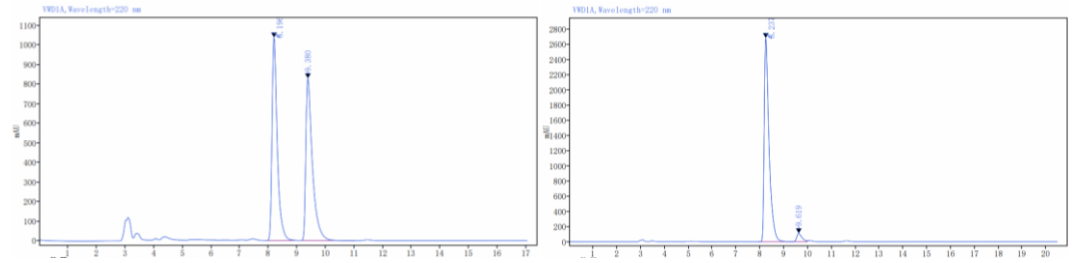
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.368	VV	2.1499	59978.9262	1693.5624	49.6117
	14.442	VB	4.3390	60917.9114	1465.0577	50.3883

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.528	VV	2.1040	3682.9793	95.9689	10.2951
	15.570	VBA	5.3567	32091.1282	749.0466	89.7049

***tert*-Butyl (*S*)-3-methyl-1-oxo-1,2,3,4-tetrahydroisoquinoline-3-carboxylate (9k):**



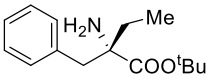
Colorless oil (27.2 mg, 52%); R_f = 0.52 (petroleum ether/ ethyl acetate = 3:2); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IF column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 8.237 min, t_R(minor) 9.619 min; $[\alpha]_D^{25}$ = 6.55 (c = 0.39, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.06 (d, *J* = 12.0 Hz, 1H), 7.45 (t, *J* = 6.0 Hz, 1H), 7.35 (t, *J* = 9.0 Hz, 1H), 7.21 (d, *J* = 12.0 Hz, 1H), 3.32 (d, *J* = 12.0 Hz, 1H), 3.06 (d, *J* = 18.0 Hz, 1H), 1.71 (s, 1H), 1.49 (s, 3H), 1.37 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.36, 165.34, 136.13, 132.41, 128.00, 127.71, 127.34, 82.61, 58.93, 37.98, 27.73, 25.33; **HRMS(ESI)** m/z: $[M+Na]^+$ Calculated for $C_{15}H_{19}NO_3Na^+$ 284.1257; found 284.1252.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.196	BB	1.1919	13211.2842	1034.7351	49.9447
	9.380	BB	1.9115	13240.5150	826.0238	50.0553

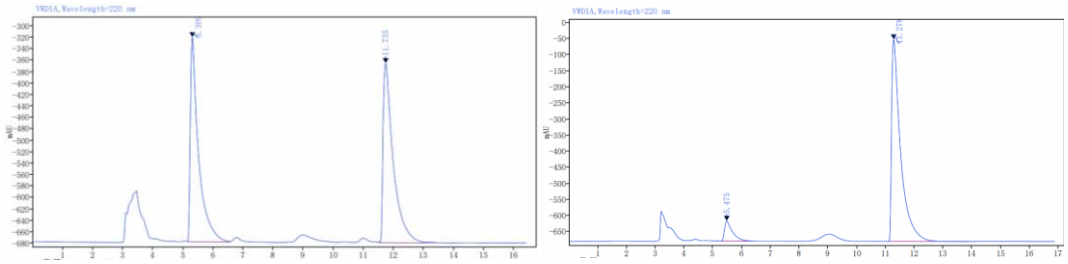
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.237	BV	1.4215	37900.0085	2680.4135	95.8424
	9.619	VV	0.6402	1644.0963	106.2072	4.1576

***tert*-Butyl (*S*)-2-amino-2-benzylbutanoate (9l)** [7]**:**



Colorless oil (22.9 mg, 46%); R_f = 0.42 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 84% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 11.278 min, t_R(minor) 5.475 min; $[\alpha]_D^{25}$ = -15.43 (c = 0.32, $CHCl_3$); **^{1}H NMR**

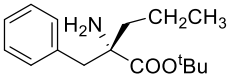
(600 MHz, $CDCl_3$) δ 7.27 (t, *J* = 6.0 Hz, 2H), 7.22 (t, *J* = 6.0 Hz, 3H), 3.16 (d, *J* = 18.0 Hz, 1H), 2.74 (d, *J* = 12.0 Hz, 1H), 1.94 – 1.88 (m, 1H), 1.59 (s, 2H), 1.57 – 1.55 (m, 1H), 1.46 (s, 9H), 0.91 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.62, 136.81, 130.23, 128.17, 126.76, 81.18, 62.28, 45.55, 33.58, 28.07, 8.16.



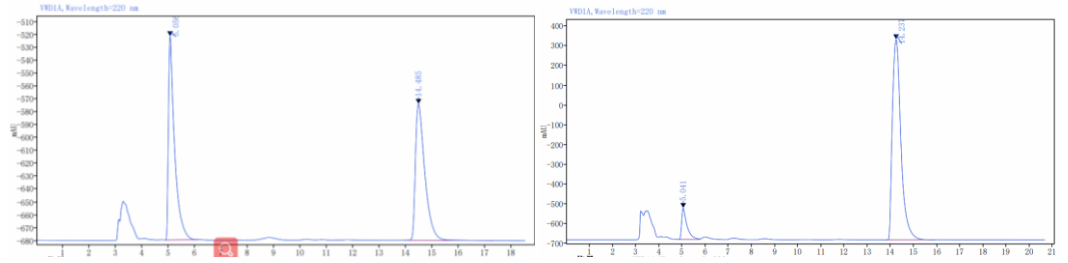
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.309	VV	1.4225	6760.7503	356.9086	48.0063
2	11.735	VB	2.5568	7322.2900	313.1000	51.9937

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.475	BB	1.5967	1188.7560	62.3062	8.0367
2	11.278	BB	2.7900	13602.8999	627.1181	91.9633

***tert*-Butyl (*S*)-2-amino-2-benzylpentanoate (9m):**



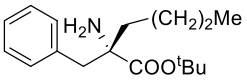
Colorless oil (23.2 mg, 44%); R_f = 0.36 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 83% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 14.237 min, t_R(minor) 5.041 min; $[\alpha]_D^{25}$ = -14.84 (c = 0.38, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 – 7.25 (m, 2H), 7.22 (t, *J* = 6.0 Hz, 3H), 3.15 (d, *J* = 12.0 Hz, 1H), 2.73 (d, *J* = 12.0 Hz, 1H), 1.86 – 1.81 (m, 1H), 1.58 (s, 2H), 1.56 – 1.51 (m, 1H), 1.45 (s, 9H), 1.42 – 1.39 (m, 1H), 1.23 – 1.20 (m, 1H), 0.94 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.77, 136.76, 130.24, 128.16, 126.76, 81.15, 61.98, 45.85, 43.17, 28.07, 17.24, 14.43; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{16}H_{25}NO_2^+$ 264.1958; found 264.1953.



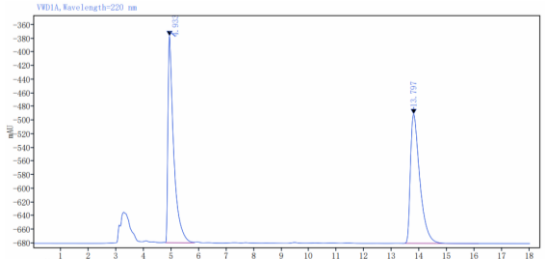
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.056	BB	1.2167	2566.6487	158.0930	49.5010
2	14.485	BB	3.3833	2618.3987	105.7623	50.4990

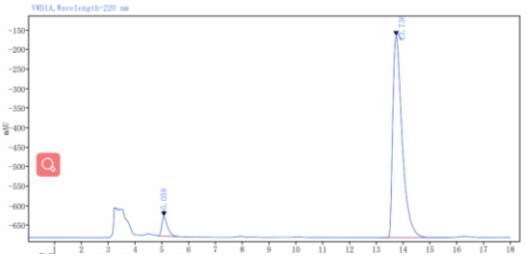
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.041	BV	0.9062	2486.1057	157.6024	8.7021
2	14.237	BB	2.1033	26082.8104	1013.4075	91.2979

***tert*-Butyl (*S*)-2-amino-2-benzylhexanoate (9n):**



Colorless oil (22.7 mg, 41%); R_f = 0.5 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 89% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 13.736 min, t_R(minor) 5.059 min; $[\alpha]_D^{25}$ = -12.36 (c = 0.30, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 – 7.25 (m, 2H), 7.22 (t, *J* = 6.0 Hz, 3H), 3.15 (d, *J* = 12.0 Hz, 1H), 2.74 (d, *J* = 18.0 Hz, 1H), 1.88 – 1.83 (m, 1H), 1.58 (s, 2H), 1.55 – 1.52 (m, 1H), 1.46 (s, 9H), 1.41 – 1.29 (m, 3H), 1.19 – 1.12 (m, 1H), 0.91 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.79, 136.78, 130.23, 128.16, 126.75, 81.13, 61.96, 45.89, 40.54, 28.08, 26.05, 23.00, 13.89; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{17}H_{27}NO_2^+$ 278.2115; found 278.2113.

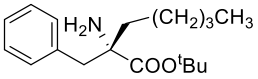




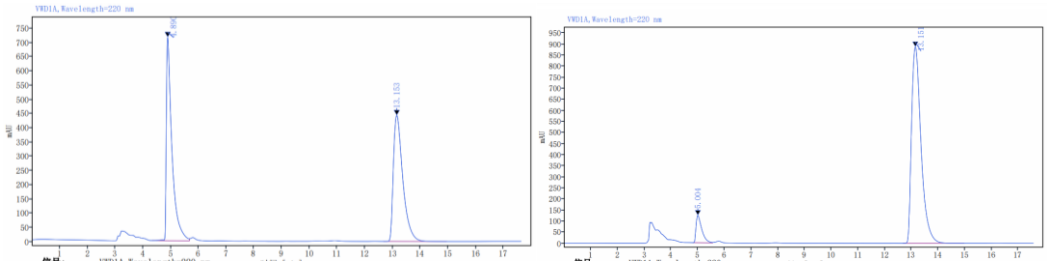
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.933	VV	1.0589	4388.7260	302.4166	49.4426
	13.797	BB	2.7567	4487.6723	189.1713	50.5574

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.059	VB	1.0662	748.8926	50.0759	5.6477
	13.736	BB	2.5517	12511.1642	515.8001	94.3523

***tert*-Butyl (*S*)-2-amino-2-benzylheptanoate (9o):**



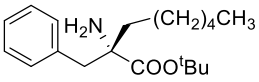
Colorless oil (26.8 mg, 46%); R_f = 0.75 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 85% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 13.151 min, t_R(minor) 5.004 min; $[\alpha]_D^{25}$ = -10.13 (c = 0.46, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 – 7.25 (m, 2H), 7.22 (d, *J* = 6.0 Hz, 3H), 3.15 (d, *J* = 12.0 Hz, 1H), 2.73 (d, *J* = 6.0 Hz, 1H), 1.87 – 1.82 (m, 1H), 1.64 (s, 2H), 1.56 – 1.51 (m, 1H), 1.45 (s, 9H), 1.42 – 1.36 (m, 1H), 1.33 – 1.27 (m, 4H), 1.21 – 1.16 (m, 1H), 0.89 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.78, 136.76, 130.23, 128.16, 126.76, 81.14, 61.99, 45.88, 40.83, 32.12, 28.07, 23.52, 22.44, 13.91; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{29}NO_2^+$ 292.2271; found 292.2262.



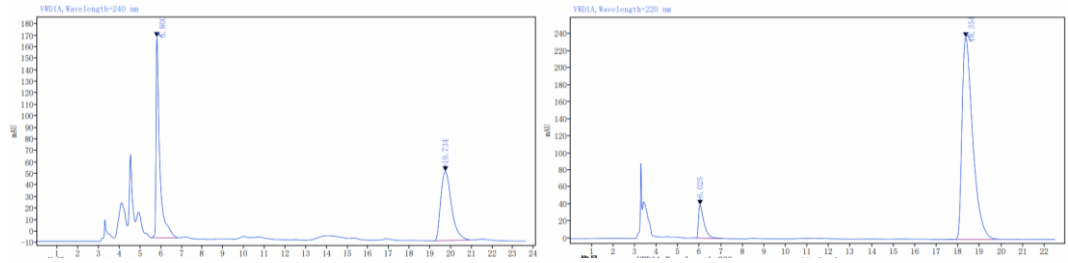
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.890	BV	1.3550	10113.8655	715.2091	49.1637
2	13.153	BB	2.2867	10457.9371	443.2493	50.8363

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.004	BV	0.7477	1837.3185	123.7025	7.7362
2	13.151	BB	2.2950	21912.1589	888.2301	92.2638

***tert*-Butyl (*S*)-2-amino-2-benzyloctanoate (9p):**



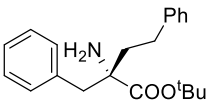
Colorless oil (26.8 mg, 46%); R_f = 0.39 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 85% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 220 nm, t_R(major) 18.354 min, t_R(minor) 6.025 min; $[\alpha]_D^{25}$ = -9.07 (c = 0.57, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.28 – 7.25 (m, 2H), 7.22 (t, *J* = 6.0 Hz, 3H), 3.15 (d, *J* = 12.0 Hz, 1H), 2.73 (d, *J* = 12.0 Hz, 1H), 1.87 – 1.83 (m, 1H), 1.57 (s, 2H), 1.54 – 1.51 (m, 1H)1.45 (s, 9H), 1.41 – 1.37 (m, 1H), 1.30 – 1.27 (m, 7H), 1.17 – 1.15 (m, 1H), 0.88 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.80, 136.78, 130.23, 128.16, 126.75, 81.12, 61.99, 45.90, 40.89, 31.64, 29.58, 28.08, 23.82, 22.50, 13.96. **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{31}NO_2^+$ 306.2428; found 306.2421.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.800	BB	1.3230	2162.7978	173.8553	50.0898
2	19.734	BB	1.8917	2155.0423	59.8318	49.9102

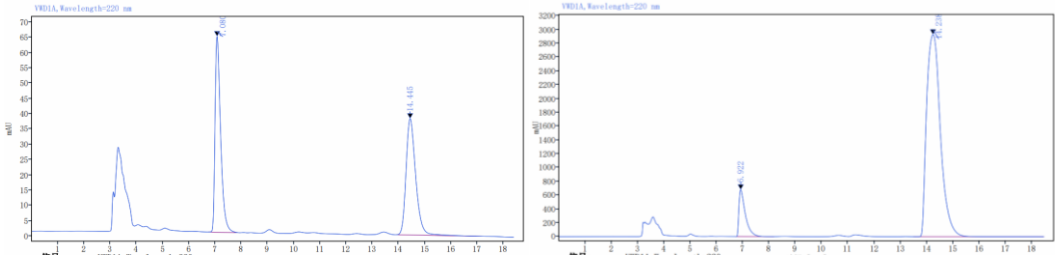
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.025	BB	1.6067	679.5234	38.6784	7.6797
2	18.354	BB	3.3667	8168.7541	237.0730	92.3203

***tert*-Butyl (*S*)-2-amino-2-benzyl-4-phenylbutanoate (9q):**



Colorless oil (31.2 mg, 48%); R_f = 0.63 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 81% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 220 nm, t_R(major) 14.238 min, t_R(minor) 6.922 min; $[\alpha]_D^{25}$ = -7.58 (c = 0.55, $CHCl_3$); **^{1}H NMR (600**

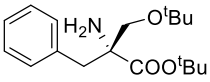
MHz, $CDCl_3$) δ 7.30 – 7.27 (m, 4H), 7.24 – 7.20 (m, 3H), 7.19 (d, *J* = 6.0 Hz, 3H), 3.18 (d, *J* = 12.0 Hz, 1H), 2.79 (d, *J* = 12.0 Hz, 1H), 2.75 – 2.70 (m, 1H), 2.53 – 2.48 (m, 1H), 2.19 – 2.14 (m, 1H), 1.89 – 1.84 (m, 1H), 1.61 (s, 2H), 1.51 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.50, 141.87, 136.49, 130.26, 128.48, 128.33, 128.24, 126.88, 125.95, 81.45, 62.01, 45.95, 42.86, 30.62, 28.16; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{27}NO_2^+$ 326.2115; found 326.2115.



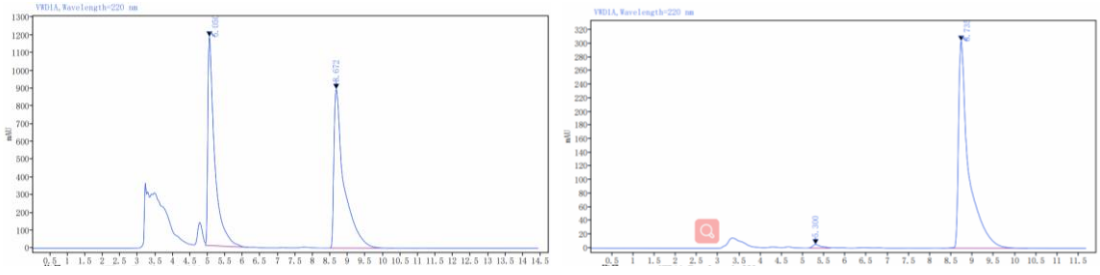
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.080	BB	1.1967	949.6387	64.1236	49.2953
2	14.445	BB	3.3067	976.7885	38.1240	50.7047

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.922	VV	1.4428	11486.4019	678.8972	9.7063
2	14.238	BBA	4.9633	106853.4383	2928.3938	90.2937

***tert*-Butyl (*R*)-2-amino-2-benzyl-3-(*tert*-butoxy)propanoate (9r)** [7]**:**



Colorless oil (28.9 mg, 47%); R_f = 0.56 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IC column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 220 nm, t_R(major) 8.735 min, t_R(minor) 5.300 min; $[\alpha]_D^{25}$ = 2.73 (c = 0.37, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.26 (t, *J* = 6.0 Hz, 2H), 7.22 (t, *J* = 6.0 Hz, 3H), 3.72 (d, *J* = 6.0 Hz, 1H), 3.31 (d, *J* = 6.0 Hz, 1H), 3.04 (d, *J* = 12.0 Hz, 1H), 2.70 (d, *J* = 12.0 Hz, 1H), 1.77 (s, 2H), 1.44 (s, 9H), 1.17 (s, 9H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 174.55, 136.10, 130.18, 128.13, 126.76, 80.90, 72.79, 68.52, 62.57, 42.15, 28.05, 27.44.

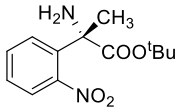
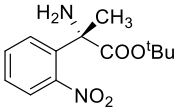


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.050	VB	1.2147	15982.6790	1175.0382	47.2404
2	8.672	BB	1.9533	17849.9903	893.7907	52.7596

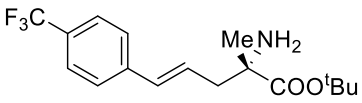
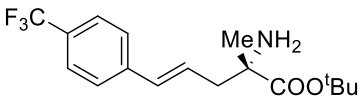
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.300	BV	0.5800	72.9428	5.1355	1.4062
2	8.735	BB	2.0267	5114.1983	304.3673	98.5938

4. Determination of the absolute configuration

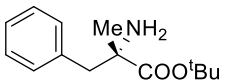
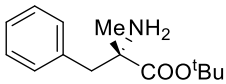
The absolute configuration of compound **3a** was established by comparing its optical rotation value with the literature data:

(*S*)-product (**3a**) in this work	(*S*)-product in literature[6]
 *tert*-butyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate	 *tert*-butyl (*S*)-2-amino-2-(2-nitrophenyl)propanoate
$[\alpha]_D^{28}$ = -58.93 (c 0.67, $CHCl_3$)	$[\alpha]_D^{28}$ = -71.10 (c 1.50, $CHCl_3$)

The absolute configuration of compound **6b** was established by comparing its optical rotation value with the literature data:

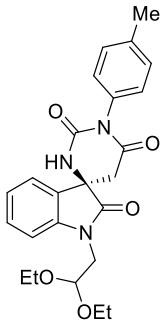
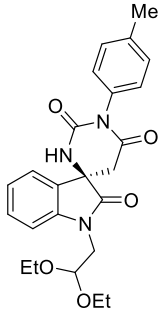
(*S*)-product (**6b**) in this work	(*S*)-product in literature[3]
 *tert*-butyl (*S*,*E*)-2-amino-2-methyl -5-(4-(trifluoromethyl)phenyl)pent-4-enoate	 *tert*-butyl (*S*,*E*)-2-amino-2-methyl -5-(4-(trifluoromethyl)phenyl)pent-4-enoate
$[\alpha]_D^{20}$ = -6.56 (c 0.78, $CHCl_3$)	$[\alpha]_D^{20}$ = -8.30 (c 1.0, $CHCl_3$)

The absolute configuration of compound **9a** was established by comparing its optical rotation value with the literature data:

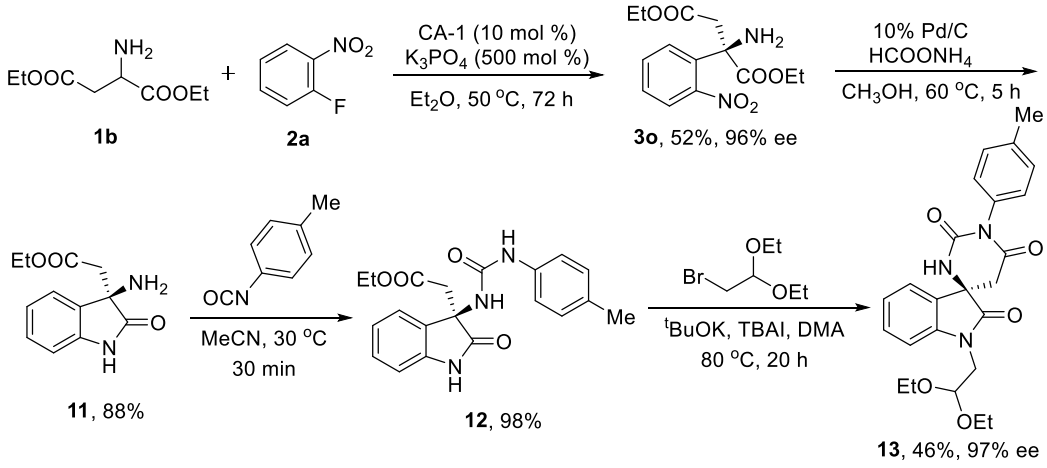
(*S*)-product (**9a**) in this work	(*S*)-product in literature[7]
 *tert*-butyl (*S*)-2-amino-2-methyl-3-phenylpropanoate	 *tert*-butyl (*S*)-2-amino-2-methyl-3-phenylpropanoate
$[\alpha]_D^{25}$ = -12.96 (c 0.58, $CHCl_3$)	$[\alpha]_D^{25}$ = -27.54 (c 0.47, $CHCl_3$)

The absolute configuration of compound **13** was established by comparing its optical rotation value with the literature data:

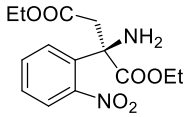
(*R*)-product (**13**) in this work	(*R*)-product in literature[8]

 (*R*)-1-(2,2-diethoxyethyl)-1'-(*p*-tolyl)-1'*H*-spiro [indoline-3,4'-pyrimidine]-2,2',6'(3'*H*,5'*H*)-trione	 (*R*)-1-(2,2-diethoxyethyl)-1'-(*p*-tolyl)-1'*H*-spiro [indoline-3,4'-pyrimidine]-2,2',6'(3'*H*,5'*H*)-trione
$[\alpha]_D^{24}$ = 59.16 (c 0.22, $CHCl_3$)	$[\alpha]_D^{24}$ = 61.30 (c 1.28, $CHCl_3$)

5. The formal synthesis of (+)-AG-041R

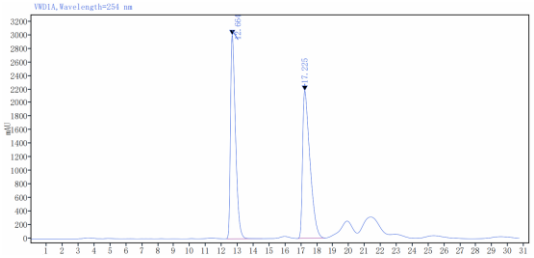


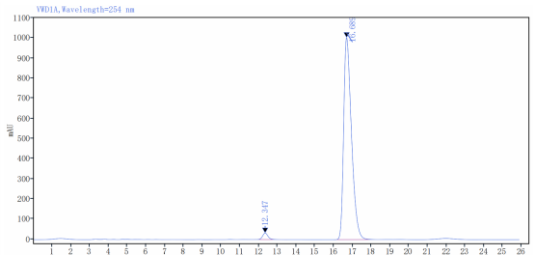
Diethyl (*R*)-2-amino-2-(2-nitrophenyl)succinate (3o)



Chiral aldehyde **CA-1** (6.3 mg, 0.02 mmol), amino acid ester **1b** (75.6 mg, 0.04 mmol), Et_2O (2 mL) and K_3PO_4 (212 mg, 1 mmol) were added successively to a 10 mL reaction tube with stirring magneton. The mixture was stirred for 10 min at room temperature, and then compound **2a** (28.2 mg, 0.02 mmol) was added. The reaction system was sealed and continuously stirred at 50 ℃ for 72 h. After the reaction completed (detected by TLC), the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =300/100/4) to give a pale yellow oil **3o** (32.2 mg, 52%); R_f= 0.42 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IG column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃), UV 254 nm, t_R(major) 16.689 min, t_R(minor) 12.347 min; $[\alpha]_D^{25}$ = -57.86 (c = 0.58, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.91 (d, *J* = 6.0 Hz, 1H), 7.77 (d,

J = 6.0 Hz, 1H), 7.58 (t, J = 9.0 Hz, 1H), 7.45 (t, J = 9.0 Hz, 1H), 4.19 (q, J = 6.0 Hz, 2H), 4.11 (q, J = 6.0 Hz, 2H), 3.25 (d, J = 18.0 Hz, 1H), 3.12 (d, J = 18.0 Hz, 1H), 2.61 (s, 2H), 1.25 – 1.20 (m, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 172.73, 170.80, 149.24, 136.29, 132.22, 128.80, 128.77, 124.94, 62.20, 61.95, 60.75, 42.76, 14.03, 13.84; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{18}H_{20}NO_3^+$ 298.1438; found 298.1435.

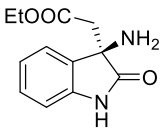




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.664	BB	2.3317	65794.4445	2997.1415	48.3356
	17.225	BB	1.7646	70325.7028	2172.0285	51.6644

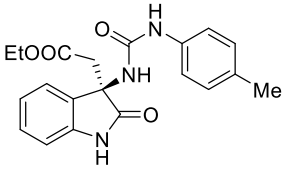
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.347	BB	1.8233	640.0913	32.3327	2.1559
	16.689	BB	2.3383	29050.3166	1003.7082	97.8441

Ethyl (*R*)-2-(3-amino-2-oxo`indolin-3-yl)acetate (11)



The compound **3o** (31.3 mg, 0.01 mmol), NH_4HCO_2 (63.1 mg, 1 mmol), 10% Pd/C (3.0 mg, 0.001 mmol) and MeOH (1 mL) were added into a 10 mL reaction tube. The reaction system was sealed and stirred for 5 h at 60 ℃. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ =1/3) to give white solid **11** (20.6 mg, 0.088 mmol, 88%); m.p. = 143-145 ºC; R_f = 0.26 (petroleum ether/ ethyl acetate = 1:3); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 8.22 (s, 1H), 7.38 (d, J = 12.0 Hz, 1H), 7.28 – 7.22 (m, 1H), 7.04 (t, J = 9.0 Hz, 1H), 6.89 (d, J = 12.0 Hz, 1H), 4.01 (m, 2H), 2.94 (s, 2H), 1.85 (s, 2H), 1.10 (t, J = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 180.96, 169.47, 140.71, 131.34, 129.36, 124.14, 122.83, 110.08, 60.65, 58.90, 42.66, 13.87; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{12}H_{15}N_2O_3^+$ 235.1077; found 235.1079.

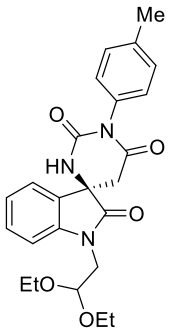
Ethyl (*R*)-2-(2-oxo-3-(3-(*p*-tolyl)ureido)indolin-3-yl)acetate (12)



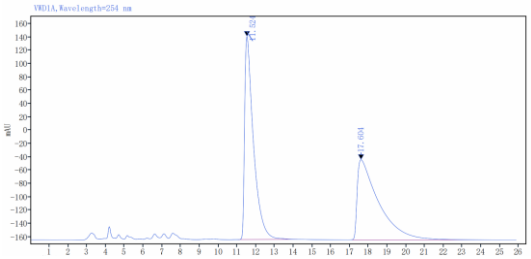
To a solution of **11** (20.6 mg, 0.088 mmol) in MeCN (1.0 mL) was added *p*-tolyl isocyanate (10.0 μL, 0.11 mmol), and the mixture was stirred for 30 min at room temperature, After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ =1/2) to give white solid **12** (31.7 mg, 0.086

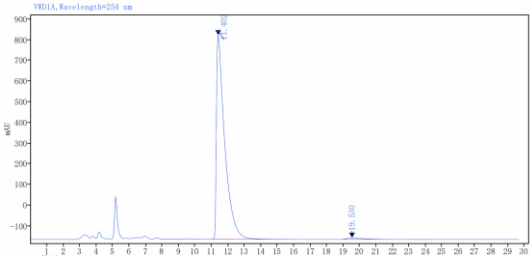
mmol, 98%); R_f = 0.53 (petroleum ether/ ethyl acetate = 1:3); **^{1}H NMR (600 MHz, CD_3OD)** δ 7.27 (d, *J* = 6.0 Hz, 1H), 7.22 (t, *J* = 6.0 Hz, 1H), 7.10 (d, *J* = 12.0 Hz, 2H), 7.02 – 6.97 (m, 3H), 6.90 (d, *J* = 6.0 Hz, 1H), 4.09 (m, 2H), 2.88 (d, *J* = 18.0 Hz, 1H), 2.68 (d, *J* = 18.0 Hz, 1H), 2.22 (s, 3H), 1.15 (t, *J* = 6.0 Hz, 3H); **^{13}C NMR (151 MHz, CD_3OD)** δ 178.75, 169.39, 154.72, 141.50, 136.29, 132.03, 130.44, 128.82, 128.68, 122.85, 121.93, 119.25, 109.94, 60.77, 59.60, 19.29, 12.87; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{22}N_3O_4^+$ 368.1605; found 368.1606.

(*R*)-1-(2,2-diethoxyethyl)-1'-(*p*-tolyl)-1'*H*-spiro[indoline-3,4'-pyrimidine]-2,2',6'(3'*H*,5'*H*)-trione (13)



To a solution of **12** (31.7 mg, 0.086 mmol) in DMA (1.5 mL) were added potassium *tert*-butoxide (19.3 mg, 0.172 mmol, 2.0 equiv), bromoacetaldehyde diethyl acetal (19.7 μL, 0.13 mmol) and tetrabutylammonium iodide (7.9 mg, 0.02 mmol). The mixture was stirred at 80 ℃ for 20 h and then cooled to ambient temperature. Saturated NH_4Cl (3 mL) was added and the mixture was extracted with Et_2O (2×20 mL). The combined organic layers were washed with brine, dried over $MgSO_4$, and concentrated in vacuo. The residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ =1/1) to give white solid **13** (17.3 mg, 0.040 mmol, 46%); m.p. = 162 -163 ℃; R_f = 0.46 (petroleum ether/ ethyl acetate = 1:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IA column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ℃), UV 254 nm, t_R(major) 11.402 min, t_R(minor) 19.530 min; $[\alpha]_D^{24}$ = 59.16 (c = 0.22 $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$)** δ 7.41 – 7.37 (m, 2H), 7.28 (d, *J* = 6.0 Hz, 2H) ,7.23 (d, *J* = 6.0 Hz, 2H), 7.17 – 7.12 (m, 2H), 5.58 (s, 1H), 4.70 (t, *J* = 6.0 Hz, 1H), 3.87 (dd, *J* = 12.0, 6.0 Hz, 1H), 3.77 – 3.72 (m, 3H), 3.54 – 3.49 (m, 2H), 3.21 (d, *J* = 18.0 Hz, 1H), 2.89 (d, *J* = 18.0 Hz, 1H), 2.39 (s, 3H), 1.14 (m, 6H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 175.29, 167.03, 154.23, 143.08, 138.54, 132.15, 130.81, 129.88, 128.42, 126.60, 123.70, 123.31, 111.01, 100.21, 63.69, 63.56, 43.64, 39.99, 21.22, 15.24, 15.23; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{24}H_{28}N_3O_5^+$ 438.2023; found 438.2024.





Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.524	BM m	0.4728	9977.5374	304.8973	51.2040
	17.604	BB	8.1100	9508.3359	120.2702	48.7960

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	11.402	BB	7.1400	34640.9449	985.7359	98.4711
	19.530	BB	5.8200	537.8391	7.2280	1.5289

6. References

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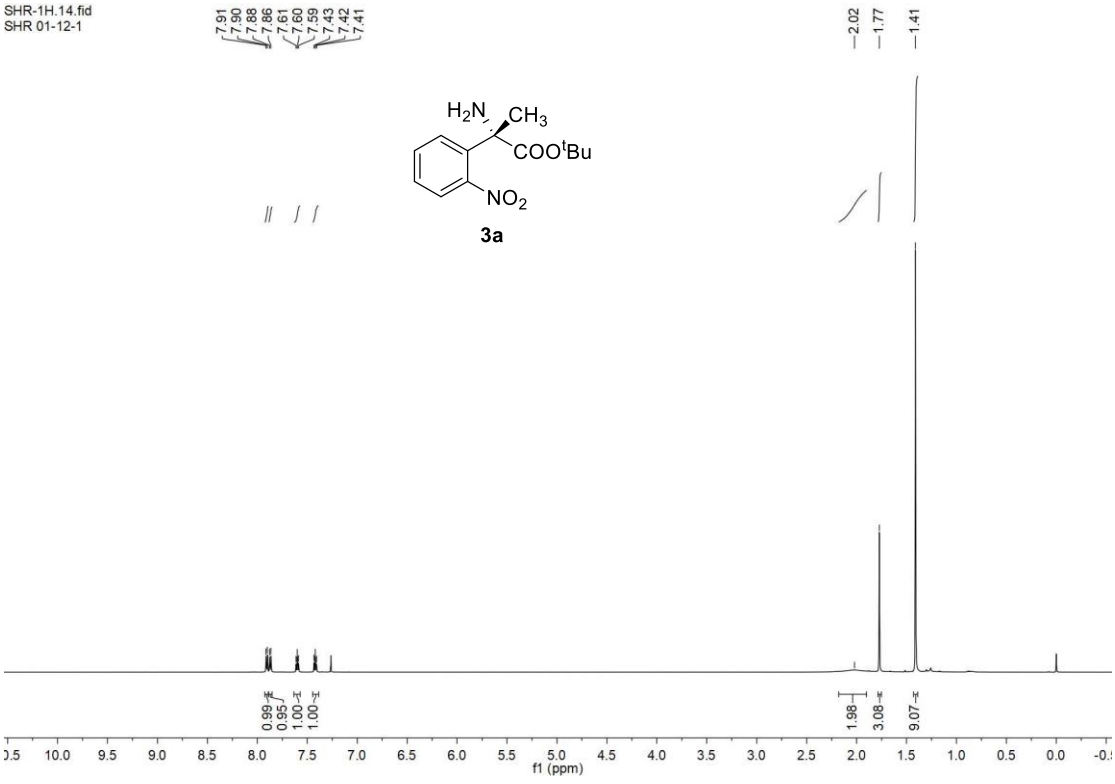
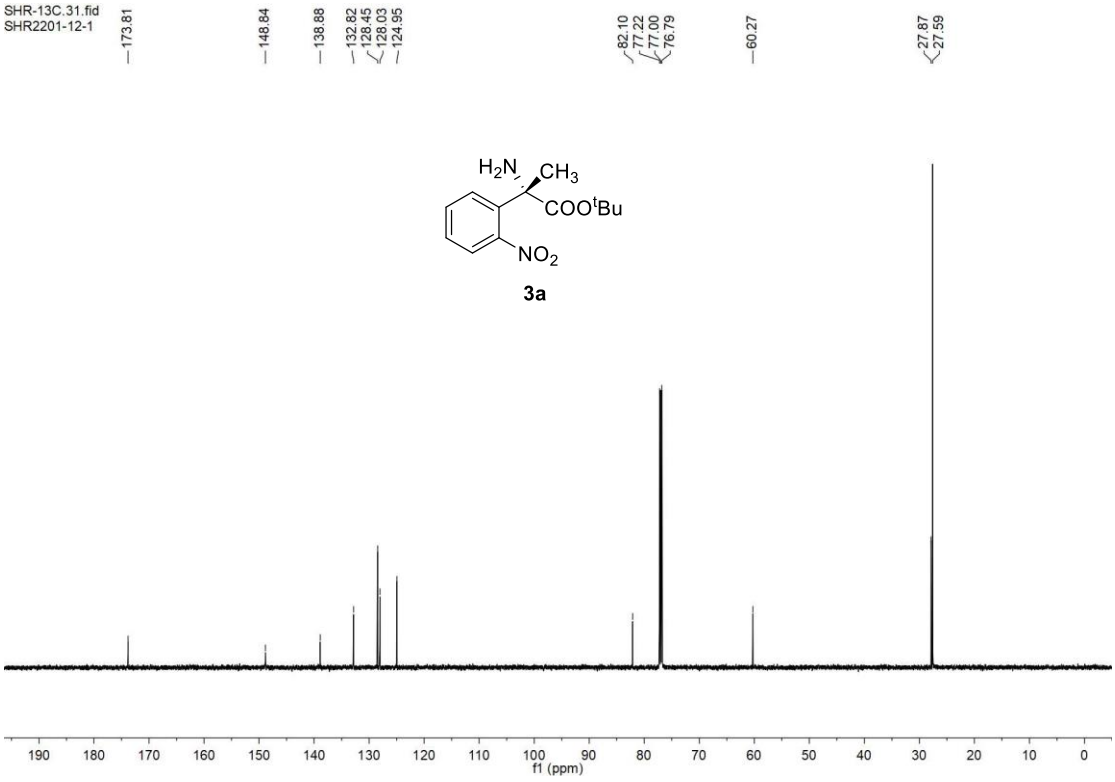
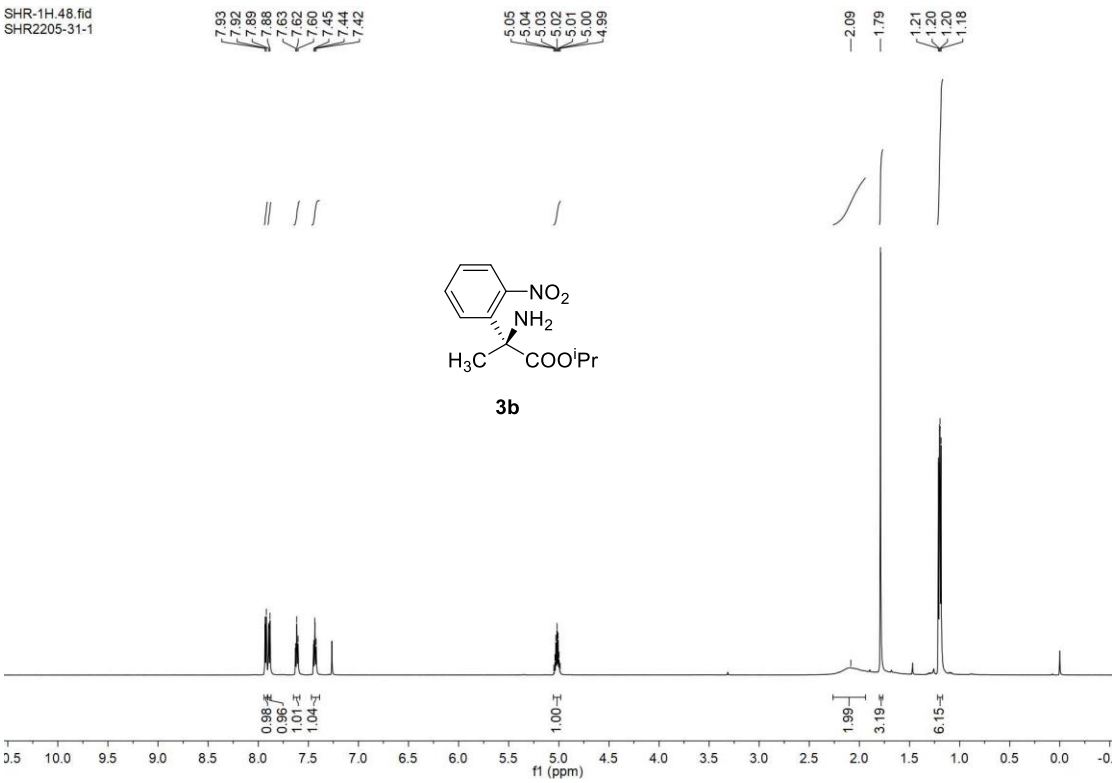
[7] Liu, J. H., Wen, W., Liao, J., Shen, Q. W., Lin, Y., Wu, Z. L., Guo, Q. X. *Nat. Commun.* **2022**, *13*, 2509.

[8] Sato, S., Shibuya, M., Kanoh, N., Iwabuchi, Y. *J. Org. Chem*. **2009**, *74*, 7522–7524.

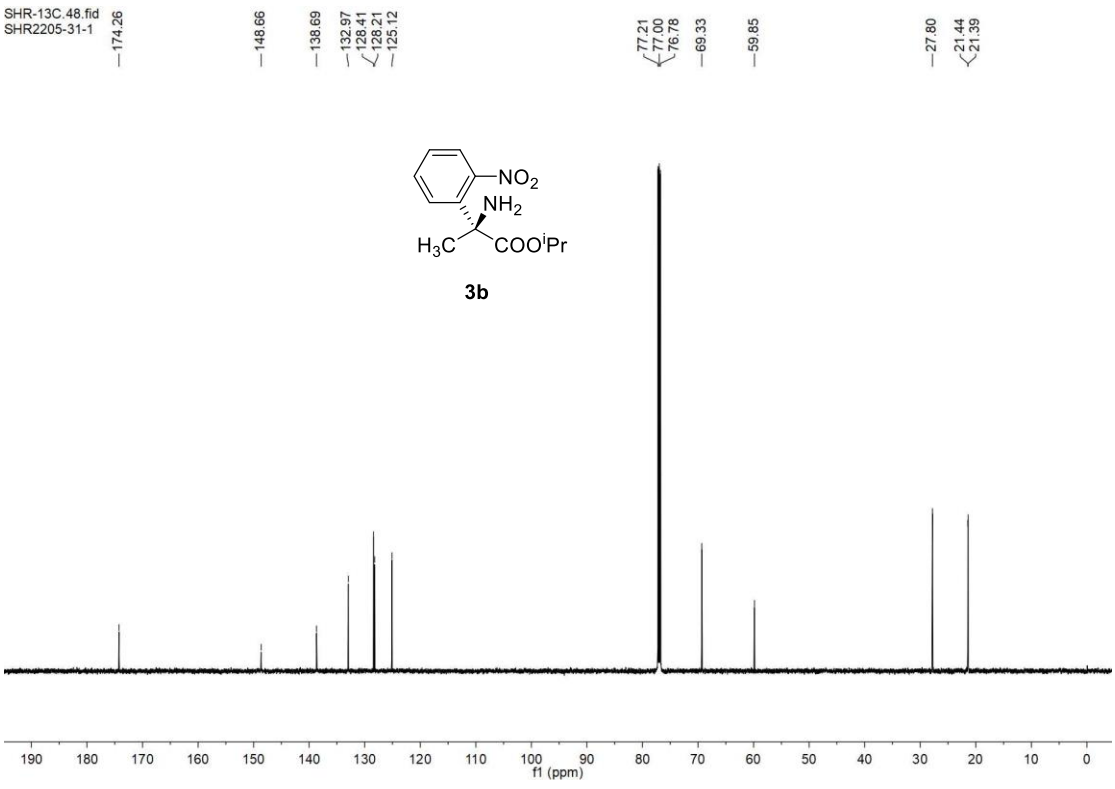
7. The spectra of ^{1}H NMR and ^{13}C NMR



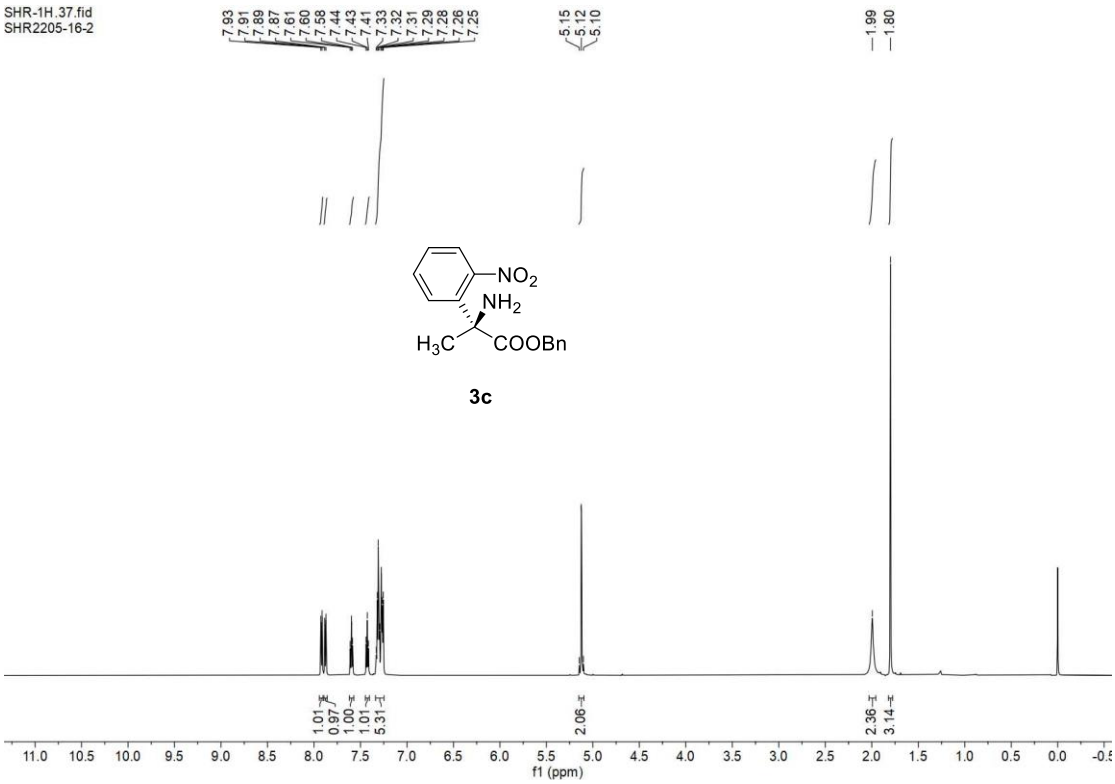



SHR-1H.48.fid
SHR2205-31-1
7.93
7.92
7.89
7.88
7.63
7.62
7.60
7.45
7.44
7.42
5.05
5.04
5.03
5.02
5.01
5.00
4.99
2.09
1.79
1.21
1.20
1.20
1.18
NO2
NH2
H3C
COOiPr
0.98
0.96
1.01
1.04
1.00
1.99
3.19
6.15
f1 (ppm)

3b


SHR-13C.48.fid
SHR2205-31-1
174.26
148.66
138.69
132.97
128.41
128.21
125.12
77.21
77.00
76.78
69.33
59.85
27.80
21.44
21.39
NO2
NH2
H3C
COOiPr
f1 (ppm)

3b


SHR-1H.37.fid
SHR2205-16-2
7.93
7.91
7.89
7.87
7.61
7.60
7.58
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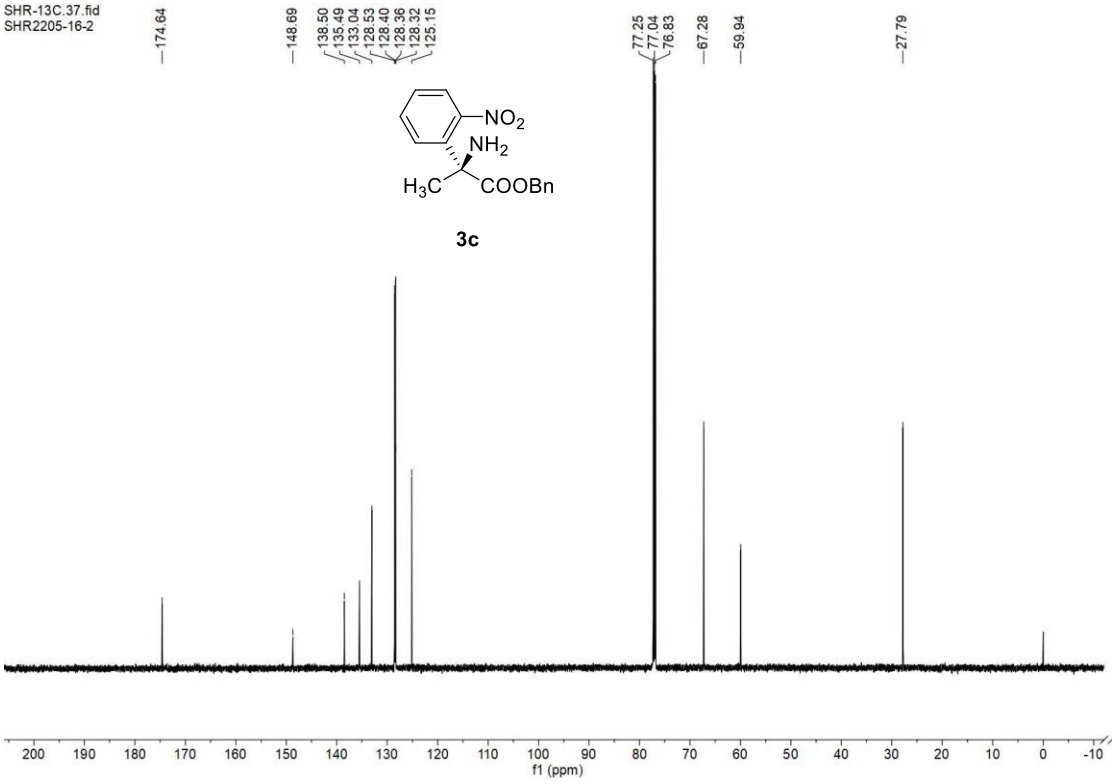
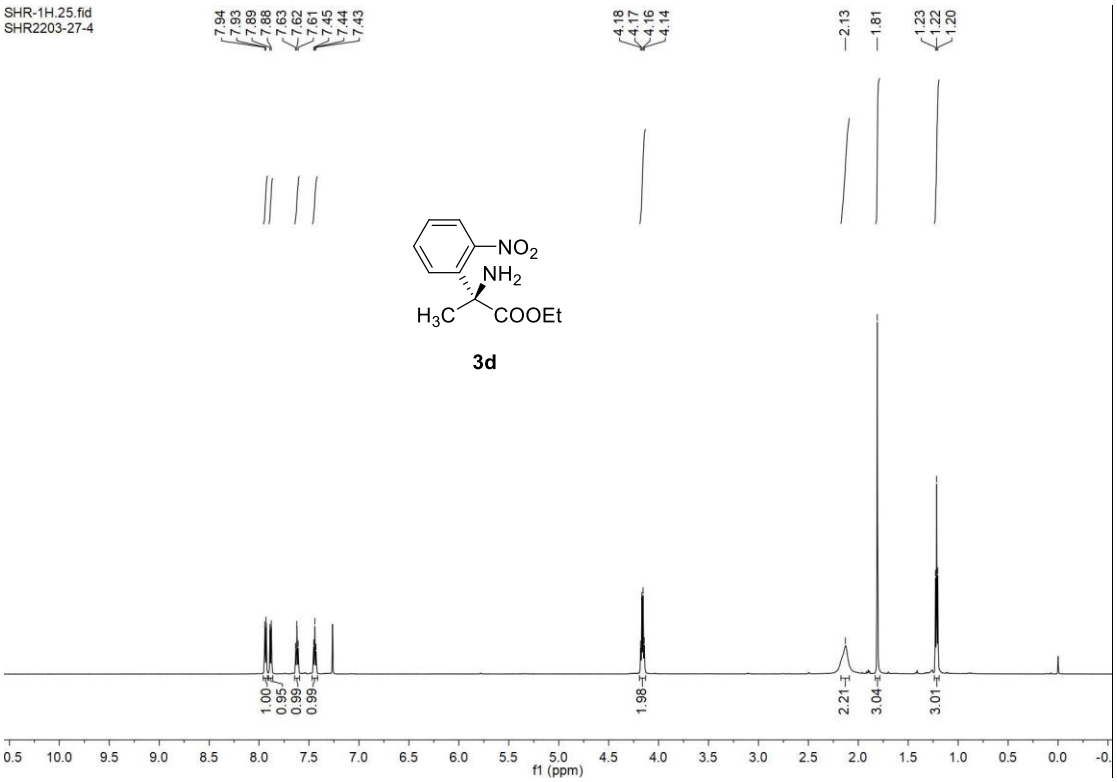
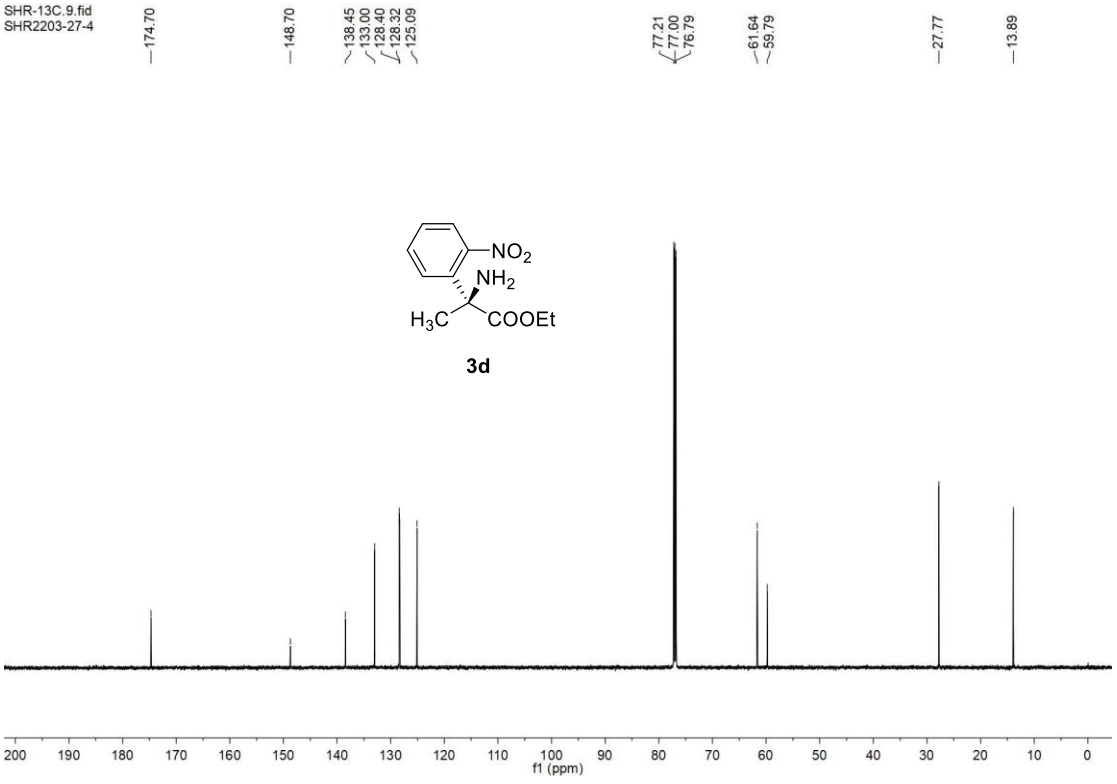
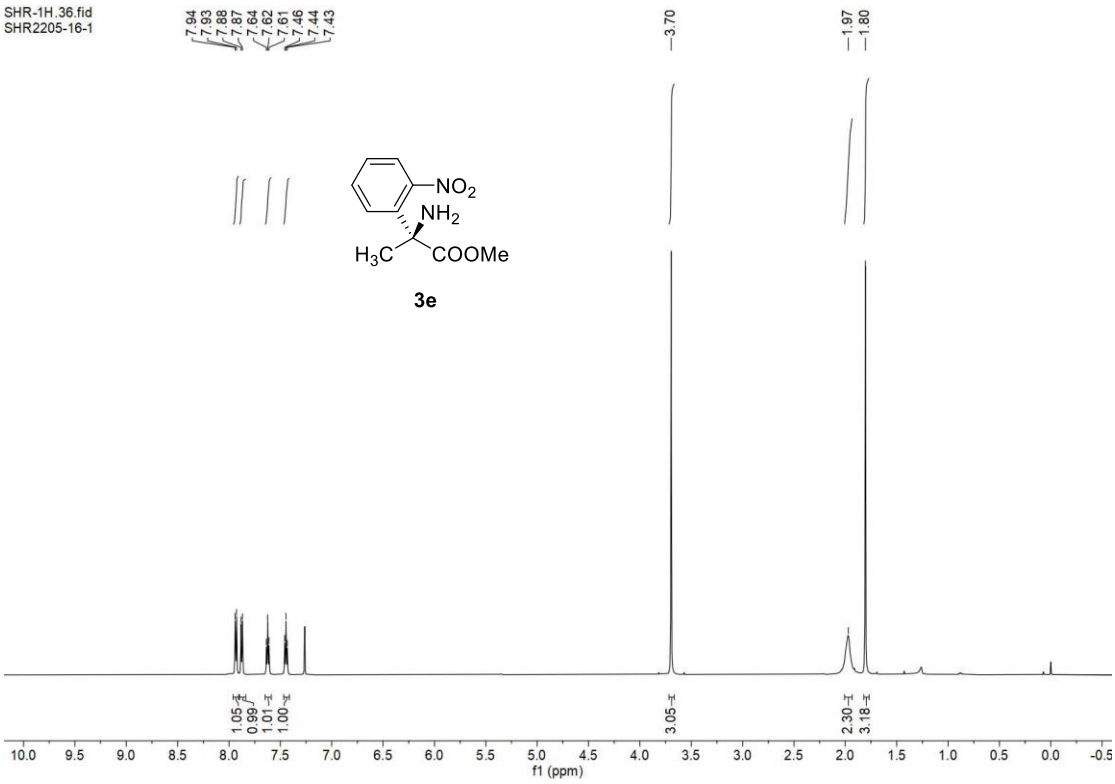
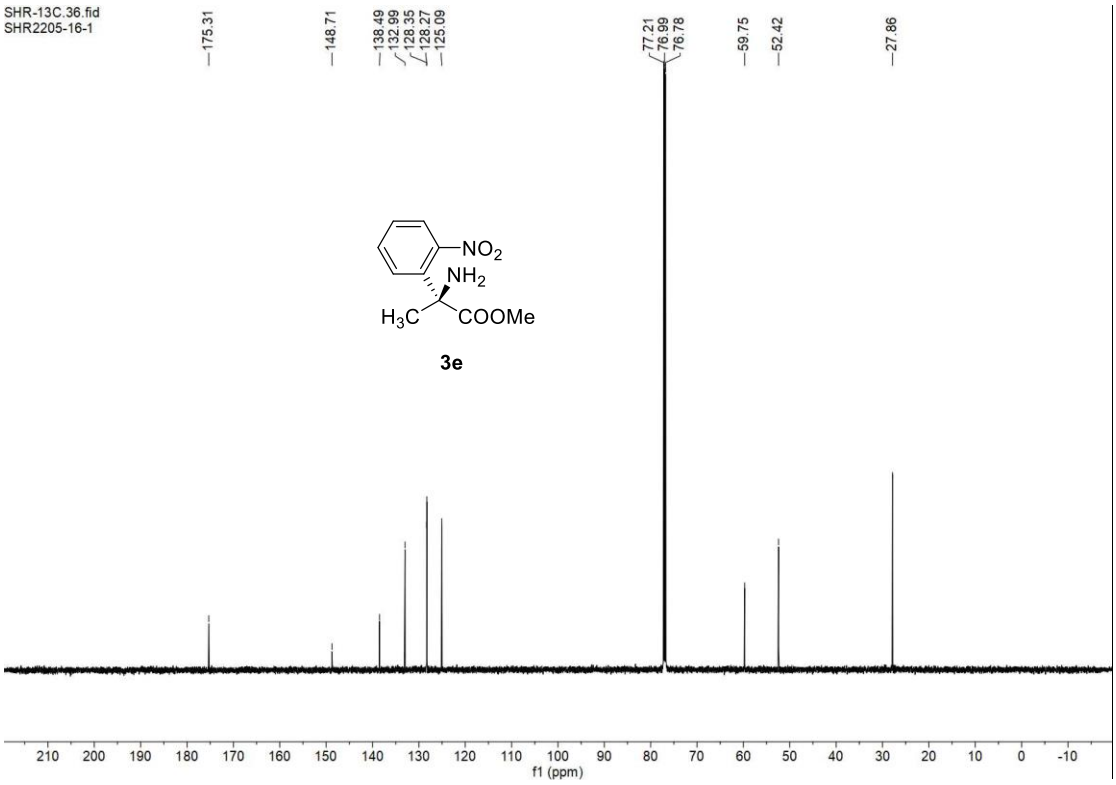
7.41
7.33
7.32
7.31
7.29
7.28
7.26
7.25
5.15
5.12
5.10
1.99
1.80
NO2
NH2
H3C
COOBn
3c
1.01
0.97
1.00
1.01
5.31
2.06
2.36
3.14
11.0 10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

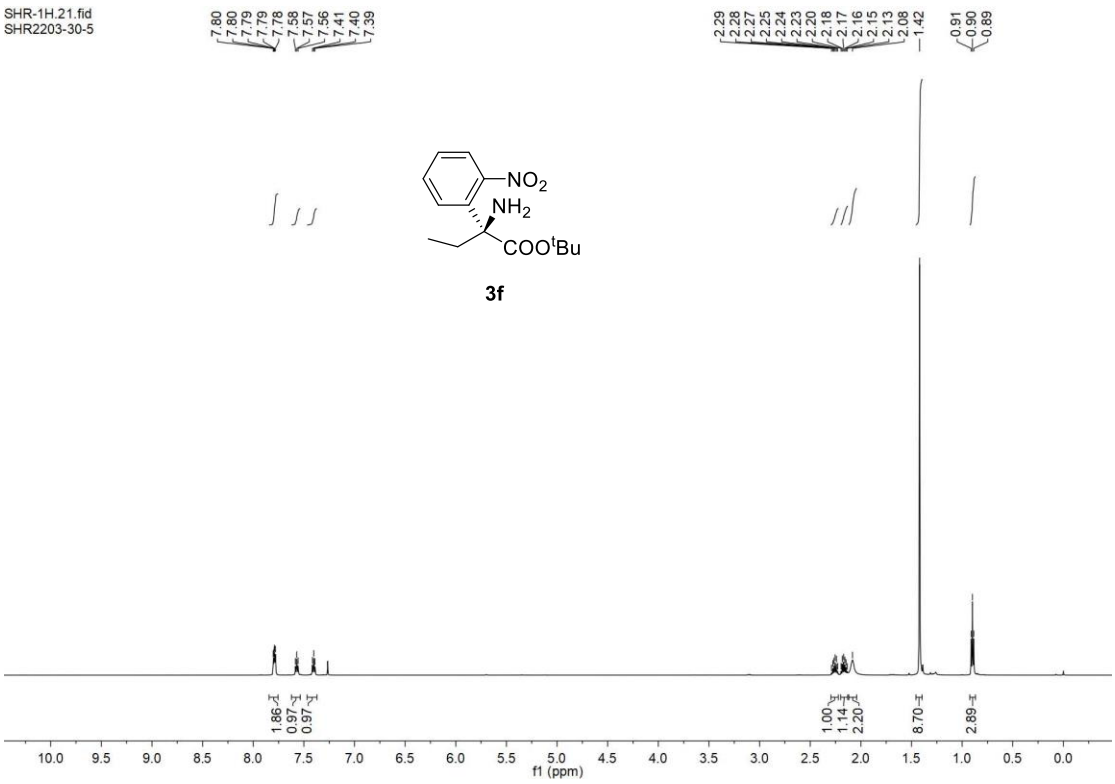

SHR-13C.37.fid
SHR2205-16-2
174.64
148.69
138.50
135.49
133.04
128.53
128.40
128.36
128.32
125.15
77.25
77.04
76.83
67.28
59.94
27.79
NO2
NH2
H3C
COOBn
3c
200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)

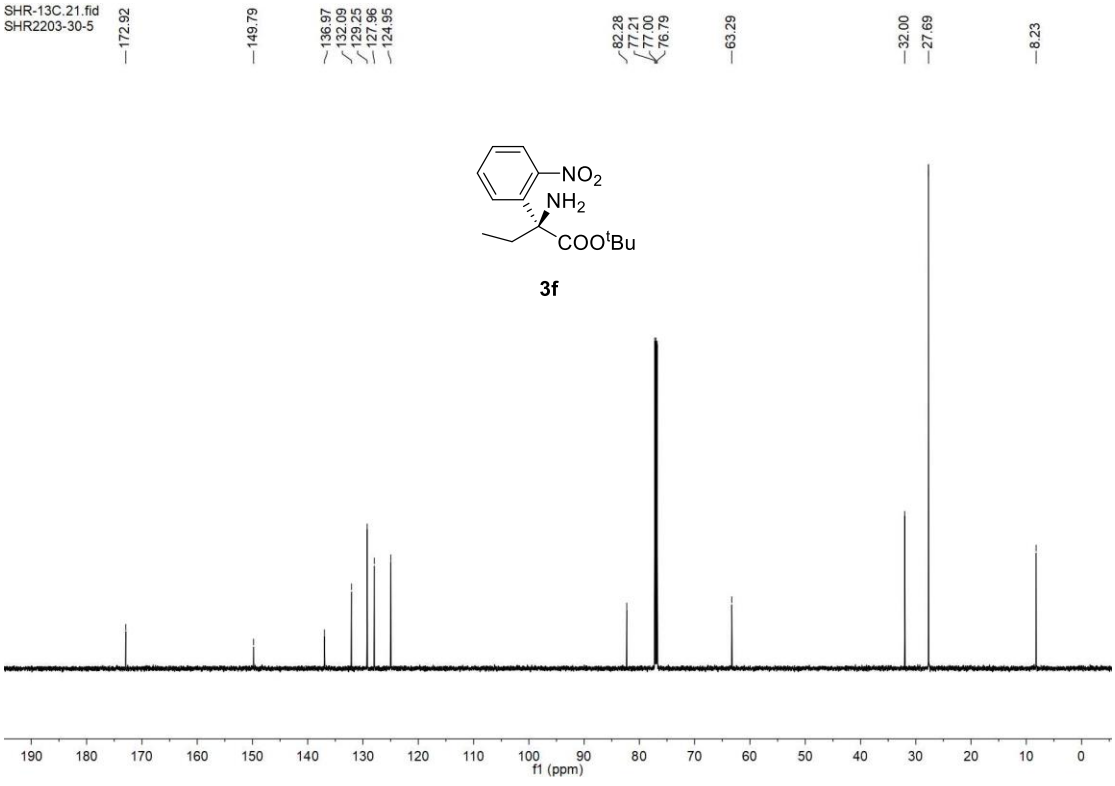

SHR-1H.25.fid
SHR2203-27-4
7.94
7.93
7.89
7.88
7.63
7.62
7.61
7.45
7.44
7.43
4.18
4.17
4.16
4.14
2.13
1.81
1.23
1.22
1.20
NO2
NH2
H3C
COOEt
3d
1.00
0.95
0.99
0.99
1.98
2.21
3.04
3.01
f1 (ppm)

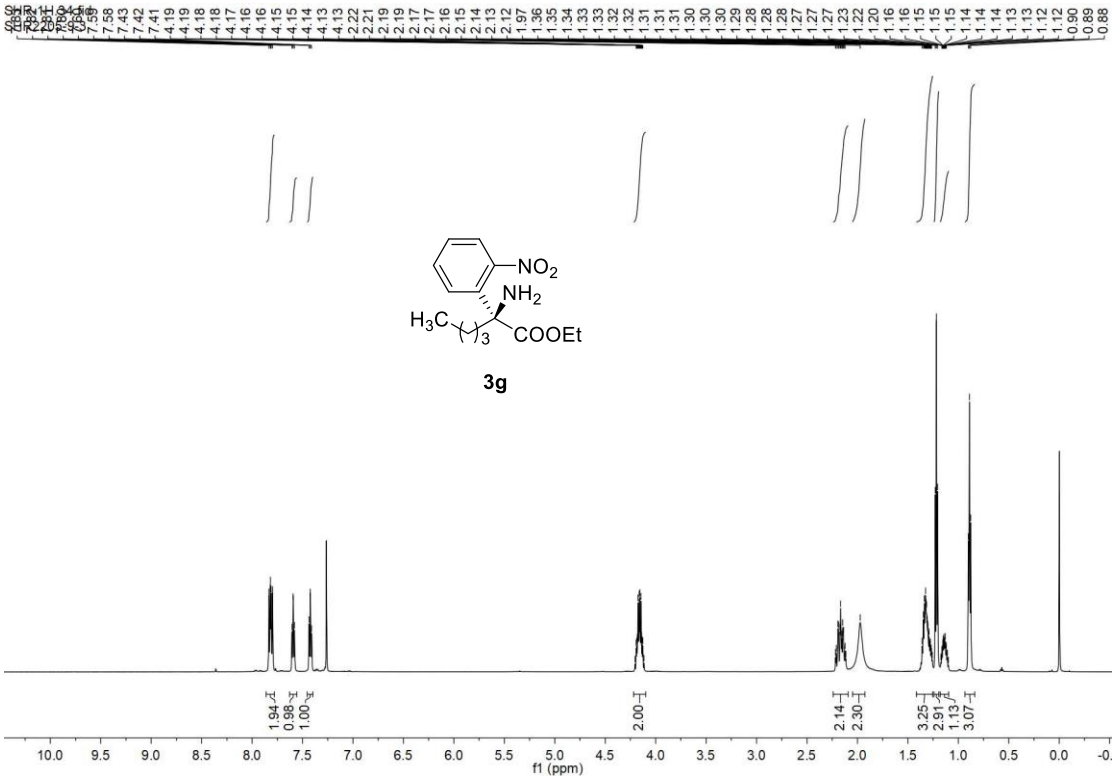

SHR-13C.9.fid
SHR2203-27-4
174.70
148.70
138.45
133.00
128.40
128.32
125.09
77.21
77.00
76.79
61.64
59.79
27.77
13.89
NO2
NH2
H3C
COOEt
3d
f1 (ppm)


SHR-1H.36.fid
SHR2205-16-1
7.94
7.93
7.88
7.87
7.64
7.62
7.61
7.46
7.44
7.43
3.70
1.97
1.80
NO2
NH2
H3C
COOMe
3e
1.05
0.99
1.01
1.00
3.05
2.30
3.18
f1 (ppm)

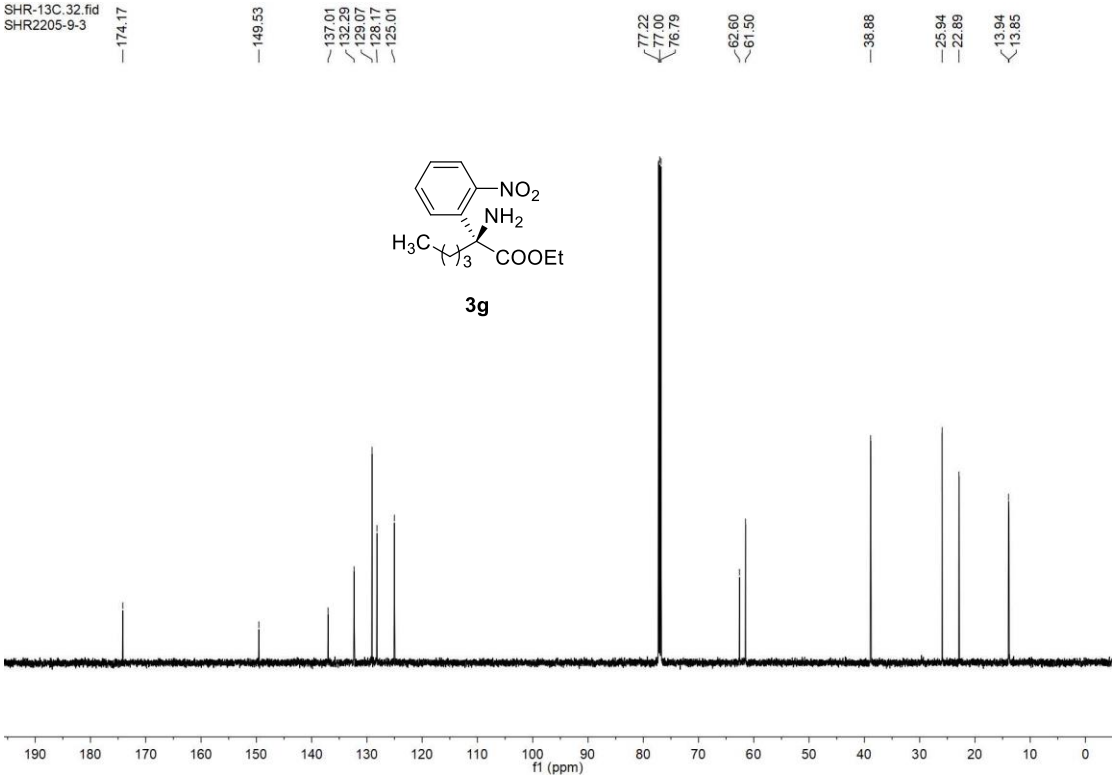

SHR-13C.36.fid
SHR2205-16-1
175.31
148.71
138.49
132.99
128.35
128.27
125.09
77.21
76.99
76.78
59.75
52.42
27.86
NO2
NH2
H3C
COOMe
3e
f1 (ppm)


SHR-1H.21.fid
SHR2203-30-5
7.80
7.80
7.79
7.79
7.78
7.58
7.57
7.56
7.41
7.40
7.39
2.29
2.28
2.27
2.25
2.24
2.23
2.20
2.18
2.17
2.16
2.15
2.13
2.08
1.42
0.91
0.90
0.89
NO2
NH2
COOtBu
3f
1.86
0.97
0.97
1.00
1.14
2.20
8.70
2.89
10.0
9.5
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)

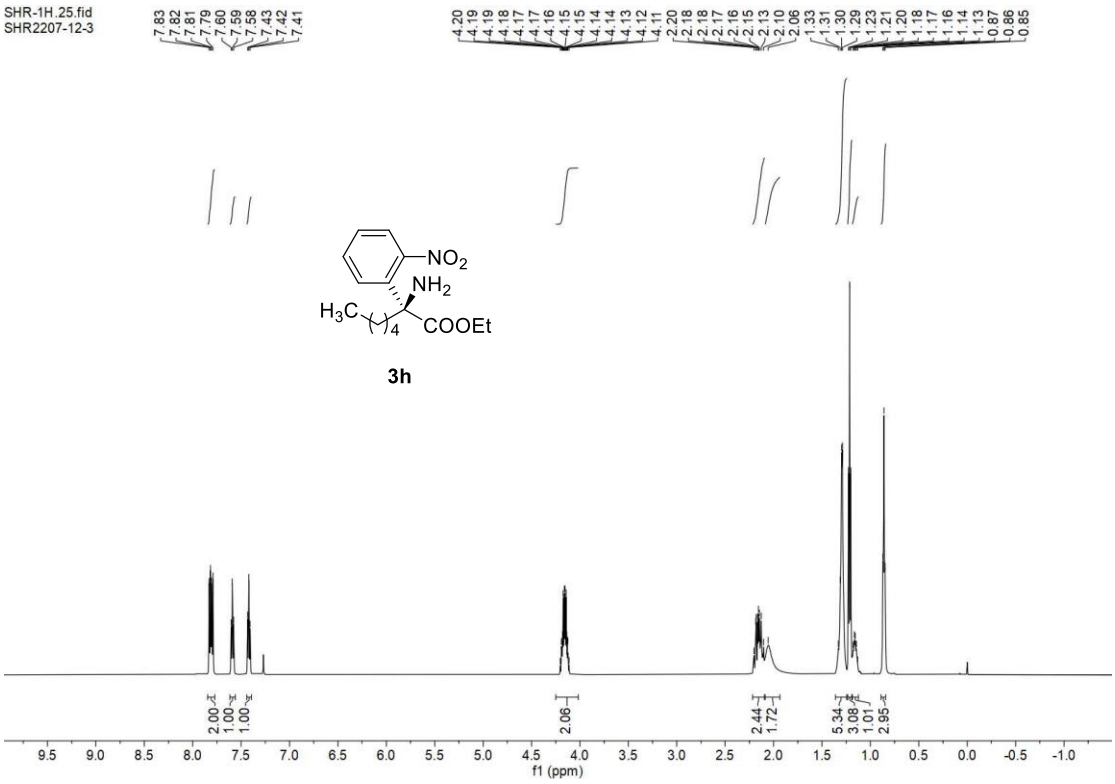

SHR-13C.21.fid
SHR2203-30-5
172.92
149.79
136.97
132.09
129.25
127.96
124.95
82.28
77.21
77.00
76.79
63.29
32.00
27.69
8.23
NO2
NH2
COOtBu
3f
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)

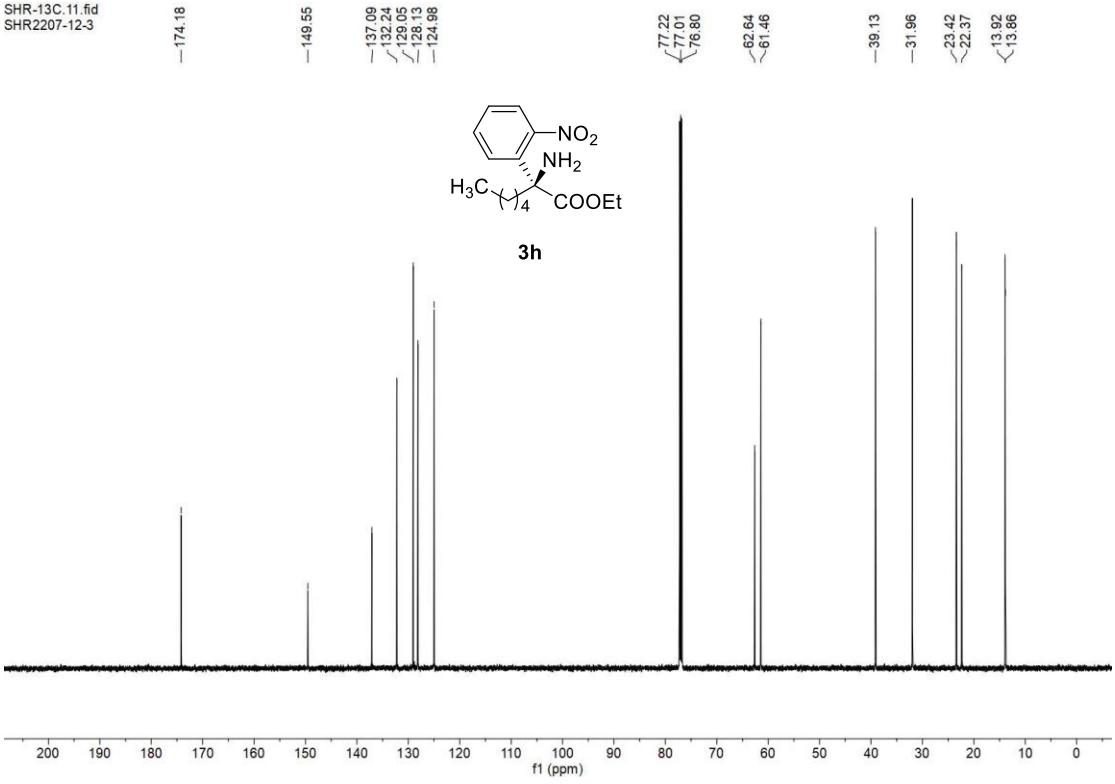

NO2
NH2
H3C
3
COOEt
1.94
0.98
1.00
2.00
2.14
2.30
3.25
2.91
1.13
3.07
f1 (ppm)

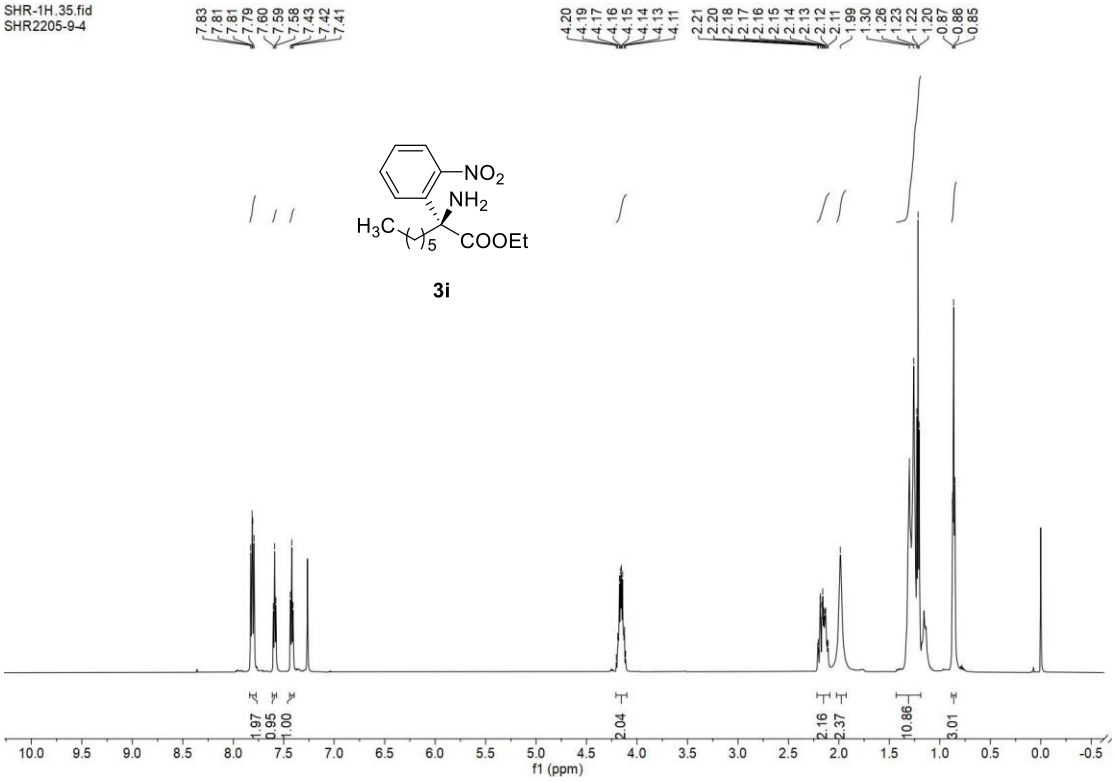
3g

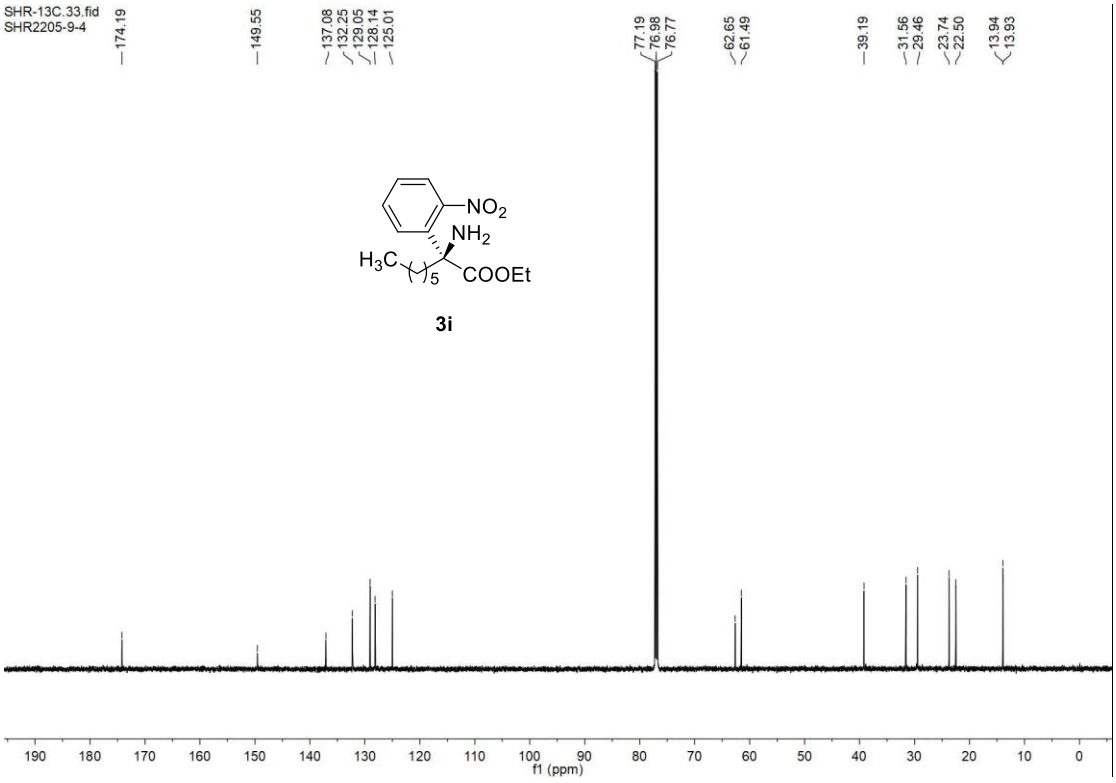

SHR-13C.32.fid
SHR2205-9-3
174.17
149.53
137.01
132.29
129.07
128.17
125.01
77.22
77.00
76.79
62.60
61.50
38.88
25.94
22.89
13.94
13.85
NO2
NH2
H3C
3
COOEt
f1 (ppm)

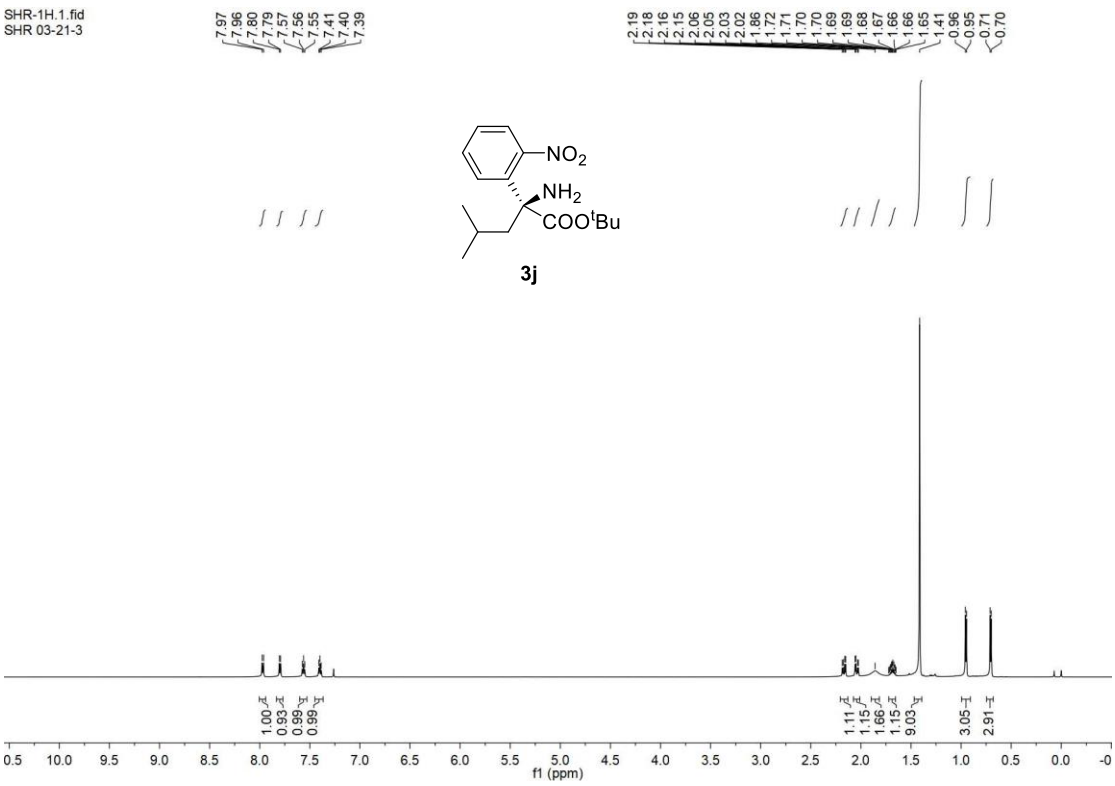
3g

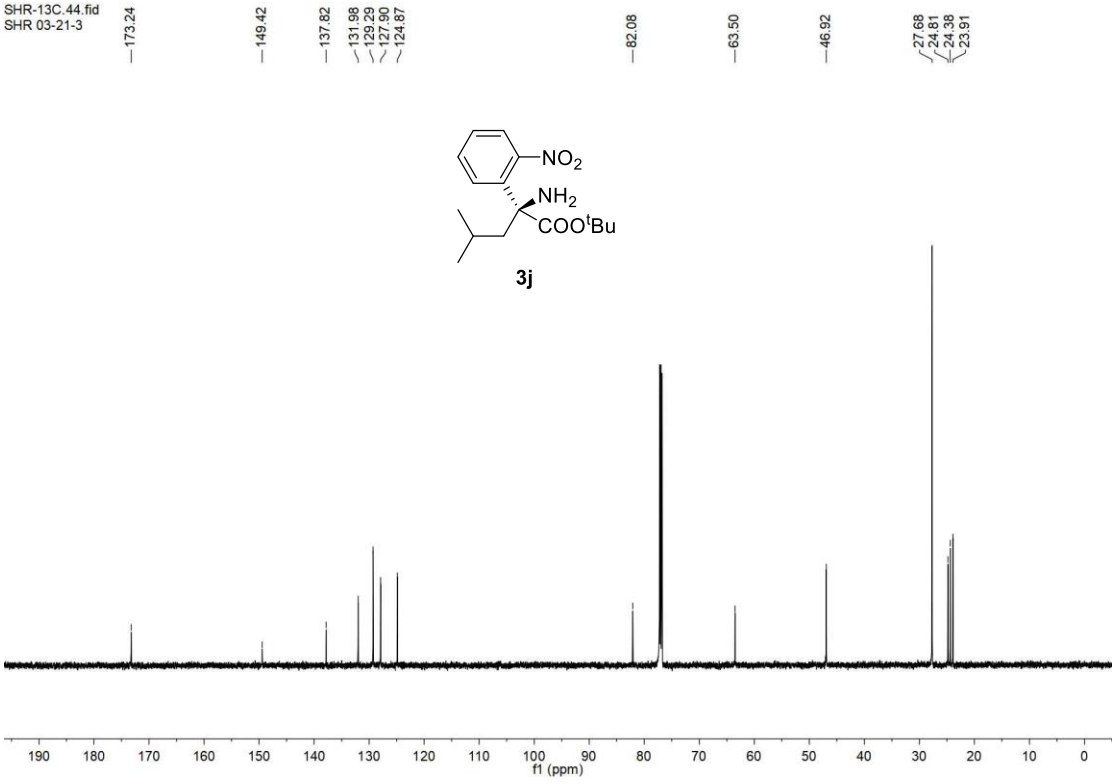

SHR-1H.25.fid
SHR2207-12-3
NO2
NH2
H3C
4
COOEt
3h
f1 (ppm)

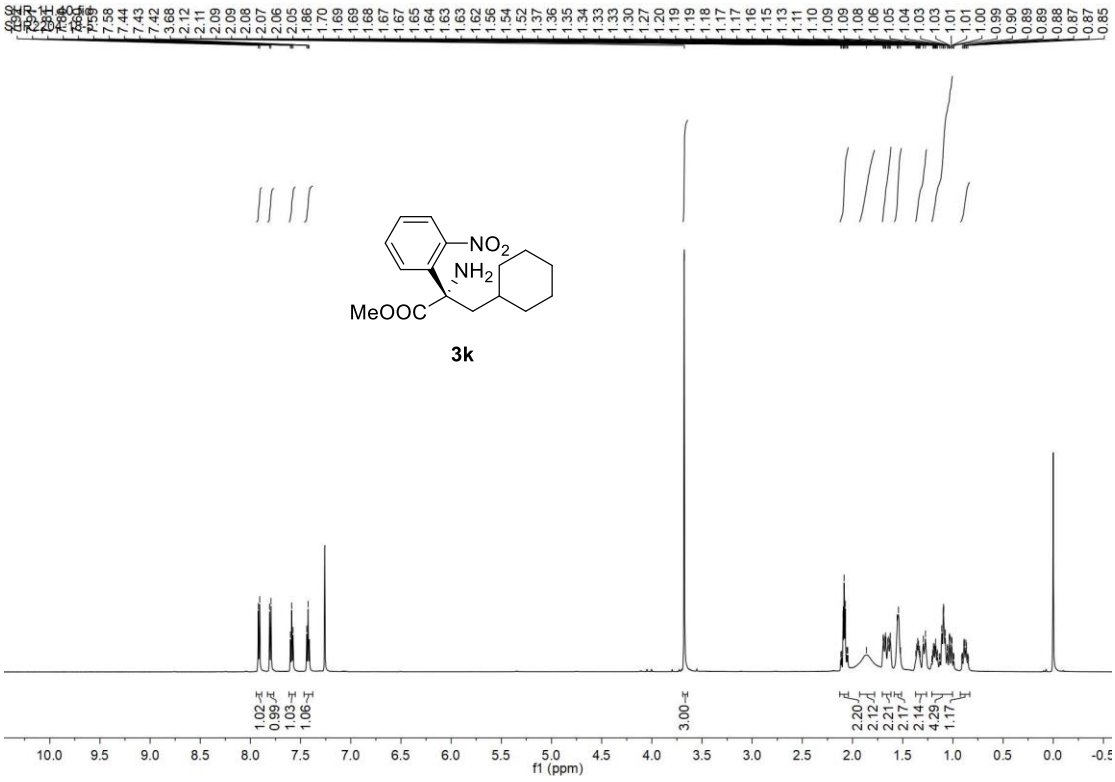

SHR-13C.11.fid
SHR2207-12-3
NO2
NH2
H3C
4
COOEt
3h
f1 (ppm)


SHR-1H.35.fid
SHR2205-9-4
7.83
7.81
7.81
7.79
7.60
7.59
7.58
7.43
7.42
7.41
4.20
4.19
4.17
4.16
4.15
4.14
4.13
4.11
2.21
2.20
2.18
2.17
2.16
2.15
2.14
2.13
2.12
2.11
1.99
1.30
1.26
1.23
1.22
1.20
0.87
0.86
0.85
NO2
NH2
H3C
5
COOEt
3i
1.97
0.95
1.00
2.04
2.16
2.37
10.86
3.01
f1 (ppm)

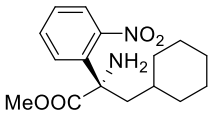

SHR-13C.33.fid
SHR2205-9-4
174.19
149.55
137.08
132.25
129.05
128.14
125.01
77.19
76.98
76.77
62.65
61.49
39.19
31.56
29.46
23.74
22.50
13.94
13.93
NO2
NH2
H3C
5
COOEt
3i
f1 (ppm)


SHR-1H.1.fid
SHR 03-21-3
7.97
7.96
7.80
7.79
7.57
7.56
7.55
7.41
7.40
7.39
2.19
2.18
2.16
2.15
2.06
2.05
2.03
2.02
1.86
1.72
1.71
1.70
1.70
1.69
1.69
1.68
1.67
1.66
1.66
1.65
1.41
0.96
0.95
0.71
0.70
NO2
NH2
COOtBu
3j
1.00
0.93
0.99
0.99
1.11
1.15
1.66
1.15
9.03
3.05
2.91
f1 (ppm)

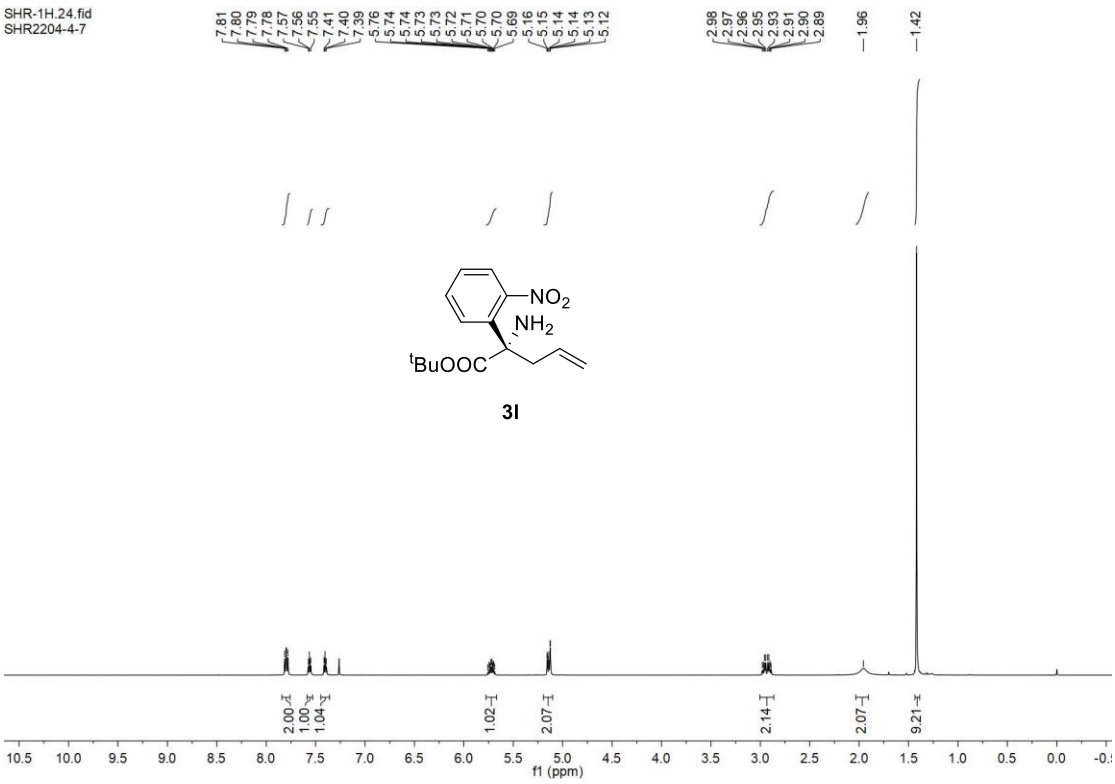

SHR-13C.44.fid
SHR 03-21-3
173.24
149.42
137.82
131.98
129.29
127.90
124.87
82.08
63.50
46.92
27.68
24.81
24.38
23.91
NO2
NH2
COOtBu
3j
f1 (ppm)



3k



3k


SHR-1H.24.fid
SHR2204-4-7
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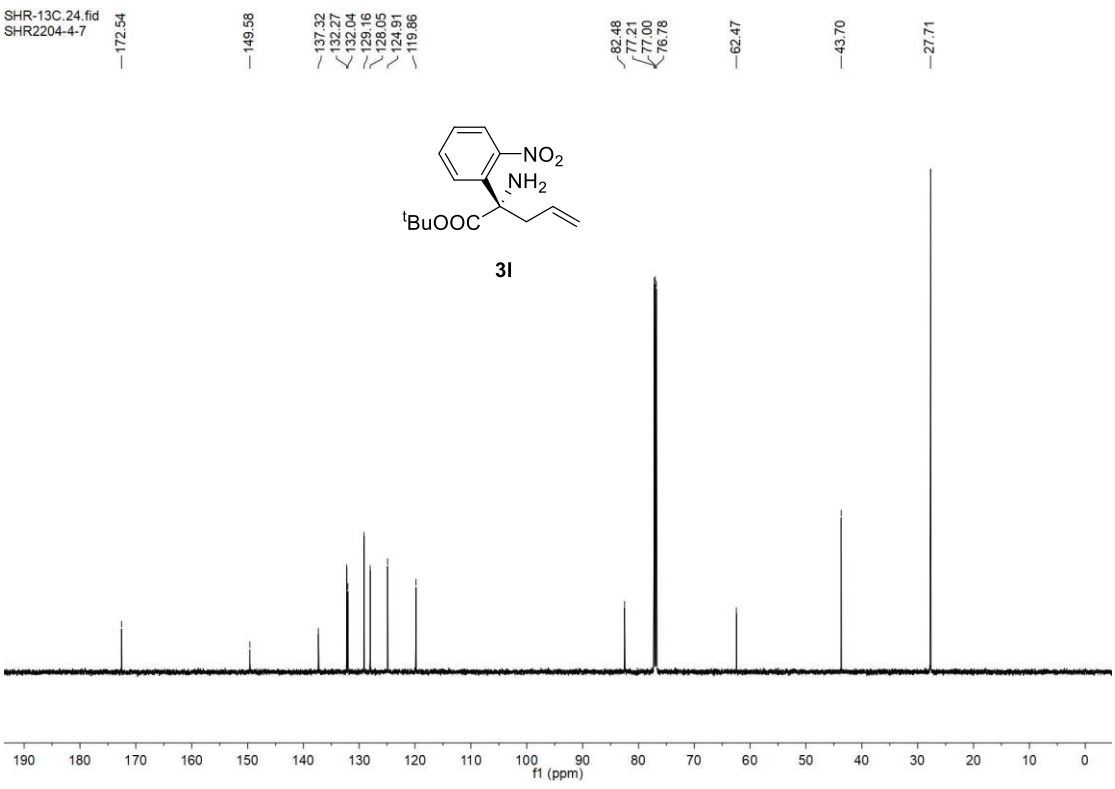
7.80
7.79
7.78
7.57
7.56
7.55
7.41
7.40
7.39
5.76
5.74
5.74
5.73
5.73
5.72
5.71
5.70
5.70
5.69
5.16
5.15
5.14
5.14
5.13
5.12
2.98
2.97
2.96
2.95
2.93
2.91
2.90
2.89
1.96
1.42
NO2
NH2
tBuOOC
3l
2.00
1.00
1.04
1.02
2.07
2.14
2.07
9.21
f1 (ppm)


SHR-13C.24.fid
SHR2204-4-7
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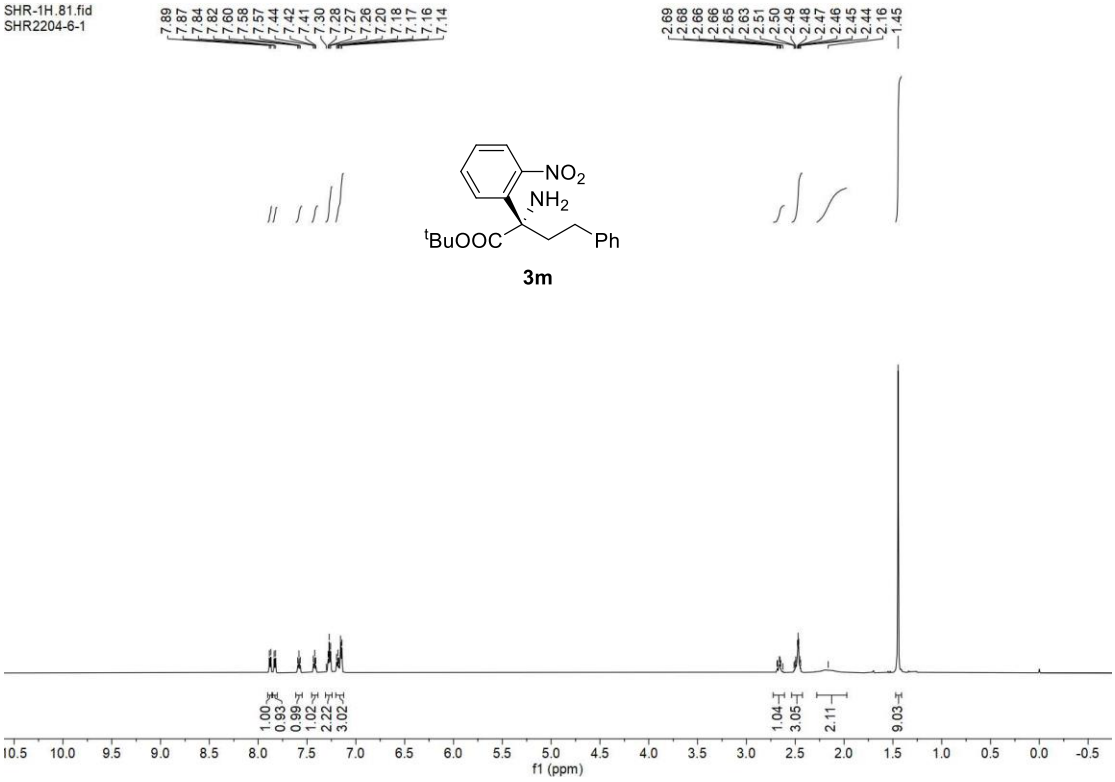
149.58
137.32
132.27
132.04
129.16
128.05
124.91
119.86
82.48
77.21
77.00
76.78
62.47
43.70
27.71
NO2
NH2
tBuOOC
3l
f1 (ppm)


SHR-1H.81.fid
SHR2204-6-1
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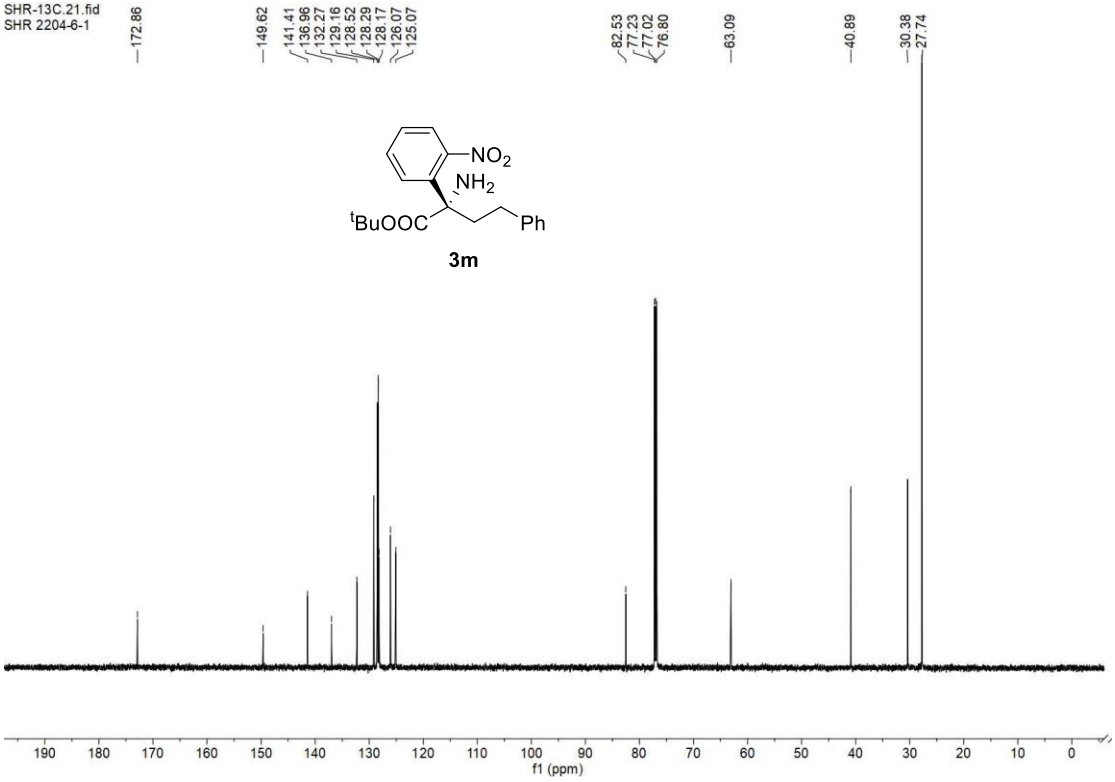
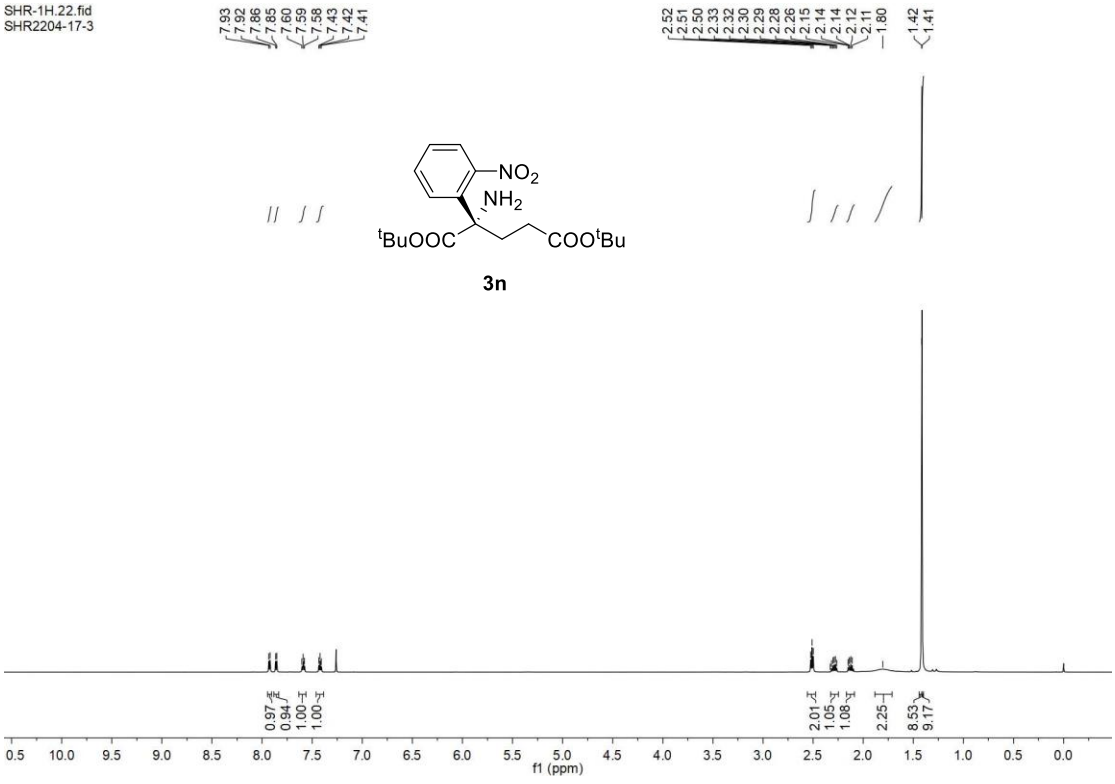
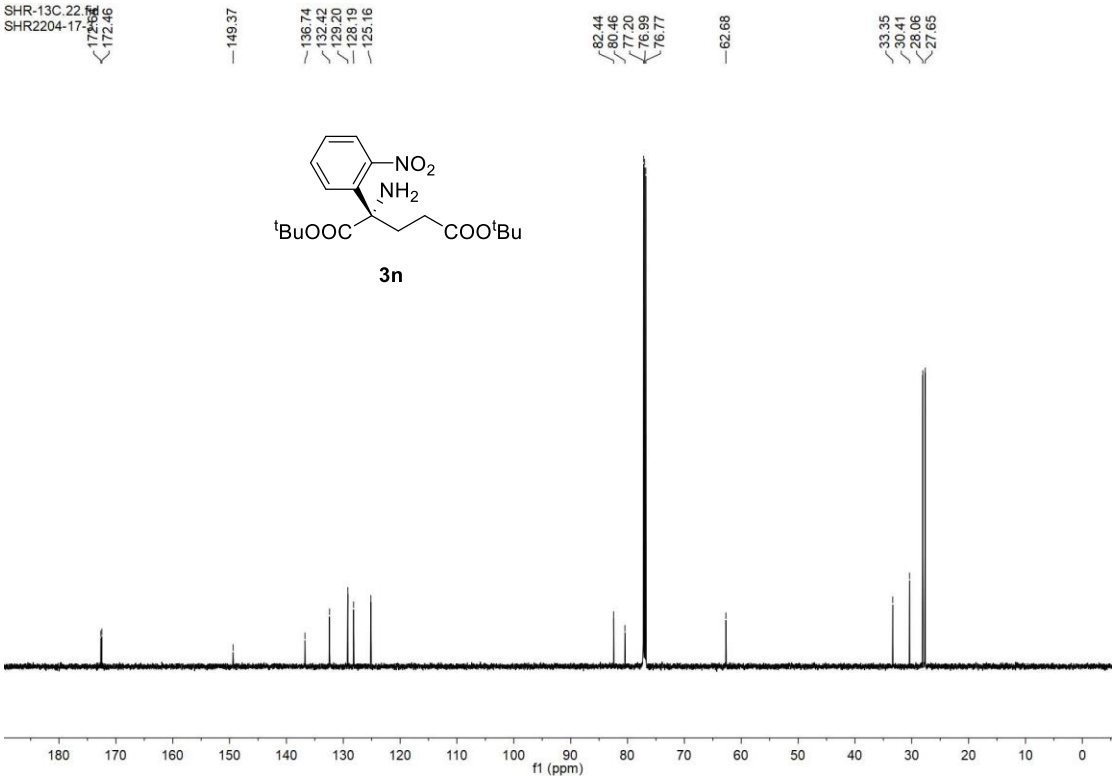
7.87
7.84
7.82
7.60
7.58
7.57
7.44
7.42
7.41
7.30
7.28
7.27
7.26
7.20
7.18
7.17
7.16
7.14
2.69
2.68
2.66
2.66
2.65
2.63
2.51
2.50
2.49
2.48
2.47
2.46
2.45
2.44
2.16
1.45
NO2
NH2
tBuOOC
Ph
3m
1.00
0.93
0.99
1.02
2.22
3.02
1.04
3.05
2.11
9.03
f1 (ppm)


SHR-13C.21.fid
SHR 2204-6-1
172.86
149.62
141.41
136.96
132.27
129.16
128.52
128.29
128.17
126.07
125.07
82.53
77.23
77.02
76.80
63.09
40.89
30.38
27.74
NO2
NH2
tBuOOC
Ph
3m
f1 (ppm)


SHR-1H.22.fid
SHR2204-17-3
7.93
7.92
7.86
7.85
7.60
7.59
7.58
7.43
7.42
7.41
2.52
2.51
2.50
2.33
2.32
2.30
2.29
2.28
2.26
2.15
2.14
2.14
2.12
2.11
1.80
1.42
1.41
NO2
NH2
tBuOOC
COOtBu
3n
0.97
0.94
1.00
1.00
2.01
1.05
1.08
2.25
8.53
9.17
f1 (ppm)


SHR-13C.22.fid
SHR2204-17-3
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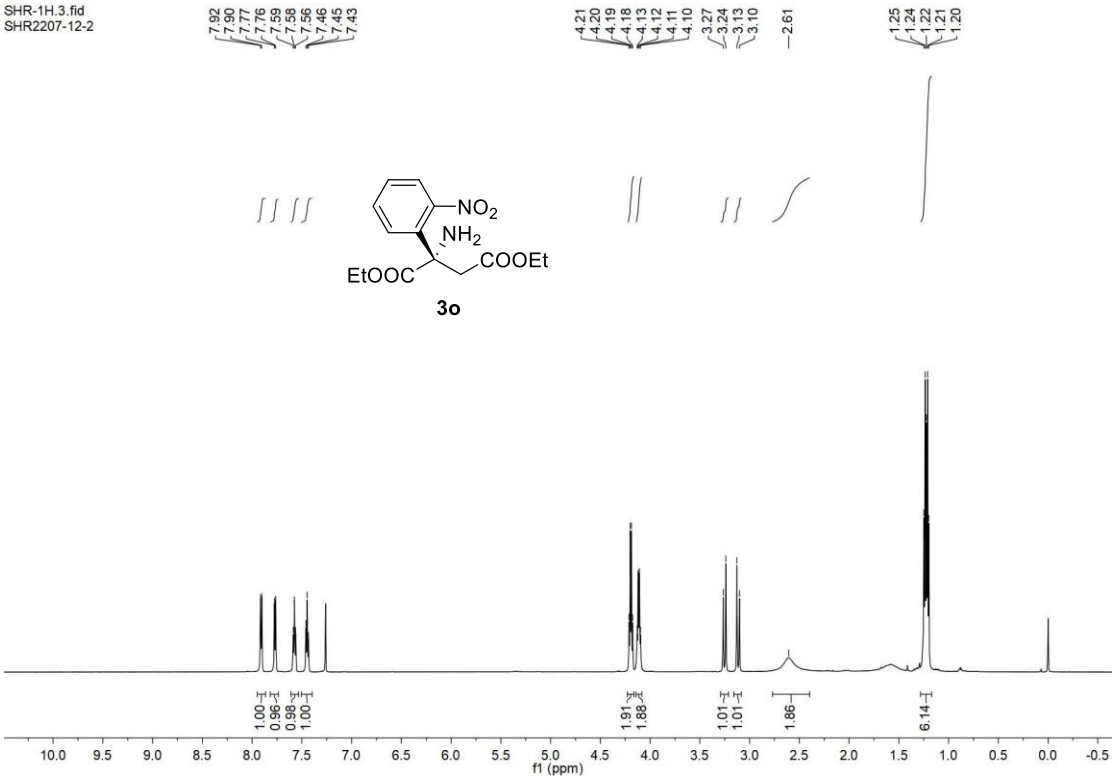
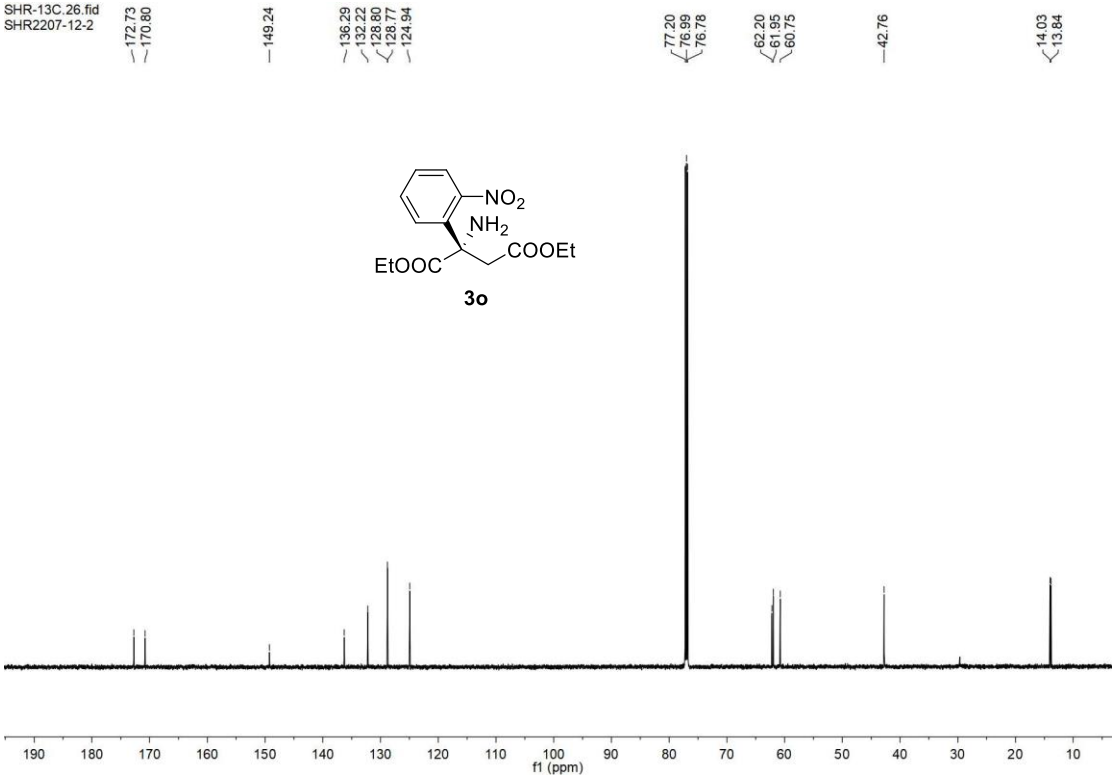
172.46
149.37
136.74
132.42
129.20
128.19
125.16
82.44
80.46
77.20
76.99
76.77
62.68
33.35
30.41
28.06
27.65
NO2
NH2
tBuOOC
COOtBu
3n
f1 (ppm)

SHR-1H.3.fid
SHR2207-12-2

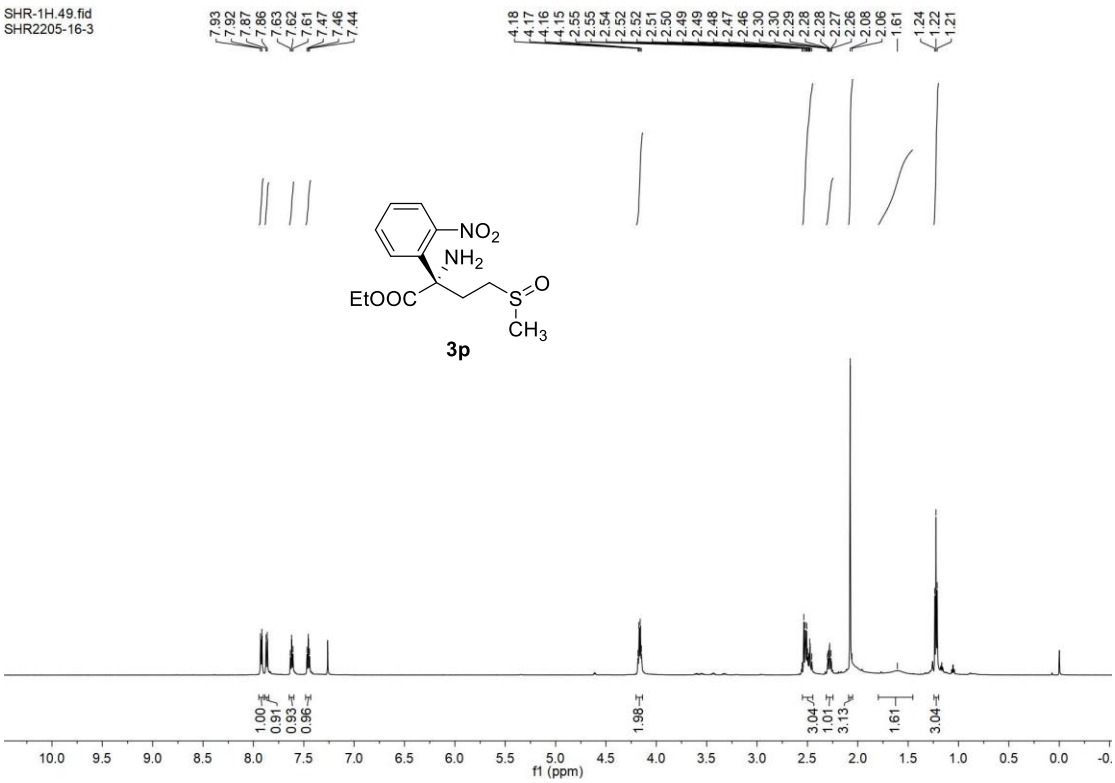


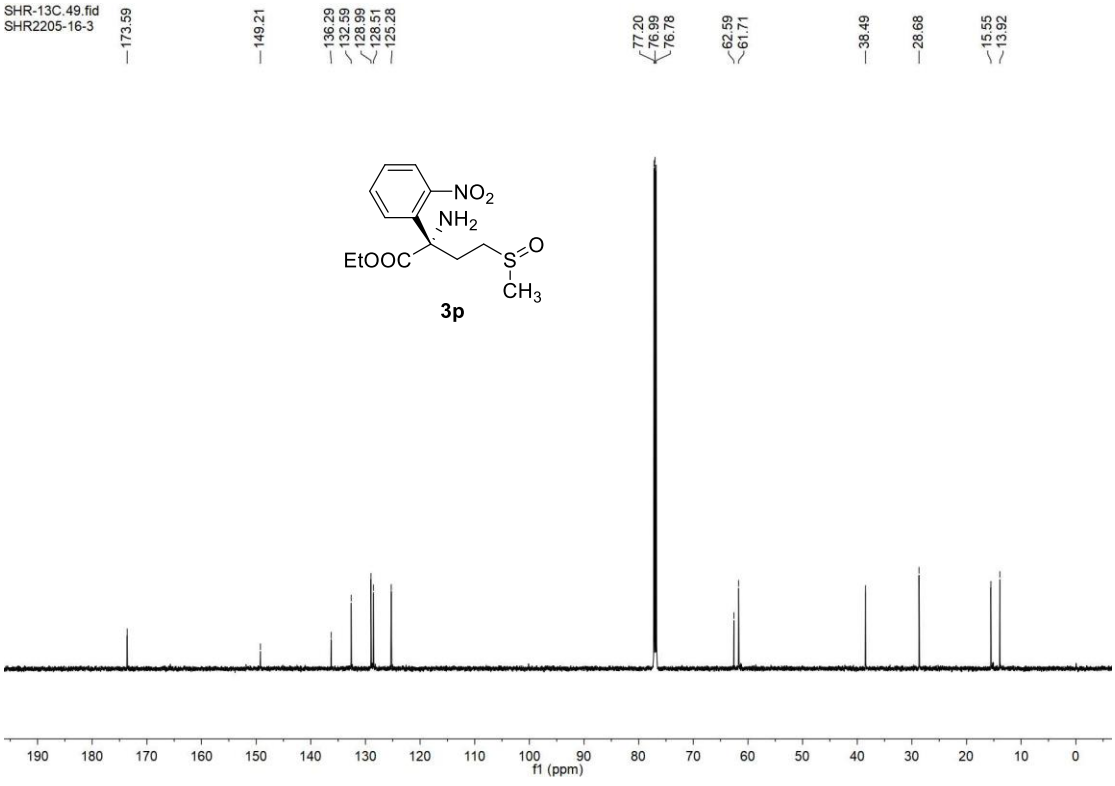
3o

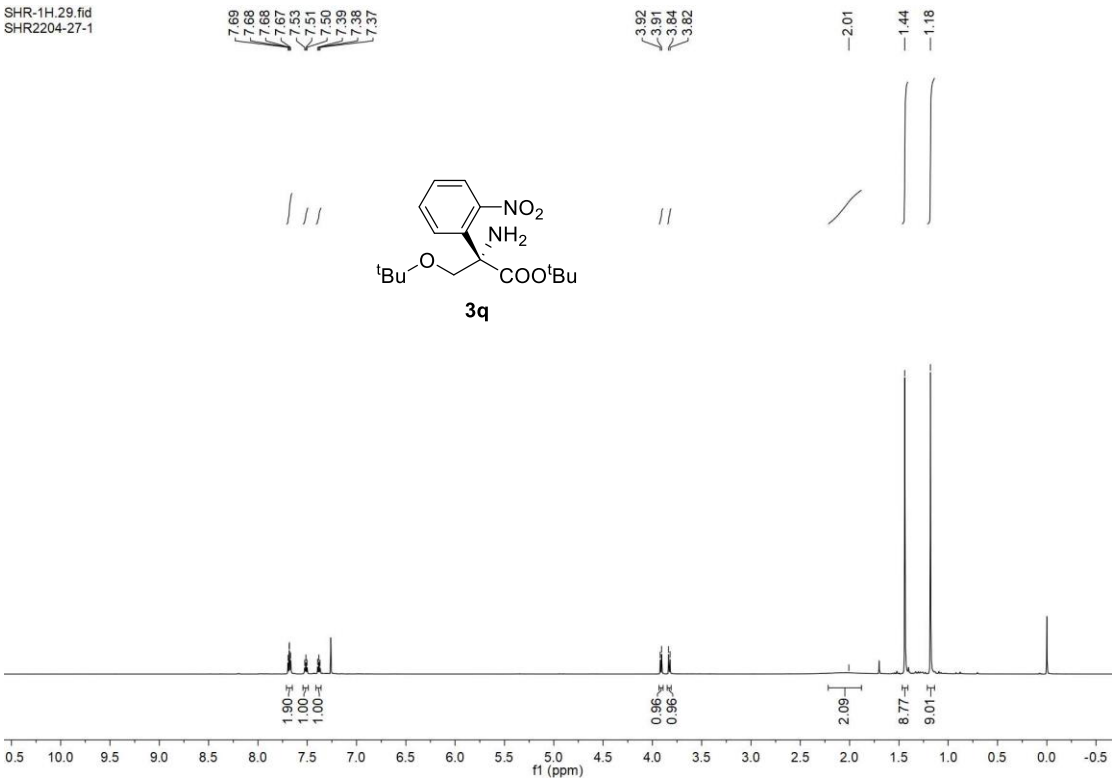
SHR-13C.26.fid
SHR2207-12-2

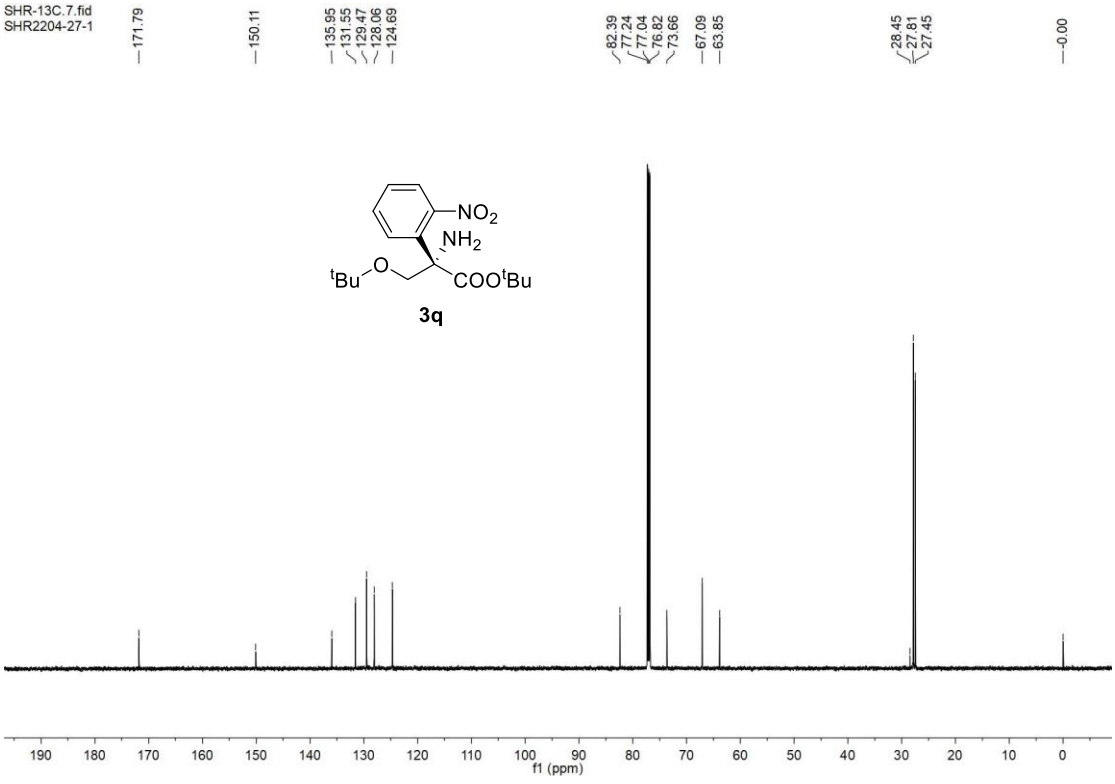


3o


SHR-1H.49.fid
SHR2205-16-3
7.93
7.92
7.87
7.86
7.63
7.62
7.61
7.47
7.46
7.44
4.18
4.17
4.16
4.15
2.55
2.55
2.54
2.52
2.52
2.51
2.50
2.49
2.49
2.48
2.47
2.46
2.30
2.30
2.29
2.28
2.28
2.27
2.26
2.08
2.06
1.61
1.24
1.22
1.21
NO2
NH2
EtOOC
S
O
CH3
3p
1.00
0.91
0.93
0.96
1.98
3.04
1.01
3.13
1.61
3.04
f1 (ppm)


SHR-13C.49.fid
SHR2205-16-3
173.59
149.21
136.29
132.59
128.99
128.51
125.28
77.20
76.99
76.78
62.59
61.71
38.49
28.68
15.55
13.92
NO2
NH2
EtOOC
S
O
CH3
3p
f1 (ppm)


SHR-1H.29.fid
SHR2204-27-1
7.69
7.68
7.68
7.68
7.67
7.53
7.51
7.50
7.39
7.38
7.37
3.92
3.91
3.84
3.82
2.01
1.44
1.18
NO2
NH2
tBu
O
COOtBu
3q
1.90
1.00
1.00
0.96
0.96
2.09
8.77
9.01
f1 (ppm)


SHR-13C.7.fid
SHR2204-27-1
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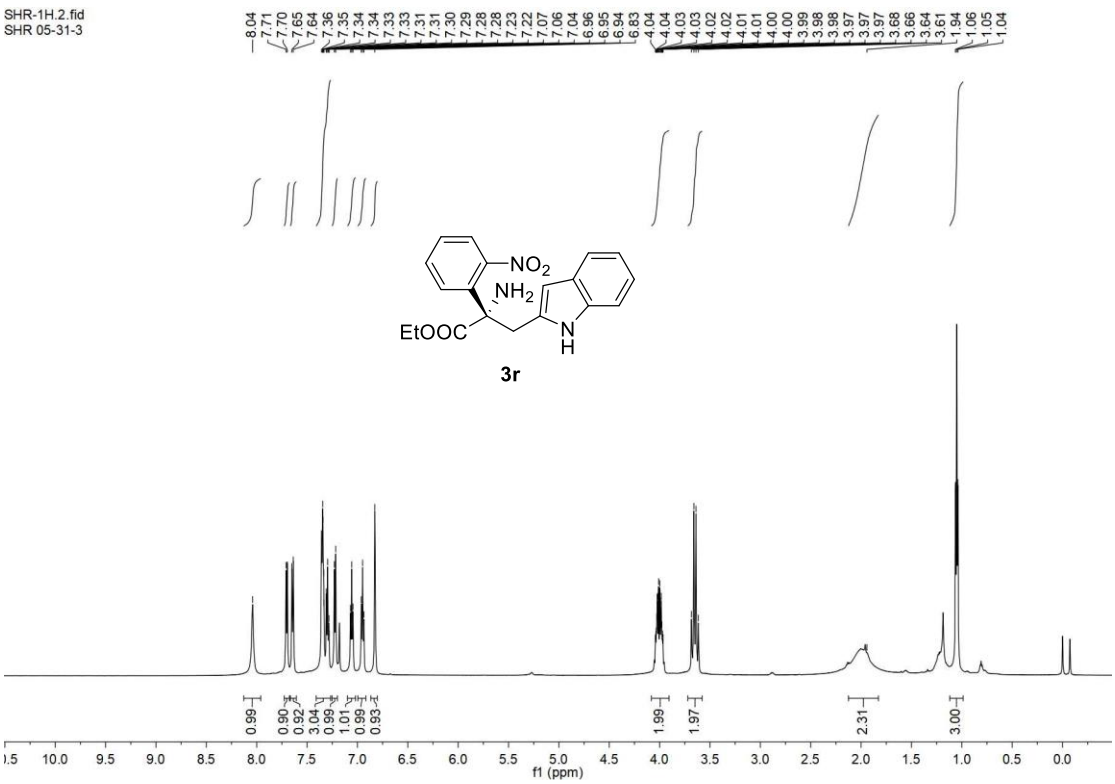
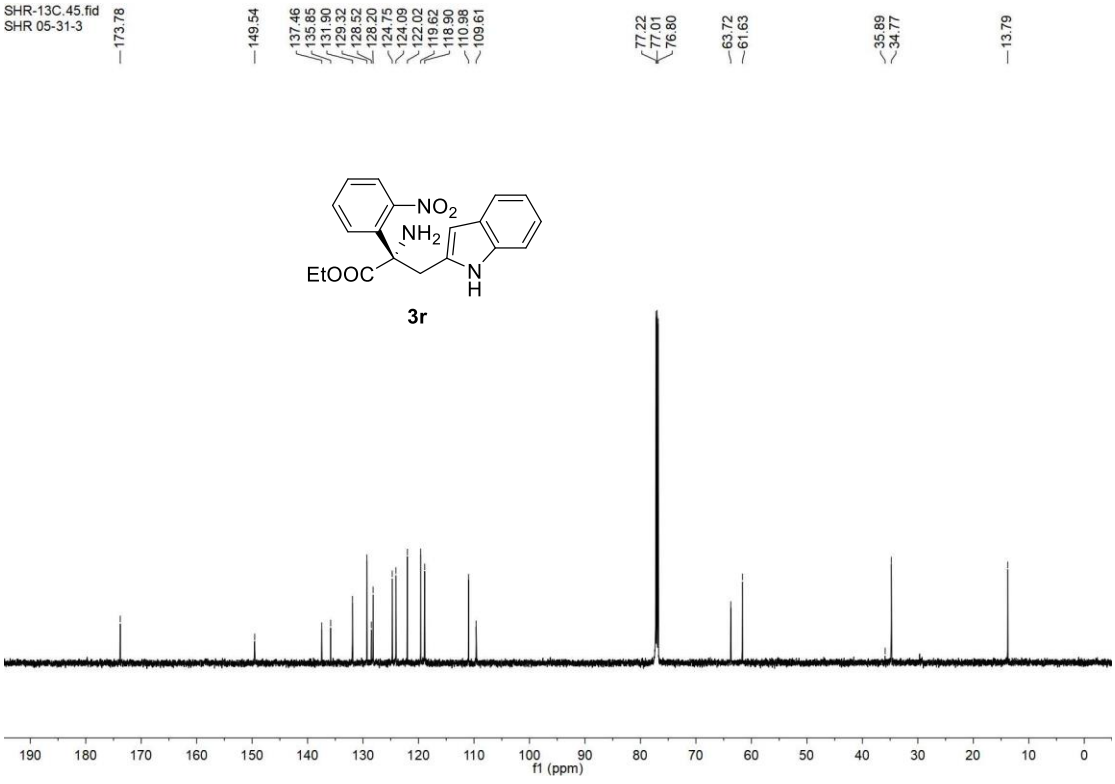
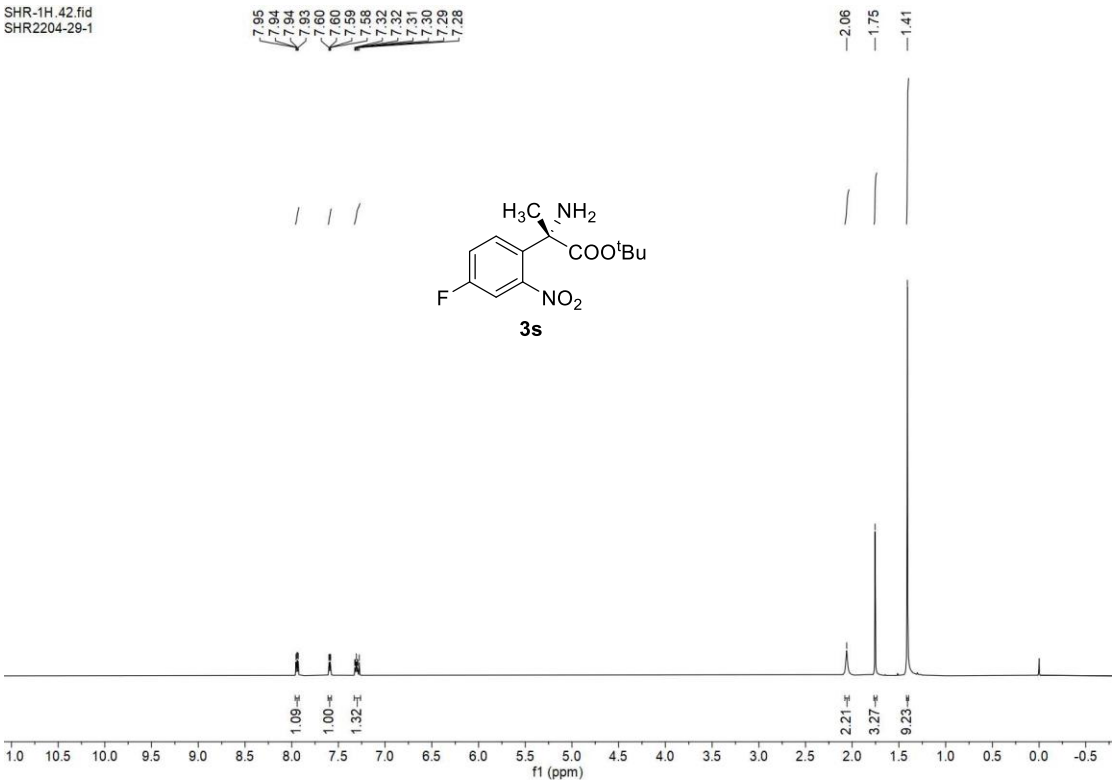
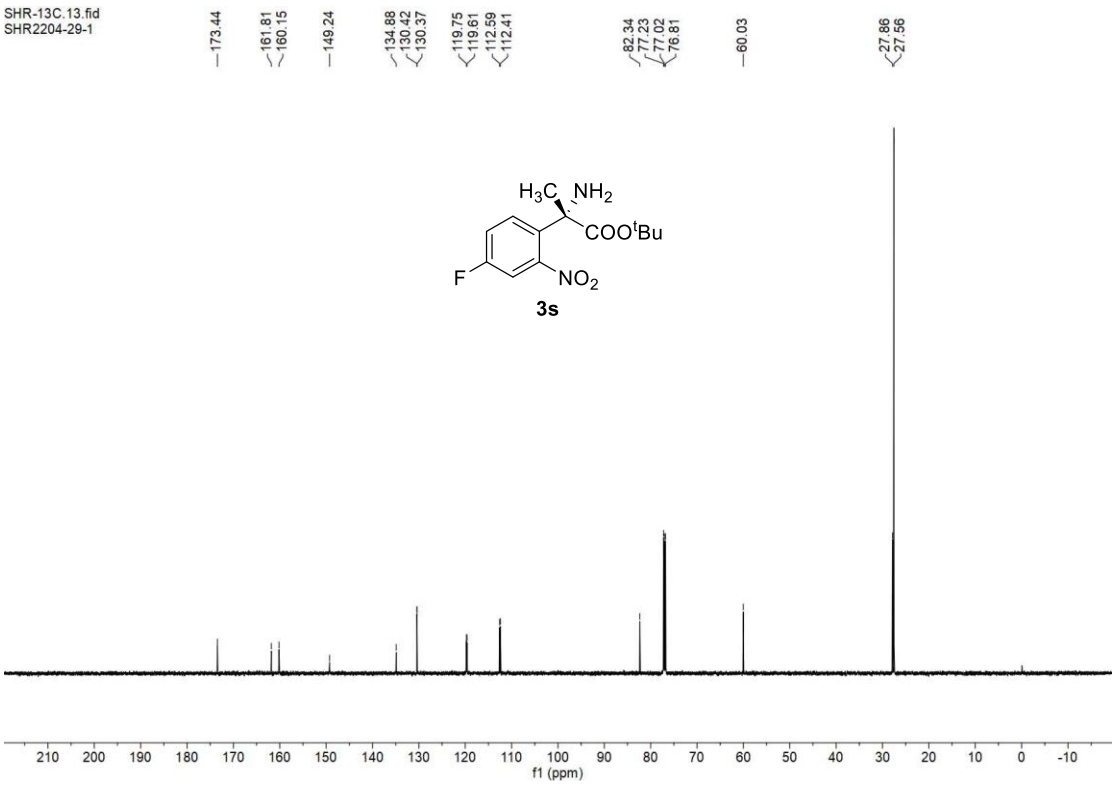
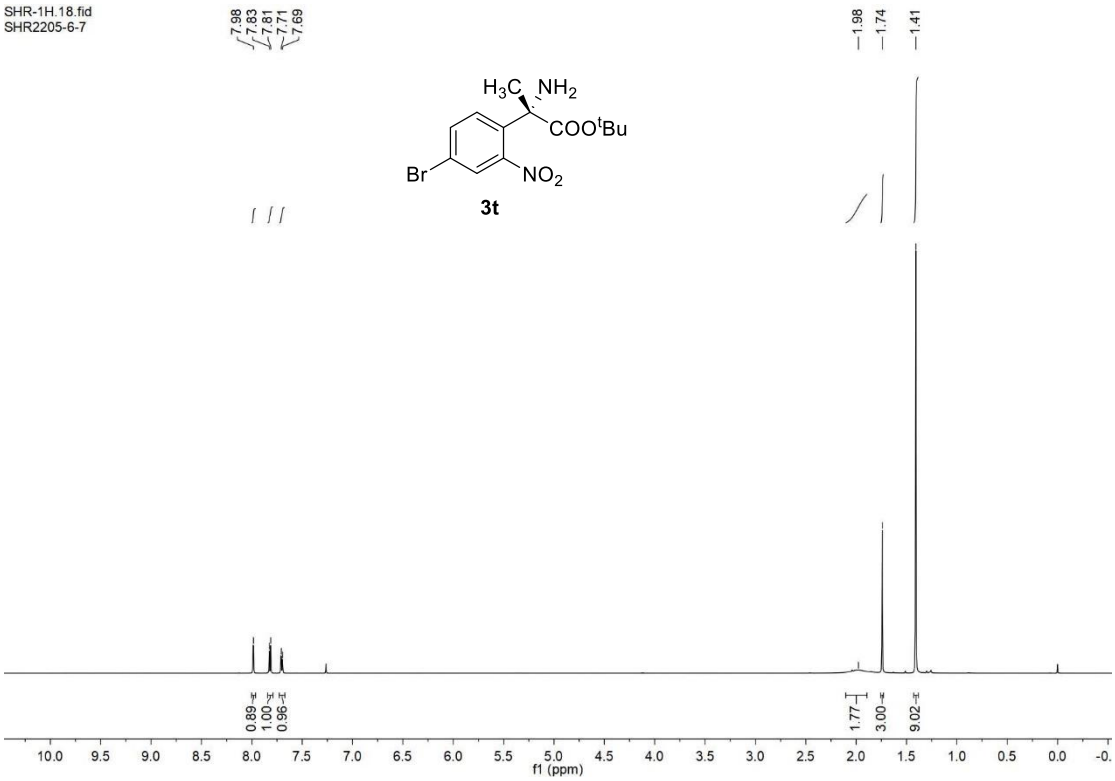
150.11
135.95
131.55
129.47
128.06
124.69
82.39
77.24
77.04
76.82
73.66
67.09
63.85
28.45
27.81
27.45
0.00
NO2
NH2
tBu
O
COOtBu
3q
f1 (ppm)

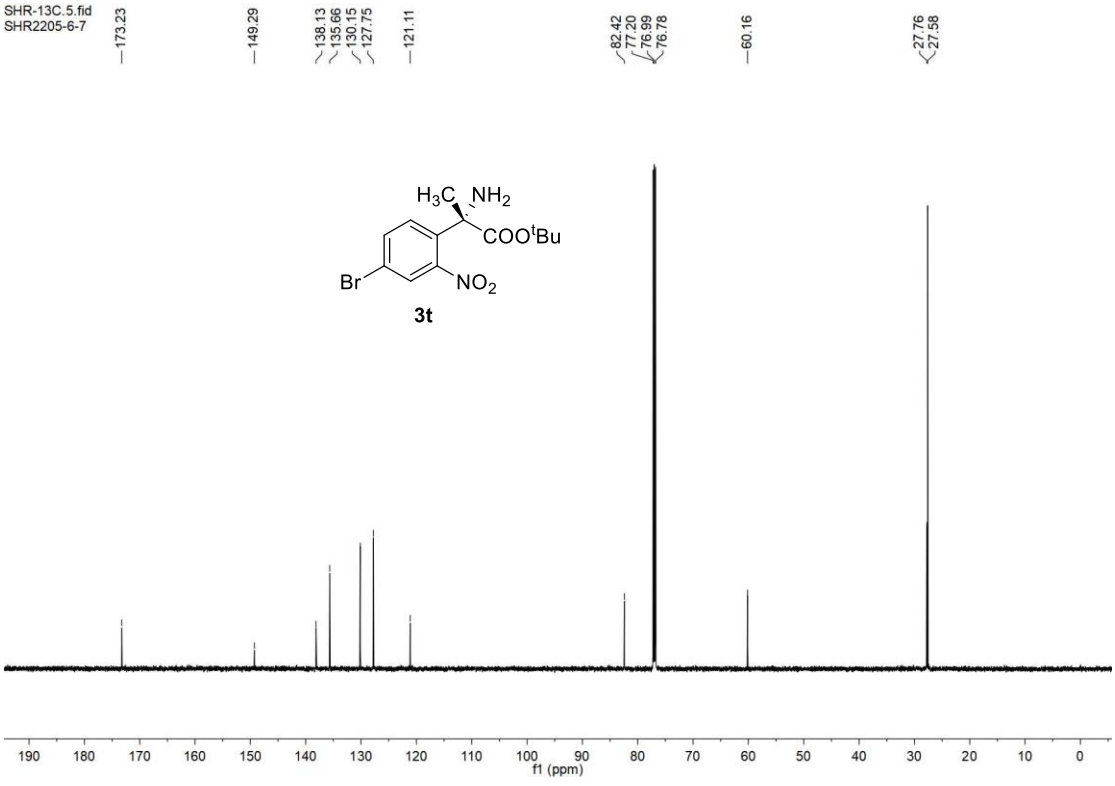

SHR-1H.2.fid
SHR 05-31-3
8.04
7.71
7.70
7.65
7.64
7.36
7.35
7.34
7.34
7.33
7.33
7.31
7.31
7.30
7.29
7.28
7.28
7.23
7.22
7.07
7.06
7.04
6.96
6.95
6.94
6.83
4.04
4.04
4.03
4.03
4.02
4.02
4.01
4.01
4.00
4.00
3.99
3.98
3.98
3.97
3.97
3.97
3.68
3.66
3.64
3.61
1.94
1.06
1.05
1.04
NO2
NH2
EtOOC
N
H
3r
0.99
0.90
0.92
3.04
0.99
1.01
0.99
0.93
1.99
1.97
2.31
3.00
f1 (ppm)


SHR-13C.45.fid
SHR 05-31-3
173.78
149.54
137.46
135.85
131.90
129.32
128.52
128.20
124.75
124.09
122.02
119.62
118.90
110.98
109.61
77.22
77.01
76.80
63.72
61.63
35.89
34.77
13.79
NO2
NH2
EtOOC
N
H
3r
f1 (ppm)

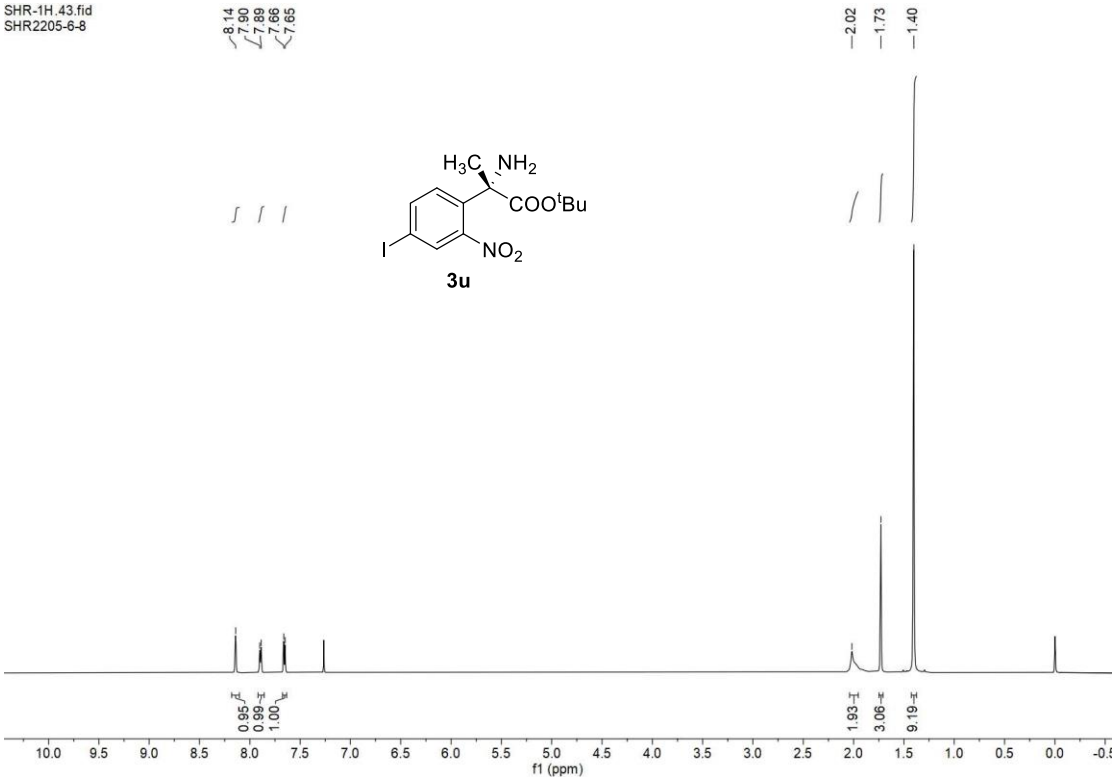

SHR-1H.42.fid
SHR2204-29-1
7.95
7.94
7.94
7.93
7.60
7.60
7.59
7.58
7.32
7.31
7.30
7.29
7.28
2.06
1.75
1.41
H3C
NH2
COOtBu
F
NO2
3s
1.09
1.00
1.32
2.21
3.27
9.23
f1 (ppm)


SHR-13C.13.fid
SHR2204-29-1
173.44
161.81
160.15
149.24
134.88
130.42
130.37
119.75
119.61
112.59
112.41
82.34
77.23
77.02
76.81
60.03
27.86
27.56
H3C
NH2
COOtBu
F
NO2
3s
f1 (ppm)


SHR-1H.18.fid
SHR2205-6-7
7.98
7.83
7.81
7.71
7.69
1.98
1.74
1.41
H3C
NH2
COOtBu
Br
NO2
3t
0.89
1.00
0.98
1.77
3.00
9.02
f1 (ppm)

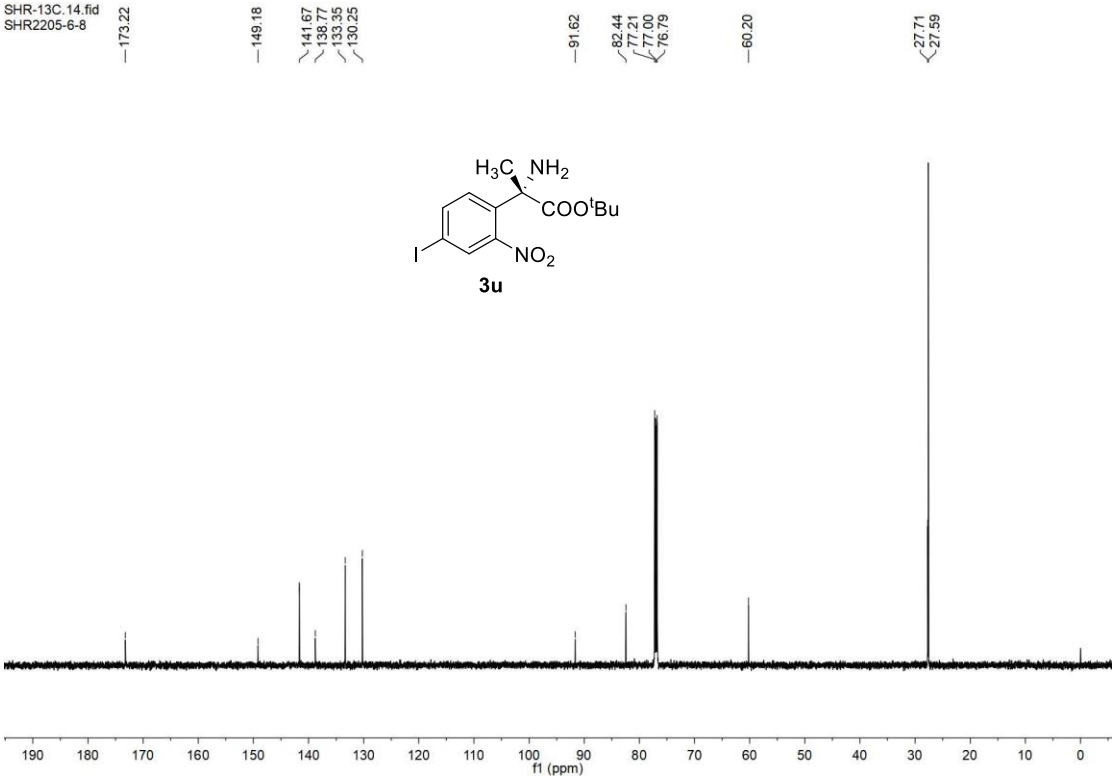

SHR-13C.5.fid
SHR2205-6-7
173.23
149.29
138.13
135.66
130.15
127.75
121.11
82.42
77.20
76.99
76.78
60.16
27.76
27.58
H3C
NH2
COOtBu
Br
NO2
3t
f1 (ppm)

SHR-1H.43.fid
SHR2205-6-8



3u

SHR-13C.14.fid
SHR2205-6-8



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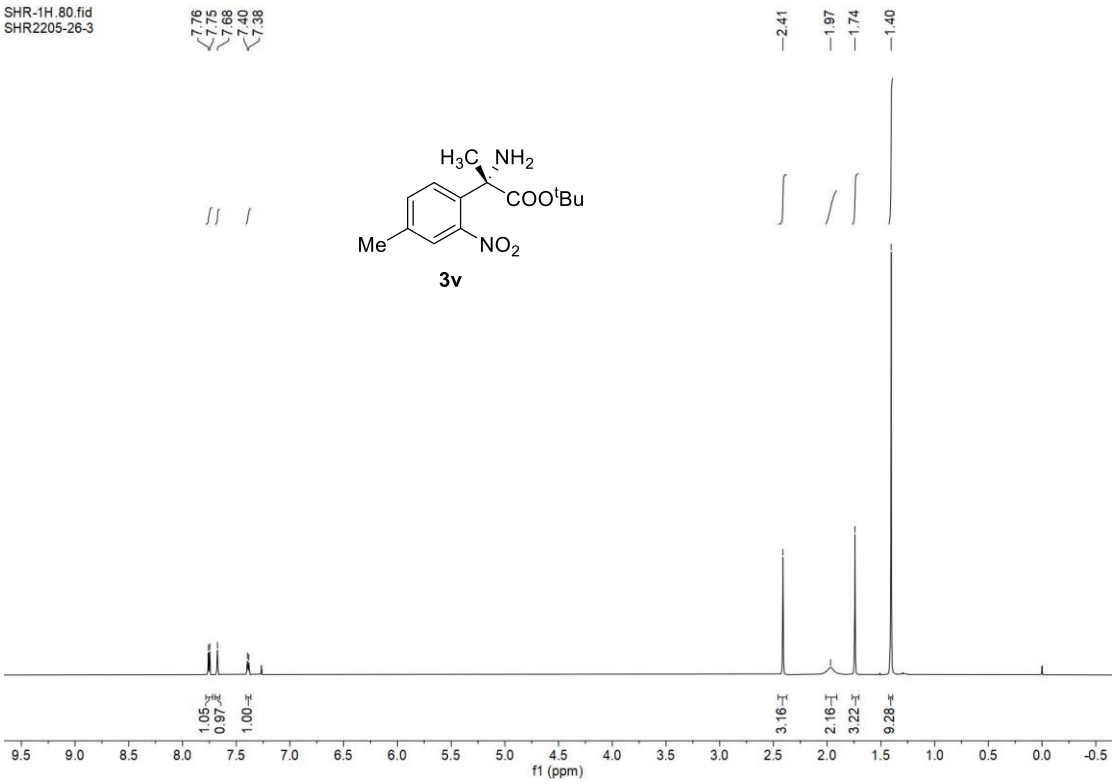
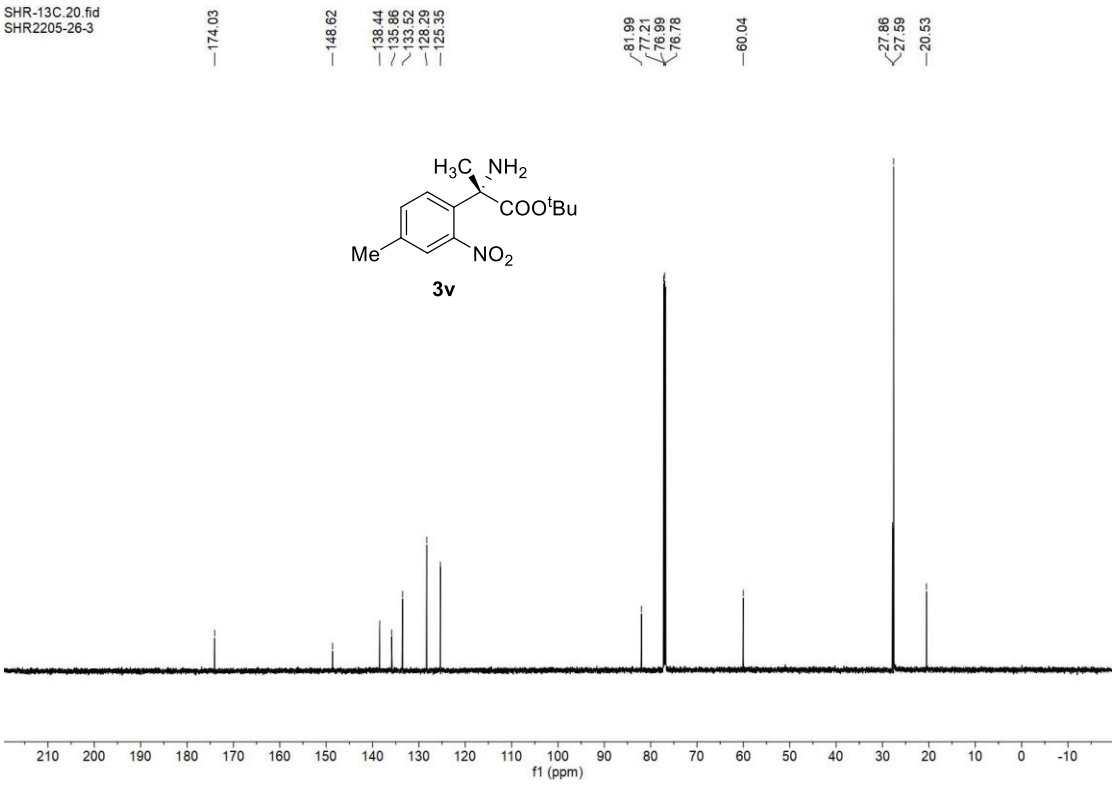
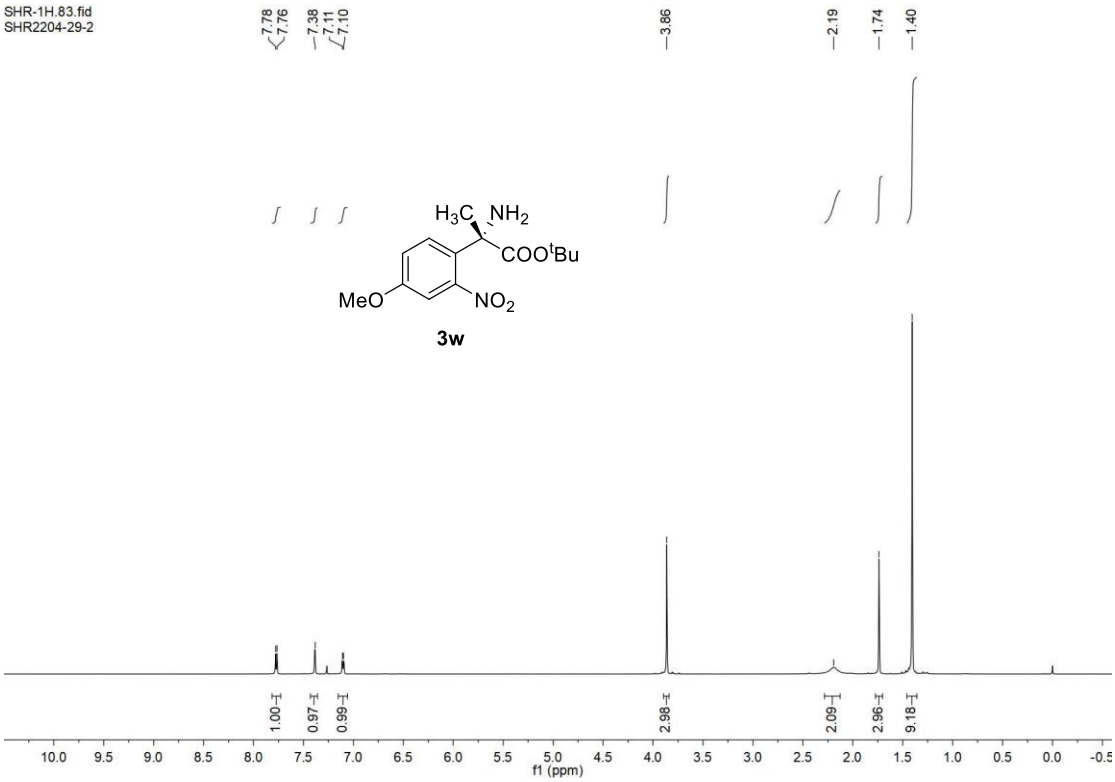
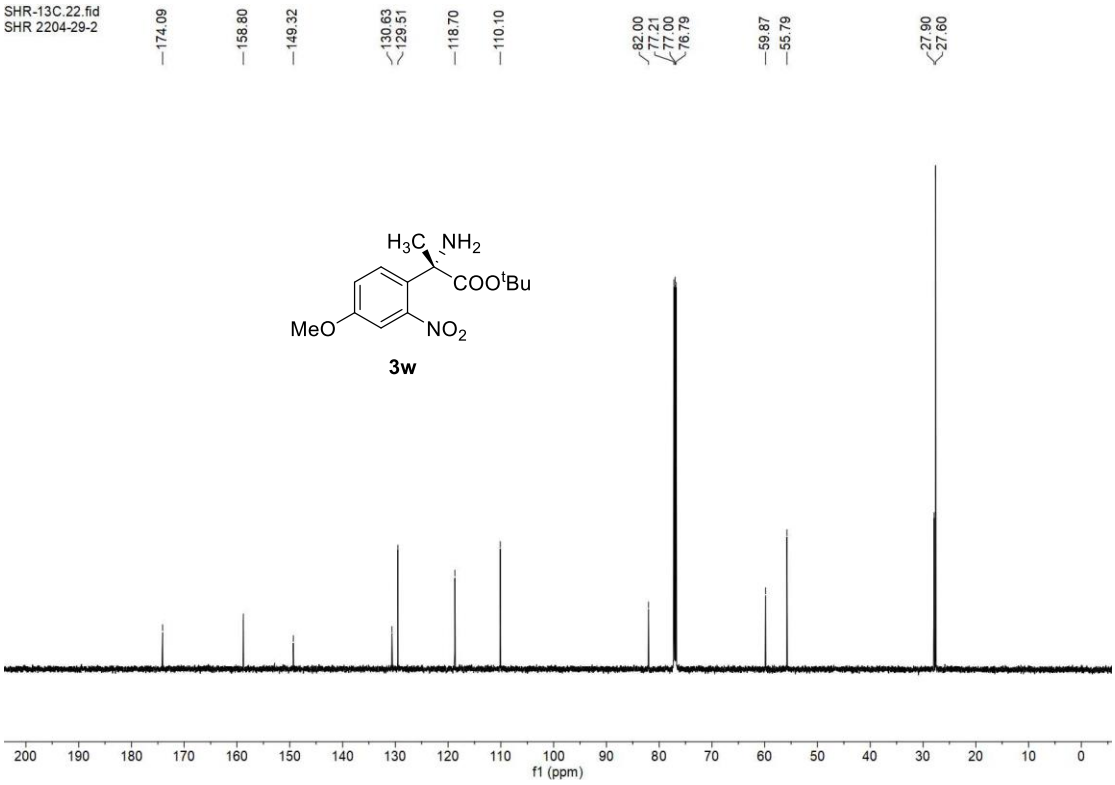
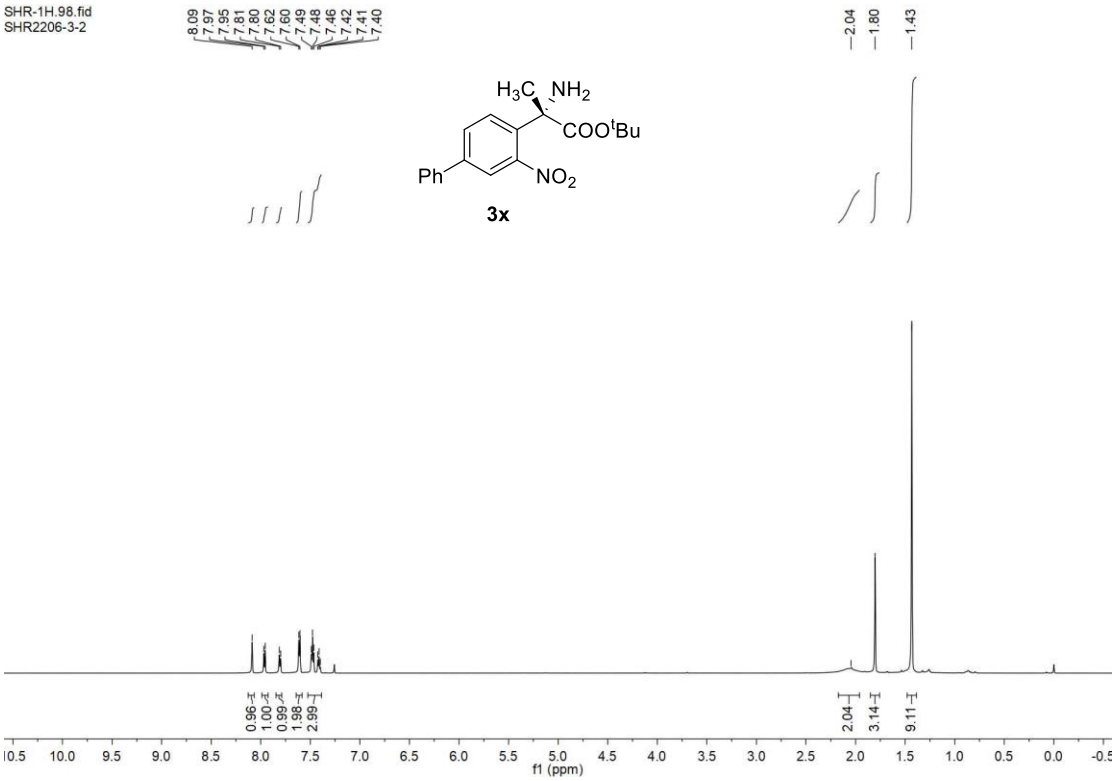

SHR-1H.80.fid
SHR2205-26-3
7.76
7.75
7.68
7.40
7.38
2.41
1.97
1.74
1.40
H3C
NH2
COOtBu
Me
NO2
3v
1.05
0.97
1.00
3.16
2.16
3.22
9.28
f1 (ppm)


SHR-13C.20.fid
SHR2205-26-3
174.03
148.62
138.44
135.86
133.52
128.29
125.35
81.99
77.21
76.99
76.78
60.04
27.86
27.59
20.53
H3C
NH2
COOtBu
Me
NO2
3v
f1 (ppm)

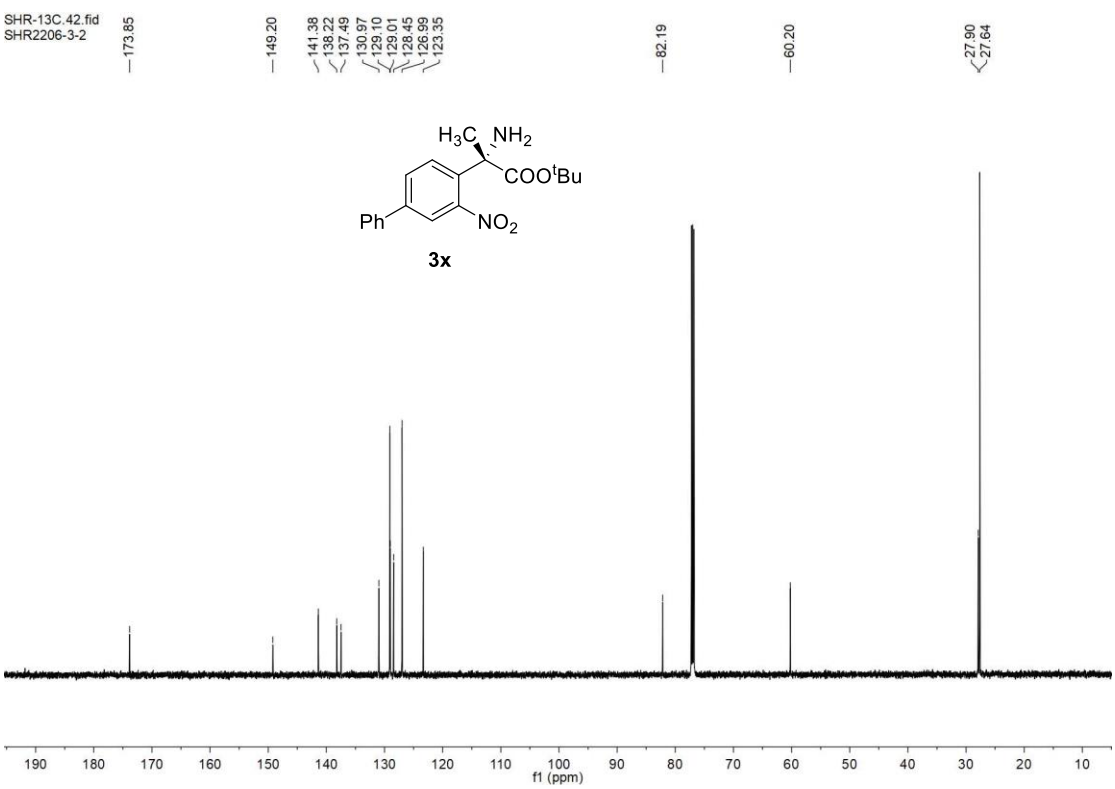

SHR-1H.83.fid
SHR2204-29-2
7.78
7.76
7.38
7.11
7.10
3.86
2.19
1.74
1.40
H3C
NH2
COOtBu
MeO
NO2
3w
1.00
0.97
0.99
2.98
2.09
2.96
9.18
f1 (ppm)

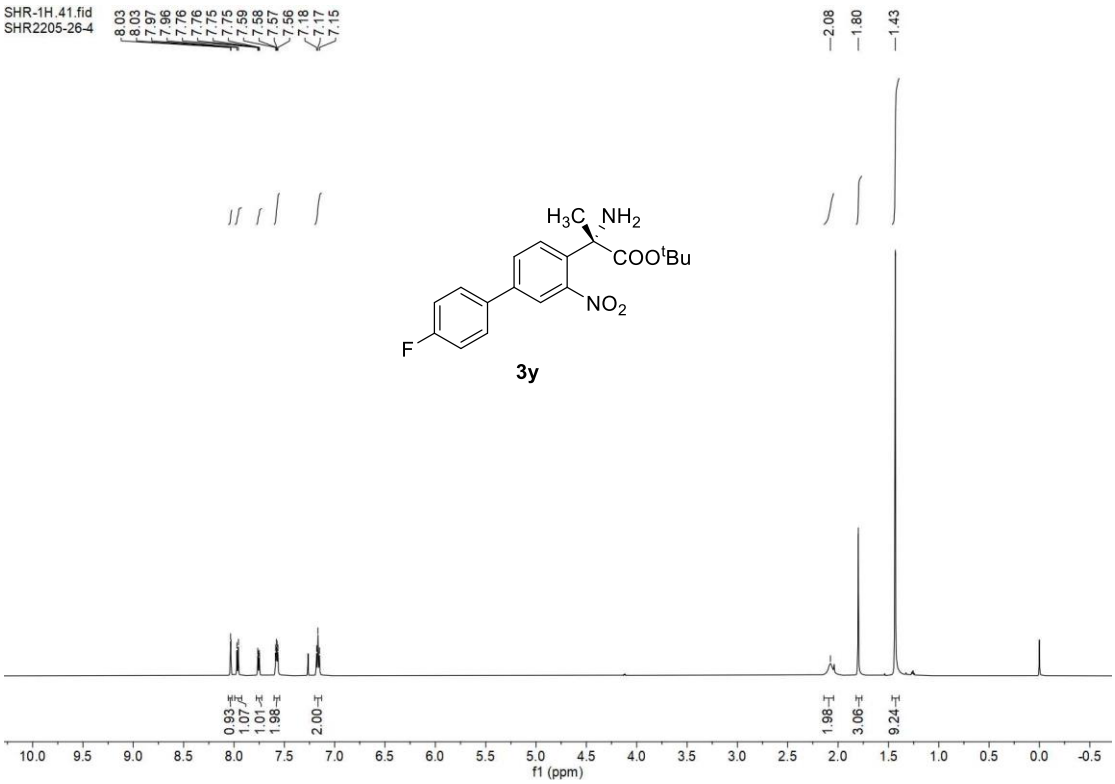

SHR-13C.22.fid
SHR 2204-29-2
174.09
158.80
149.32
130.63
129.51
118.70
110.10
82.00
77.21
77.00
76.79
59.87
55.79
27.90
27.60
H3C
NH2
COOtBu
MeO
NO2
3w
f1 (ppm)

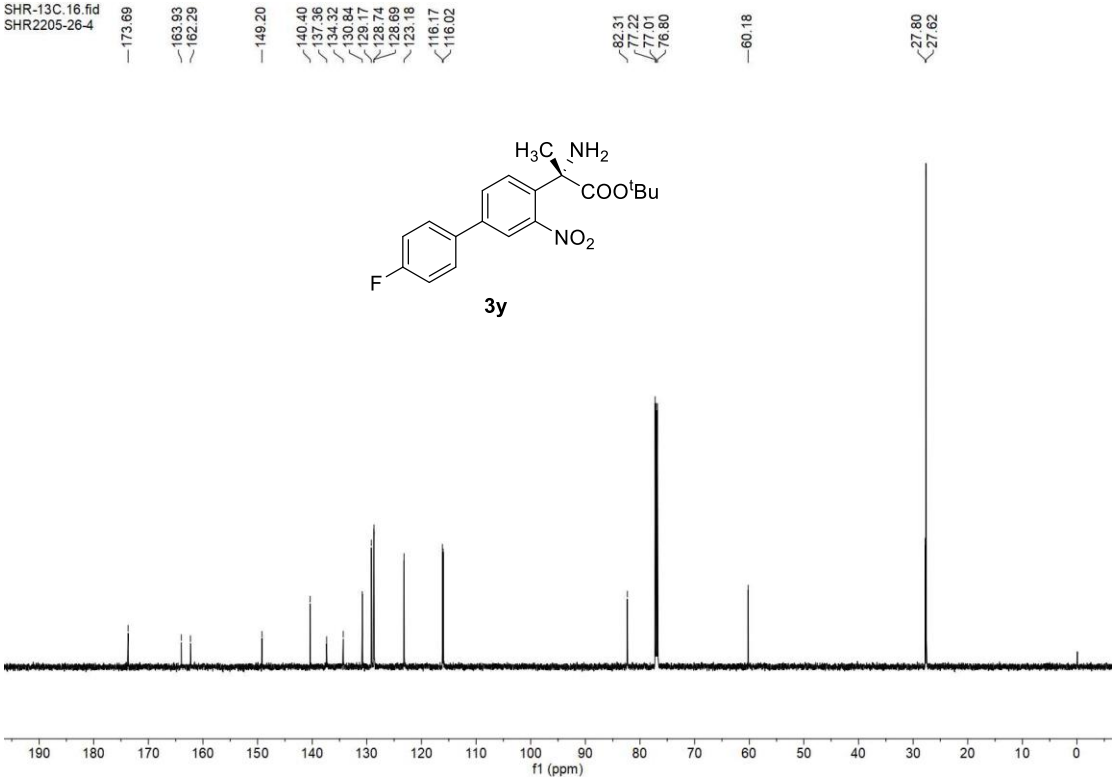
SHR-1H.98.fid
SHR2206-3-2

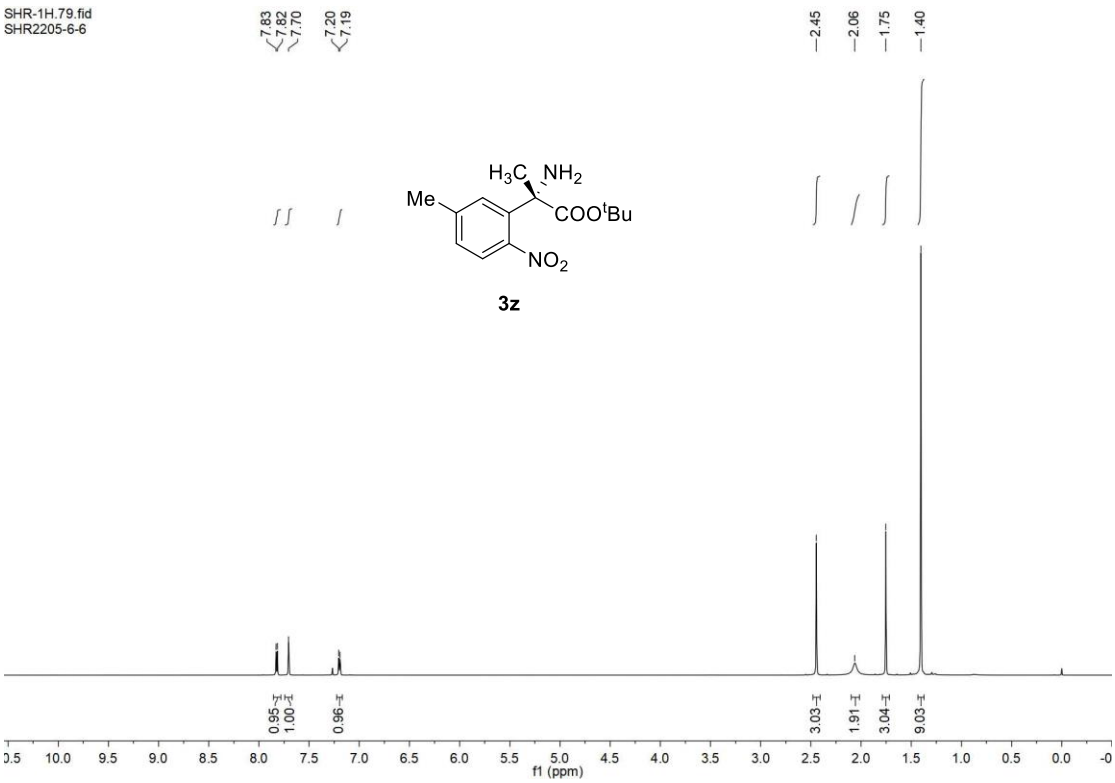


SHR-13C.42.fid
SHR2206-3-2

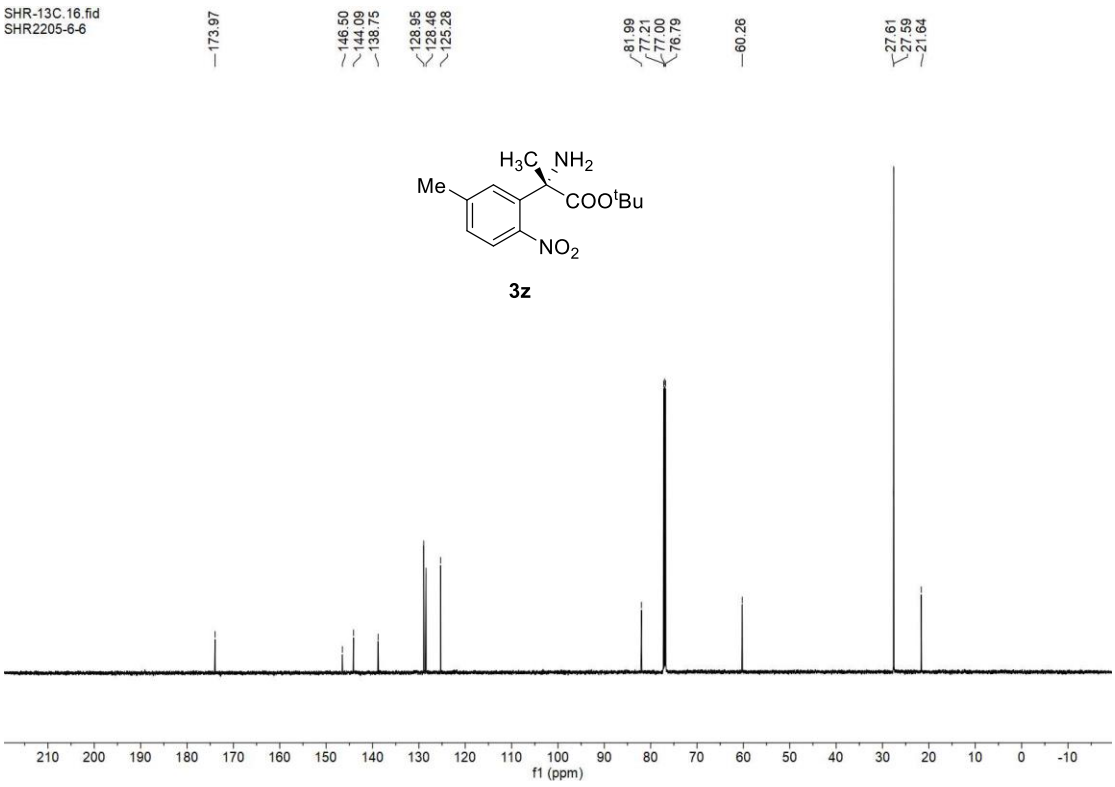



SHR-1H.41.fid
SHR2205-26-4
8.03
8.03
7.97
7.96
7.76
7.76
7.75
7.75
7.59
7.58
7.57
7.56
7.18
7.17
7.15
2.08
1.80
1.43
H3C
NH2
COOtBu
NO2
F
3y
0.93
1.07
1.01
1.98
2.00
1.98
3.06
9.24
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)

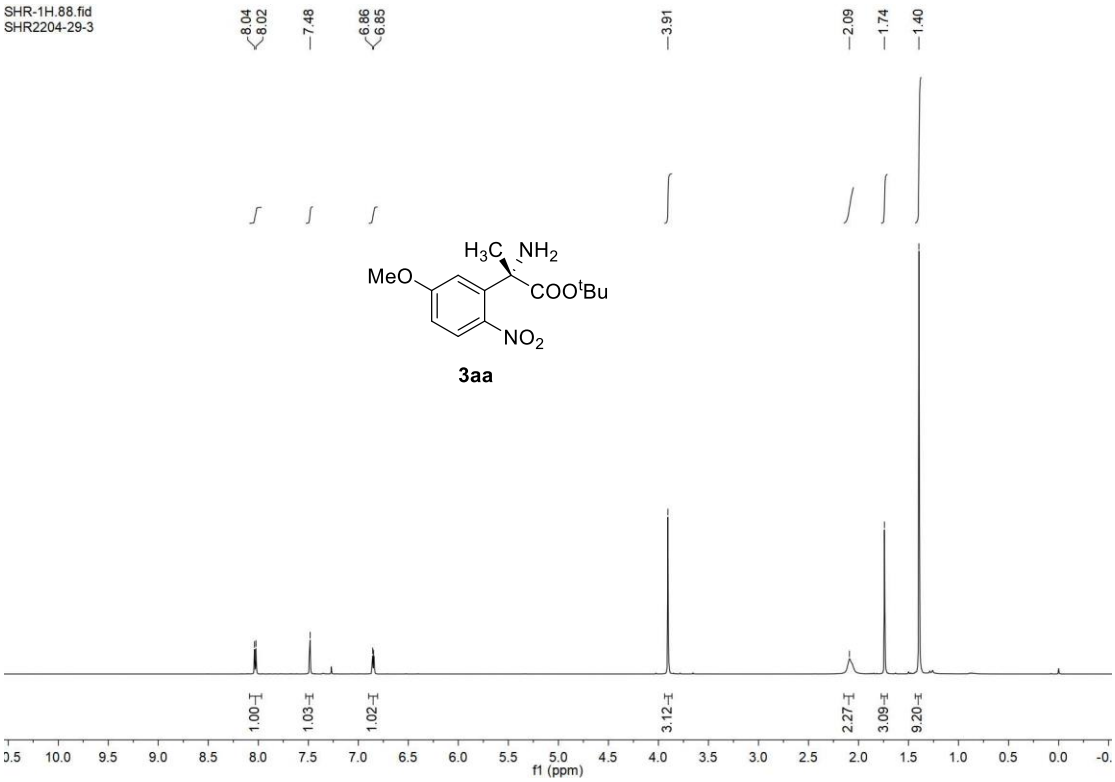

SHR-13C.16.fid
SHR2205-26-4
173.69
163.93
162.29
149.20
140.40
137.36
134.32
130.84
129.17
128.74
128.69
123.18
116.17
116.02
82.31
77.22
77.01
76.80
60.18
27.80
27.62
H3C
NH2
COOtBu
NO2
F
3y
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SHR-1H.79.fid
SHR2205-6-6
7.83
7.82
7.70
7.20
7.19
2.45
2.06
1.75
1.40
Me
H3C
NH2
COOtBu
NO2
0.95
1.00
0.96
3.03
1.91
3.04
9.03
f1 (ppm)

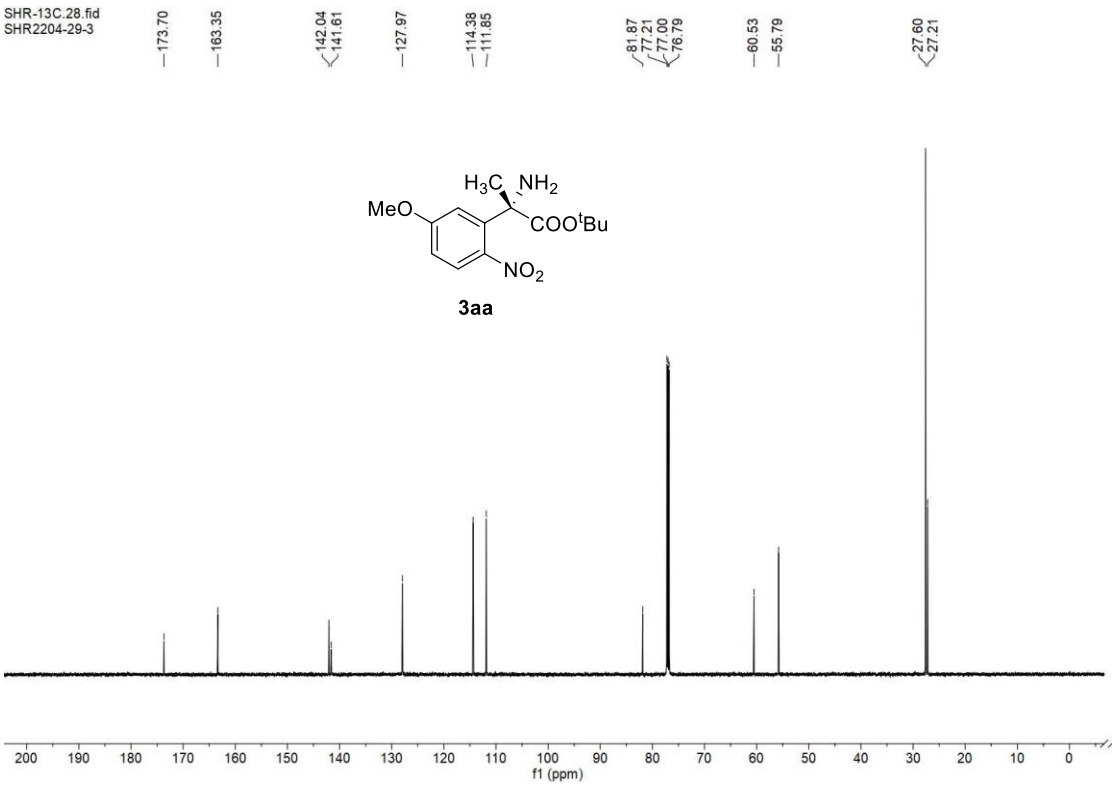
3z


SHR-13C.16.fid
SHR2205-6-6
173.97
146.50
144.09
138.75
128.95
128.46
125.28
81.99
77.21
77.00
76.79
60.26
27.61
27.59
21.64
Me
H3C
NH2
COOtBu
NO2
f1 (ppm)

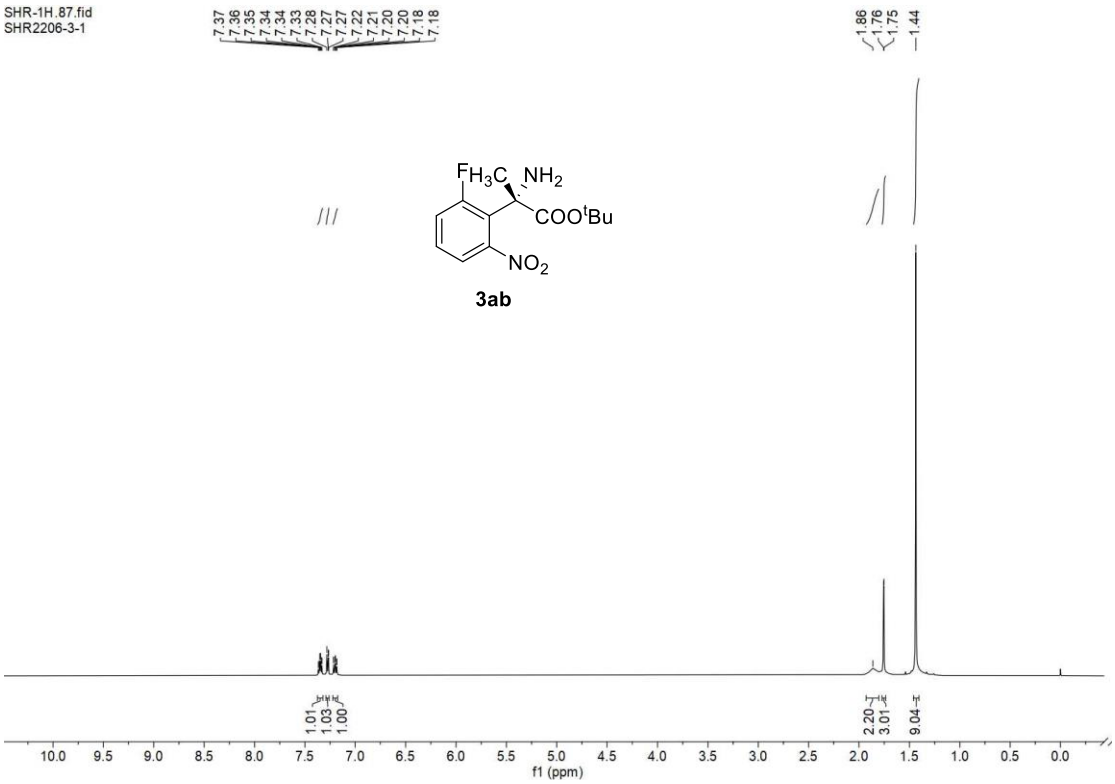
3z

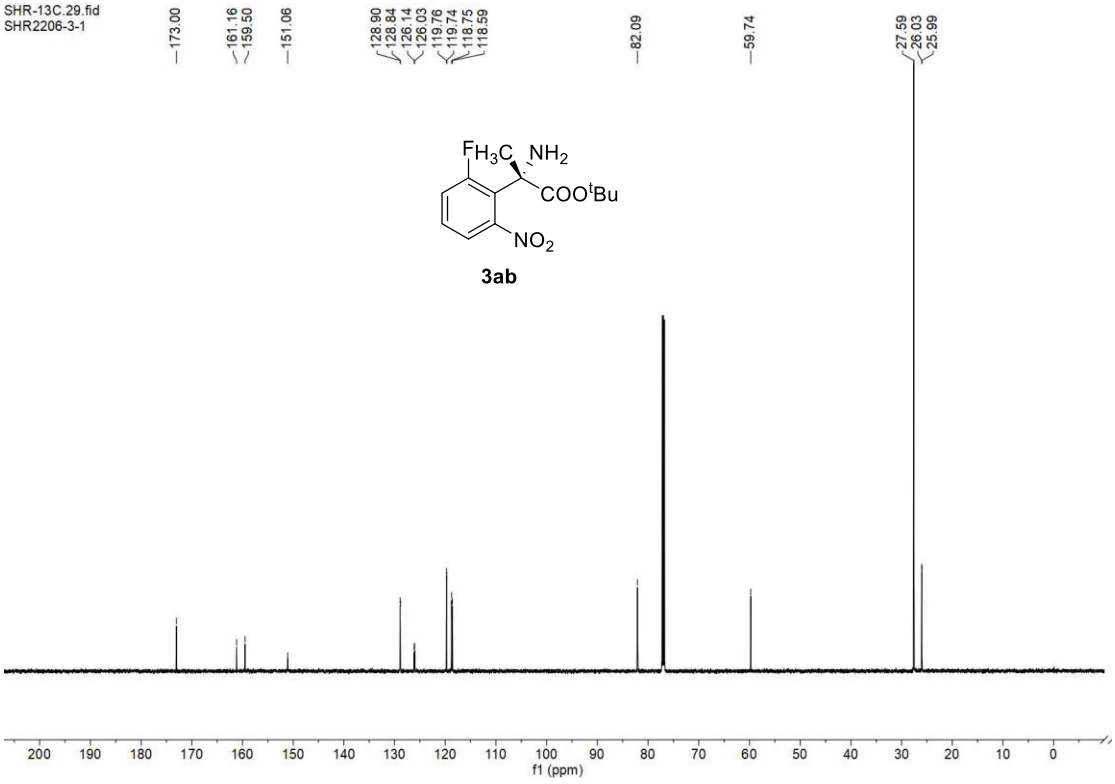

SHR-1H.88.fid
SHR2204-29-3
8.04
8.02
7.48
6.86
6.85
3.91
2.09
1.74
1.40
MeO
H3C
NH2
COOtBu
NO2
1.00
1.03
1.02
3.12
2.27
3.09
9.20
f1 (ppm)

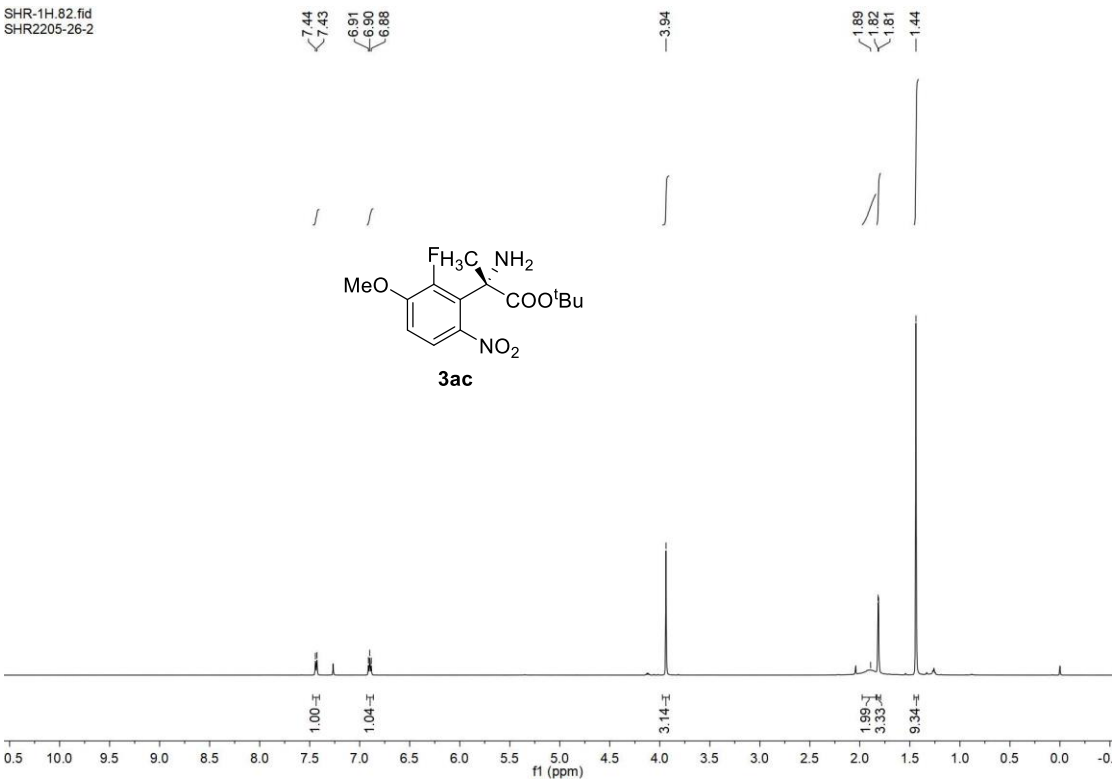
3aa


SHR-13C.28.fid
SHR2204-29-3
173.70
163.35
142.04
141.61
127.97
114.38
111.85
81.87
77.21
77.00
76.79
60.53
55.79
27.60
27.21
MeO
H3C
NH2
COOtBu
NO2
f1 (ppm)

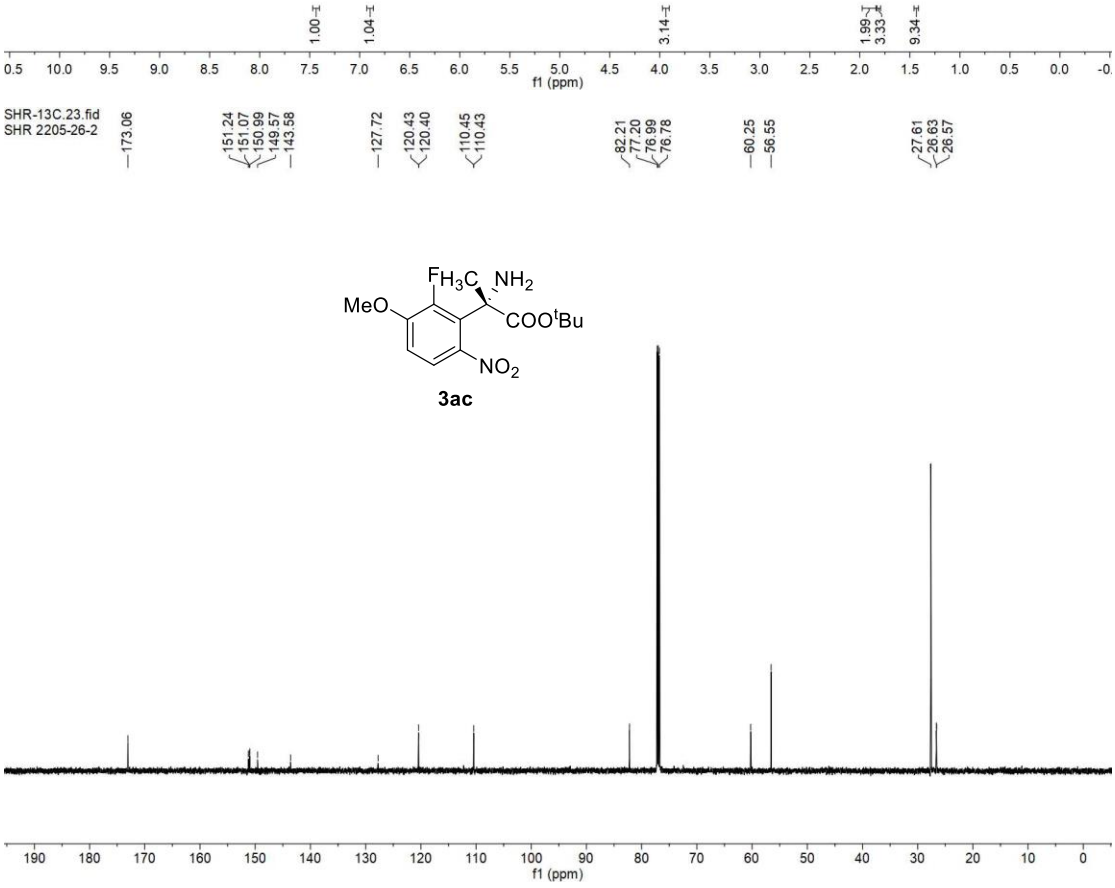
3aa


SHR-1H.87.fid
SHR2206-3-1
7.37
7.36
7.35
7.34
7.34
7.33
7.28
7.27
7.27
7.22
7.21
7.20
7.20
7.18
7.18
1.86
1.76
1.75
1.44
F3C
NH2
COOtBu
NO2
3ab
1.01
1.03
1.00
2.20
3.01
9.04
f1 (ppm)

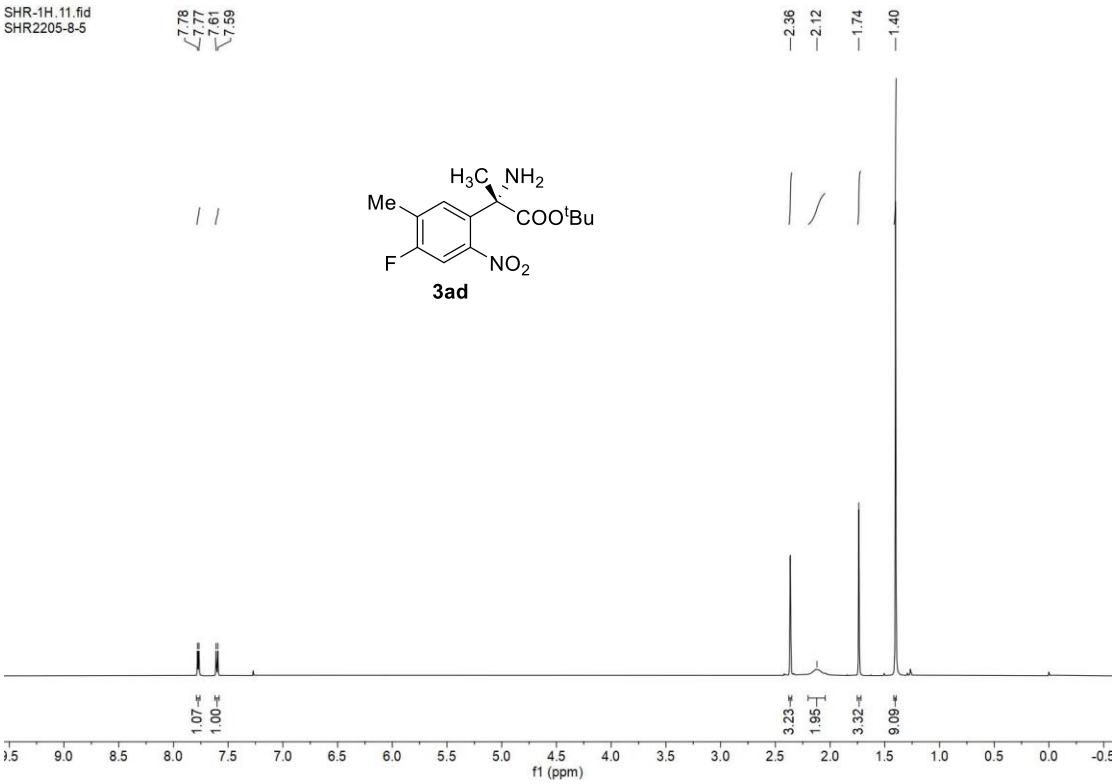

SHR-13C.29.fid
SHR2206-3-1
173.00
161.16
159.50
151.06
128.90
128.84
126.14
126.03
119.76
119.74
118.75
118.59
82.09
59.74
27.59
26.03
25.99
F3C
NH2
COOtBu
NO2
3ab
f1 (ppm)

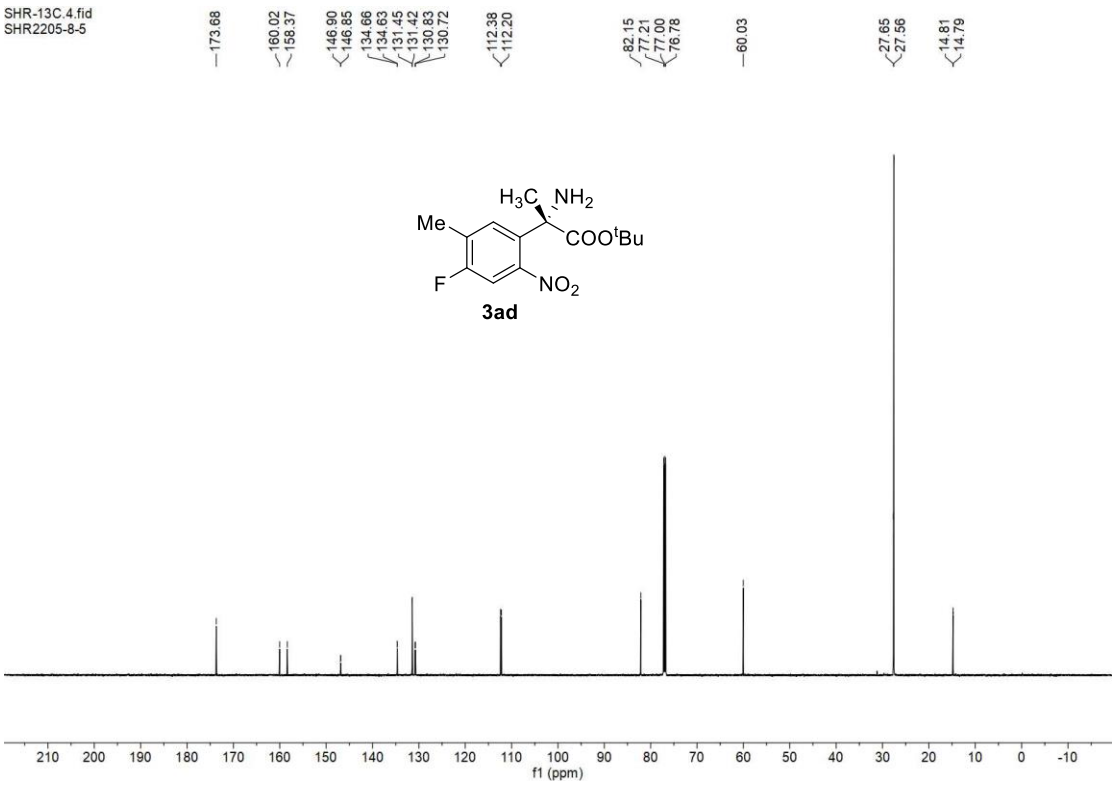

SHR-1H.82.fid
SHR2205-26-2
7.44
7.43
6.91
6.90
6.88
3.94
1.89
1.82
1.81
1.44
F3C
NH2
MeO
COOtBu
NO2
1.00
1.04
3.14
1.99
3.33
9.34
f1 (ppm)

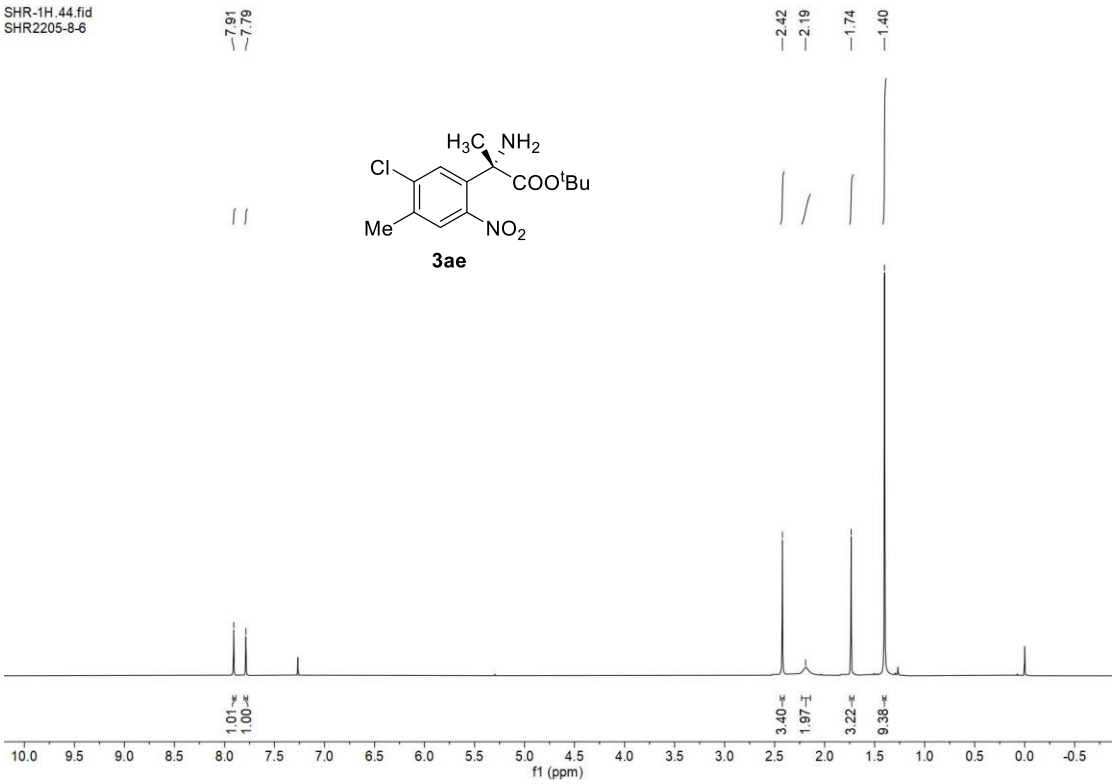
3ac

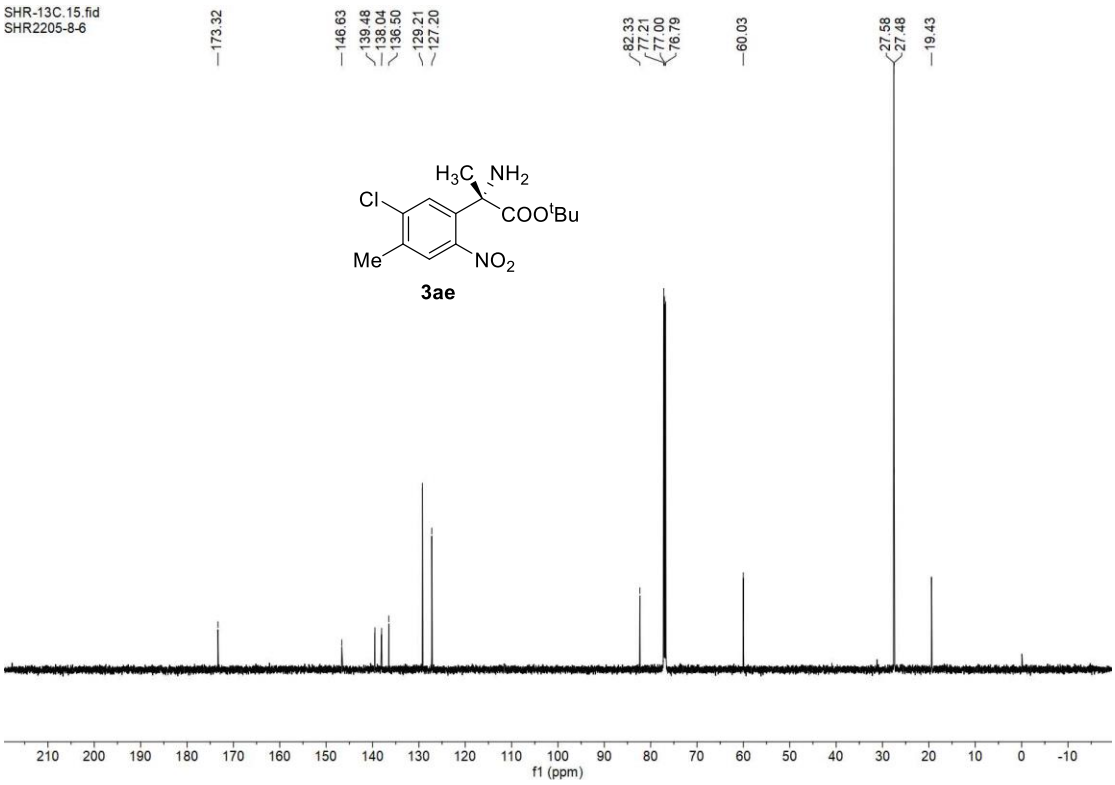

SHR-13C.23.fid
SHR 2205-26-2
173.06
151.24
151.07
150.99
149.57
143.58
127.72
120.43
120.40
110.45
110.43
82.21
77.20
76.99
76.78
60.25
56.55
27.61
26.63
26.57
F3C
NH2
MeO
COOtBu
NO2
f1 (ppm)

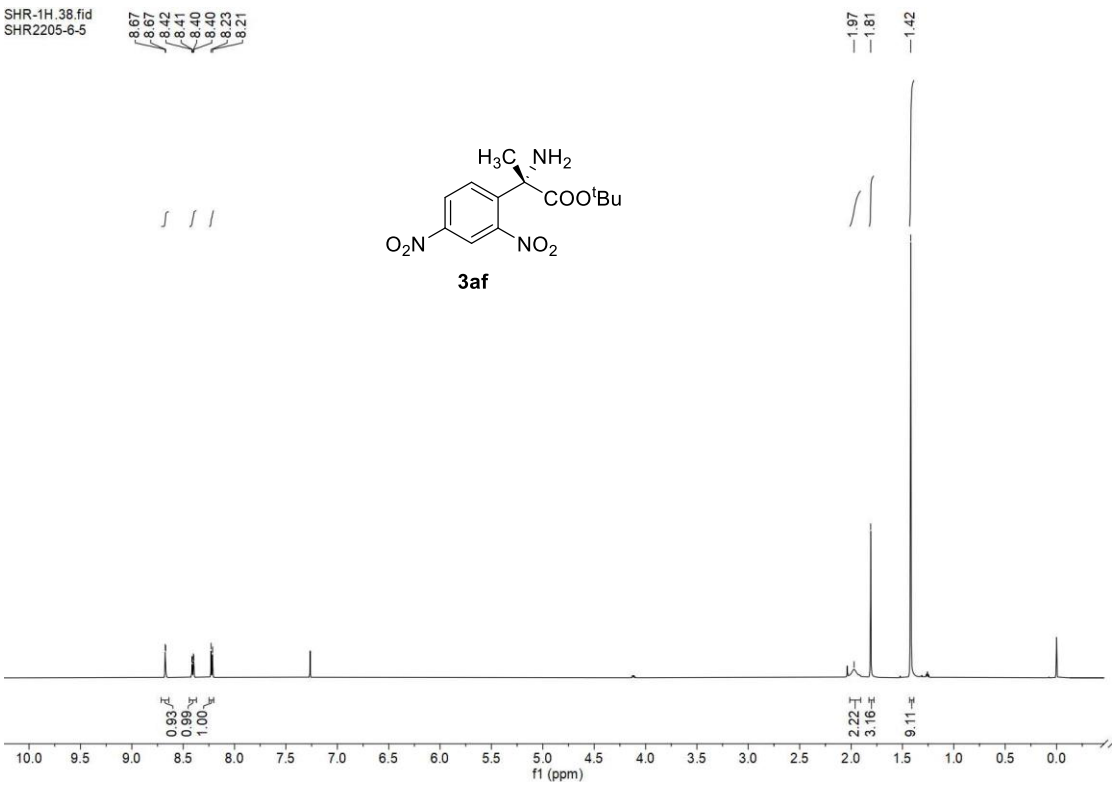
3ac

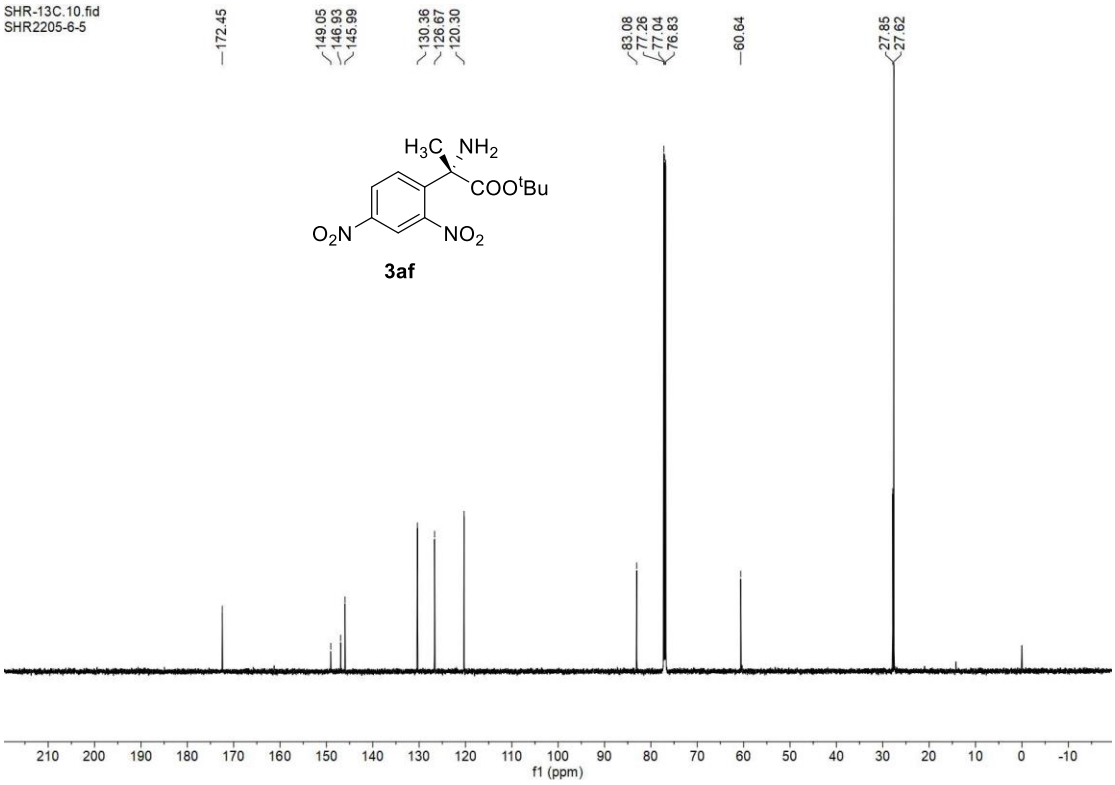

SHR-1H.11.fid
SHR2205-8-5
7.78
7.77
7.61
7.59
2.36
2.12
1.74
1.40
Me
F
NO2
3ad
1.07
1.00
3.23
1.95
3.32
9.09
f1 (ppm)

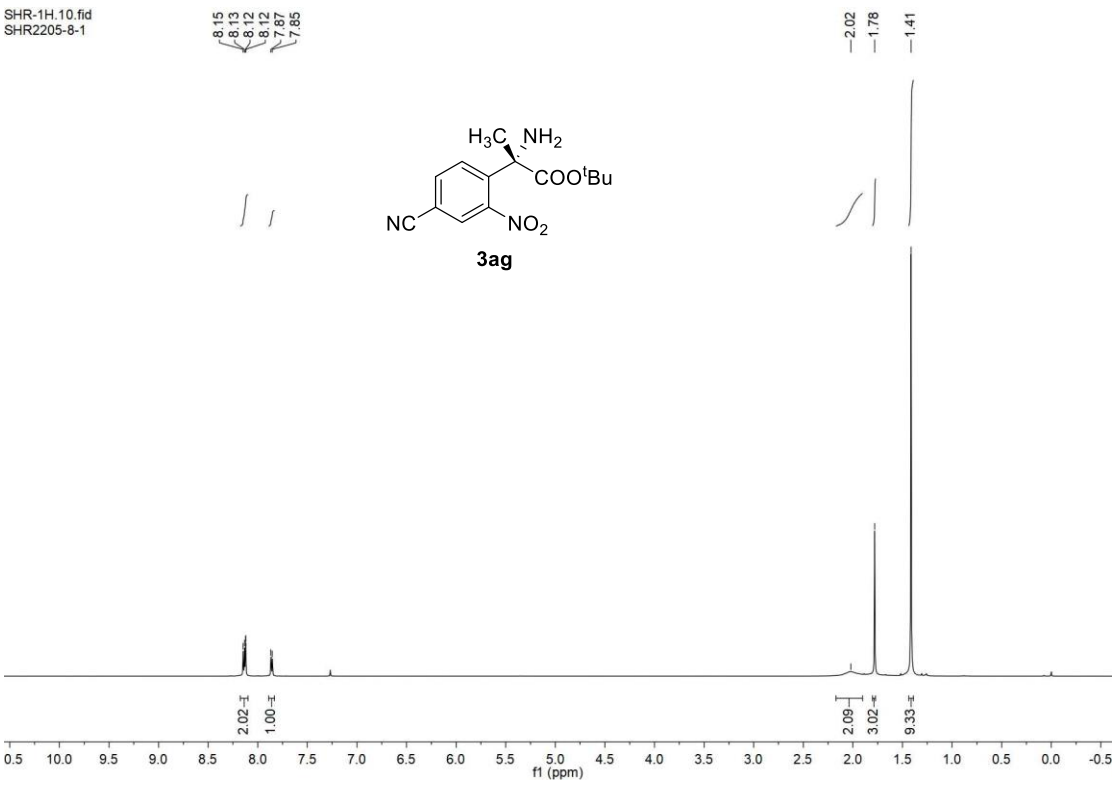

SHR-13C.4.fid
SHR2205-8-5
173.68
160.02
158.37
146.90
146.85
134.66
134.63
131.45
131.42
130.83
130.72
112.38
112.20
82.15
77.21
77.00
76.78
60.03
27.65
27.56
14.81
14.79
Me
F
NO2
3ad
f1 (ppm)

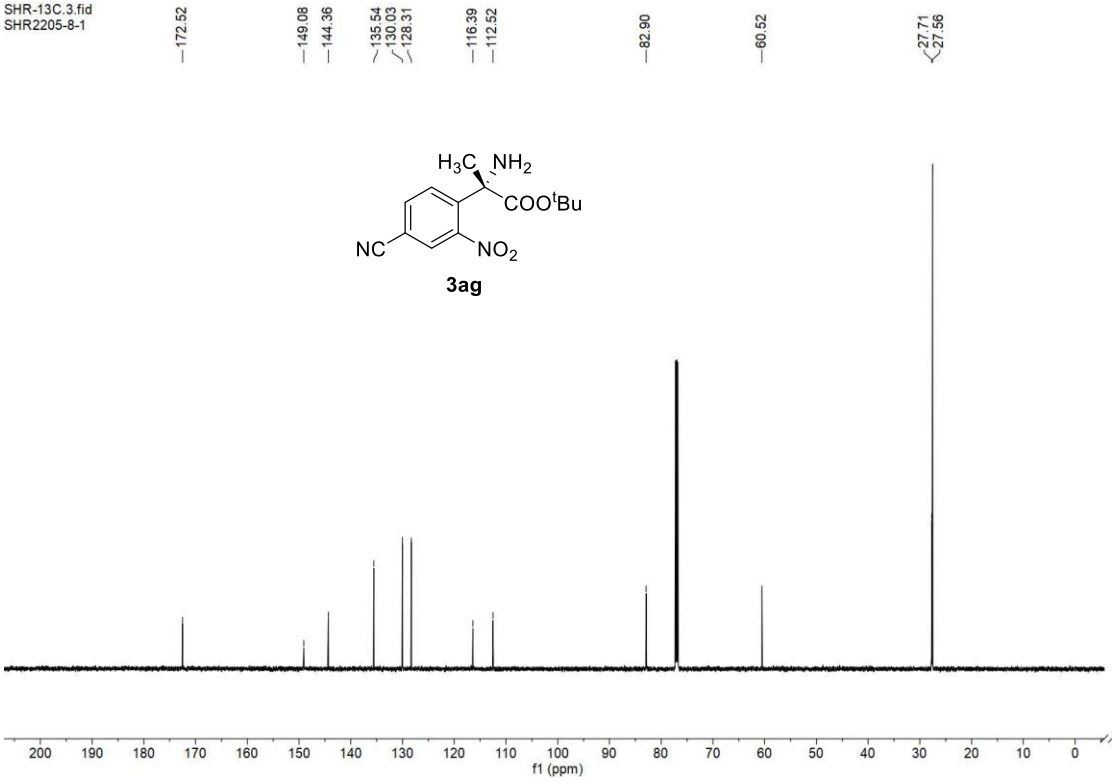

SHR-1H.44.fid
SHR2205-8-6
7.91
7.79
2.42
2.19
1.74
1.40
H3C
NH2
Cl
COOtBu
Me
NO2
3ae
1.01
1.00
3.40
1.97
3.22
9.38
f1 (ppm)

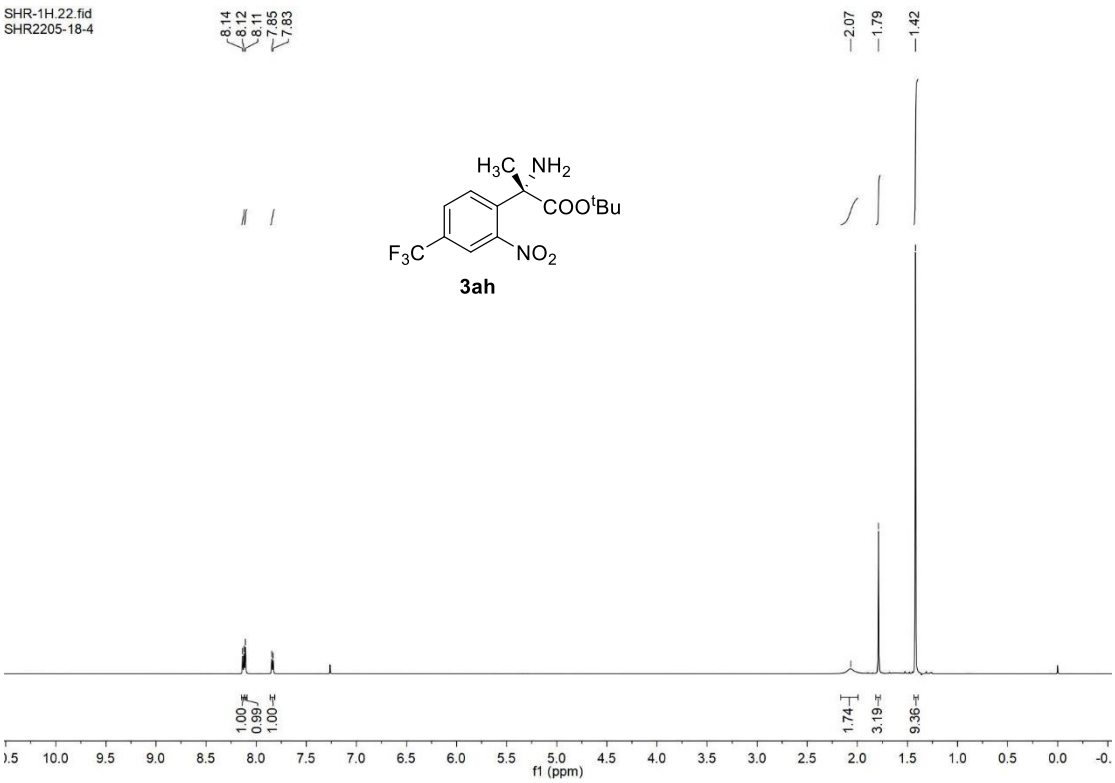

SHR-13C.15.fid
SHR2205-8-6
173.32
146.63
139.48
138.04
136.50
129.21
127.20
82.33
77.21
77.00
76.79
60.03
27.58
27.48
19.43
H3C
NH2
Cl
COOtBu
Me
NO2
3ae
f1 (ppm)

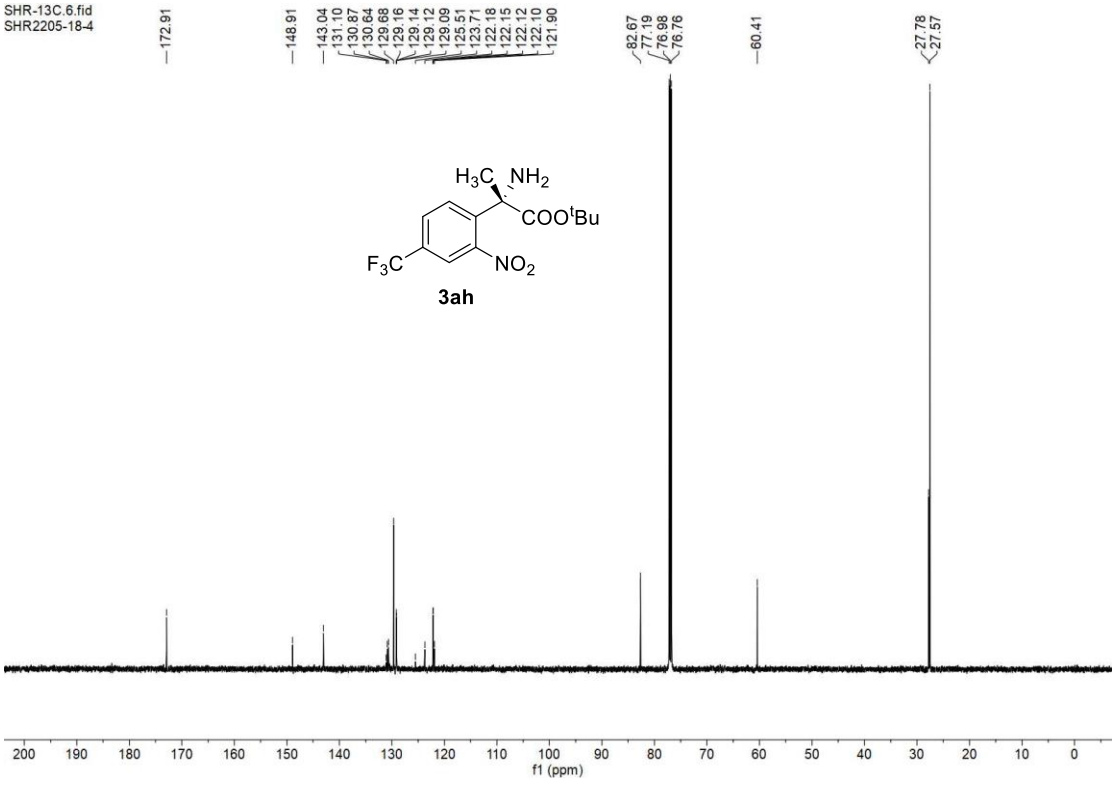

SHR-1H.38.fid
SHR2205-6-5
8.67
8.67
8.42
8.41
8.40
8.40
8.23
8.21
1.97
1.81
1.42
H3C NH2
COOtBu
O2N
NO2
3af
0.93
0.99
1.00
2.22
3.16
9.11
f1 (ppm)

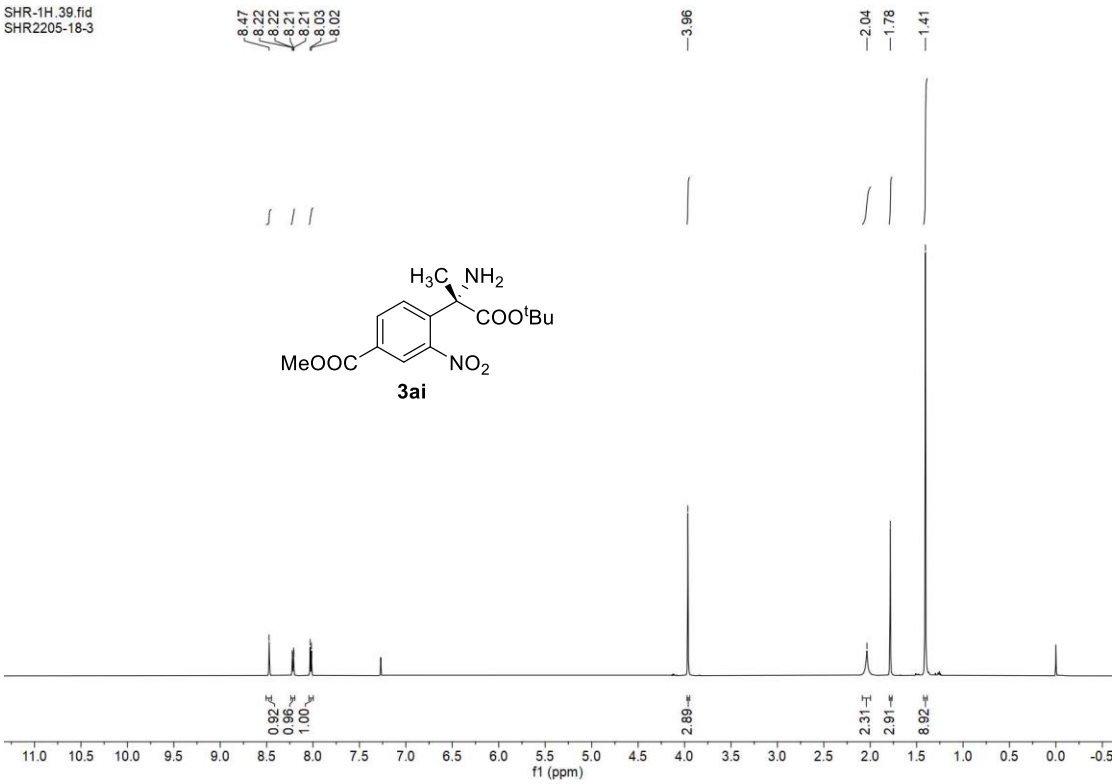

SHR-13C.10.fid
SHR2205-6-5
172.45
149.05
146.93
145.99
130.36
126.67
120.30
83.08
77.26
77.04
76.83
60.64
27.85
27.62
H3C NH2
COOtBu
O2N
NO2
3af
f1 (ppm)

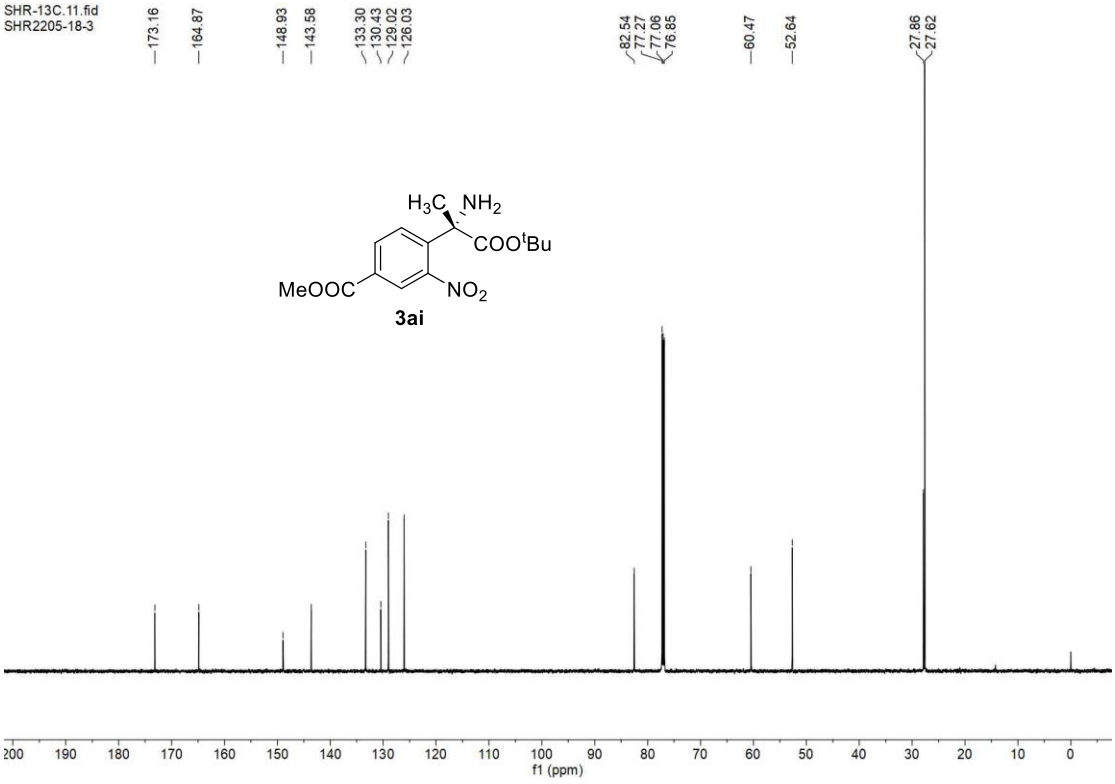

SHR-1H.10.fid
SHR2205-8-1
8.15
8.13
8.12
8.12
7.87
7.85
2.02
1.78
1.41
H3C
NH2
COOtBu
NC
NO2
3ag
2.02
1.00
2.09
3.02
9.33
f1 (ppm)

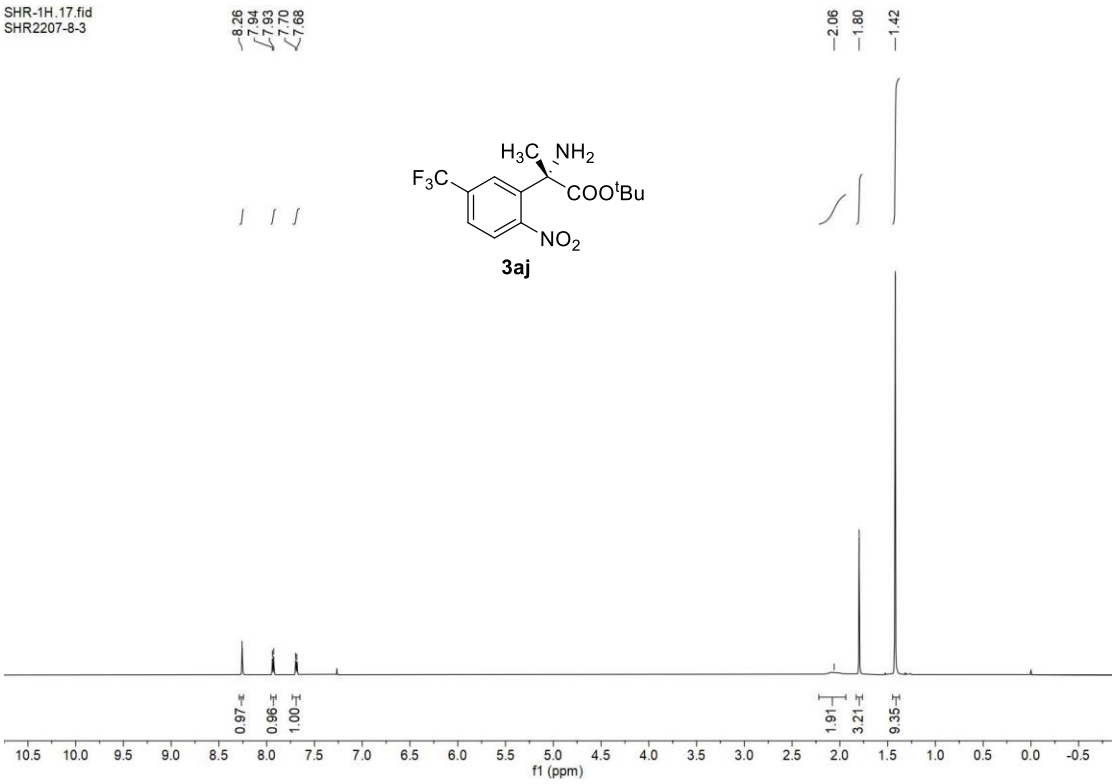

SHR-13C.3.fid
SHR2205-8-1
172.52
149.08
144.36
135.54
130.03
128.31
116.39
112.52
82.90
60.52
27.71
27.56
H3C
NH2
COOtBu
NC
NO2
3ag
f1 (ppm)

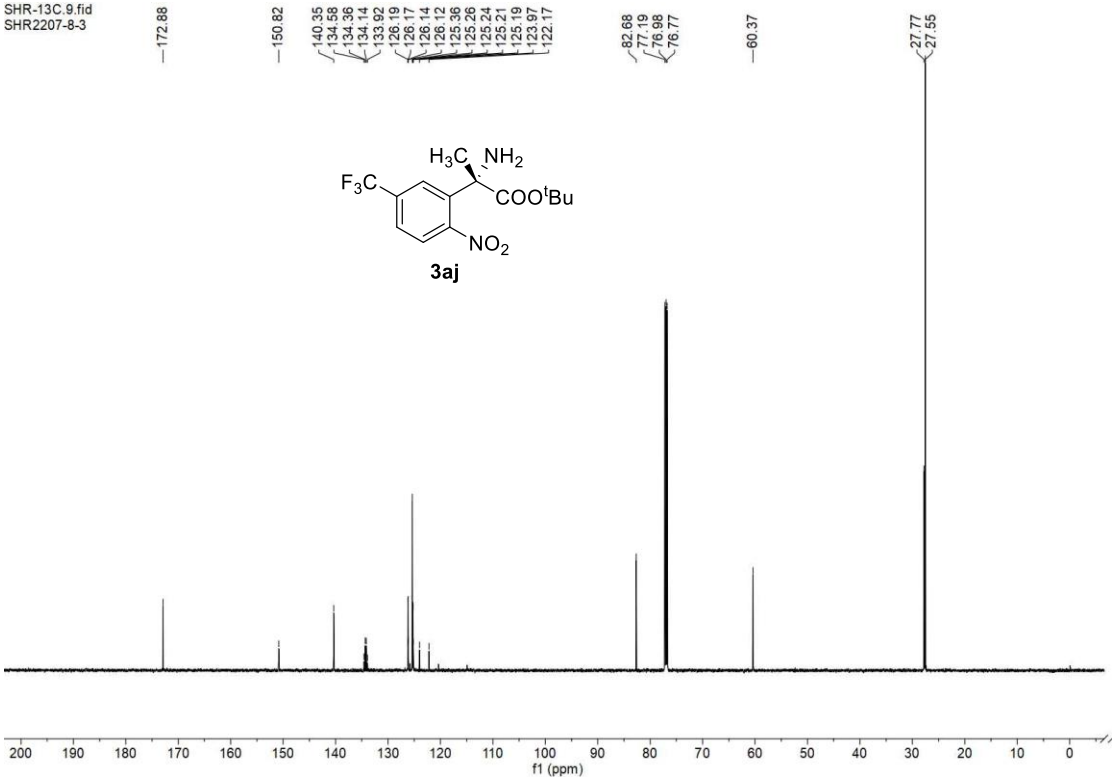

SHR-1H.22.fid
SHR2205-18-4
8.14
8.12
8.11
7.85
7.83
2.07
1.79
1.42
H_3C NH_2
COO^tBu
F_3C
NO_2
3ah
1.00
0.99
1.00
1.74
3.19
9.36
f1 (ppm)

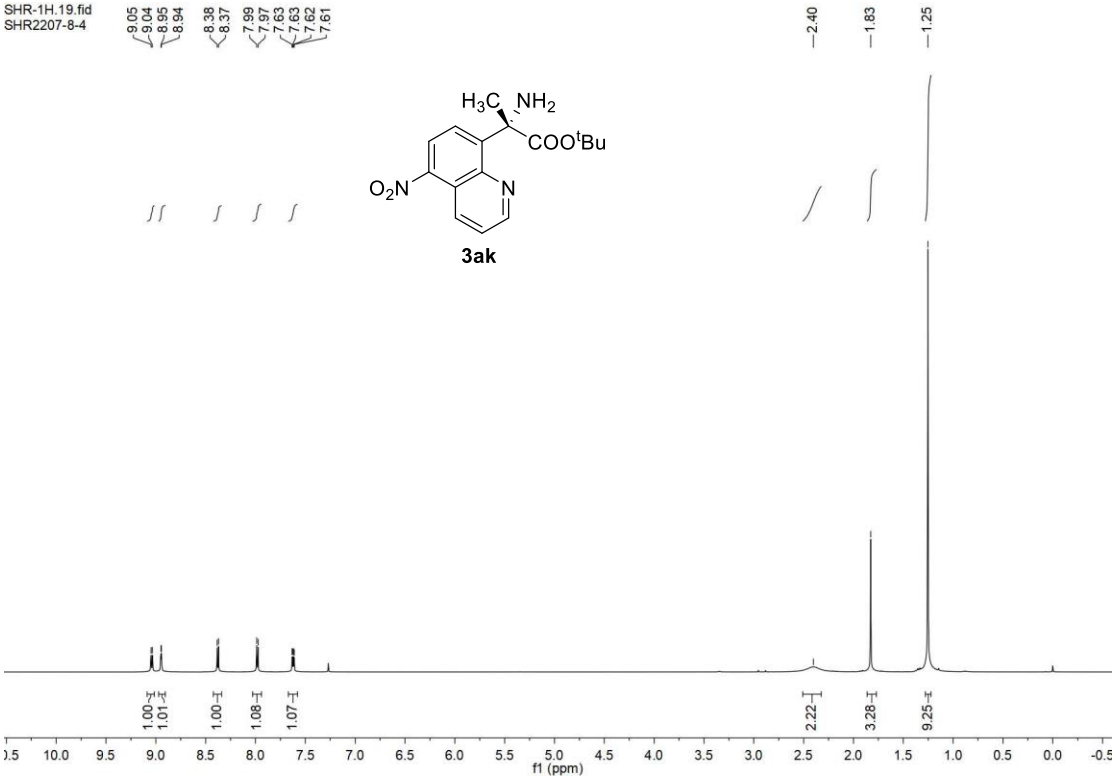

SHR-13C.6.fid
SHR2205-18-4
172.91
148.91
143.04
131.10
130.87
130.64
129.88
129.16
129.14
129.12
129.09
125.51
123.71
122.18
122.15
122.12
122.10
121.90
82.67
77.19
76.98
76.76
60.41
27.78
27.57
H_3C NH_2
COO^tBu
F_3C
NO_2
3ah
f1 (ppm)

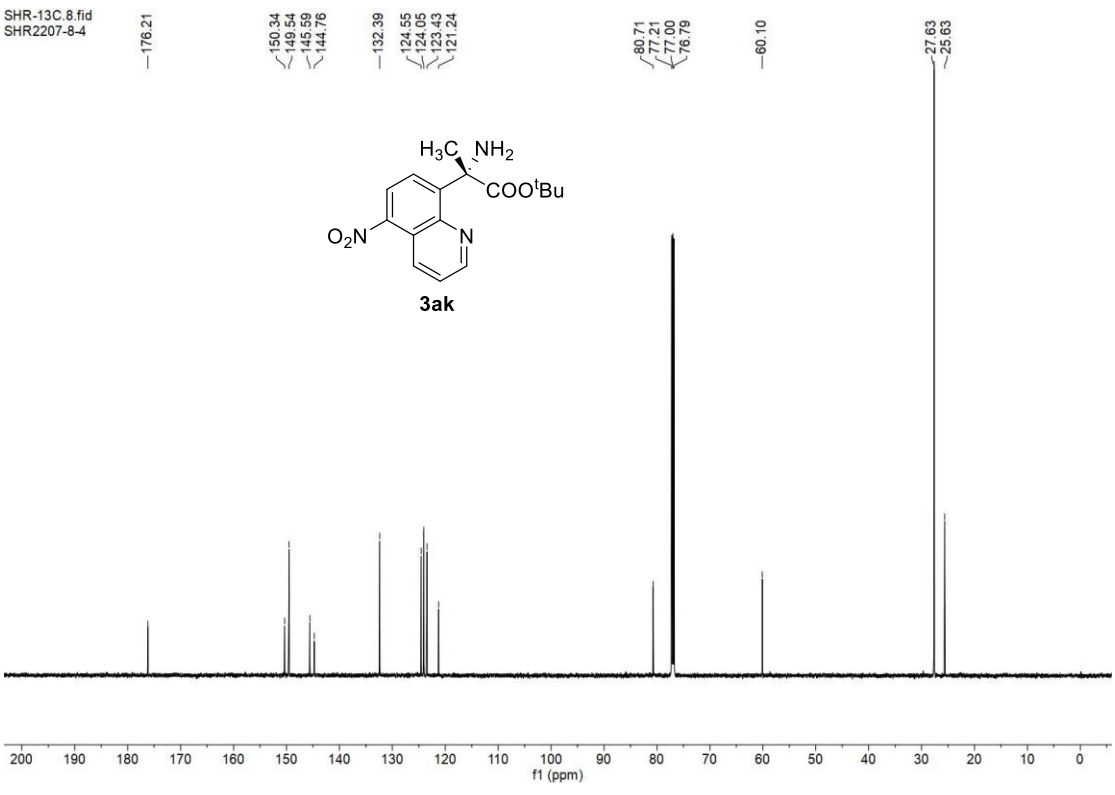

SHR-1H.39.fid
SHR2205-18-3
8.47
8.22
8.22
8.21
8.21
8.03
8.02
3.96
2.04
1.78
1.41
H3C
NH2
COOtBu
MeOOC
NO2
3ai
0.92
0.96
1.00
2.89
2.31
2.91
8.92
f1 (ppm)

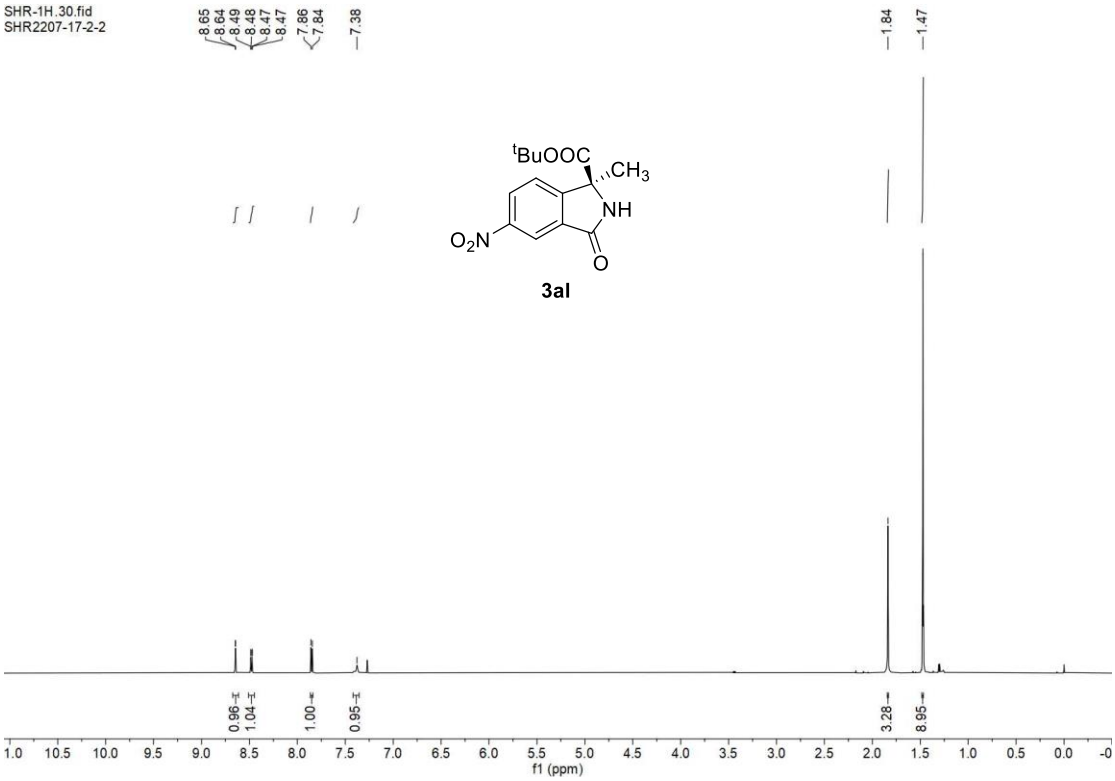

SHR-13C.11.fid
SHR2205-18-3
173.16
164.87
148.93
143.58
133.30
130.43
129.02
126.03
82.54
77.27
77.06
76.85
60.47
52.64
27.86
27.62
H3C
NH2
COOtBu
MeOOC
NO2
3ai
f1 (ppm)

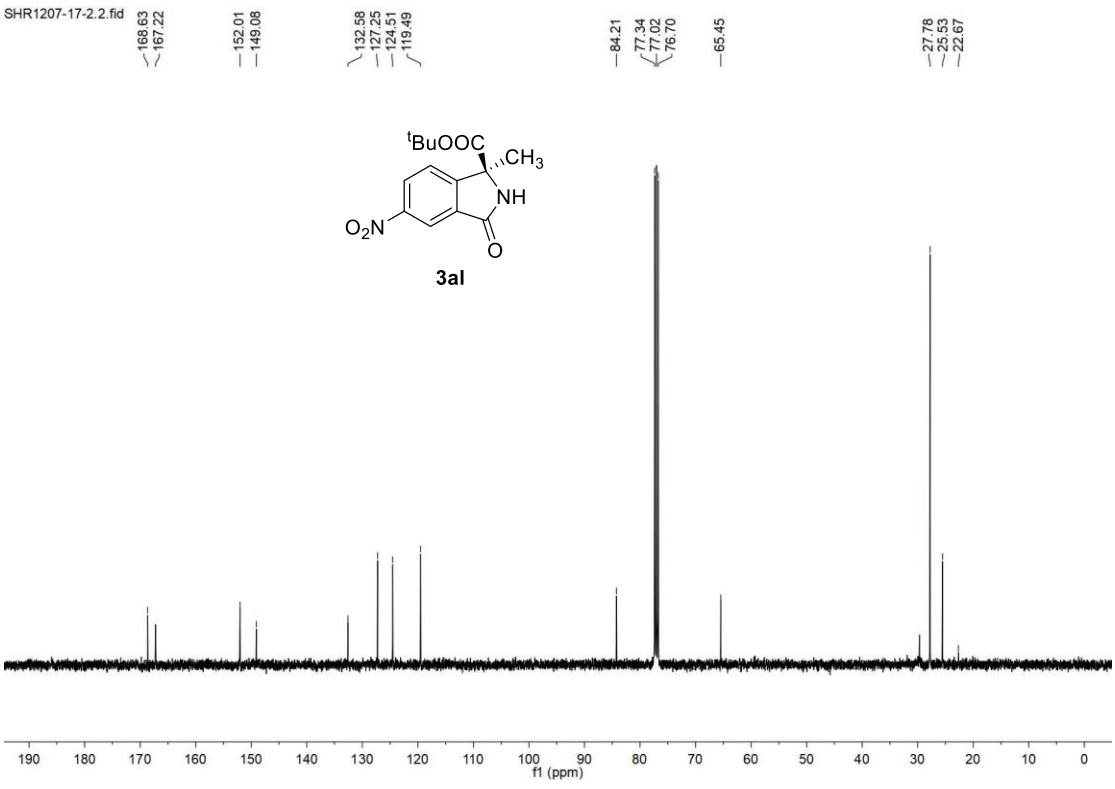

SHR-1H.17.fid
SHR2207-8-3
8.26
7.94
7.93
7.70
7.68
2.06
1.80
1.42
H_3C NH_2
F_3C
COO^tBu
NO_2
3aj
0.97
0.96
1.00
1.91
3.21
9.35
f1 (ppm)

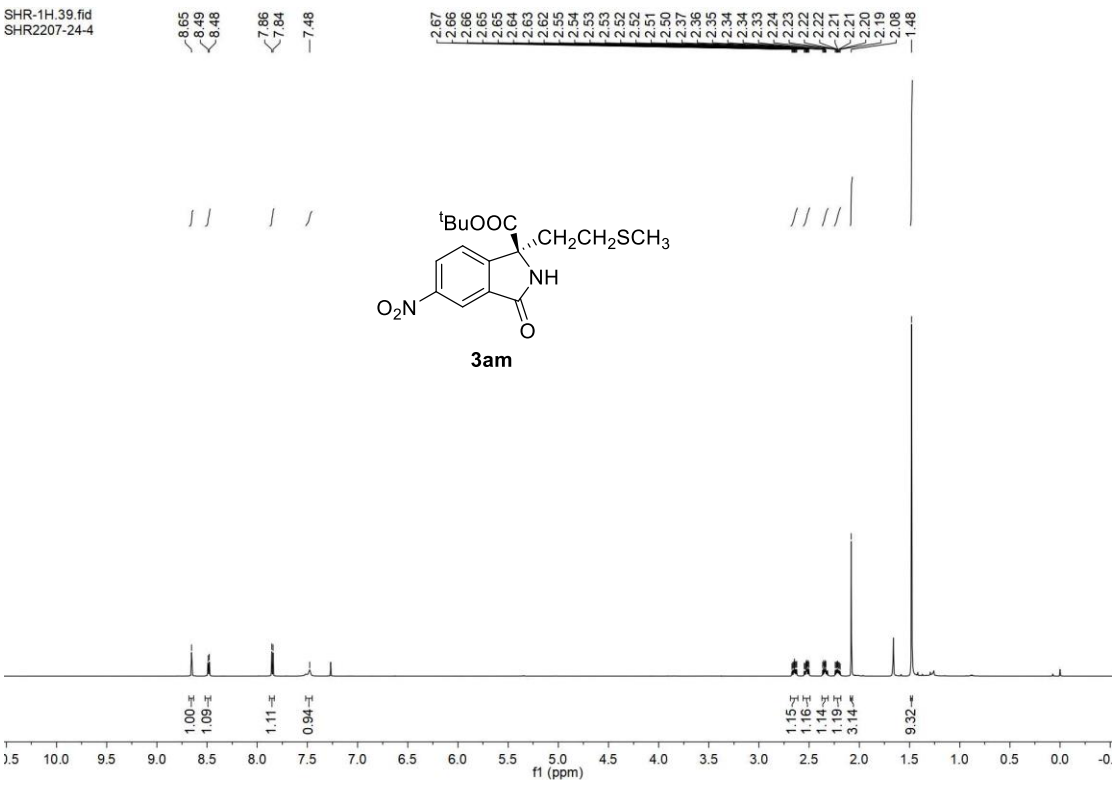

SHR-13C.9.fid
SHR2207-8-3
172.88
150.82
140.35
134.58
134.36
134.14
133.92
126.19
126.17
126.14
126.12
125.36
125.26
125.24
125.21
125.19
123.97
122.17
82.68
77.19
76.98
76.77
60.37
27.77
27.55
H_3C NH_2
F_3C
COO^tBu
NO_2
3aj
f1 (ppm)

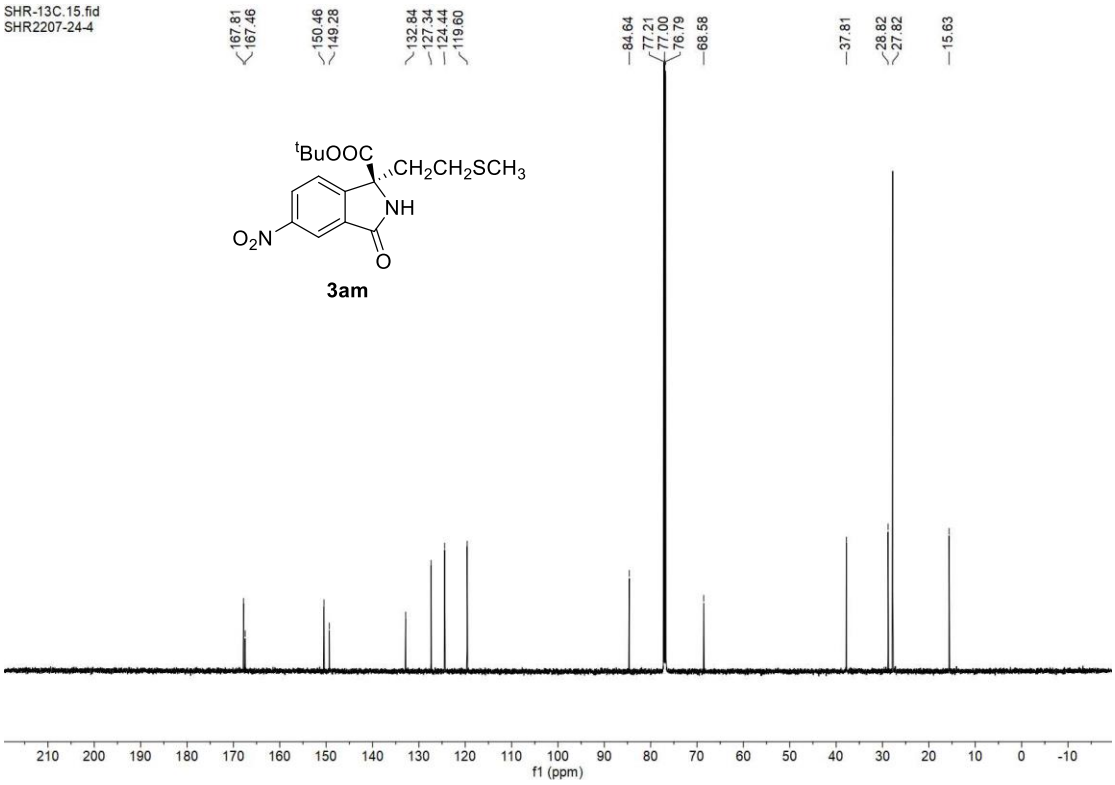

SHR-1H.19.fid
SHR2207-8-4
9.05
9.04
8.95
8.94
8.38
8.37
7.99
7.97
7.63
7.63
7.62
7.61
2.40
1.83
1.25
H3C NH2
COOtBu
O2N
N
3ak
1.00
1.01
1.00
1.08
1.07
2.22
3.28
9.25
f1 (ppm)

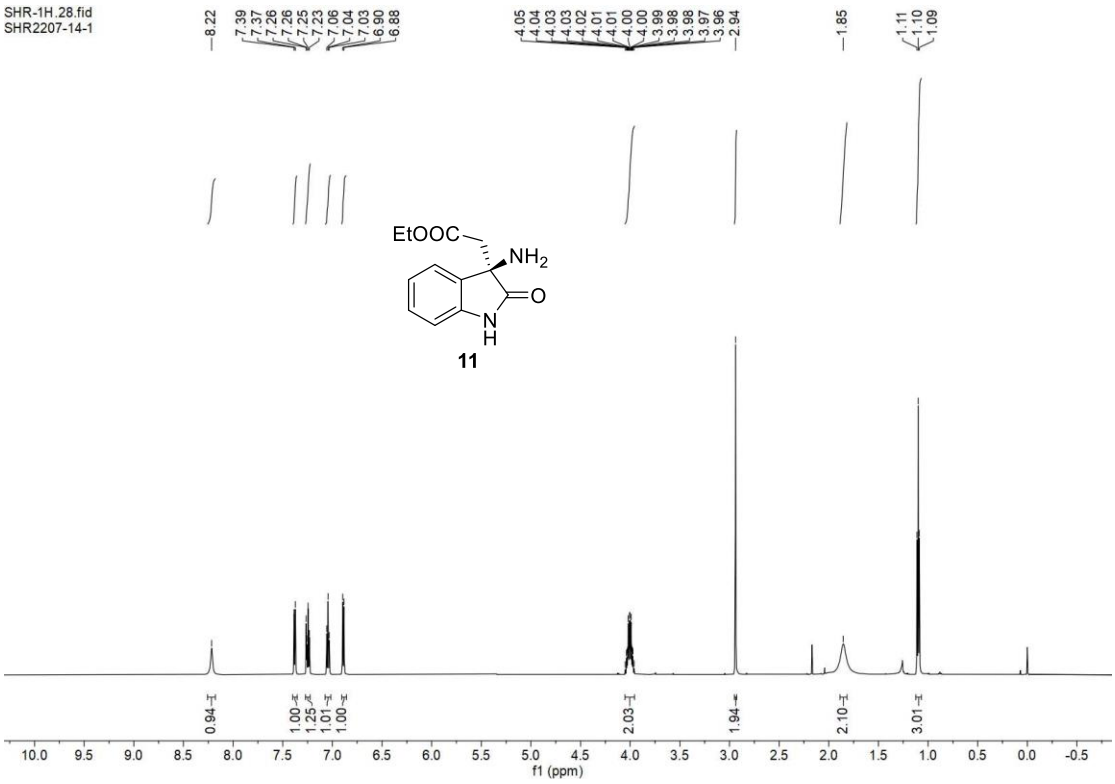

SHR-13C.8.fid
SHR2207-8-4
176.21
150.34
149.54
145.59
144.76
132.39
124.55
124.05
123.43
121.24
80.71
77.21
77.00
76.79
60.10
27.63
25.63
H3C NH2
COOtBu
O2N
N
3ak
f1 (ppm)

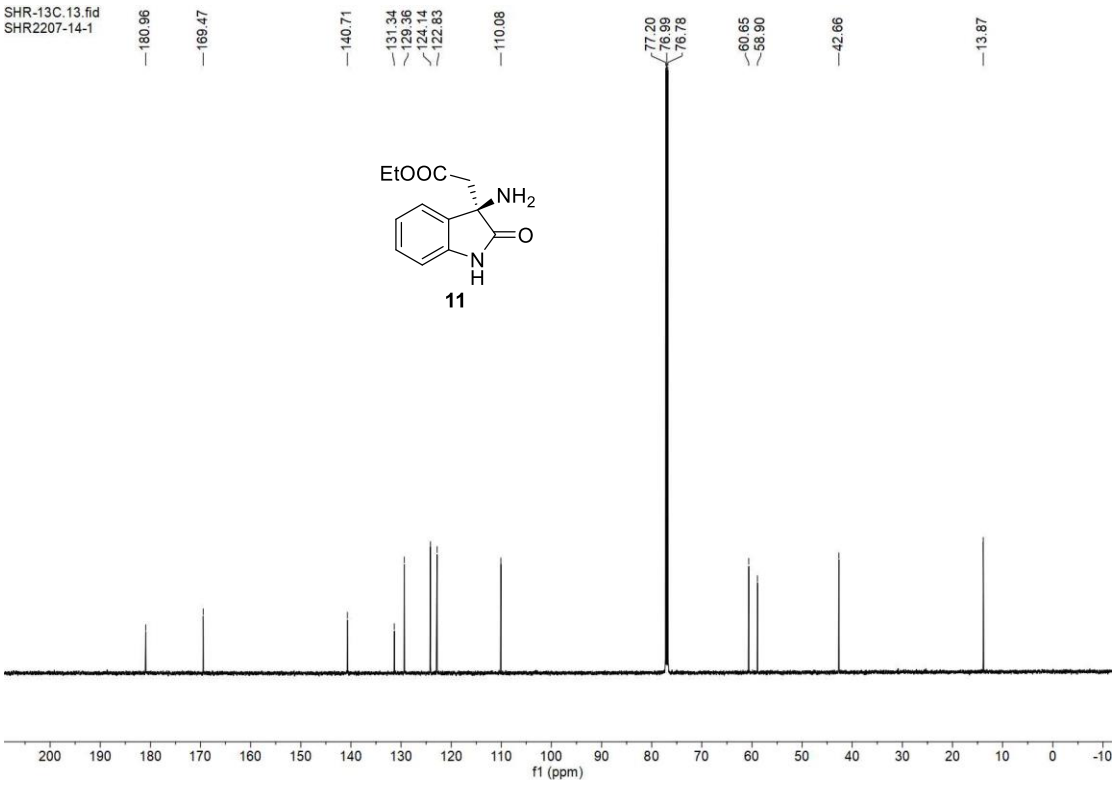

SHR-1H.30.fid
SHR2207-17-2-2
8.65
8.64
8.49
8.48
8.47
8.47
7.86
7.84
7.38
1.84
1.47
tBuOOC
CH3
NH
O2N
O
3al
0.96
1.04
1.00
0.95
3.28
8.95
f1 (ppm)

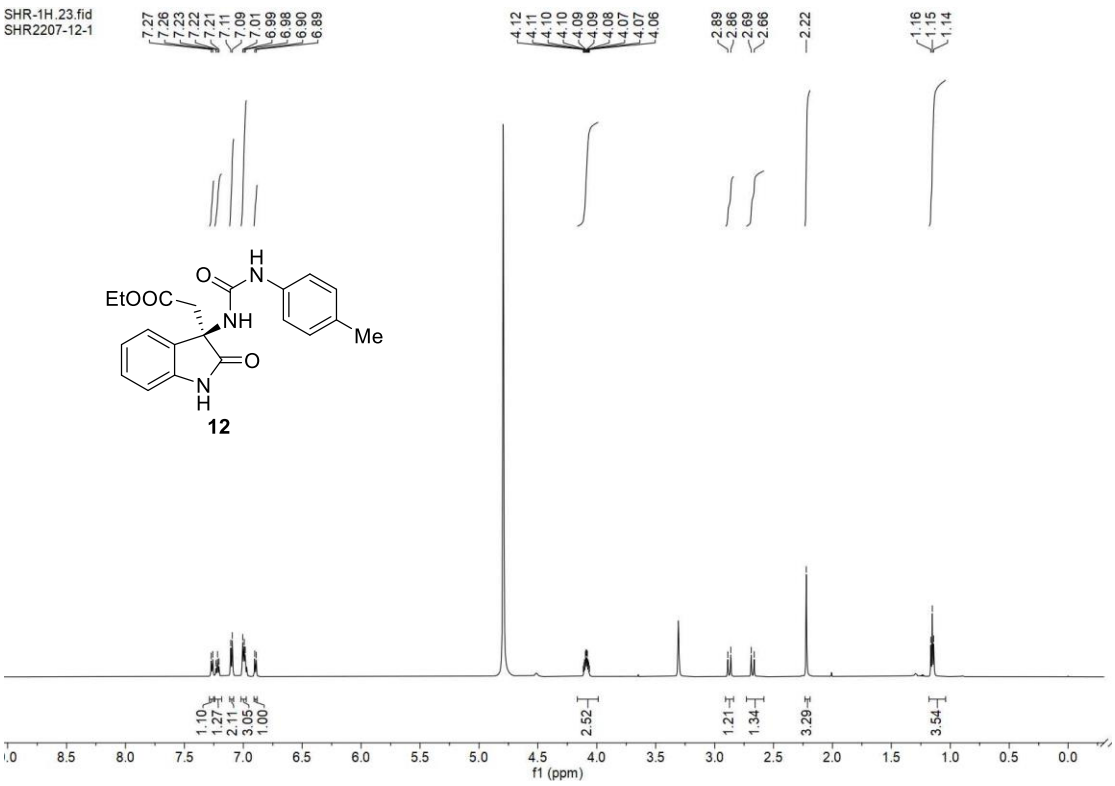

SHR1207-17-2.2.fid
168.63
167.22
152.01
149.08
132.58
127.25
124.51
119.49
84.21
77.34
77.02
76.70
65.45
27.78
25.53
22.67
tBuOOC
CH3
NH
O2N
O
3al
f1 (ppm)

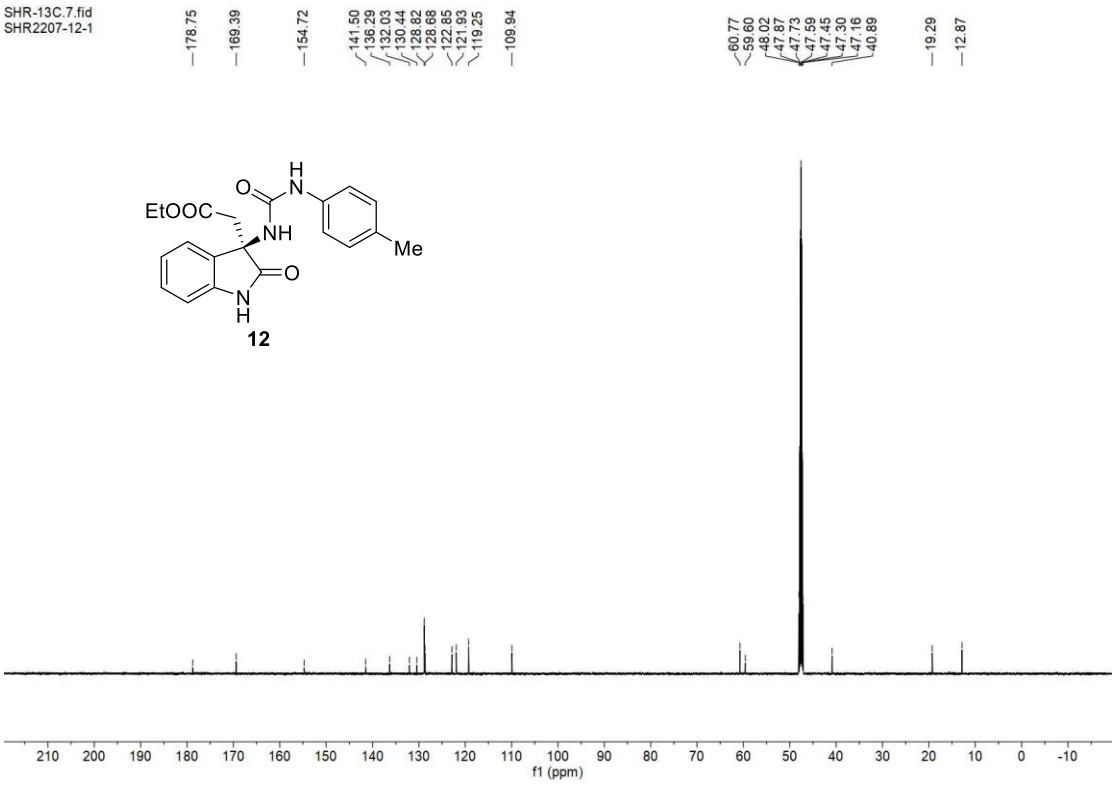

SHR-1H.39.fid
SHR2207-24-4
8.65
8.49
8.48
7.86
7.84
7.48
2.67
2.66
2.66
2.65
2.65
2.64
2.63
2.62
2.55
2.54
2.53
2.53
2.52
2.52
2.51
2.50
2.37
2.36
2.35
2.34
2.34
2.33
2.24
2.23
2.22
2.22
2.21
2.21
2.20
2.19
2.08
1.48
tBuOOC
CH2CH2SCH3
NH
O2N
O
3am
1.00
1.09
1.11
0.94
1.15
1.16
1.14
1.19
3.14
9.32
f1 (ppm)

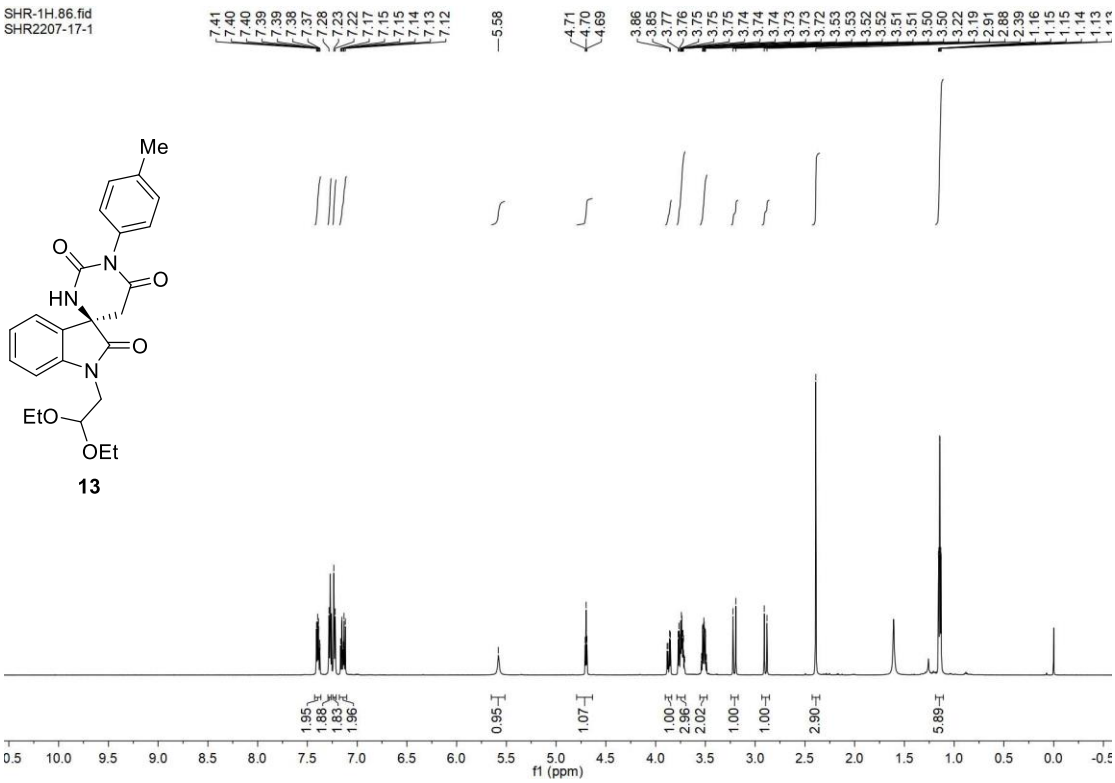

SHR-13C.15.fid
SHR2207-24-4
167.81
167.46
150.46
149.28
132.84
127.34
124.44
119.60
84.64
77.21
77.00
76.79
68.58
37.81
28.82
27.82
15.63
tBuOOC
CH2CH2SCH3
NH
O2N
O
3am
f1 (ppm)

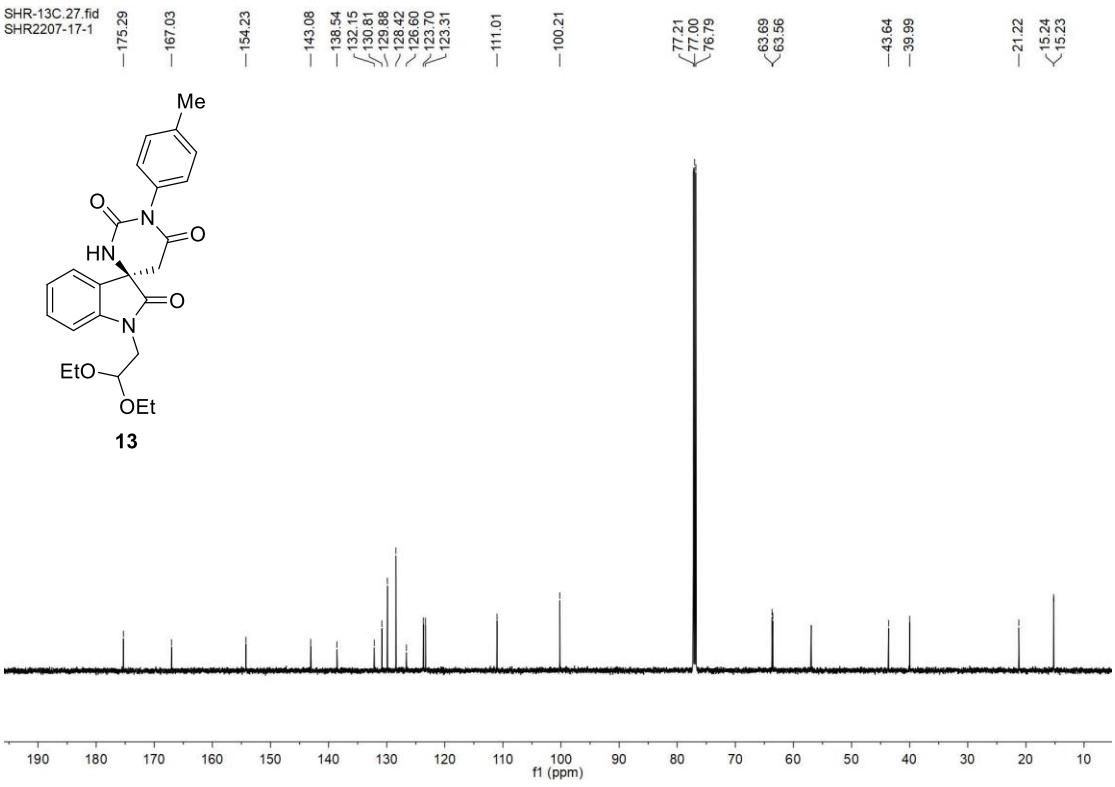

SHR-1H.28.fid
SHR2207-14-1
EtOOC
NH2
O
N
H
11
f1 (ppm)

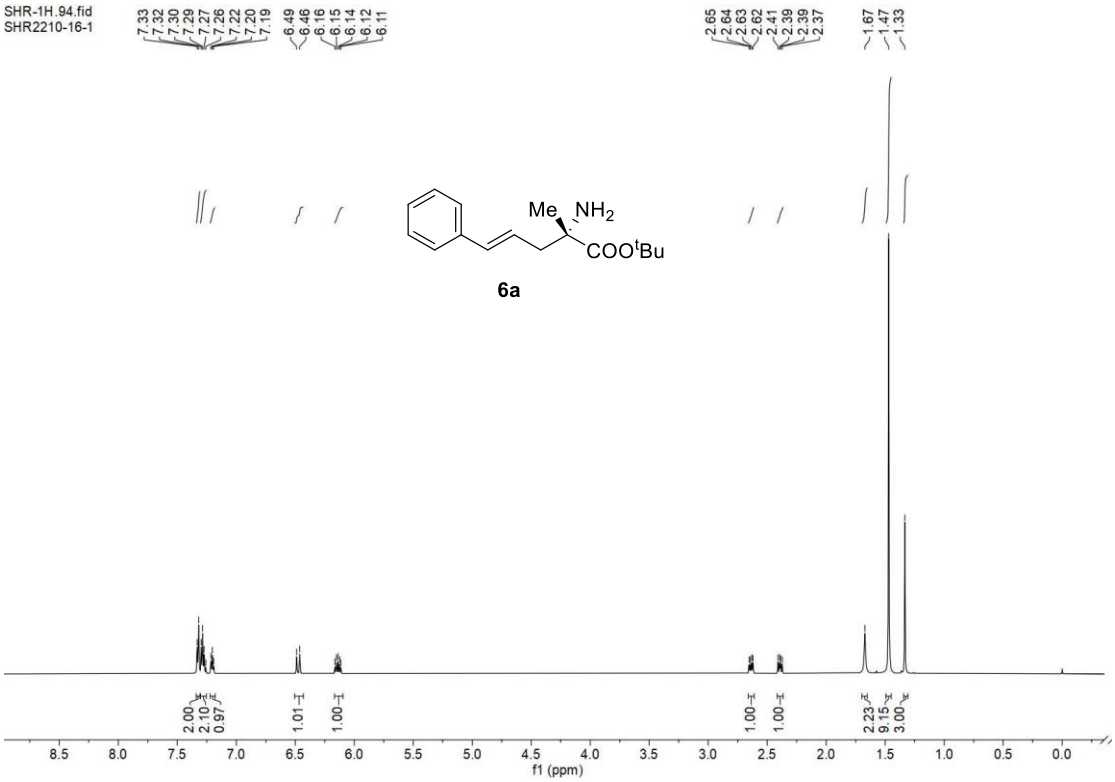

SHR-13C.13.fid
SHR2207-14-1
EtOOC
NH2
O
N
H
11
f1 (ppm)

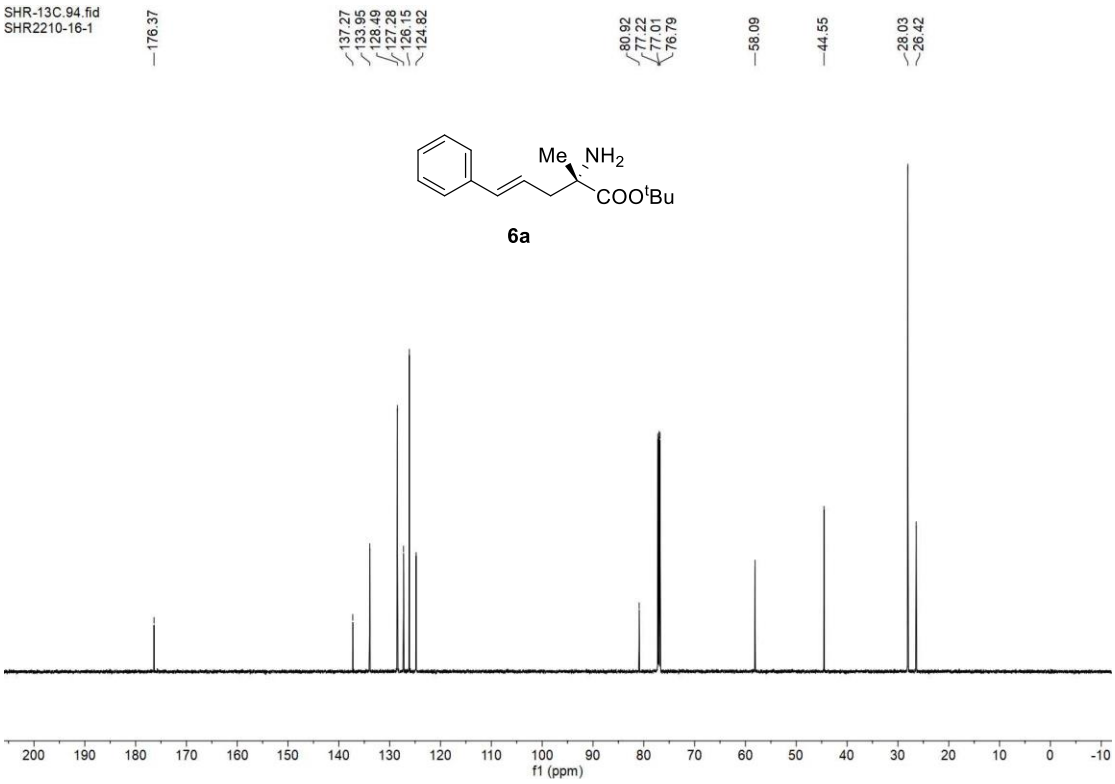

SHR-1H.23.fid
SHR2207-12-1
EtOOC
NH
O
H
N
Me
O
N
H
12
f1 (ppm)


SHR-13C.7.fid
SHR2207-12-1
EtOOC
NH
O
H
N
Me
O
N
H
12
f1 (ppm)


SHR-1H.86.fid
SHR2207-17-1
Me
O
N
O
HN
O
N
EtO
OEt
13
f1 (ppm)


SHR-13C.27.fid
SHR2207-17-1
Me
O
N
O
HN
O
N
EtO
OEt
13
f1 (ppm)


SHR-1H.94.fid
SHR2210-16-1
7.33
7.32
7.30
7.29
7.27
7.26
7.22
7.20
7.19
6.49
6.46
6.16
6.15
6.14
6.12
6.11
2.65
2.64
2.63
2.62
2.41
2.39
2.39
2.37
1.67
1.47
1.33
Me
NH2
COOtBu
6a
2.00
2.10
0.97
1.01
1.00
1.00
1.00
2.23
9.15
3.00
f1 (ppm)


SHR-13C.94.fid
SHR2210-16-1
176.37
137.27
133.95
128.49
127.28
126.15
124.82
80.92
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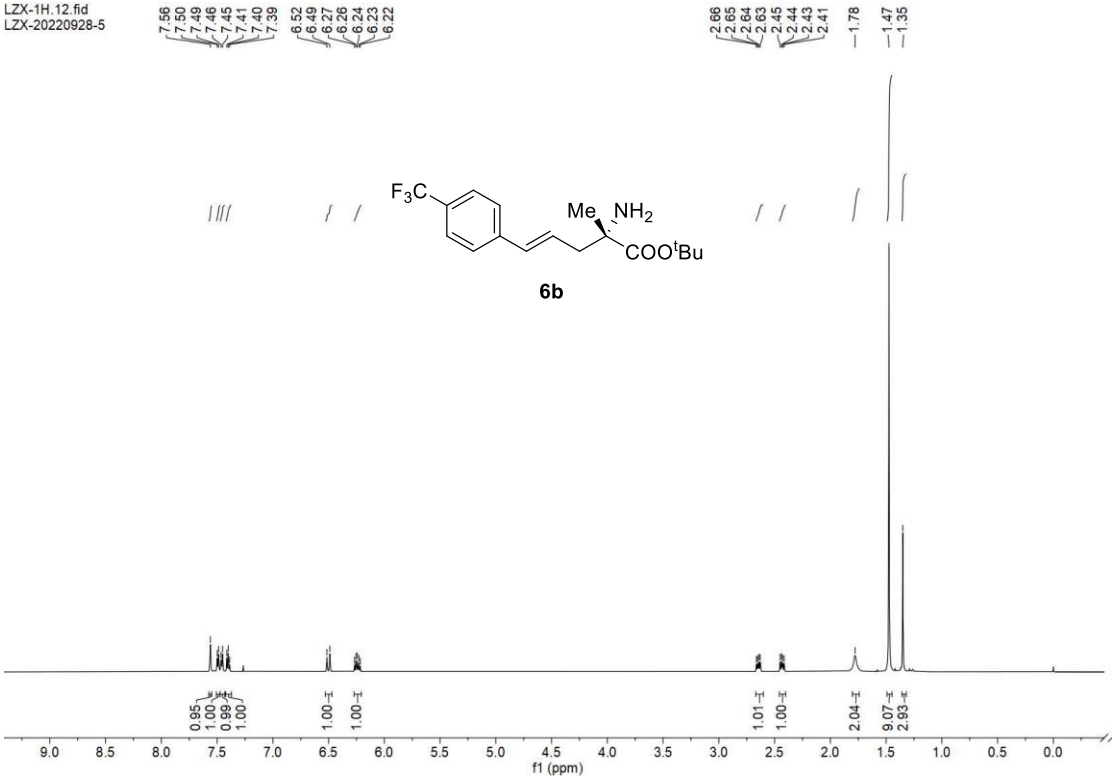
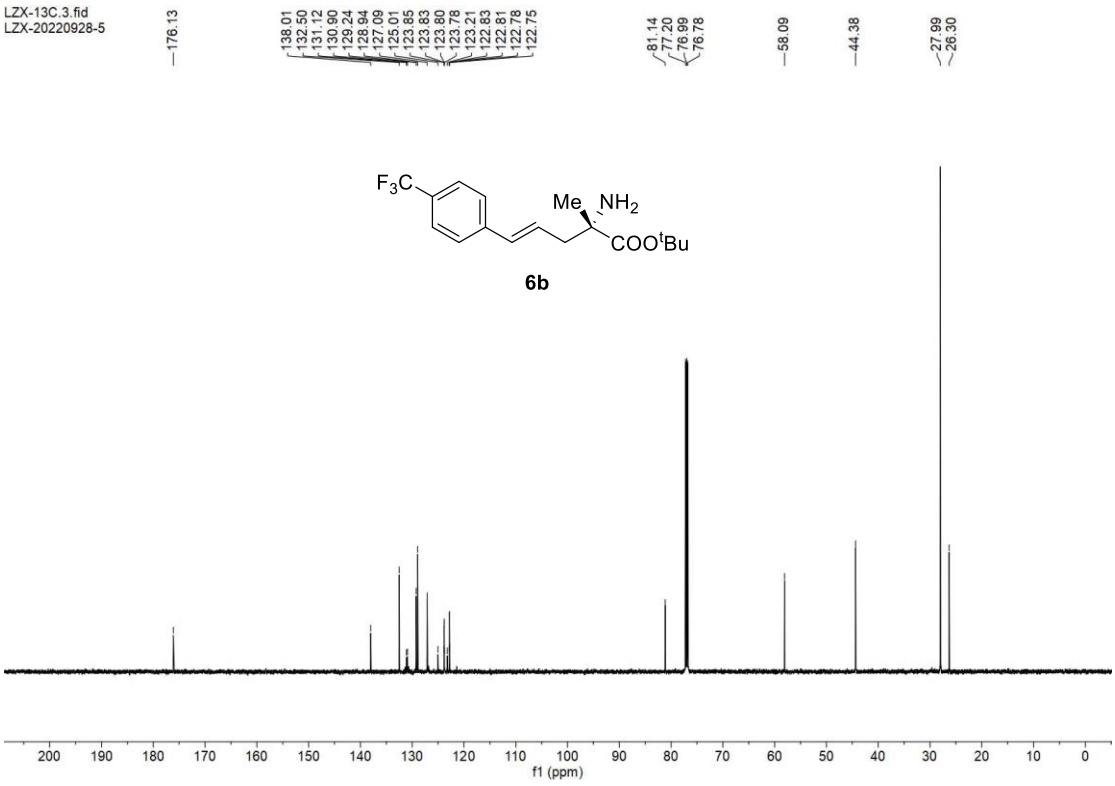
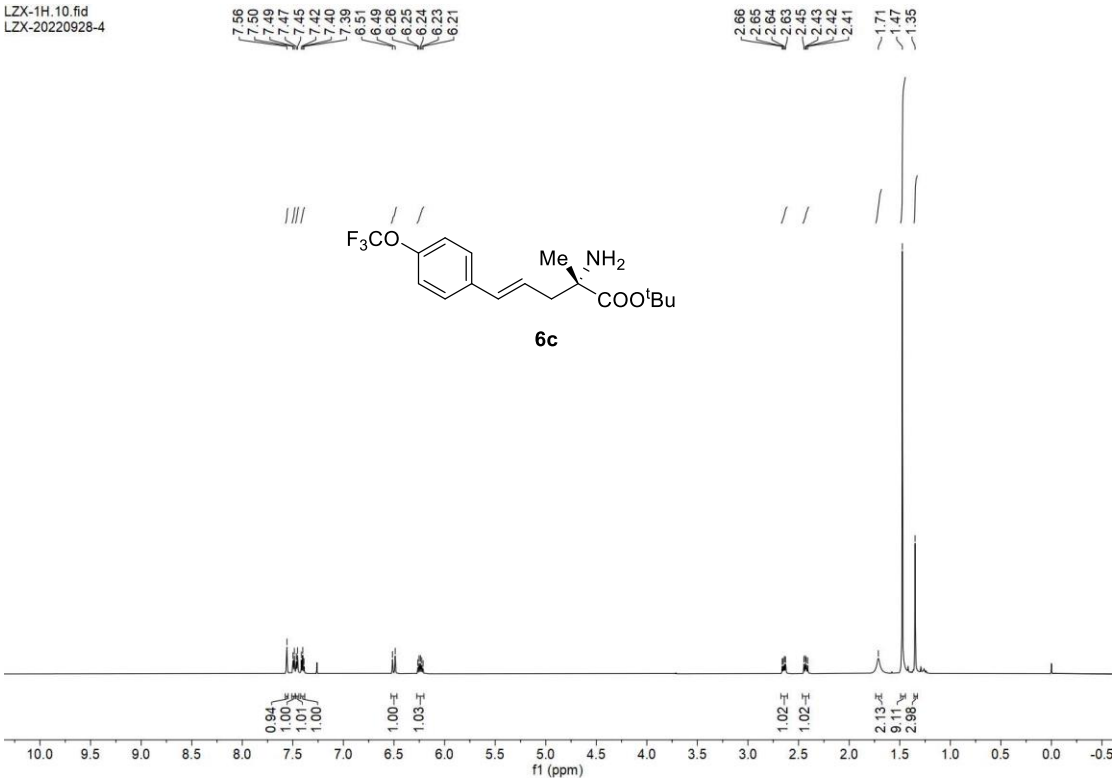
26.42
Me
NH2
COOtBu
6a
f1 (ppm)


LZX-1H.12.fid
LZX-20220928-5
7.56
7.50
7.49
7.46
7.45
7.41
7.40
7.39
6.52
6.49
6.27
6.26
6.24
6.23
6.22
2.66
2.65
2.64
2.63
2.45
2.44
2.43
2.41
1.78
1.47
1.35
F3C
Me
NH2
COOtBu
6b
0.95
1.00
0.99
1.00
1.00
1.00
1.01
1.00
2.04
9.07
2.93
f1 (ppm)


LZX-13C.3.fid
LZX-20220928-5
176.13
138.01
132.50
131.12
130.90
129.24
128.94
127.09
125.01
123.85
123.83
123.80
123.78
123.21
122.83
122.81
122.78
122.75
81.14
77.20
76.99
76.78
58.09
44.38
27.99
26.30
F3C
Me
NH2
COOtBu
6b
f1 (ppm)


LZX-1H.10.fid
LZX-20220928-4
7.56
7.50
7.49
7.47
7.45
7.42
7.40
7.39
6.51
6.49
6.26
6.25
6.24
6.23
6.21
2.66
2.65
2.64
2.63
2.45
2.43
2.42
2.41
1.71
1.47
1.35
F3CO
Me
NH2
COOtBu
6c
0.94
1.00
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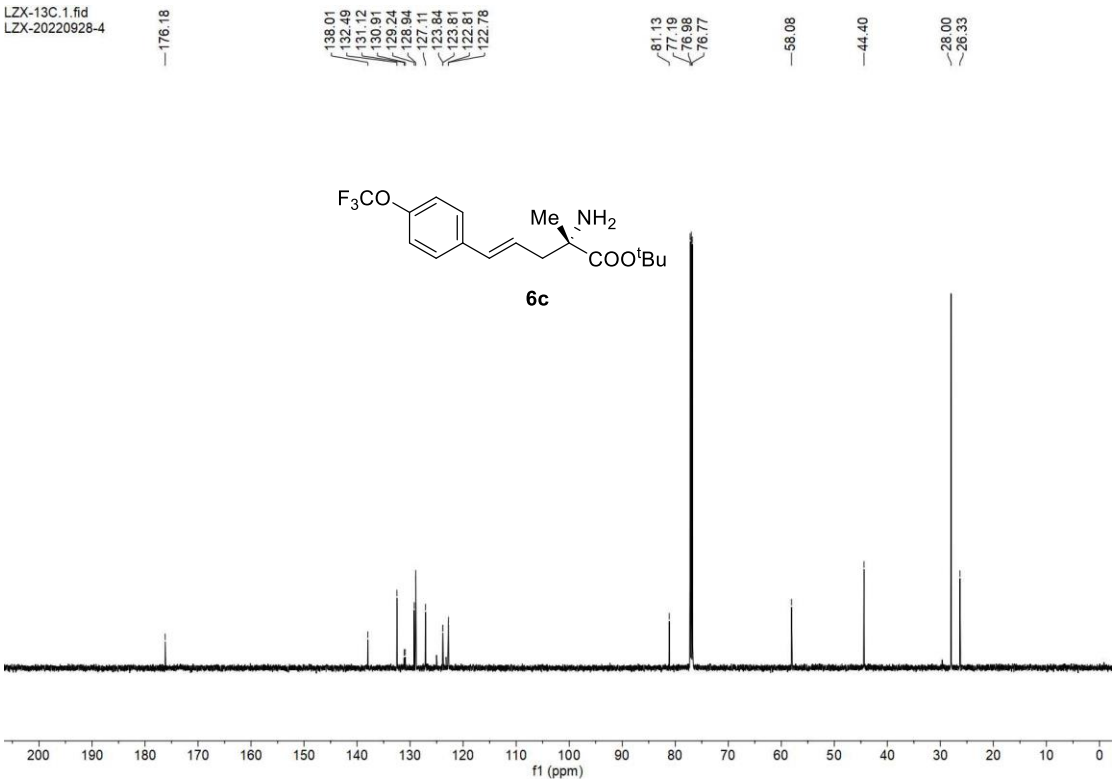
1.00
1.00
1.03
1.02
1.02
2.13
9.11
2.98
f1 (ppm)


LZX-13C.1.fid
LZX-20220928-4
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138.01
132.49
131.12
130.91
129.24
128.94
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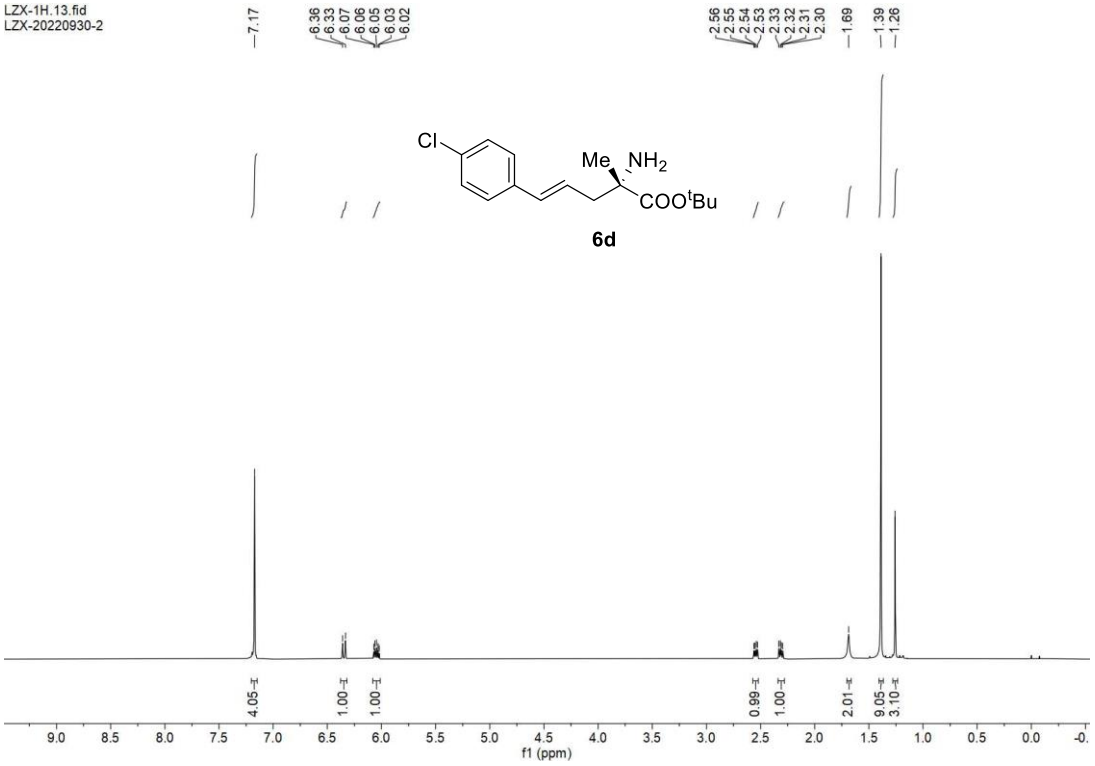
123.84
123.81
122.81
122.78
81.13
77.19
76.98
76.77
58.08
44.40
28.00
26.33
F3CO
Me
NH2
COOtBu
6c
f1 (ppm)


LZX-1H.13.fid
LZX-20220930-2
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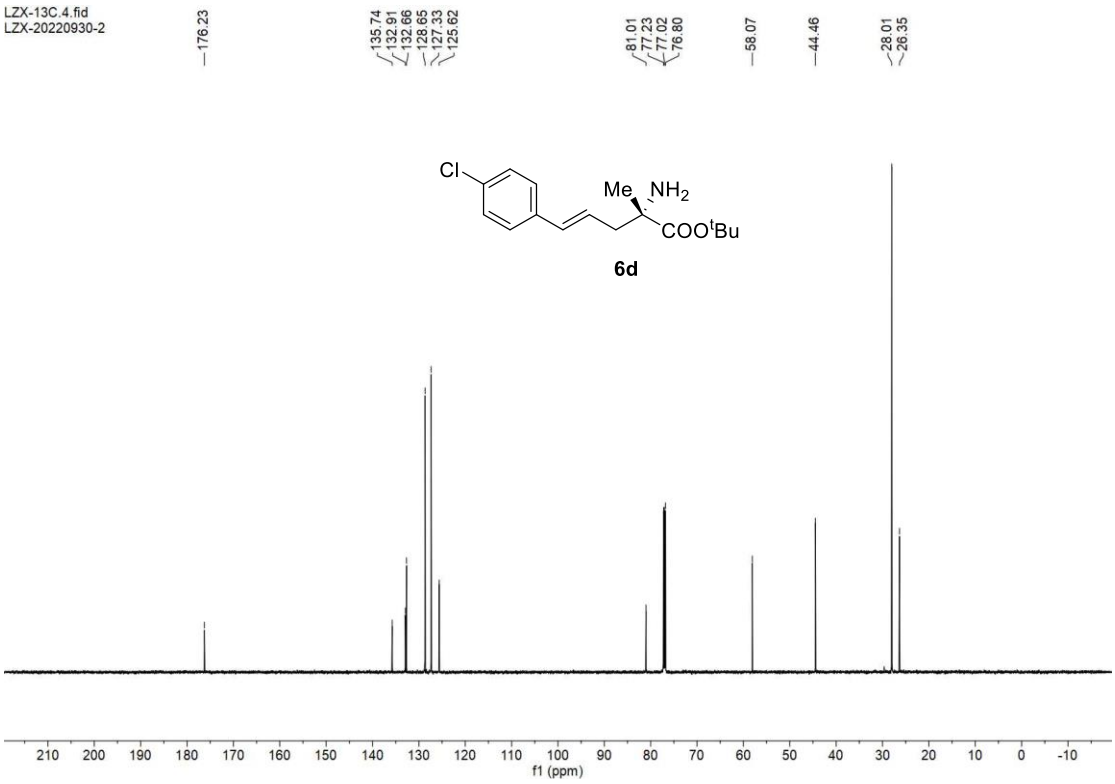
6.36
6.33
6.07
6.06
6.05
6.03
6.02
2.56
2.55
2.54
2.53
2.33
2.32
2.31
2.30
1.69
1.39
1.26
Cl
Me
NH2
COOtBu
6d
4.05
1.00
1.00
0.99
1.00
2.01
9.05
3.10
f1 (ppm)


LZX-13C.4.fid
LZX-20220930-2
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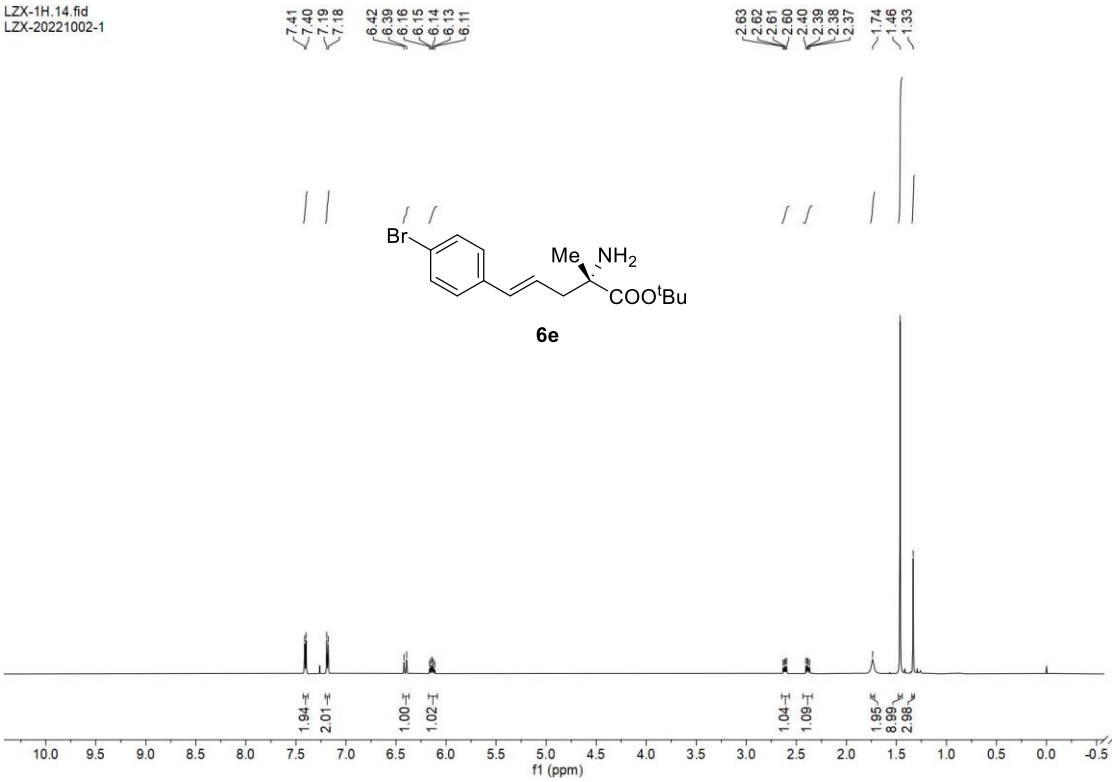
135.74
132.91
132.66
128.65
127.33
125.62
81.01
77.23
77.02
76.80
58.07
44.46
28.01
26.35
Cl
Me
NH2
COOtBu
6d
f1 (ppm)


LZX-1H.14.fid
LZX-20221002-1
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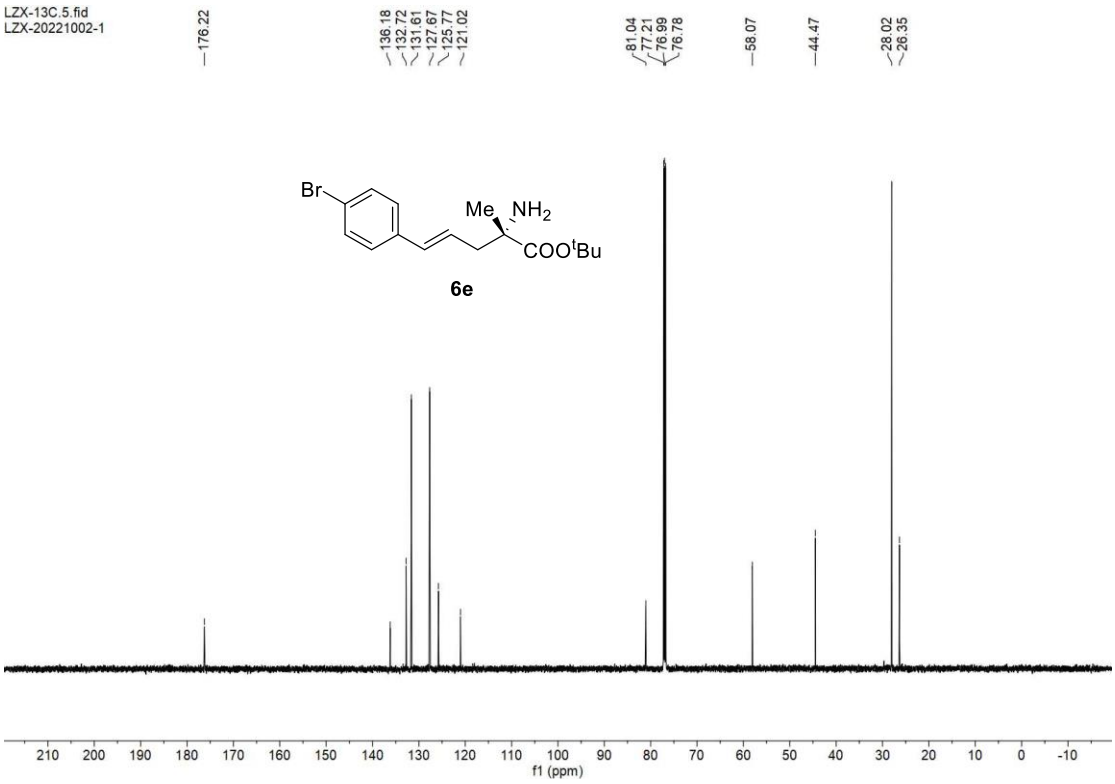
7.40
7.19
7.18
6.42
6.39
6.16
6.15
6.14
6.13
6.11
2.63
2.62
2.61
2.60
2.40
2.39
2.38
2.37
1.74
1.46
1.33
Br
Me
NH2
COOtBu
6e
1.94
2.01
1.00
1.02
1.04
1.09
1.95
8.99
2.98
10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


LZX-13C.5.fid
LZX-20221002-1
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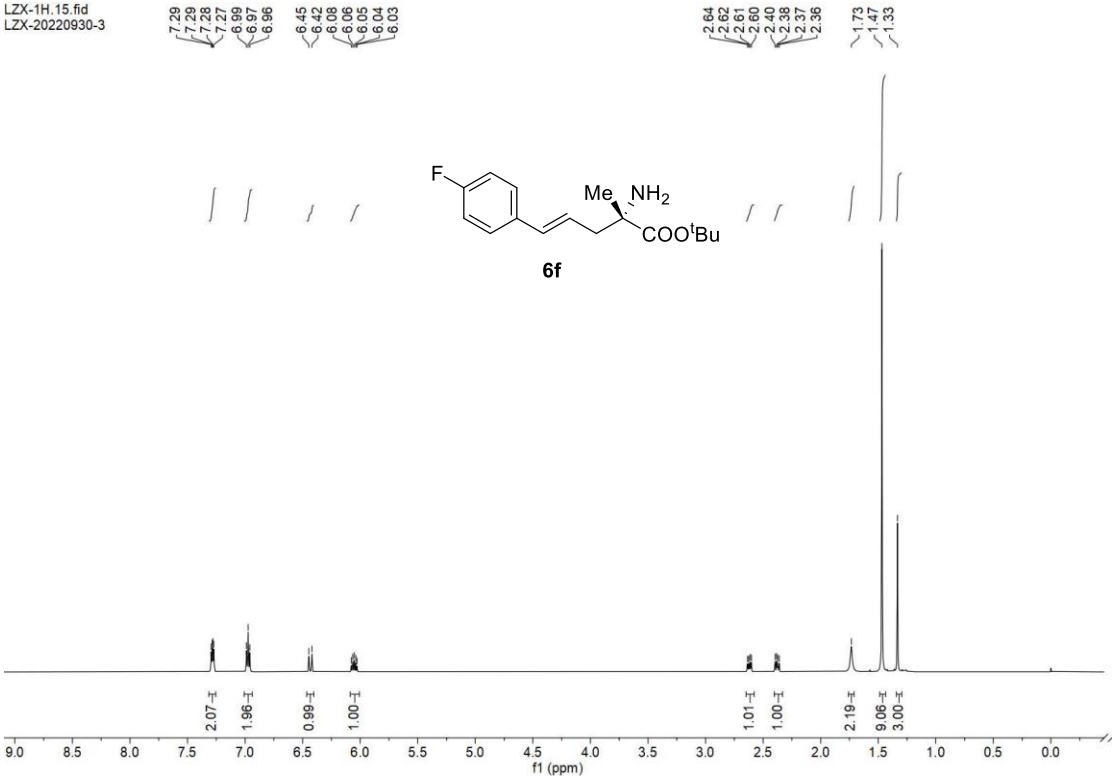
136.18
132.72
131.61
127.67
125.77
121.02
81.04
77.21
76.99
76.78
58.07
44.47
28.02
26.35
Br
Me
NH2
COOtBu
6e
210 200 190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0 -10
f1 (ppm)


LZX-1H.15.fid
LZX-20220930-3
7.29
7.29
7.28
7.27
6.99
6.97
6.96
6.45
6.42
6.08
6.06
6.05
6.04
6.03
2.64
2.62
2.61
2.60
2.40
2.38
2.37
2.36
1.73
1.47
1.33
F
Me
NH2
COOtBu
6f
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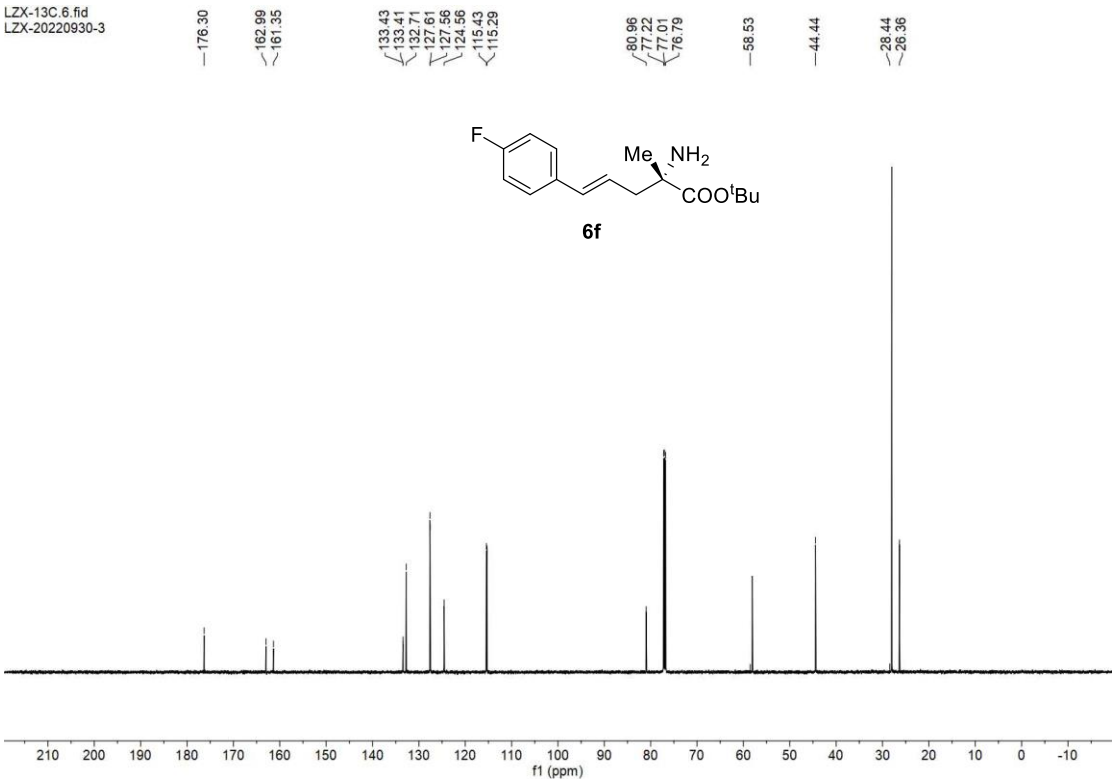
1.96
0.99
1.00
1.01
1.00
2.19
9.06
3.00
f1 (ppm)


LZX-13C.6.fid
LZX-20220930-3
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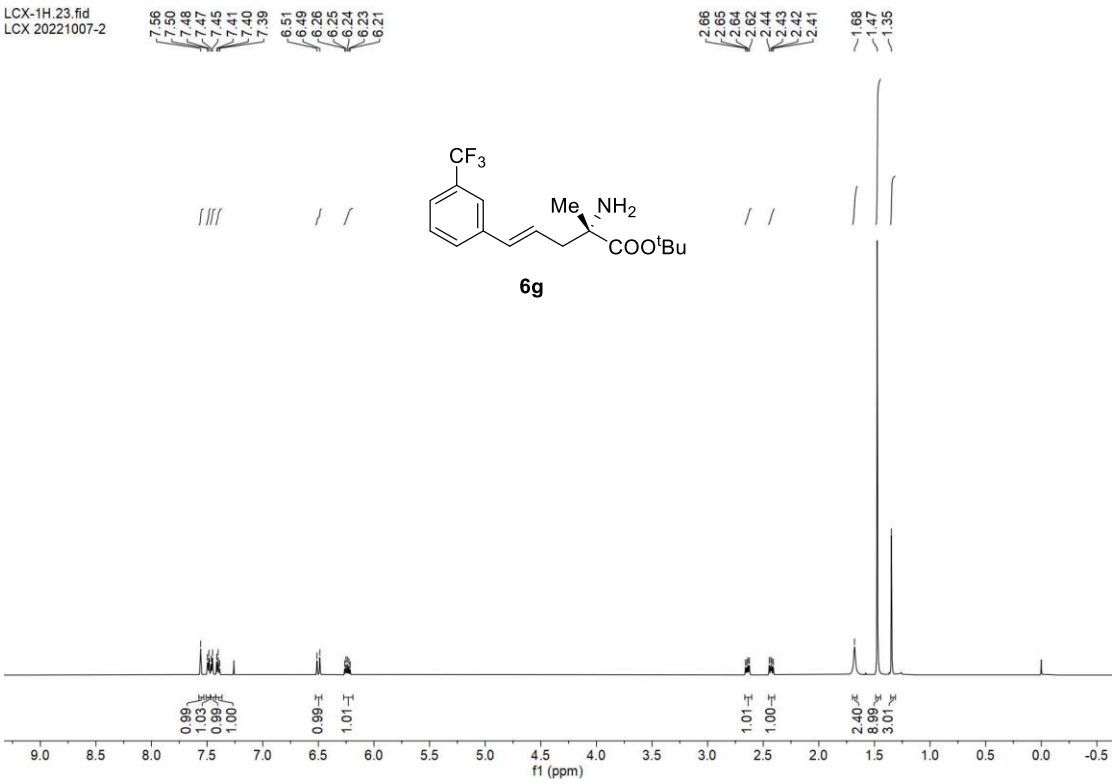
161.35
133.43
133.41
132.71
127.61
127.56
124.56
115.43
115.29
80.96
77.22
77.01
76.79
58.53
44.44
28.44
26.36
F
Me
NH2
COOtBu
6f
f1 (ppm)


LCX-1H.23.fid
LCX 20221007-2
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7.48
7.47
7.45
7.41
7.40
7.39
6.51
6.49
6.26
6.25
6.24
6.23
6.21
2.66
2.65
2.64
2.62
2.44
2.43
2.42
2.41
1.68
1.47
1.35
CF3
Me
NH2
COOtBu
6g
0.99
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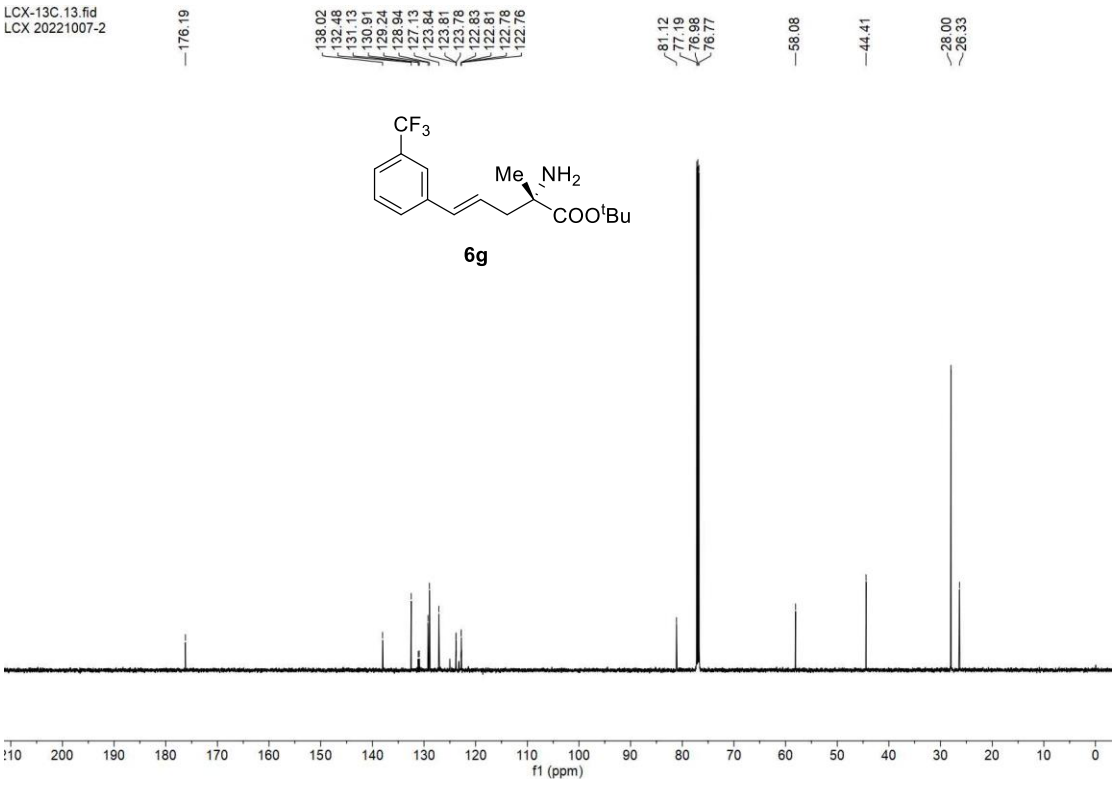
1.00
0.99
1.01
1.01
1.00
2.40
8.99
3.01
f1 (ppm)


LCX-13C.13.fid
LCX 20221007-2
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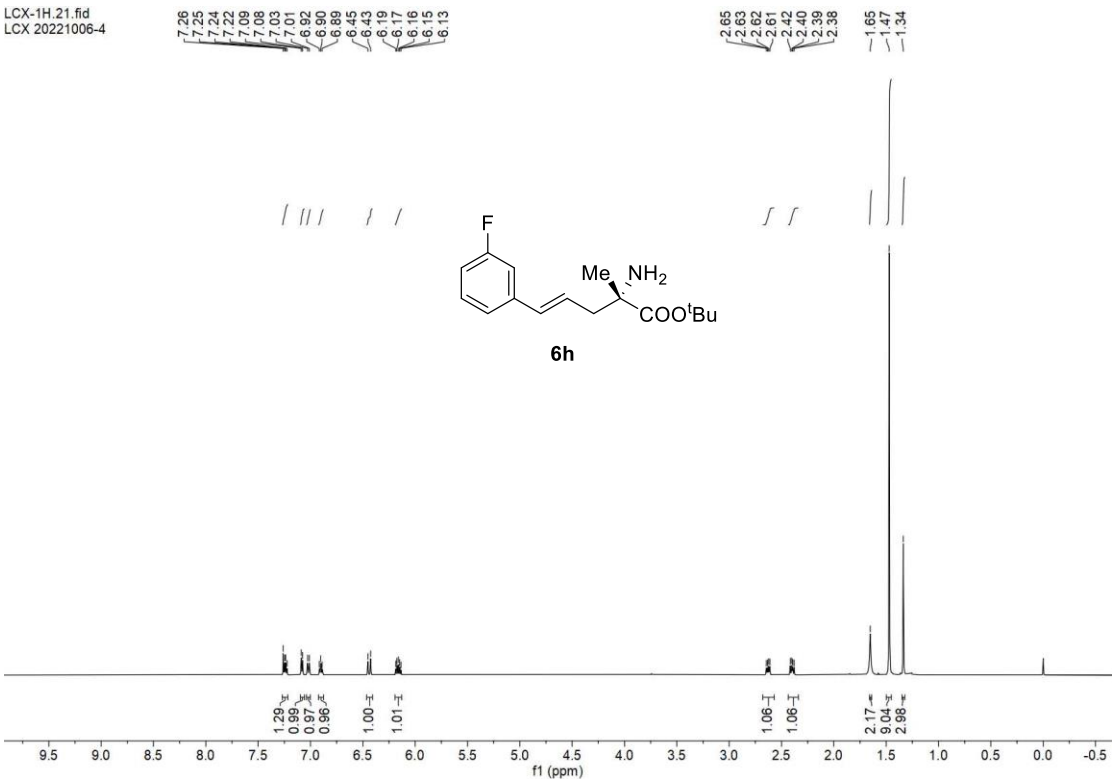
129.24
128.94
127.13
123.84
123.81
123.78
122.83
122.81
122.78
122.76
81.12
77.19
76.98
76.77
58.08
44.41
28.00
26.33
CF3
Me
NH2
COOtBu
6g
f1 (ppm)


LCX-1H.21.fid
LCX 20221006-4
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7.24
7.22
7.09
7.08
7.03
7.01
6.92
6.90
6.89
6.45
6.43
6.19
6.17
6.16
6.15
6.13
2.65
2.63
2.62
2.61
2.42
2.40
2.39
2.38
1.65
1.47
1.34
F
Me
NH2
COOtBu
6h
1.29
0.99
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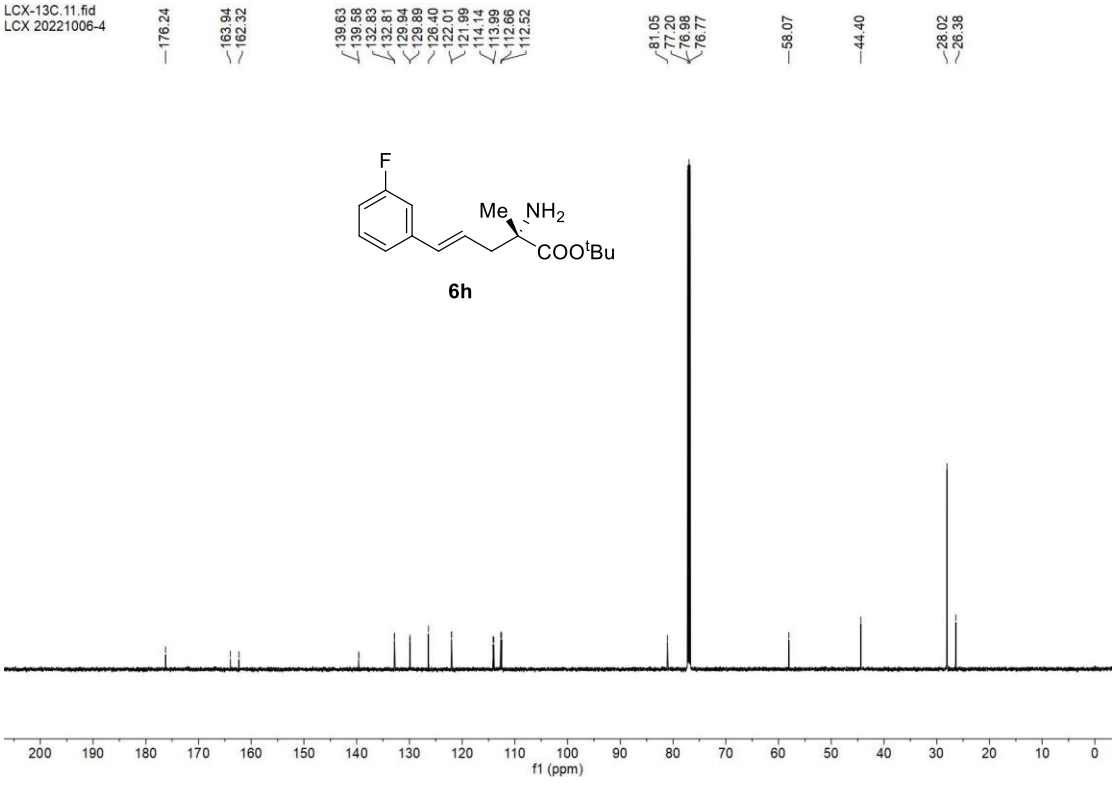
0.98
1.00
1.01
1.06
1.06
2.17
9.04
2.98
f1 (ppm)


LCX-13C.11.fid
LCX 20221006-4
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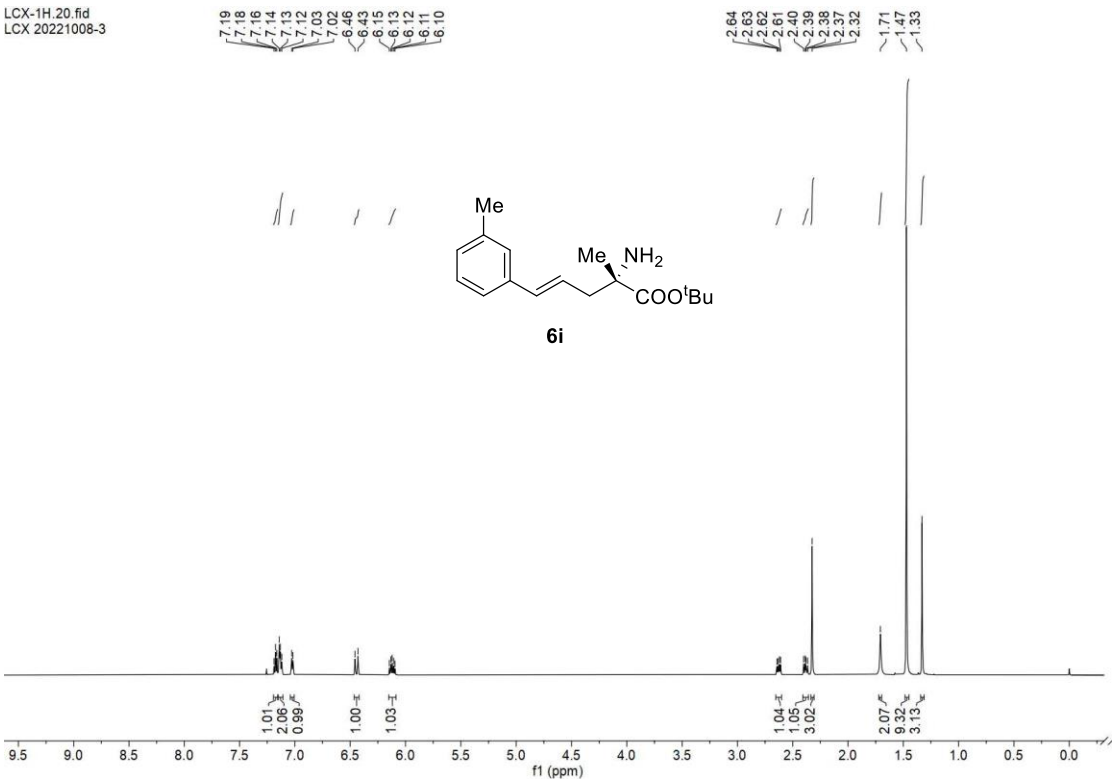
162.32
139.63
139.58
132.83
132.81
129.94
129.89
126.40
122.01
121.99
114.14
113.99
112.66
112.52
81.05
77.20
76.98
76.77
58.07
44.40
28.02
26.38
F
Me
NH2
COOtBu
6h
f1 (ppm)


LCX-1H.20.fid
LCX 20221008-3
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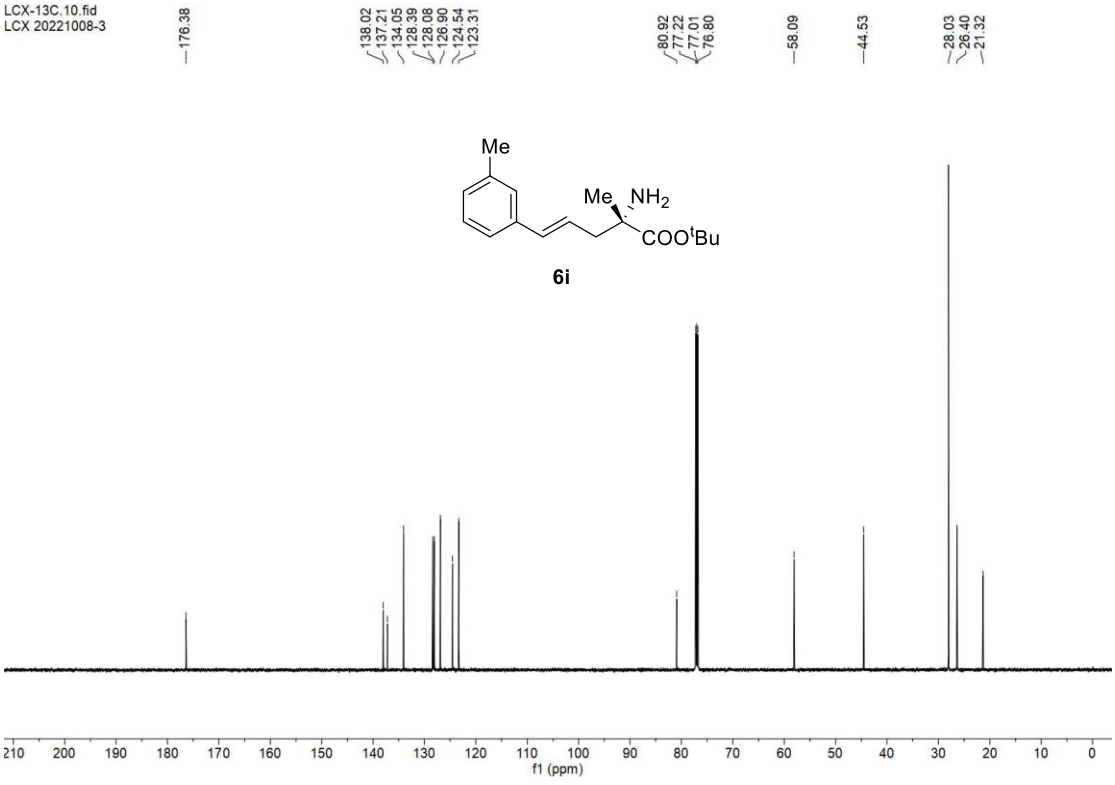
7.18
7.16
7.14
7.13
7.12
7.03
7.02
6.46
6.43
6.15
6.13
6.12
6.11
6.10
2.64
2.63
2.62
2.61
2.40
2.39
2.38
2.37
2.32
1.71
1.47
1.33
Me
Me
NH2
COOtBu
6i
1.01
2.08
0.99
1.00
1.03
1.04
1.05
3.02
2.07
9.32
3.13
f1 (ppm)


LCX-13C.10.fid
LCX 20221008-3
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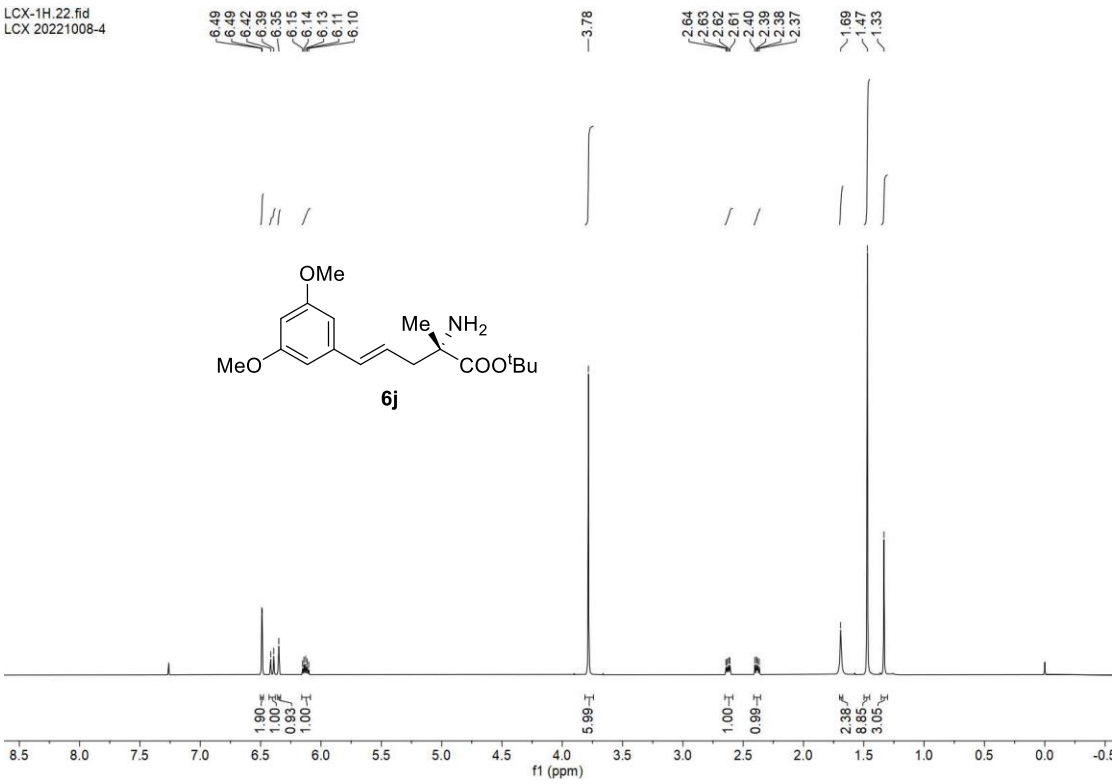
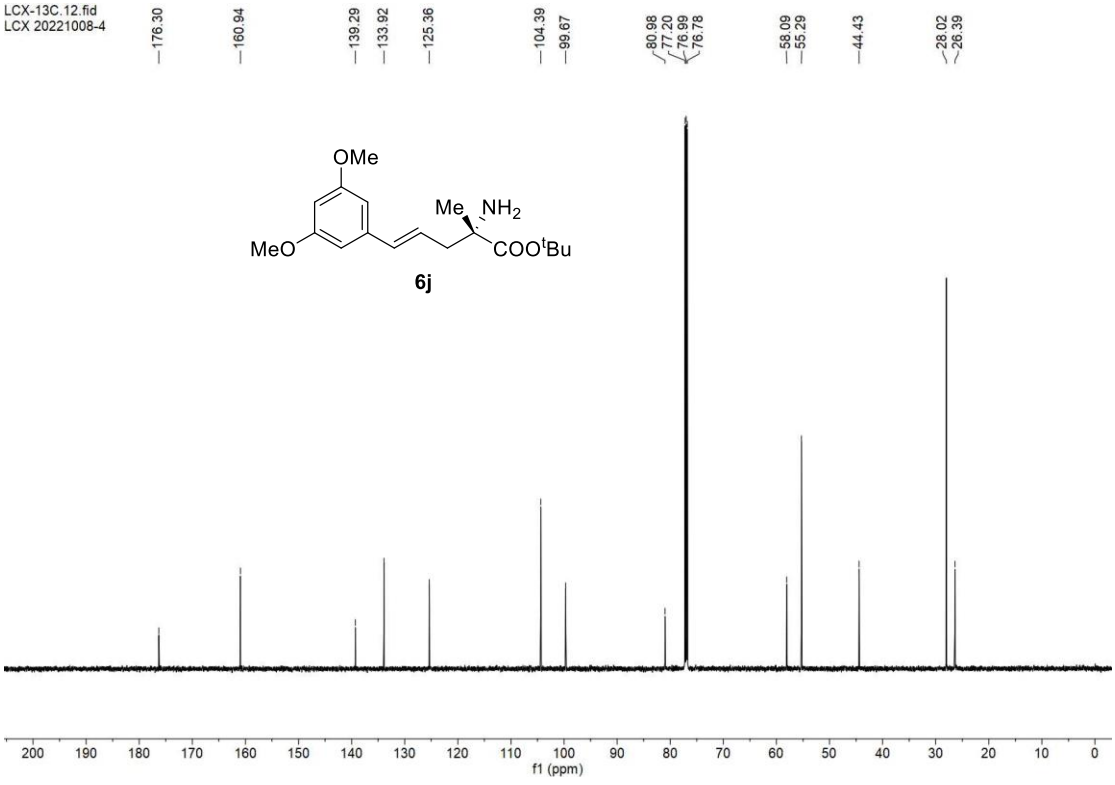
137.21
134.05
128.39
128.08
126.90
124.54
123.31
80.92
77.22
77.01
76.80
58.09
44.53
28.03
26.40
21.32
Me
Me
NH2
COOtBu
6i
f1 (ppm)


LCX-1H.22.fid
LCX 20221008-4
6.49
6.49
6.42
6.39
6.35
6.15
6.14
6.13
6.11
6.10
3.78
2.64
2.63
2.62
2.61
2.40
2.39
2.38
2.37
1.69
1.47
1.33
OMe
MeO
Me
NH2
COOtBu
6j
1.90
1.00
0.93
1.00
5.99
1.00
0.99
2.38
8.85
3.05
f1 (ppm)


LCX-13C.12.fid
LCX 20221008-4
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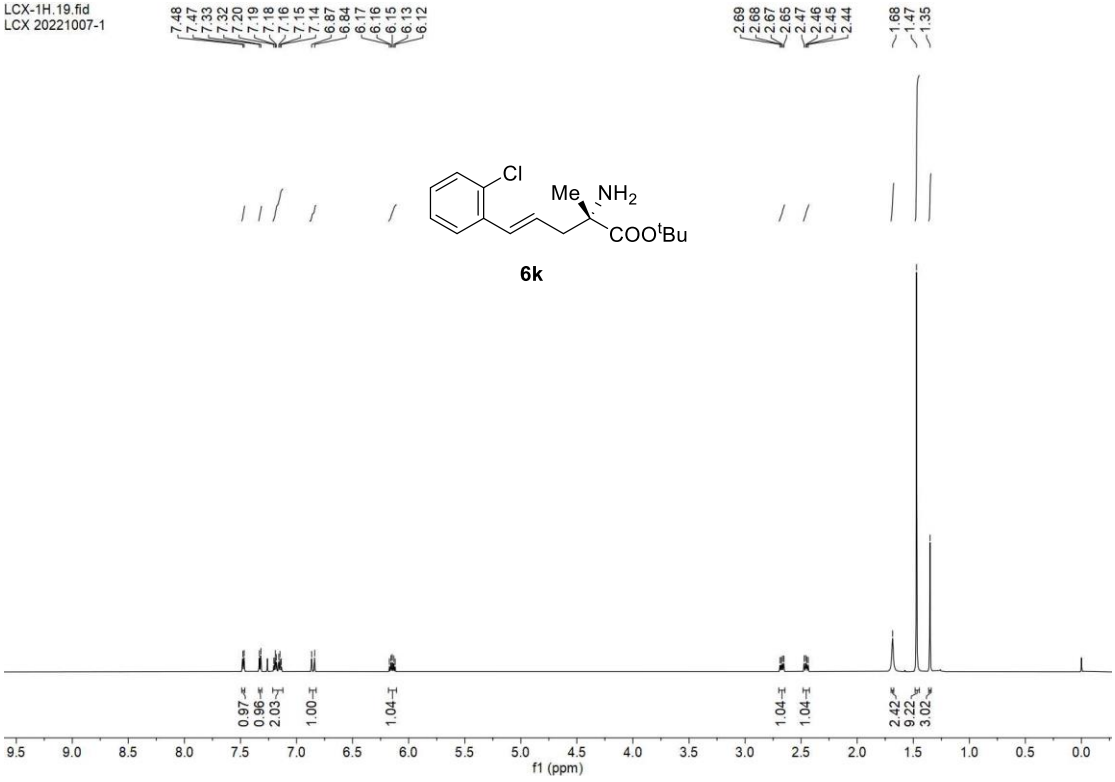
139.29
133.92
125.36
104.39
99.67
80.98
77.20
76.99
76.78
58.09
55.29
44.43
28.02
26.39
OMe
MeO
Me
NH2
COOtBu
6j
f1 (ppm)


LCX-1H.19.fid
LCX 20221007-1
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7.20
7.19
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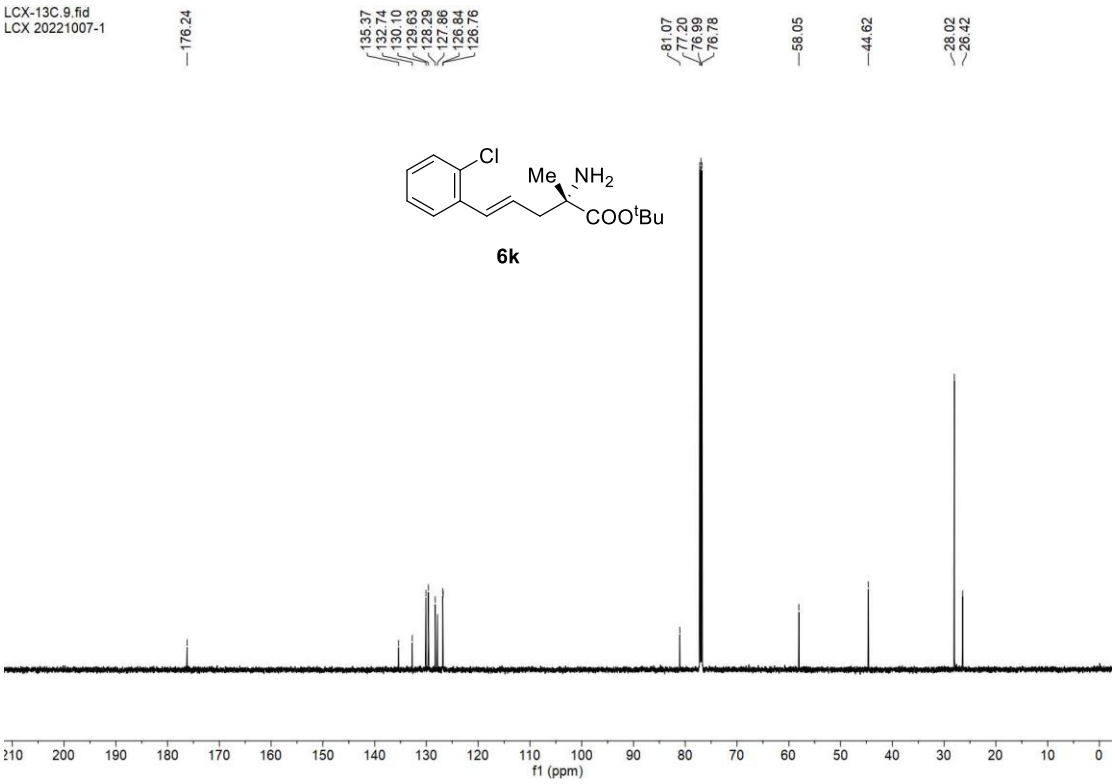
7.16
7.15
7.14
6.87
6.84
6.17
6.16
6.15
6.13
6.12
2.69
2.68
2.67
2.65
2.47
2.46
2.45
2.44
1.68
1.47
1.35
Cl
Me
NH2
COOtBu
6k
0.97
0.96
2.03
1.00
1.04
1.04
1.04
2.42
9.22
3.02
f1 (ppm)


LCX-13C.9.fid
LCX 20221007-1
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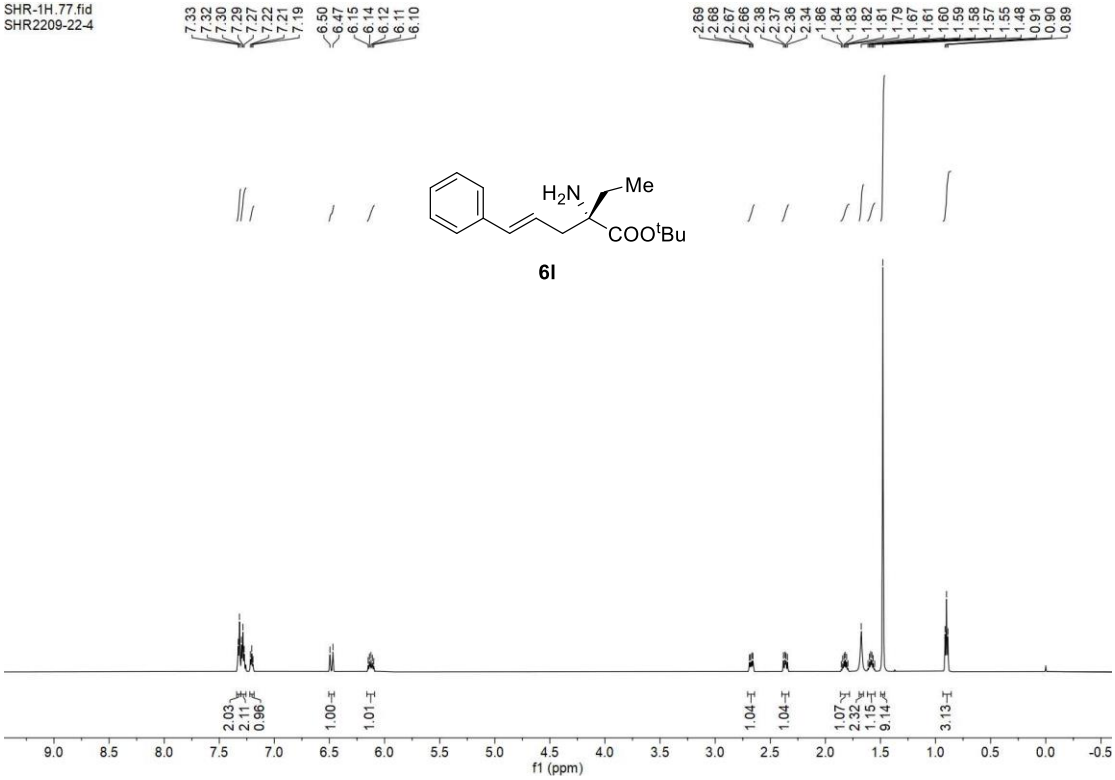
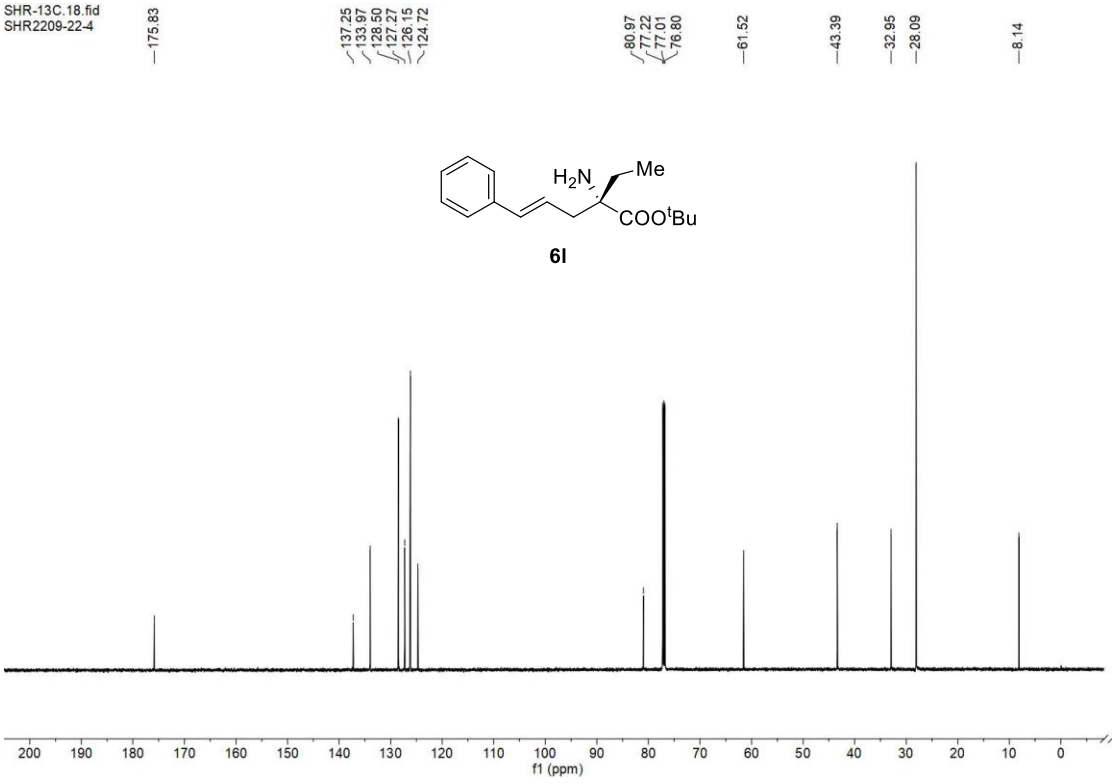
135.37
132.74
130.10
129.63
128.29
127.86
126.84
126.76
81.07
77.20
76.99
76.78
58.05
44.62
28.02
26.42
Cl
Me
NH2
COOtBu
6k
f1 (ppm)

SHR-1H.77.fid
SHR2209-22-4

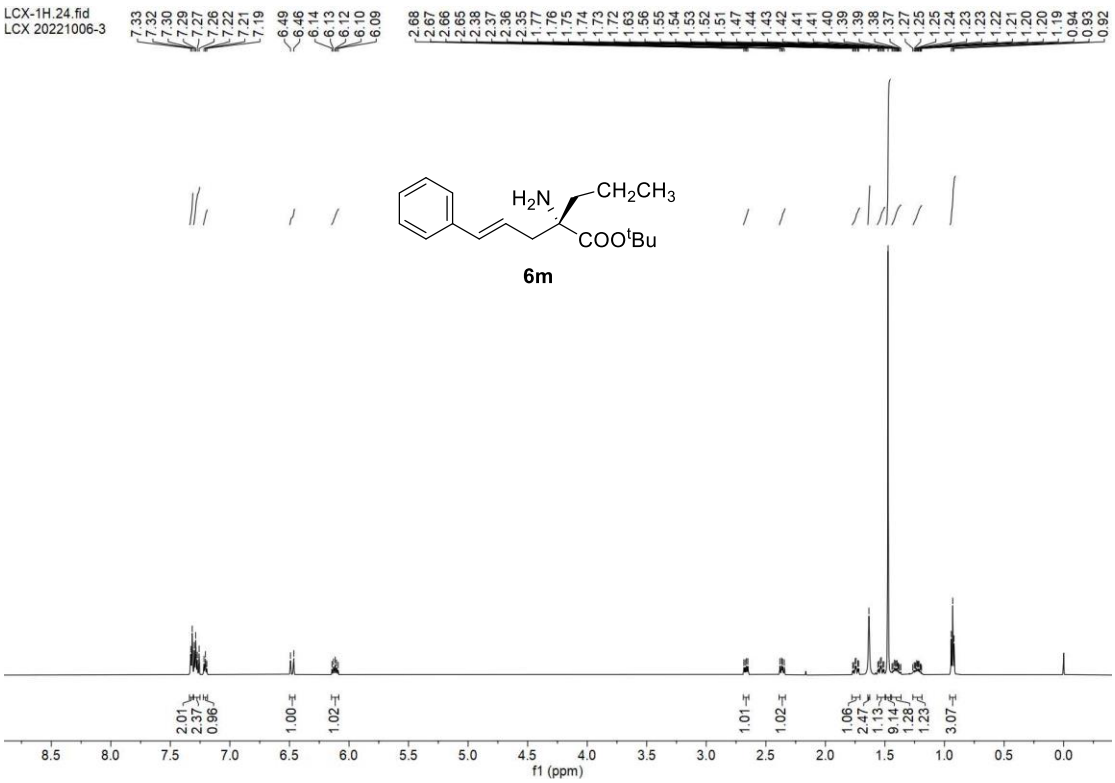


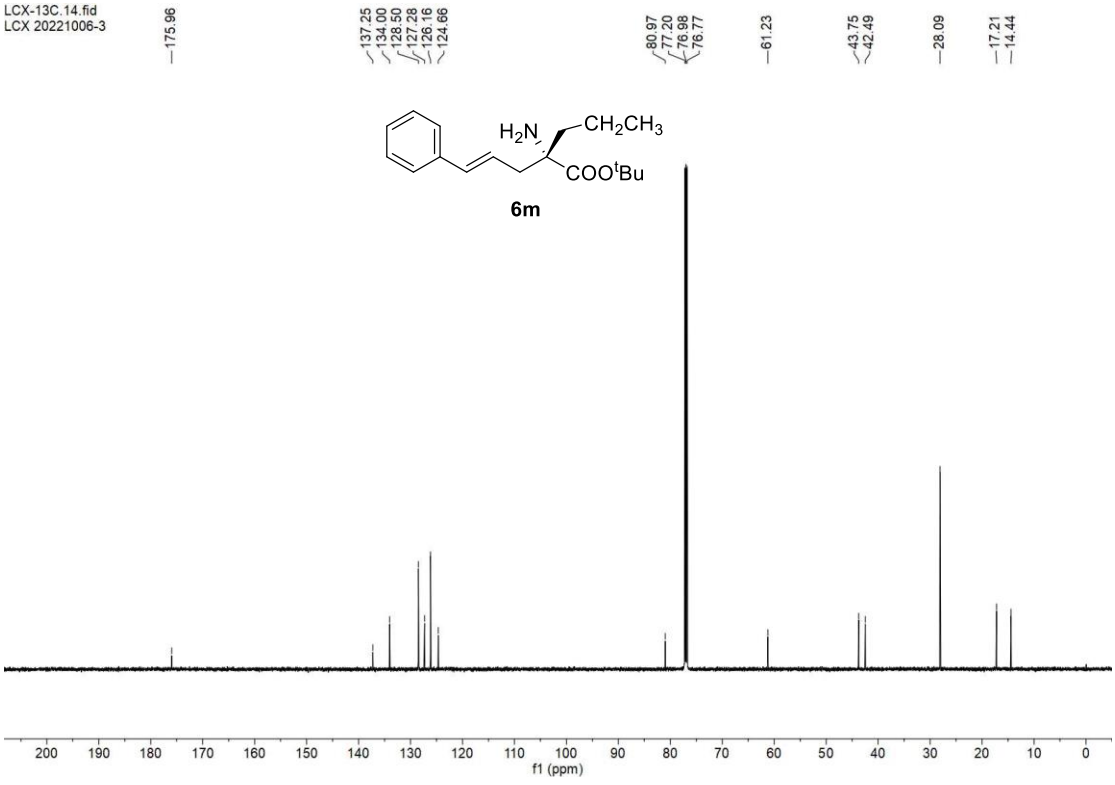
6l

SHR-13C.18.fid
SHR2209-22-4

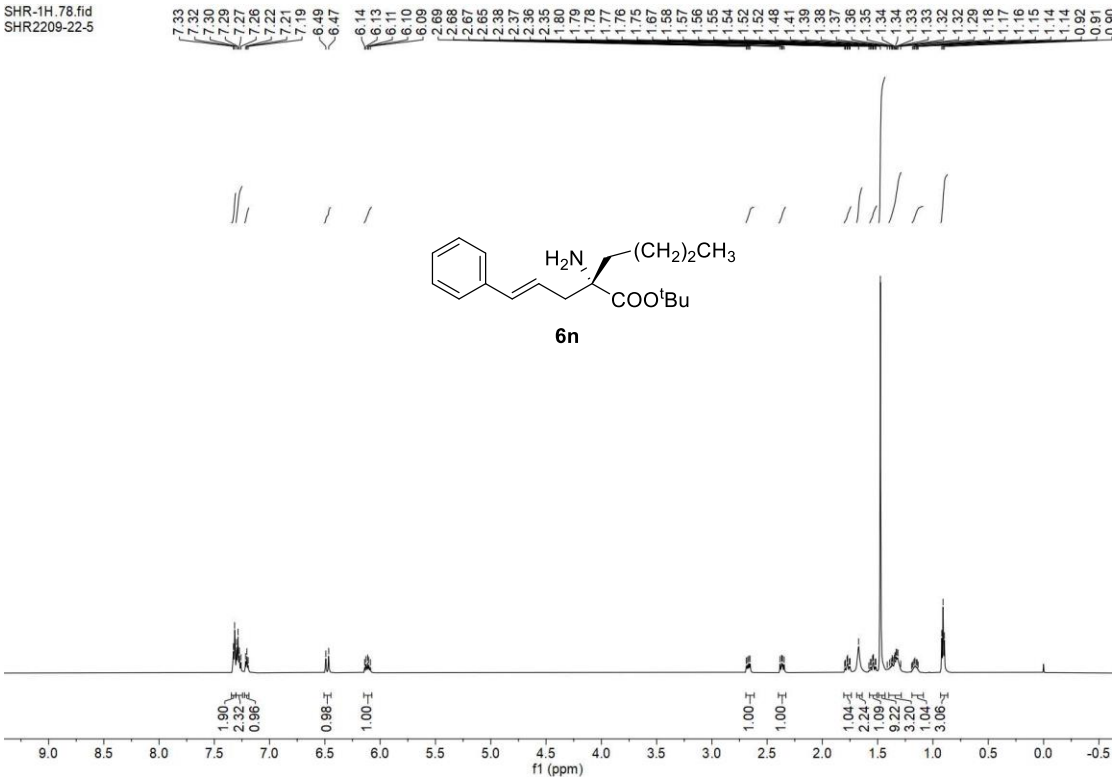


6l


LCX-1H.24.fid
LCX 20221006-3
H2N
CH2CH3
COOtBu
6m
f1 (ppm)

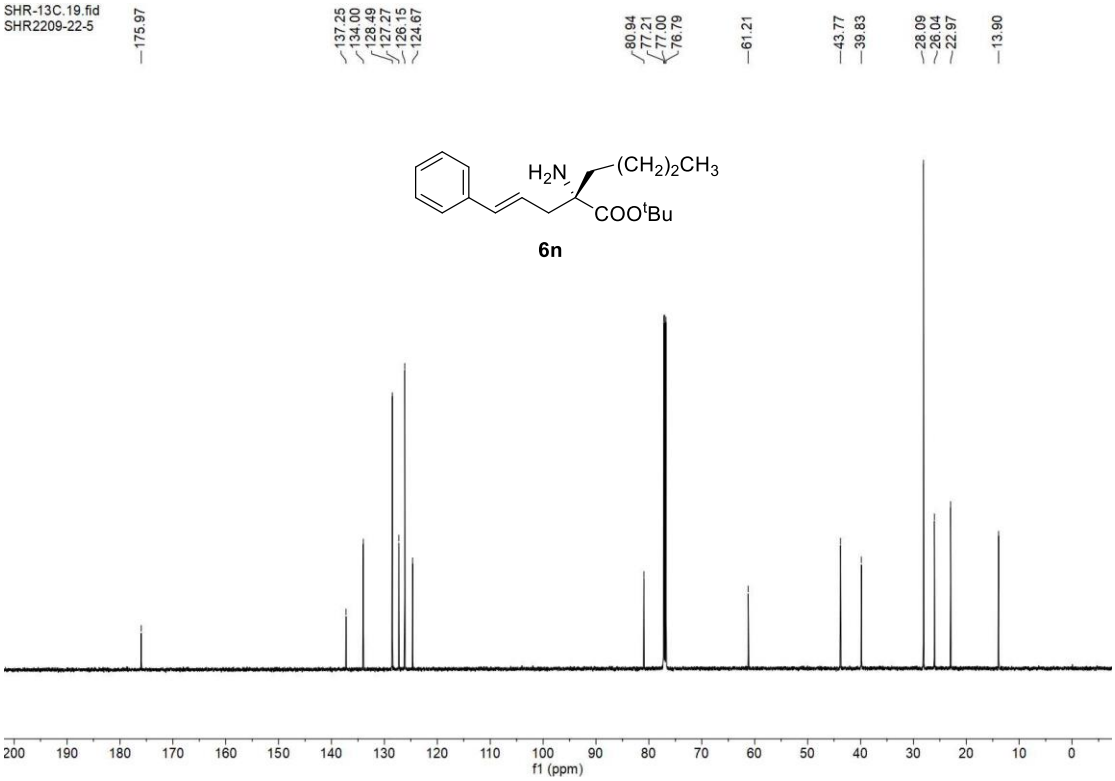

LCX-13C.14.fid
LCX 20221006-3
H2N
CH2CH3
COOtBu
6m
f1 (ppm)

SHR-1H.78.fid
SHR2209-22-5

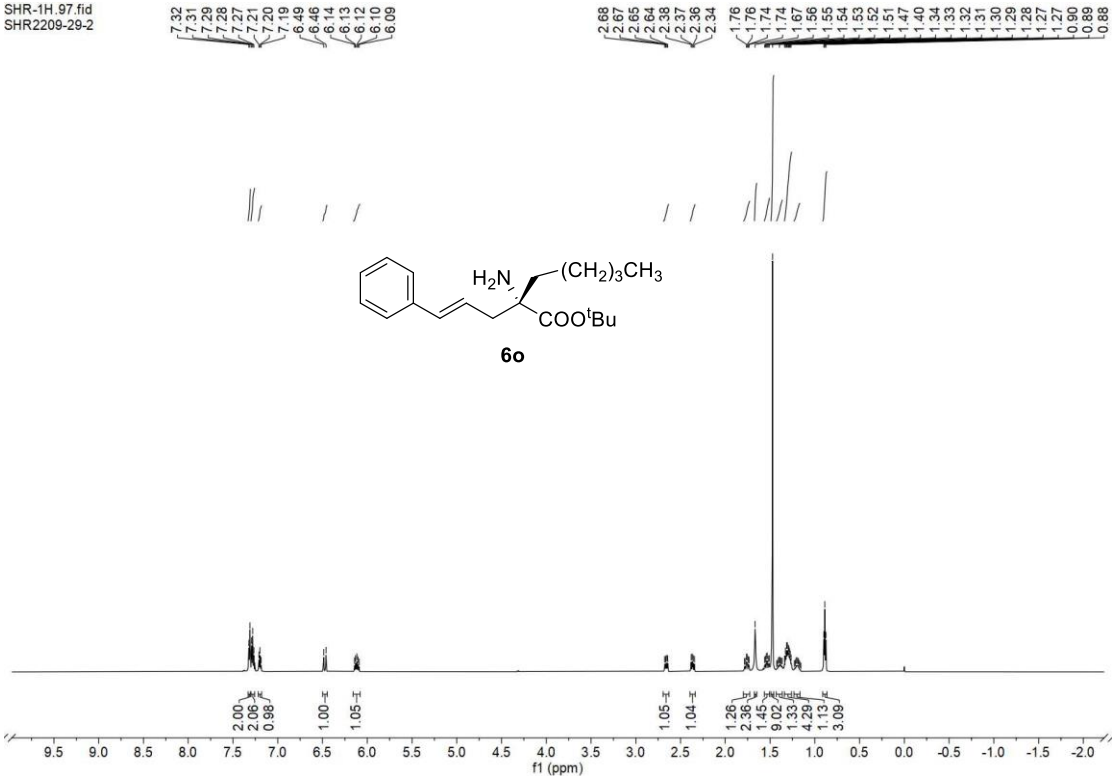


6n

SHR-13C.19.fid
SHR2209-22-5



6n


SHR-1H.97.fid
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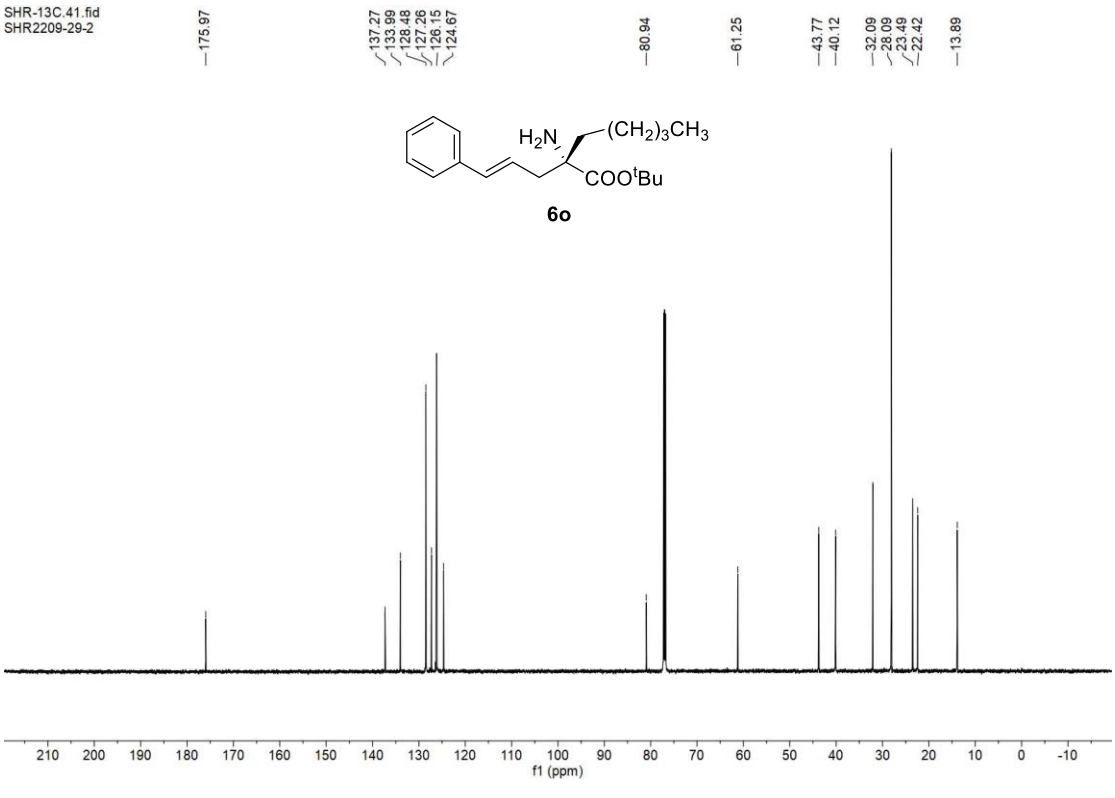
7.27
7.21
7.20
7.19
6.49
6.46
6.14
6.13
6.12
6.10
6.09
2.68
2.67
2.65
2.64
2.38
2.37
2.36
2.34
1.76
1.76
1.74
1.74
1.67
1.56
1.55
1.54
1.53
1.52
1.51
1.47
1.40
1.34
1.33
1.32
1.31
1.30
1.29
1.28
1.27
1.27
0.90
0.89
0.88
H2N
(CH2)3CH3
COOtBu
6o
2.00
2.06
0.98
1.00
1.05
1.05
1.04
1.26
2.36
1.45
9.02
1.33
4.29
1.13
3.09
f1 (ppm)


SHR-13C.41.fid
SHR2209-29-2
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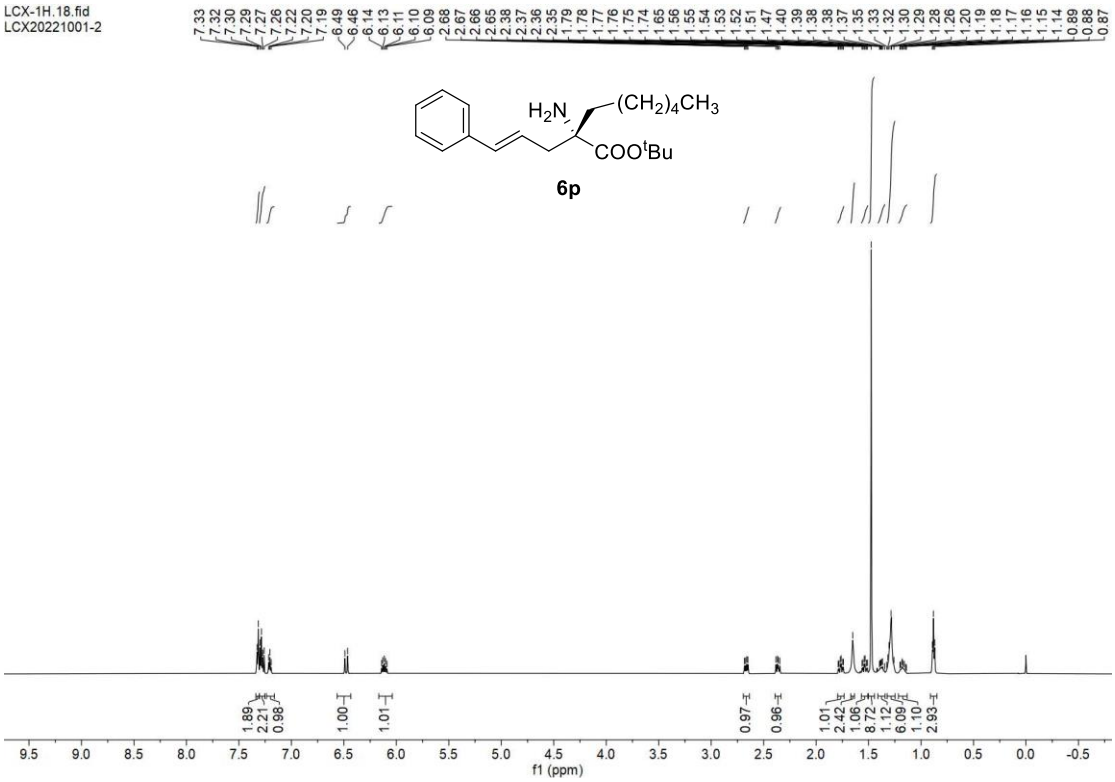
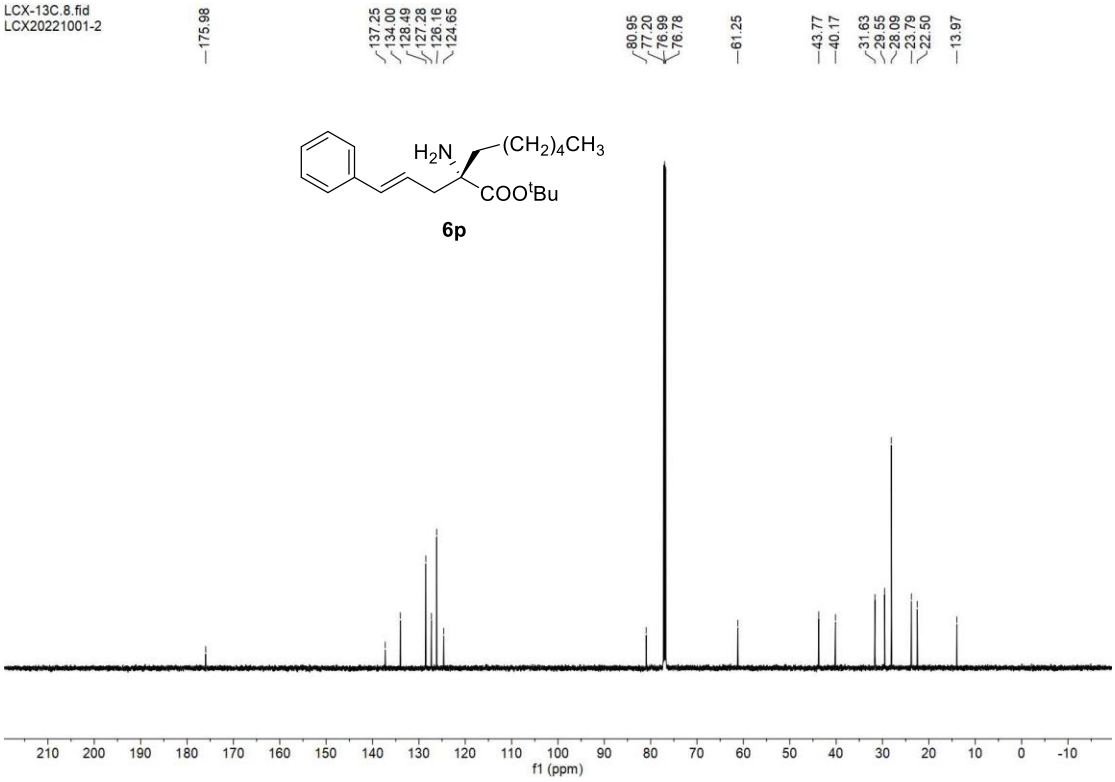
128.48
127.26
126.15
124.67
80.94
61.25
43.77
40.12
32.09
28.09
23.49
22.42
13.89
H2N
(CH2)3CH3
COOtBu
6o
f1 (ppm)

LCX-1H.18.fid
LCX20221001-2

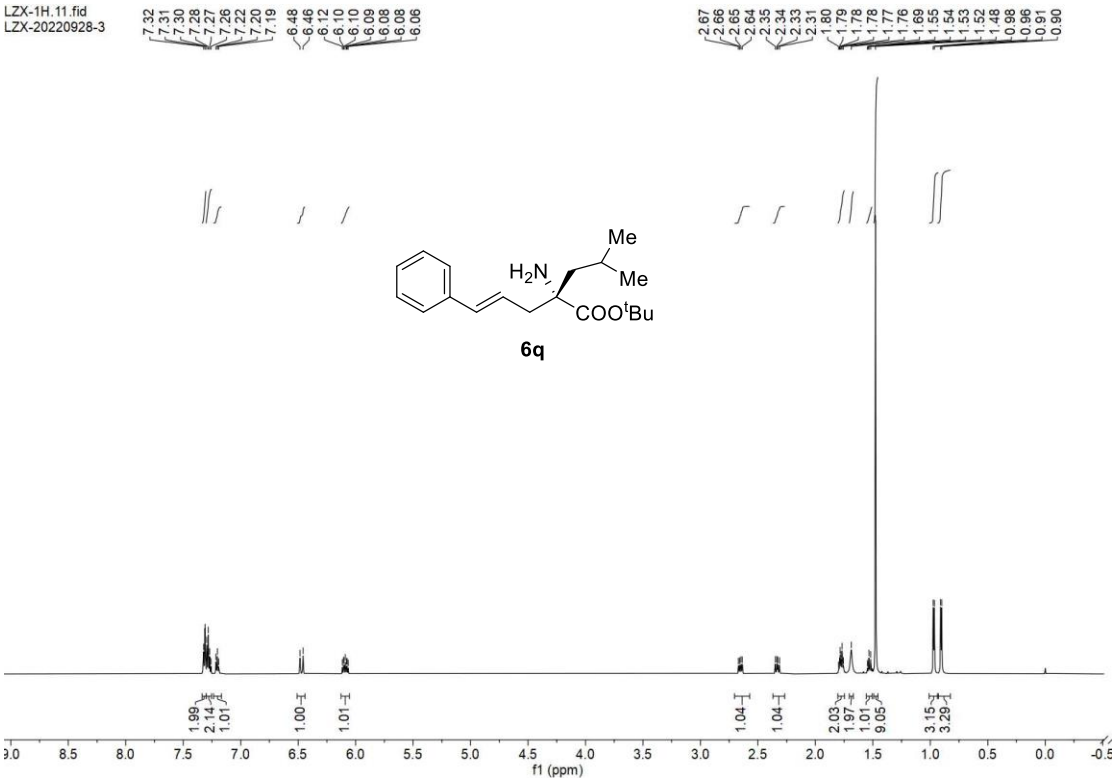


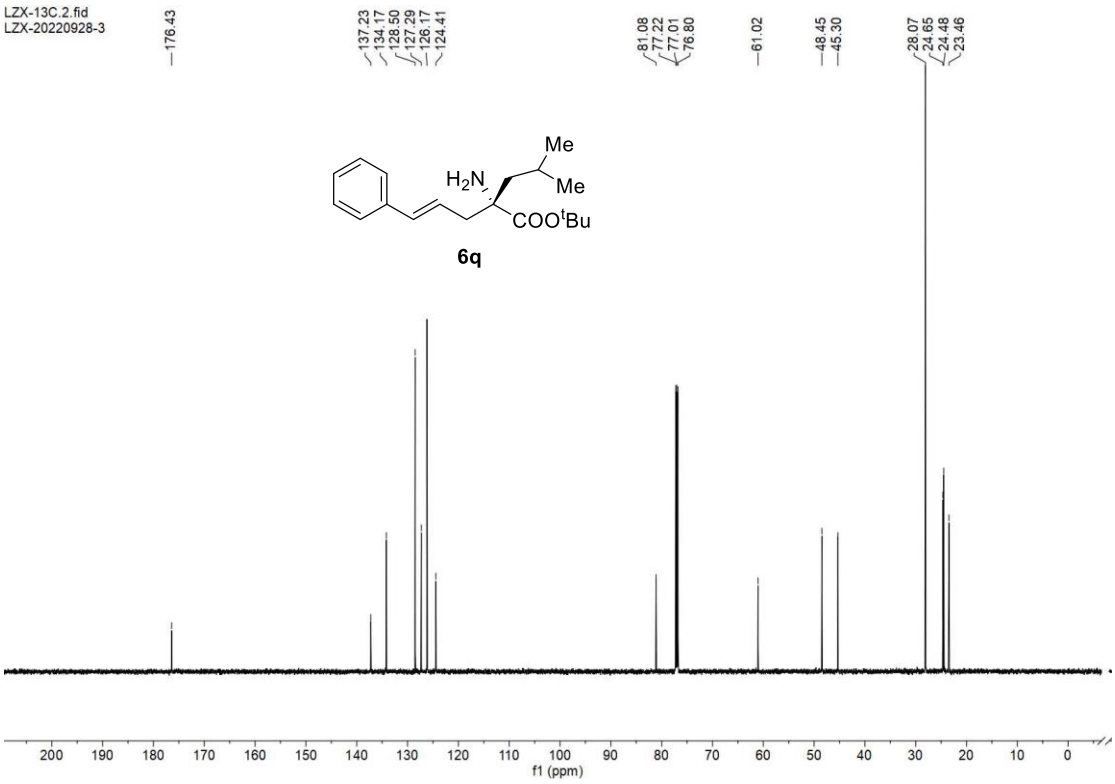
6p

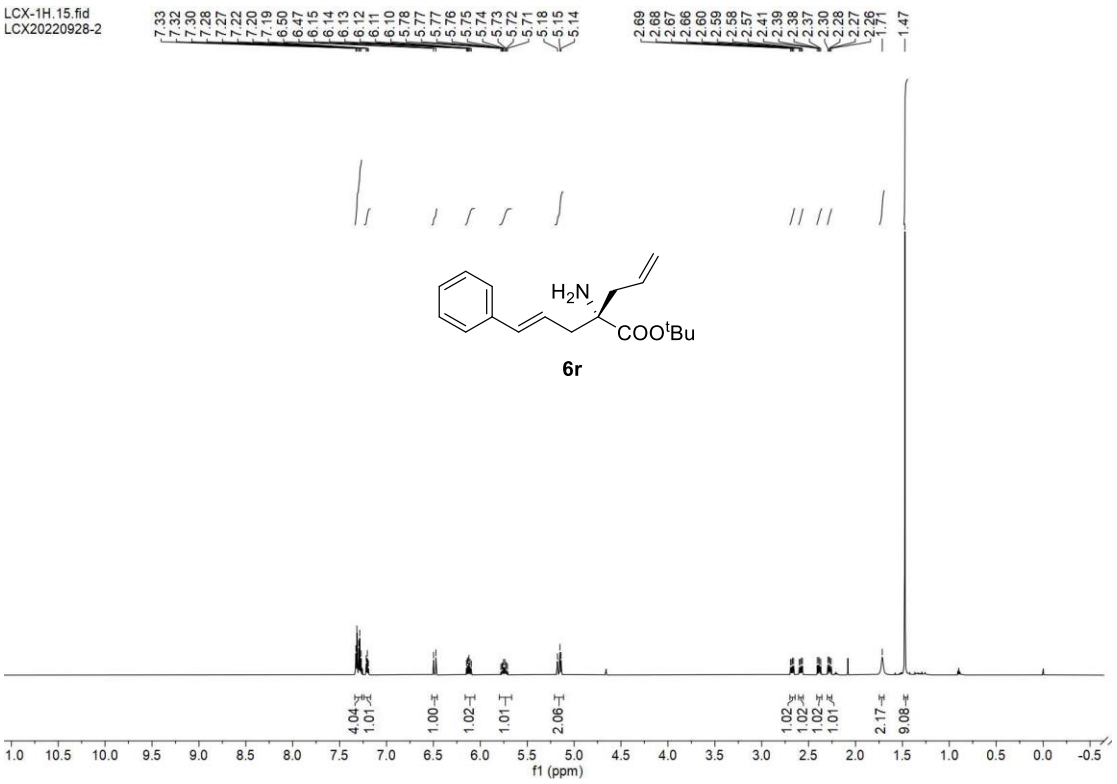
LCX-13C.8.fid
LCX20221001-2



6p


LZX-1H.11.fid
LZX-20220928-3
Me
H2N
Me
COOtBu
6q
f1 (ppm)


LZX-13C.2.fid
LZX-20220928-3
Me
H2N
Me
COOtBu
6q
f1 (ppm)


LCX-1H.15.fid
LCX20220928-2
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7.27
7.22
7.20
7.19
6.50
6.47
6.15
6.14
6.13
6.12
6.11
6.10
5.78
5.77
5.77
5.76
5.75
5.74
5.73
5.72
5.71
5.18
5.15
5.14
2.69
2.68
2.67
2.66
2.60
2.59
2.58
2.57
2.41
2.39
2.38
2.37
2.30
2.28
2.27
2.26
1.71
1.47
H2N
COOtBu
6r
4.04
1.01
1.00
1.02
1.01
2.06
1.02
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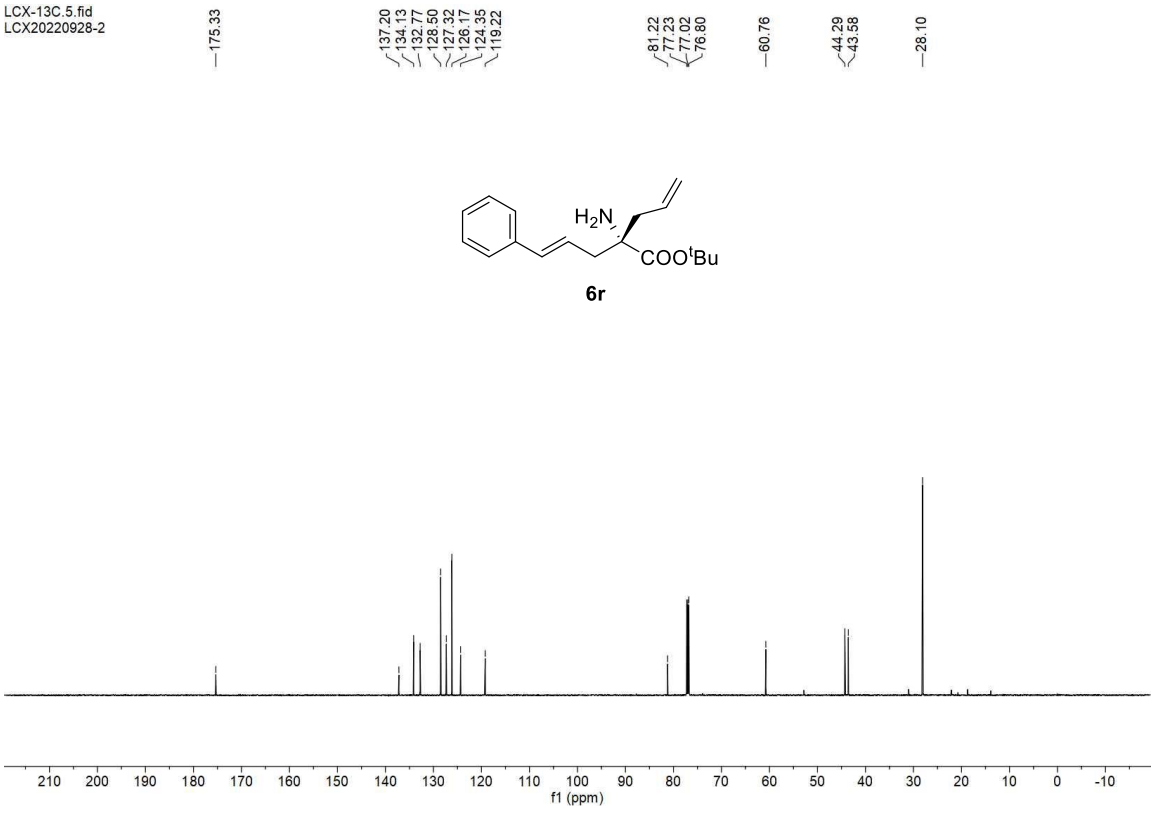
1.02
1.01
2.17
9.08
f1 (ppm)


LCX-13C.5.fid
LCX20220928-2
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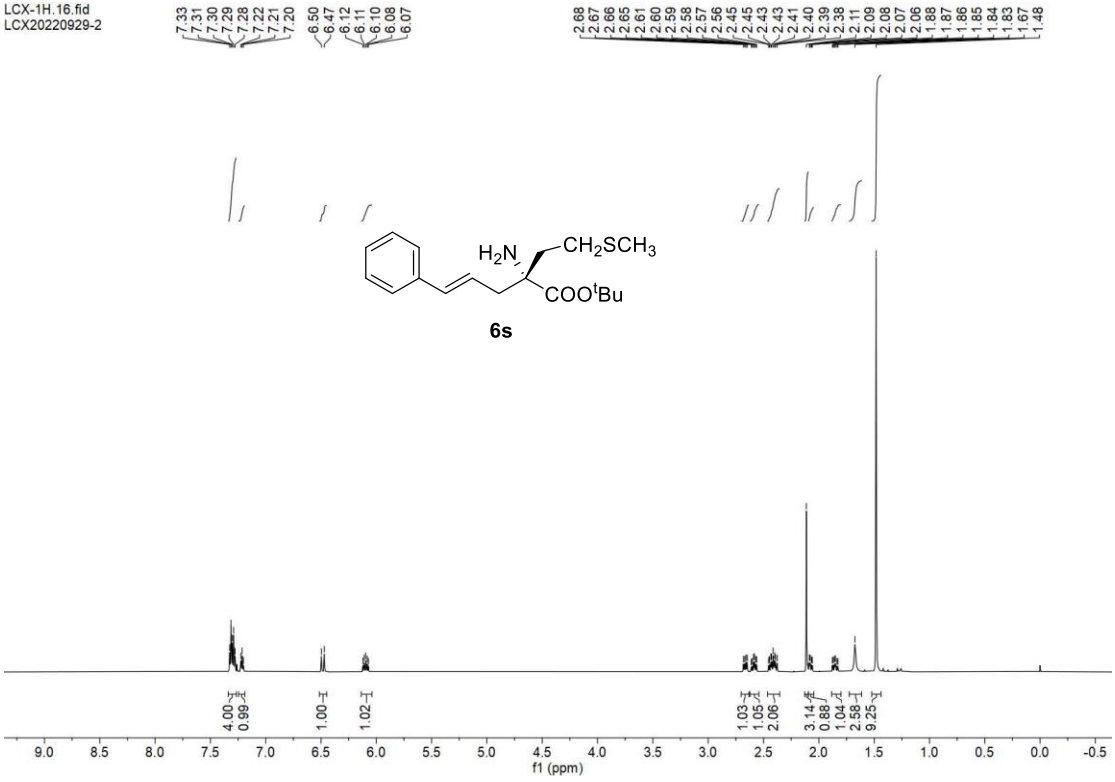
134.13
132.77
128.50
127.32
126.17
124.35
119.22
81.22
77.23
77.02
76.80
60.76
44.29
43.58
28.10
H2N
COOtBu
6r
f1 (ppm)


LCX-1H.16.fid
LCX20220929-2
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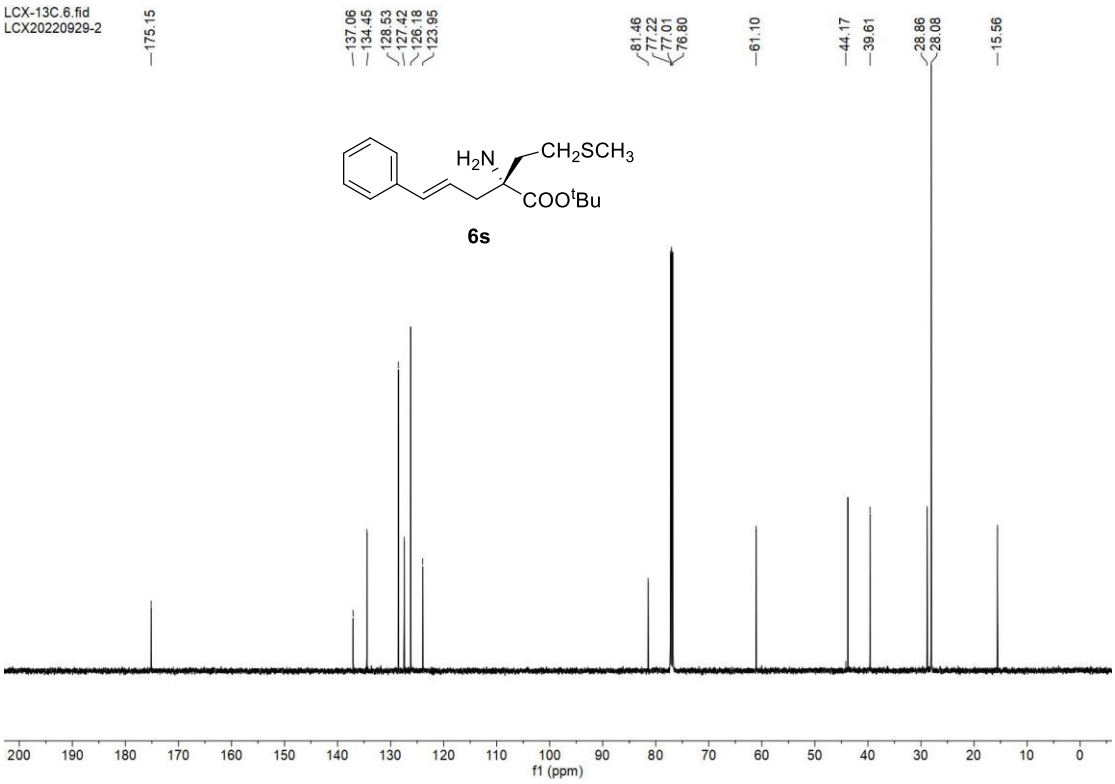
7.31
7.30
7.29
7.28
7.22
7.21
7.20
6.50
6.47
6.12
6.11
6.10
6.08
6.07
2.68
2.67
2.66
2.65
2.61
2.60
2.59
2.58
2.57
2.56
2.45
2.43
2.41
2.40
2.39
2.38
2.11
2.09
2.08
2.07
2.06
1.88
1.87
1.86
1.85
1.84
1.83
1.67
1.48
H2N
CH2SCH3
COOtBu
6s
4.00
0.99
1.00
1.02
1.03
1.05
2.06
3.14
0.88
1.04
2.58
9.25
f1 (ppm)


LCX-13C.6.fid
LCX20220929-2
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134.45
128.53
127.42
126.18
123.95
81.46
77.22
77.01
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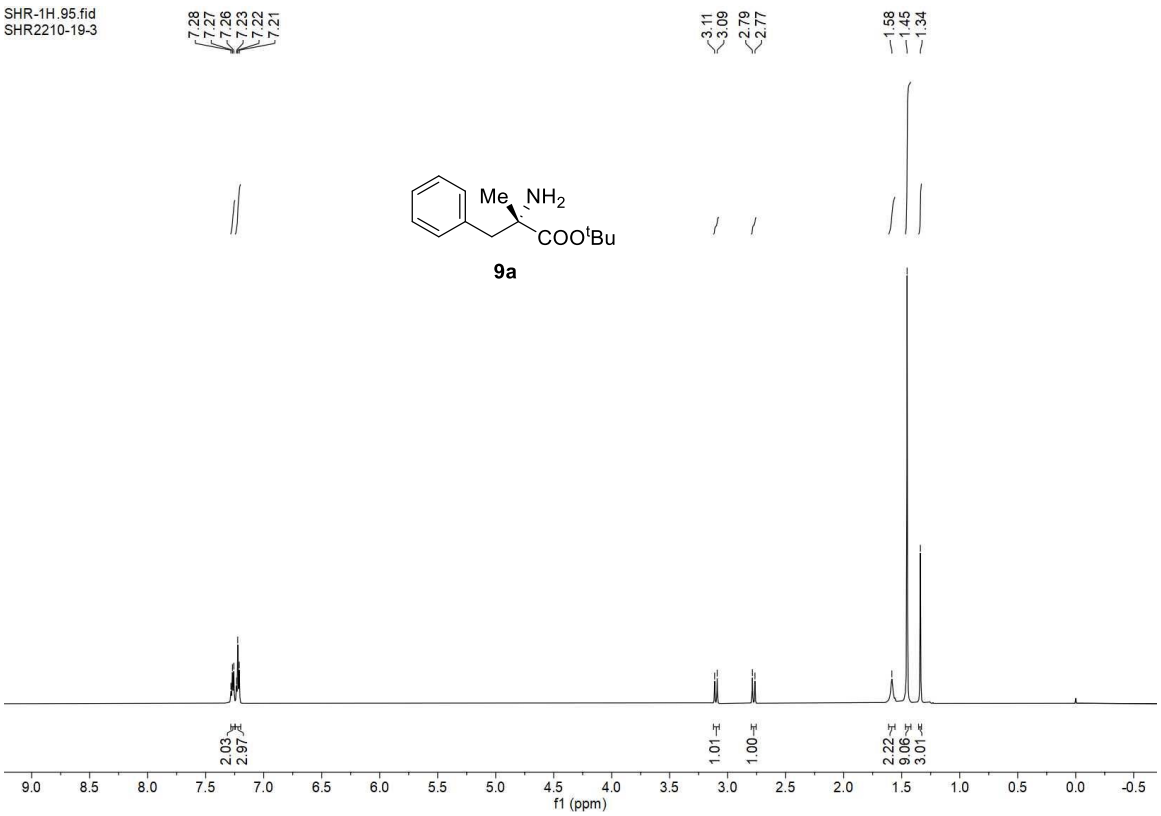
H2N
CH2SCH3
COOtBu
6s
f1 (ppm)


SHR-1H.95.fid
SHR2210-19-3
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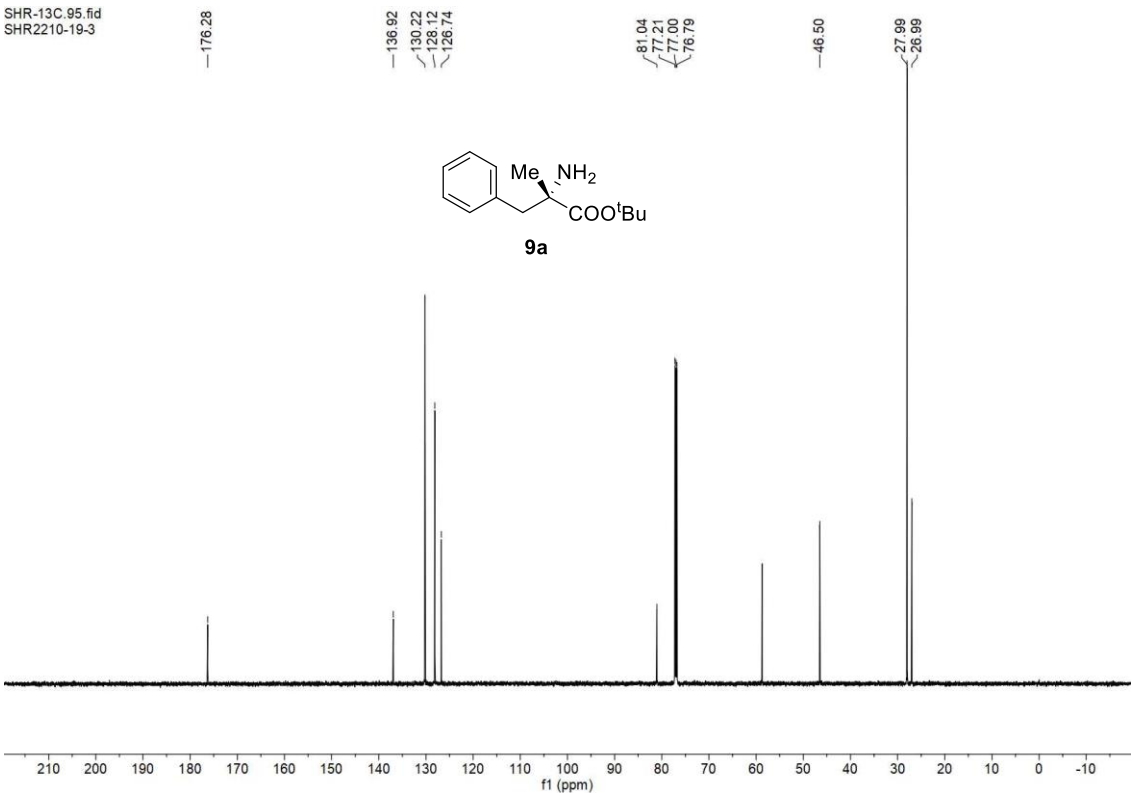
7.27
7.26
7.23
7.22
7.21
3.11
3.09
2.79
2.77
1.58
1.45
1.34
Me
NH2
COOtBu
9a
2.03
2.97
1.01
1.00
2.22
9.06
3.01
f1 (ppm)


SHR-13C.95.fid
SHR2210-19-3
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136.92
130.22
128.12
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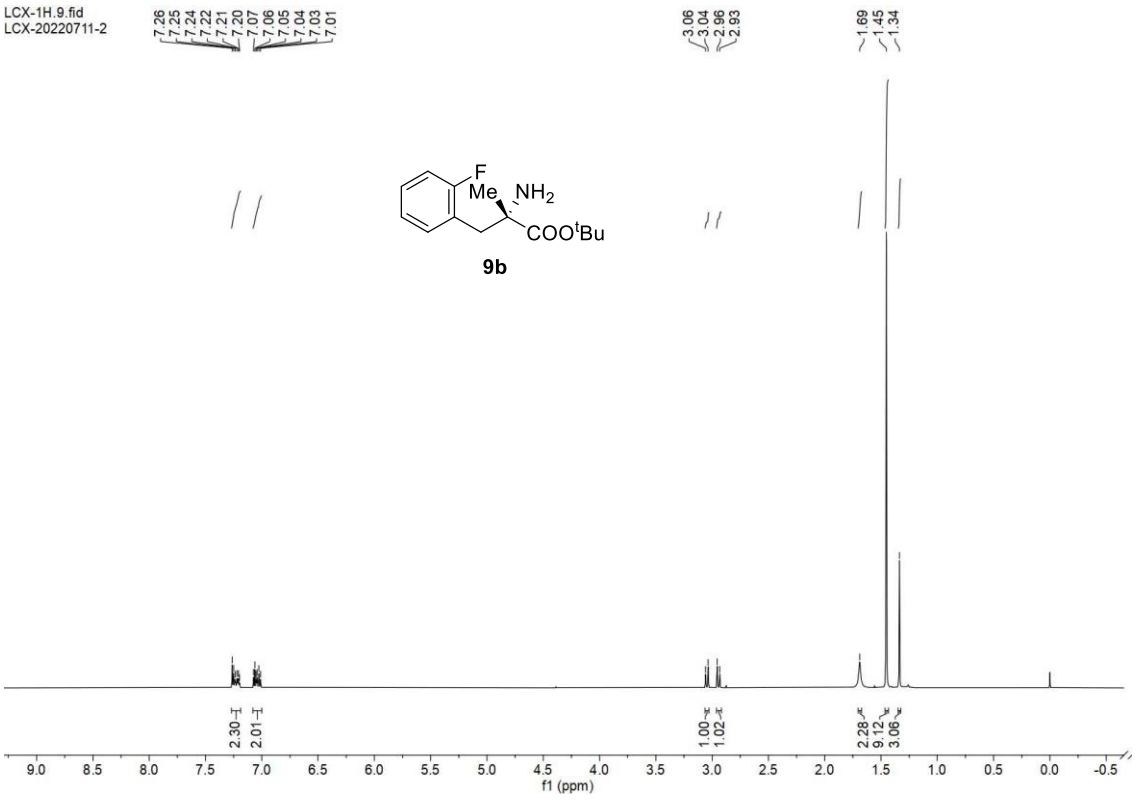
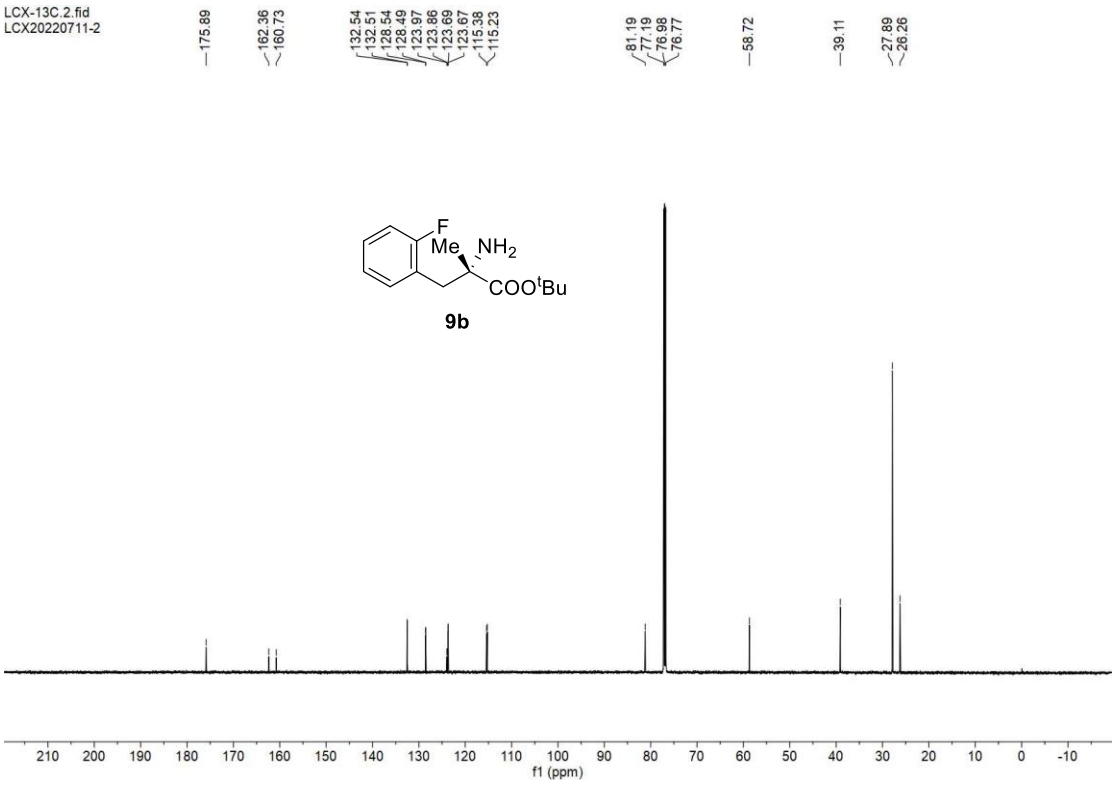
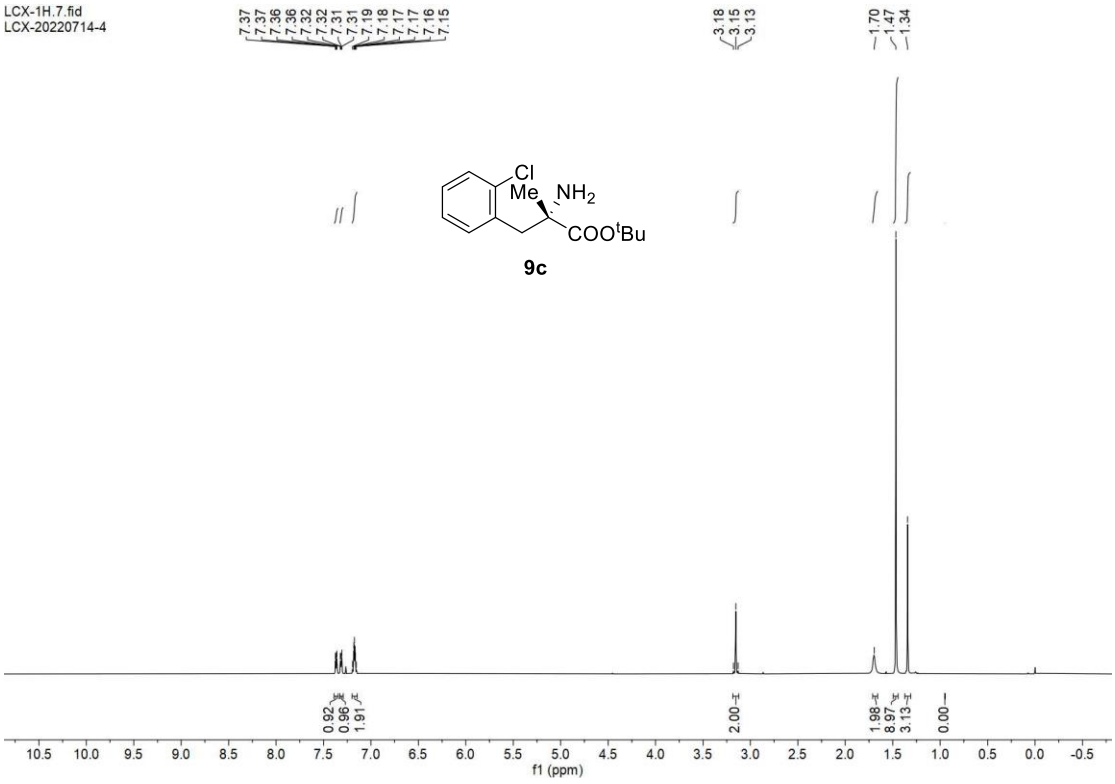
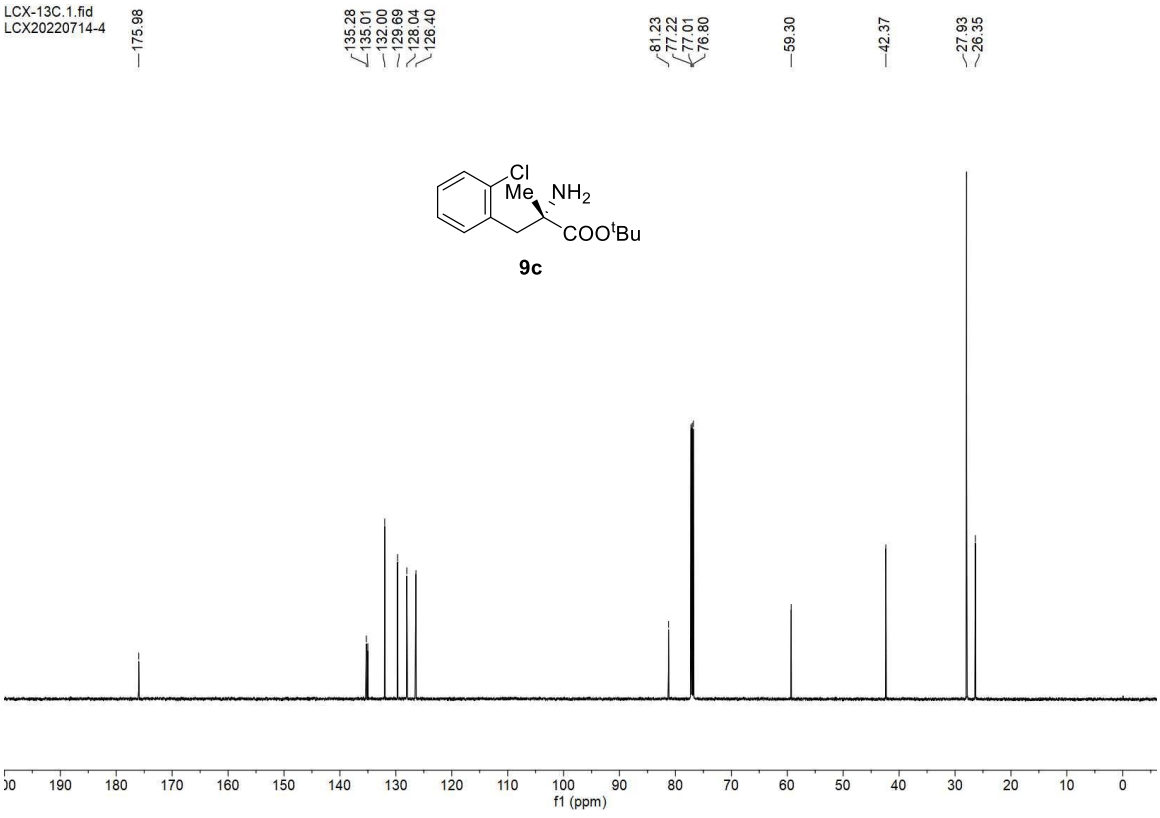
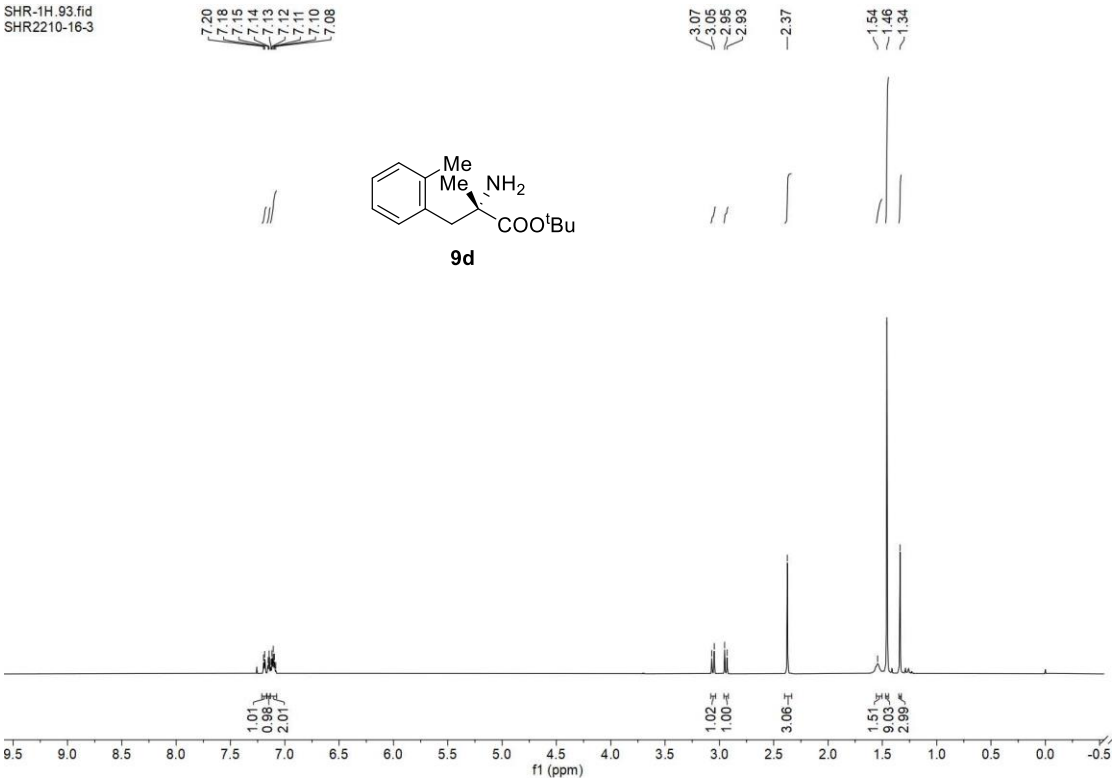
81.04
77.21
77.00
76.79
46.50
27.99
26.99
Me
NH2
COOtBu
9a
f1 (ppm)

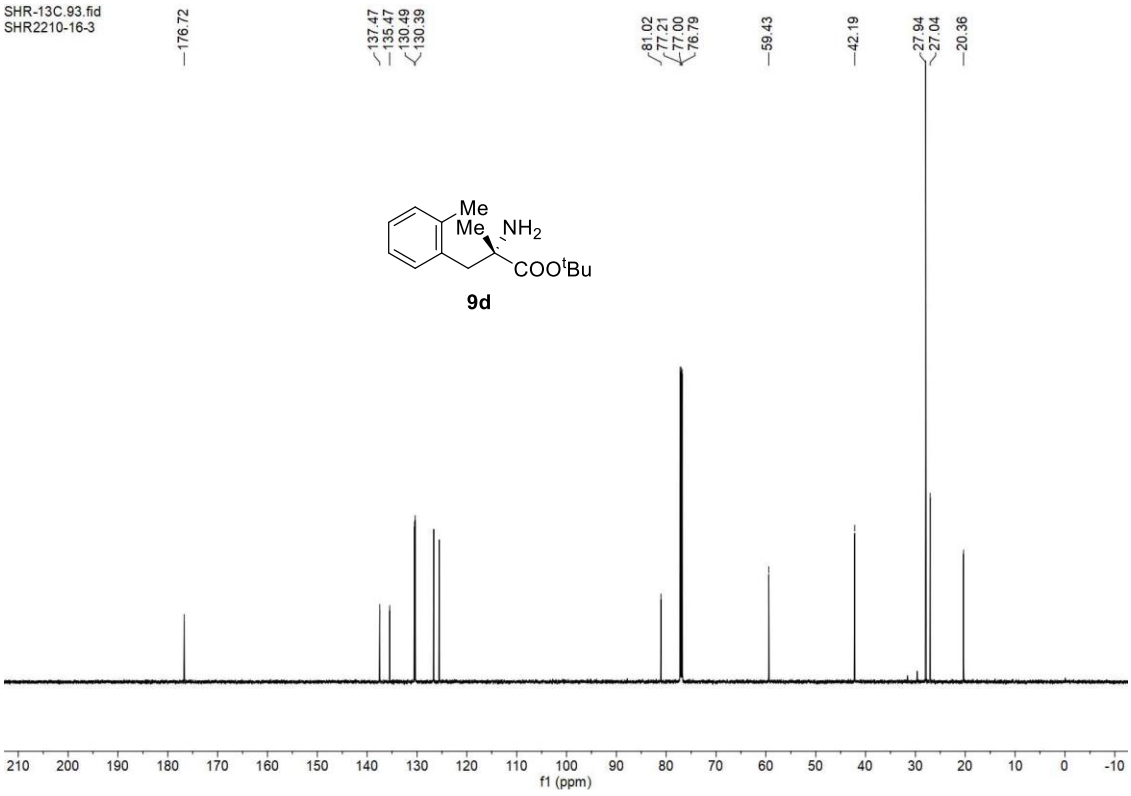

LCX-1H.9.fid
LCX-20220711-2
7.26
7.25
7.24
7.22
7.21
7.20
7.07
7.06
7.05
7.04
7.03
7.01
3.06
3.04
2.96
2.93
1.69
1.45
1.34
F
Me
NH2
COOtBu
9b
2.30
2.01
1.00
1.02
2.28
9.12
3.06
f1 (ppm)


LCX-13C.2.fid
LCX20220711-2
175.89
162.36
160.73
132.54
132.51
128.54
128.49
123.97
123.86
123.69
123.67
115.38
115.23
81.19
77.19
76.98
76.77
58.72
39.11
27.89
26.26
F
Me
NH2
COOtBu
9b
f1 (ppm)

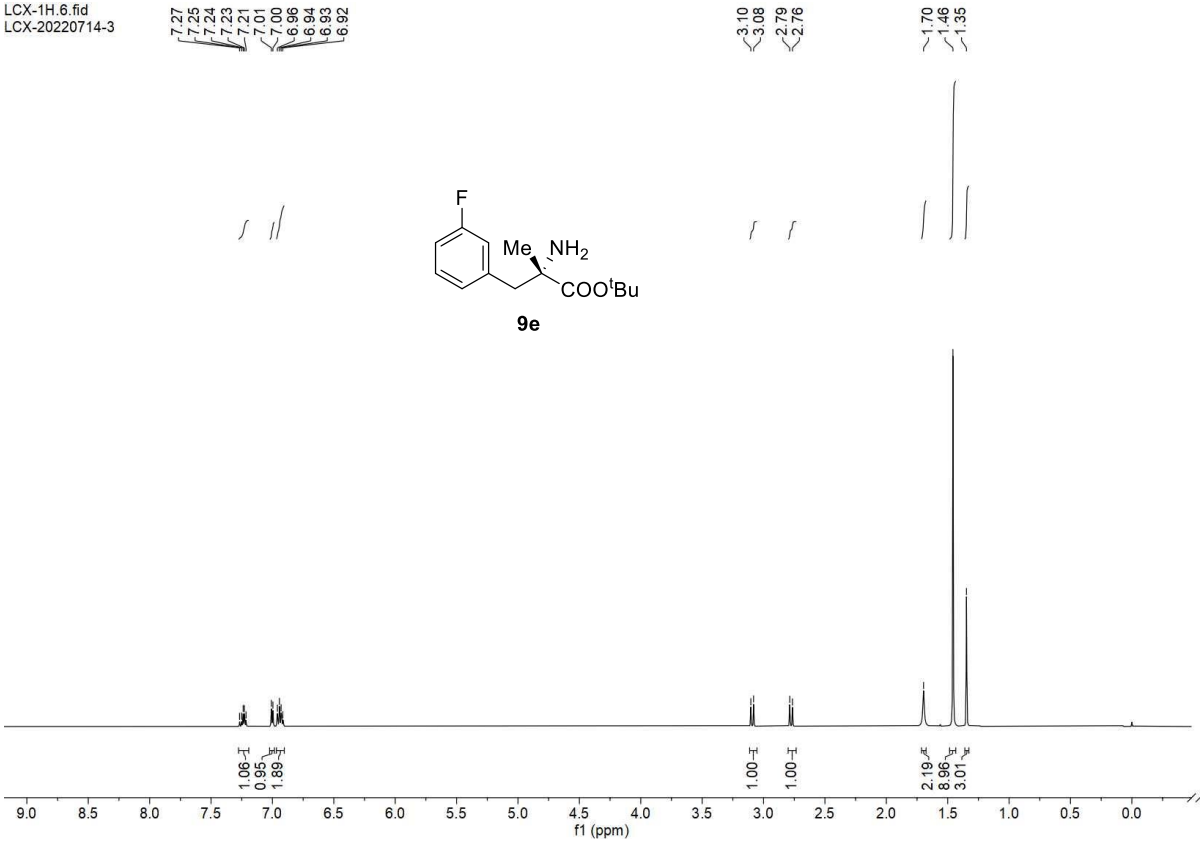

LCX-1H.7.fid
LCX-20220714-4
7.37
7.37
7.36
7.36
7.32
7.32
7.31
7.31
7.19
7.18
7.17
7.17
7.16
7.15
3.18
3.15
3.13
1.70
1.47
1.34
Cl
Me
NH2
COOtBu
9c
0.92
0.96
1.91
2.00
1.98
8.97
3.13
0.00
10.5 10.0 9.5 9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


LCX-13C.1.fid
LCX20220714-4
175.98
135.28
135.01
132.00
129.69
128.04
126.40
81.23
77.22
77.01
76.80
59.30
42.37
27.93
26.35
Cl
Me
NH2
COOtBu
9c
190 180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


SHR-1H.93.fid
SHR2210-16-3
7.20
7.18
7.15
7.14
7.13
7.12
7.11
7.10
7.08
3.07
3.05
2.95
2.93
2.37
1.54
1.46
1.34
Me
Me
NH2
COOtBu
9d
1.01
0.98
2.01
1.02
1.00
3.06
1.51
9.03
2.99
f1 (ppm)

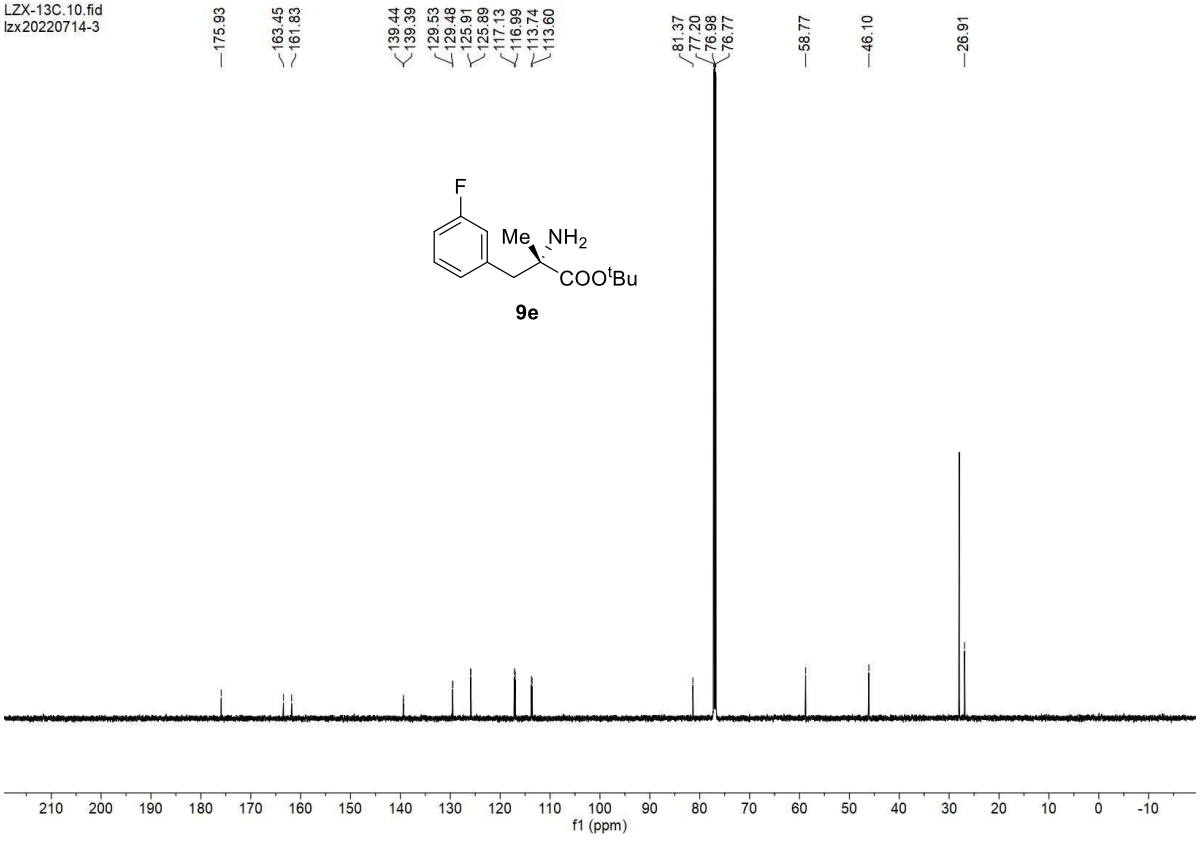

SHR-13C.93.fid
SHR2210-16-3
176.72
137.47
135.47
130.49
130.39
81.02
77.21
77.00
76.79
59.43
42.19
27.94
27.04
20.36
Me
Me
NH2
COOtBu
9d
f1 (ppm)

LCX-1H.6.fid
LCX-20220714-3

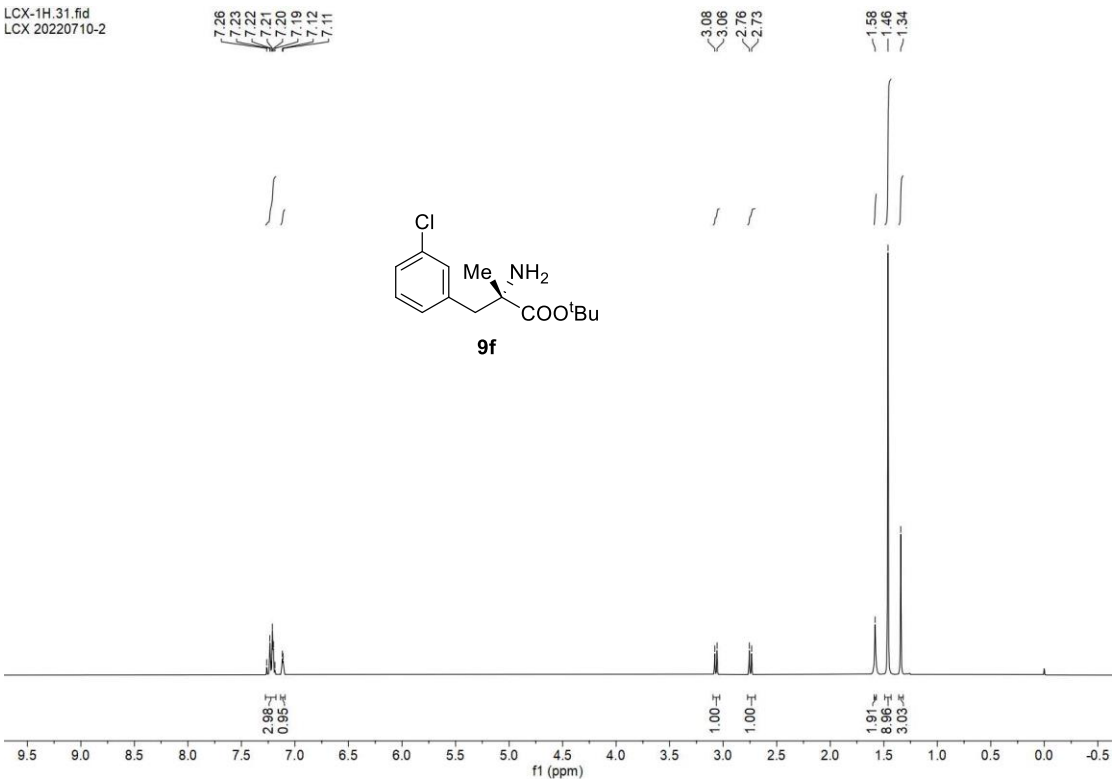


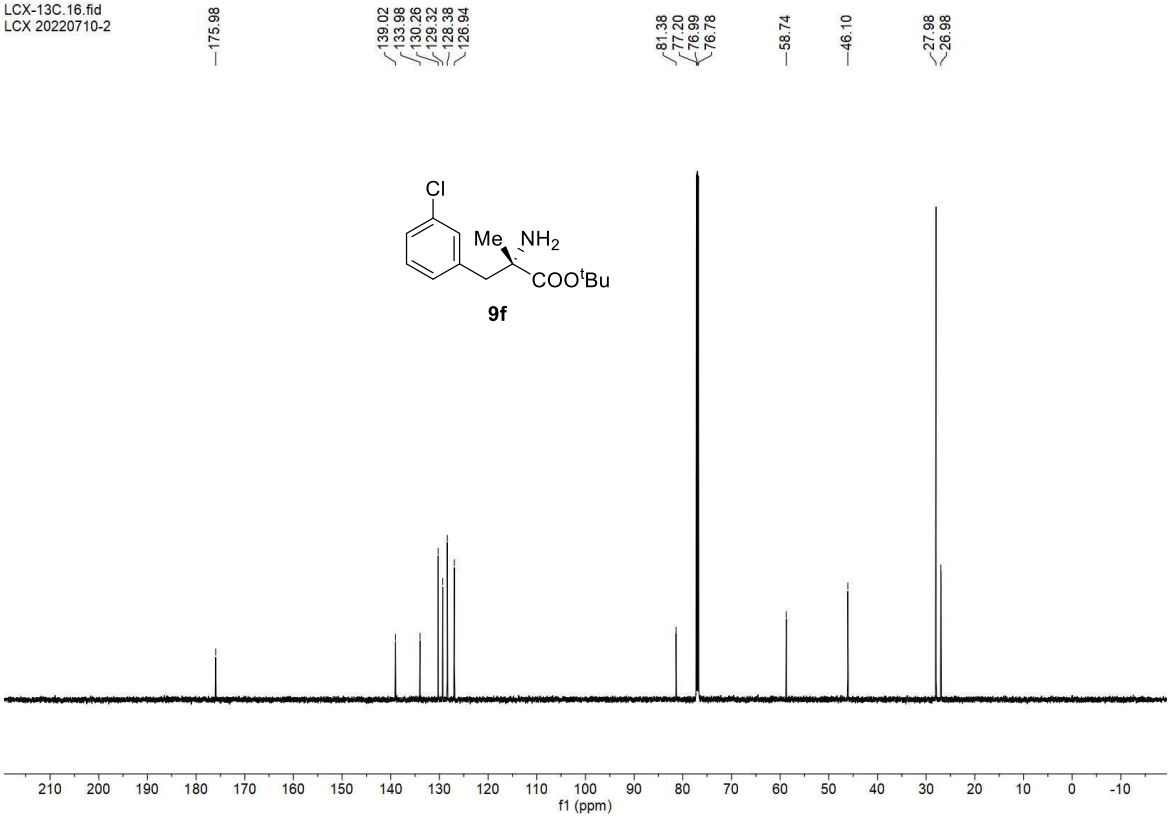
9e

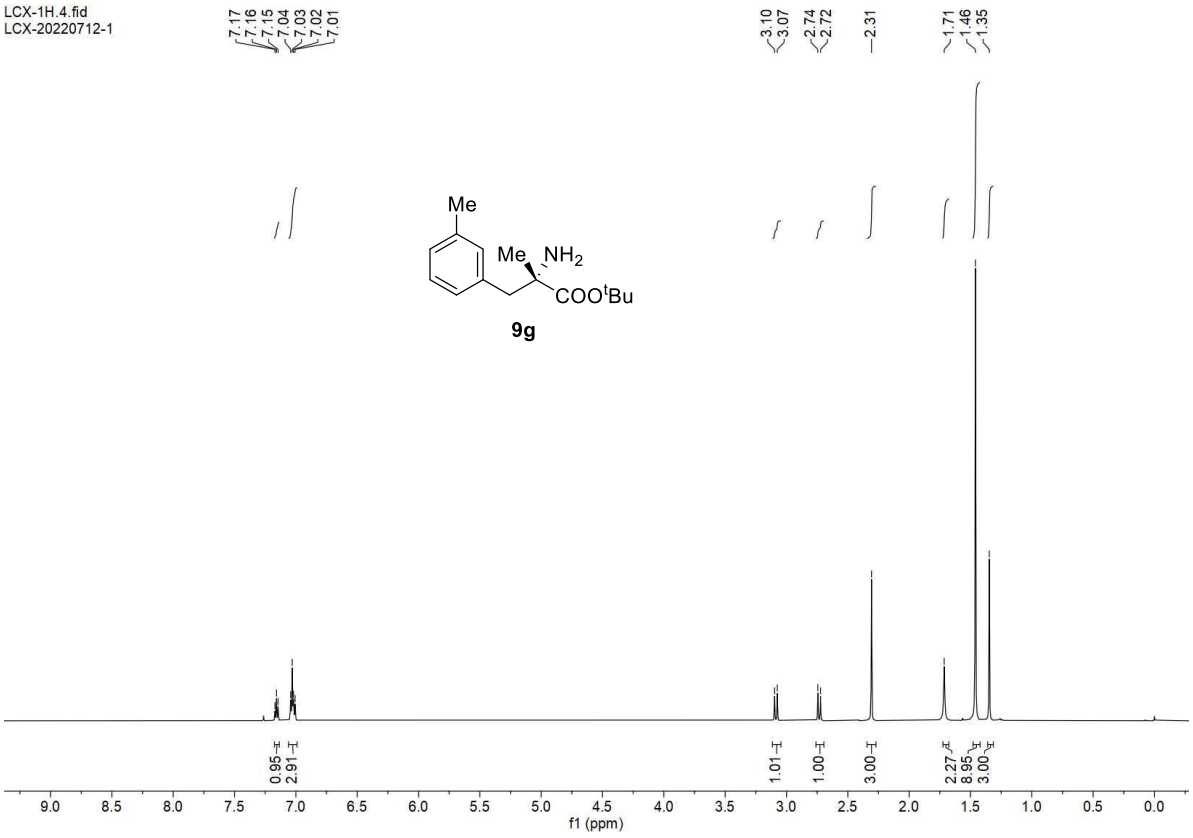
LZX-13C.10.fid
lzx20220714-3

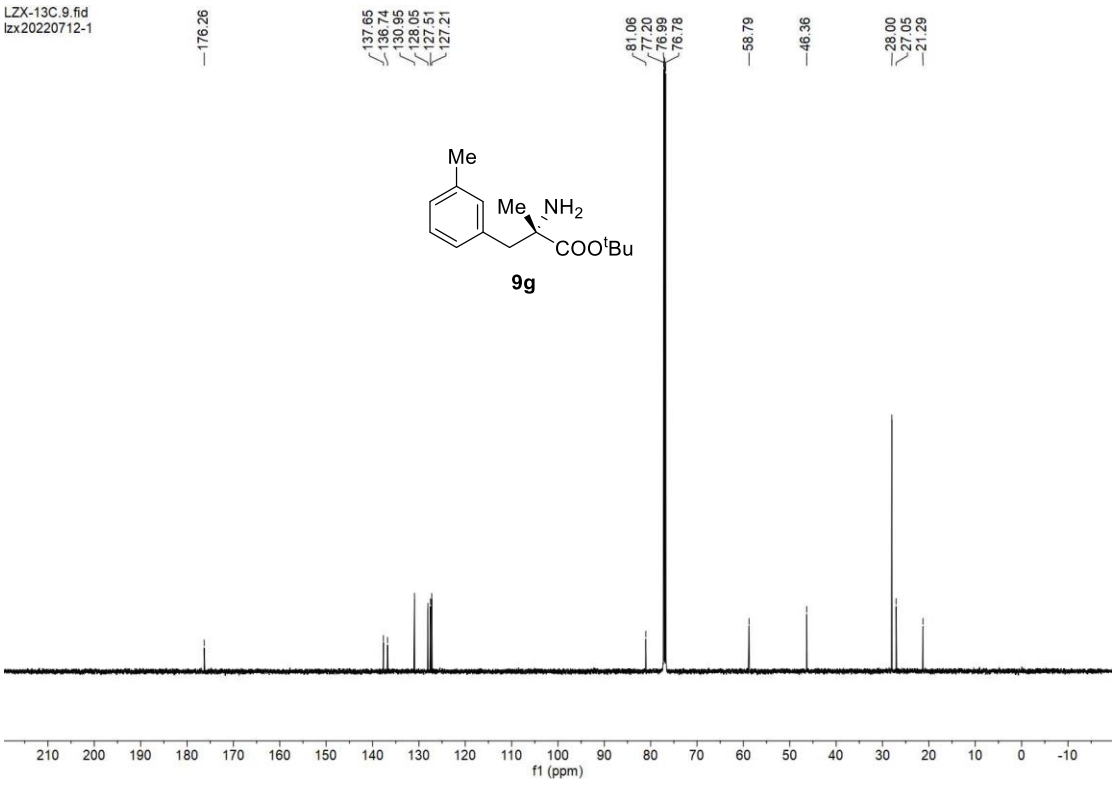


9e

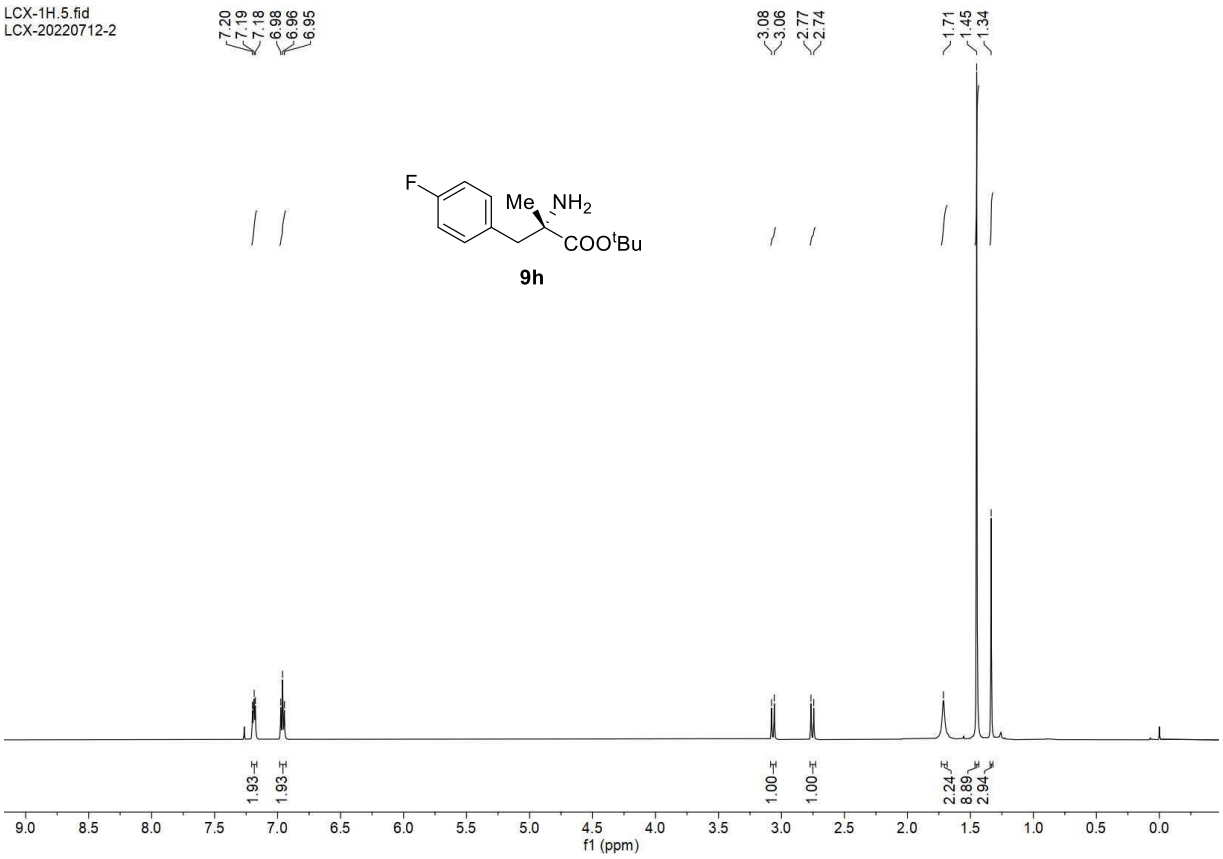

LCX-1H.31.fid
LCX 20220710-2
7.26
7.23
7.22
7.21
7.20
7.19
7.12
7.11
3.08
3.06
2.76
2.73
1.58
1.46
1.34
Cl
Me
NH2
COOtBu
9f
2.98
0.95
1.00
1.00
1.91
8.96
3.03
f1 (ppm)


LCX-13C.16.fid
LCX 20220710-2
175.98
139.02
133.98
130.26
129.32
128.38
126.94
81.38
77.20
76.99
76.78
58.74
46.10
27.98
26.98
Cl
Me
NH2
COOtBu
9f
f1 (ppm)


LCX-1H.4.fid
LCX-20220712-1
7.17
7.16
7.15
7.04
7.03
7.02
7.01
3.10
3.07
2.74
2.72
2.31
1.71
1.46
1.35
Me
Me
NH2
COOtBu
9g
0.95
2.91
1.01
1.00
3.00
2.27
8.95
3.00
f1 (ppm)

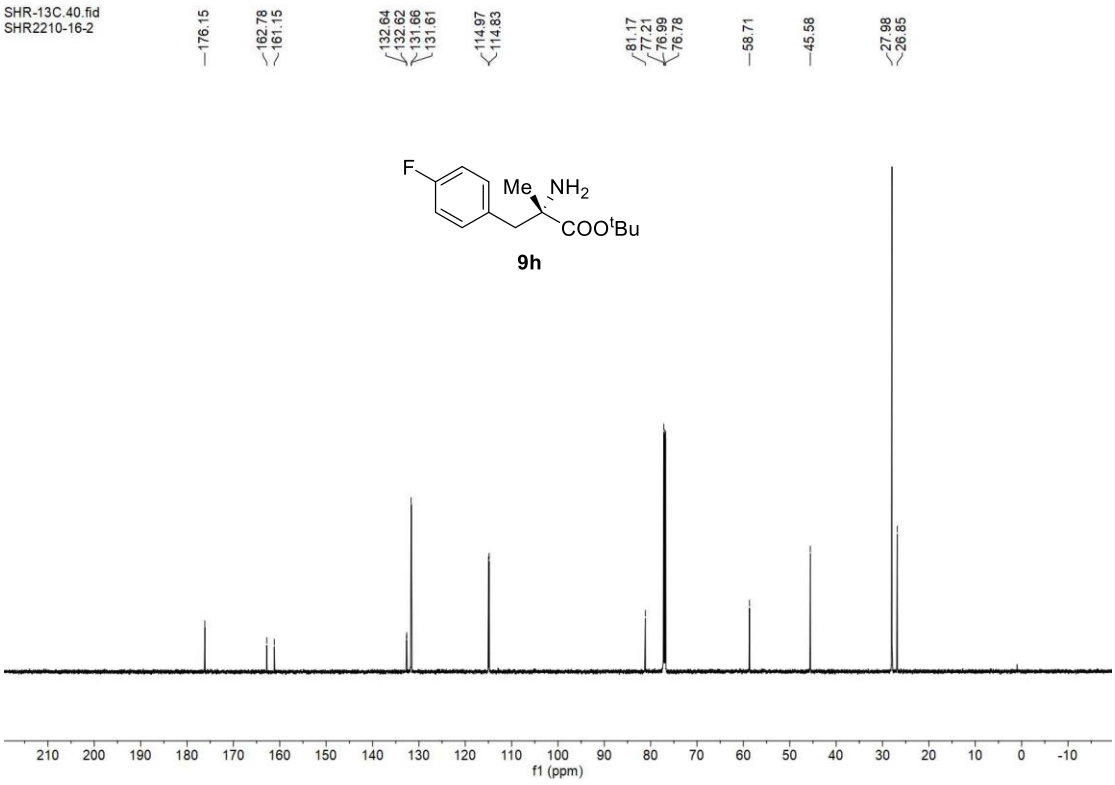

LZX-13C.9.fid
lzx20220712-1
176.26
137.65
136.74
130.95
128.05
127.51
127.21
81.06
77.20
76.99
76.78
58.79
46.36
28.00
27.05
21.29
Me
Me
NH2
COOtBu
9g
f1 (ppm)

LCX-1H.5.fid
LCX-20220712-2

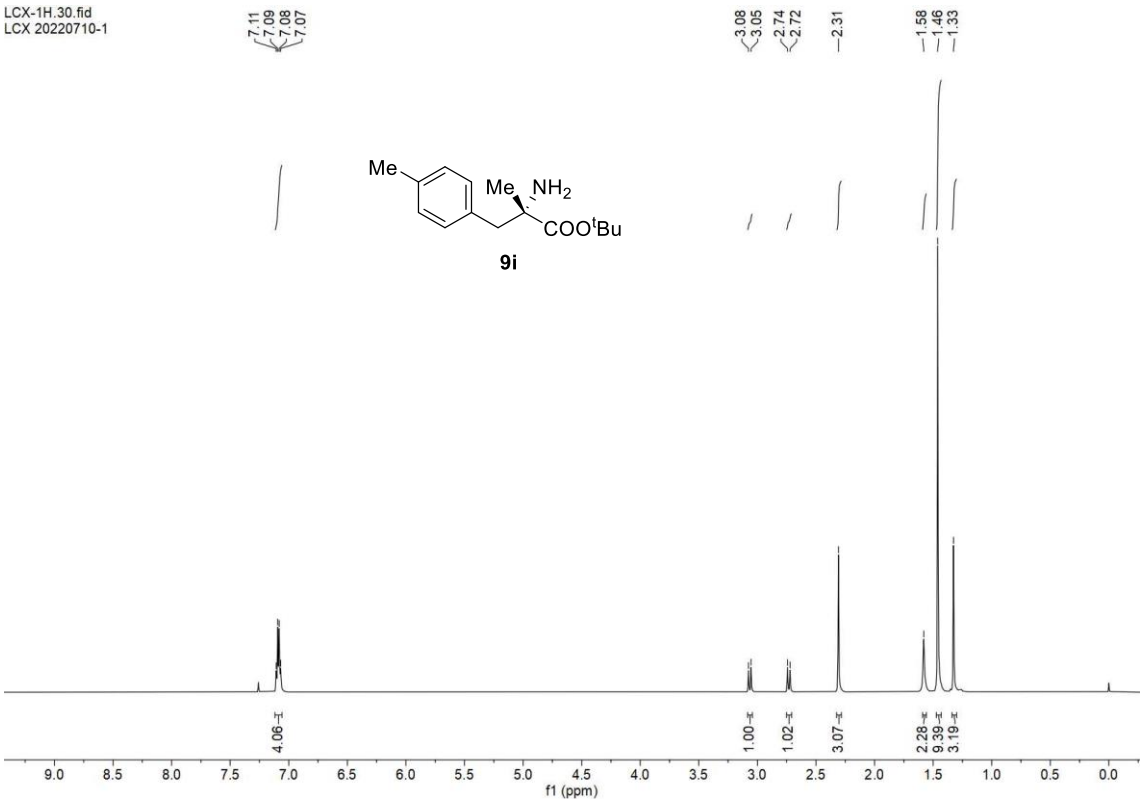


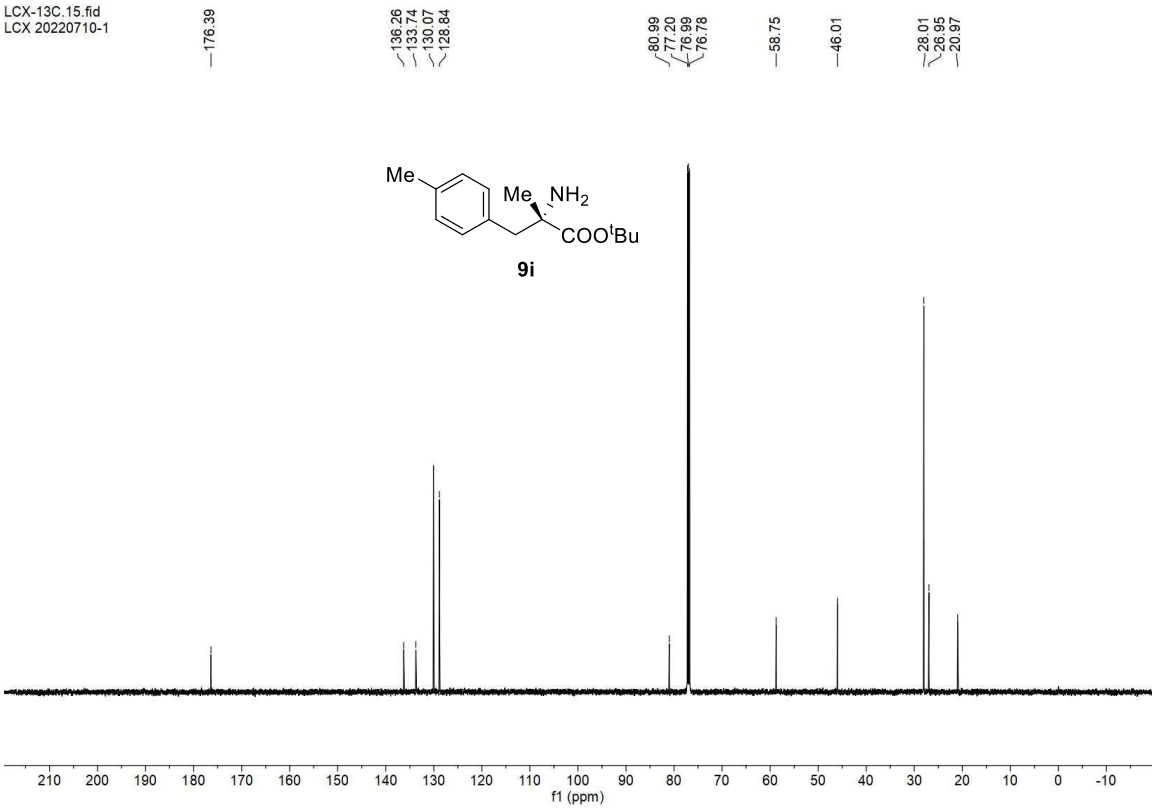
9h

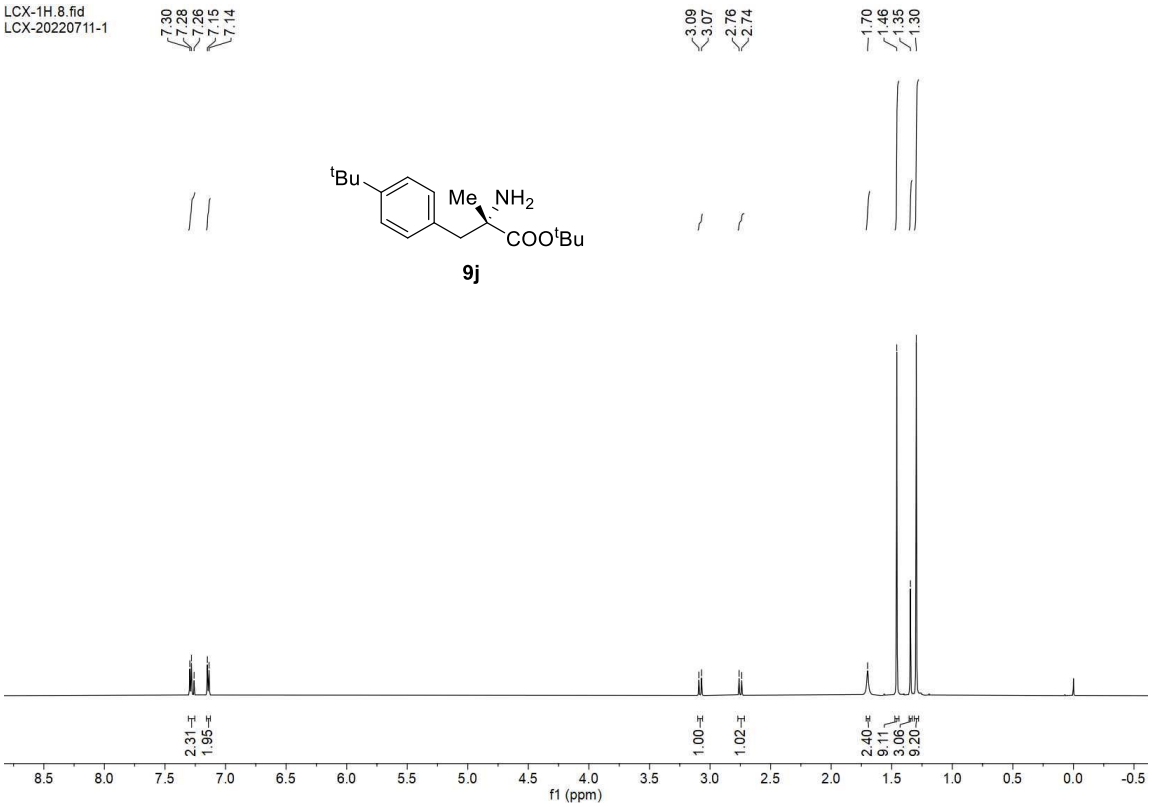
SHR-13C.40.fid
SHR2210-16-2

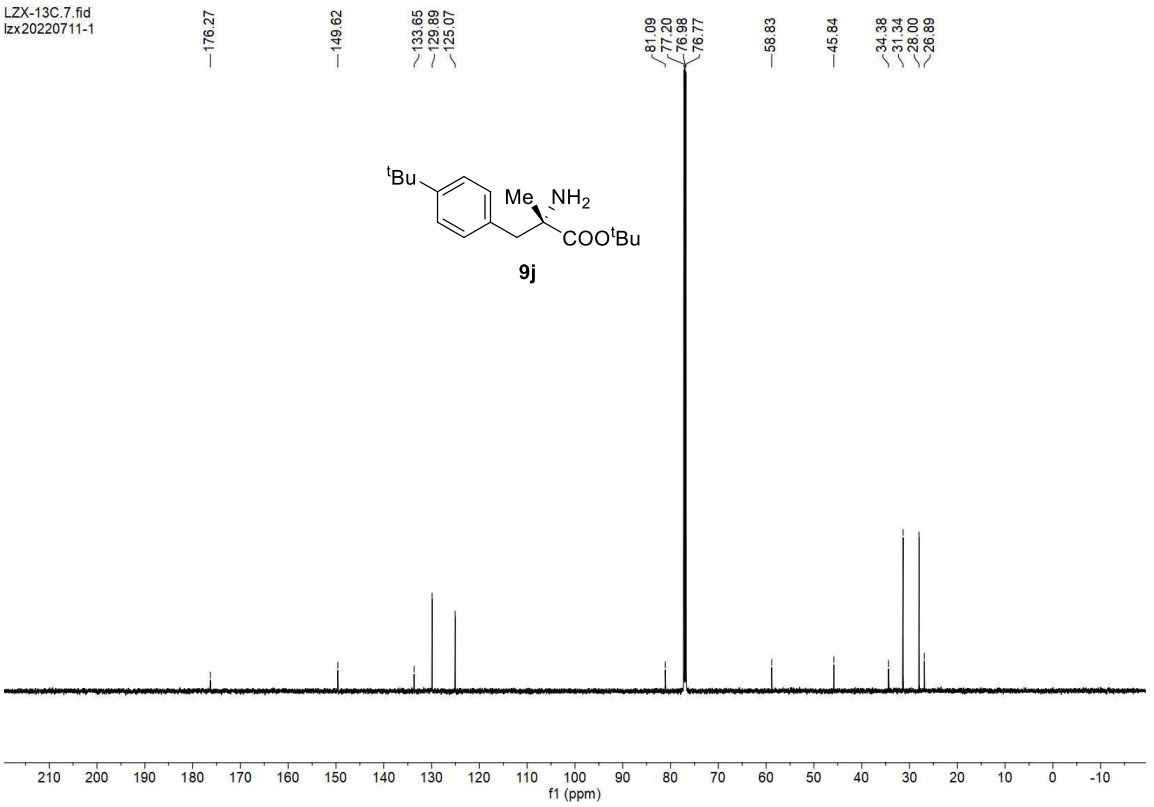


9h

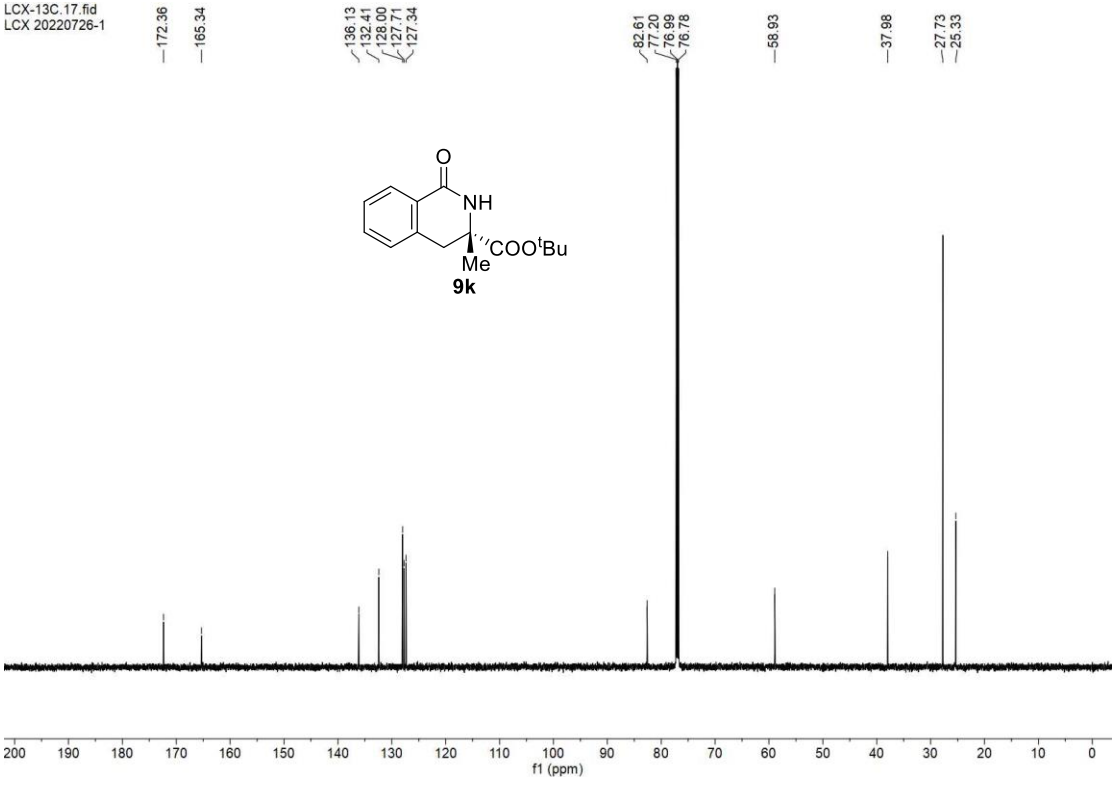

LCX-1H.30.fid
LCX 20220710-1
7.11
7.09
7.08
7.07
3.08
3.05
2.74
2.72
2.31
1.58
1.46
1.33
Me
Me
NH2
COOtBu
9i
4.06
1.00
1.02
3.07
2.28
9.39
3.19
f1 (ppm)

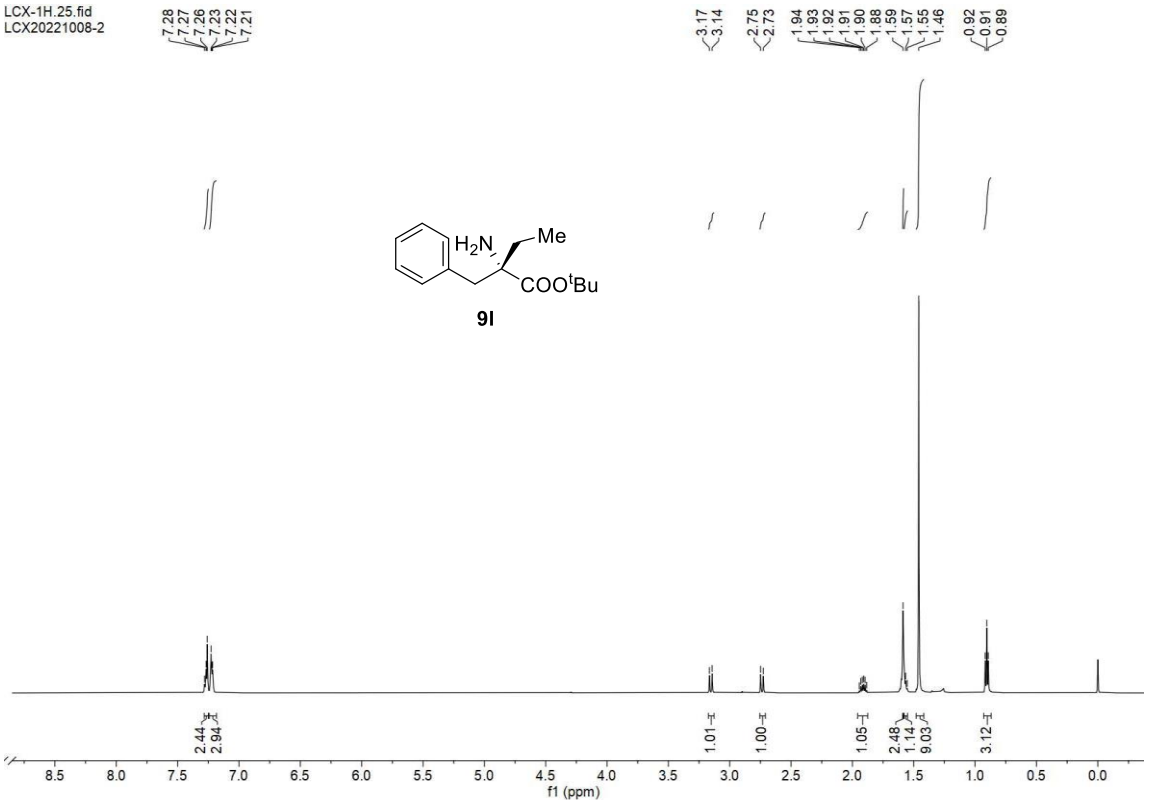

LCX-13C.15.fid
LCX 20220710-1
176.39
136.26
133.74
130.07
128.84
80.99
77.20
76.99
76.78
58.75
46.01
28.01
26.95
20.97
Me
Me
NH2
COOtBu
9i
f1 (ppm)


LCX-1H.8.fid
LCX-20220711-1
7.30
7.28
7.26
7.15
7.14
3.09
3.07
2.76
2.74
1.70
1.46
1.35
1.30
tBu
Me
NH2
COOtBu
9j
2.31
1.95
1.00
1.02
2.40
9.11
3.06
9.20
f1 (ppm)


LZX-13C.7.fid
lzx20220711-1
176.27
149.62
133.65
129.89
125.07
81.09
77.20
76.98
76.77
58.83
45.84
34.38
31.34
28.00
26.89
tBu
Me
NH2
COOtBu
9j
f1 (ppm)


LCX-1H.33.fid
LCX20220726-1
8.07
8.05
7.46
7.45
7.44
7.37
7.35
7.34
7.22
7.20
3.33
3.31
3.07
3.04
1.71
1.49
1.37
O
NH
COO^{t}Bu
Me
9k
0.98
1.02
1.00
1.00
0.98
1.00
0.95
3.01
9.01
f1 (ppm)


LCX-13C.17.fid
LCX 20220726-1
172.36
165.34
136.13
132.41
128.00
127.71
127.34
82.61
77.20
76.99
76.78
58.93
37.98
27.73
25.33
O
NH
COO^{t}Bu
Me
9k
f1 (ppm)


LCX-1H.25.fid
LCX20221008-2
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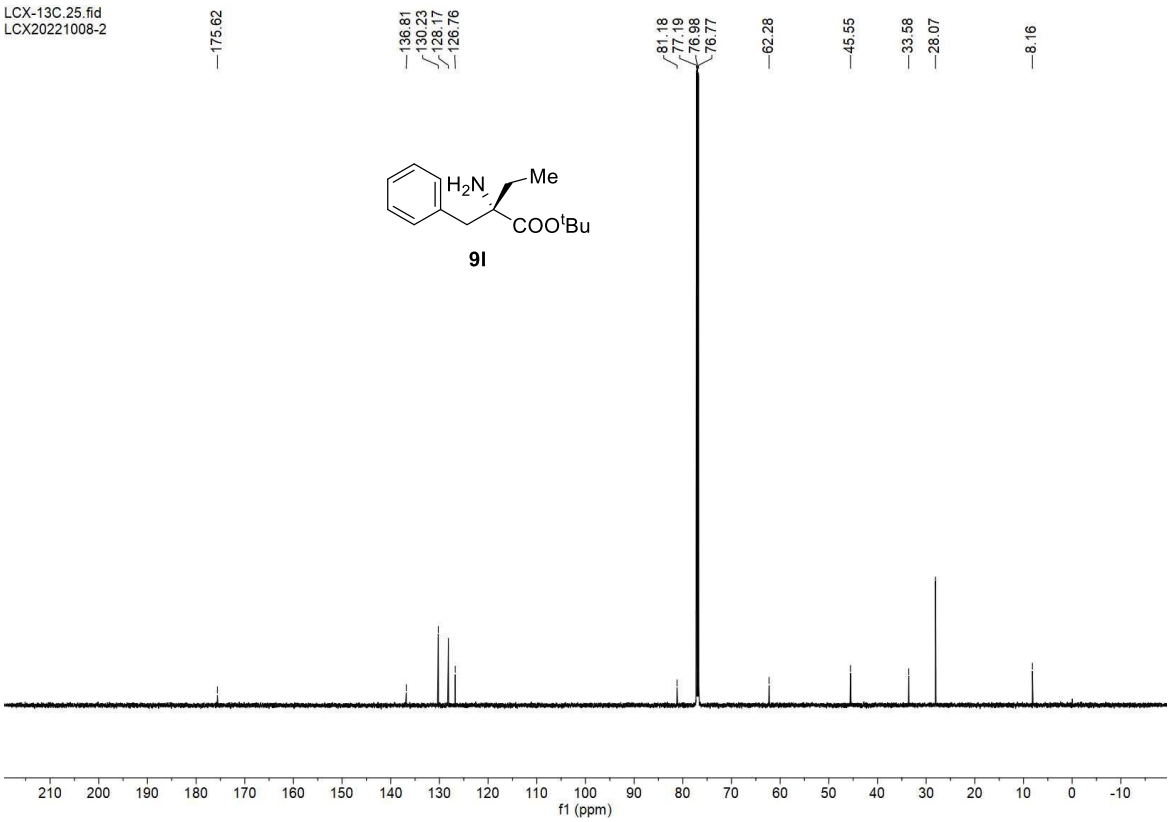
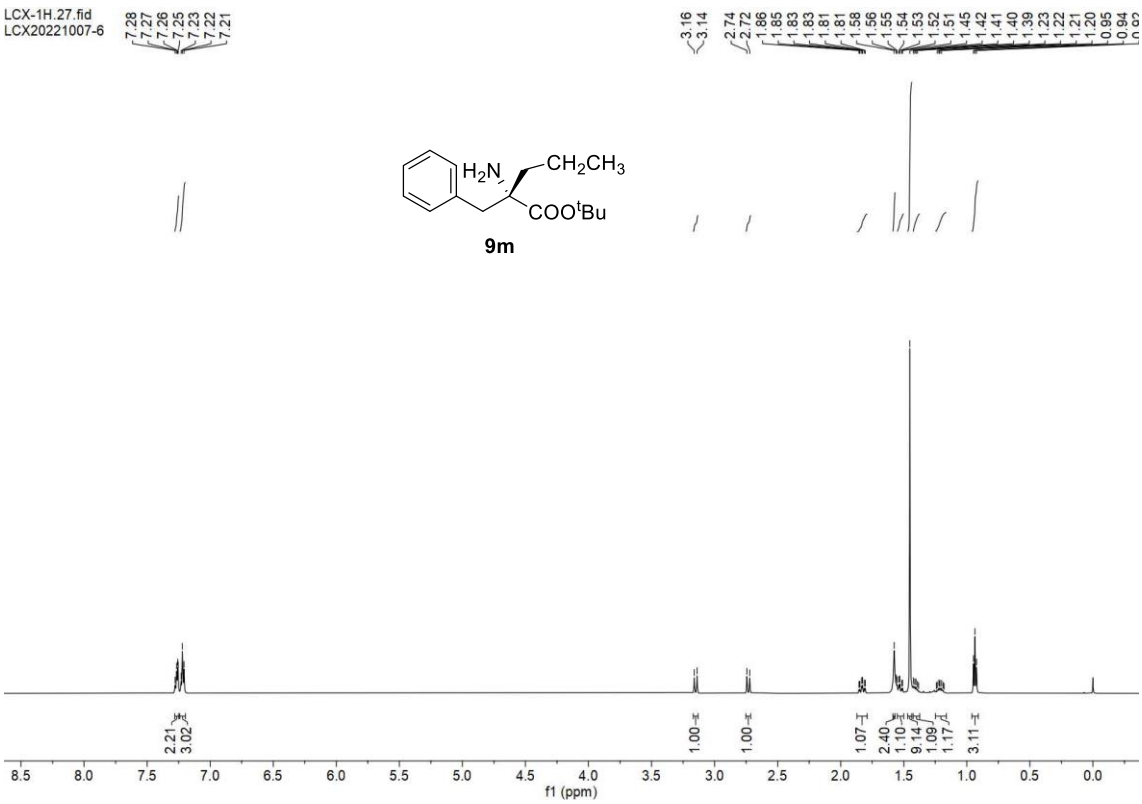
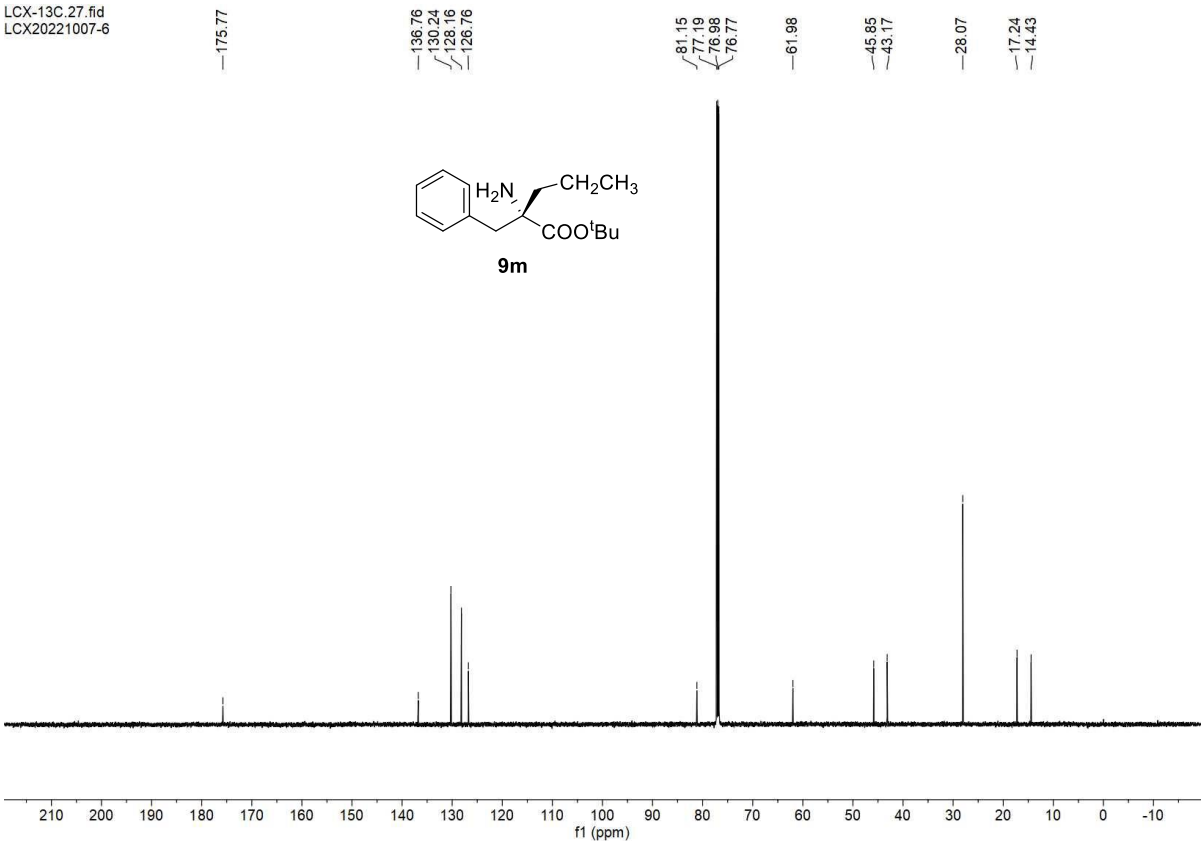
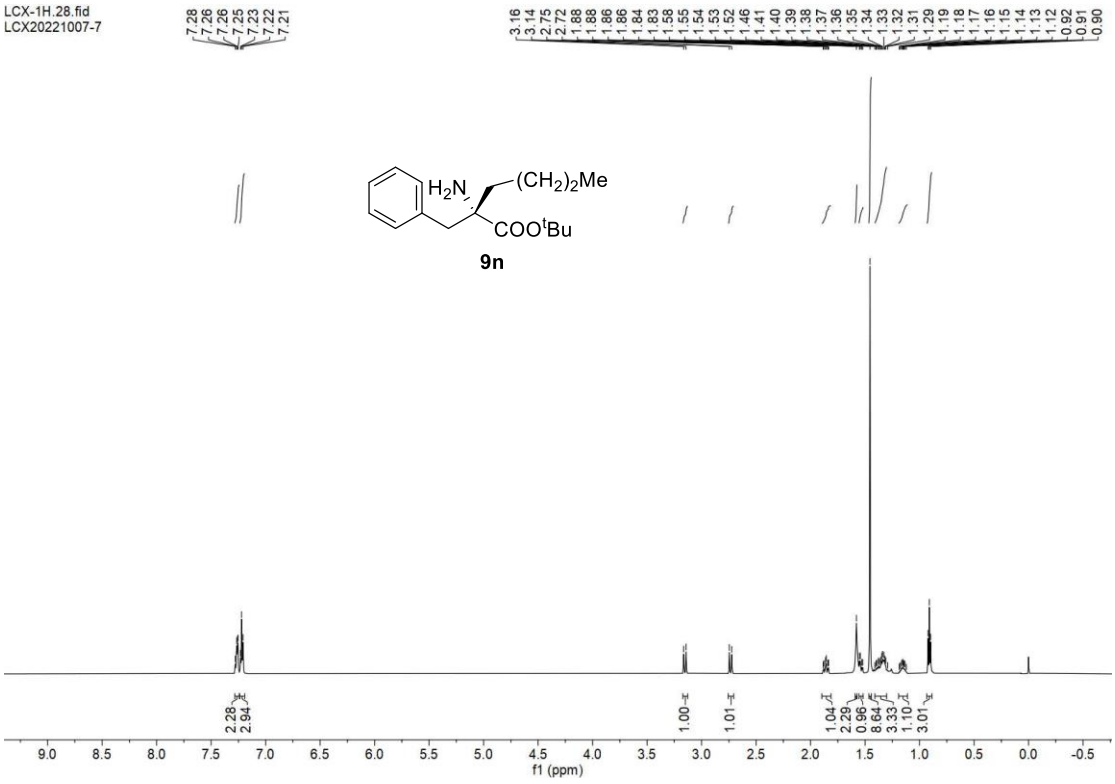
7.27
7.26
7.23
7.22
7.21
3.17
3.14
2.75
2.73
1.94
1.93
1.92
1.91
1.90
1.88
1.59
1.57
1.55
1.46
0.92
0.91
0.89
H2N
Me
COOtBu
9l
2.44
2.94
1.01
1.00
1.05
2.48
1.14
9.03
3.12
f1 (ppm)


LCX-13C.25.fid
LCX20221008-2
175.62
136.81
130.23
128.17
126.76
81.18
77.19
76.98
76.77
62.28
45.55
33.58
28.07
8.16
H2N
Me
COOtBu
9l
f1 (ppm)


LCX-1H.27.fid
LCX20221007-6
7.28
7.27
7.26
7.25
7.23
7.22
7.21
3.16
3.14
2.74
2.72
1.86
1.85
1.83
1.83
1.81
1.81
1.58
1.56
1.55
1.54
1.53
1.52
1.51
1.45
1.42
1.41
1.40
1.39
1.23
1.22
1.21
1.20
0.95
0.94
H2N
CH2CH3
COOtBu
9m
2.21
3.02
1.00
1.00
1.07
2.40
1.10
9.14
1.09
1.17
3.11
f1 (ppm)


LCX-13C.27.fid
LCX20221007-6
175.77
136.76
130.24
128.16
126.76
81.15
77.19
76.98
76.77
61.98
45.85
43.17
28.07
17.24
14.43
H2N
CH2CH3
COOtBu
9m
f1 (ppm)


LCX-1H.28.fid
LCX20221007-7
7.28
7.26
7.26
7.25
7.23
7.22
7.21
3.16
3.14
2.75
2.72
1.88
1.88
1.86
1.86
1.84
1.83
1.58
1.55
1.54
1.53
1.52
1.46
1.41
1.40
1.39
1.38
1.37
1.36
1.35
1.34
1.33
1.32
1.31
1.29
1.19
1.18
1.17
1.16
1.15
1.14
1.13
1.12
0.92
0.91
0.90
H2N
(CH2)2Me
COOtBu
9n
2.28
2.94
1.00
1.01
1.04
2.29
0.96
8.64
3.33
1.10
3.01
9.0
8.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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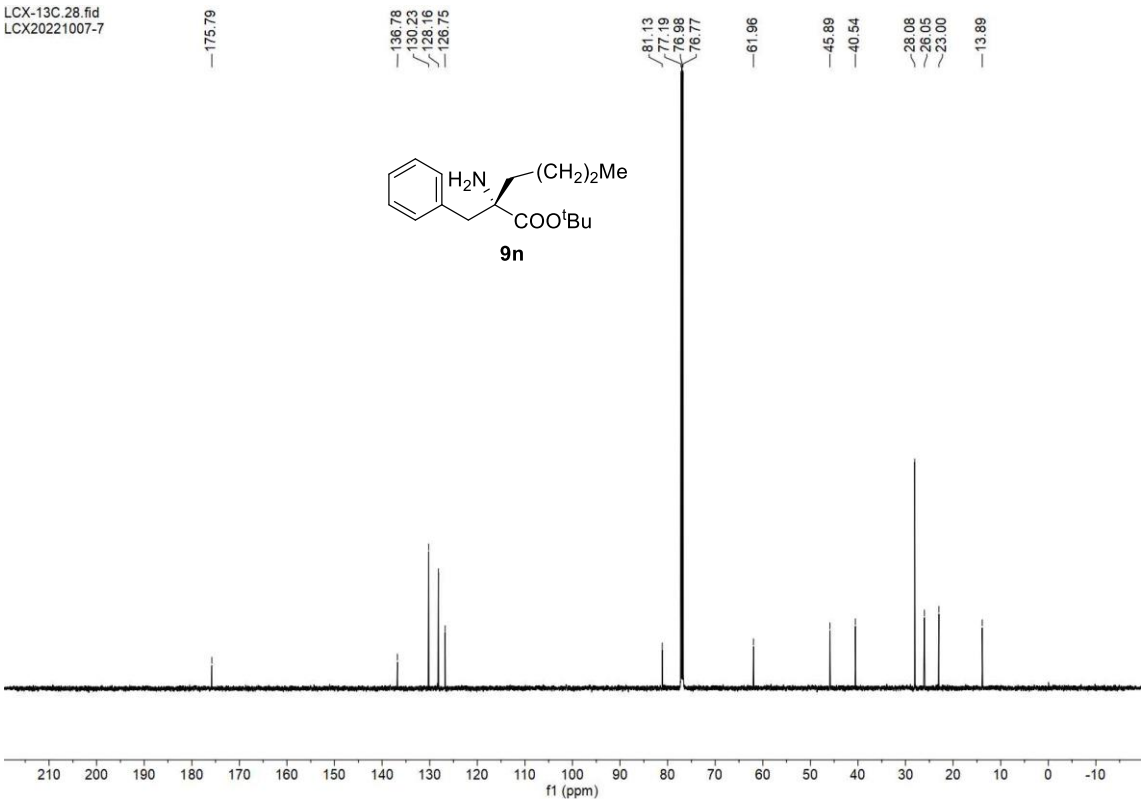
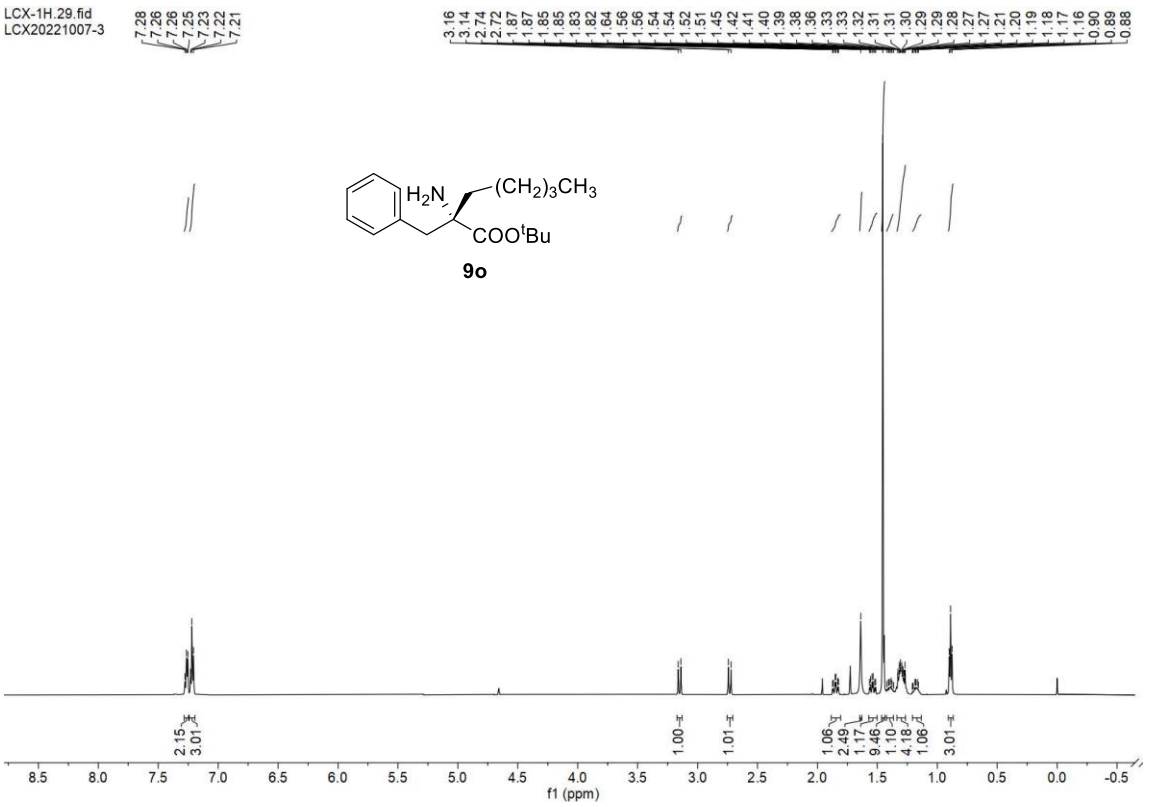
3.0
2.5
2.0
1.5
1.0
0.5
0.0
-0.5
f1 (ppm)


LCX-13C.28.fid
LCX20221007-7
175.79
136.78
130.23
128.16
126.75
81.13
77.19
76.98
76.77
61.96
45.89
40.54
28.08
26.05
23.00
13.89
H2N
(CH2)2Me
COOtBu
9n
210
200
190
180
170
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
-10
f1 (ppm)

LCX-1H.29.fid
LCX20221007-3



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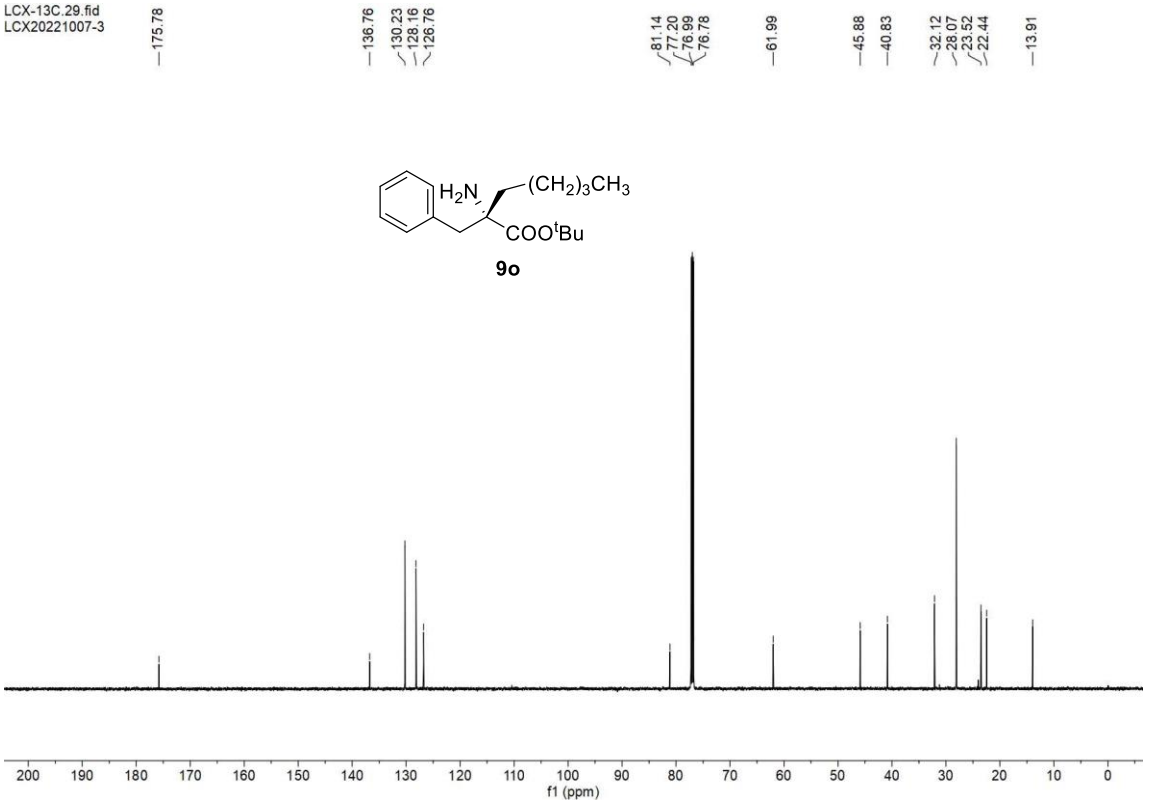
LCX-13C.29.fid
LCX20221007-3



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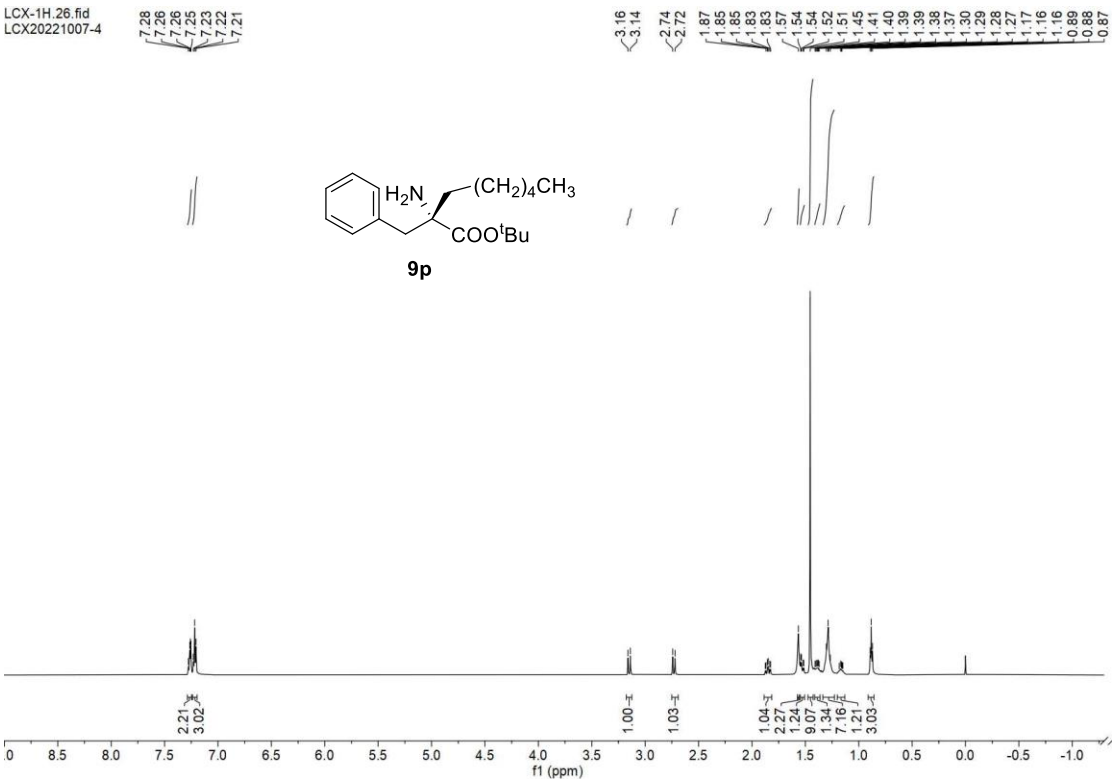
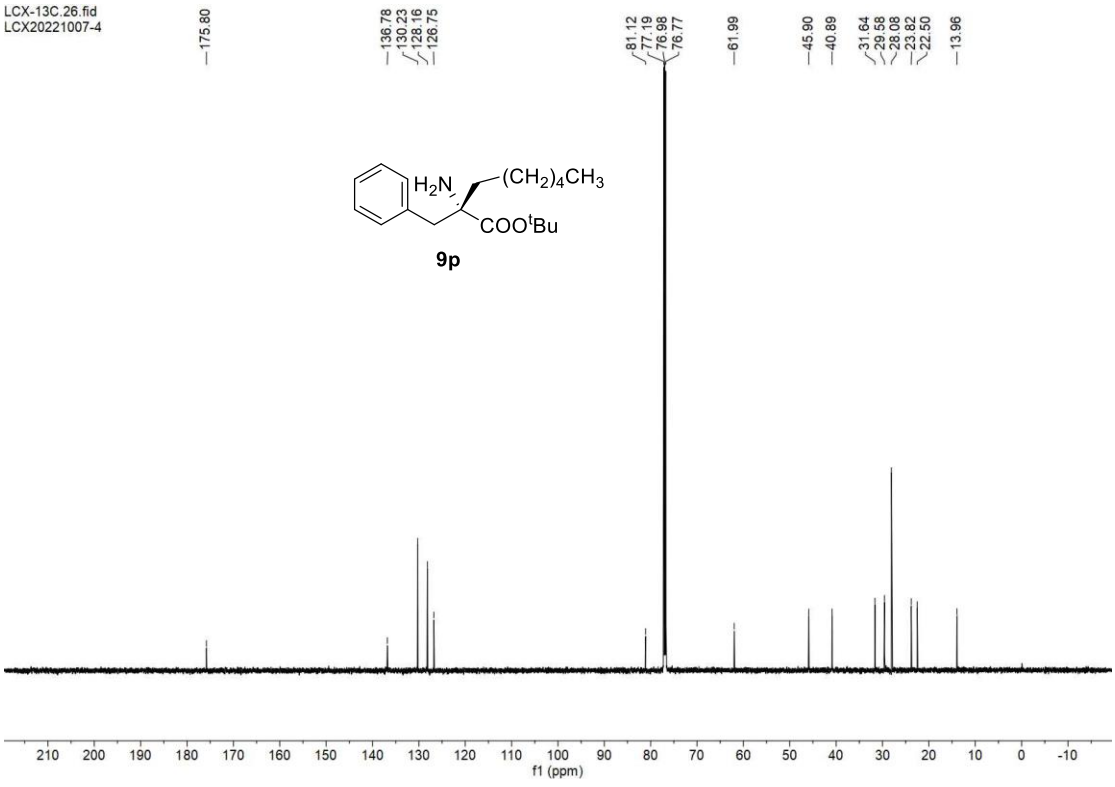
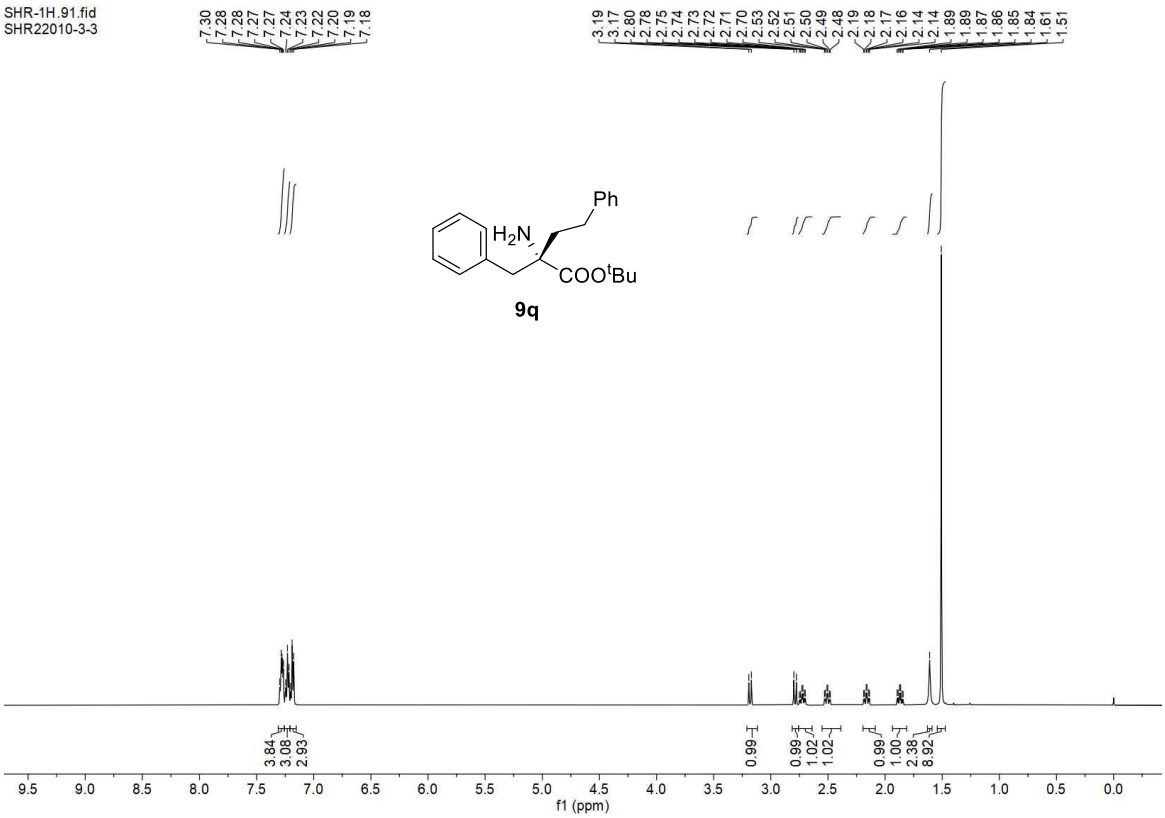
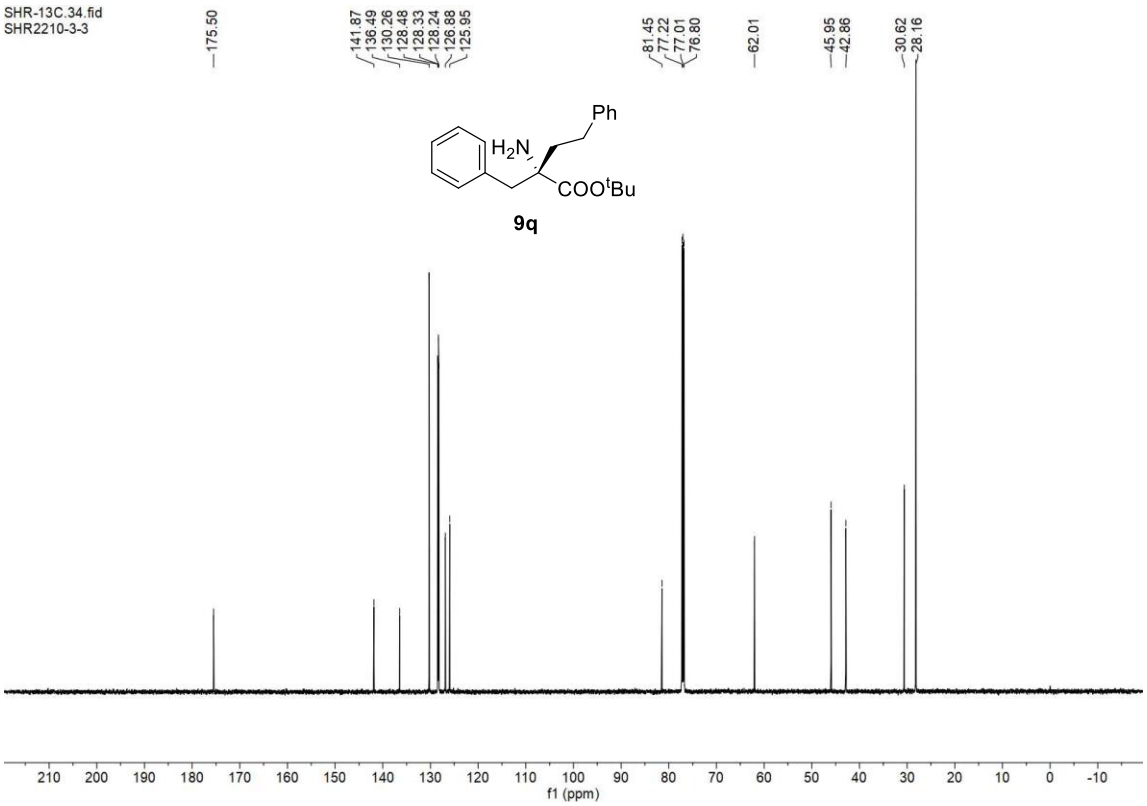
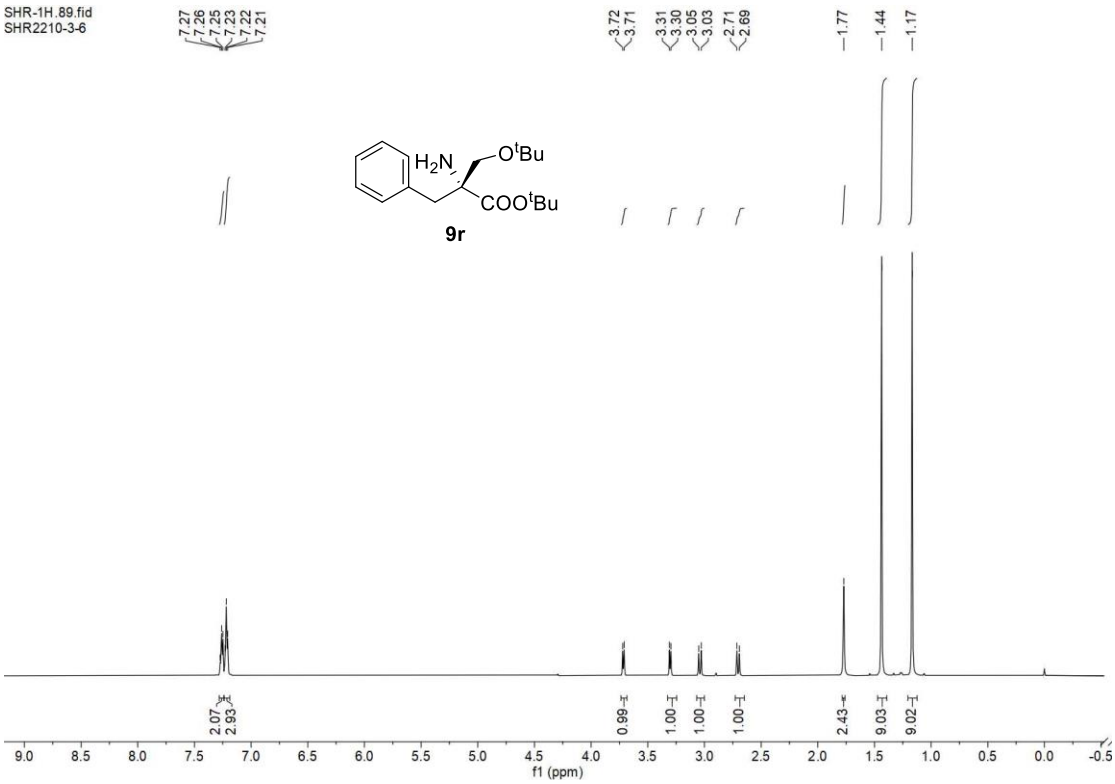
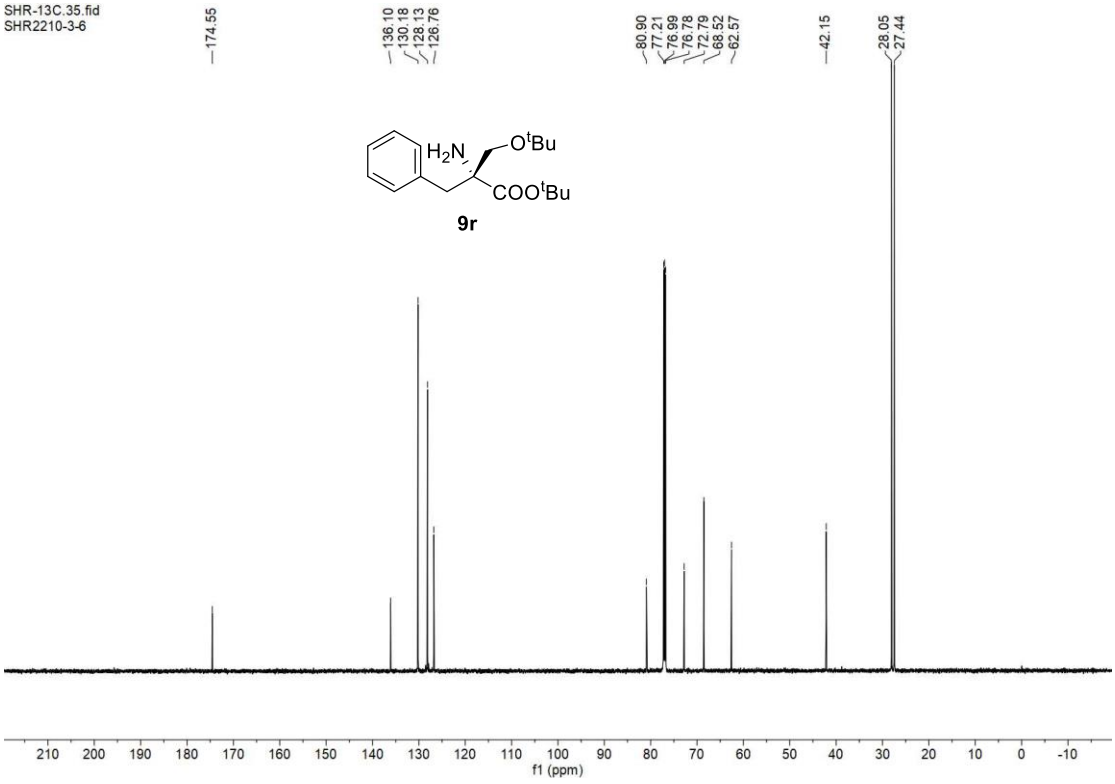

LCX-1H.26.fid
LCX20221007-4
7.28
7.26
7.26
7.25
7.23
7.22
7.21
3.16
3.14
2.74
2.72
1.87
1.85
1.85
1.83
1.83
1.57
1.54
1.54
1.52
1.51
1.45
1.41
1.40
1.39
1.39
1.38
1.37
1.30
1.29
1.28
1.27
1.17
1.16
1.16
0.89
0.88
0.87
H2N
(CH2)4CH3
COOtBu
9p
2.21
3.02
1.00
1.03
1.04
2.27
1.24
9.07
1.34
7.16
1.21
3.03
f1 (ppm)


LCX-13C.26.fid
LCX20221007-4
175.80
136.78
130.23
128.16
126.75
81.12
77.19
76.98
76.77
61.99
45.90
40.89
31.64
29.58
28.08
23.82
22.50
13.96
H2N
(CH2)4CH3
COOtBu
9p
f1 (ppm)


SHR-1H.91.fid
SHR22010-3-3
7.30
7.28
7.28
7.27
7.27
7.24
7.23
7.22
7.20
7.19
7.18
3.19
3.17
2.80
2.78
2.75
2.74
2.73
2.72
2.71
2.70
2.53
2.52
2.51
2.50
2.49
2.48
2.19
2.18
2.17
2.16
2.14
2.14
1.89
1.89
1.87
1.86
1.85
1.84
1.61
1.51
Ph
H2N
COOtBu
9q
3.84
3.08
2.93
0.99
0.99
1.02
1.02
0.99
1.00
2.38
8.92
f1 (ppm)


SHR-13C.34.fid
SHR2210-3-3
175.50
141.87
136.49
130.26
128.48
128.33
128.24
126.88
125.95
81.45
77.22
77.01
76.80
62.01
45.95
42.86
30.62
28.16
Ph
H2N
COOtBu
9q
f1 (ppm)


SHR-1H.89.fid
SHR2210-3-6
7.27
7.26
7.25
7.23
7.22
7.21
3.72
3.71
3.31
3.30
3.05
3.03
2.71
2.69
1.77
1.44
1.17
H2N
OtBu
COOtBu
9r
2.07
2.93
0.99
1.00
1.00
1.00
2.43
9.03
9.02
f1 (ppm)


SHR-13C.35.fid
SHR2210-3-6
174.55
136.10
130.18
128.13
126.76
80.90
77.21
76.99
76.78
72.79
68.52
62.57
42.15
28.05
27.44
H2N
OtBu
COOtBu
9r
f1 (ppm)