Supporting Information

for

Asymmetric Bifunctionalization of Allenes with Aryl Iodides and Amino Acids Enabled by Chiral Aldehyde/Palladium Combined Catalysis

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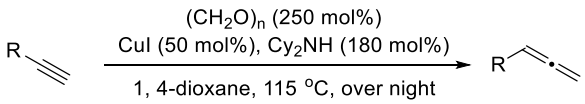
1. General data

All non-aqueous reactions were carried out in a flame-dried glassware under nitrogen atmosphere 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. All other reagents were directly used as purchased from Aladdin, Adamas-beta® and Energy Chemical. Imino-tris(dimethylamino)phosphorane (TDMAIP) purchased from Sigmaaldrich. ^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, AS-H, IA-H, IB-H, IC-H, ID-H, IE-H, IF-H, IG-H, IH-H, OJ-H, OD-H 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. allenes substrates[1], amino acid ethyl esters[2] and chiral aldehydes catalysts[3] were prepared according to the literature. The yield of all compounds was the isolated yield, and the enantiomeric excess was determined by chiral HPLC analysis.

2. Preparation of starting materials

2.1 General Procedure for the Synthesis of Allenes from Alkynes

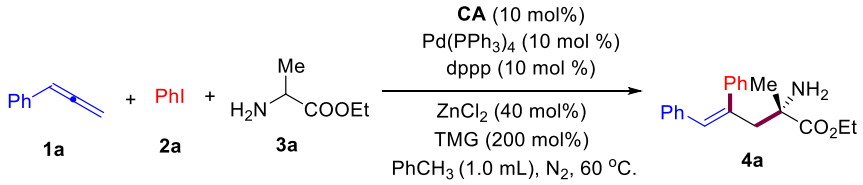


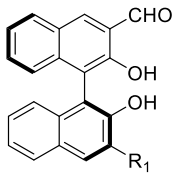
According to the literature procedure,[1] the corresponding aryl alkyne (10.0 mmol), paraformaldehyde (750.0 mg, 25.0 mmol, 2.5 equiv.), CuI (950.0 mg, 5.0 mmol, 0.5 equiv.) and dicyclohexylamine (3.6 mL, 18.0 mmol, 1.8 equiv.) were dissolved in dry 1, 4-dioxane (40.0 mL) under nitrogen, and the reaction mixture was placed in an oil bath and heated for over night at 115 ℃. The reaction was quenched with H_2O (20.0 mL), followed by the addition of Et_2O (20.0 mL). The organic layer was separated and the aqueous layer was extracted with Et_2O (3 × 20.0 mL). The combined organic layers were dried over $MgSO_4$, and the solvents were evaporated

under vacuum. Flash chromatography on silica gel using petroleum ether provided the desired allene in analytically pure form. Substituted allene derivatives were prepared and characterized before in literature.

3. Reaction condition optimization

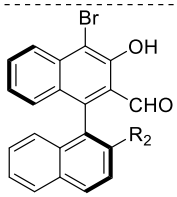
Table S1: Screening of the chiral aldehyde[a]





I

CA-1: R_1 = H; **CA-2**: R_1 = $SiMe_3$
CA-3: R_1 = CN; **CA-4**: R_1 = 9-anthryl ;
CA-5: R_1 = 3, 5-$(t\text{-Bu})_2C_6H_3$; **CA-6**: R_1 = 3, 5-$(F)_2C_6H_3$
CA-12: R_1 = Br; **CA-13**: R_1 = 4-FC_6H_4
CA-14: R_1 = 4-$MeOC_6H_4$; **CA-15**: R_1 = Me
CA-16: R_1 = 3, 5-$(CF_3)_2C_6H_3$; **CA-17:** R_1 = 4-ClC_6H_4
CA-18: R_1 = 3, 4-$Me_2C_6H_3$; **CA-19**: R_1 = 4-$(CF_3)C_6H_4$



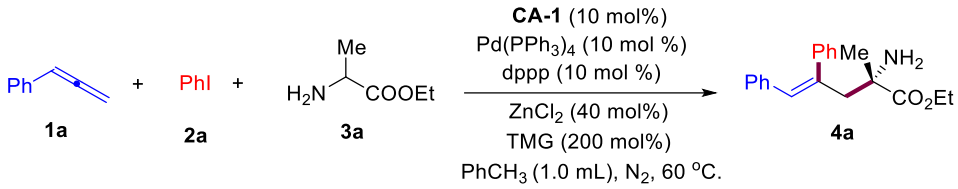
II

CA-7: R_2 = Ph; **CA-8:** R_2 = 3, 5-$(t\text{-Bu})_2C_6H_3$
CA-9: R_2 = 3, 5-$(CF_3)_2C_6H_3$; **CA-10**: R_2 = 2-Naphthalene
CA-11: R_2 = 1-Naphthalene; **CA-20**: R_2 = H
CA-21: R_2 = 4-Biphenyl; **CA-22**: R_2 = 4-$MeOC_6H_4$
CA-23: R_2 = 4-MeC_6H_4; **CA-24**: R_2 = 4-$(t\text{-Bu})C_6H_4$
CA-25: R_2 = Br; **CA-26**: R_2 = 3, 5-$(Me)_2C_6H_3$

entry	CA	yield (%)	ee (%)	entry	CA	yield (%)	ee (%)
1	**CA-1**	83	81	14	**CA-14**	68	68
2	**CA-2**	39	28	15	**CA-15**	42	44
3	**CA-3**	34	12	16	**CA-16**	90	70
4	**CA-4**	71	20	17	**CA-17**	91	68
5	**CA-5**	81	80	18	**CA-18**	71	70
6	**CA-6**	74	68	19	**CA-19**	66	72
7	**CA-7**	34	70	20	**CA-20**	61	26
8	**CA-8**	19	95	21	**CA-21**	26	89
9	**CA-9**	32	96	22	**CA-22**	11	79
10	**CA-10**	28	89	23	**CA-23**	44	84
11	**CA-11**	16	84	24	**CA-24**	29	85
12	**CA-12**	74	60	25	**CA-25**	37	58
13	**CA-13**	82	74	26	**CA-26**	47	66

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TMG (200 mol%) in toluene (1.0 mL) at 60 ℃.

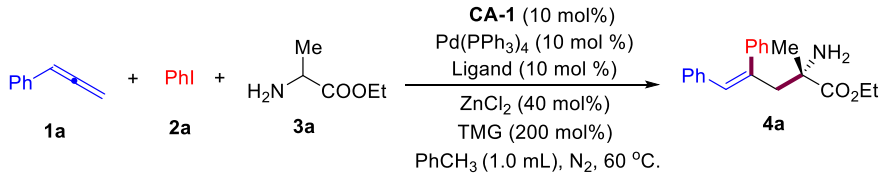
Table S2: Screening of the equivalents of 3a[a]

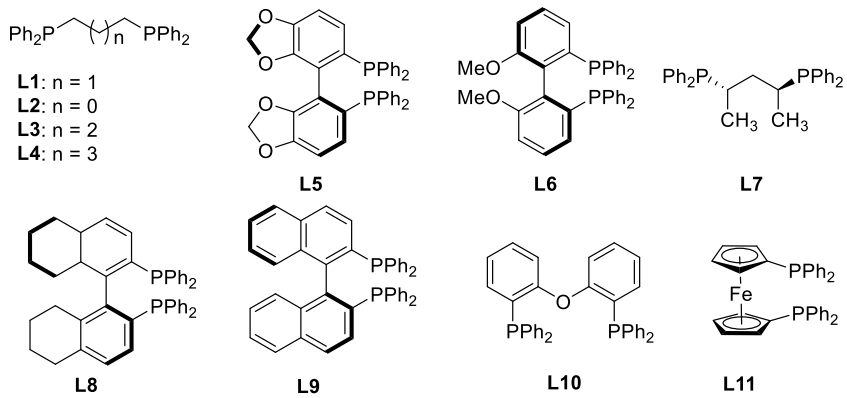


entry	3a (x mol%)	yield (%)	ee (%)
1	100	80	76
2	125	83	80
3	150	83	81
4	175	82	78
5	200	83	80
6	225	84	74
7	250	32	76

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (x mol%), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TMG (200 mol%) in toluene (1.0 mL) at 60 ℃.

Table S3: Screening of the ligand[a]



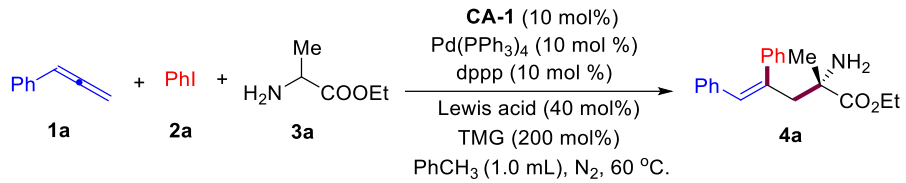


entry	ligand	yield (%)	ee (%)	entry	ligand	yield (%)	ee (%)
1	**L1**	83	81	8	**L7**	67	86
2	**L2**	24	62	9[c]	**L7**	21	-29
3	**L3**	19	50	10	**L8**	24	52
4	**L4**	10	32	11	**L9**	37	60
5[b]	**PPh_3**	13	26	12	**L10**	24	62
6	**L5**	19	56	13	**L11**	32	66
7	**L6**	34	34				

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), Ligand (10 mol%), $ZnCl_2$ (40 mol%) and TMG (200 mol%) in toluene (1.0 mL)

at 60 ℃, [b] 20 mol% **PPh$_3$**, [c] Use *ent*-**CA-1** (10 mol%).

Table S4: Screening of the Lewis acid[a]

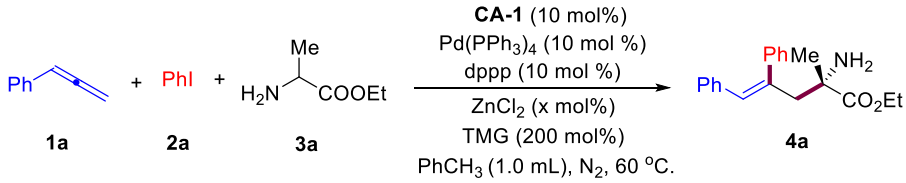


1a **2a** **3a** **4a**

entry	Lewis acid	yield (%)	ee (%)
1	$ZnCl_2$	83	81
2	$Zn(OAc)_2$	50	68
3	$Zn(OTf)_2$	28	44
4	$ZnBr_2$	69	60
5	ZnF_2	44	58
6	$Zn(ClO_4)\cdot 6H_2O$	26	57
7	ZnI_2	39	52
8	$Zn(CN)_2$	40	68
9	$Zn_3(PO_4)_2$	11	32

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), Lewis acid (40 mol%) and TMG (200 mol%) in toluene (1.0 mL) at 60 ℃.

Table S5: Screening of the equivalents of Lewis acid[a]

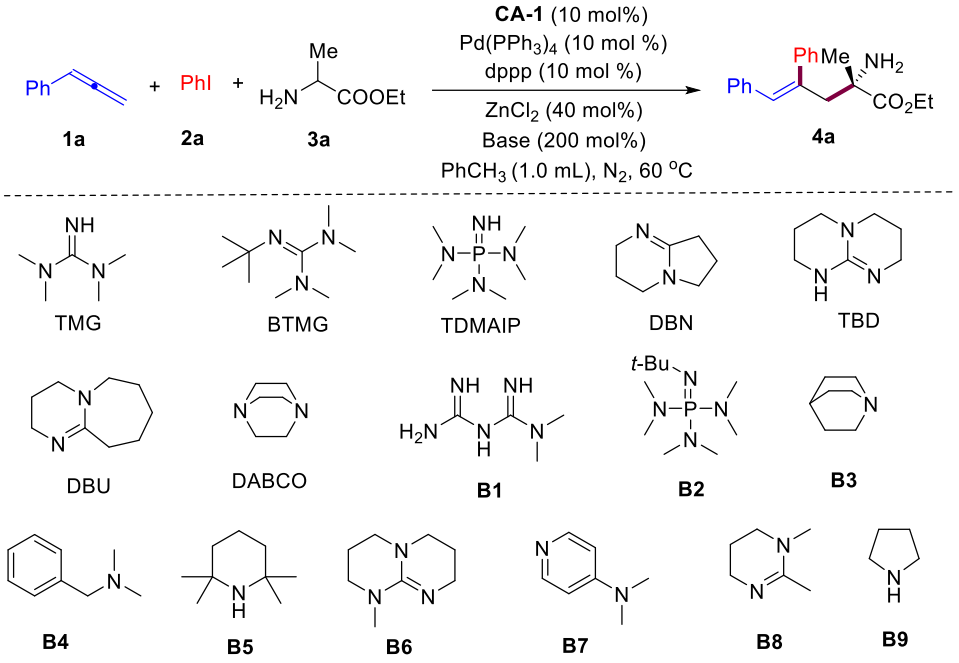


1a **2a** **3a** **4a**

entry	$ZnCl_2$ (x mol%)	yield (%)	ee (%)
1	-	8	8
2	20	45	76
3	30	74	80
4	40	83	81
5	50	78	78
6	60	80	80
7	80	83	72
8	100	80	60

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (x mol%) and TMG (200 mol%) in toluene (1.0 mL) at 60 ℃.

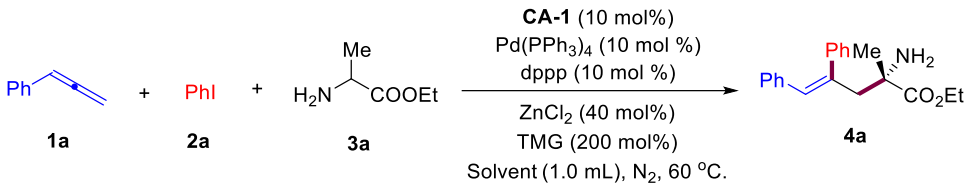
Table S6: Screening of the base[a]



entry	Base	yield (%)	ee (%)	entry	Base	yield (%)	ee (%)
1	**TMG**	83	81	11	**B1**	10	54
2	**BTMG**	68	42	12	**B2**	90	20
3	**TDMAIP**	70	90	13	**B3**	47	66
4	**DBN**	10	60	14	**B4**	0	-
5	**TBD**	11	58	15	**B5**	58	66
6	**DBU**	50	66	16	**B6**	52	58
7	**DABCO**	18	54	17	**B7**	6	54
8	**Cs_2CO_3**	78	38	18	**B8**	32	56
9	***t*-BuOK**	0	-	19	**B9**	0	-
10	**Et_3N**	10	42				

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and Base (200 mol%) in toluene (1.0 mL) at 60 ℃.

Table S7: Screening of the solvent[a]

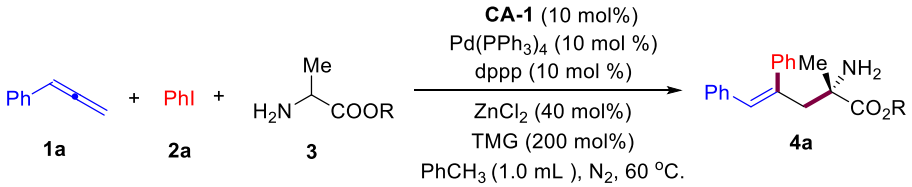


1a 2a 3a 4a

entry	solvent	yield (%)	ee (%)
1	Toluene	83	81
2	Acetonitrile	40	4
3	*o*-xylene	66	76
4	DME	32	66
5	Mesitylene	55	78
6	DCE	25	54
7	Ethylbenzene	71	78
8	Hexafluorobenzene	10	59
9	Chlorobenzene	60	72
10	1, 2-Difluorobenzene	61	68
11	Benzotrifluoride	50	66
12	THF	34	56
13	DCM	50	66

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TMG (200 mol%) in solvent (1.0 mL) at 60 ℃.

Table S8: Screening of the alkoxyl groups of amino acid esters

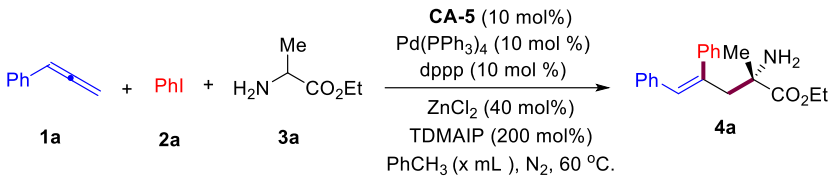


1a 2a 3 4a

entry	-R	yield (%)	ee (%)
1	-Et	83	81
2[b]	-Et	81	80
3[c]	-Et	70	90
4[d]	-Et	80	90
5	-Me	69	79
6	-^{t}Bu	68	66
7	-Bn	39	68

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3** (0.30 mmol), **CA-1** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TMG (200 mol%) in toluene (1.0 mL) at 60 ℃. [b] **CA-5** replace **CA-1** (10 mol%). [c] TDMAIP replace TMG (200 mol%). [d] **CA-5** replace **CA-1** (10 mol%) and TDMAIP replace TMG (200 mol%).

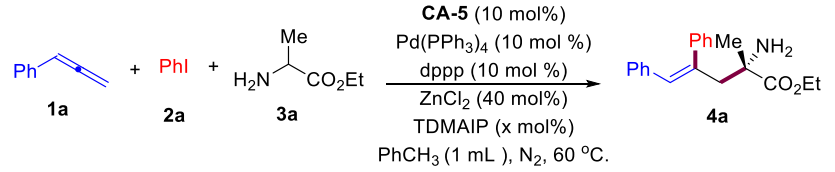
Table S9: Screening of the reactant concentration[a]



Entry	$PhCH_3$ (X mL)	yield (%)	ee (%)
1	0.50	83	88
2	0.75	61	82
3	1.00	80	90
4	1.25	76	90
5	1.50	78	92
6	1,75	49	88
7	2.00	45	80

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-5** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TDMAIP (200 mol%) in toluene (x mL) at 60 ℃.

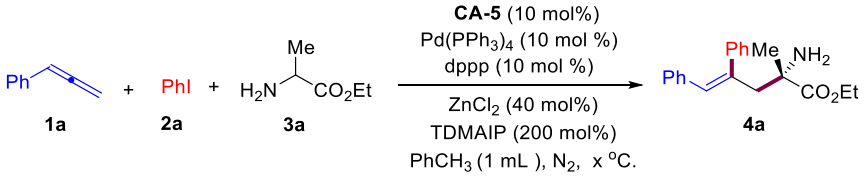
Table S10: Screening of the equivalents of the base[a]



entry	TDMAIP (x mol%)	yield (%)	ee (%)
1	200	80	90
2	175	78	90
3	150	78	88

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-5** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TDMAIP (x mol%) in toluene (1.0 mL) at 60 ℃.

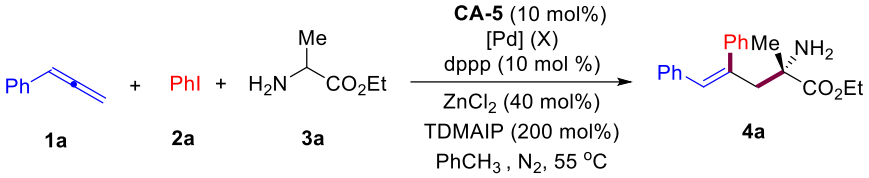
Table S11: Screening of the temperature[a]



entry	T (x ℃)	yield (%)	ee (%)
1	40	58	88
2	45	65	90
3	50	80	90
4	55	83	90
5	60	80	90

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-5** (10 mol%), $Pd(PPh_3)_4$ (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TDMAIP (200 mol%) in toluene (1.0 mL) at x ℃.

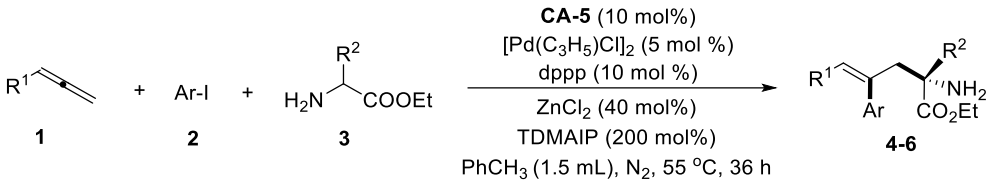
Table S12: Screening of the palladium sources[a]



entry	$PhCH_3$ (mL)	[Pd] (X)	T (℃)	yield (%)	ee (%)
1	1.0	[b]$Pd(PPh_3)_4$	60	83	90
2	1.0	[b]$Pd(dppe)_2$	60	52	84
3	1.0	[c]$[Pd(C_3H_5)Cl]_2$	60	93	89
4	1.0	[c]$[Pd(C_3H_5)Cl]_2$	50	78	90
5	1.0	[c]$[Pd(C_3H_5)Cl]_2$	55	83	90
6	1.5	[c]$[Pd(C_3H_5)Cl]_2$	55	89	90

[a] Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.20 mmol), **3a** (0.30 mmol), **CA-5** (10 mol%), dppp (10 mol%), $ZnCl_2$ (40 mol%) and TDMAIP (200 mol%). [b] X = 10 mol%. [c] X = 5 mol%.

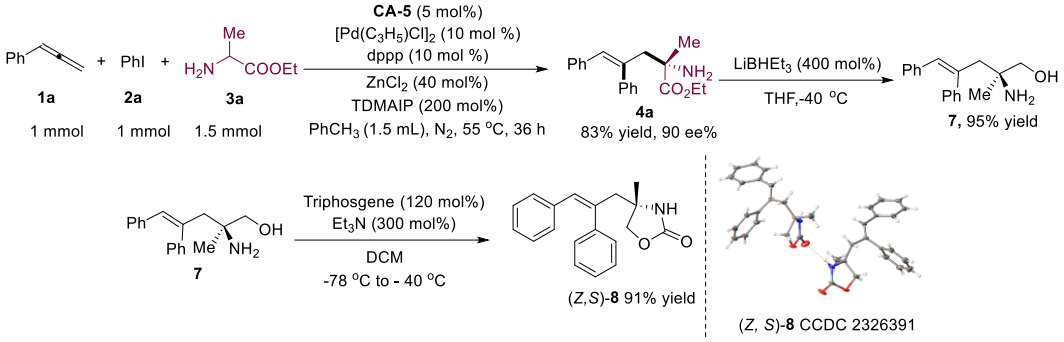
4. General procedure for the catalytic asymmetric reaction



To a 10 mL flame dried Schlenk tube with $[Pd(C_3H_5)Cl]_2$ (4 mg, 0.01 mmol) and dppp (9 mg, 0.02 mmol) was added 0.5 mL $PhCH_3$, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, allenes **1** (0.2 mmol), iodobenzene **2** (0.2 mmol), ethyl amino acid ester **3** (0.3 mmol), chiral aldehyde **CA-5** (11 mg, 0.02 mmol), $ZnCl_2$ (11 mg, 0.08 mmol), TDMAIP (72 mg, 0.40 mmol) and another 1.0 mL toluene were added. The mixture was continuously stirred at indicated reaction temperature under a nitrogen atmosphere. After the reaction was completed, the solvent was removed by rotary evaporation, and the residue was purified by flash silica gel column chromatography separation to afford **4-6** (eluent: petroleum ether/ ethyl acetate/ triethylamine = 300/100/2).

5. Determination of the absolute configuration

5.1 Determination of the absolute configuration of (*Z*, *S*)-8



1) To a 10 mL flame dried Schlenk tube with $[Pd(C_3H_5)Cl]_2$ (19.0 mg, 0.05 mmol) and dppp (42.0 mg, 0.1 mmol) was added 1.5 mL $PhCH_3$, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, allenes **1** (1.0 mmol, 116 mg), iodobenzene **2** (1.0 mmol, 204 mg), ethyl amino acid ester **3** (1.5 mmol, 176.0 mg), chiral aldehyde **CA-5** (50.0 mg, 0.1 mmol), $ZnCl_2$ (55.0 mg, 0.4 mmol), TDMAIP (356.0 mg, 2.0 mmol) and another 1.5 mL toluene were added. The mixture was continuously stirred at indicated reaction temperature under a nitrogen atmosphere. After the reaction was completed, the solvent was removed by rotary evaporation, and the residue was purified by flash silica gel column chromatography separation to afford compound **4a** (eluent: petroleum ether/ ethyl acetate/ triethylamine =300/100/2) (256.0 mg, 85%, 90% ee).

2) $LiBHEt_3$ (2.58 mmol, 2.58 mL, 1M in THF) was slowly added to a solution of the resulting compound **4a** (200.0 mg, 0.645 mmol) in anhydrous THF at -40 ℃ under a nitrogen atmosphere. The resulting mixture was stirred at -40 ℃ for 1 h and quenched with H_2O at 0 ℃. The mixture was filtered through Celite and washed thoroughly with DCM. The organic layer was extracted with DCM (3 x 20.0 mL) and washed with water (20.0 mL) and brine (20.0 mL) before drying over Na_2SO_4, filtering and concentrating under reduced pressure. The residue was purified by flash chromatography column on silica gel to afford compound **7** (eluent: MeOH/ DCM =1/20) (164.0 mg, 95%). The resulting compound **7** was used for next step without further characterized.

3) the compound **7** (160.0 mg, 0.6 mmol) was dissolved in dry CH_2Cl_2 (5.0 mL). To the solution, Et_3N (0.25 mL, 1.8 mmol) and triphosgene (214.0 mg, 0.72 mmol) were added at -78 ℃. The mixture was gradually warmed to -40 ℃, and stirred for 15 min. 1 M HCl was slowly added to the mixture, and the product was extracted with CH_2Cl_2. The combined organic layer was

washed with satd $NaHCO_3$ and brine, and dried over Na_2SO_4, filtering and concentrating under reduced pressure. The residue was purified by flash chromatography column on silica gel to afford compound **8** (eluent: petroleum ether/ ethyl acetate =2/1) (158.0 mg, 91%, 90% ee).

Precautions for safe use of triphosgene and Safe use of triphosgene:

(1) Sparks and fires should be avoided, and equipment should be equipped with explosion safety protection devices;

(2) Excessive use should be avoided to avoid overheating, overload, and other situations;

(3) Regularly check the temperature and pressure of the equipment to ensure compliance with requirements;

(4) Equipment operators should wear safety clothing and protective equipment to carry out safe operations;

(5) Explosion safety devices should be installed to prevent sparks and fires.

Crystal data and structure refinement for Compound (*Z*, *S*)-8

The absolute configuration of compound (*Z*, *S*)-**8** was confirmed by the single crystal X-ray analysis. The corresponding single crystal was obtained via evaporation of its solution prepared from 20.0 mg compound (*Z*, *S*)-**8** and 4.0 mL mixed solvents (petroleum ether/ethyl acetate = 100/10). The intensity data were collected on an (Dual, Cu, Eos) diffractometer using graphitemonochromated Cu Kα radiation. Crystallographic data collection and structure solution parameters are summarized in **Table S13**. This data can be obtained free of charge from The Cambridge Crystallographic Data Center via www.ccdc.cam.uk/data_request/cif.

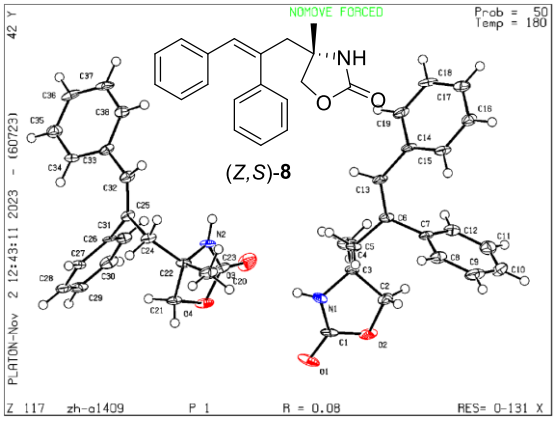


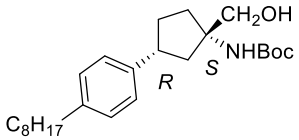
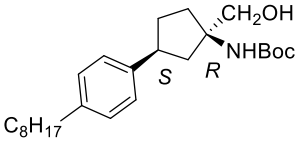
Table S13: Crystal data and structure refinement for Compound (*Z*, *S*)-8

Chemical Formula	$C_{19}H_{19}NO_2$
CCDC Deposit number	2326391

Formula weight	293.35
Temperature/K	179.98(10)
Wavelength	1.54184
Crystal system, space group	Triclinic, P1
a/Å	5.9905(4)
b/Å	8.0684(5)
c/Å	16.5496(9)
α/°	96.029(5)
β/°	98.627(5)
γ/°	92.934(5)
Volume/Å^3	784.65(8)
F(000)	312.0
Z, Calculated density	2
Flack	-0.3（3）

5.2 Determination of the absolute configuration of compound 13

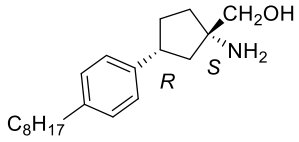
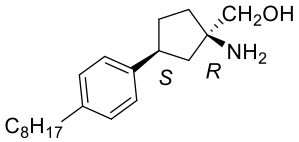
The NMR of compound **13** was identical to that reported in the literature [4].

Tert-butyl ((*1S*, *3R*)-1-(hydroxymethyl)-3-(4-octylphenyl)cyclopentyl)carbamate in this work (**13**):	Tert-butyl (*1R*, *3S*)-1-(Hydroxymethyl)-3-(4-octylphenyl)cyclopentylcarbamate, a total product in literature: [4]
	
$[\alpha]_D^{20}$= +9.63, 90% ee (c 0.36 , $CHCl_3$)	
^{1}H NMR (600 MHz, $CDCl_3$): δ 7.15 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.88 (s, 1H), δ 3.85 (s, 1H), 3.74 (d, *J* = 11.7 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.57 (t, *J* = 7.9 Hz, 2H), 2.46 (q, *J* = 13.4, 7.7 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.99 – 1.89 (m, 2H), 1.73 (t, *J* = 12.1 Hz, 1H), 1.66 – 1.53 (m, 3H), 1.45 (s, 9H), 1.34 – 1.23 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 156.69, 141.81, 141.11, 128.69, 127.10, 80.30, 64.95, 44.58, 44.03, 43.85, 36.08, 35.84, 32.94, 32.19, 31.85, 29.78, 29.69, 29.56, 28.69, 22.97, 14.40; **HRMS(ESI) m/z:** $[M+H]^+$ Calculated for $C_{25}H_{42}NO_3^+$ 404.3159; found 404.3160.	**^{1}H NMR (300 MHz, $CDCl_3$)** δ: 7.18–7.07 (m, 4H), 4.93 (s, 1H), 3.72 (q, *J* = 11.27 Hz, 1H), 3.08 (m, 1H), 2.57 (app t, *J* = 7.75 Hz, 1H), 2.46 (dd, *J* = 13.29, 7.55 Hz, 1H), 2.16–2.03 (m, 1H), 2.00–1.80 (m, 3H), 1.73 (dd, *J* = 13.16, 11.13 Hz, 1H), 1.59 (m, 2H), 1.45 (s, 9H), 1.38–1.18 (m, 10H), 0.88 (t, *J* = 6.74 Hz, 3H); **^{13}C NMR (75 MHz, $CDCl_3$)** δ: 156.6, 141.8, 141.0, 128.6, 127.1, 80.2, 69.4, 65.0, 44.4, 44.0, 43.3, 35.9, 35.8, 32.9, 32.1, 31.8, 29.7, 29.6, 29.5, 22.9, 14.4.

5.3 Determination of the absolute configuration of (*S*, *R*)-VPC01091

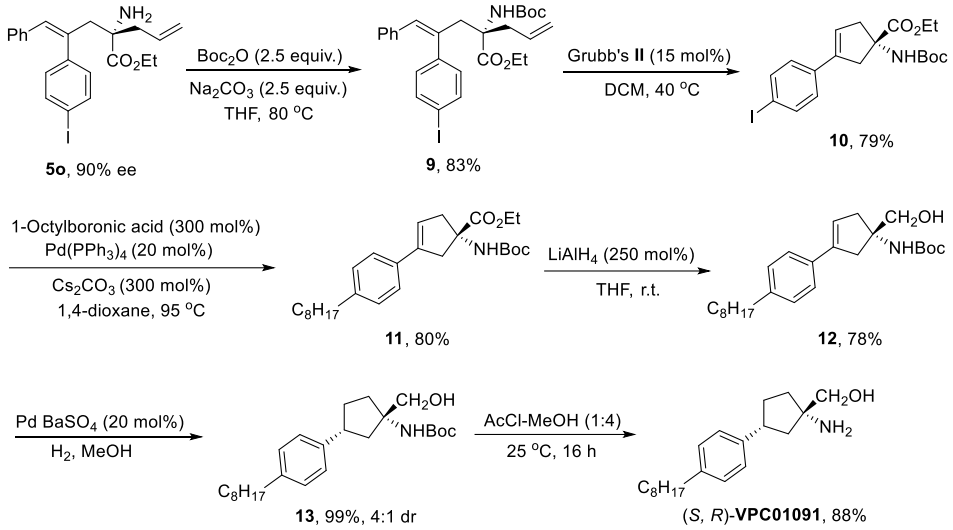
The NMR of (*S*, *R*)-VPC01091 was identical to that reported in the literature, and the

absolute configuration of VPC01091 was assigned by comparing its optical rotation with literature values [4].

(*S, R*)-VPC01091 in this work	((*1R,3S*)-1-Amino-3-(4-octylphenyl)cyclopentyl)-methanol Hydrochloride **VPC01091** in literature[4]
	
$[\alpha]_D^{20}$= +2.4, 90% ee (c 0.033, $CHCl_3$)	$[\alpha]_D^{20}$= -2.8 (c 1.05, $CHCl_3$)

6. The synthesis of (*S, R*)-VPC01091

Scheme S1: The synthesis of (*S, R*)-VPC01091.



6.1 The synthesis of compound 9

A round-bottomed flask equipped with a reflux condenser and a nitrogen inlet adapter was charged with compound **5o** (168.0 mg, 0.364 mmol), di-tert-butyldicarbonate (198.0 mg, 2.5 equiv.), and sodium carbonate (97.0 mg, 2.5 equiv.) in 30.0 mL of THF. The mixture was heated at 80 ℃ for 16 h and then allowed to cool to ambient temperature and filtered through a sintered glass funnel. The filtrate was concentrated under reduced pressure to provide the crude material as a yellow oil. The residue was purified by silica gel chromatography to afford compound **9** as colorless oil (169.0 mg, 83%) (eluent: petroleum ether/ ethyl acetate=30/1). The resulting compound **9** was used for next step without further characterized (**Scheme S1**).

6.2 The synthesis of compound 10

To a solution of compound **9** (393.0 mg, 0.7 mmol) in anhydrous DCM (30.0 mL), under N_2, it was added the 2nd generation Grubbs catalyst (G-II) (89.0 mg, 15 mol%) and the reaction

mixture refluxed for 5 h. The progress of the reaction was checked by TCL. On completion of the reaction, the solvent was evaporated at low pressure on rotary evaporator. The residue was purified by silica gel chromatography to afford compound **10** (269.0 mg, 79% yield) (eluent: petroleum ether/ ethyl = 1:10) (**Scheme S1**).

6.3 The synthesis of compound 11

To a suspension of the compound **10** (241.0 mg, 0.528 mmol), n-octylboronic acid (250.0 mg, 300 mol%), $Pd(PPh_3)_4$ (124.0 mg, 20 mol %) and Cs_2CO_3 (517.0 mg, 300 mol%), in 1, 4-dioxane (20.0 mL). The mixture was stirred at room temperature for 12 hours under nitrogen. Next, the reaction mixture was allowed to cool to ambient temperature and filtered through a pad of celite with the aid of ether. The filtrate was concentrated under reduced pressure. The resulting residue was purified by silica gel chromatography to to give compound **11** (186.0 mg, 80% yield) (**Scheme S1**).

6.4 The synthesis of compound 12

$LiAlH_4$ (44.0 mg, 250 mol%) was slowly added to a solution of the compound **11** (203.0 mg, 0.46 mmol) in THF (10.0 mL) at 0 ℃. The resulting mixture was stirred at room temperature for 2 hours and quenched with saturated $NaHCO_3$ (aq, 10.0 mL) at 0 ℃. The mixture was filtered through Celite and washed thoroughly with EtOAc. The organic layer was extracted with EtOAc (3 x 20.0 mL) and washed with water (20.0 mL) and brine (20.0 mL) before drying over Na_2SO_4, filtering and concentrating under reduced pressure. The crude product was purified via column chromatography (petroleum ether/ ethyl acetate=5:1) to isolate compound **12** (144.1 mg, 78% yield, 90% ee) (**Scheme S1**).

6.6 The synthesis of compound 13

A suspension of the compound **12** (71.0 mg, 0.175 mmol) and $Pd/BaSO_4$ (30.0 mg; 20 mol%) in methanol (5.0 mL), was stirred for 9 hours under hydrogen (balloon). Next, the mixture was filtered through a plug of silica and concentrated under reduced pressure to provide product **13** (petroleum ether/ ethyl acetate=3:1) (70.1 mg, 99% yield, 90% ee) (**Scheme S1**).

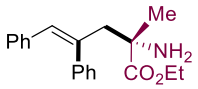
6.7 The synthesis of (*S, R*)-VPC01091

The reaction was carried out following literature procedure[5]: Compound **13** (34.0 mg, 0.0856 mmol) was dissolved in a carefully pre-mixed methanol and acetyl chloride (methanol: chloride = 4:1, 5 ml), and stirred at 25 ^{o}C for 16 h. Upon completion of the reaction, the solvent

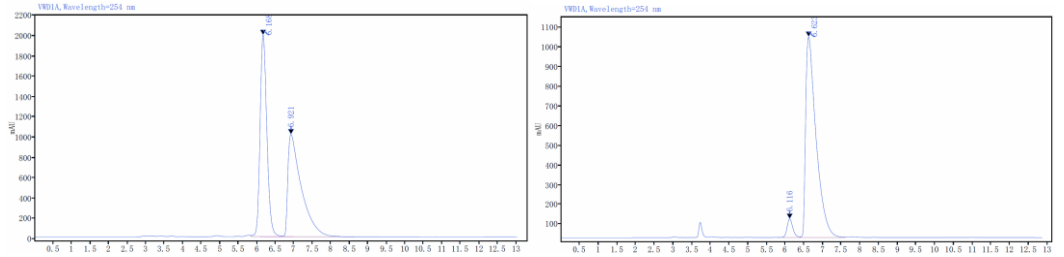
was evaporated. The residue was dissolved in 10% NaOH aqueous solution and extracted with DCM. The combined organic layers were dried on Na_2SO_4, filtered and concentration on rotary evaporator into **VPC01091**, the residue was purified by chromatography [DCM /MeOH= 10:1] to afford pure (*S*, *R*)-**VPC01091** as a white solid (23.0 mg, 88% yield) (**Scheme S1**).

7. Characterization date of products

Ethyl (*S*, *Z*)-2-amino-2-methyl-4, 5-diphenylpent-4-enoate (4a):



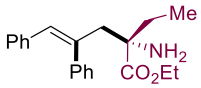
White solid (55.1 mg, 89%); m.p. = 46-48 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R (major) 6.623 min, t_R(minor) 6.116 min; $[\alpha]_D^{20}$ = -77.37 (c= 1, DCM); **^{1}H NMR (400 MHz, $CDCl_3$):** δ 7.30 – 7.18 (m, 3H), 7.18 – 7.12 (m, 2H), 7.11 – 7.02 (m, 3H), 6.92 – 6.77 (m, 2H), 6.54 (s, 1H), 3.85 – 3.66 (m, 1H), 3.55 – 3.43 (m, 1H), 3.15 (d, *J* = 13.4 Hz, 1H), 2.75 (d, *J* = 14.2 Hz, 1H), 1.72 (s, 2H), 1.33 (s, 3H), 1.08 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (101 MHz, $CDCl_3$):** δ 176.9, 140.0, 138.3, 136.8, 131.2, 129.2, 129.1, 128.4, 127.8, 127.3, 126.6, 60.8, 57.6, 51.0, 27.7, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{24}NO_2^+$ 310.1802; found 310.1800.



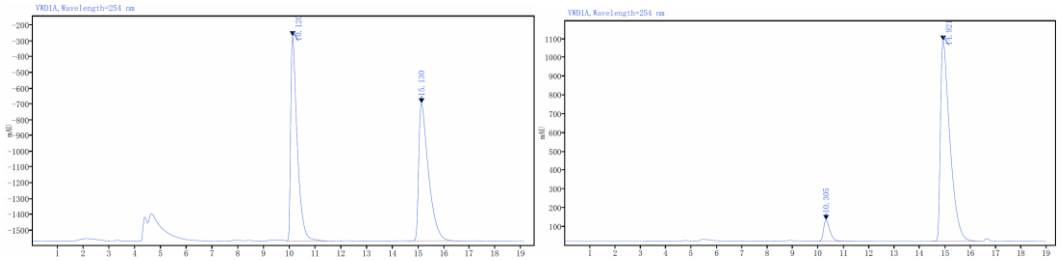
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.168	VV	0.8679	25235.6680	1984.7077	49.8202
	6.921	VB	1.9279	25417.8233	1007.0467	50.1798

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.116	VV	0.6001	1026.3702	94.8671	4.9419
	6.623	VV	1.2079	19742.4191	1021.1331	95.0581

Ethyl (*S*, *Z*)-2-amino-2-ethyl-4, 5-diphenylpent-4-enoate (4b):



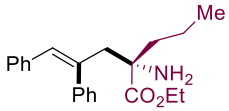
White solid (49.0 mg, 76%); m.p. = 46-48 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 87% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 14.921 min, t_R(minor) 10.305 min; $[\alpha]_D^{20}$ = -88.11 (c= 0.948, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.29 – 7.19 (m, 3H), 7.17 – 7.12 (m, 2H), 7.11 – 7.01 (m, 3H), 6.91 – 6.81 (m, 2H), 6.54 (s, 1H), 3.83 – 3.69 (m, 1H), 3.50 – 3.39 (m, 1H), 3.18 (d, *J* = 13.5 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 1.88 – 1.78 (m, 1H), 1.73 (s, 2H), 1.61 – 1.53 (m, 1H), 1.07 (t, *J* = 7.1 Hz, 3H), 0.82 (t, *J* = 7.5 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.3, 140.1, 138.2, 136.8, 131.2, 129.2, 129.1, 128.4, 127.8, 127.3, 126.6, 61.0, 60.7, 49.9, 34.2, 14.0, 8.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{26}NO_2^+$ 324.1958; found 324.1957.



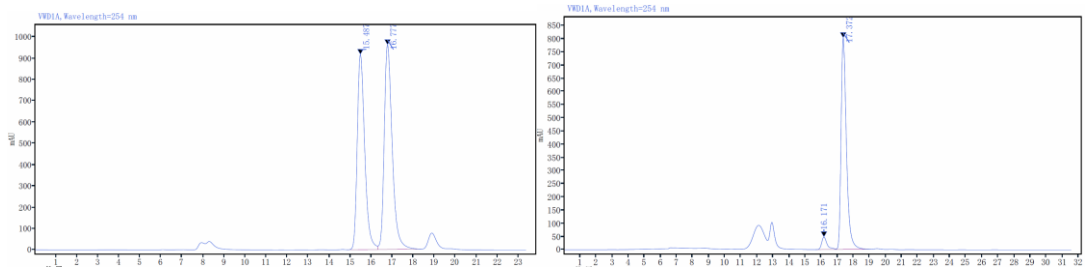
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.120	VB	1.8202	23020.3751	1297.8368	50.1995
2	15.130	BB	2.0700	22837.3691	870.3706	49.8005

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.305	BB	1.4700	1973.1785	112.8287	6.6785
2	14.921	BV	2.0238	27571.9443	1066.7623	93.3215

Ethyl (*S*, *Z*)-2-amino-4, 5-diphenyl-2-propylpent-4-enoate (4c):



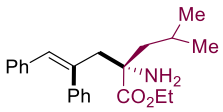
White solid (53.3 mg, 79%); m.p. = 60-62 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 89% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 17.372 min, t_R(minor) 16.171 min; $[\alpha]_D^{20}$ = -77.99 (c= 1.236, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.18 (m, 3H), 7.16 – 7.12 (m, 2H), 7.09 – 7.03 (m, 3H), 6.87 (dd, *J* = 7.6, 2.1 Hz, 2H), 6.54 (s, 1H), 3.87 – 3.64 (m, 1H), 3.49 – 3.33 (m, 1H), 3.18 (d, *J* = 13.4 Hz, 1H), 2.71 (d, *J* = 13.4 Hz, 1H), 1.81 – 1.73 (m, 1H), 1.71 (s, 2H), 1.53 (td, *J* = 13.2, 12.8, 4.6 Hz, 1H), 1.47 – 1.19 (m, 2H), 1.07 (t, *J* = 7.2 Hz, 3H), 0.88 (t, *J* = 7.3 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 176.4, 140.1, 138.2, 136.8 131.3, 129.2, 129.1, 128.3, 127.8, 127.3, 126.6, 60.6, 50.2, 43.7, 17.1, 14.3, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{28}NO_2^+$ 338.2115; found 338.2113.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	15.487	VV	1.4377	22683.6504	915.8064	47.1479
2	16.777	VB	2.0704	25428.0121	959.9157	52.8521

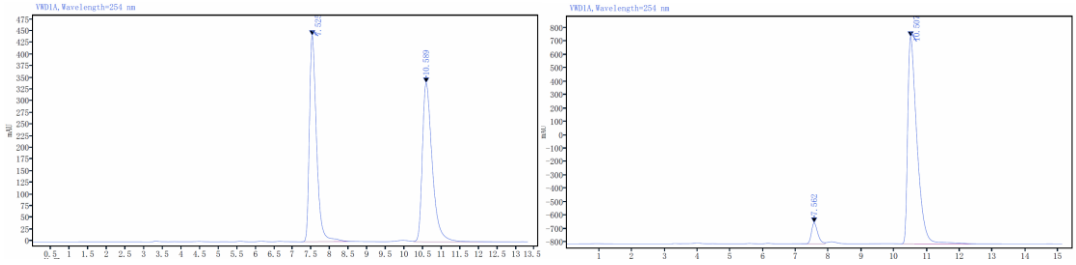
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	16.171	BV	1.2893	1110.2376	47.4207	5.6217
2	17.372	VB	2.1786	18638.7881	802.7928	94.3783

Ethyl (*S*, *Z*)-2-amino-2-isobutyl-4, 5-diphenylpent-4-enoate (4d):



Colorless oil (44.2 mg, 63%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 87% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 10.507 min, t_R(minor) 7.562 min; $[\alpha]_D^{20}$ = -74.37 (c= 0.736, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.18 (m, 3H), 7.13 (d, *J* = 8.5 Hz,2H), 7.09 – 7.01 (m, 3H), 6.87 – 6.83 (m, 2H), 6.53 (s, 1H), 3.77 – 3.69 (m, 1H), 3.45 – 3.35 (m, 1H), 3.15 (d, *J* = 13.3 Hz, 1H), 2.69 (d, *J* = 13.3 Hz, 1H), 1.83 – 1.77 (m, 1H), 1.75 (s, 2H), 1.71 – 1.64 (m, 1H), 1.54 (dd, *J* = 13.8, 4.8 Hz, 1H), 1.08 (t, *J* = 7.2 Hz, 3H), 0.94 (d, *J* = 6.6 Hz, 3H), 0.78 (d, *J* = 6.6 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 176.9, 140.1, 138.0, 136.8, 131.5, 129.2, 129.1, 128.3, 127.8, 127.3, 126.6, 60.6, 60.4, 51.4, 49.9, 24.8, 24.2, 22.8, 13.9; **HRMS(ESI)**

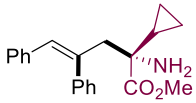
m/z: $[M+H]^+$ Calculated for $C_{23}H_{30}NO_2^+$ 352.2271; found 352.2269.



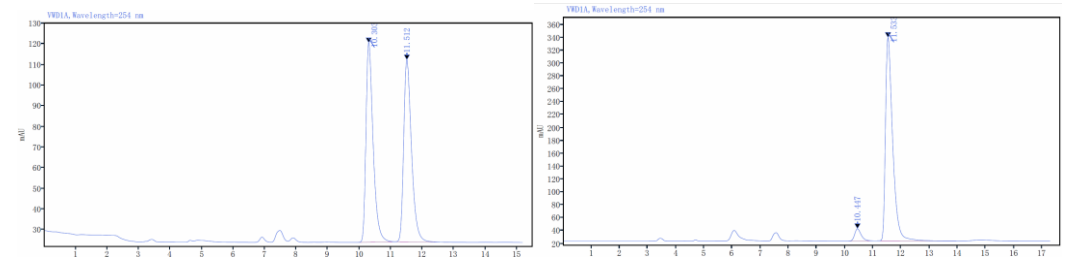
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.525	BB	1.4417	5883.0028	441.4291	48.3245
2	10.589	VB	2.5913	6290.9476	340.2337	51.6755

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.562	BV	0.7228	2079.5527	155.8736	6.3978
2	10.507	VB	3.6973	30424.6132	1546.4773	93.6022

Ethyl (*S*, *Z*)-2-amino-2-cyclopropyl-4, 5-diphenylpent-4-enoate (4e):



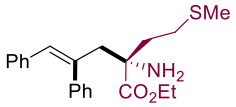
White solid (39.0 mg, 61%); m.p. = 96-98 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IE-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 11.533 min, t_R(minor) 10.447 min; $[\alpha]_D^{20}$ = -67.71 (c= 0.636, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.23 (m, 2H), 7.24 – 7.18 (m, 1H), 7.15 – 7.12 (m, 2H), 7.11 – 7.04 (m, 3H), 6.89 – 6.84 (m, 2H), 6.52 (s, 1H), 3.31 (d, *J* = 13.6 Hz, 1H), 3.21 (s, 3H), 2.76 (d, *J* = 13.6 Hz, 1H), 1.49 (s, 2H), 1.22 – 1.10 (m, 1H), 0.56 – 0.44 (m, 1H), 0.41 – 0.22 (m, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 176.7, 139.7, 138.0, 136.5, 131.1, 128.9, 128.8, 128.1, 127.6, 126.9, 126.3, 58.6, 51.3, 49.6, 19.6, 0.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{24}NO_2^+$ 322.1802; found 322.1800.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.303	BB	1.1656	1520.5581	96.5298	49.9677
2	11.512	BB	1.7000	1522.5244	88.1346	50.0323

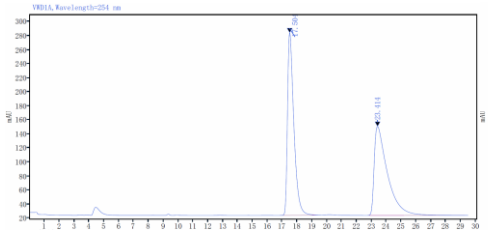
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	10.447	BB	0.9200	300.3809	18.8674	5.0873
2	11.533	BB	2.9033	5604.1259	315.5443	94.9127

Ethyl (*S*, *Z*)-2-amino-2-(2-(methylthio)ethyl)-4, 5-diphenylpent-4-enoate (4f):



Colorless oil (67.3 mg, 90%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 86% by HPLC analysis on Daicel Chirapak ID-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 21.852 min, t_R(minor) 17.103 min; $[\alpha]_D^{20}$ = -47.01 (c= 1.448, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.19 (m, 3H), 7.16 – 7.12 (m, 2H), 7.10 – 7.01 (m, 3H), 6.89 – 6.84 (m, 2H), 6.53 (s, 1H), 3.84 – 3.70 (m, 1H), 3.57 – 3.37 (m, 1H), 3.17 (d, *J* = 13.4 Hz, 1H), 2.74 (d, *J* = 13.4 Hz, 1H), 2.57 – 2.49 (m, 1H), 2.34 – 2.27 (m, 1H), 2.13 – 2.07 (m, 1H), 2.06 (s, 3H), 1.84 (ddd, *J* = 13.5, 11.4, 5.1 Hz, 1H), 1.70 (s, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.7, 139.9, 137.7, 136.6, 131.6, 129.1, 129.1, 128.4, 127.9, 127.4, 126.7, 61.0, 60.6, 50.1, 40.7, 28.7, 15.5, 14.0; **HRMS(ESI)** m/z:

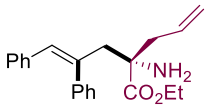
$[M+H]^+$ Calculated for $C_{22}H_{28}NO_2S^+$ 370.1835; found 370.1834.



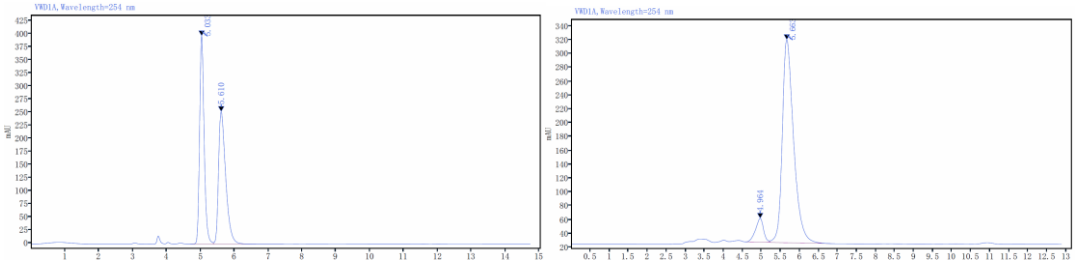
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	17.504	BB	2.8050	7718.1544	259.9885	49.5791
2	23.414	BB	6.6450	7849.2006	126.7668	50.4209

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	17.103	MM m	0.4199	2537.8841	91.7095	6.9020
2	21.852	BB	9.3167	34232.3945	506.7939	93.0980

Ethyl (*S*, *Z*)-2-allyl-2-amino-4, 5-diphenylpent-4-enoate (4g):



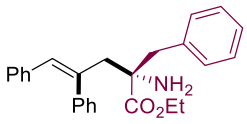
Colorless oil (40 mg, 59%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 85% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.663 min, t_R(minor) 4.964 min; $[\alpha]_D^{20}$ = -9.88 (c= 0.172, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.29 – 7.18 (m, 3H), 7.17 – 7.11 (m, 2H), 7.10 – 7.03 (m, 3H), 6.98 – 6.77 (m, 2H), 6.55 (s, 1H), 5.74 – 5.56 (m, 1H), 5.17 – 5.08 (m, 2H), 3.83 – 3.63 (m, 1H), 3.53 – 3.40 (m, 1H), 3.17 (d, *J* = 13.3 Hz, 1H), 2.74 (d, *J* = 13.4 Hz, 1H), 2.59 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.26 (dd, *J* = 13.4, 8.5 Hz, 1H), 1.73 (s, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.8, 140.0, 137.9, 136.8, 132.4, 131.4, 129.2, 129.1, 128.4, 127.9, 127.3, 126.6, 119.6, 60.8, 60.4, 49.9, 45.4, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{26}NO_2^+$ 336.1958; found 336.1958.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.033	BV	0.7057	3701.5617	397.7907	49.7850
2	5.610	VB	2.2040	3733.5390	253.0860	50.2150

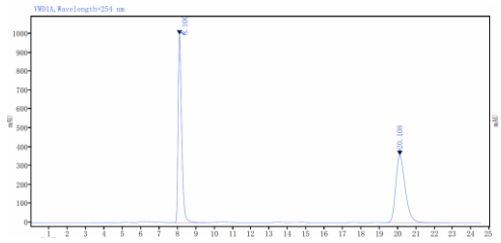
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.964	BV	0.6310	504.3401	34.3329	7.6619
2	5.663	VB	1.6338	6078.1102	293.3594	92.3381

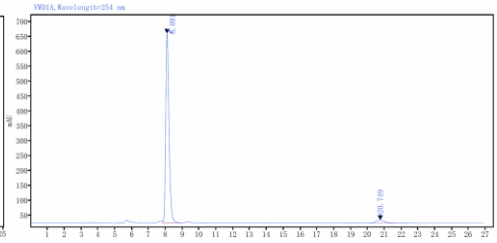
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4, 5-diphenylpent-4-enoate (4h):



White solid (64 mg, 83%); m.p. = 78-80 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 8.091 min, t_R(minor) 20.749 min; $[\alpha]_D^{20}$ = -48.49 (c= 1.102, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.27 – 7.17 (m, 6H), 7.14 (t, *J* = 7.8 Hz, 4H), 7.10 – 7.03 (m, 3H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.59 (s, 1H), 3.75 – 3.63 (m, 1H), 3.49 – 3.38 (m, 1H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.80 (dd, *J* = 21.9, 13.2 Hz, 2H), 1.63 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 140.1, 138.0, 136.8, 136.2, 131.6, 130.0, 129.2, 129.1, 128.4, 128.3, 127.9, 127.3,

126.9, 126.6, 61.8, 60.7, 50.5, 47.1, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{28}NO_2^+$ 386.2115; found 386.2113.

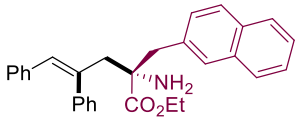




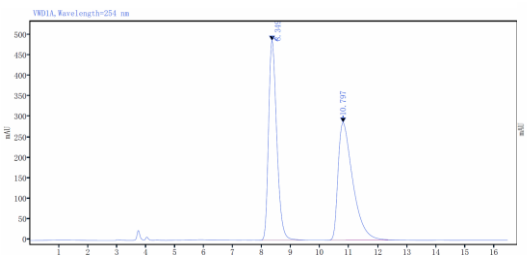
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.100	VB	1.7907	13422.3172	994.3670	51.3037
2	20.108	BB	3.4967	12740.1665	355.5914	48.6963

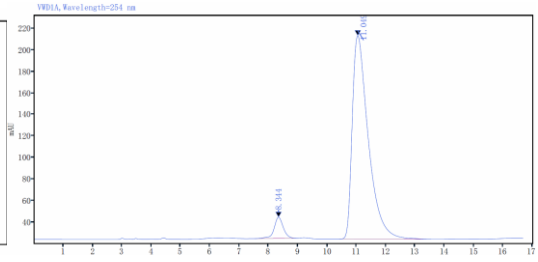
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.091	VV	1.1628	8653.5491	636.5519	95.7706
2	20.749	BB	2.2450	382.1576	9.8391	4.2294

Ethyl (*S*, *Z*)-2-amino-2-(naphthalen-2-ylmethyl)-4, 5-diphenylpent-4-enoate (4i):



White solid (65.0 mg, 75%); m.p. = 74-76 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 89% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 11.049 min, t_R(minor) 8.344 min; $[\alpha]_D^{20}$ = -23.92 (c= 1.300, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.80 – 7.69 (m, 3H), 7.63 (s, 1H), 7.45 – 7.38 (m, 2H), 7.28 – 7.18 (m, 4H), 7.15 (d, *J* = 7.4 Hz, 2H), 7.09 – 7.01 (m, 3H), 6.91 – 6.85 (m, 2H), 6.61 (s, 1H), 3.75 – 3.68 (m, 1H), 3.48 – 3.42 (m, 1H), 3.40 (dd, *J* = 13.3, 3.3 Hz, 2H), 2.95 (d, *J* = 13.1 Hz, 1H), 2.86 (d, *J* = 13.3 Hz, 1H), 1.66 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 139.9, 137.9, 136.8, 133.7, 133.4, 132.5, 131.6, 129.3, 129.1, 128.9, 128.4, 128.2, 127.9, 127.7, 127.6, 127.4, 126.7, 126.0, 125.6, 61.9, 60.9, 50.6, 47.2, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{30}H_{30}NO_2^+$ 436.2271; found 436.2270.

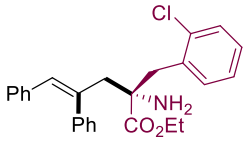




Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.349	BB	1.7450	9547.0214	485.7884	48.6267
2	10.797	BB	2.4700	10086.2787	286.0933	51.3733

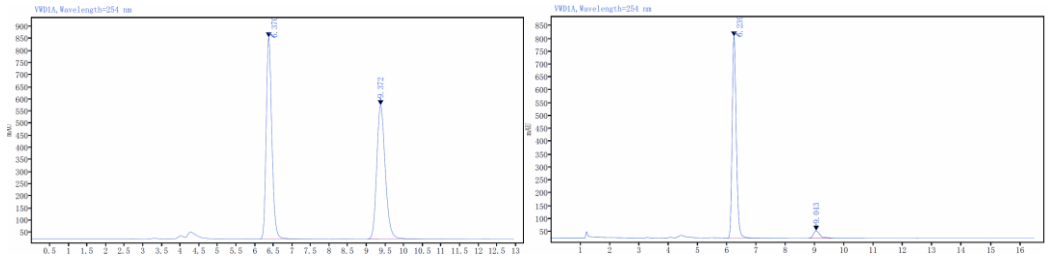
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.344	BB	1.4217	429.8048	19.7570	5.6417
2	11.049	BB	3.3667	7188.5351	189.1076	94.3583

Ethyl (*Z*, *S*)-2-amino-2-(2-chlorobenzyl)-4, 5-diphenylpent-4-enoate(4j):



White solid (51.1 mg, 61%); m.p. = 72-74 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.239 min, t_R(minor) 9.043 min; $[\alpha]_D^{20}$ = -41.14 (c= 1.008, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.38 – 7.32 (m, 1H), 7.28 – 7.20 (m, 4H), 7.18 – 7.12 (m, 4H), 7.09 – 7.00 (m, 3H), 6.89 – 6.82 (m, 2H), 6.57 (s, 1H), 3.78 – 3.67 (m, 1H), 3.51 – 3.40 (m, 1H), 3.38 (d, *J* =

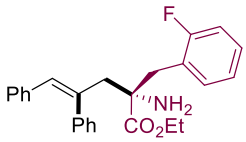
13.5 Hz, 1H), 3.27 – 3.13 (m, 2H), 2.82 (d, *J* = 13.3 Hz, 1H), 1.65 (s, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 140.2, 137.9, 136.8, 135.2, 134.5, 132.1, 131.8, 129.7, 129.2, 129.1, 128.4, 128.2, 127.8, 127.3, 126.6, 126.5, 61.8, 61.0, 49.9, 43.0, 13.8; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}ClNO_2^+$ 420.1725; found 420.1723.



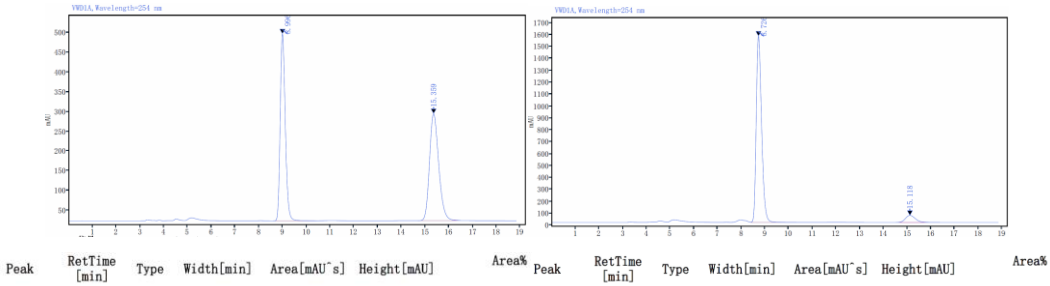
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.370	BB	1.4295	8703.8843	830.0960	49.9749
2	9.372	BB	1.6042	8712.6162	550.4959	50.0251

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.239	BB	1.4930	7673.1576	783.5538	94.3894
2	9.043	BB	1.2000	456.1027	28.6810	5.6106

Ethyl (*Z*, *S*)-2-amino-2-(2-fluorobenzyl)-4, 5-diphenylpent-4-enoate (4k):



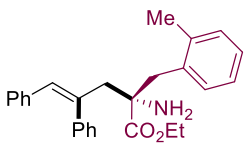
Colorless oil (39.1 mg, 48%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 86% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 8.726 min, t_R(minor) 15.118 min; $[\alpha]_D^{20}$ = -50.34 (c= 0.484, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.29 – 7.11 (m, 7H), 7.08 – 6.96 (m, 5H), 6.88 – 6.83 (m, 2H), 6.58 (s, 1H), 3.80 – 3.68 (m, 1H), 3.45 – 3.37 (m, 1H), 3.36 (d, *J* = 13.3 Hz, 1H), 3.16 (d, *J* = 13.4 Hz,1H), 2.94 (d, *J* = 13.4 Hz, 1H), 2.81 (d, *J* = 13.4 Hz, 1H), 1.68 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 162.3, 160.7, 140.1, 137.9, 136.7, 132.5 (d, *J* = 4.4 Hz), 131.7, 129.1 (d, *J* = 13.2 Hz), 128.7 (d, *J* = 8.3 Hz), 128.4, 127.9, 127.3, 126.6, 123.8 (d, *J* = 3.5 Hz), 123.3 (d, *J* = 15.9 Hz), 115.4 (d, *J* = 22.8 Hz), 61.3, 61.0, 49.9, 39.9, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}FNO_2^+$ 404.2020; found 404.2019.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.996	BB	1.8767	7024.9237	474.4785	49.0811
2	15.359	BB	1.9250	7287.9638	271.5443	50.9189

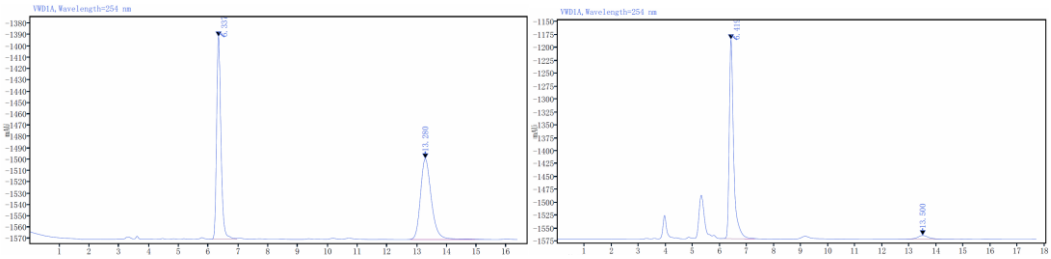
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.726	VB	1.9219	24598.2447	1563.3542	93.3710
2	15.118	BB	2.8033	1746.3784	59.0108	6.6290

Ethyl (*Z*, *S*)-2-amino-2-(2-methylbenzyl)-4, 5-diphenylpent-4-enoate (4l):



Colorless oil (45.0 mg, 56%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1,0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 6.419 min, t_R(minor) 13.500 min; $[\alpha]_D^{20}$ = -32.18 (c= 0.778, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.28 –

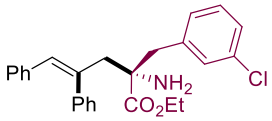
7.17 (m, 3H), 7.17 – 7.01 (m, 9H), 6.90 – 6.84 (m, 2H), 6.58 (s, 1H), 3.75 – 3.65 (m, 1H), 3.48 – 3.38 (m, 1H), 3.36 (d, *J* = 13.2 Hz, 1H), 3.16 (d, *J* = 13.7 Hz, 1H), 2.96 (d, *J* = 13.7 Hz, 1H), 2.83 (d, *J* = 13.3 Hz, 1H), 2.35 (s, 3H), 1.56 (s, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.1, 140.2, 138.1, 137.6, 136.8, 134.8, 131.7, 130.6, 130.4, 129.2, 129.1, 128.4, 127.9, 127.3, 126.8, 126.6, 125.7, 62.2, 60.8, 50.6, 43.0, 20.3, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2270.



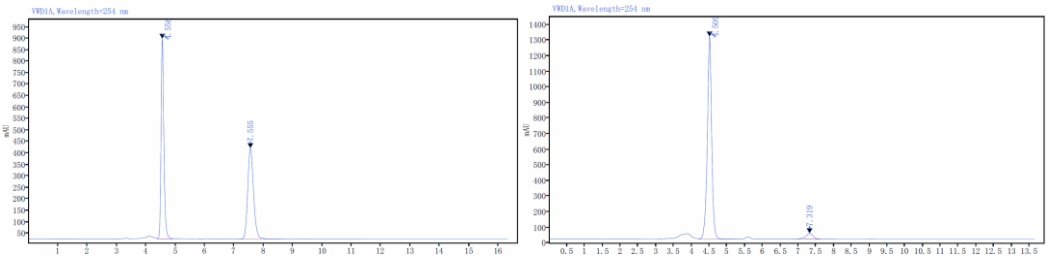
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.337	BV	0.9173	1814.5646	178.5249	49.9173
2	13.280	BB	3.0667	1820.5735	71.2430	50.0827

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.419	VB	1.7217	4378.7754	385.7163	95.8094
2	13.500	MM m	0.4174	191.5246	6.8888	4.1906

Ethyl (*S*, *Z*)-2-amino-2-(3-chlorobenzyl)-4, 5-diphenylpent-4-enoate (4m):



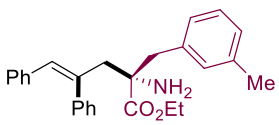
Colorless oil (67.3 mg, 80%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.509 min, t_R(minor) 7.319 min; $[\alpha]_D^{20}$ = -46,78 (c= 1.5, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.28 – 7.17 (m, 5H), 7.17 – 7.11 (m, 3H), 7.09 – 7.04 (m, 3H), 7.02 (d, *J* = 7.2 Hz, 1H), 6.87 (dd, *J* = 7.4, 2.3 Hz, 2H), 6.58 (s, 1H), 3.76 – 3.65 (m, 1H), 3.50 – 3.41 (m, 1H), 3.32 (d, *J* = 13.5 Hz, 1H), 3.18 (d, *J* = 13.1 Hz, 1H), 2.80 (d, *J* = 13.4 Hz, 1H), 2.75 (d, *J* = 13.1 Hz, 1H), 1.58 (s, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.3, 139.9, 138.2, 137.7, 136.6, 134.1, 131.7, 130.1, 129.5, 129.2, 129.1, 128.4, 128.1, 127.9, 127.4, 127.2, 126.7, 61.7, 60.9, 50.4, 46.6, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}ClNO_2^+$ 420.1725; found 420.1723.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.556	VV	0.6730	5782.9200	871.3408	51.5782
2	7.555	BB	1.6267	5429.0362	395.2288	48.4218

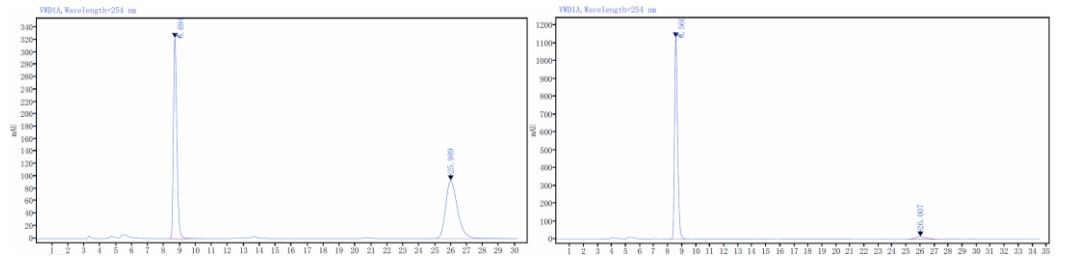
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.509	VB	1.1689	11063.6031	1296.8887	95.3182
2	7.319	BB	1.5067	543.4206	36.2886	4.6818

Ethyl (*S*, *Z*)-2-amino-2-(3-methylbenzyl)-4, 5-diphenylpent-4-enoate (4n):



White solid (45.4 mg, 56%); m.p. = 68-70 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 8.560

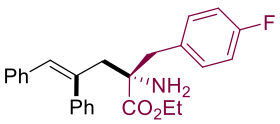
min, t_R(minor) 26.007 min; $[\alpha]_D^{20}$ = -40.85 (c= 0.9, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.28 – 7.18 (m,3H), 7.17 – 7.09 (m, 3H), 7.09 – 7.03 (m, 3H), 7.01 (d, *J* = 7.6 Hz, 1H), 6.95 (s, 1H), 6.91 (d, *J* = 7.7 Hz, 1H), 6.89 – 6.85 (m, 2H), 6.59 (s, 1H), 3.75 – 3.64 (m, 1H), 3.48 – 3.37 (m, 1H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.21 (d, *J* = 13.1 Hz, 1H), 2.81 (d, *J* = 13.3 Hz, 1H), 2.74 (d, *J* = 13.0 Hz, 1H), 2.27 (s, 3H), 1.60 (s, 2H), 1.07 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 140.0, 137.9, 137.8, 136.8, 136.0, 131.5, 130.8, 129.2, 129.1, 128.4, 128.2, 127.9, 127.7, 127.3, 126.9, 126.6, 61.7, 60.7, 50.6, 46.9, 21.3, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2270.



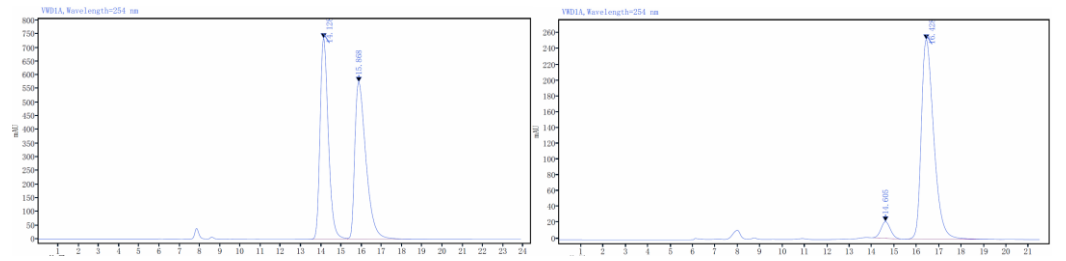
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.694	BB	2.4483	4831.4574	323.4224	50.0513
2	25.989	BB	5.4617	4821.5596	93.7158	49.9487

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	8.560	VB	1.3336	17120.0509	1130.8173	95.5745
2	26.007	BB	4.3083	792.7292	14.4796	4.4255

Ethyl (*S*, *Z*)-2-amino-2-(4-fluorobenzyl)-4, 5-diphenylpent-4-enoate (4o):



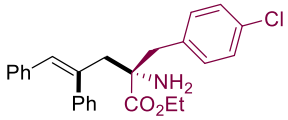
White solid (47.3 mg, 58%); m.p. = 90-92 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 16.428 min, t_R(minor) 14.605 min; $[\alpha]_D^{20}$ = -47.54 (c= 0.906, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.28 – 7.17 (m, 3H), 7.16 – 7.02 (m, 7H), 6.92 (t, *J* = 8.7 Hz, 2H), 6.87 (dd, *J* = 7.3, 2.4 Hz, 2H), 6.58 (s, 1H), 3.74 – 3.63 (m, 1H), 3.46 – 3.38 (m, 1H), 3.32 (d, *J* = 13.2 Hz, 1H), 3.19 (d, *J* = 13.3 Hz, 1H), 2.77 (dd, *J* = 27.4, 13.3 Hz, 2H), 1.63 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.4, 162.0 (d, *J* = 245.0 Hz), 139.9, 137.8, 136.7, 131.8 (d, *J* = 3.2 Hz), 131.6, 131.4 (d, *J* = 8.0 Hz), 129.2, 129.1, 128.4, 127.9, 127.4, 126.7, 115.1 (d, *J* = 21.2 Hz), 61.7, 60.8, 50.4, 46.2, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}FNO_2^+$ 404.2020; found 404.2019.



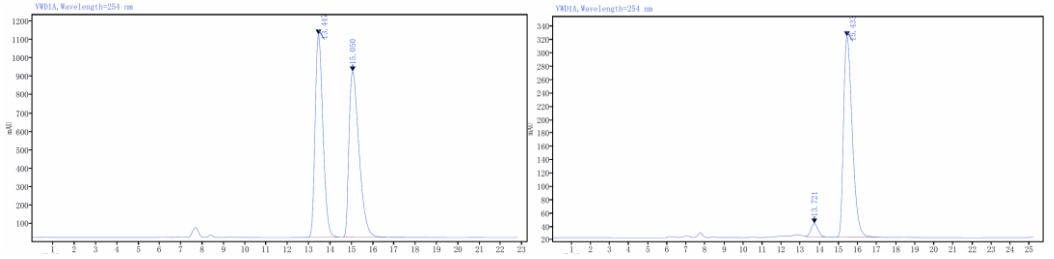
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	14.128	BV	1.9203	20984.6593	735.0726	48.7752
2	15.868	VB	3.1447	22038.5493	574.9763	51.2248

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	14.605	BB	1.4167	625.4248	21.1460	5.9958
2	16.428	BB	4.3133	9805.5915	252.6684	94.0042

Ethyl (*S*, *Z*)-2-amino-2-(4-chlorobenzyl)-4, 5-diphenylpent-4-enoate (4p):



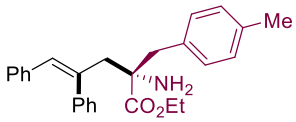
White solid (71.9 mg, 86%); m.p. = 117-119 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 98/2, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 15.433 min, t_R(minor) 13.721 min; $[\alpha]_D^{20}$ = -34.98 (c= 1.436, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.28 – 7.16 (m, 5H), 7.15 – 7.11 (m, 2H), 7.09 – 7.03 (m, 5H), 6.89 – 6.83 (m, 2H), 6.57 (s, 1H), 3.73 – 3.64 (m, 1H), 3.47 – 3.38 (m, 1H), 3.32 (d, *J* = 13.3 Hz, 1H), 3.18 (d, *J* = 13.2 Hz, 1H), 2.77 (dd, *J* = 28.5, 13.3 Hz, 2H), 1.57 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.3, 139.9, 137.7, 136.7, 134.7, 132.9, 131.7, 131.3, 129.2, 129.1, 128.4, 127.9, 127.4, 126.7, 61.7, 60.9, 50.4, 46.3, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}ClNO_2^+$ 420.1725; found 420.1724.



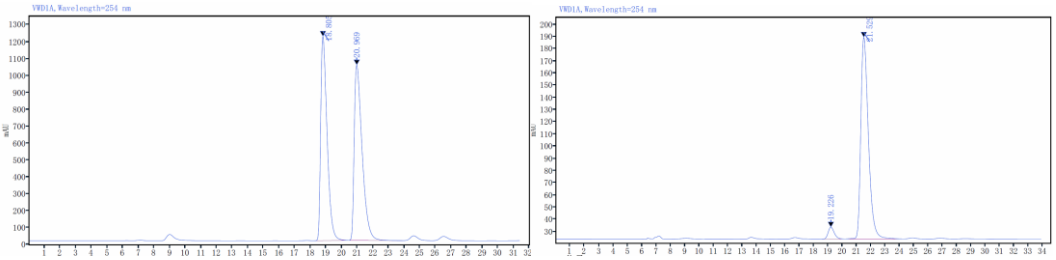
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.447	VB	1.6712	28106.7169	1102.8975	48.7880
	15.050	BB	3.0102	29503.1574	901.5473	51.2120

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.721	VB	1.5421	511.7543	19.6483	5.0696
	15.433	BB	2.8000	9582.8156	300.8944	94.9304

Ethyl (*S*, *Z*)-2-amino-2-(4-methylbenzyl)-4, 5-diphenylpent-4-enoate (4q):

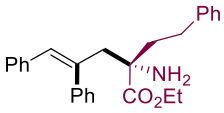


White solid (46.0 mg, 58%); m.p. = 95-97 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IF-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 21.529 min, t_R(minor) 19.226 min; $[\alpha]_D^{20}$ = -44.17 (c= 0.52, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.28 – 7.18 (m, 3H), 7.15 – 7.12 (m, 2H), 7.10 – 6.95 (m, 7H), 6.87 (d, *J* = 7.4 Hz, 2H), 6.59 (s, 1H), 3.76 – 3.63 (m, 1H), 3.46 – 3.37 (m, 1H), 3.33 (d, *J* = 13.3 Hz, 1H), 3.19 (d, *J* = 13.1 Hz, 1H), 2.80 (d, *J* = 13.3 Hz, 1H), 2.74 (d, *J* = 13.1 Hz, 1H), 2.28 (s, 3H), 1.58 (s, 2H), 1.07 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.7, 140.0, 138.0, 136.8, 136.5, 132.9, 131.5, 129.8, 129.2, 129.1, 129.0, 128.4, 127.9, 127.3, 126.6, 61.7, 60.7, 50.5, 46.6, 21.1, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2270.

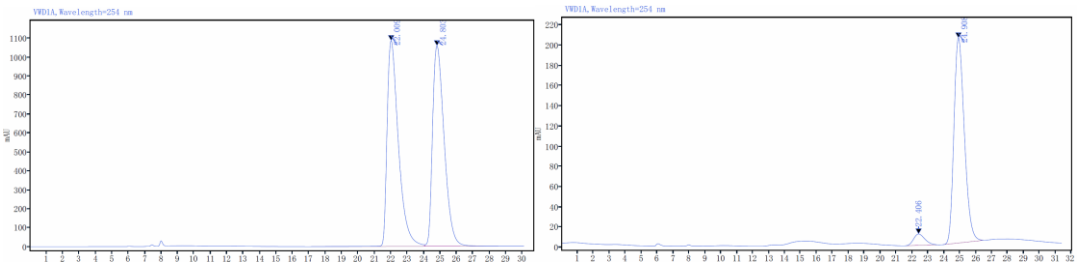


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	18.805	BB	2.1564	34382.6213	1206.7216	48.5809		19.226	BB	1.5983	288.8049	9.7487	4.5296
	20.969	BB	3.4469	36391.3330	1036.4913	51.4191		21.529	BB	4.0733	6087.1142	165.5799	95.4704

Ethyl (*S*, *Z*)-2-amino-2-phenethyl-4, 5-diphenylpent-4-enoate (4r):

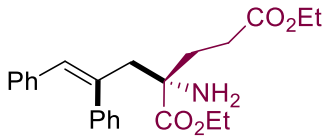


White solid (40.0 mg, 50%); m.p. = 71-73 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 24.908 min, t_R(minor) 22.406 min; $[\alpha]_D^{20}$ = -72.63 (c= 0.486, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.29 – 7.21 (m, 5H), 7.19 – 7.10 (m, 5H), 7.10 – 7.02 (m, 3H), 6.87 (dd, *J* = 7.3, 2.3 Hz, 2H), 6.55 (s, 1H), 3.84 – 3.70 (m, 1H), 3.53 – 3.38 (m, 1H), 3.21 (d, *J* = 13.4 Hz, 1H), 2.76 (d, *J* = 13.4 Hz, 1H), 2.67 (td, *J* = 12.7, 5.3 Hz, 1H), 2.38 (td, *J* = 12.8, 4.6 Hz, 1H), 2.10 (td, *J* = 12.8, 4.7 Hz, 1H), 1.88 (td, *J* = 12.8, 5.3 Hz, 1H), 1.77 (s, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.1, 141.6, 140.1, 138.0, 136.8, 131.5, 129.2, 129.1, 127.9, 127.3, 126.6, 125.9, 60.8, 60.8, 50.1, 43.3, 30.4, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2270.

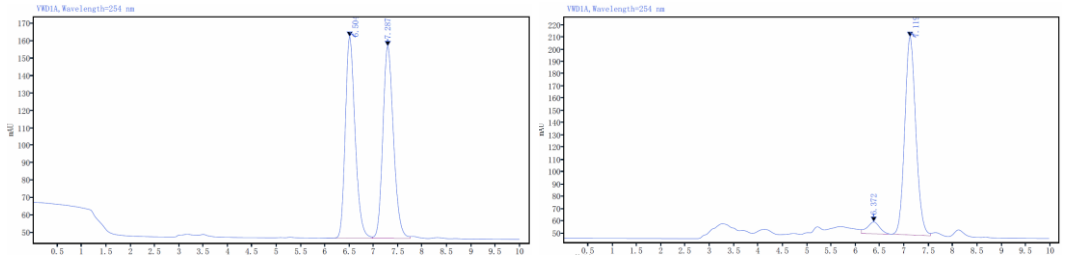


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	22.009	BV	6.9876	51982.1566	1086.1087	49.9376		22.406	BB	2.1933	556.5428	11.2501	5.7016
	24.803	VB	4.4808	52112.1317	1058.6024	50.0624		24.908	BB	2.5783	9204.6105	202.8058	94.2984

Diethyl (*S*, *Z*)-2-amino-2-(2,3-diphenylallyl)pentanedioate (4s):



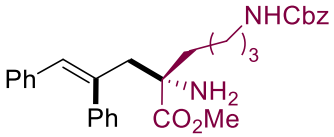
Light yellow oil (32.0 mg, 41%); R_f = 0.2 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 87% by HPLC analysis on Daicel Chirapak AS-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.119 min, t_R(minor) 6.372 min; $[\alpha]_D^{20}$ = -17.56 (c= 0.3, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.21 – 7.12 (m, 3H), 7.06 (d, *J* = 8.4 Hz, 2H), 7.03 – 6.97 (m, 3H), 6.82 – 6.76 (m, 2H), 6.45 (s, 1H), 4.03 (q, *J* = 7.2 Hz, 2H), 3.74 – 3.62 (m, 1H), 3.47 – 3.35 (m, 1H), 3.10 (d, *J* = 13.5 Hz, 1H), 2.67 (d, *J* = 13.5 Hz, 1H), 2.39 – 2.29 (m, 1H), 2.17 – 2.08 (m, 1H), 2.07 – 1.98 (m, 1H), 1.88 – 1.77 (m, 1H), 1.60 (s, 2H), 1.16 (t, *J* = 7.2 Hz, 3H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 173.2, 140.0, 137.8, 136.7, 131.6, 129.1, 129.1, 128.4, 127.8, 127.3, 126.6, 61.0, 60.4, 60.3, 49.9, 35.8, 29.2, 14.2, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{24}H_{30}NO_4^+$ 396.2169; found 396.2167.



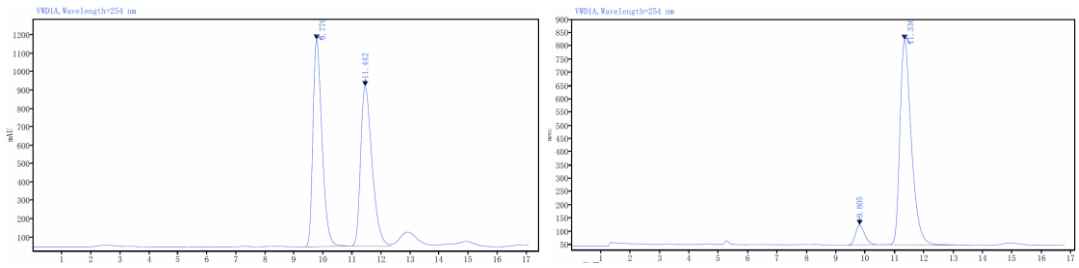
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.504	BV	0.9402	1624.8139	115.5437	49.2092
	7.287	VV	0.7748	1677.0389	110.2351	50.7908

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.372	VB	0.6108	173.4765	9.6526	6.3441
	7.119	BV	0.8065	2560.9838	161.3445	93.6559

Methyl (*S*, *Z*)-2-amino-6-(((benzyloxy)carbonyl)amino)-2-(2,3-diphenylallyl)hexanoate (4t):



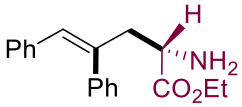
Colorless oil (41.0 mg, 42%); R_f = 0.35 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 86% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 1.336 min, t_R(minor) 9.805 min; $[\alpha]_D^{20}$ = -63.77 (c= 0.38, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.25 (m, 4H), 7.25 – 7.21 (m, 1H), 7.20 – 7.11 (m, 3H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.02 – 6.96 (m, 3H), 6.80 (dd, *J* = 7.1, 2.6 Hz, 2H), 6.45 (s, 1H), 5.01 (s, 2H), 4.70 (s, 1H), 3.12 (s, 3H), 3.08 (d, *J* = 13.5 Hz, 2H), 2.63 (d, *J* = 13.4 Hz, 1H), 1.74 – 1.59 (m, 4H), 1.52 – 1.44 (m, 1H), 1.41 – 1.34 (m, 2H), 1.35 – 1.25 (m, 1H), 1.06 – 0.93 (m, 1H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 176.6, 156.4, 139.8, 137.8, 136.7, 136.6, 131.5, 129.2, 129.1, 128.5, 128.4, 128.1, 127.9, 127.3, 126.7, 66.6, 60.7, 51.6, 50.1, 40.7, 30.0, 20.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{30}H_{35}N_2O_4^+$ 487.2591; found 487.2589.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	9.770	BB	1.6115	24322.5563	1124.9995	50.4926
	11.442	BV	1.3937	23848.0145	869.0115	49.5074

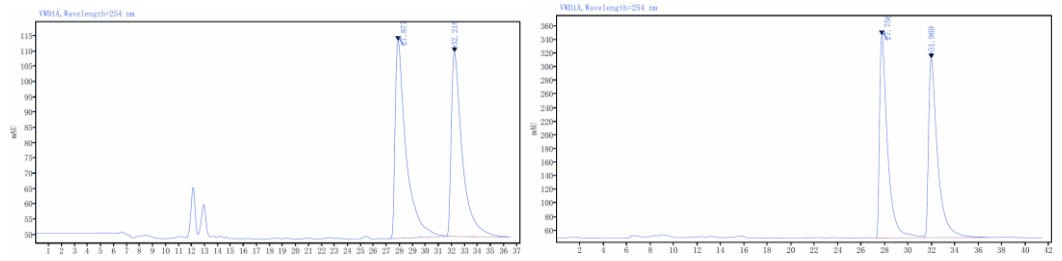
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	9.805	BB	1.2129	1622.3047	74.1899	7.2105
	11.336	BB	2.8767	20876.8145	773.2218	92.7895

Ethyl (*S*, *Z*)-2-amino-4,5-diphenylpent-4-enoate (4u):



Light yellow oil (36.0 mg, 61%); R_f = 0.28 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 0% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R 27.756 min, t_R 31.969 min; $[\alpha]_D^{20}$ = 0 (c= 0.32, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.36 – 7.25 (m, 3H), 7.20 (d, *J* = 8.4 Hz, 2H), 7.14 – 7.02 (m, 3H), 6.92 (d, *J* = 8.1 Hz, 2H), 6.52 (s, 1H), 4.14 – 3.93 (m, 2H), 3.45 (dd, *J* = 8.1, 5.6 Hz, 1H), 3.01 (dd, *J* = 13.7, 5.5 Hz, 1H), 2.74 (dd, *J* = 13.7, 8.1 Hz, 1H), 1.61 (s, 2H), 1.22 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.2, 139.7, 138.4, 136.7, 129.9,

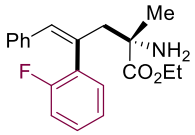
129.1, 128.8, 128.7, 127.9, 127.4, 126.6, 60.9, 52.7, 46.1, 14.2; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{22}NO_2^+$ 296.1645; found 296.1645.



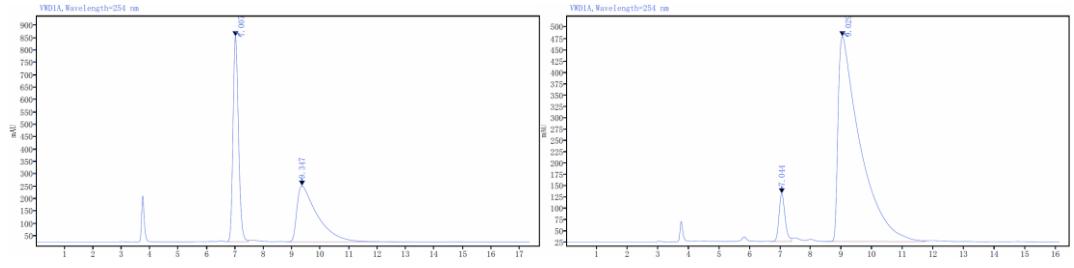
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	27.877	BB	4.5297	3796.4377	64.4010	51.7226
2	32.218	BBA	4.9500	3543.5600	60.0667	48.2774

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	27.756	BV	4.1799	14126.1184	296.8656	49.9471
2	31.969	VB	5.8251	14156.0595	262.7622	50.0529

Ethyl (*S*, *Z*)-2-amino-4-(2-fluorophenyl)-2-methyl-5-phenylpent-4-enoate (5a):



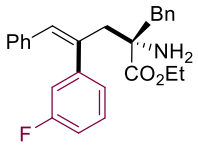
Colorless oil (34.5 mg, 52%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 9.029 min, t_R(minor) 7.044 min; $[\alpha]_D^{20}$ = -58.08 (c= 0.842, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.25 – 7.18 (m, 1H), 7.13 – 7.06 (m, 4H), 7.05 – 6.97 (m, 2H), 6.93 – 6.86 (m, 2H), 6.68 (s, 1H), 3.85 – 3.62 (m, 1H), 3.56 – 3.39 (m, 1H), 3.22 (d, *J* = 13.6 Hz, 1H), 2.74 (d, *J* = 13.6 Hz, 1H), 1.77 (s, 2H), 1.34 (s, 3H), 1.08 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 177.0, 160.0 (d, *J* = 246.9 Hz), 136.6, 133.8, 132.0, 131.5 (d, *J* = 3.8 Hz), 129.3 (d, *J* = 8.0 Hz), 128.6, 128.0 , 127.4 (d, *J* = 15.8 Hz), 126.9, 124.1 (d, *J* = 3.4 Hz), 115.8 (d, *J* = 22.3 Hz), 60.8, 57.3, 50.0, 27.8, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{23}FNO_2^+$ 328.1707; found 328.1706.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.007	VV	0.7727	11124.0804	828.9050	49.8971
2	9.347	BB	3.9196	11169.9834	225.4376	50.1029

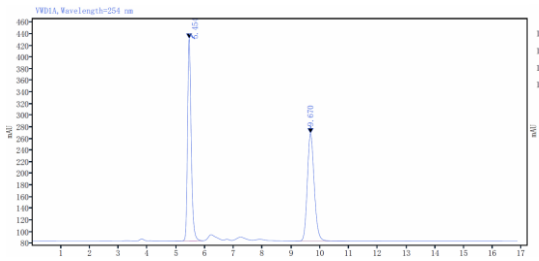
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.044	BV	0.6553	1441.9680	105.6181	5.9779
2	9.029	BV	3.2423	22679.8027	452.5030	94.0221

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(3-fluorophenyl)-5-phenylpent-4-enoate (5b):

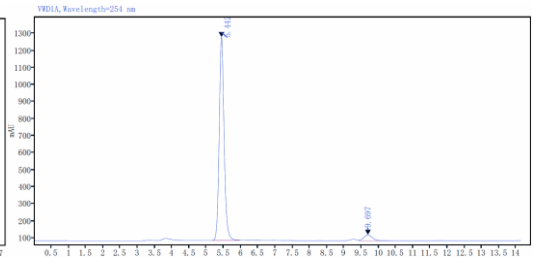


White solid (57.0 mg, 71%); m.p. = 61-63 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.442 min, t_R(minor) 9.697 min; $[\alpha]_D^{20}$ = -47.72 (c= 1.128, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.28 – 7.15 (m, 4H), 7.13 (d, *J* = 9.6 Hz, 2H), 7.10 – 7.04 (m, 3H), 6.97 – 6.83 (m, 5H), 6.62 (s, 1H), 3.83 – 3.71 (m, 1H), 3.59 – 3.45 (m, 1H), 3.32 (d, *J* = 13.6 Hz, 1H), 3.24 (d, *J* = 13.1 Hz, 1H), 2.79 (t, *J* =

12.8 Hz, 2H), 1.63 (s, 2H), 1.10 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 162.8 (d, *J* = 246.4 Hz), 142.4 (d, *J* = 7.2 Hz), 136.5, 136.3, 136.0, 132.4, 130.1, 130.0, 129.9, 129.1, 128.4, 128.0, 127.0 (d, *J* = 17.7 Hz), 125.2 (d, *J* = 2.9 Hz), 116.1 (d, *J* = 21.3 Hz), 114.2 (d, *J* = 21.0 Hz), 61.8, 60.9, 50.2, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}FNO_2^+$ 404.2020; found 404.2018.

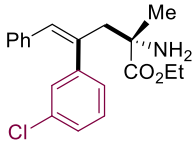


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.454	BV	0.9660	3051.4466	347.3775	49.8117
	9.670	BB	1.8800	3074.5206	184.8126	50.1883

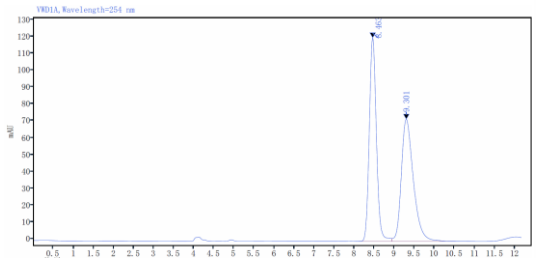


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.442	BV	0.8776	11711.3380	1192.6251	95.2291
	9.697	VB	1.0138	586.7317	33.8672	4.7709

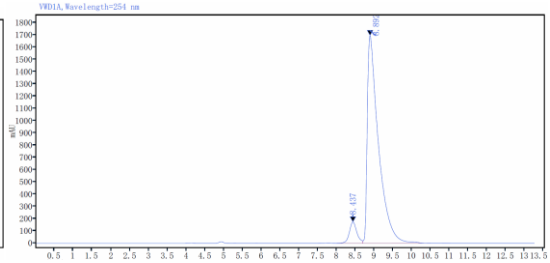
Ethyl (*S*, *Z*)-2-amino-4-(3-chlorophenyl)-2-methyl-5-phenylpent-4-enoate (5c):



Colorless oil (45.2 mg, 66%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 87% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R(major) 8.892 min, t_R(minor) 8.437 min; $[\alpha]_D^{20}$ = -61.9 (c= 0.812, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.20 (d, *J* = 12.7 Hz, 2H), 7.15 (t, *J* = 7.6 Hz, 1H), 7.09 (s, 3H), 6.99 (d, *J* = 7.5 Hz, 1H), 6.88 (d, *J* = 6.8 Hz, 2H), 6.58 (s, 1H), 3.84 – 3.72 (m, 1H), 3.59 – 3.47 (m, 1H), 3.13 (d, *J* = 13.5 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 1.70 (s, 2H), 1.34 (s, 3H), 1.19 – 1.02 (m, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.8, 142.0, 136.7, 136.3, 134.2, 132.2, 129.6, 129.1, 129.0, 128.0, 127.8, 127.4, 126.9, 61.0, 57.5, 50.7, 27.6, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{23}ClNO_2^+$ 344.1412; found 344.1411.

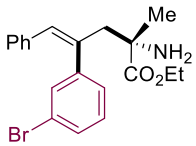


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.463	BV	0.8188	1492.5176	120.6377	49.7532
	9.301	VB	1.5862	1507.3268	72.3594	50.2468



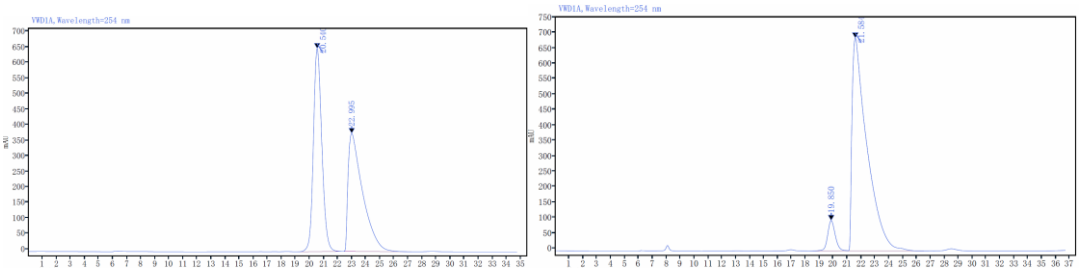
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	8.437	VV	0.7120	2430.4574	174.1027	6.4970
	8.892	VB	1.7970	34978.2291	1694.5482	93.5030

Ethyl (*S*, *Z*)-2-amino-4-(3-bromophenyl)-2-methyl-5-phenylpent-4-enoate (5d):



Colorless oil (58.5 mg, 75%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 86% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 21.584 min, t_R(minor) 19.850 min; $[\alpha]_D^{20}$ = -59.09 (c= 1.192, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.38 – 7.31 (m, 2H),

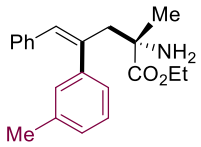
7.17 – 7.05 (m, 4H), 7.08 – 6.98 (m, 1H), 6.88 (dd, *J* = 7.3, 2.2 Hz, 2H), 6.57 (s, 1H), 3.88 – 3.68 (m, 1H), 3.64 – 3.42 (m, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 1.73 (s, 2H), 1.34 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.8, 142.3, 136.6, 136.3, 132.2, 131.9, 130.3, 129.9, 129.1, 128.2, 128.0, 126.9, 122.3, 61.0, 57.4, 50.7, 27.6, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{23}BrNO_2^+$ 388.0907; found 388.0905.



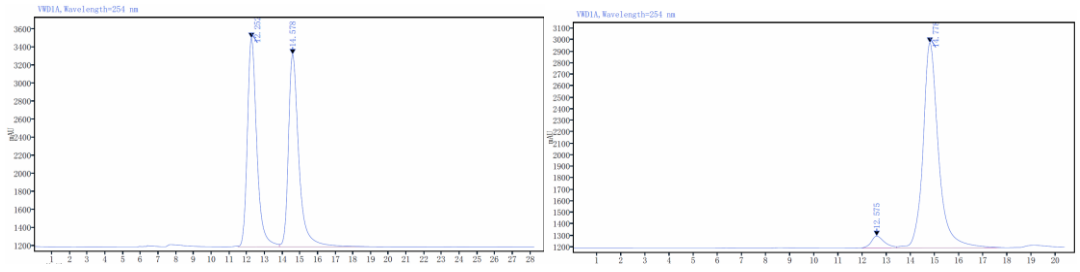
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	20.540	BB	3.2183	27211.2673	653.0698	49.9772
2	22.995	BB	4.8633	27236.1059	379.6965	50.0228

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	19.850	BV	2.7194	3740.1115	98.4961	6.7508
2	21.584	VB	5.4456	51662.5372	690.2695	93.2492

Ethyl (*S*, *Z*)-2-amino-2-methyl-5-phenyl-4-(m-tolyl)pent-4-enoate (5e):



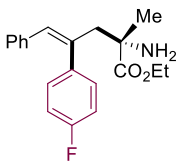
Colorless oil (58.2 mg, 90%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak AS-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 14.778 min, t_R(minor) 12.575 min; $[\alpha]_D^{20}$ = -49.52 (c= 1.102, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.12 (t, *J* = 7.6 Hz, 1H), 7.09 – 7.00 (m, 4H), 6.98 (d, *J* = 2.3 Hz, 1H), 6.94 – 6.86 (m, 3H), 6.51 (s, 1H), 3.91 – 3.66 (m, 1H), 3.60 – 3.47 (m, 1H), 3.13 (d, *J* = 13.4 Hz, 1H), 2.74 (d, *J* = 13.4 Hz, 1H), 2.28 (s, 3H), 1.72 (s, 2H), 1.33 (s, 3H), 1.09 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.9, 140.0, 138.4, 137.9, 136.9, 131.0, 129.5, 129.0, 128.3, 128.0, 127.8, 126.5, 126.3, 60.8, 57.7, 51.1, 27.8, 21.4, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{26}NO_2^+$ 324.1958; found 324.1957.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.252	VV	2.3386	85277.5715	2306.3264	49.4559
2	14.578	VB	5.8582	87154.0758	2125.1197	50.5441

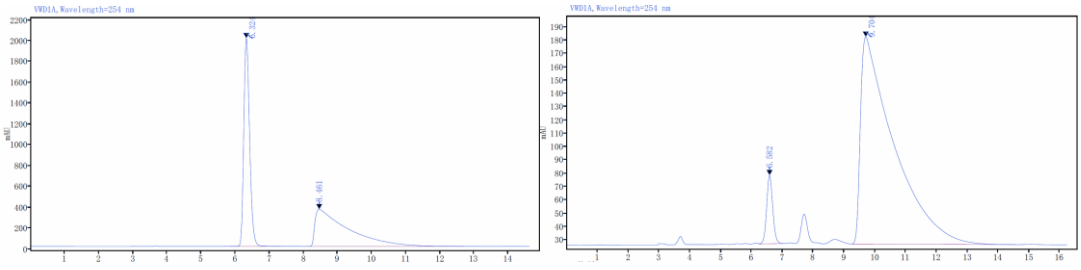
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.575	BV	1.7035	3923.1187	102.8734	4.7028
2	14.778	VB	4.5734	79497.6236	1780.5101	95.2972

Ethyl (*S*, *Z*)-2-amino-4-(4-fluorophenyl)-2-methyl-5-phenylpent-4-enoate (5f):



White solid (42.2 mg, 63%); m.p. = 49-51 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 9.704 min,

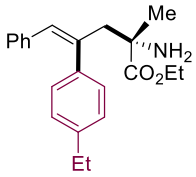
t_R(minor) 6.582 min; $[\alpha]_D^{20}$ = -58.20 (c= 0.768, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.14 – 7.05 (m, 5H), 6.95 (t, *J* = 8.7 Hz, 2H), 6.88 – 6.84 (m, 2H), 6.55 (s, 1H), 3.94 – 3.70 (m, 1H), 3.69 – 3.36 (m, 1H), 3.12 (d, *J* = 13.5 Hz, 1H), 2.74 (d, *J* = 13.5 Hz, 1H), 1.70 (s, 2H), 1.33 (s, 3H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.9, 162.8, 161.2, 136.9 (d, *J* = 78.7 Hz), 135.9 (d, *J* = 3.6 Hz), 131.6, 130.9 (d, *J* = 7.9 Hz), 129.0, 128.0, 126.7, 115.3 (d, *J* = 21.3 Hz), 60.9, 57.6, 50.9, 27.6, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{23}FNO_2^+$ 328.1707; found 328.1706.



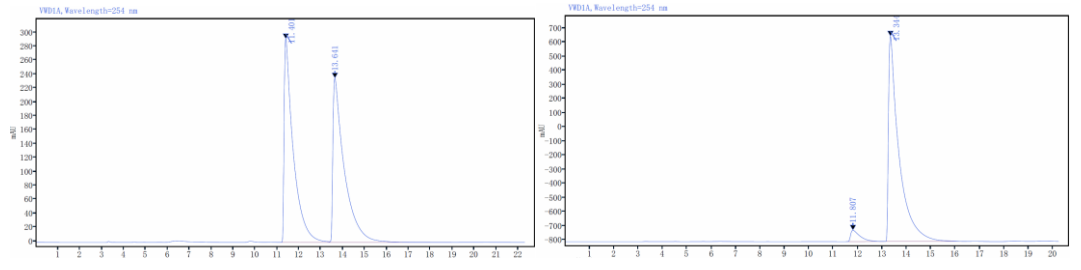
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.324	VB	1.5162	23667.0302	1998.0240	49.7543
2	8.461	BB	4.6537	23900.7440	355.4215	50.2457

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.582	VB	0.7885	700.0148	51.5081	5.6370
2	9.704	VB	5.3752	11718.2784	155.7881	94.3630

Ethyl (*S*, *Z*)-2-amino-4-(4-ethylphenyl)-2-methyl-5-phenylpent-4-enoate (5g):



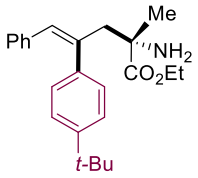
White solid (57.1 mg, 85%); m.p. = 53-55 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 13.344 min, t_R(minor) 11.807 min; $[\alpha]_D^{20}$ = -66.8 (c= 1.032, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.06 (q, *J* = 8.2 Hz, 7H), 6.90 (d, *J* = 6.0 Hz, 2H), 6.51 (s, 1H), 3.97 – 3.67 (m, 1H), 3.56 – 3.39 (m, 1H), 3.13 (d, *J* = 13.3 Hz, 1H), 2.73 (d, *J* = 13.4 Hz, 1H), 2.61 (q, *J* = 7.6 Hz, 2H), 1.69 (s, 2H), 1.33 (s, 3H), 1.20 (t, *J* = 7.6 Hz, 3H), 1.07 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 177.0, 143.3, 138.3, 137.1, 137.0, 130.8, 129.1, 129.0, 127.8, 127.8, 126.4, 60.8, 57.6, 51.1, 28.6, 27.7, 15.5, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{28}NO_2^+$ 338.2115; found 338.2113.



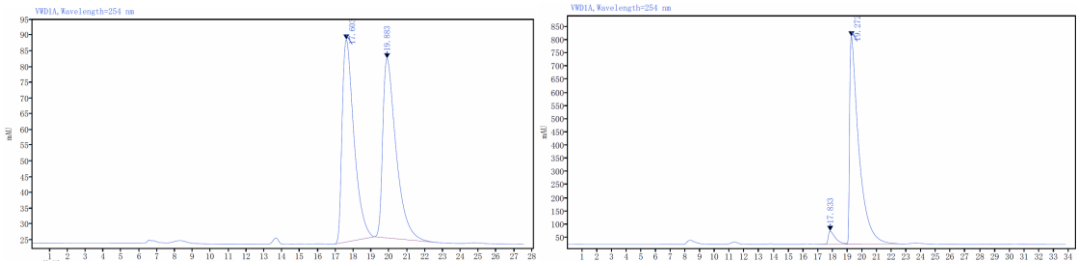
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	11.401	BV	2.2236	8407.5098	292.4021	49.7234
2	13.641	VB	5.5431	8501.0608	236.0137	50.2766

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	11.807	BB	1.6067	2118.1326	80.0693	4.6667
2	13.344	BB	3.3692	43269.8002	1455.1874	95.3333

Ethyl (*S*, *Z*)-2-amino-4-(4-(tert-butyl)phenyl)-2-methyl-5-phenylpent-4-enoate (5h):



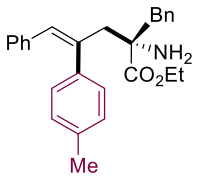
White solid (44.4 mg, 60%); m.p. = 76-78 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak ID-H column (hexane/isopropanol = 98/2, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 19.272 min, t_R(minor) 17.833 min; $[\alpha]_D^{20}$ = -71.75 (c= 0.806, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.28 – 7.24 (m, 2H), 7.08 – 7.01 (m, 5H), 6.89 (d, *J* = 7.7 Hz, 2H), 6.51 (s, 1H), 3.82 – 3.57 (m, 1H), 3.47 – 3.30 (m, 1H), 3.15 (d, *J* = 13.3 Hz, 1H), 2.72 (d, *J* = 13.3 Hz, 1H), 1.72 (s, 2H), 1.33 (s, 3H), 1.29 (s, 9H), 1.04 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 177.0, 150.2, 138.2, 137.0, 136.8, 130.9, 129.0, 128.8, 127.8, 126.4, 125.2, 60.7, 57.4, 51.0, 34.5, 31.3, 27.8, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{24}H_{32}NO_2^+$ 366.2428; found 366.2428.



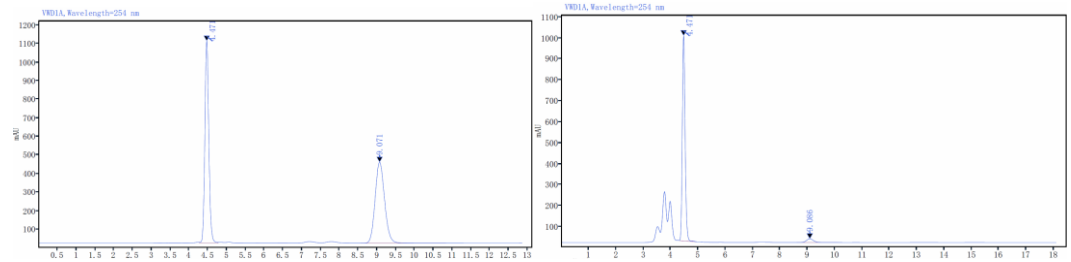
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	17.603	BB	2.2380	2970.2925	64.2276	50.1224
2	19.883	BB	3.5367	2955.7870	56.9721	49.8776

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	17.833	BV	1.7398	1652.9967	49.6281	4.6040
2	19.272	VB	3.8568	34250.4733	788.0380	95.3960

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-phenyl-4-(p-tolyl)pent-4-enoate(5i):



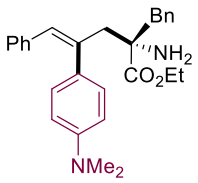
Colorless oil (51.1 mg, 64%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.471 min, t_R(minor) 9.086 min; $[\alpha]_D^{20}$ = -38.46 (c= 1.066, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.31 – 7.17 (m, 3H), 7.13 (d, *J* = 6.7 Hz, 2H), 7.11 – 6.99 (m, 7H), 6.92 – 6.87 (m, 2H), 6.55 (s, 1H), 3.85 – 3.59 (m, 1H), 3.53 – 3.42 (m, 1H), 3.31 (d, *J* = 13.3 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.79 (dd, *J* = 19.3, 13.2 Hz, 2H), 2.30 (s, 3H), 1.61 (s, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 138.0, 137.0, 136.9, 136.2, 131.1, 130.0, 129.1, 129.1, 128.3, 127.8, 126.9, 126.5, 61.9, 60.8, 50.6, 47.0, 21.2, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2269.



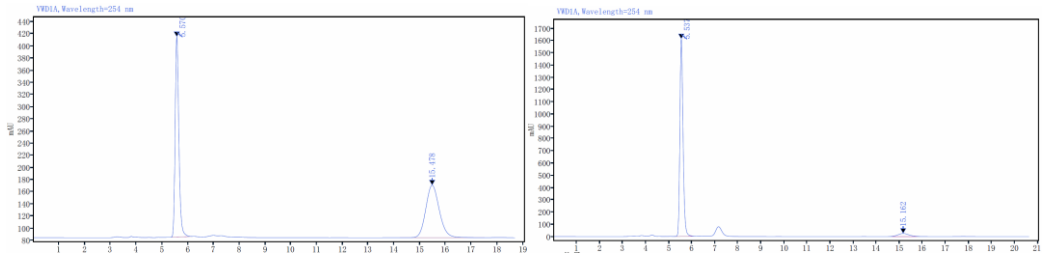
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.471	VV	0.4968	7954.5725	1087.8458	51.0636
	9.071	BB	2.2667	7623.2030	436.1167	48.9364

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.471	VB	0.6613	6911.4065	977.2289	95.6483
	9.086	BB	1.8800	314.4446	17.6748	4.3517

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-(dimethylamino)phenyl)-5-phenylpent-4-enoate (5j):



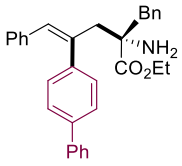
White solid (55.2 mg, 64%); m.p. = 70-72 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.537 min, t_R(minor) 15.162 min; $[\alpha]_D^{20}$ = -40.32 (c= 1.102, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.26 – 7.18 (m, 3H), 7.16 – 7.12 (m, 2H), 7.11 – 7.06 (m, 2H), 7.06 – 6.99 (m, 3H), 6.96 (d, *J* = 7.2 Hz, 2H), 6.60 (d, *J* = 8.7 Hz, 2H), 6.48 (s, 1H), 3.83 – 3.66 (m, 1H), 3.63 – 3.50 (m, 1H), 3.27 (dd, *J* = 25.8, 13.3 Hz, 2H), 2.91 (s, 6H), 2.78 (dd, *J* = 13.2, 10.1 Hz, 2H), 1.59 (s, 2H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.7, 149.8, 138.1, 137.5, 136.4, 130.0, 130.0, 129.9, 129.0, 128.2, 127.8, 127.4, 126.9, 126.2, 112.3, 62.1, 60.7, 50.5, 47.0, 40.5, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{28}H_{33}N_2O_2^+$ 429.2537; found 429.2532.



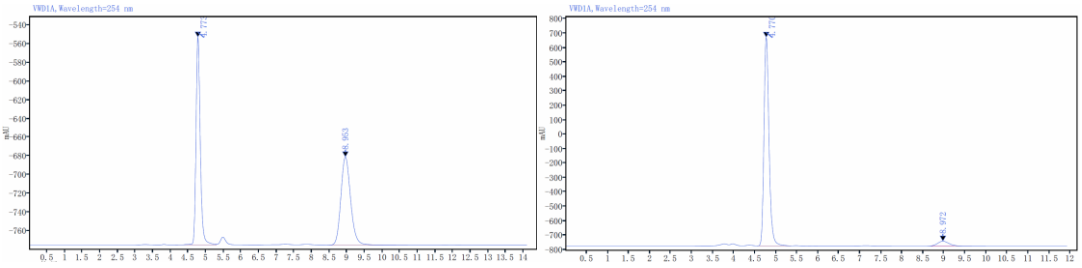
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.570	BB	0.8310	3296.2948	329.7378	51.2770
	15.478	BB	3.2717	3132.1154	86.3216	48.7230

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.537	BB	0.9462	15518.6533	1612.6188	94.6607
	15.162	BB	2.7083	875.3155	25.3840	5.3393

Ethyl (*S*, *Z*)-4-([1,1'-biphenyl]-4-yl)-2-amino-2-benzyl-5-phenylpent-4-enoate (5k):



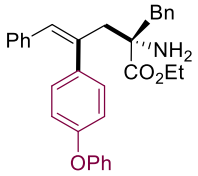
Colorless oil (67.1 mg, 73%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.770 min, t_R(minor) 8.972 min; $[\alpha]_D^{20}$ = -57.73 (c= 1.284, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.50 (d, *J* = 8.2 Hz, 2H), 7.42 (t, *J* = 7.8 Hz, 2H), 7.33 (t, *J* = 7.4 Hz, 1H), 7.26 – 7.17 (m, 5H), 7.14 (d, *J* = 6.3 Hz, 2H), 7.12 – 7.02 (m, 3H), 6.94 (d, *J* = 7.6 Hz, 2H), 6.63 (s, 1H), 3.76 – 3.62 (m, 1H), 3.52 – 3.42 (m, 1H), 3.38 (d, *J* = 13.3 Hz, 1H), 3.26 (d, *J* = 13.2 Hz, 1H), 2.82 (dd, *J* = 27.3, 13.3 Hz, 2H), 1.66 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 140.6, 140.0, 139.0, 137.5, 136.7, 136.1, 131.7, 130.0, 129.8, 129.1, 128.8, 128.4, 128.0, 127.4, 127.0, 127.0, 126.9, 126.7, 61.8, 60.8, 50.4, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{32}H_{32}NO_2^+$ 462.2428; found 462.2427.



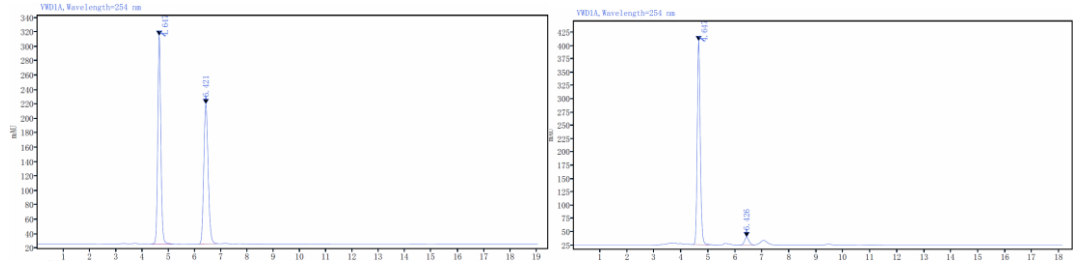
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.773	BV	1.1700	1848.7805	221.3740	50.7894
2	8.953	BB	2.2733	1791.3101	93.8501	49.2106

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.770	BV	0.7960	12025.8042	1445.1636	94.9718
2	8.972	BB	1.1417	636.6984	33.4973	5.0282

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-phenoxyphenyl)-5-phenylpent-4-enoate (5l):



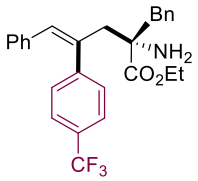
Colorless oil (54.9 mg, 58%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.647 min, t_R(minor) 6.426 min; $[\alpha]_D^{20}$ = -60.84 (c= 1.064, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.35 – 7.29 (m, 2H), 7.27 – 7.18 (m, 3H), 7.15 (d, *J* = 6.6 Hz,2H), 7.12 – 7.06 (m, 6H), 6.99 (d, *J* = 8.7 Hz, 2H), 6.90 (dd, *J* = 13.1, 7.6 Hz, 4H), 6.59 (s, 1H), 3.89 – 3.72 (m, 1H), 3.63 – 3.51 (m, 1H), 3.33 (d, *J* = 13.4 Hz, 1H), 3.26 (d, *J* = 13.1 Hz, 1H), 2.85 – 2.75 (m, 2H), 1.64 (s, 2H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 157.0, 156.5, 137.3, 136.8, 136.1, 134.8, 131.6, 130.7, 130.0, 129.8, 129.1, 128.4, 127.9, 127.0, 126.7, 123.4, 118.9, 118.7, 61.8, 60.8, 50.4, 47.0, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{32}H_{32}NO_3^+$ 478.2377; found 478.2378.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.647	VB	1.0766	2361.2240	288.7155	51.2893
2	6.421	BB	0.8345	2242.5116	193.8275	48.7107

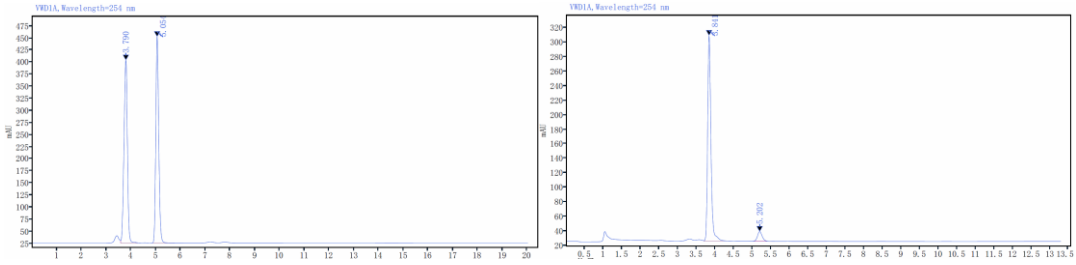
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.647	BB	0.9581	2983.5654	382.1668	94.7794
2	6.426	BV	0.5542	164.3385	14.2259	5.2206

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)pent-4-enoate (5m):



White solid (46.8 mg, 52%); m.p. = 95-97 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 3.841 min, t_R(minor) 5.202 min; $[\alpha]_D^{20}$ = -50.81 (c= 0.982, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.51 (d, *J* = 8.1 Hz, 2H), 7.31 – 7.18 (m, 5H), 7.15 – 7.06 (m, 5H), 6.93 – 6.81 (m, 2H), 6.68 (s, 1H), 3.72 – 3.62 (m, 1H), 3.42 – 3.36 (m, 1H), 3.34 (d, *J* = 13.5 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.80 (dd, *J* = 28.7, 13.3 Hz, 2H), 1.60 (s, 2H), 1.04 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.5, 144.0, 136.4, 136.1, 135.9, 132.9, 130.0, 129.8, 129.4 (d, *J* = 32.4 Hz), 129.1, 128.4, 128.1, 127.1 (d, *J* = 5.3 Hz), 125.3 (q, *J* = 3.8 Hz), 124.1 (d, *J* = 271.9 Hz), 61.7, 60.9, 50.1, 46.9, 13.9;

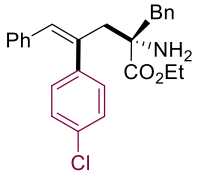
HRMS(ESI) m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}F_3NO_2^+$ 454.1988; found 454.1987.



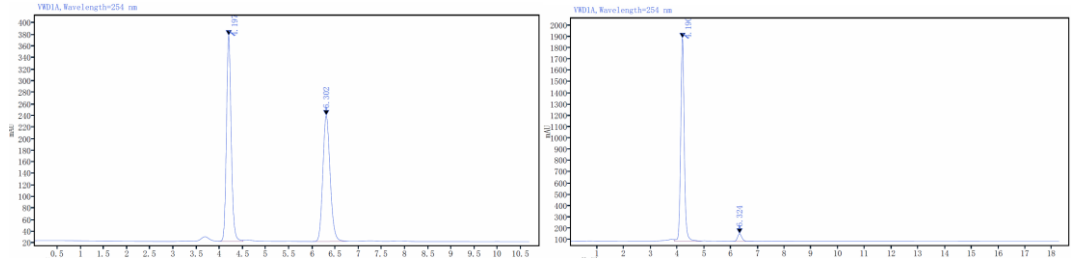
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	3.790	VB	0.7802	3634.4229	378.5458	50.6988
2	5.054	BB	0.9164	3534.2371	426.9388	49.3012

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	3.841	VB	0.7180	1730.8803	282.3624	93.7073
2	5.202	BB	0.6967	116.2326	13.2555	6.2927

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-chlorophenyl)-5-phenylpent-4-enoate (5n):



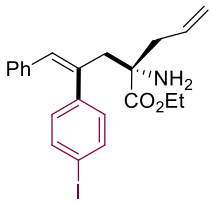
White solid (61.4 mg, 73%); m.p. = 89-91 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.190 min, t_R(minor) 6.324 min; $[\alpha]_D^{20}$ = -47.5 (c= 1.2, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.17 (m, 5H), 7.16 – 7.02 (m, 7H), 6.95 – 6.83 (m, 2H), 6.61 (s, 1H), 3.80 – 3.70 (m, 1H), 3.55 – 3.44 (m, 1H), 3.30 (d, *J* = 13.4 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.78 (t, *J* = 13.4 Hz, 2H), 1.60 (s, 2H), 1.09 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.5, 138.5, 136.6, 136.4, 136.0, 133.2, 132.2, 130.7, 129.9, 129.1, 128.6, 128.4, 128.0, 127.0, 126.9, 61.8, 60.9, 50.2, 46.9, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}ClNO_2^+$ 420.1725; found 420.1723.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.197	VV	0.5327	2527.4239	355.3273	51.4228
2	6.302	BB	0.8625	2387.5647	217.4201	48.5772

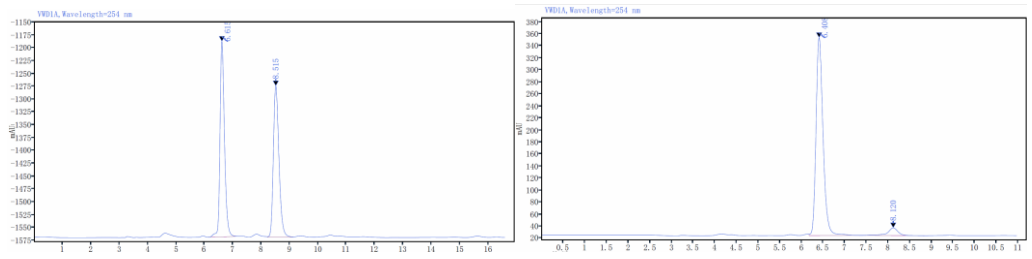
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.190	VV	0.9963	16696.9192	1800.1824	95.6757
2	6.324	BB	0.7633	754.6600	67.2431	4.3243

Ethyl (*S*, *Z*)-2-allyl-2-amino-4-(4-iodophenyl)-5-phenylpent-4-enoate (5o):



Colorless oil (52.7 mg, 56%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 6.408 min, t_R(minor) 8.120 min; $[\alpha]_D^{20}$ = -51.84 (c= 1.030, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.58 (d, *J* = 8.4 Hz, 2H), 7.15 – 7.05 (m, 3H), 6.92 – 6.85 (m, 4H), 6.57 (s, 1H), 5.77 – 5.46 (m, 1H), 5.19 – 4.99 (m, 2H), 3.90 – 3.64 (m, 1H), 3.59 – 3.44 (m, 1H), 3.12 (d, *J* = 13.4 Hz, 1H), 2.71 (d, *J* = 13.4 Hz, 1H), 2.59 (dd, *J* = 13.4, 6.3 Hz, 1H), 2.25 (dd, *J* = 13.4, 8.5 Hz, 1H), 1.69 (s, 2H), 1.11 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.8, 139.6, 137.5, 136.6,

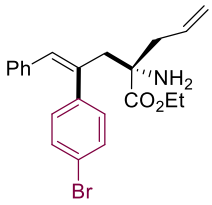
136.4, 132.3, 132.0, 131.2, 129.0, 128.0, 126.9, 119.8, 92.8, 60.9, 60.4, 49.6, 45.2, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{25}INO_2^+$ 462.0924; found 462.0923.



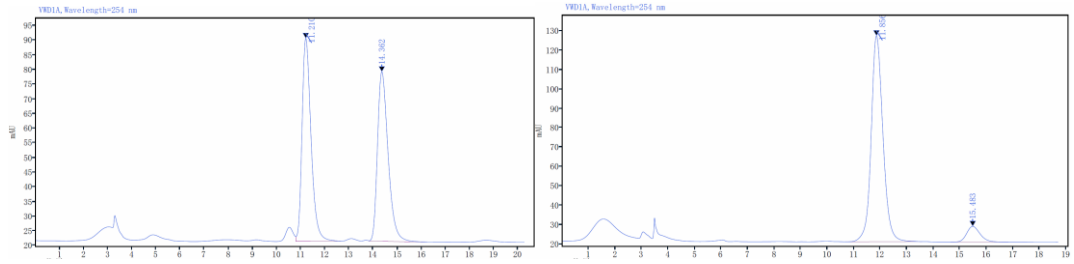
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.615	BB	1.0407	4184.3292	380.6025	50.9907
2	8.515	VV	0.9055	4021.7409	294.5783	49.0093

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.408	VB	1.2078	3698.8110	329.1166	94.5577
2	8.120	BB	1.4500	212.8870	12.7723	5.4423

Ethyl (*S*, *Z*)-2-allyl-2-amino-4-(4-bromophenyl)-5-phenylpent-4-enoate (5p):



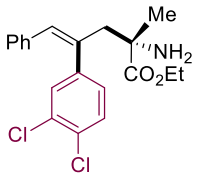
Colorless oil (52.7 mg, 63%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 84% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 11.856 min, t_R(minor) 15.483 min; $[\alpha]_D^{20}$ = -51.12 (c= 1.010, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.40 – 7.35 (m, 2H), 7.14 – 7.07 (m, 3H), 7.04 – 7.00 (m, 2H), 6.94 – 6.80 (m, 2H), 6.58 (s, 1H), 5.70 – 5.55 (m, 1H), 5.18 – 5.09 (m, 2H), 3.86 – 3.73 (m, 1H), 3.59 – 3.47 (m, 1H), 3.13 (d, *J* = 14.5 Hz, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 2.59 (dd, *J* = 13.4, 6.4 Hz, 1H), 2.25 (dd, *J* = 13.4, 8.5 Hz, 1H), 1.68 (s, 2H), 1.11 (t, *J* = 7.1 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.8, 139.0, 136.6, 136.4, 132.2, 132.0, 131.5, 131.0, 129.0, 128.0, 126.9, 121.3, 119.8, 60.9, 60.4, 49.6, 45.2, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{25}BrNO_2^+$ 414.1063; found 414.1062.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	11.210	VB	1.8717	1796.2068	69.2391	50.3700
2	14.362	VB	2.5390	1769.8152	57.8373	49.6300

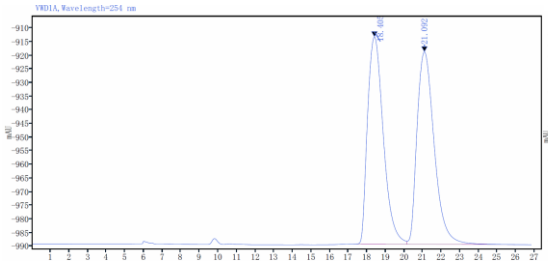
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	11.856	BB	2.8833	3267.8654	105.8601	92.0247
2	15.483	BB	2.1633	283.2086	8.0812	7.9753

Ethyl (*S*, *Z*)-2-amino-4-(3, 4-dichlorophenyl)-2-methyl-5-phenylpent-4-enoate (5q):

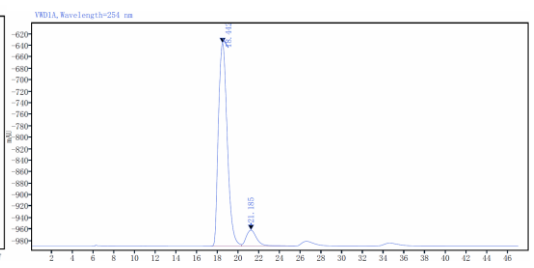


Colorless oil (48.2 mg, 64%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 84% by HPLC analysis on Daicel Chirapak AD-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 18.442 min, t_R(minor) 21.185 min; $[\alpha]_D^{20}$ = -63.26 (c= 0.744, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.35 – 7.22 (m, 2H), 7.17 – 7.08 (m, 3H), 6.94 (dd, *J* = 8.3, 2.1 Hz, 1H), 6.89 (dd, *J* = 7.6, 1.9 Hz, 2H), 6.59 (s, 1H), 3.95 – 3.73 (m, 1H), 3.65 – 3.55 (m, 1H), 3.09 (d, *J* = 13.6 Hz, 1H), 2.72 (d, *J* = 13.7 Hz, 1H), 1.70 (s, 2H), 1.34 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.8,

140.2, 136.0, 135.6, 132.7, 132.4, 131.2, 130.9, 130.3, 129.1, 129.0, 128.1, 127.1, 61.0, 57.6, 50.5, 27.5, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{20}H_{22}Cl_2NO_2^+$ 378.1022; found 378.1021.

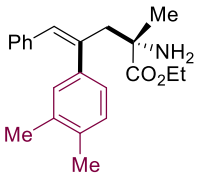


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	18.405	BV	2.8630	4470.3229	75.9839	49.6130
	21.092	VB	5.8003	4540.0641	70.5630	50.3870

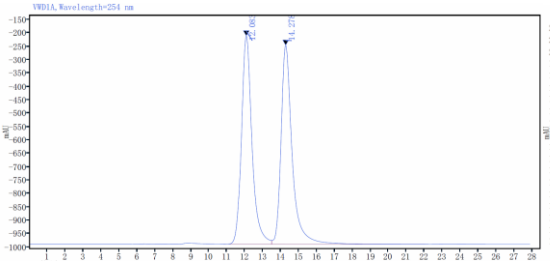


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	18.442	BV	4.0128	20960.6856	353.6487	91.4008
	21.185	VB	5.1272	1972.0200	27.8650	8.5992

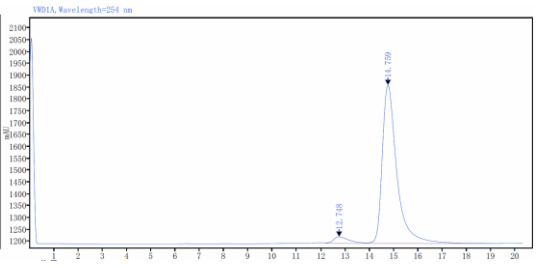
Ethyl (*S*, *Z*)-2-amino-4-(3,4-dimethylphenyl)-2-methyl-5-phenylpent-4-enoate (5r):



Colorless oil (58.3 mg, 86%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak AS-H column (hexane/isopropanol = 99/1, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 14.759 min, t_R(minor) 12.748 min; $[\alpha]_D^{20}$ = -57.26 (c= 1.152, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.11 – 7.01 (m, 3H), 6.98 (d, *J* = 7.7 Hz, 1H), 6.94 – 6.89 (m, 3H), 6.83 (d, *J* = 7.7 Hz, 1H), 6.47 (s, 1H), 3.93 – 3.69 (m, 1H), 3.63 – 3.44 (m, 1H), 3.11 (d, *J* = 13.3 Hz, 1H), 2.72 (d, *J* = 13.4 Hz, 1H), 2.22 (s, 3H), 2.18 (s, 3H), 1.69 (s, 2H), 1.32 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 177.0, 138.4, 137.4, 137.1, 136.4, 135.5, 130.5, 130.0, 129.6, 129.0, 127.8, 126.6, 126.4, 60.8, 57.8, 51.1, 27.8, 19.7, 19.5, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{28}NO_2^+$ 338.2115; found 338.2114.

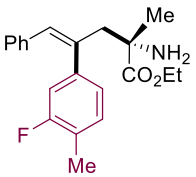


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.083	BV	2.6768	31555.2598	777.1472	49.5448
	14.278	VB	8.7398	32135.0863	742.4016	50.4552



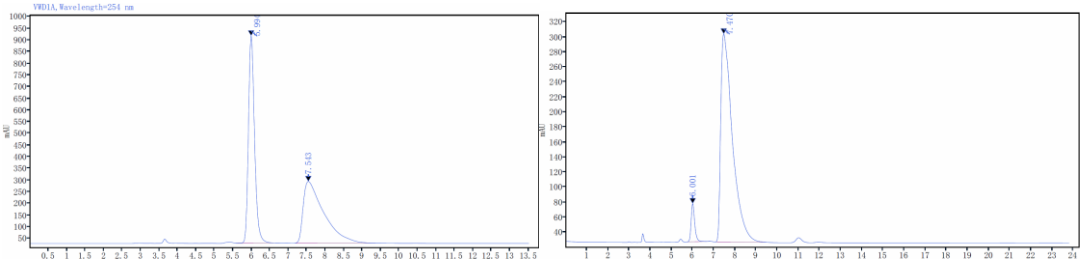
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	12.748	VV	1.6754	1233.3326	27.8134	4.2434
	14.759	VB	5.2350	27831.1458	667.6381	95.7566

Ethyl (*S*, *Z*)-2-amino-4-(3-fluoro-4-methylphenyl)-2-methyl-5-phenylpent-4-enoate (5s):



Colorless oil (53.3 mg, 78%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.470 min, t_R(minor) 6.001 min; $[\alpha]_D^{20}$ = -58.61 (c= 1.022, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.17 – 7.06 (m, 3H), 7.03 (t, J = 7.9 Hz, 1H), 6.95 – 6.87 (m, 2H), 6.85 – 6.75 (m, 2H), 6.53 (s, 1H), 3.88 – 3.76 (m, 1H),

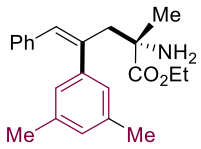
3.68 – 3.55 (m, 1H), 3.31 – 2.93 (m, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 2.24 (d, *J* = 1.8 Hz, 3H), 1.71 (s, 2H), 1.33 (s, 3H), 1.13 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.8, 161.2 (d, *J* = 245.0 Hz), 139.5 (d, *J* = 7.5 Hz), 137.0, 136.6, 131.6, 131.3 (d, *J* = 5.5 Hz), 129.0, 127.9, 126.7, 124.8 (d, *J* = 3.2 Hz), 123.7 (d, *J* = 17.2 Hz), 115.6 (d, *J* = 22.5 Hz), 60.9, 57.7, 50.8, 27.6, 14.3 (d, *J* = 3.3 Hz), 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{21}H_{25}FNO_2^+$ 342.1864; found 342.1863.



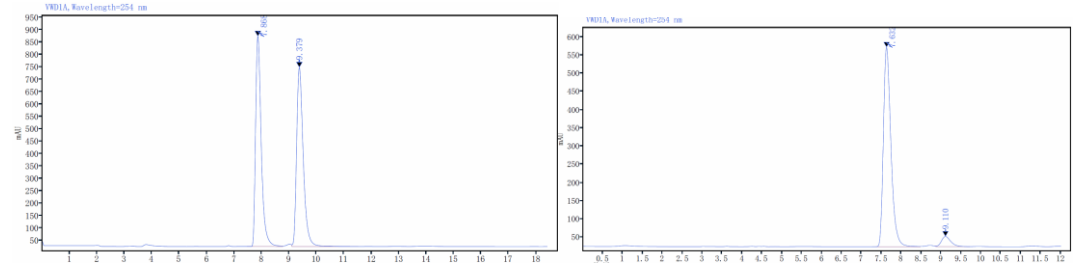
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.994	VB	1.1717	10215.1147	886.8878	50.0363
2	7.543	BB	2.2543	10200.3132	263.8356	49.9637

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.001	MM m	0.1777	594.2795	50.7118	5.2993
2	7.470	MM m	0.5256	10620.0443	276.8353	94.7007

Ethyl (*S*, *Z*)-2-amino-4-(3, 5-dimethylphenyl)-2-methyl-5-phenylpent-4-enoate (5t):



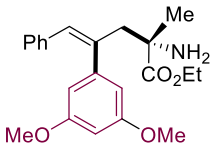
Colorless oil (60.1 mg, 89%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak IG-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.632 min, t_R(minor) 9.110 min; $[\alpha]_D^{20}$ = -32.92 (c=1.144, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.11 – 7.01 (m, 3H), 6.94 – 6.87 (m, 2H), 6.84 (s, 1H), 6.75 (s, 2H), 6.47 (s, 1H), 3.86 – 3.76 (m, 1H), 3.60 – 3.51 (m, 1H), 3.11 (d, *J* = 13.4 Hz, 1H), 2.72 (d, *J* = 13.5 Hz, 1H), 2.22 (s, 6H), 1.73 (s, 2H), 1.33 (s, 3H), 1.10 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 177.0, 140.0, 138.6, 137.7, 136.9, 130.7, 129.0, 128.8, 127.8, 126.7, 126.5, 60.7, 57.7, 51.1, 27.8, 21.3, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{28}NO_2^+$ 338.2115; found 338.2115.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.868	BV	1.3018	12160.5924	849.1489	50.0503
2	9.379	VB	2.4146	12136.1641	723.5266	49.9497

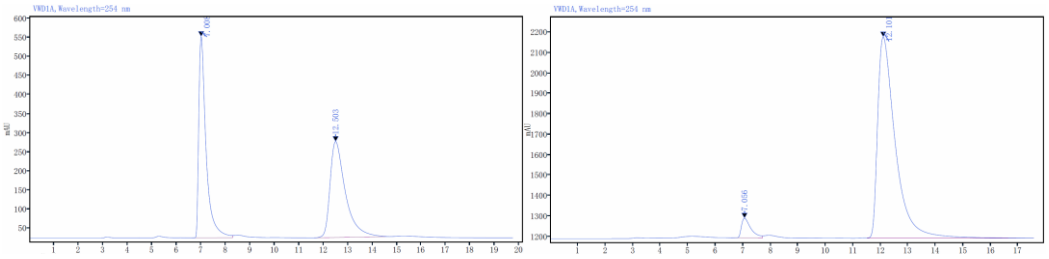
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.632	BV	1.2117	7215.3649	547.4041	94.0517
2	9.110	VB	0.8516	456.3324	28.0058	5.9483

Ethyl (*S*, *Z*)-2-amino-4-(3, 5-dimethoxyphenyl)-2-methyl-5-phenylpent-4-enoate (5u):



Colorless oil (69.4 mg, 93%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak AS-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 12.101 min,

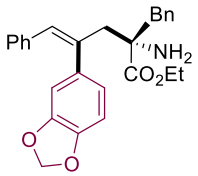
t_R(minor) 7.056 min; $[\alpha]_D^{20}$ = -34.41 (c= 1.304, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.12 – 7.05 (m, 3H), 6.94 (d, *J* = 6.7 Hz, 2H), 6.50 (s, 1H), 6.33 (t, *J* = 2.3 Hz, 1H), 6.29 (d, *J* = 2.3 Hz, 2H), 3.92 – 3.84 (m, 1H), 3.67 (s, 6H), 3.66 – 3.63 (m, 1H), 3.10 (d, *J* = 13.4 Hz, 1H), 2.73 (d, *J* = 13.5 Hz, 1H), 1.77 (s, 2H), 1.34 (s, 3H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.9, 160.7, 142.2, 138.2, 136.7, 131.1, 129.0, 127.9, 126.6, 107.0, 99.6, 60.9, 57.8, 55.3, 50.9, 27.7, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{22}H_{28}NO_4^+$ 370.2013; found 370.2011.



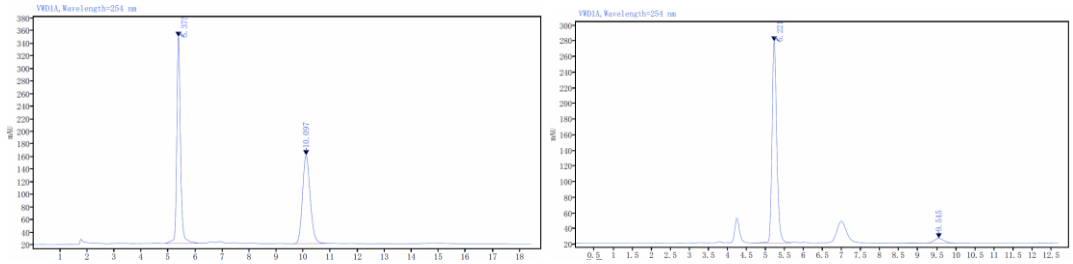
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.008	BV	1.6506	10997.2461	528.2042	50.0729
2	12.503	BB	3.0908	10965.2200	251.7991	49.9271

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.056	BV	1.1413	2292.8376	96.1560	4.9284
2	12.101	VBA	6.0649	44229.8871	986.6496	95.0716

Ethyl (*S*, *Z*)-2-amino-4-(benzo[d][1, 3]dioxol-5-yl)-2-benzyl-5-phenylpent-4-enoate (5v):



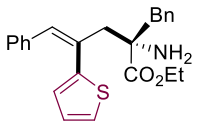
White solid (74.6 mg, 86%); m.p. = 61-63 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.221 min, t_R(minor) 9.545 min; $[\alpha]_D^{20}$ = -44.39 (c= 1.466, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.30 – 7.18 (m, 3H), 7.17 – 7.03 (m, 5H), 6.93 (d, *J* = 8.5 Hz, 2H), 6.68 (d, *J* = 7.9 Hz,1H), 6.65 (s, 1H), 6.60 (d, *J* = 8.0 Hz, 1H), 6.53 (s, 1H), 5.92 (s, 2H), 3.88 – 3.79 (m, 1H), 3.70 – 3.60 (m, 1H), 3.26 (dd, *J* = 21.1, 13.2 Hz, 2H), 2.77 (d, *J* = 13.2 Hz, 2H), 1.59 (s, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 147.6, 146.8, 137.4, 136.8, 136.1, 133.7, 131.4, 130.0, 129.0, 128.3, 127.9, 127.0, 126.6, 122.7, 109.6, 108.4, 101.0, 62.0, 60.8, 50.5, 47.0, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{28}NO_4^+$ 430.2013; found 430.2012.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.375	BV	1.3722	3172.7522	327.5160	53.2457
2	10.097	BB	1.4717	2785.9461	139.9836	46.7543

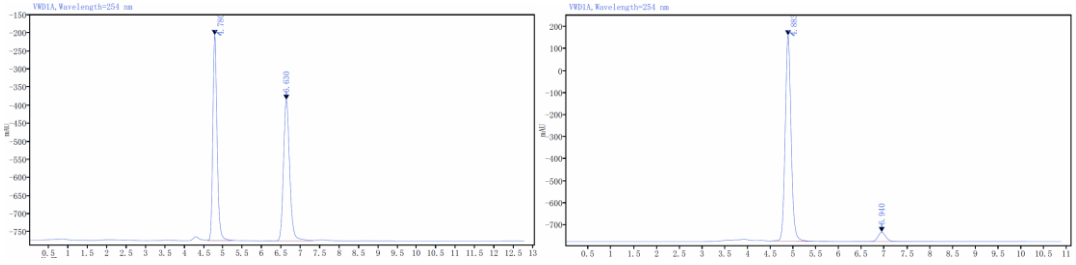
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.221	BV	0.9875	2235.8335	257.3511	94.8498
2	9.545	MM m	0.3040	121.4021	6.0790	5.1502

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-phenyl-4-(thiophen-2-yl)pent-4-enoate (5w):



White solid (33.7 mg, 42%); m.p. = 54-56 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.883 min, t_R(minor) 6.940

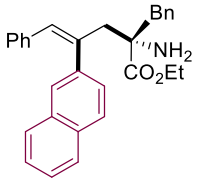
min; $[\alpha]_D^{20}$ = -28.82 (c= 0.664, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.29 – 7.19 (m, 4H), 7.18 – 7.09 (m, 5H), 7.05 – 6.99 (m, 2H), 6.91 – 6.85 (m, 1H), 6.86 – 6.76 (m, 1H), 6.64 (s, 1H), 3.92 – 3.81 (m, 1H), 3.74 – 3.64 (m, 1H), 3.28 (dd, *J* = 13.3, 8.5 Hz, 2H), 2.81 (dd, *J* = 19.1, 13.3 Hz, 2H), 1.64 (s, 2H), 1.15 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 141.7, 136.7, 136.1, 133.3, 130.4, 130.1, 129.0, 128.3, 128.0, 127.2, 127.1, 127.0, 126.8, 126.0, 62.1, 61.0, 50.97, 46.8, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{24}H_{26}NO_2S^+$ 392.1679; found 392.1677.



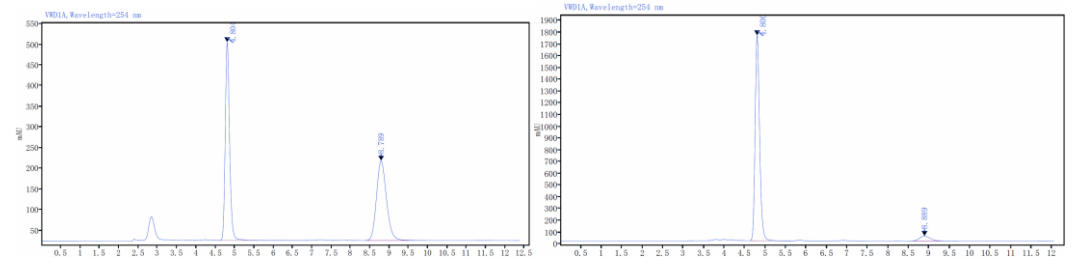
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.780	VB	0.9340	4350.7108	568.1740	50.1214
2	6.630	BV	1.2678	4329.6348	389.6011	49.8786

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.883	BB	1.2541	8409.1560	932.6255	94.2985
2	6.940	BB	1.7800	508.4337	41.9250	5.7015

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(naphthalen-2-yl)-5-phenylpent-4-enoate (5x):



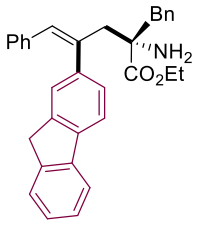
Colorless oil (58,0 mg, 67%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.800 min, t_R(minor) 8.889 min; $[\alpha]_D^{20}$ = -42.2 (c= 1.154, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.84 – 7.63 (m, 4H), 7.49 – 7.36 (m, 2H), 7.27 – 7.16 (m, 4H), 7.14 – 7.08 (m, 2H), 7.07 – 6.95 (m, 3H), 6.94 – 6.84 (m, 2H), 6.69 (s, 1H), 3.51 – 3.41 (m, 2H), 3.25 (d, *J* = 13.1 Hz, 1H), 3.19 – 3.09 (m, 1H), 2.91 (d, *J* = 13.4 Hz, 1H), 2.80 (d, *J* = 13.1 Hz, 1H), 1.66 (s, 2H), 0.87 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 137.7, 137.5, 136.7, 136.1, 133.4, 132.6, 131.9, 130.0, 129.2, 128.3, 128.0, 127.9, 127.9, 127.8, 127.6, 127.0, 126.7, 126.0, 61.8, 60.7, 50.7, 47.0, 13.8; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{30}H_{30}NO_2^+$ 436.2271; found 436.2270.



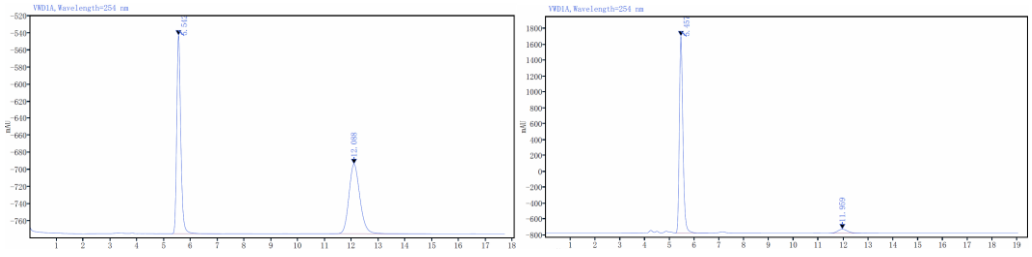
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.804	VB	0.9651	3763.2562	479.1080	52.0589
2	8.789	BB	2.2967	3465.5893	192.8161	47.9411

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.800	BB	1.0863	13517.5147	1745.2214	94.7071
2	8.889	BB	2.0067	755.4608	40.3784	5.2929

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(9H-fluoren-2-yl)-5-phenylpent-4-enoate (5y):



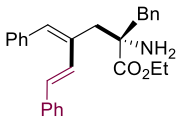
Colorless oil (46.1 mg, 49%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.457 min, t_R(minor) 11.959 min; $[\alpha]_D^{20}$ = -40.85 (c= 0.86, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.75 (d, *J* = 7.5 Hz, 1H), 7.66 (d, *J* = 7.8 Hz, 1H), 7.53 (d, *J* = 7.4 Hz, 1H), 7.41 – 7.33 (m, 2H), 7.30 (t, *J* = 7.4 Hz, 1H), 7.25 – 7.18 (m, 3H), 7.18 – 7.11 (m, 3H), 7.08 – 7.01 (m, 3H), 6.94 – 6.87 (m, 2H), 6.61 (s, 1H), 3.83 (q, 2H), 3.70 – 3.60 (m, 1H), 3.45 – 3.36 (m, 2H), 3.26 (d, *J* = 13.1 Hz, 1H), 2.83 (dd, *J* = 40.4, 13.3 Hz, 2H), 1.62 (s, 2H), 1.02 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 143.4, 143.3, 141.4, 140.9, 138.6, 138.2, 136.9, 136.1, 131.5, 130.0, 129.1, 128.3, 128.0, 127.9, 127.0, 126.8, 126.8, 126.6, 125.7, 125.1, 119.9, 119.8, 61.9, 60.8, 50.7, 47.0, 36.9, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{33}H_{32}NO_2^+$ 474.2428; found 474.2427.



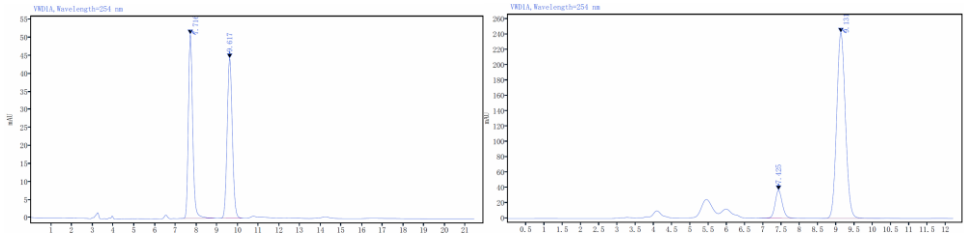
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.542	BB	1.8467	2422.2235	231.6394	51.2140
	12.088	BB	3.9033	2307.3902	81.3406	48.7860

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.457	VB	1.3326	25001.0226	2478.0296	94.7157
	11.959	BB	1.3843	1394.8403	50.6962	5.2843

Ethyl (*S*, *E*)-2-amino-2-benzyl-4-((*Z*)-benzylidene)-6-phenylhex-5-enoate (5z):

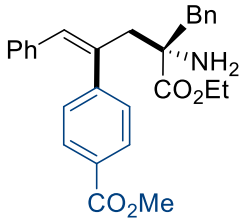


Colorless oil (33.3 mg, 40%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 78% by HPLC analysis on Daicel Chirapak IG-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 9.131 min, t_R(minor) 7.425 min; $[\alpha]_D^{20}$ = -25.11 (c= 0.312, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.42 – 7.32 (m, 4H), 7.31 – 7.15 (m, 12H), 6.85 (d, *J* = 16.4 Hz, 1H), 6.63 (s, 1H), 4.03 – 3.94 (m, 1H), 3.93 – 3.85 (m, 1H), 3.44 (d, *J* = 13.1 Hz, 1H), 3.26 (d, *J* = 13.6 Hz, 1H), 2.88 (d, *J* = 13.1 Hz, 1H), 2.77 (d, *J* = 13.6 Hz, 1H), 1.65 (s, 2H), 1.17 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 176.1, 137.4, 137.2, 136.5, 133.8, 133.5, 131.1, 130.2, 129.5, 128.7, 128.4, 128.2, 127.6, 127.0, 126.9, 126.6, 126.6, 62.4, 61.2, 46.6, 44.3, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{28}H_{30}NO_2^+$ 412.2271; found 412.2271.

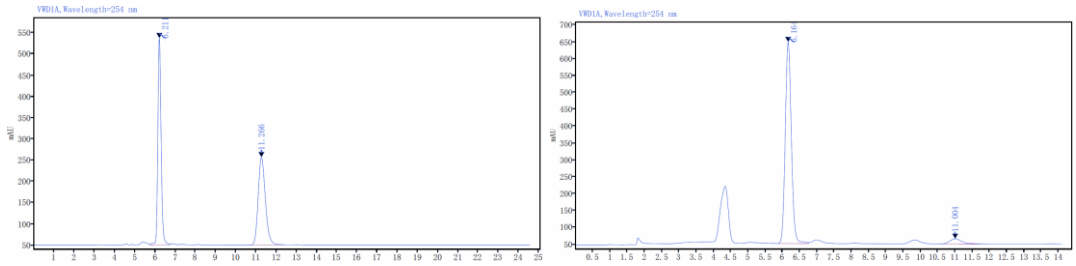


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.716	BB	1.7250	742.5220	50.9969	49.0559		7.425	BB	1.3500	504.2156	36.4248	11.1393
	9.617	BB	1.2200	771.1019	44.3303	50.9441		9.131	BB	1.5833	4022.2425	242.1411	88.8607

Methyl (*S*, *Z*)-4-(4-amino-4-benzyl-5-ethoxy-5-oxo-1-phenylpent-1-en-2-yl)benzoate (5aa):

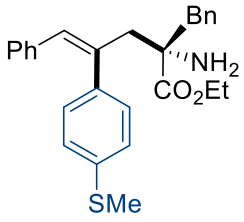


White solid (50.0 mg, 56%); m.p. = 101-103 ºC; R_f = 0.35 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 6.164 min, t_R(minor) 11.004 min; $[\alpha]_D^{20}$ = -52.45 (c= 0.3, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.84 (d, *J* = 8.3 Hz, 2H), 7.19 – 7.11 (m, 5H), 7.05 (d, *J* = 8.3 Hz, 2H), 7.01 – 6.96 (m, 3H), 6.79 – 6.74 (m, 2H), 6.58 (s, 1H), 3.81 (s, 3H), 3.62 (dq, *J* = 10.3, 7.0 Hz, 1H), 3.35 (dq, *J* = 10.5, 7.1 Hz, 1H), 3.27 (d, *J* = 13.4 Hz, 1H), 3.15 (d, *J* = 13.2 Hz, 1H), 2.73 (dd, *J* = 33.9, 13.3 Hz, 2H), 1.53 (s, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.4, 166.8, 145.3, 137.0, 136.3, 136.0, 132.7, 130.0, 129.6, 129.4, 129.1, 128.3, 128.0, 127.0, 126.9, 119.5, 61.8, 60.8, 52.0, 50.1, 46.9, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{28}H_{30}NO_4^+$ 444.2169; found 444.2166.

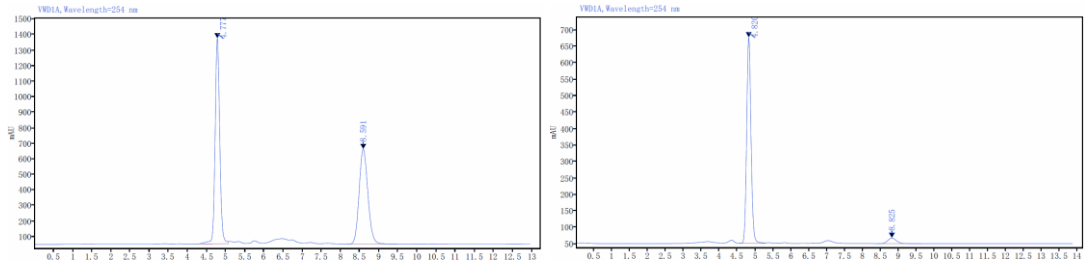


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%	Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.211	VV	1.0388	5434.3755	485.8943	51.6230		6.164	BV	0.9139	7329.2832	596.7906	95.0798
	11.266	BB	2.0517	5092.6692	206.2410	48.3770		11.004	BB	1.8767	379.2738	14.9942	4.9202

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-(methylthio)phenyl)-5-phenylpent-4-enoate (5ab):



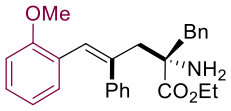
White solid (40.0 mg, 46%); m.p. = 90-92 ºC; R_f = 0.30 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.820 min, t_R(minor) 8.825 min; $[\alpha]_D^{20}$ = -40.58 (c= 0.4, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.28 – 7.20 (m, 4H), 7.15 – 7.04 (m, 8H), 6.91 (d, J = 7.1 Hz, 2H), 6.57 (s, 1H), 3.78 – 3.69 (m, 1H), 3.53 – 3.45 (m, 1H), 3.27 (dd, J = 42.1, 13.2 Hz, 2H), 2.79 (t, J = 13.7 Hz, 2H), 2.45 (s, 3H), 1.64 (s, 2H), 1.09 (t, J = 7.3 Hz, 3H).; **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 137.6, 137.2, 136.7, 136.6, 136.1, 131.6, 130.0, 129.7, 129.1, 128.3, 128.0, 127.0, 126.7, 126.3, 61.8, 60.8, 50.33 , 46.9, 15.6, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2S^+$ 432.1992 ; found 432.1989.



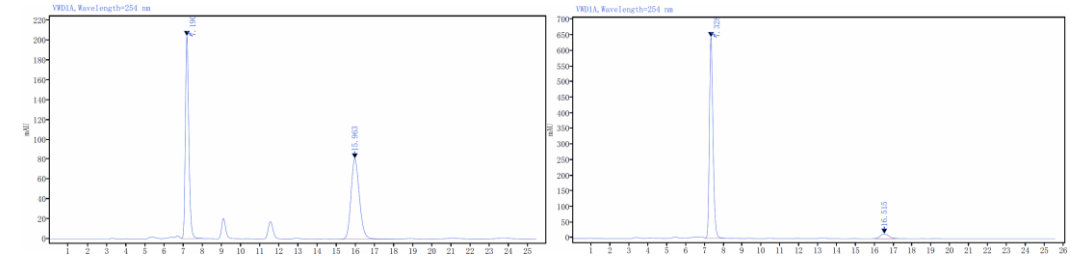
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.777	BV	0.8649	11143.6943	1322.7082	53.4189
	8.591	BB	1.2767	9717.2564	611.2528	46.5811

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.820	BV	0.7095	5288.5536	625.6254	94.8397
	8.825	BB	1.2267	287.7529	17.0101	5.1603

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(2-methoxyphenyl)-4-phenylpent-4-enoate (6a):



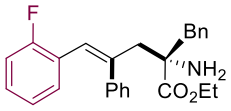
Colorless oil (36.3 mg, 43%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.328 min, t_R(minor) 16.515 min; $[\alpha]_D^{20}$ = -62.95 (c= 0.592, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.32 – 7.09 (m, 10H), 7.07 – 7.02 (m, 1H), 6.77 (d, *J* = 8.3 Hz, 1H), 6.73 (s, 1H), 6.59 – 6.51 (m, 2H), 3.77 (s, 3H), 3.75 – 3.68 (m, 1H), 3.48 – 3.38 (m, 1H), 3.35 (d, *J* = 13.5 Hz, 1H), 3.25 (d, *J* = 13.1 Hz, 1H), 2.83 (dd, *J* = 36.0, 13.2 Hz, 2H), 1.67 (s, 2H), 1.08 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 157.2, 140.3, 137.4, 136.4, 130.2, 130.0, 129.3, 128.3, 128.0, 127.8, 127.2, 127.0, 126.9, 126.1, 119.8, 110.1, 61.9, 60.7, 55.2, 49.8, 46.9, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_3^+$ 416.2220; found 416.2218.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.190	VB	1.2918	2571.9233	204.1881	51.0640
	15.963	BB	2.9750	2464.7422	81.1442	48.9360

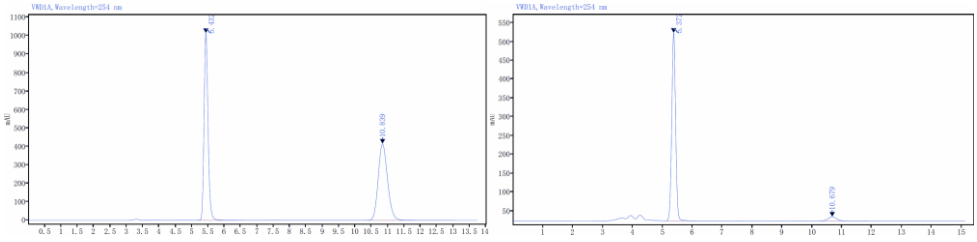
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.328	VB	1.4463	8570.7416	644.5328	94.6212
	16.515	BB	2.2333	487.2122	15.2044	5.3788

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(2-fluorophenyl)-4-phenylpent-4-enoate (6b):



White solid (49.0 mg, 61%); m.p. = 72-74 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.372 min, t_R(minor) 10.679 min; $[\alpha]_D^{20}$ = -30.65 (c= 0.882, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.34 – 7.17 (m, 6H), 7.17 – 7.09 (m, 4H), 7.04 (q, *J* = 6.5, 5.6 Hz, 1H), 6.93 (t, *J* = 9.3 Hz, 1H), 6.76 – 6.67 (m, 1H), 6.66 (s, 1H), 6.60 (t, *J* = 7.7 Hz, 1H), 3.89 – 3.72 (m, 1H), 3.60 – 3.50 (m, 1H), 3.34 (d, *J* = 13.2 Hz, 1H), 3.26 (d, *J* = 13.1 Hz, 1H), 2.88 (d, *J* = 13.2 Hz, 1H), 2.79 (d, *J* = 13.1 Hz, 1H), 1.54 (s, 2H), 1.12 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.5, 161.3, 159.7, 140.0

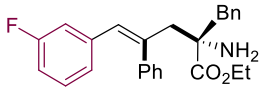
(d, *J* = 70.9 Hz), 136.1, 130.5 (d, *J* = 3.3 Hz), 130.0, 129.1, 128.3, 128.2 (d, *J* = 8.3 Hz), 127.5, 127.0, 124.8 (d, *J* = 13.5 Hz), 123.7 (d, *J* = 3.9 Hz), 123.2 (d, *J* = 3.4 Hz), 115.1 (d, *J* = 22.1 Hz), 62.1, 60.9, 50.1, 46.8, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}FNO_2^+$ 404.2020; found 404.2018.



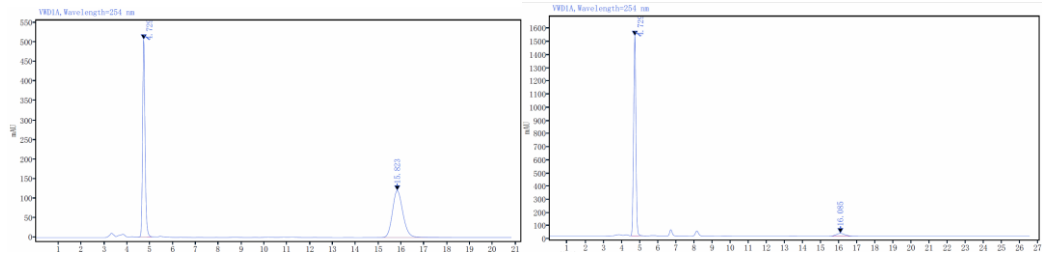
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.432	VB	1.3926	8588.1056	1013.1880	51.0320
2	10.839	BB	3.3233	8240.7618	414.4431	48.9680

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.372	BB	1.0133	4472.6560	499.5375	95.4718
2	10.679	BB	1.6833	212.1386	10.7968	4.5282

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3-fluorophenyl)-4-phenylpent-4-enoate (6c):



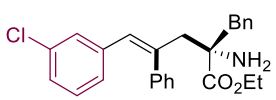
White solid (43.0 mg, 53%); m.p. = 76-78 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.729 min, t_R(minor) 16.085 min; $[\alpha]_D^{20}$ = -47.13 (c= 0.778, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.30 – 7.18 (m, 6H), 7.15 – 7.10 (m, 4H), 7.07 – 6.98 (m, 1H), 6.75 (td, *J* = 8.2, 2.4 Hz, 1H), 6.67 (d, *J* = 8.1 Hz, 1H), 6.55 (s, 1H), 6.51 (d, *J* = 10.7 Hz, 1H), 3.77 – 3.63 (m, 1H), 3.49 – 3.38 (m, 1H), 3.34 (d, *J* = 13.4 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.79 (dd, *J* = 18.9, 13.2 Hz, 2H), 1.59 (s, 2H), 1.06 (t, *J* = 7.2 Hz,3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 163.2, 161.6, 139.5, 139.0 (d, *J* = 8.0 Hz), 136.0, 130.3 (d, *J* = 2.3 Hz), 130.0, 129.2 (d, *J* = 8.3 Hz), 129.0, 128.5, 128.3, 127.7, 127.0, 125.0 (d, *J* = 2.8 Hz), 115.6 (d, *J* = 22.1 Hz), 113.5 (d, *J* = 21.3 Hz), 61.7, 60.8, 50.4, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}FNO_2^+$ 404.2020; found 404.2019.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.729	BB	0.6867	3781.0388	504.5756	49.9023
2	15.823	BB	3.2567	3795.8434	119.8604	50.0977

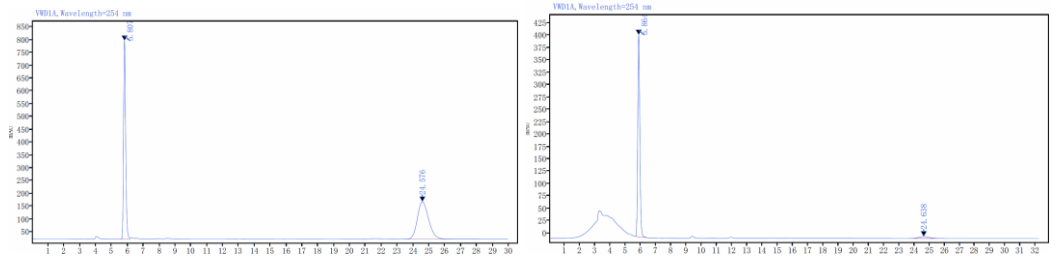
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.729	BB	0.8690	13520.9897	1517.3410	95.3261
2	16.085	BB	2.7133	662.9356	20.4104	4.6739

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3-chlorophenyl)-4-phenylpent-4-enoate (6d):



White solid; (45.5 mg, 54%); m.p. = 63-65 ºC R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 5.864 min, t_R(minor) 24.638 min; $[\alpha]_D^{20}$ = -47.53 (c= 0.836, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.30 – 7.17 (m, 6H), 7.16 –

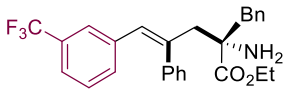
7.08 (m, 4H), 7.02 (d, *J* = 8.2 Hz, 1H), 6.97 (t, *J* = 7.9 Hz, 1H), 6.84 (t, *J* = 1.8 Hz, 1H), 6.71 (d, *J* = 7.7 Hz, 1H), 6.52 (s, 1H), 3.74 – 3.64 (m, 1H), 3.48 – 3.39 (m, 1H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.79 (dd, *J* = 17.8, 13.2 Hz, 2H), 1.58 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 139.7, 139.4, 138.6, 136.0, 133.7, 130.1, 130.0, 129.0, 128.5, 128.3, 127.7, 127.2, 127.0, 126.6, 61.7, 60.8, 50.4, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}ClNO_2^+$ 420.1725; found 420.1723.



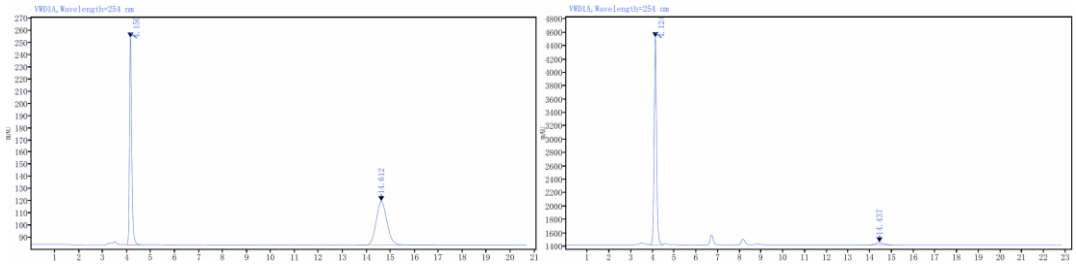
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.807	BV	0.6424	7089.5060	773.8288	49.7575
	24.576	BB	4.7500	7158.6083	145.8275	50.2425

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	5.864	BB	0.8800	3858.2904	408.1971	95.3059
	24.638	BB	2.8433	190.0319	3.9125	4.6941

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(3-(trifluoromethyl)phenyl)pent-4-enoate (6e):



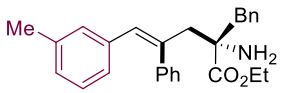
White solid (43.0 mg, 47%); m.p. = 86-88 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 ºC), UV 254 nm, t_R(major) 4.124 min, t_R(minor) 14.437 min; $[\alpha]_D^{20}$ = -43.36 (c= 0.818, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.33 – 7.19 (m, 7H), 7.19 – 7.08 (m, 6H), 7.02 (d, *J* = 7.9 Hz, 1H), 6.60 (s, 1H), 3.75 – 3.61 (m, 1H), 3.46 – 3.39 (m, 1H), 3.37 (d, *J* = 13.3 Hz, 1H), 3.24 (d, *J* = 13.1 Hz, 1H), 2.81 (dd, *J* = 24.1, 13.2 Hz, 2H), 1.65 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.4, 140.2, 139.2, 137.5, 136.0, 132.1, 130.3, 130.1, 130.0, 129.0, 128.6, 128.4, 128.2, 127.8, 127.0, 125.8 (q, *J* = 3.9 Hz), 123.1 (q, *J* = 3.8 Hz), 123.0, 61.6, 60.8, 50.3, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}F_3NO_2^+$ 454.1988; found 454.1987.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.150	BB	0.7291	1104.4868	169.4622	49.8012
	14.612	BB	3.2450	1113.3028	35.7199	50.1988

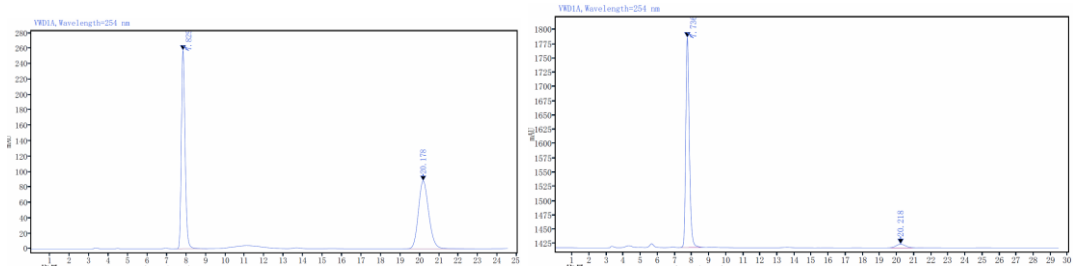
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.124	VV	0.5827	24197.2499	3103.9327	95.4349
	14.437	MM m	0.4784	1157.4659	37.4683	4.5651

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(m-tolyl)pent-4-enoate (6f):



White solid (55.0 mg, 69%); m.p. = 70-72 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5,

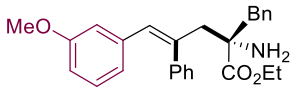
flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.736 min, t_R(minor) 20.218 min; $[\alpha]_D^{20}$ = -50.03 (c= 1.098, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.31 – 7.18 (m, 6H), 7.16 – 7.10 (m, 4H), 6.93 (t, *J* = 7.6 Hz, 1H), 6.86 (d, *J* = 7.5 Hz, 1H), 6.70 (s, 1H), 6.64 (d, *J* = 7.7 Hz, 1H), 6.56 (s, 1H), 3.78 – 3.61 (m, 1H), 3.48 – 3.38 (m, 1H), 3.36 – 3.27 (m, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.79 (dd, *J* = 16.9, 13.2 Hz, 2H), 2.13 (s, 3H), 1.60 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 140.1, 137.7, 137.3, 136.7, 136.2, 131.7, 130.0, 129.2, 128.3, 128.3, 127.7, 127.4, 127.3, 127.0, 126.1, 61.7, 60.7, 50.5, 47.0, 21.3, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2270.



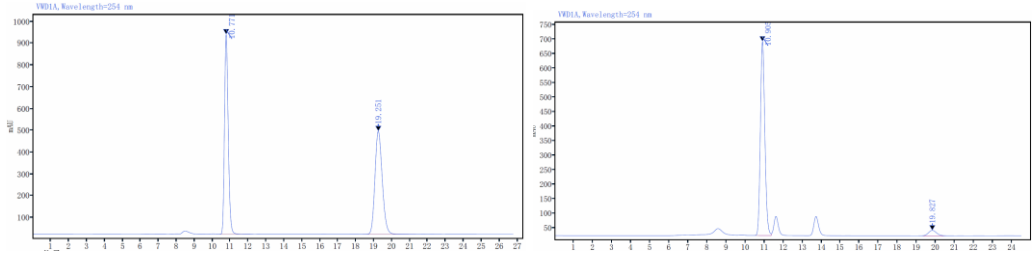
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.829	BB	1.6850	3431.8060	257.3327	51.2951
	20.178	BB	3.6850	3258.5101	88.0299	48.7049

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.736	BB	1.6310	5385.4913	368.1001	95.5969
	20.218	BB	2.3283	248.0492	6.3877	4.4031

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3-methoxyphenyl)-4-phenylpent-4-enoate (6g):



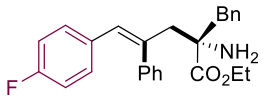
White solid (42.2 mg, 51%); m.p. = 75-77 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 10.905 min, t_R(minor) 19.827 min; $[\alpha]_D^{20}$ = -42.06 (c= 0.42, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.31 – 7.18 (m, 6H), 7.18 – 7.14 (m, 2H), 7.14 – 7.10 (m, 2H), 7.00 (t, *J* = 7.9 Hz, 1H), 6.62 (dd, *J* = 8.0, 2.6 Hz, 1H), 6.57 (s, 1H), 6.53 (d, *J* = 7.6 Hz, 1H), 6.37 (s, 1H), 3.75 – 3.66 (m, 1H), 3.46 (s, 3H), 3.45 – 3.38 (m, 1H), 3.34 (d, *J* = 13.6 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.80 (dd, *J* = 18.8, 13.2 Hz, 2H), 1.63 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 159.0, 140.2, 138.3, 138.0, 136.2, 131.5, 130.0, 129.2, 128.8, 128.4, 128.3, 127.3, 126.9, 121.9, 113.6, 113.3, 61.8, 60.7, 54.8, 50.5, 47.1, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_3^+$ 416.2220; found 416.2219.



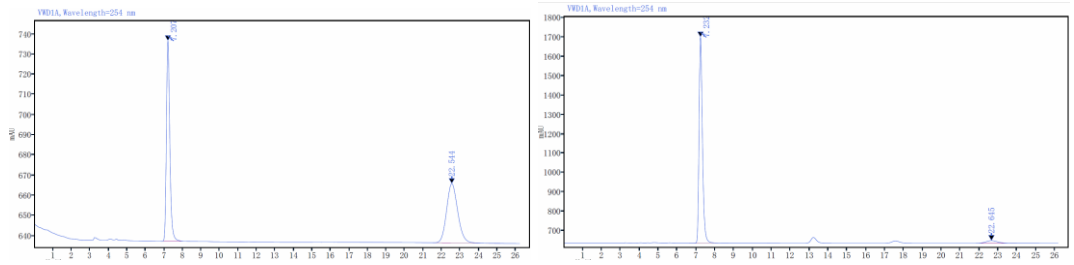
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	10.771	BB	1.7133	13278.9596	916.9998	49.8683
	19.251	BB	2.9367	13349.0811	473.3425	50.1317

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	10.905	BV	0.8733	10852.6448	668.4161	95.0784
	19.827	BB	2.1117	561.7661	18.8418	4.9216

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-fluorophenyl)-4-phenylpent-4-enoate (6h):



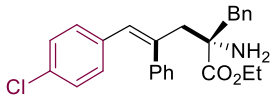
Colorless oil (69 mg, 86%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.232 min, t_R(minor) 22.645 min; $[\alpha]_D^{20}$ = -40.01 (c= 1.388, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.30 – 7.17 (m, 6H), 7.14 – 7.09 (m, 4H), 6.88 – 6.78 (m, 2H), 6.75 (t, *J* = 8.7 Hz, 2H), 6.55 (s, 1H), 3.75 – 3.63 (m, 1H), 3.46 – 3.37 (m, 1H), 3.34 (d, *J* = 13.3 Hz, 1H), 3.23 (d, *J* = 13.1 Hz, 1H), 2.84 – 2.75 (m, 2H), 1.60 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.5, 161.4 (d, *J* = 246.6 Hz), 139.7, 137.8, 136.1, 132.8 (d, *J* = 3.4 Hz), 130.6 (d, *J* = 7.8 Hz), 130.3, 130.0, 129.2, 128.5, 128.3, 127.4, 127.0, 114.8 (d, *J* = 21.4 Hz), 61.7, 60.8, 50.4, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}FNO_2^+$ 404.2020; found 404.2018.



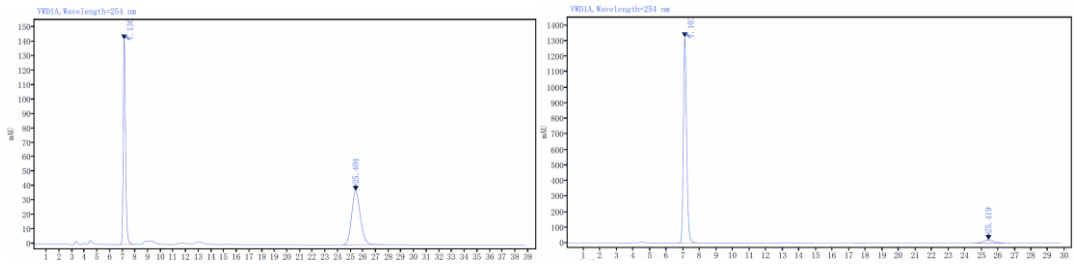
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.207	BB	1.2728	1280.0595	99.3868	51.0361
2	22.544	BB	3.6300	1228.0865	29.4044	48.9639

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.232	BB	1.5497	13297.2184	1063.9913	95.9124
2	22.645	BB	2.3950	566.7020	13.6432	4.0876

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-chlorophenyl)-4-phenylpent-4-enoate (6i):



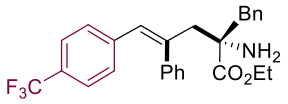
White solid (63.0 mg, 75%); m.p. = 58-60 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.103 min, t_R(minor) 25.419 min; $[\alpha]_D^{20}$ = -54.02 (c= 1.254, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.30 – 7.17 (m, 6H), 7.15 – 7.08 (m, 4H), 7.02 (d, *J* = 8.5 Hz, 2H), 6.78 (d, *J* = 6.6 Hz, 2H), 6.53 (s, 1H), 3.75 – 3.64 (m, 1H), 3.48 – 3.38 (m, 1H), 3.33 (d, *J* = 13.3 Hz, 1H), 3.22 (d, *J* = 13.1 Hz, 1H), 2.78 (dd, *J* = 17.0, 13.2 Hz, 2H), 1.59 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.5, 139.6, 138.8, 136.0, 135.2, 132.2, 130.3, 130.2, 130.0, 129.1, 128.5, 128.3, 128.1, 127.5, 127.0, 61.7, 60.8, 50.4, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{27}ClNO_2^+$ 420.1725; found 420.1723.



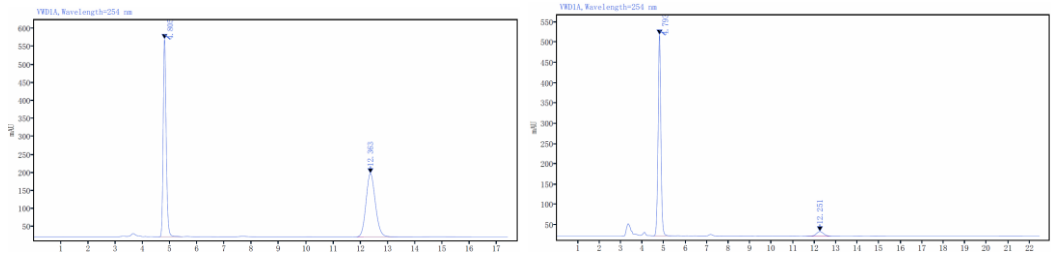
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.130	BB	1.4683	1807.1456	141.6857	50.5460
	25.404	BB	3.5650	1768.1034	37.0476	49.4540

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	7.103	BB	1.4191	17952.0359	1320.3351	95.0395
	25.419	BB	3.7883	936.9976	18.8930	4.9605

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (6j):



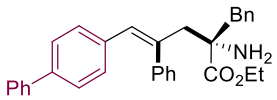
Colorless oil (48.2 mg, 53%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.793 min, t_R(minor) 12.251 min; $[\alpha]_D^{20}$ = -45 (c= 0.96, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.46 – 7.17 (m, 8H), 7.16 – 7.09 (m, 4H), 6.95 (d, *J* = 8.2 Hz, 2H), 6.61 (s, 1H), 3.76 – 3.64 (m, 1H), 3.48 – 3.39 (m, 1H), 3.37 (d, *J* = 13.3 Hz, 1H), 3.24 (d, *J* = 13.1 Hz, 1H), 2.81 (dd, *J* = 28.0, 13.2 Hz, 2H), 1.62 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.4, 140.7, 140.4, 139.4, 136.0, 130.1, 130.0, 129.2, 129.0, 128.6, 128.3, 127.7, 127.0, 125.0, 124.8 (q, *J* = 3.8 Hz), 123.2, 61.7, 60.9, 50.4, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{27}F_3NO_2^+$ 454.1988; found 454.1988.



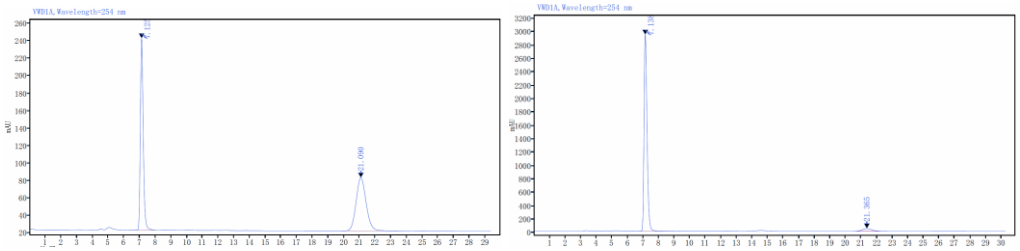
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.805	BV	0.8733	4227.3758	548.4026	50.2978
	12.363	BB	2.1883	4177.3222	175.9848	49.7022

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	4.793	BB	0.8517	4491.6270	495.4981	94.0405
	12.251	BB	2.2467	284.6429	11.5712	5.9595

Ethyl (*S*, *Z*)-5-([1,1'-biphenyl]-4-yl)-2-amino-2-benzyl-4-phenylpent-4-enoate (6k):



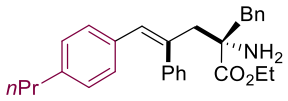
White solid (69.8 mg, 76%); m.p. = 97-99 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.138 min, t_R(minor) 21.365 min; $[\alpha]_D^{20}$ = -54.17 (c= 1.6, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.50 (d, *J* = 6.6 Hz, 2H), 7.42 – 7.17 (m, 13H), 7.14 (d, *J* = 6.5 Hz, 2H), 6.94 (d, *J* = 8.1 Hz, 2H), 6.62 (s, 1H), 3.75 – 3.66 (m, 1H), 3.48 – 3.39 (m, 1H), 3.36 (d, *J* = 13.3 Hz, 1H), 3.24 (d, *J* = 13.1 Hz, 1H), 2.81 (dd, *J* = 28.0, 13.2 Hz, 2H), 1.61 (s, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 140.6, 140.1, 139.2, 138.2, 136.1, 135.8, 131.1, 130.0, 129.5, 129.2, 128.7, 128.5, 128.3, 127.4, 127.2, 127.0, 126.8, 126.5, 61.8, 60.8, 50.6, 47.1, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{32}H_{32}NO_2^+$ 462.2428; found 462.2426.



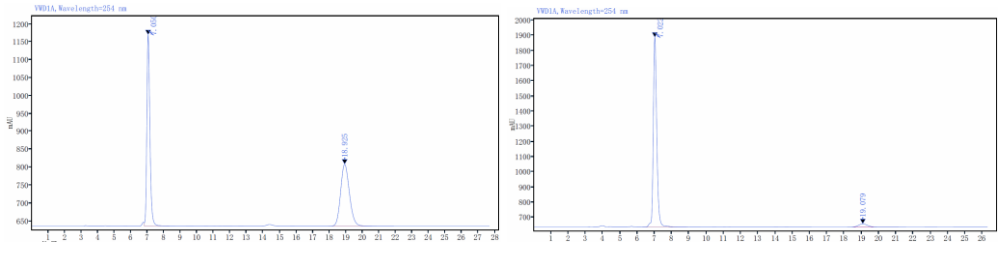
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.125	BB	1.5350	2806.5282	219.7456	51.0941
2	21.090	BB	3.5233	2686.3380	60.8620	48.9059

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.138	VB	2.2250	39347.7050	2935.2557	95.4946
2	21.365	BB	3.4767	1856.3910	41.4921	4.5054

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(4-propylphenyl)pent-4-enoate (6l):



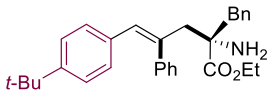
Colorless oil (45.8 mg, 60%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.022 min, t_R(minor) 19.079 min; $[\alpha]_D^{20}$ = -50.66 (c= 0.962, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.29 – 7.18 (m, 6H), 7.14 (dd, *J* = 17.3, 6.6 Hz, 4H), 6.87 (d, *J* = 8.0 Hz, 2H), 6.78 (d, *J* = 7.9 Hz, 2H), 6.56 (s, 1H), 3.81 – 3.65 (m, 1H), 3.46 – 3.37 (m, 1H), 3.33 (d, *J* = 13.3 Hz, 1H), 3.22 (d, *J* = 13.1 Hz, 1H), 2.79 (dd, *J* = 17.6, 13.3 Hz, 2H), 2.45 (t, *J* = 7.7 Hz, 2H), 1.64 (s, 2H), 1.58 – 1.47 (m, 2H), 1.06 (t, *J* = 7.2 Hz, 3H), 0.87 (t, *J* = 7.4 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 141.2, 140.3, 137.0, 136.2, 134.1, 131.5, 130.0, 129.2, 129.0, 128.4, 128.3, 128.0, 127.2, 126.9, 61.8, 60.7, 50.6, 47.0, 37.7, 24.3, 14.0, 13.8; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{29}H_{34}NO_2^+$ 428.2584; found 428.2584.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.050	VB	1.5077	6866.4800	533.9092	51.8110
2	18.925	BB	4.1000	6386.4541	172.6482	48.1890

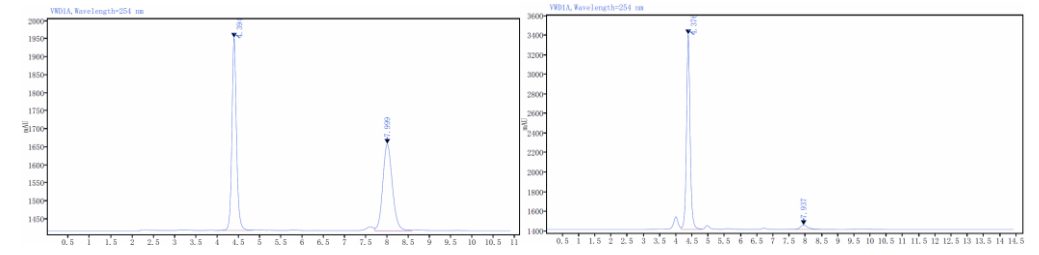
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	7.022	BB	2.6794	17597.1371	1251.4167	95.5452
2	19.079	BB	3.2217	820.4660	21.5597	4.4548

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-(tert-butyl)phenyl)-4-phenylpent-4-enoate (6m):



White solid (57.8 mg, 66%); m.p. = 70-72 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.376 min, t_R(minor) 7.937 min; $[\alpha]_D^{20}$ = -43.23 (c= 1.122, DCM); **^{1}H NMR (600 MHz, CDCl$_3$):** δ 7.33 – 7.15 (m, 8H), 7.13 (d, *J* = 8.1 Hz, 2H), 7.09 (d, *J* = 8.4 Hz, 2H), 6.81 (d, *J* = 8.4 Hz, 2H), 6.55 (s, 1H), 3.75 – 3.64 (m, 1H), 3.49 – 3.39 (m, 1H), 3.33 (d, *J* = 13.5 Hz, 1H), 3.22 (d, *J* = 13.1 Hz, 1H), 2.79 (dd, *J* = 17.9, 13.2 Hz, 2H), 1.61 (s, 2H), 1.22 (s, 9H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, CDCl$_3$):** δ 175.6, 149.7, 140.4, 137.0, 136.2, 133.7, 131.4, 130.0, 129.2, 128.8, 128.4, 128.3, 127.2, 126.9, 124.8, 61.7, 60.7,

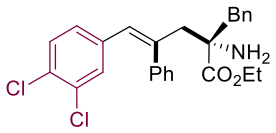
50.8, 47.1, 34.4, 31.2, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{30}H_{36}NO_2^+$ 442.2741; found 442.2739.



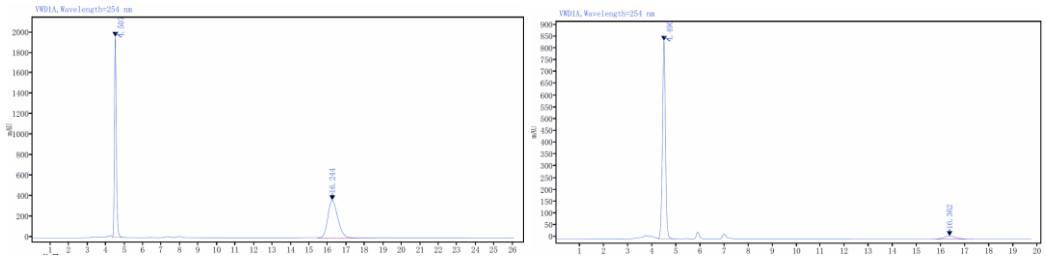
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.394	BV	0.8450	3994.6843	534.3649	51.6163
2	7.999	VV	0.8848	3744.5122	240.1256	48.3837

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.376	VV	0.6411	15510.0820	1989.5778	95.4306
2	7.937	VB	1.4598	742.6572	42.2851	4.5694

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3, 4-dichlorophenyl)-4-phenylpent-4-enoate (6n):



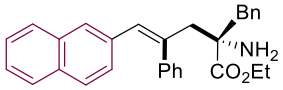
Colorless oil (47.9 mg, 53%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 4.490 min, t_R(minor) 16.362 min; $[\alpha]_D^{20}$ = -48.08 (c= 0.834, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.35 – 7.18 (m, 6H), 7.16 – 7.06 (m, 5H), 6.94 (d, *J* = 2.0 Hz, 1H), 6.63 (dd, *J* = 8.4, 2.1 Hz, 1H), 6.47 (s, 1H), 3.76 – 3.62 (m, 1H), 3.47 – 3.37 (m, 1H), 3.36 – 3.31 (m, 1H), 3.22 (d, *J* = 13.1 Hz, 1H), 2.78 (t, *J* = 13.7 Hz, 2H), 1.60 (s, 2H), 1.05 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.4, 140.5, 139.3, 136.9, 136.0, 131.9, 130.8, 130.3, 130.0, 129.7, 129.0, 128.9, 128.6, 128.3, 128.2, 127.8, 127.0, 61.7, 60.8, 50.3, 47.0, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{26}H_{26}Cl_2NO_2^+$ 454.1335; found 454.1334.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.507	VB	0.6370	13886.7339	1957.1376	50.5057
2	16.244	VB	3.1187	13608.6318	365.4383	49.4943

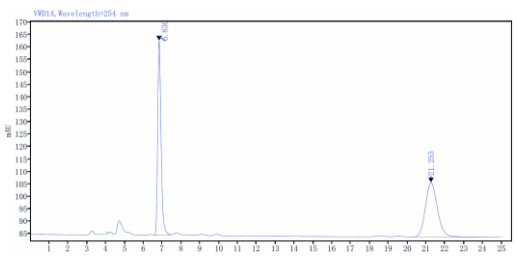
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	4.490	VB	0.6951	7277.7457	838.0467	93.9443
2	16.362	BB	2.5567	469.1236	12.5649	6.0557

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(naphthalen-2-yl)-4-phenylpent-4-enoate (6o):

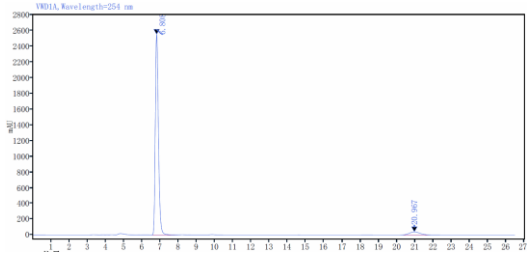


White solid (52.1 mg, 60%); m.p. = 92-94 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.808 min, t_R(minor) 20.967 min; $[\alpha]_D^{20}$ = -89.61 (c= 0.988, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.66 (dd, *J* = 6.1, 3.3 Hz, 1H), 7.57 (dd, *J* = 6.1, 3.4 Hz, 1H), 7.47 (d, *J* = 8.6 Hz, 1H), 7.41 (s, 1H), 7.36 (dd, *J* = 6.2, 3.2 Hz, 2H), 7.27 – 7.11 (m, 10H), 6.89 (d, *J* = 8.6 Hz, 1H), 6.75 (s, 1H), 3.83 – 3.64 (m, 1H), 3.55 – 3.42 (m, 1H), 3.40 (d, *J* = 13.3 Hz, 1H), 3.26 (d, *J* = 13.1 Hz, 1H), 2.87 (d, *J* = 13.4 Hz, 1H), 2.81 (d, *J* = 13.1

Hz, 1H), 1.62 (s, 2H), 1.07 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 140.0, 138.4, 136.1, 134.4, 133.2, 132.2, 131.6, 130.0, 129.4, 128.4, 128.4, 128.3, 127.9, 127.4, 127.4, 127.1, 127.0, 126.9, 125.9, 125.8, 61.8, 60.8, 50.5, 47.0, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{30}H_{30}NO_2^+$ 436.2271; found 436.2270.

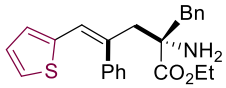


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.830	BB	0.9550	961.7991	77.9876	50.0516
2	21.255	BB	3.9033	959.8169	21.7950	49.9484

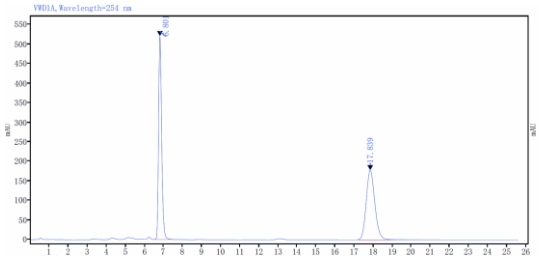


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.808	BV	1.4485	30322.6172	2549.0359	94.7490
2	20.967	BB	3.8050	1680.4794	39.5730	5.2510

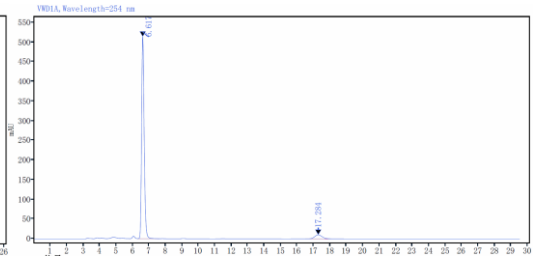
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(thiophen-2-yl)pent-4-enoate (6p):



White solid (48.9 mg, 63%); m.p. = 80-82 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 88% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.617 min, t_R(minor) 17.284 min; $[\alpha]_D^{20}$ = -35.64 (c= 0.98, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.39 – 7.17 (m, 8H), 7.12 (dd, *J* = 8.1, 1.5 Hz, 2H), 6.98 (dd, *J* = 5.1, 3.0 Hz, 1H), 6.75 (d, *J* = 1.7 Hz, 1H), 6.58 (s, 1H), 6.39 (d, *J* = 3.9 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.49 – 3.37 (m, 1H), 3.30 (d, *J* = 12.3 Hz, 1H), 3.21 (d, *J* = 13.1 Hz, 1H), 2.77 (d, *J* = 11.6 Hz, 2H), 1.63 (s, 2H), 1.04 (t, *J* = 7.2 Hz,3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 140.5, 138.1, 136.7, 136.1, 130.0, 129.0, 128.5, 128.3, 127.9, 127.5, 127.0, 125.9, 124.4, 123.8, 61.6, 60.7, 50.5, 47.1, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{24}H_{26}NO_2S^+$ 392.1679; found 392.1679.

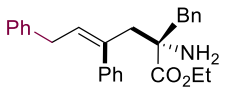


Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.801	BB	1.2229	5860.4275	519.9623	51.2479
2	17.839	BB	3.3967	5575.0281	177.5529	48.7521



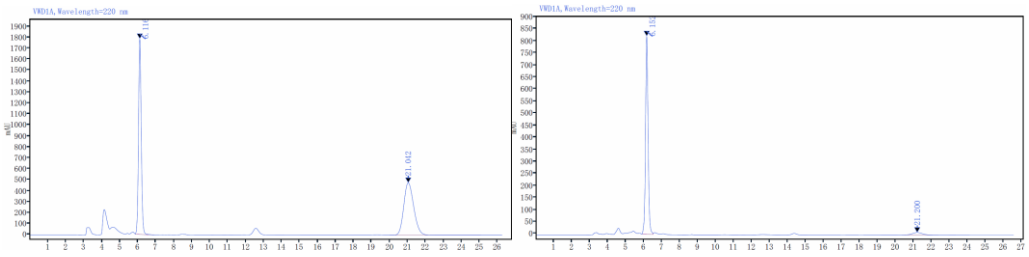
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	6.617	VB	1.3383	5565.5507	513.5254	94.4792
2	17.284	BB	2.5633	325.2174	10.1639	5.5208

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4, 6-diphenylhex-4-enoate (6q):



Colorless oil (35.9 mg, 45%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 220 nm, t_R(major) 6.152 min, t_R(minor) 21.2 min; $[\alpha]_D^{20}$ = -3.91 (c= 0.264, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.32 (t, *J* = 7.5 Hz, 2H), 7.27 – 7.13 (m, 9H), 7.12 – 7.07 (m, 4H), 5.81 (t, *J* = 7.5 Hz, 1H), 3.71 – 3.61 (m, 1H), 3.41 – 3.32 (m, 1H), 3.30 (d, *J* = 7.6 Hz, 2H),

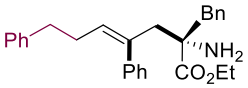
3.20 (dd, *J* = 28.5, 13.2 Hz, 2H), 2.79 – 2.68 (m, 2H), 1.59 (s, 2H), 1.01 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.7, 140.8, 139.7, 136.9, 136.2, 131.4, 130.0, 128.9, 128.4, 128.3, 128.3, 128.1, 127.1, 126.9, 125.9, 61.7, 60.7, 49.6, 46.8, 35.2, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2^+$ 400.2271; found 400.2269.



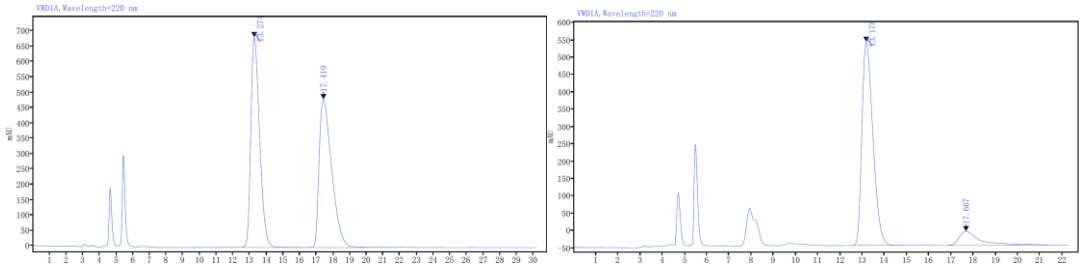
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.116	VB	1.0697	18661.6680	1784.6786	50.2965
	21.042	BB	5.0567	18441.6620	478.0740	49.7035

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	6.152	BV	0.6485	8130.2857	821.8307	95.4019
	21.200	BB	2.0200	391.8523	10.3833	4.5981

Ethyl (*S*, *Z*)-2-amino-2-benzyl-4, 7-diphenylhept-4-enoate (6r):



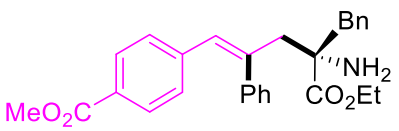
Colorless oil (34.5 mg, 41%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 76% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 99/1, flow rate 1.0 mL/min, T = 30 °C), UV 220 nm, t_R(major) 13.178 min, t_R(minor) 17.667 min; $[\alpha]_D^{20}$ = -14.71 (c=0.374, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.27 – 7.13 (m, 9H), 7.13 – 7.05 (m, 4H), 6.99 (d, *J* = 6.8 Hz, 2H), 5.64 (t, *J* = 7.3 Hz, 1H), 3.69 – 3.56 (m, 1H), 3.35 – 3.20 (m, 1H), 3.15 (dd, *J* = 13.2, 7.3 Hz, 2H), 2.70 (d, *J* = 13.1 Hz, 1H), 2.66 – 2.57 (m, 2H), 2.34 – 2.23 (m, 2H), 2.16 (d, *J* = 6.3 Hz, 1H), 1.55 (s, 2H), 0.99 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.6, 141.6, 139.9, 136.7, 136.3, 132.3, 130.0, 128.8, 128.5, 128.3, 128.2, 127.9, 126.9, 126.8, 125.9, 61.4, 60.6, 49.5, 46.9, 36.0, 30.8, 13.9; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{28}H_{32}NO_2^+$ 414.2428; found 414.2426.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.274	VB	3.7183	24972.4365	684.4464	49.7028
	17.419	BB	5.0917	25271.0575	482.2064	50.2972

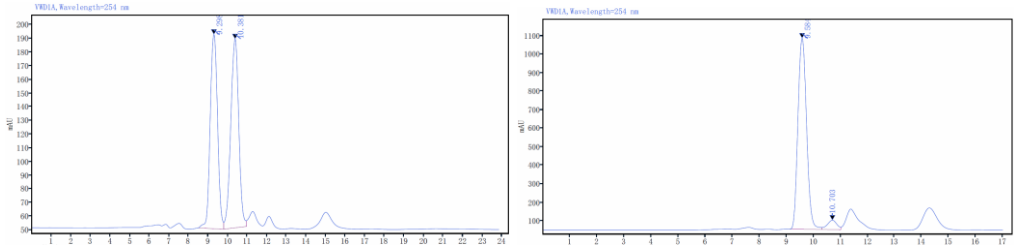
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	13.178	VB	2.2933	20148.2970	586.8442	87.9410
	17.667	BB	4.6983	2762.8527	40.3276	12.0590

Methyl (S,Z)-4-(4-amino-4-benzyl-5-ethoxy-5-oxo-2-phenylpent-1-en-1-yl)benzoate (6s):



White solid (34.0 mg, 38%); m.p. = 77- 79 °C; R_f = 0.3 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 80/20, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 9.584 min, t_R(minor) 10.703 min; $[\alpha]_D^{20}$ = -59.51 (c=0.34, DCM); **^{1}H**

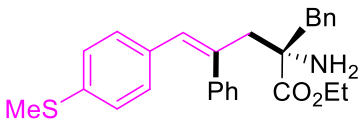
NMR (600 MHz, $CDCl_3$): δ 7.73 (d, *J* = 10.3 Hz, 2H), 7.28 – 7.19 (m, 6H), 7.13 (t, *J* = 7.4 Hz, 4H), 6.92 (d, *J* = 8.5 Hz, 2H), 6.63 (s, 1H), 3.84 (s, 3H), 3.70 (dq, *J* = 10.3, 7.3 Hz, 1H), 3.50 – 3.39 (m, 1H), 3.31 (dd, *J* = 73.3, 13.2 Hz, 2H), 2.83 (dd, *J* = 29.9, 13.2 Hz, 2H), 1.81 (s, 2H), 1.06 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.3, 166.8, 141.6, 140.5, 139.4, 135.9, 130.7, 130.0, 129.2, 129.1, 129.0, 128.5, 128.4, 128.0, 127.7, 127.1, 61.8, 60.9, 52.0, 50.3, 46.8, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{28}H_{30}NO_4^+$ 444.2169; found 444.2169.



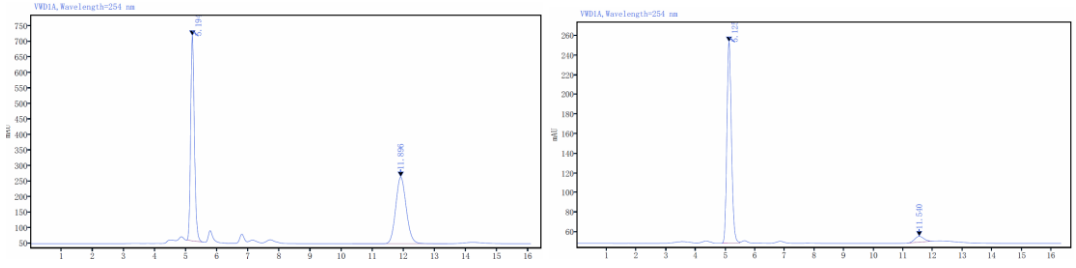
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	9.298	MM m	0.4170	3701.1982	142.0185	48.4990
2	10.381	VM m	0.4511	3930.2981	138.0693	51.5010

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	9.584	BV	1.2047	22925.1653	1031.7502	94.8730
2	10.703	VV	0.7012	1238.8992	50.4384	5.1270

Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-(methylthio)phenyl)-4-phenylpent-4-enoate (6t):



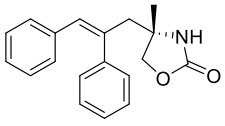
White solid (33.9 mg, 39%); m.p. = 85- 87 °C; R_f = 0.27 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90% by HPLC analysis on Daicel Chirapak IC-H column (hexane/isopropanol = 70/30, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 5.125 min, t_R(minor) 11.540 min; $[\alpha]_D^{20}$ = -60.59 (c=0.28, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):**δ 7.21 – 7.11 (m, 6H), 7.06 (dd, *J* = 12.5, 7.9 Hz, 4H), 6.87 (d, *J* = 8.2 Hz, 2H), 6.71 (d, *J* = 8.2 Hz, 2H), 6.45 (s, 1H), 3.66 – 3.57 (m, 1H), 3.39 – 3.31 (m, 1H), 3.20 (dd, *J* = 63.6, 13.2 Hz, 2H), 2.72 (dd, *J* = 16.4, 13.2 Hz, 2H), 2.31 (s, 3H), 1.58 (s, 2H), 0.98 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 175.5, 140.0, 137.6, 136.7, 136.1, 133.5, 130.9, 130.0, 129.5, 129.2, 128.5, 128.3, 127.4, 127.0, 125.8, 61.7, 60.8, 50.5, 47.0, 15.6, 14.0; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{30}NO_2S^+$ 432.1992; found 432.1990.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.194	MM m	0.1295	5575.2070	660.4728	52.5891
2	11.896	MB m	0.3632	5026.2402	214.6707	47.4109

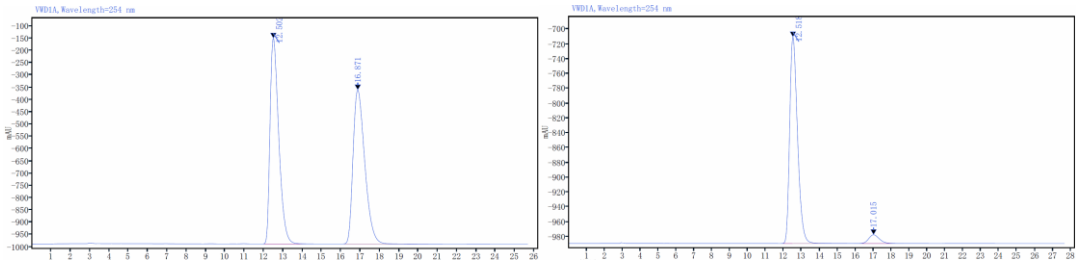
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	5.125	BV	0.7972	2193.7348	204.8186	94.5529
2	11.540	BB	0.8717	126.3780	5.8731	5.4471

(*S*, *Z*)-4-(*2*, *3*-diphenylallyl)-4-methyloxazolidin-2-one (8):



White solid (158.1 mg, 91%); m.p. = 153- 155 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 90 % by HPLC analysis on Daicel Chirapak OD-H column

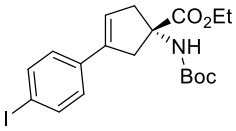
(hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R(major) 12.518 min, t_R(minor) 17.015 min; $[\alpha]_D^{20}$ = -62.96 (c=0.892, DCM); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.37 – 7.24 (m, 3H), 7.18 (d, *J* = 6.4 Hz, 2H), 7.12 – 7.07 (m, 3H), 6.92 (dd, *J* = 7.1, 2.6 Hz, 2H), 6.52 (s, 1H), 5.25 (s, 1H), 3.97 (d, *J* = 8.6 Hz, 1H), 3.84 (d, *J* = 8.5 Hz, 1H), 2.90 (d, *J* = 13.7 Hz, 1H), 2.81 (d, *J* = 13.7 Hz, 1H), 1.30 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 158.5, 140.1, 137.1, 136.4, 131.7, 129.1, 128.8, 128.0, 127.9, 126.9, 75.6, 75.6, 58.2, 50.7, 25.9; **HRMS(ESI)** m/z: $[M+Na]^+$ Calculated for $C_{19}H_{19}NNaO_2^+$ 316.1308; found 316.1308.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.502	BB	3.8161	26410.5785	838.2318	49.9051
2	16.871	BB	4.8733	26510.9976	627.7270	50.0949

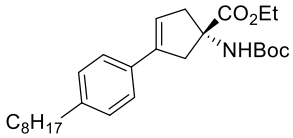
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	12.518	BB	3.7158	8480.9899	278.8340	94.6105
2	17.015	BB	2.7367	483.1177	11.7022	5.3895

Ethyl (*S*)-1-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)cyclopent-3-ene-1-carboxylate (10):



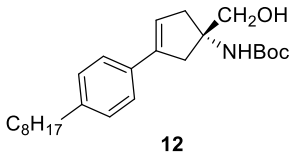
Colorless oil (269.0 mg, 79%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); $[\alpha]_D^{20}$ = -14.61 (c= 0.68, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.64 (d, *J* = 8.1 Hz, 2H), 7.13 (d, *J* = 8.1 Hz, 2H), 6.06 (s, 1H), 5.16 (s, 1H), 4.29 – 4.17 (m, 2H), 3.45 (d, *J* = 16.5 Hz, 1H), 3.19 (d, *J* = 18.0 Hz, 1H), 2.96 (d, *J* = 16.6 Hz, 1H), 2.76 (d, *J* = 18.1 Hz, 1H), 1.44 (s, 9H), 1.27 (t, *J* = 7.2 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 173.8, 154.9, 138.9, 137.5, 134.9, 127.4, 122.7, 92.8, 64.4, 61.6, 45.3, 44.7, 42.0, 28.3, 14.2; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{19}H_{25}INO_4^+$ 458.0823; found 458.0822.

Ethyl (*S*)-1-((tert-butoxycarbonyl)amino)-3-(4-octylphenyl)cyclopent-3-ene-1-carboxylate (11):



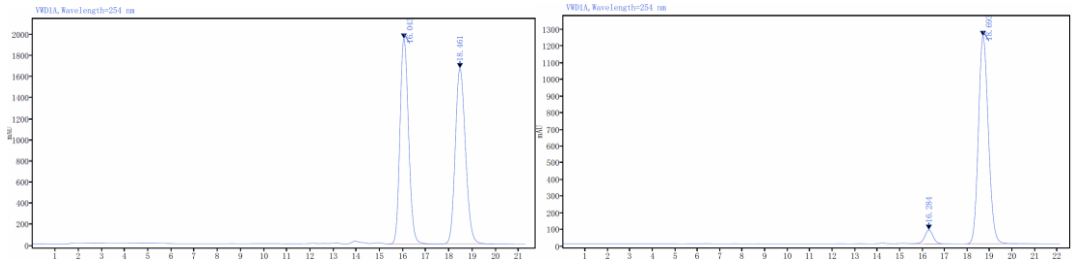
Colorless oil (186.1 mg, 80%); R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); $[\alpha]_D^{20}$ = -16.44 (c= 0.15, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 7.9 Hz, 2H), 7.13 (d, *J* = 7.9 Hz, 2H), 5.98 (s, 1H), 5.15 (s, 1H), 4.27 – 4.14 (m, 2H), 3.48 (d, *J* = 16.5 Hz, 1H), 3.21 (d, *J* = 20.1 Hz, 1H), 2.97 (d, *J* = 16.5 Hz, 1H), 2.74 (d, *J* = 17.8 Hz, 1H), 2.58 (t, *J* = 7.7 Hz, 2H), 1.63 – 1.56 (m, 2H), 1.43 (s, 9H), 1.32 – 1.23 (m, 13H), 0.87 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 174.0, 155.0, 142.4, 139.6, 132.9, 128.4, 125.5, 120.6, 79.9, 64.5, 61.6, 61.5, 45.1, 35.7, 31.9, 31.4, 29.5, 29.3, 29.2, 28.3, 22.7, 14.2, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{27}H_{42}NO_4^+$ 444.3108; found 444.3110.

Tert-butyl (*S*)-(1-(hydroxymethyl)-3-(4-octylphenyl)cyclopent-3-en-1-yl)carbamate (12):



12

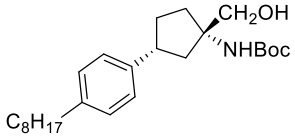
White solid (144.0 mg, 78%); m.p. = 58- 60 °C; R_f = 0.27 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90 % by HPLC analysis on Daicel Chirapak IG-H column (hexane/isopropanol = 90/10, flow rate 0.5 mL/min, T = 30 °C), UV 254 nm, t_R(major) 18.693 min, t_R(minor) 16.284 min; $[\alpha]_D^{20}$ = +11.99 (c= 0.57, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.31 (d, *J* = 8.0 Hz, 2H), 7.12 (d, *J* = 7.9 Hz, 2H), 6.00 (s, 1H), 5.12 (s, 1H), 3.87 (s, 1H), 3.74 (s, 2H), 2.98 (d, *J* = 16.3 Hz, 1H), 2.85 (d, *J* = 18.6 Hz, 1H), 2.76 (d, *J* = 17.6 Hz, 1H), 2.63 (d, *J* = 17.4 Hz, 1H), 2.57 (t, *J* = 7.8 Hz, 2H), 1.64 – 1.56 (m, 2H), 1.44 (s, 9H), 1.36 – 1.21 (m, 10H), 0.87 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 156.3, 142.3, 139.9, 133.2, 128.4, 125.4, 121.6, 80.0, 68.6, 63.9, 43.1, 43.0, 35.7, 31.9, 31.4, 29.5, 29.3, 29.3, 28.4, 22.7, 14.1; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{25}H_{40}NO_3^+$ 402.3003; found 402.3004.



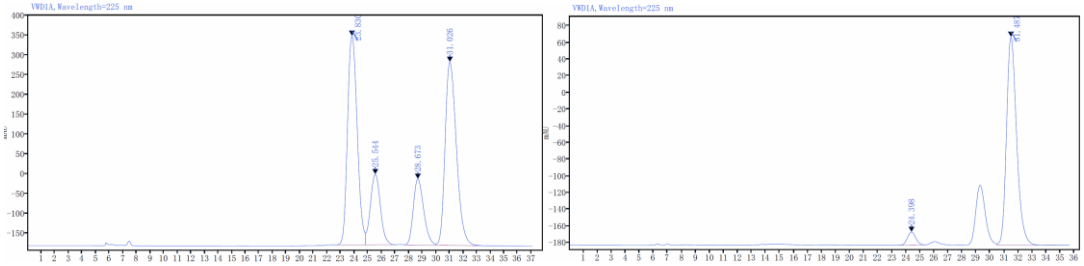
Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	16.043	VB	2.0962	50270.5194	1944.4749	49.6100
2	18.461	BB	2.4567	51060.8512	1663.8390	50.3900

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
1	16.284	VB	2.1211	2166.2002	82.5013	5.3714
2	18.693	BB	2.4900	38162.5420	1245.4410	94.6286

Tert-butyl ((*1S*, *3R*)-1-(hydroxymethyl)-3-(4-octylphenyl)cyclopentyl)carbamate (13):



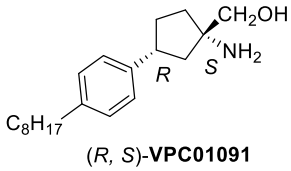
Colorless oil (70.0 mg, 99%, 4:1 dr); R_f = 0.26 (petroleum ether/ ethyl acetate = 3:1); the enantiomeric excess was determined to be 90 % by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 98/2, flow rate 0.5 mL/min, T = 30 °C), UV 225 nm, t_R(major) 31.487 min, t_R(minor) 24.398 min; $[\alpha]_D^{20}$ = +9.63 (c= 0.36, $CHCl_3$); **^{1}H NMR (600 MHz, $CDCl_3$):** δ 7.15 (d, *J* = 7.8 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 4.88 (s, 1H), δ 3.85 (s, 1H), 3.74 (d, *J* = 11.7 Hz, 1H), 3.70 (d, *J* = 11.2 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.57 (t, *J* = 7.9 Hz, 2H), 2.46 (q, *J* = 13.4, 7.7 Hz, 1H), 2.13 – 2.05 (m, 1H), 1.99 – 1.89 (m, 2H), 1.73 (t, *J* = 12.1 Hz, 1H), 1.66 – 1.53 (m, 3H), 1.45 (s, 9H), 1.34 – 1.23 (m, 10H), 0.88 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, $CDCl_3$):** δ 156.7, 141.8, 141.1, 128.7, 127.1, 80.3, 65.0, 44.6, 44.0, 43.9, 36.1, 35.8, 32.9, 32.2, 31.9, 29.8, 29.7, 29.6, 28.7, 23.0, 14.4; **HRMS(ESI)** m/z: $[M+H]^+$ Calculated for $C_{25}H_{42}NO_3^+$ 404.3159; found 404.3160.



Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	23.830	BV	2.2026	26154.8209	528.5753	36.9223
	25.544	VB	2.1710	9120.4497	178.1670	12.8752
	28.673	VV	2.3196	8804.5988	166.9696	12.4293
	31.026	VB	3.8718	26757.6339	463.9131	37.7733

Peak	RetTime [min]	Type	Width[min]	Area[mAU*s]	Height[mAU]	Area%
	24.398	BB	1.8937	645.0087	15.6123	4.8959
	31.487	VB	4.2037	12529.4439	249.5387	95.1041

((*1S, 3R*)-1-amino-3-(4-octylphenyl)cyclopentyl)methanol [(*1S, 3R*)-VPC01091]:[4]



(*R, S*)-**VPC01091**

White solid (0.023 g, 88%); m.p. = 69- 71 ºC; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); $[\alpha]_D^{20}$ = +2.4 (c= 0.033, $CHCl_3$); **^{1}H NMR (600 MHz, CD_3OD):** δ 7.20 (d, *J* = 7.9 Hz, 2H), 7.11 (d, *J* = 7.7 Hz, 2H), 3.65 (d, *J* = 11.5 Hz, 1H), 3.58 (d, *J* = 11.5 Hz, 1H), 3.12 (ddt, *J* = 18.2, 11.8, 6.7 Hz, 1H), 2.56 (t, *J* = 7.6 Hz, 2H), 2.41 (dd, *J* = 13.3, 7.0 Hz, 1H), 2.22 – 2.08 (m, 1H), 2.01 – 1.86 (m, 3H), 1.77 – 1.68 (m, 1H), 1.58 (q, *J* = 7.3 Hz, 2H), 1.42 – 1.19 (m, 10H), 0.89 (t, *J* = 6.9 Hz, 3H); **^{13}C NMR (151 MHz, CD_3OD):** δ 142.3, 141.5, 129.5, 127.8, 66.9, 65.2, 45.5, 43.1, 36.5, 34.6, 33.6, 33.0, 32.8, 30.6, 30.4, 30.3, 23.7, 14.4. HRMS(ESI) m/z: $[M+H]^+$ Calculated for $C_{20}H_{34}NO^+$ 304.2635; found 304.2632.

8. References

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[2] (a) V. P. Kasagani, S. H. Kurma, C. R. Bhimapaka, *J. Org. Chem.***2020**, *85*, 5, 2976; (b) Shmatova, O. I., Shevchenko, N. E., Balenkova, E. S., Röschenthaler, G.-V. & Nenajdenko, V. G. Friedel-Crafts alkylation of natural amino acid-derived pyrroles with CF_3-substituted cyclic imines. *Mendeleev Commun.* **2013**, *23*, 92-93.

[3] (a) W. Wen, L. Chen, M. Luo, Y. Zhang, Y. Chen, Q. Ouyang, Q.-X. Guo. *J. Am. Chem. Soc.* **2018**, *140*, 9774; (b) L. Chen, M.-J. Luo, F. Zhu, W. Wen, Q.-X. Guo, *J. Am. Chem. Soc*. **2019**, *141*, 5159; (c) Xu, B. et al. Catalytic asymmetric direct α-alkylation of amino esters by aldehydes via imine activation. *Chem. Sci.* **2014**, *5*, 1988-1991.

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Macdonald. Asymmetric Synthesis of Conformationally Constrained Fingolimod Analogues—Discovery of an Orally Active Sphingosine 1-Phosphate Receptor Type-1 Agonist and Receptor Type-3 Antagonist. *Journal of Medicinal Chemistry*, **2007**, *50*, 6428-6435.

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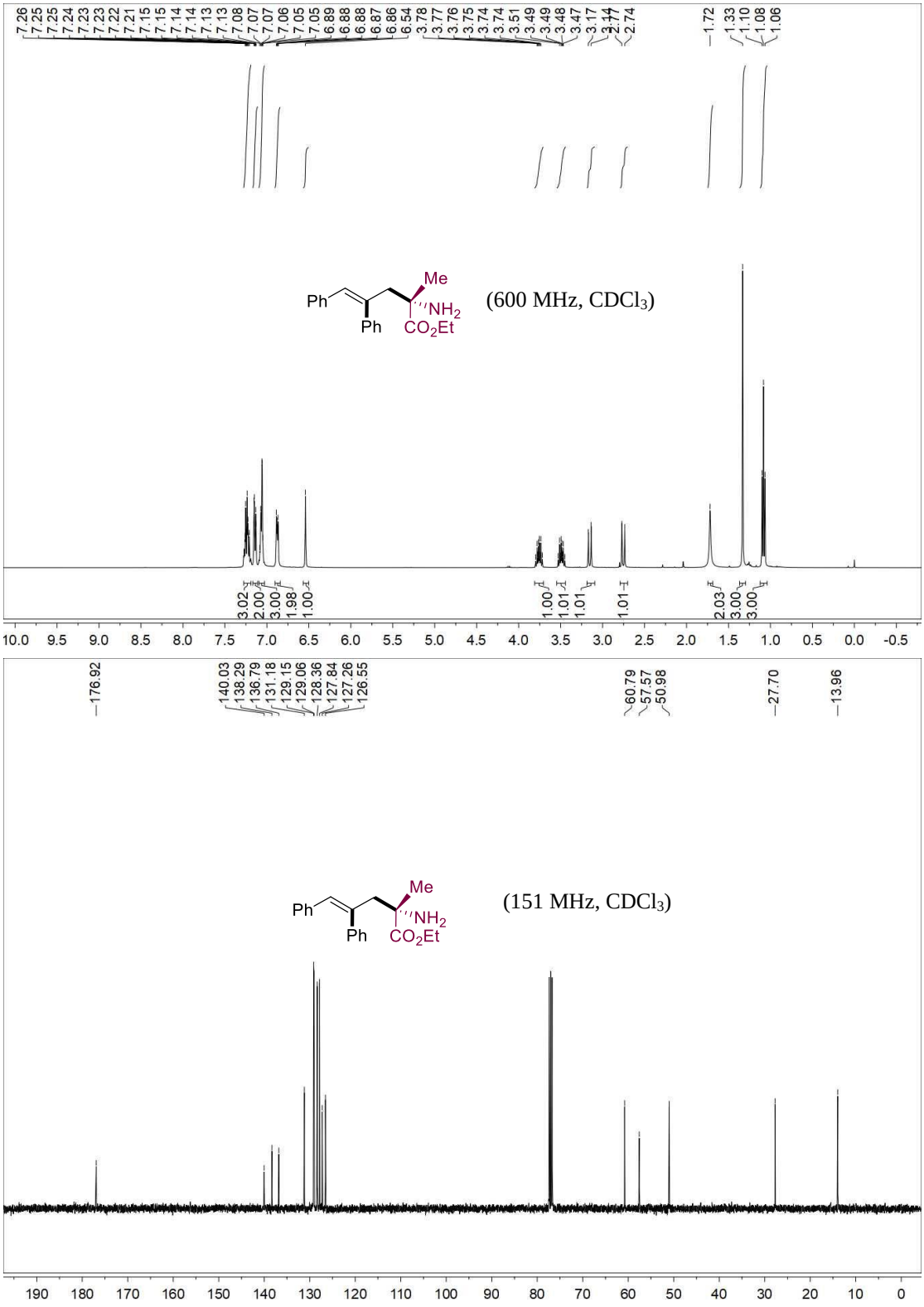
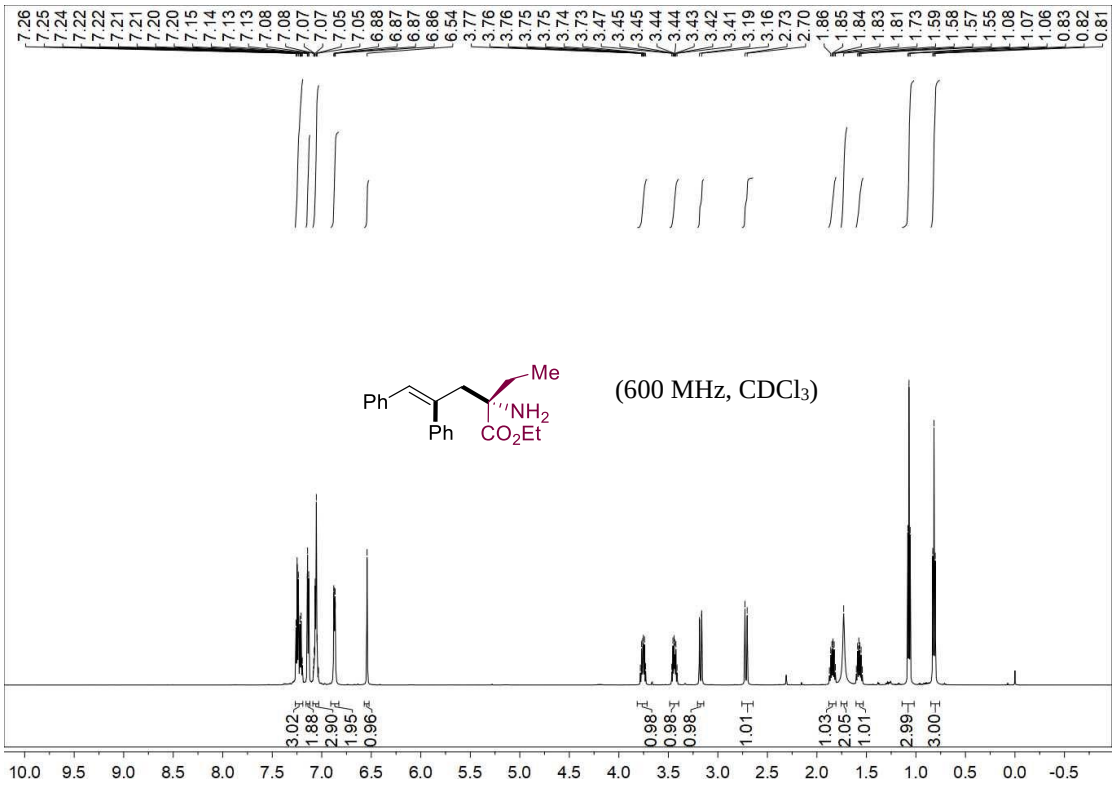
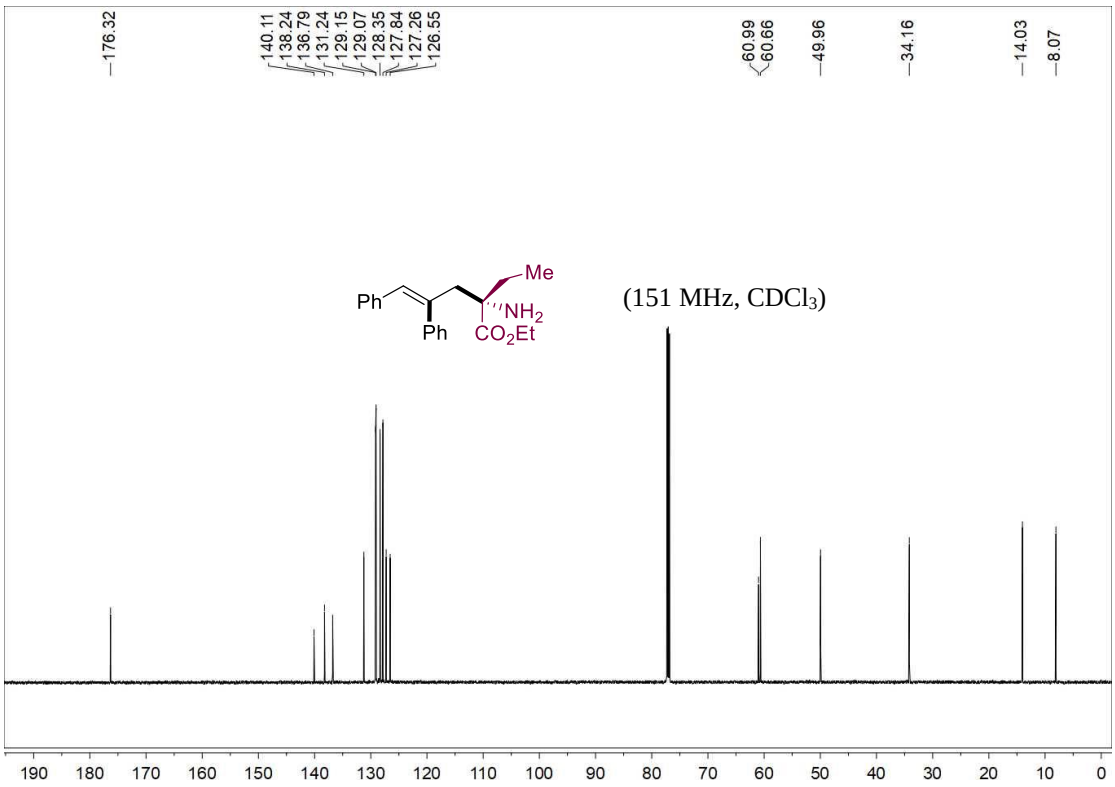
9. The spectrums of ^{1}H NMR and ^{13}C NMR

Ethyl (*S*, *Z*)-2-amino-2-methyl-4, 5-diphenylpent-4-enoate (4a):

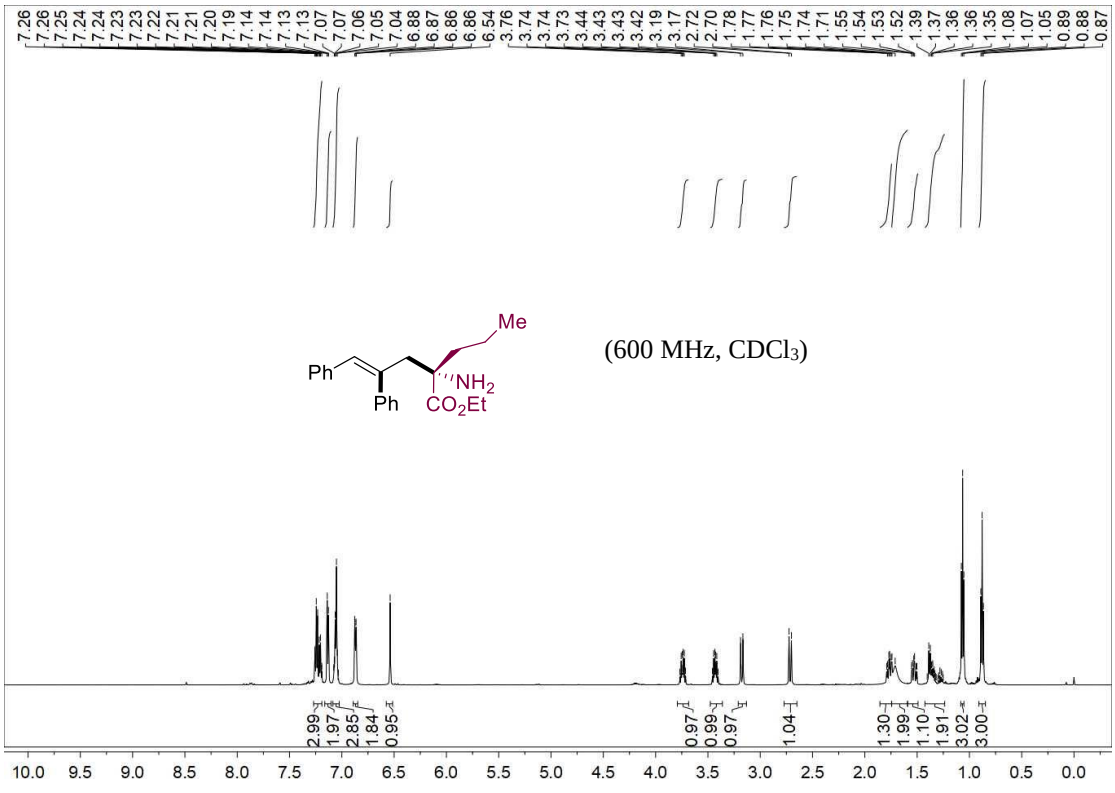


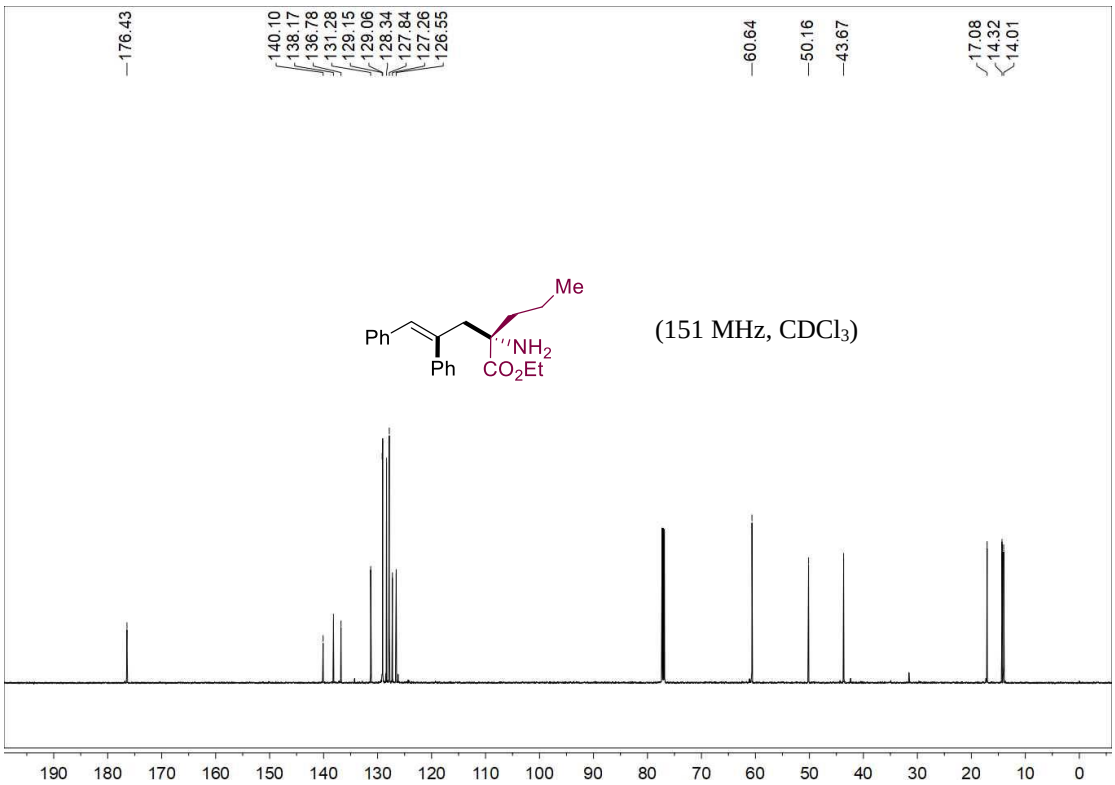
Ethyl (*S*, *Z*)-2-amino-2-ethyl-4, 5-diphenylpent-4-enoate (4b):



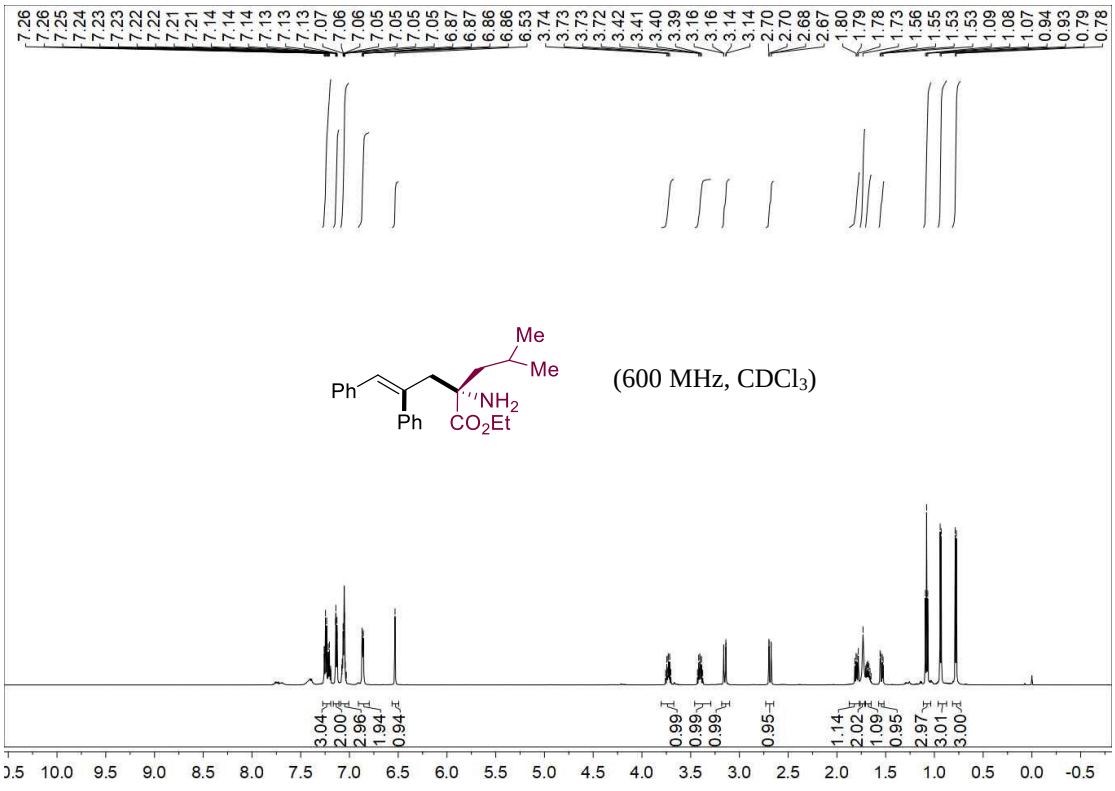


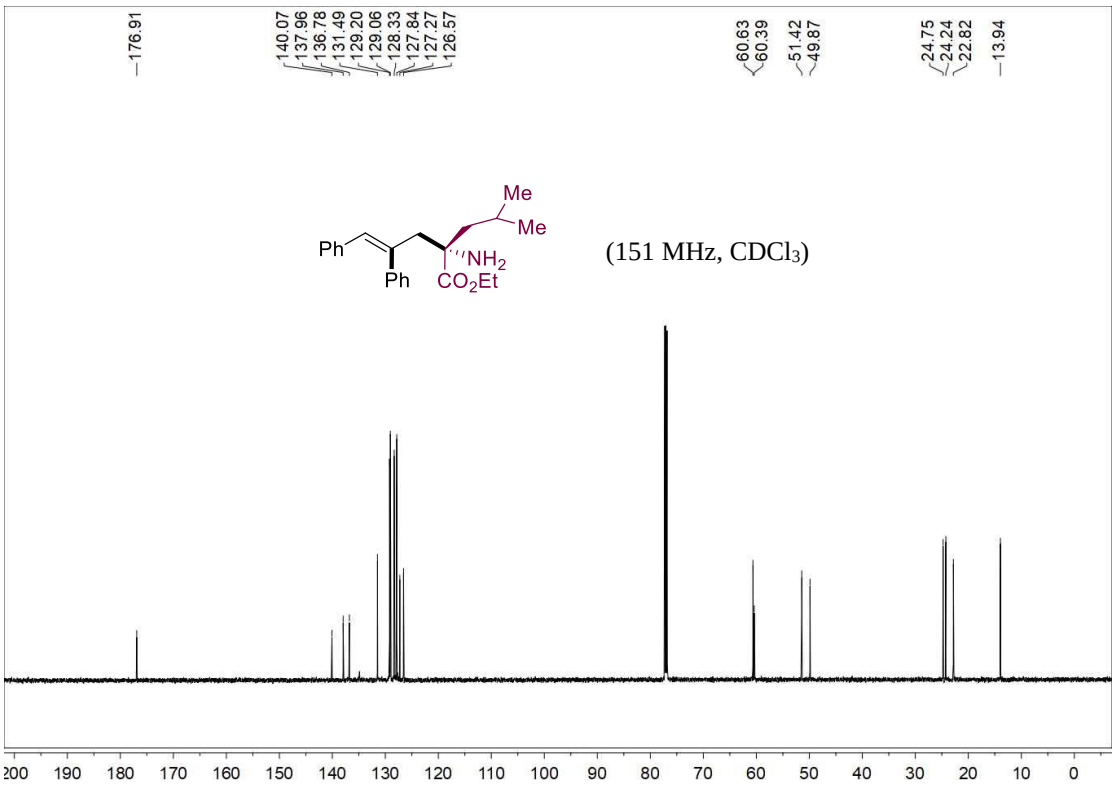
Ethyl (*S*, *Z*)-2-amino-4, 5-diphenyl-2-propylpent-4-enoate (4c):



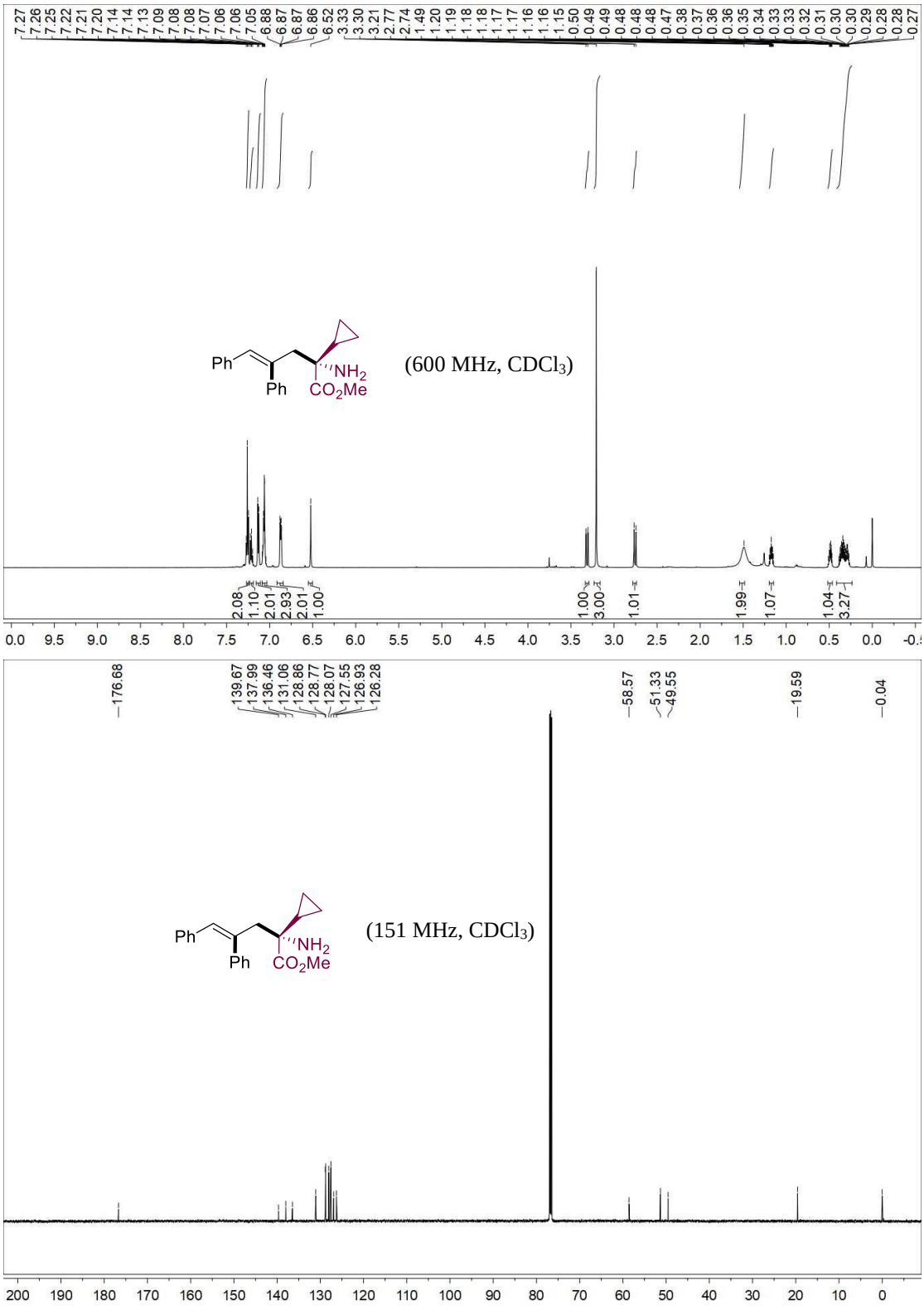


Ethyl (*S*, *Z*)-2-amino-2-isobutyl-4, 5-diphenylpent-4-enoate (4d):

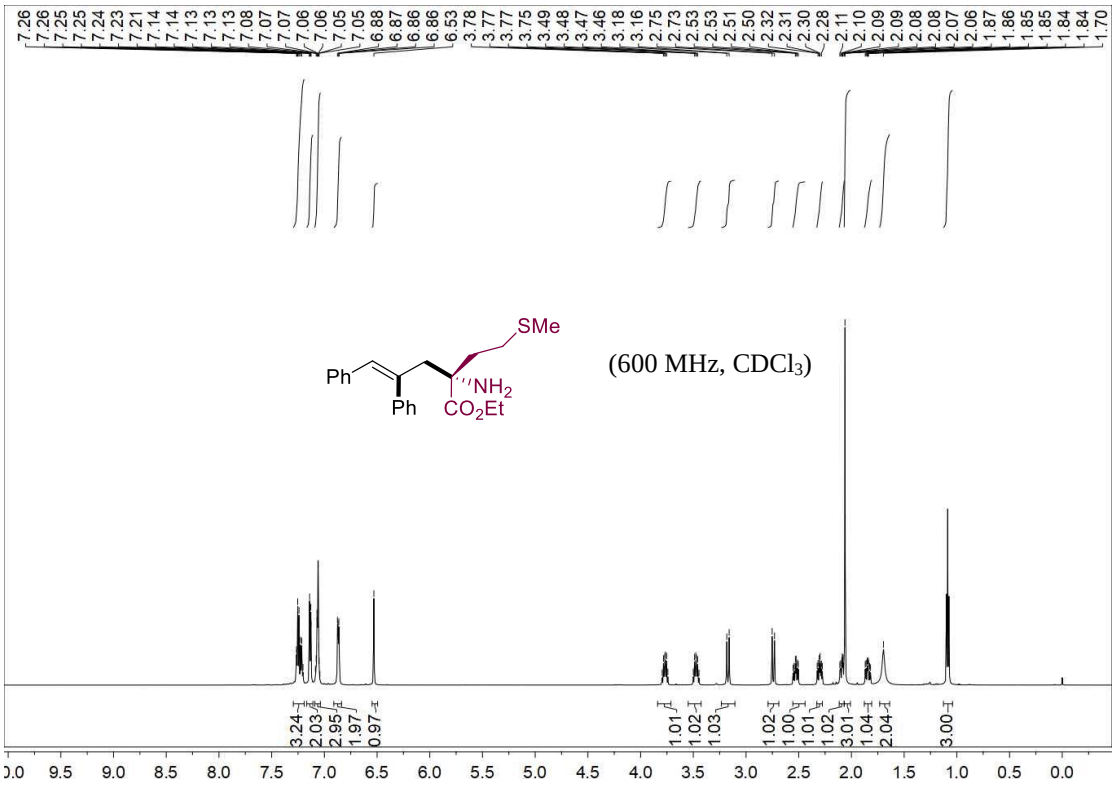


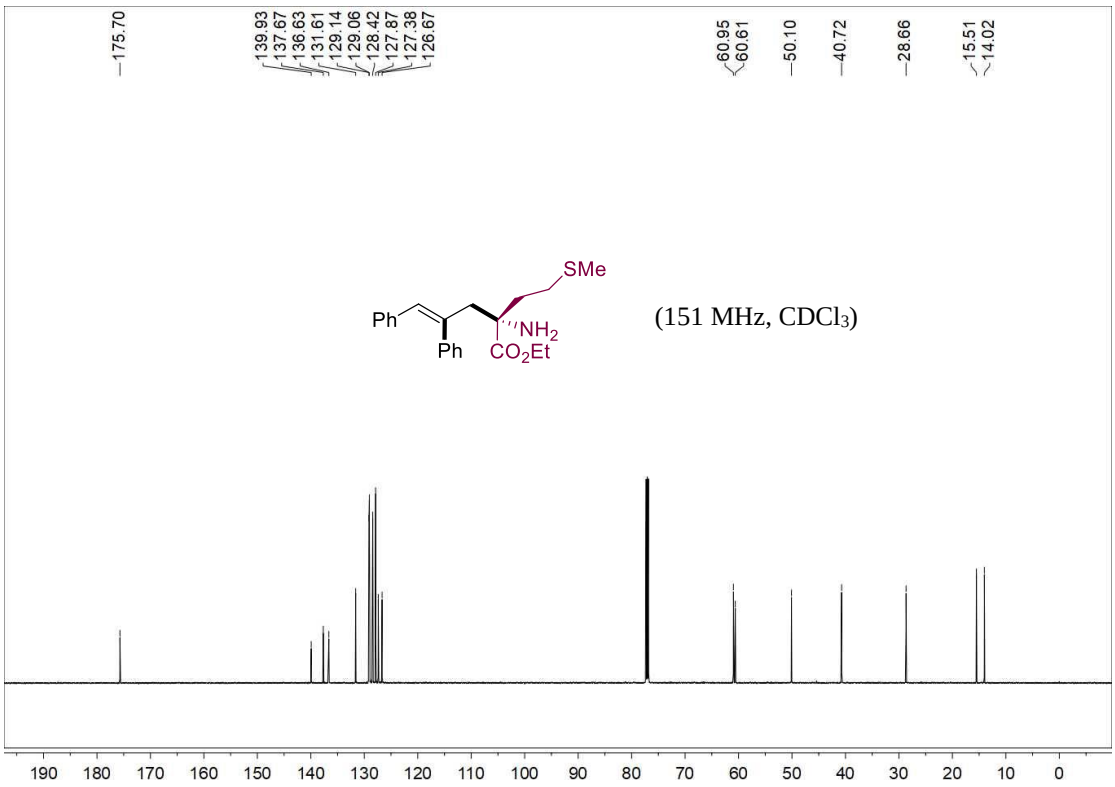


Ethyl (*S*, *Z*)-2-amino-2-cyclopropyl-4, 5-diphenylpent-4-enoate (4e):

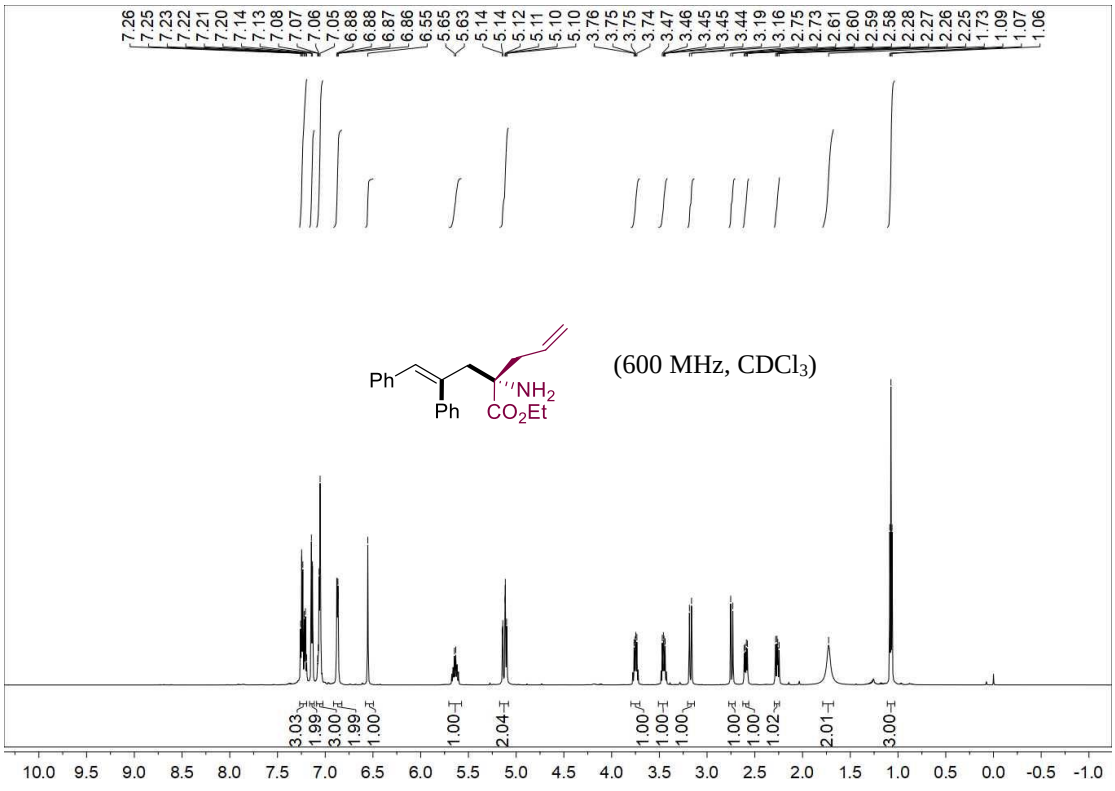


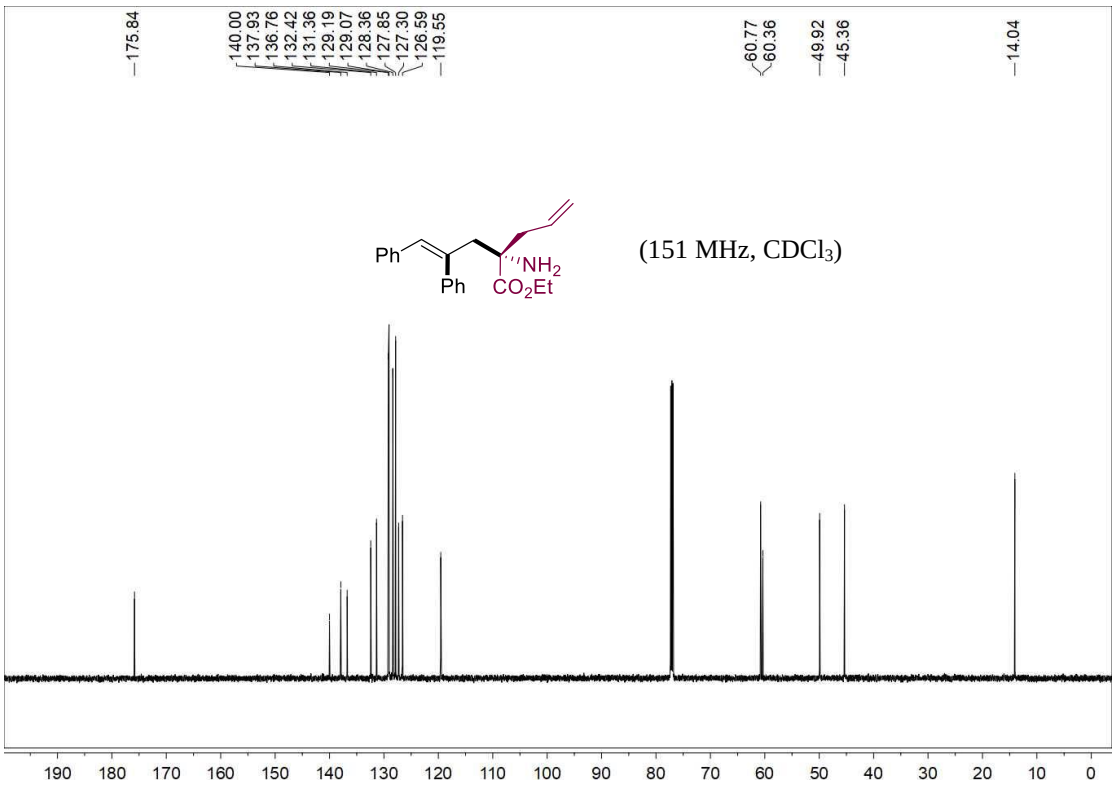
Ethyl (*S*, *Z*)-2-amino-2-(2-(methylthio)ethyl)-4, 5-diphenylpent-4-enoate (4f):



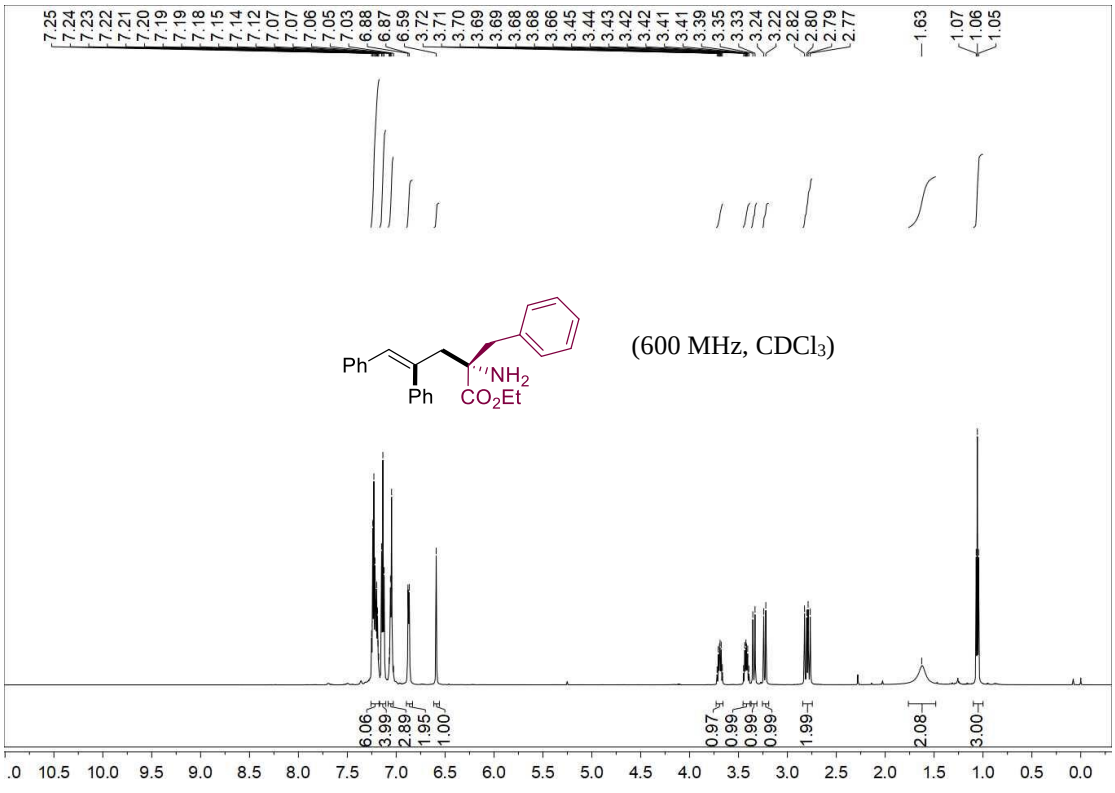


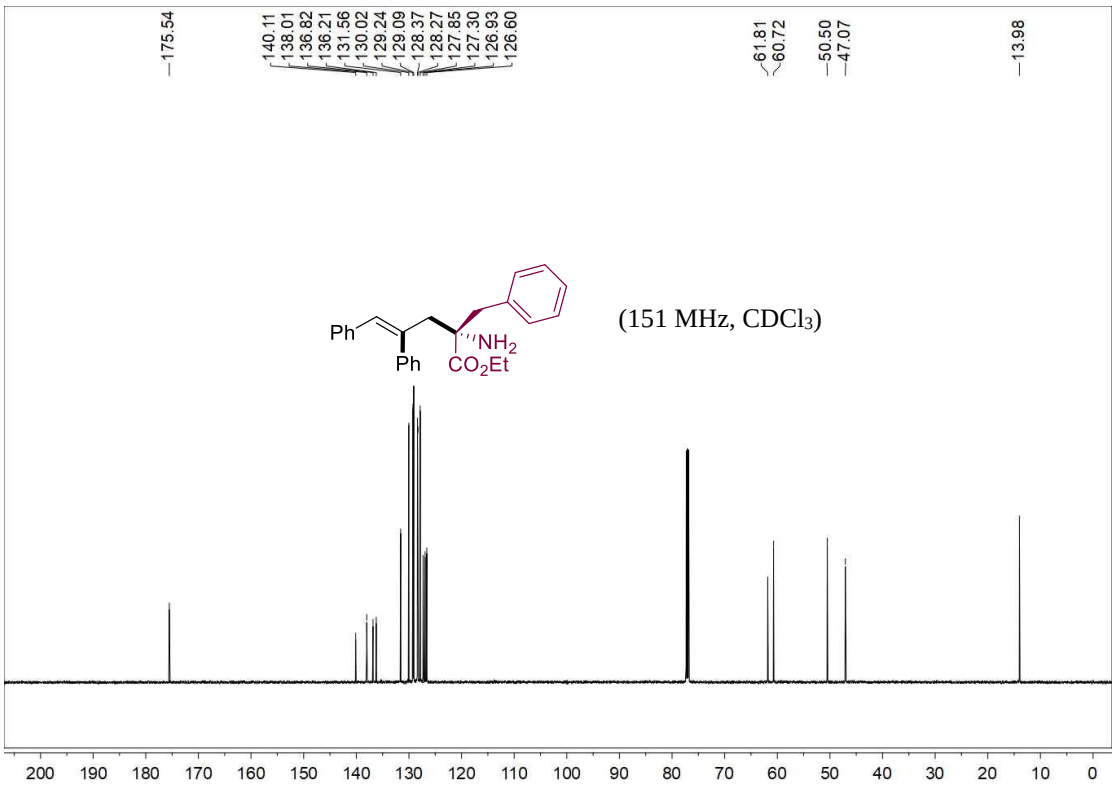
ethyl (*S*, *Z*)-2-allyl-2-amino-4, 5-diphenylpent-4-enoate (4g):



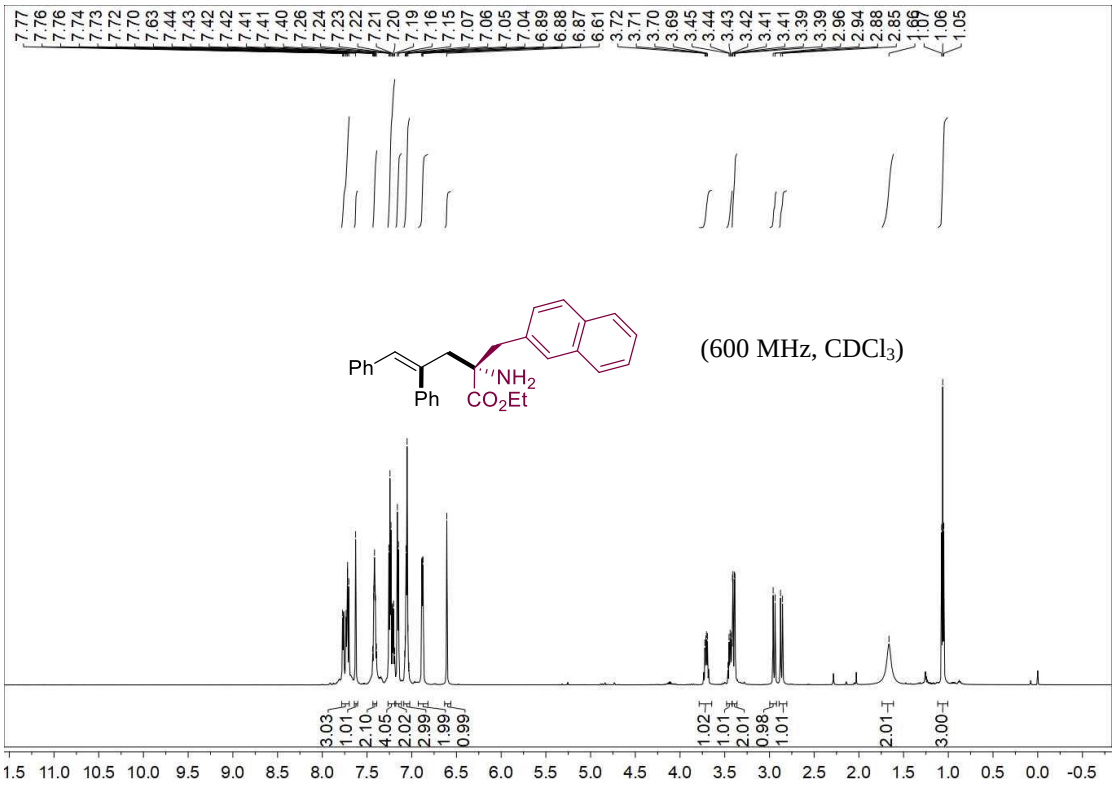


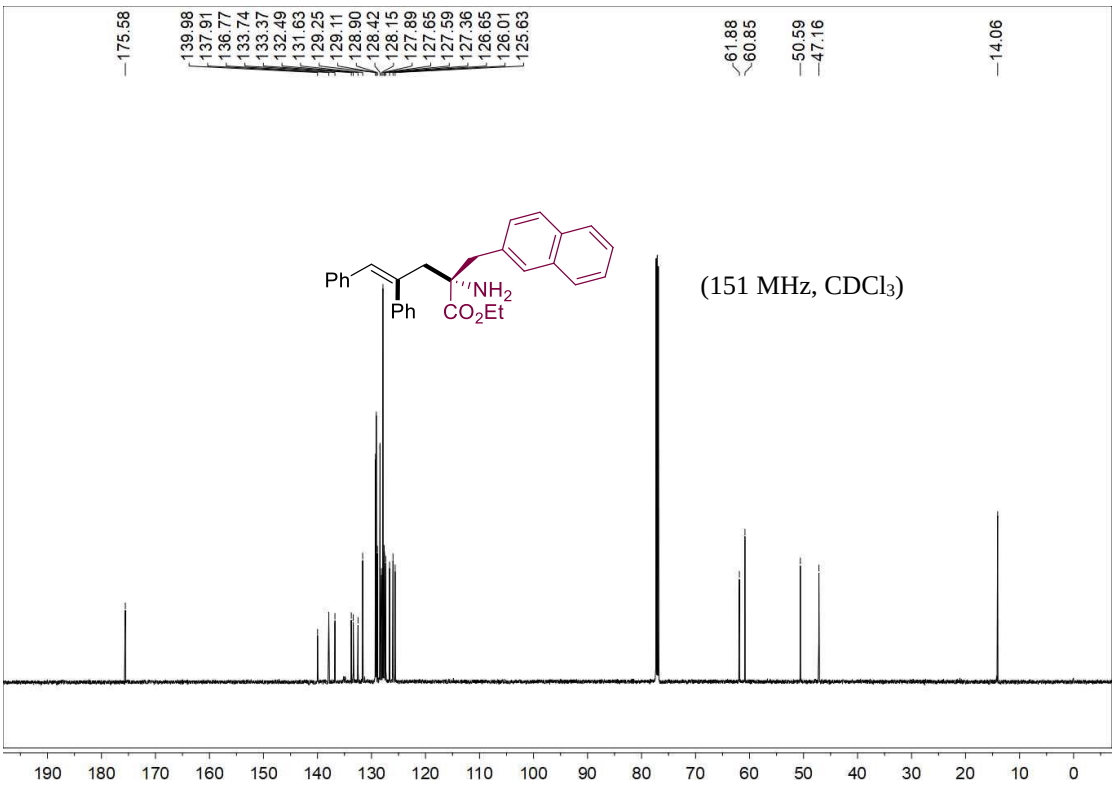
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4, 5-diphenylpent-4-enoate (4h):



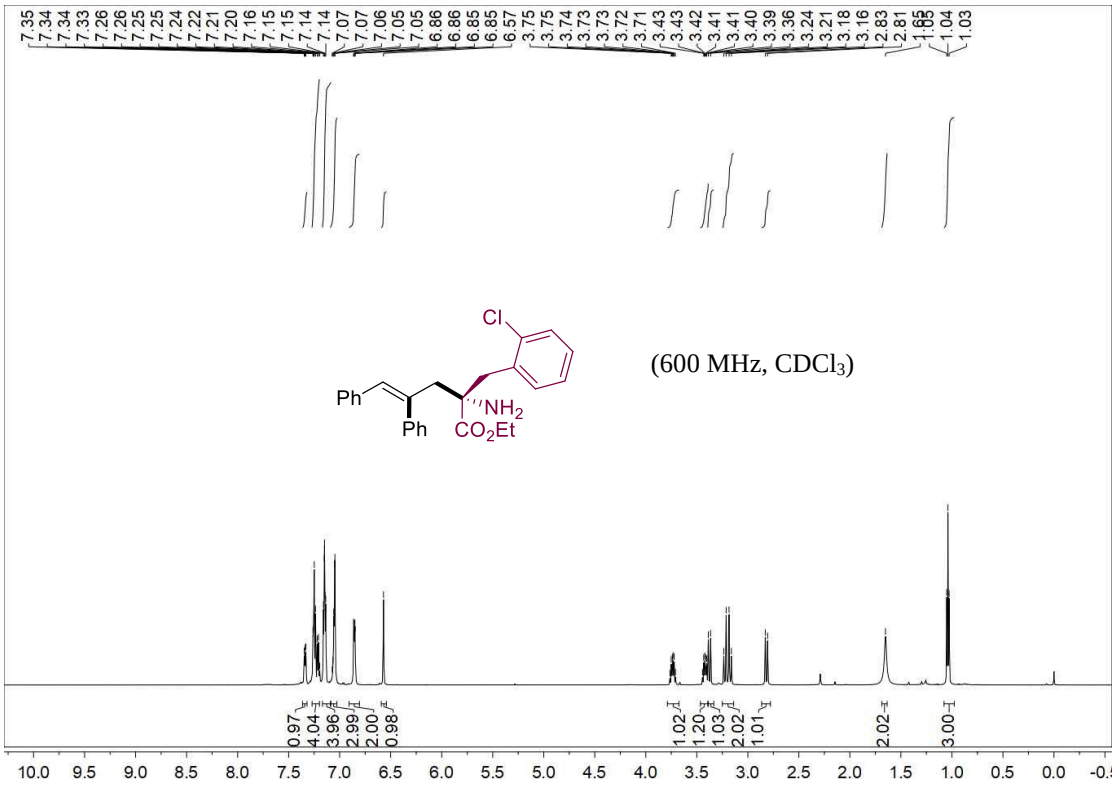


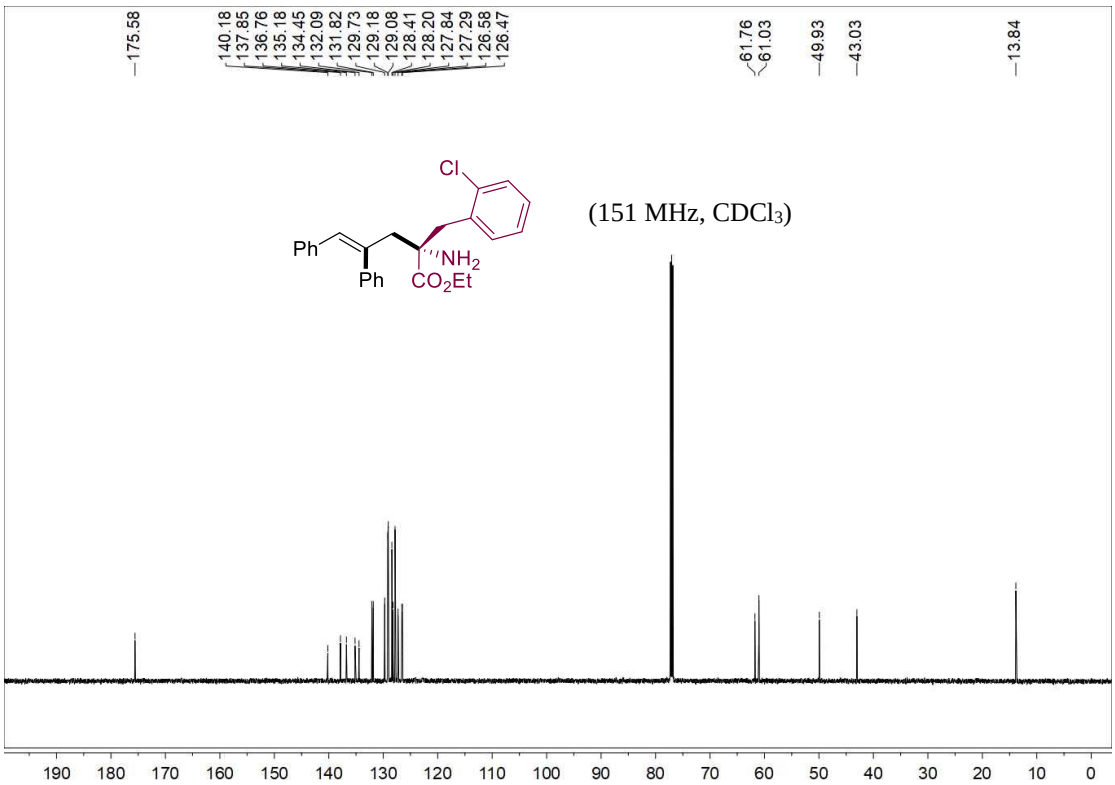
Ethyl (*S*, *Z*)-2-amino-2-(naphthalen-2-ylmethyl)-4, 5-diphenylpent-4-enoate (4i):



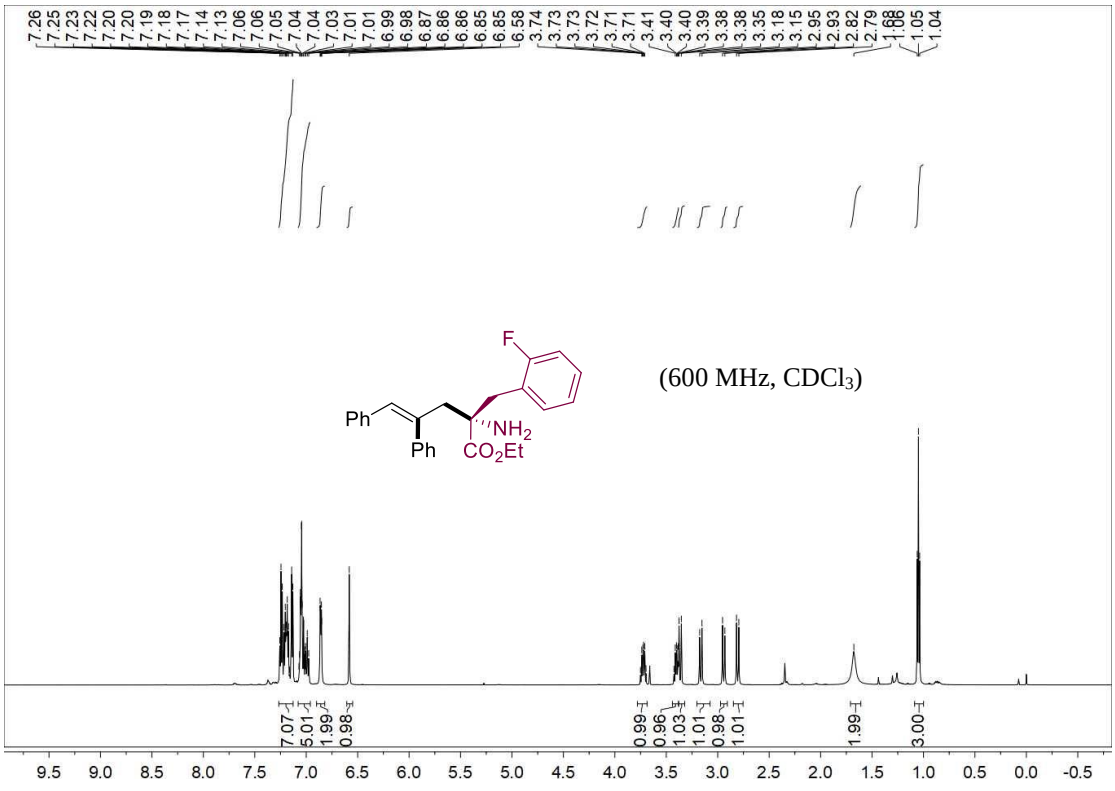


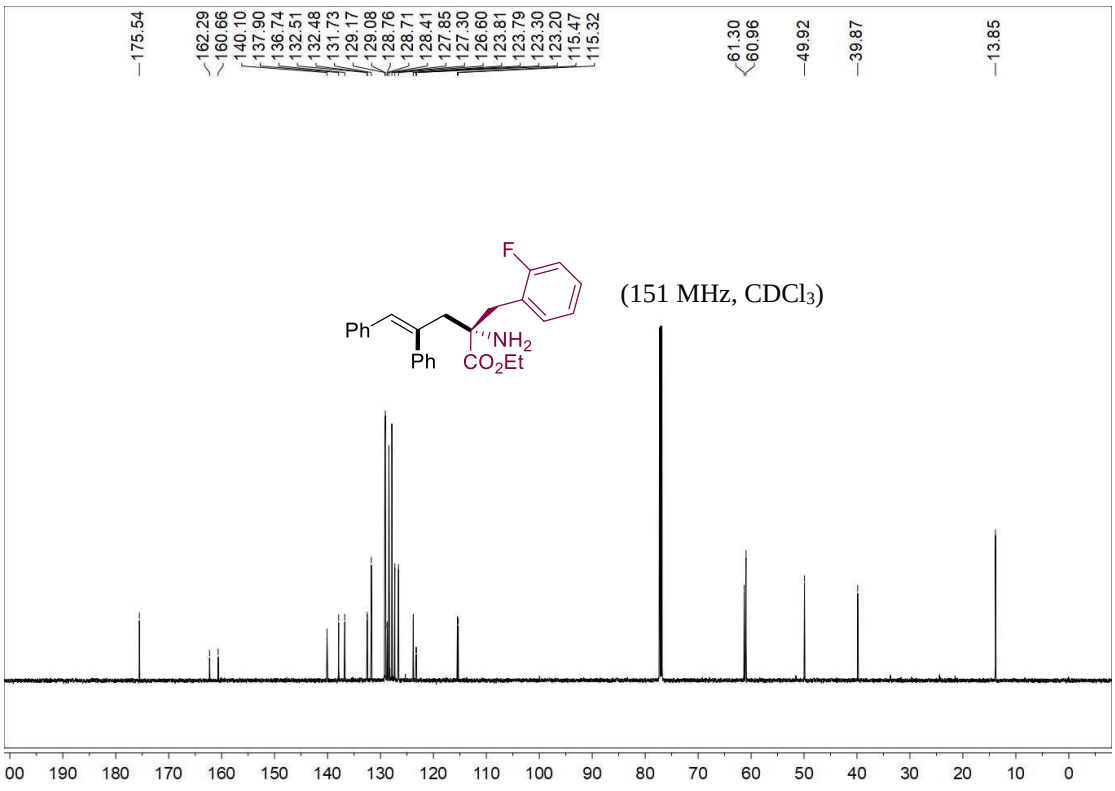
Ethyl (*Z*, *S*)-2-amino-2-(2-chlorobenzyl)-4, 5-diphenylpent-4-enoate(4j):



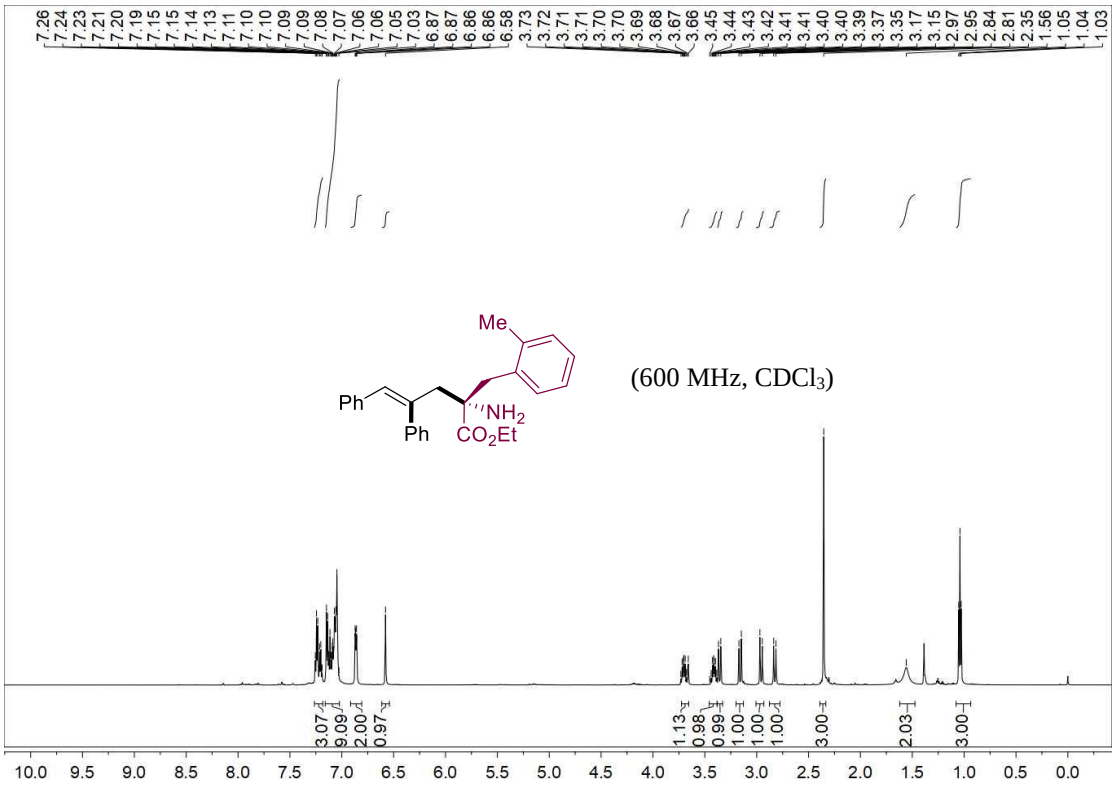


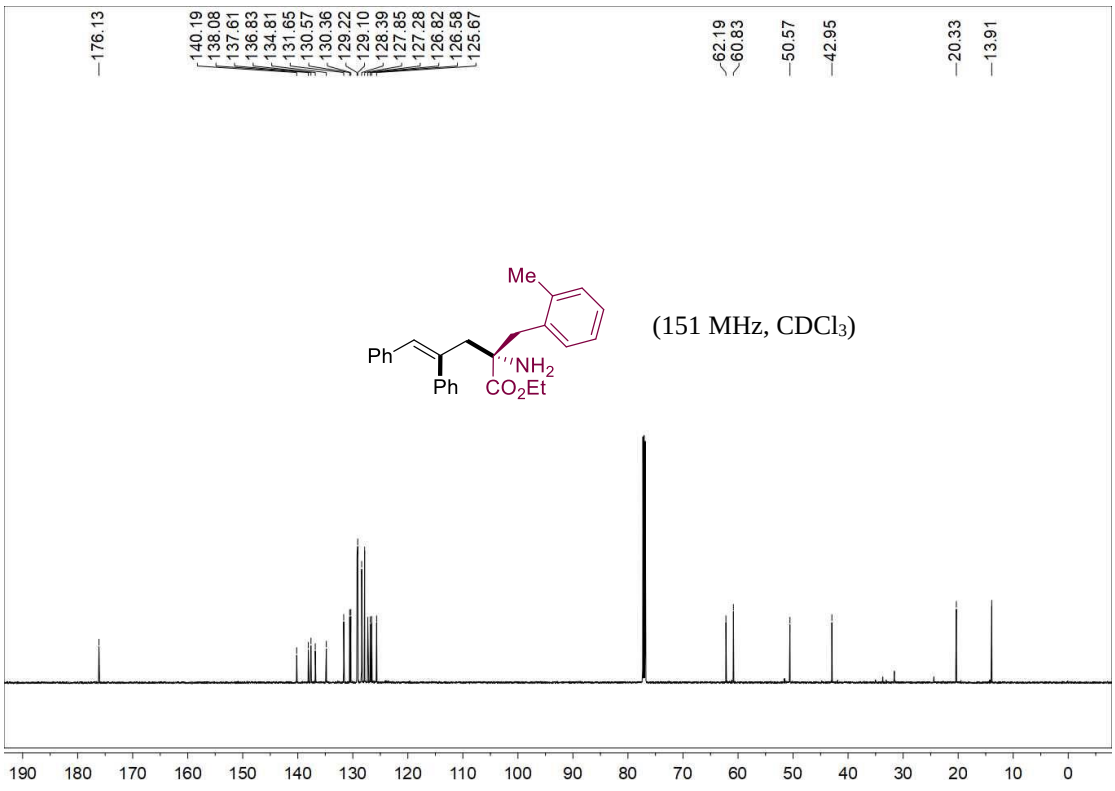
Ethyl (*Z*, *S*)-2-amino-2-(2-fluorobenzyl)-4, 5-diphenylpent-4-enoate (4k):



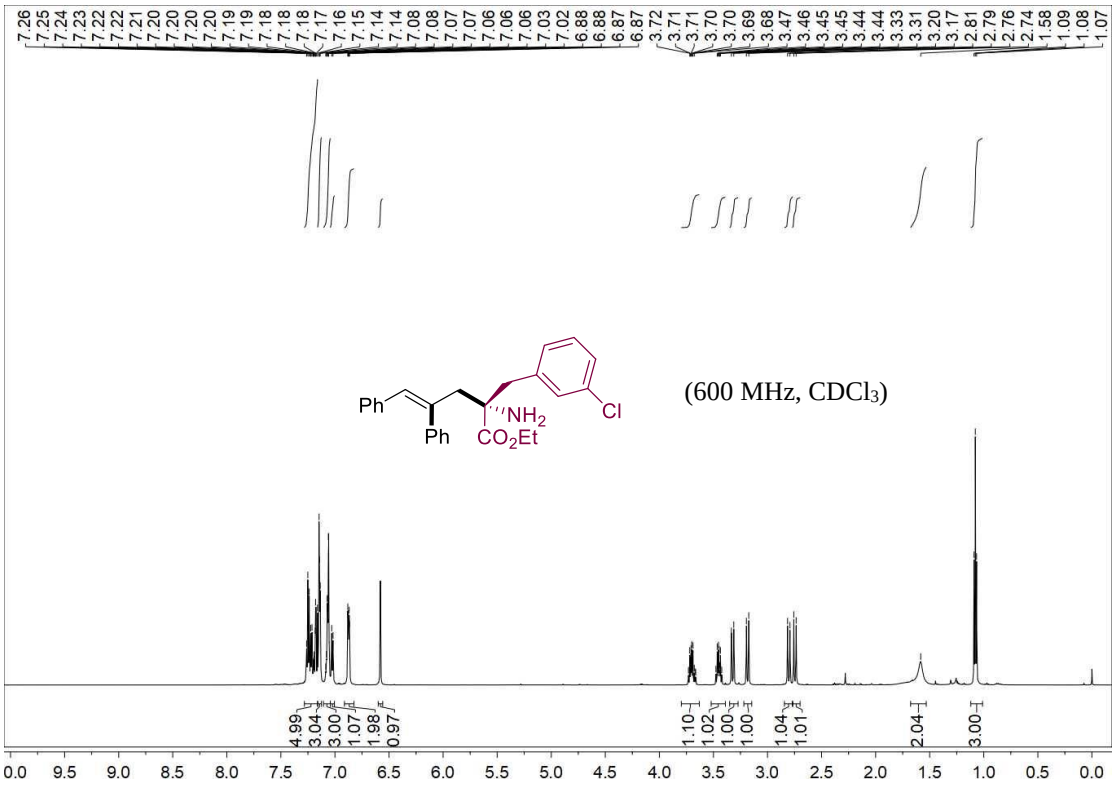


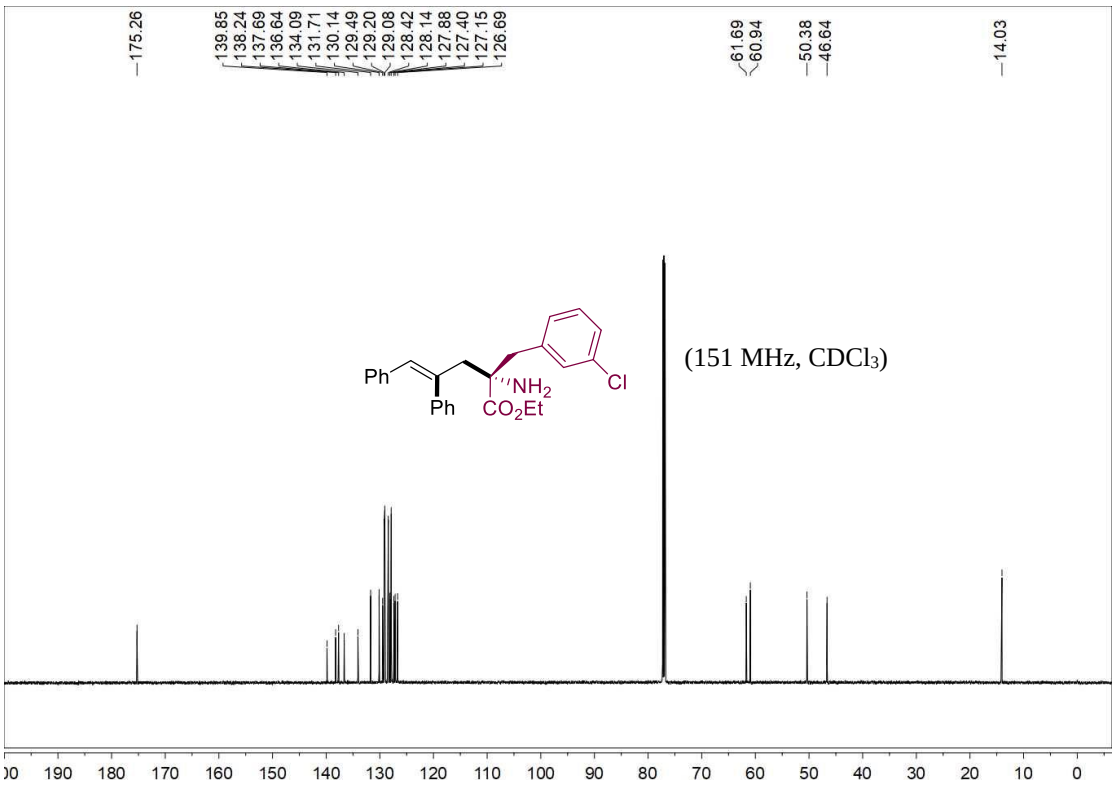
Ethyl (*Z*, *S*)-2-amino-2-(2-methylbenzyl)-4, 5-diphenylpent-4-enoate (4l):



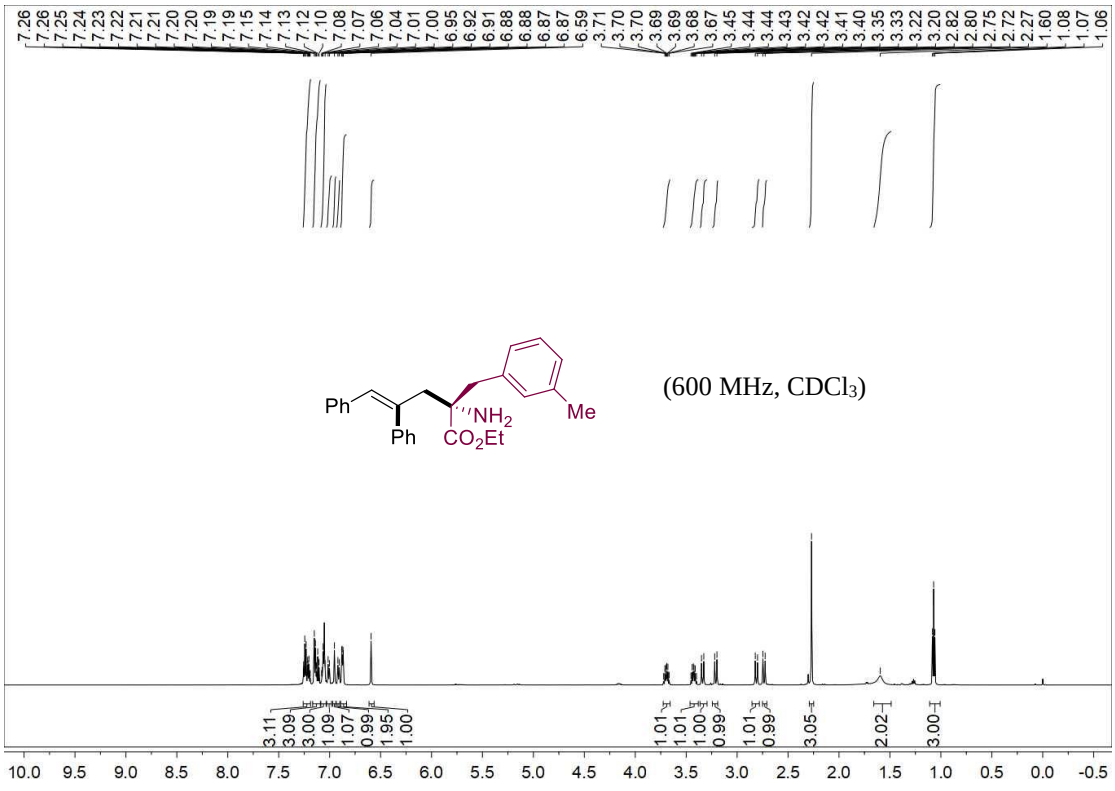


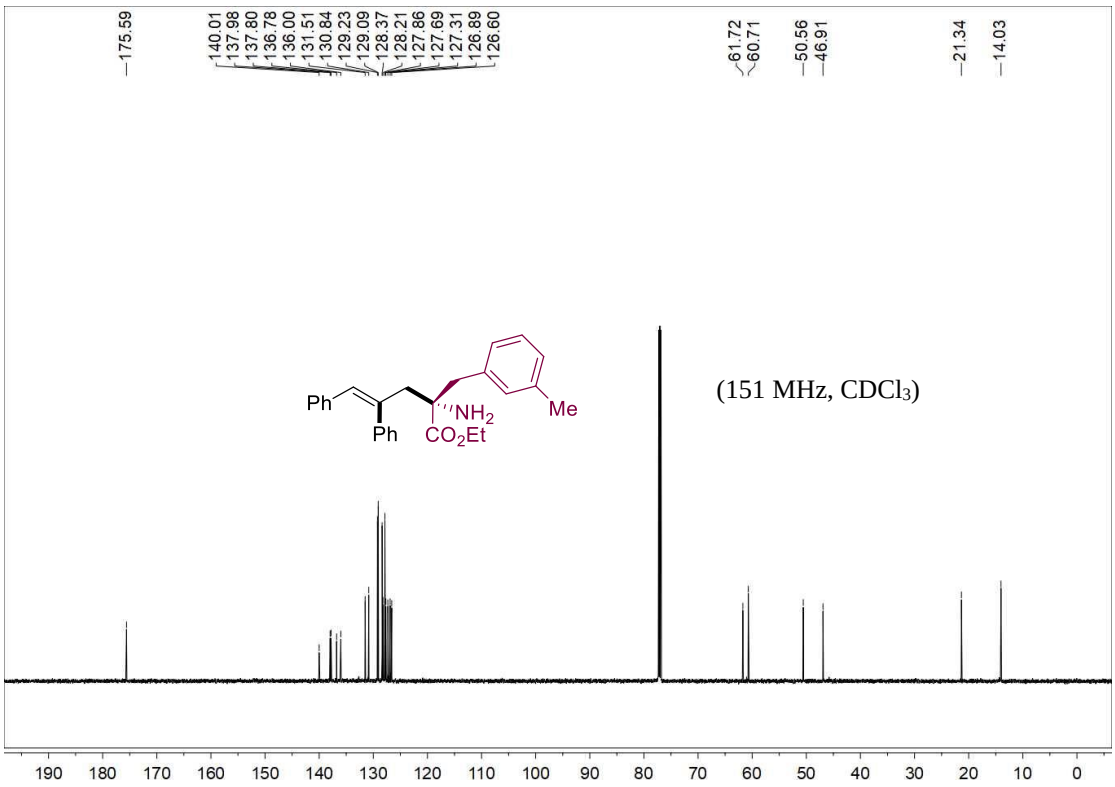
Ethyl (*S*, *Z*)-2-amino-2-(3-chlorobenzyl)-4, 5-diphenylpent-4-enoate (4m):



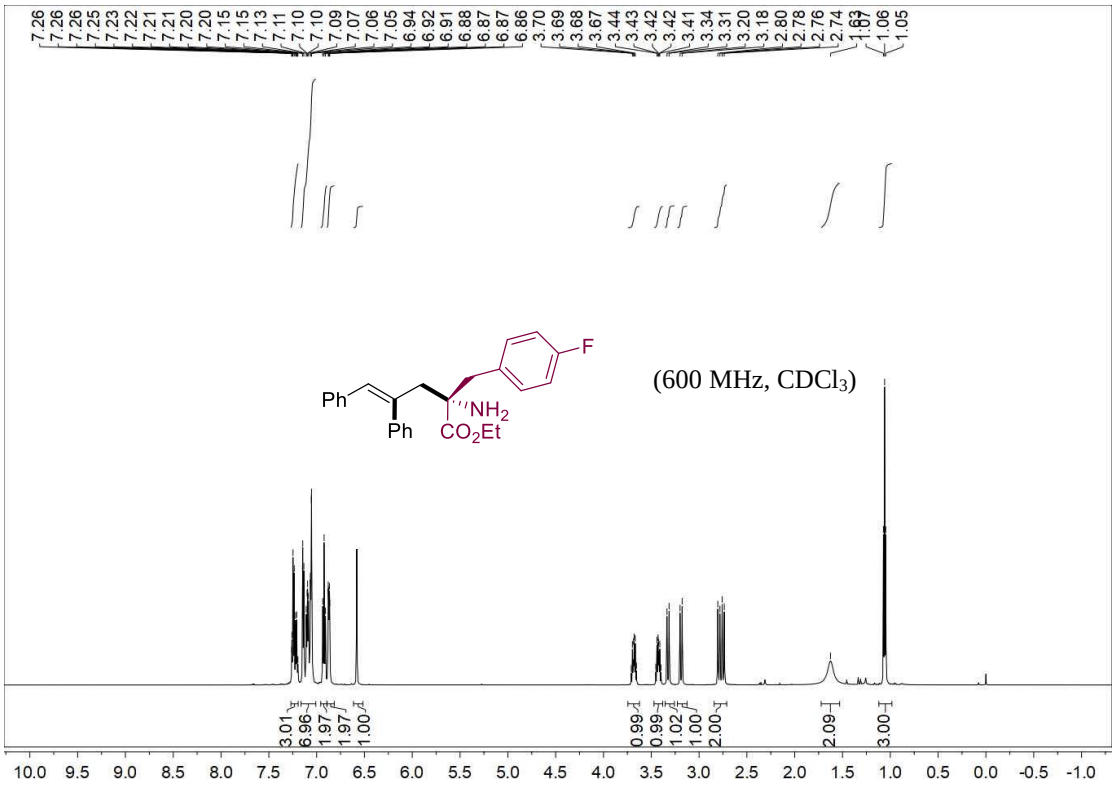


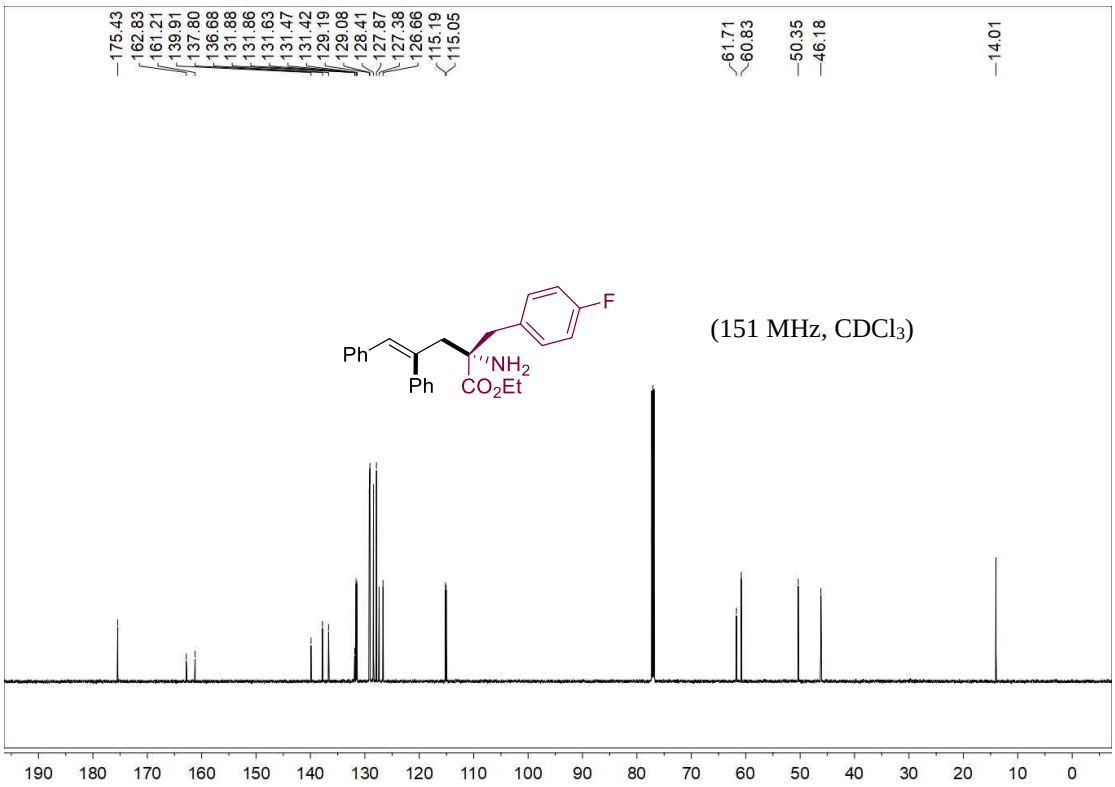
Ethyl (*S*, *Z*)-2-amino-2-(3-methylbenzyl)-4, 5-diphenylpent-4-enoate (4n):



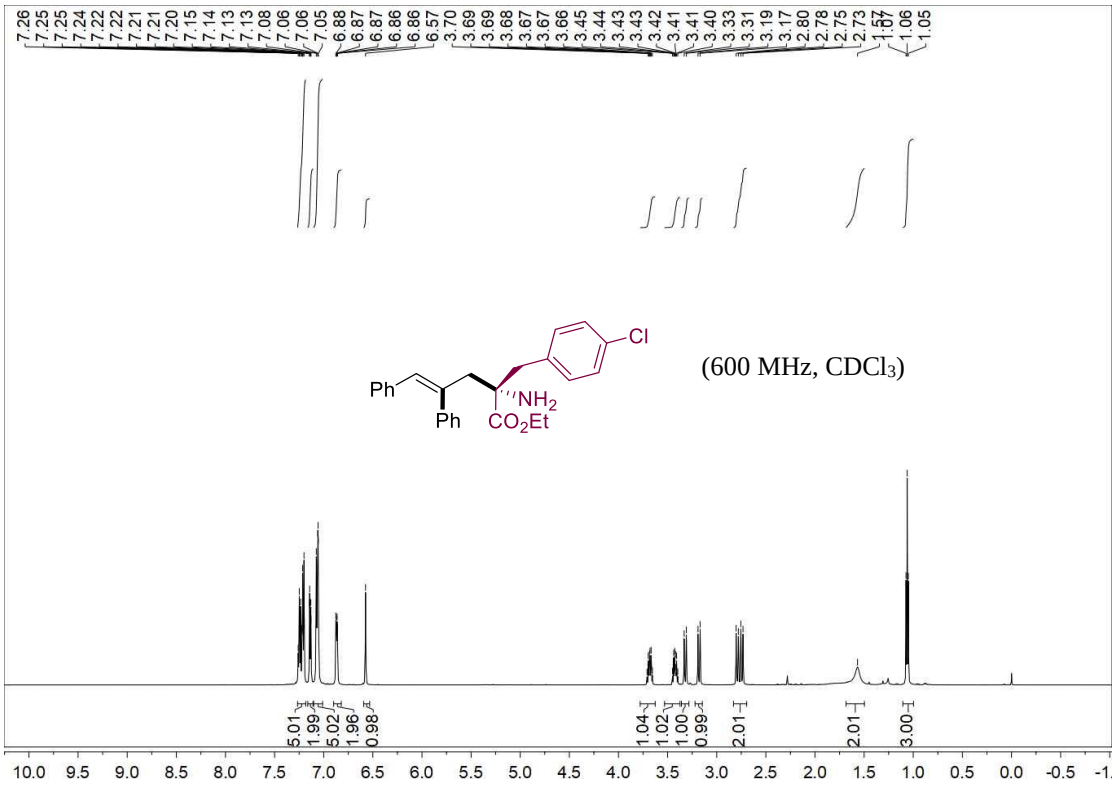


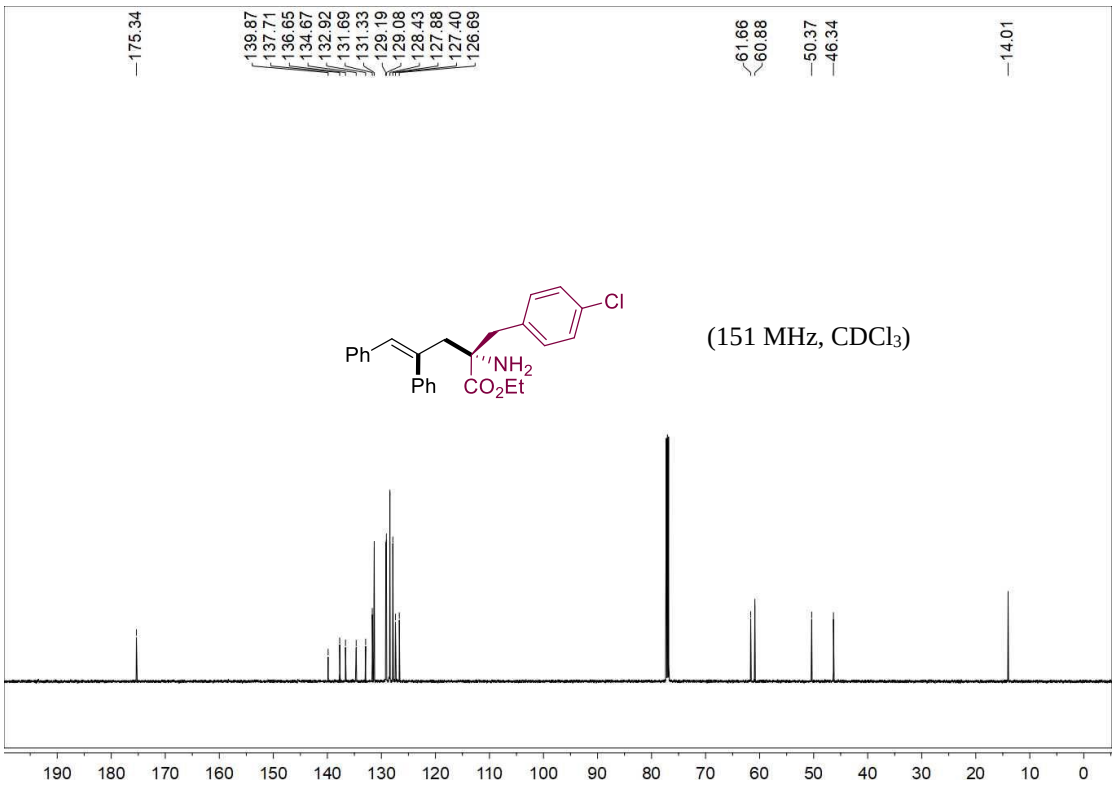
Ethyl (*S*, *Z*)-2-amino-2-(4-fluorobenzyl)-4, 5-diphenylpent-4-enoate (4o):



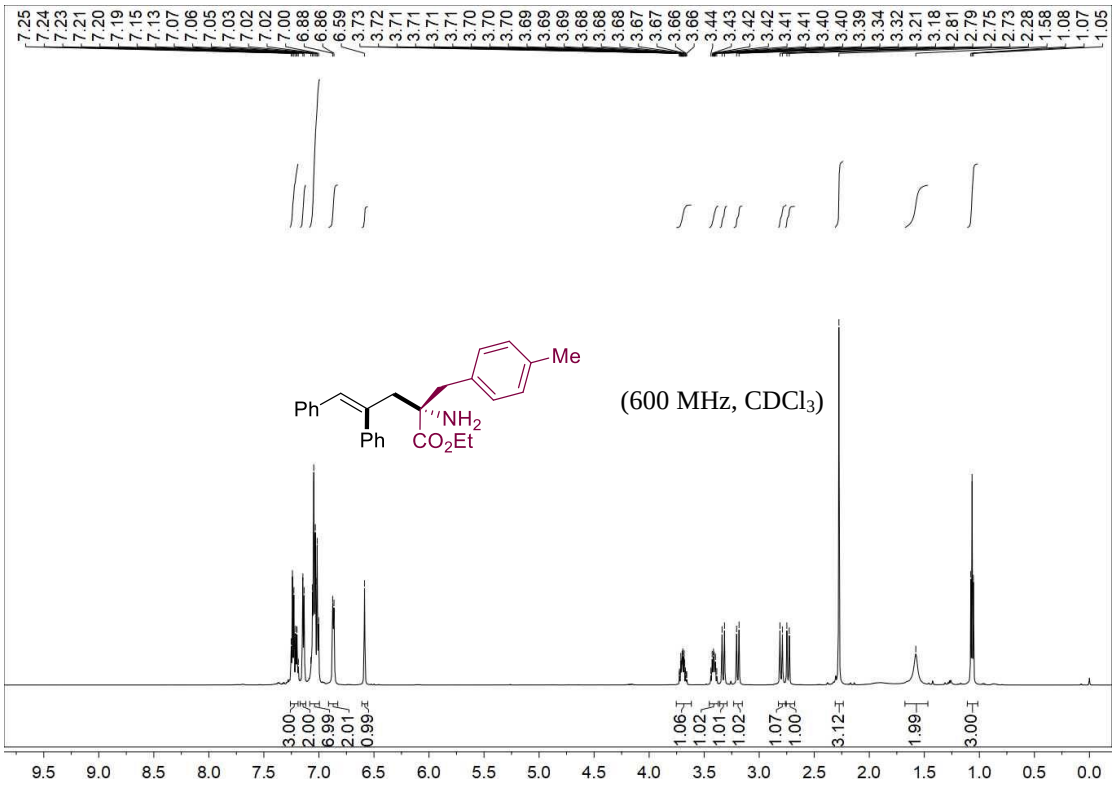


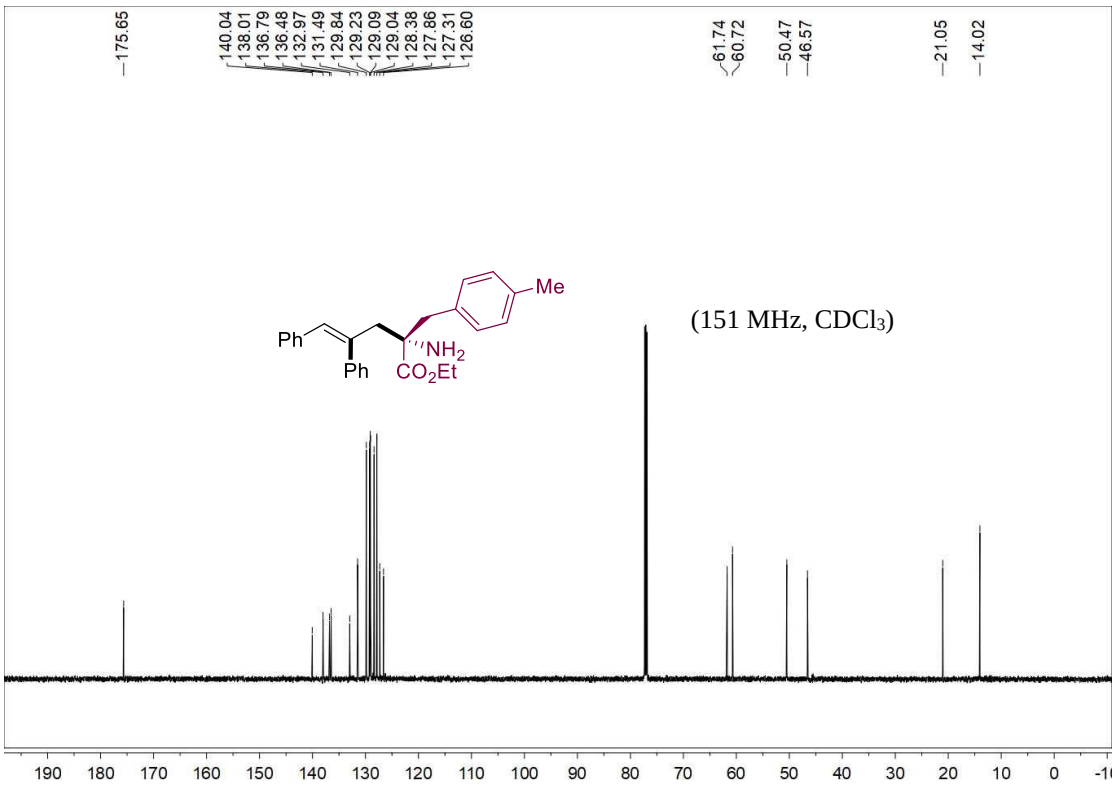
Ethyl (*S*, *Z*)-2-amino-2-(4-chlorobenzyl)-4, 5-diphenylpent-4-enoate (4p):



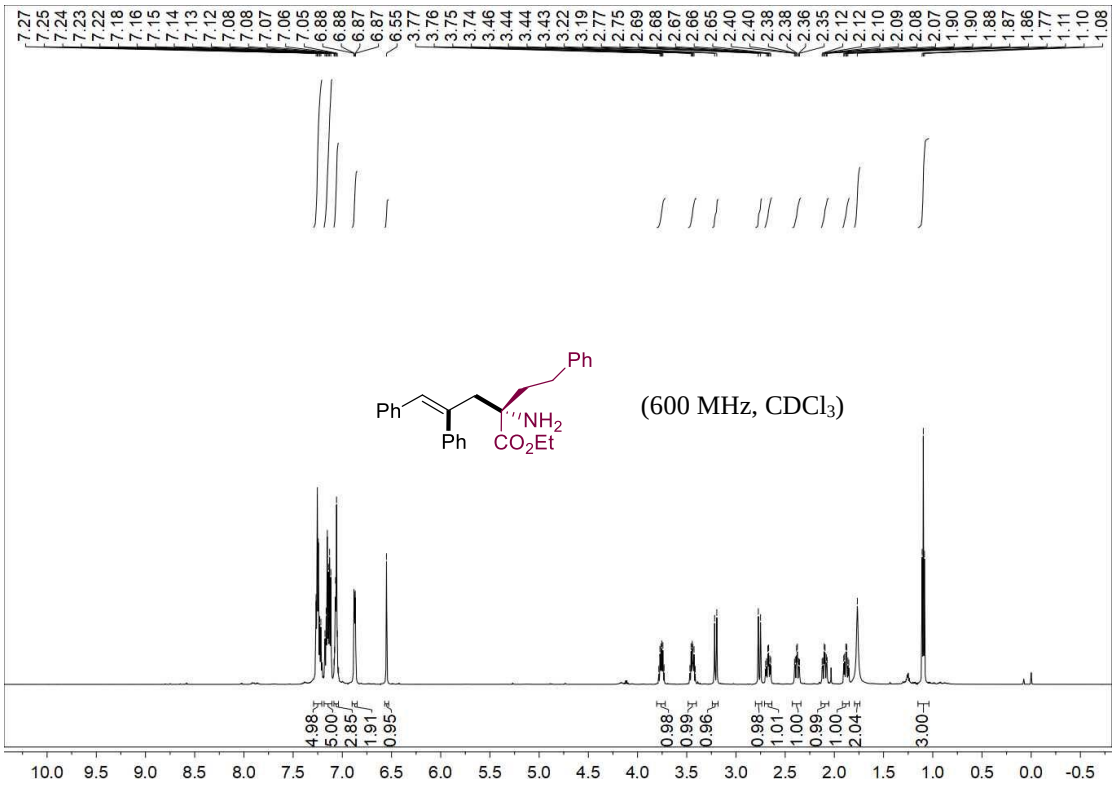


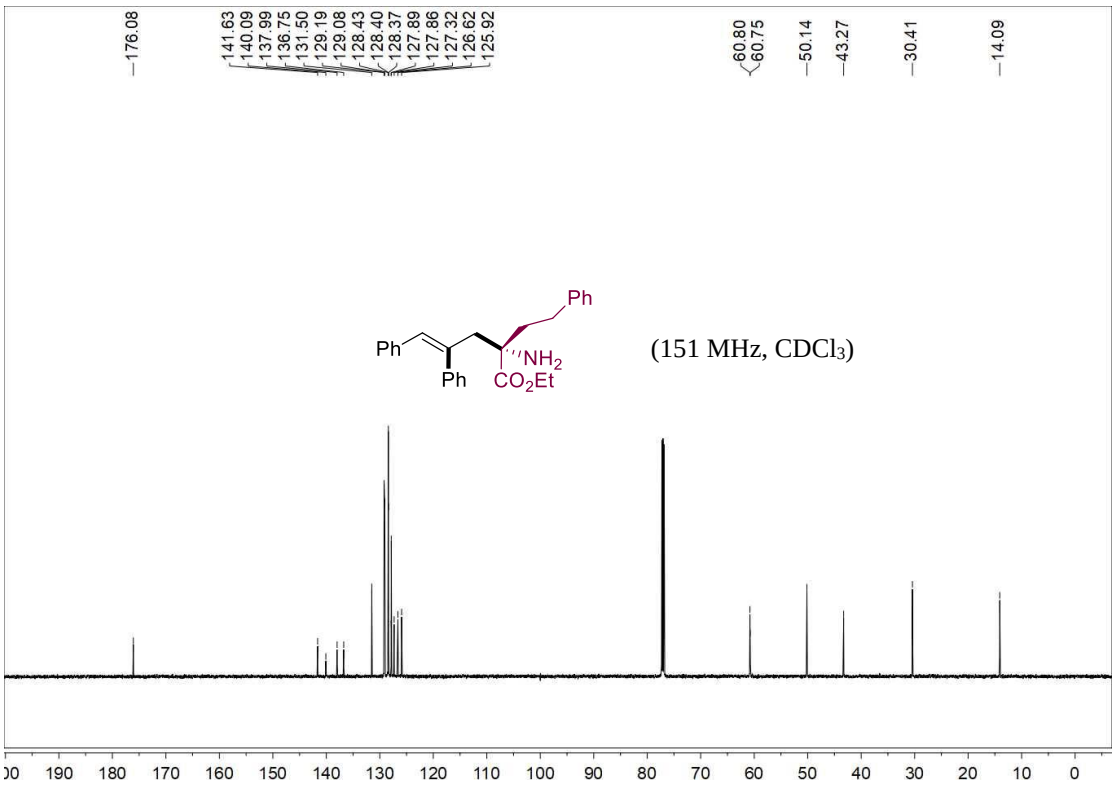
Ethyl (*S*, *Z*)-2-amino-2-(4-methylbenzyl)-4, 5-diphenylpent-4-enoate (4q):



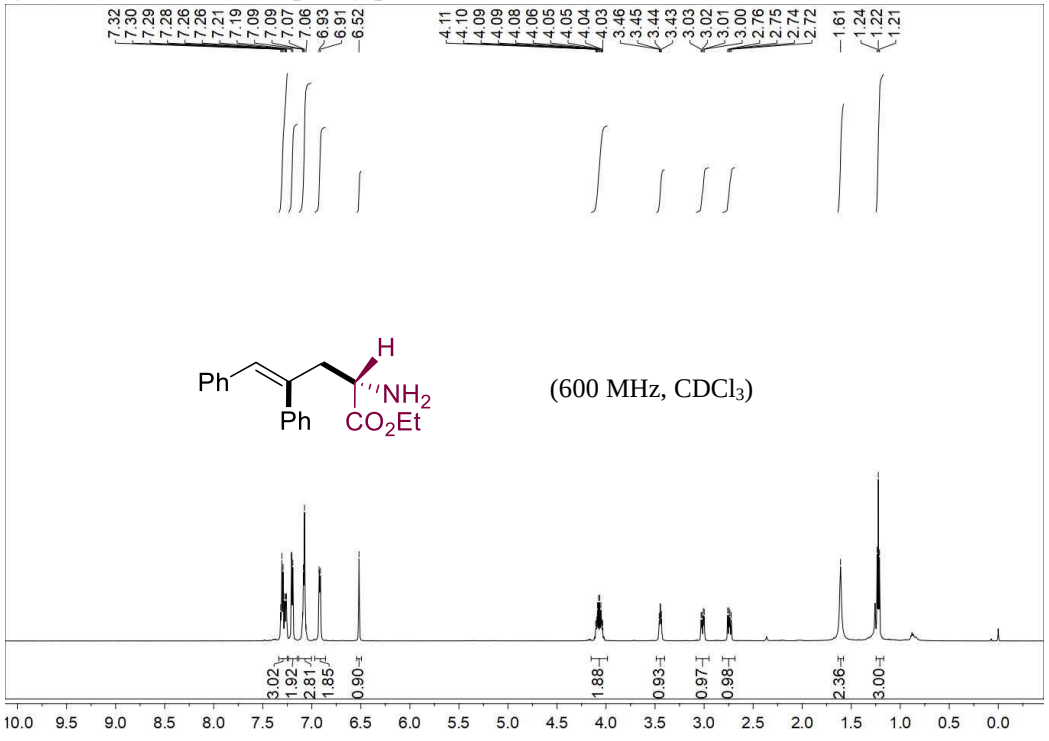


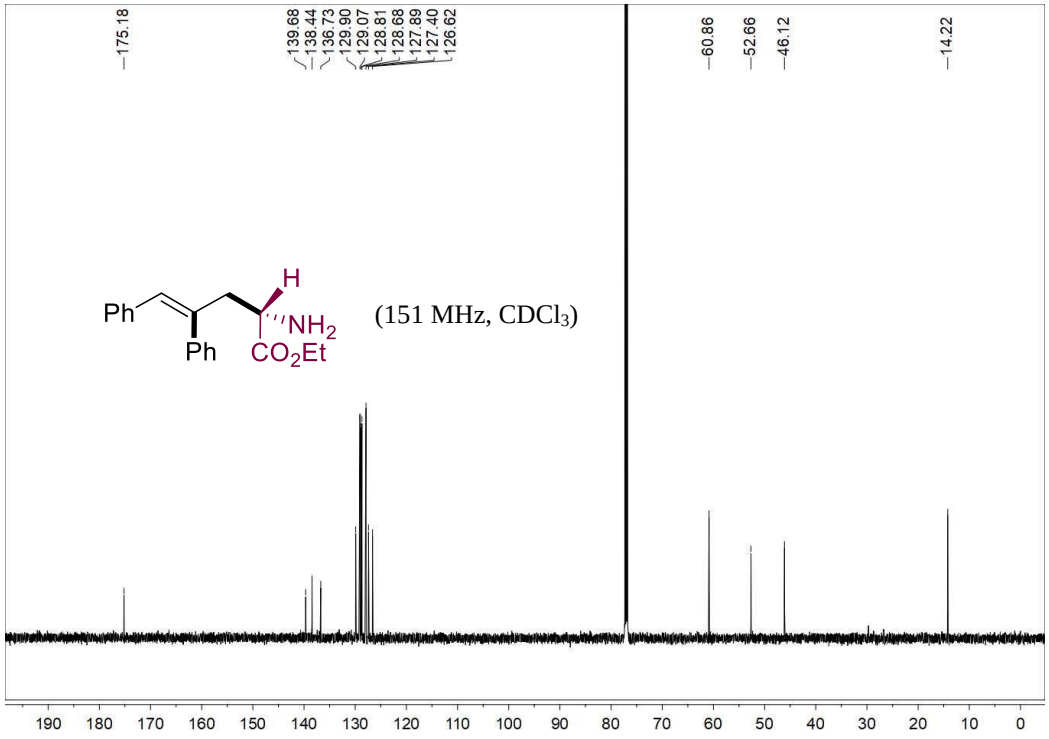
Ethyl (*S*, *Z*)-2-amino-2-phenethyl-4, 5-diphenylpent-4-enoate (4r):



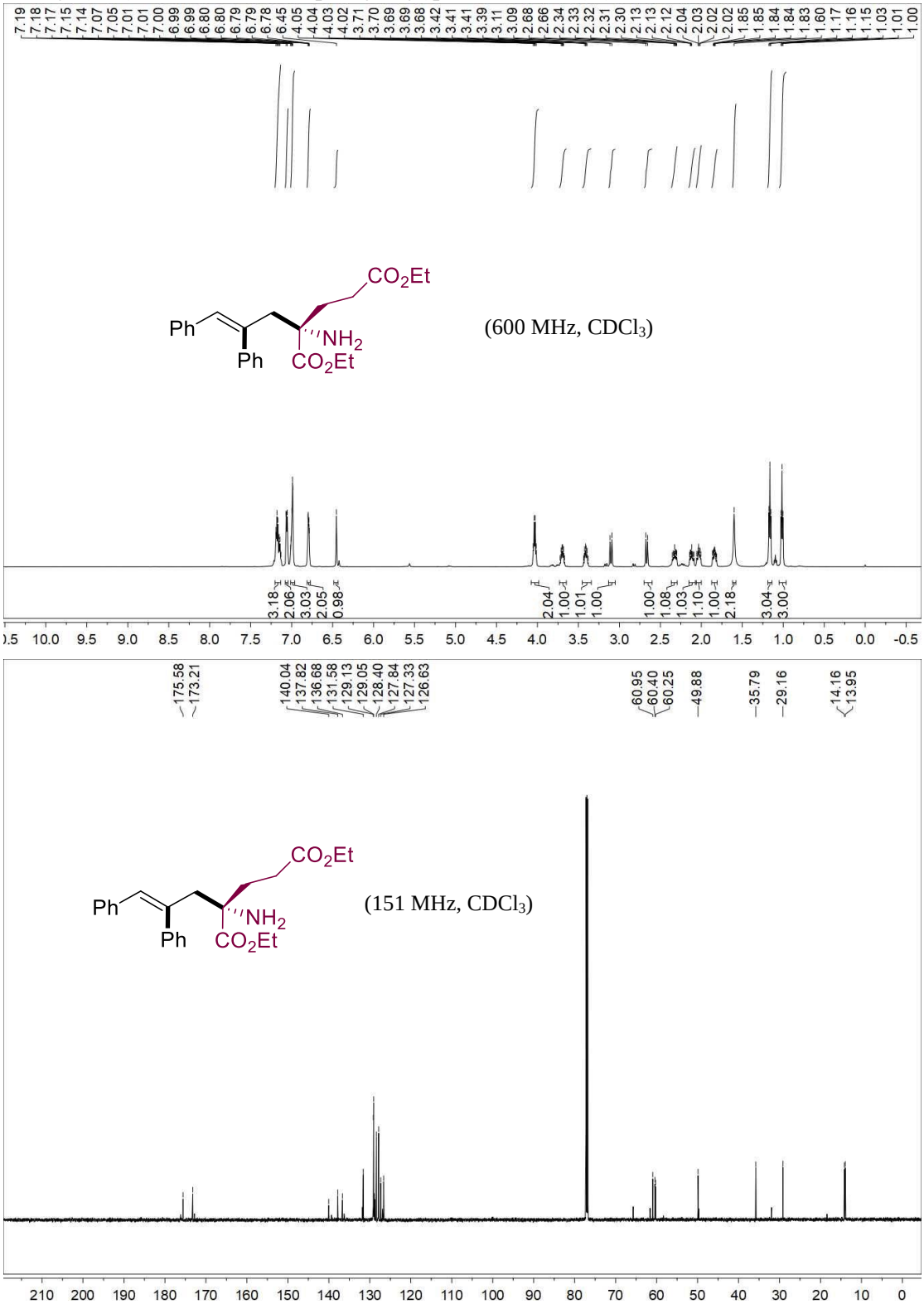


Ethyl (*S*, *Z*)-2-amino-4,5-diphenylpent-4-enoate (4s):

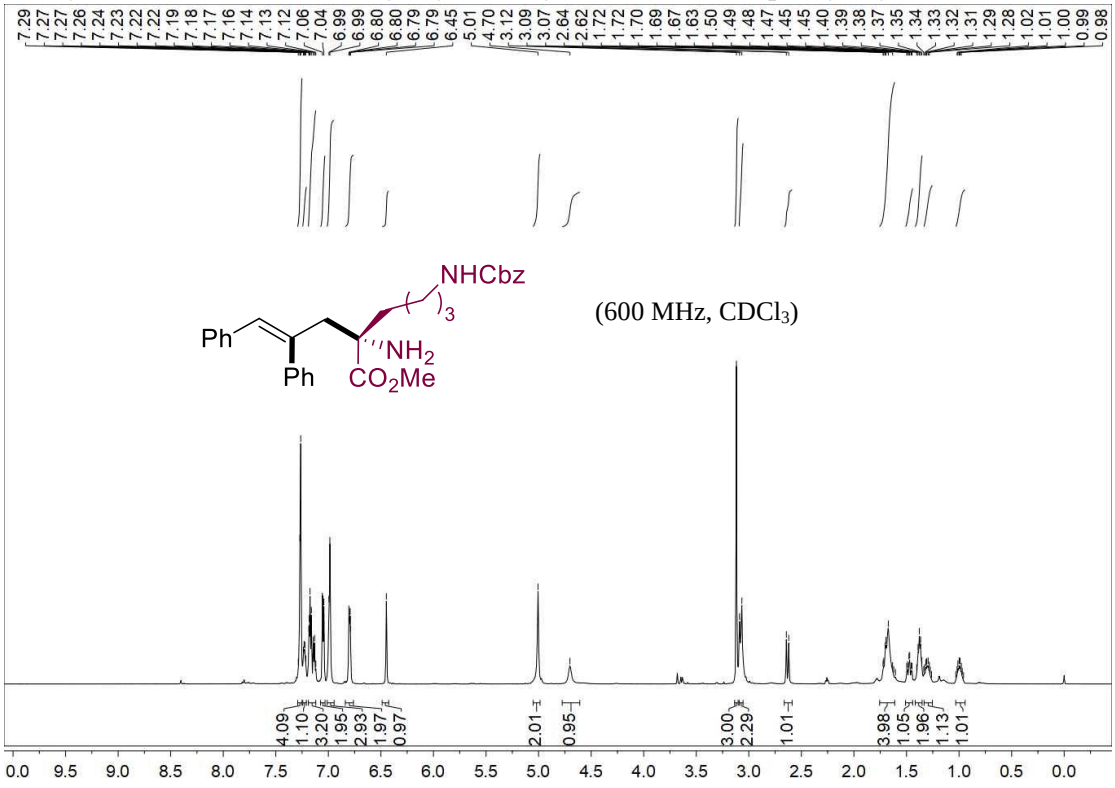


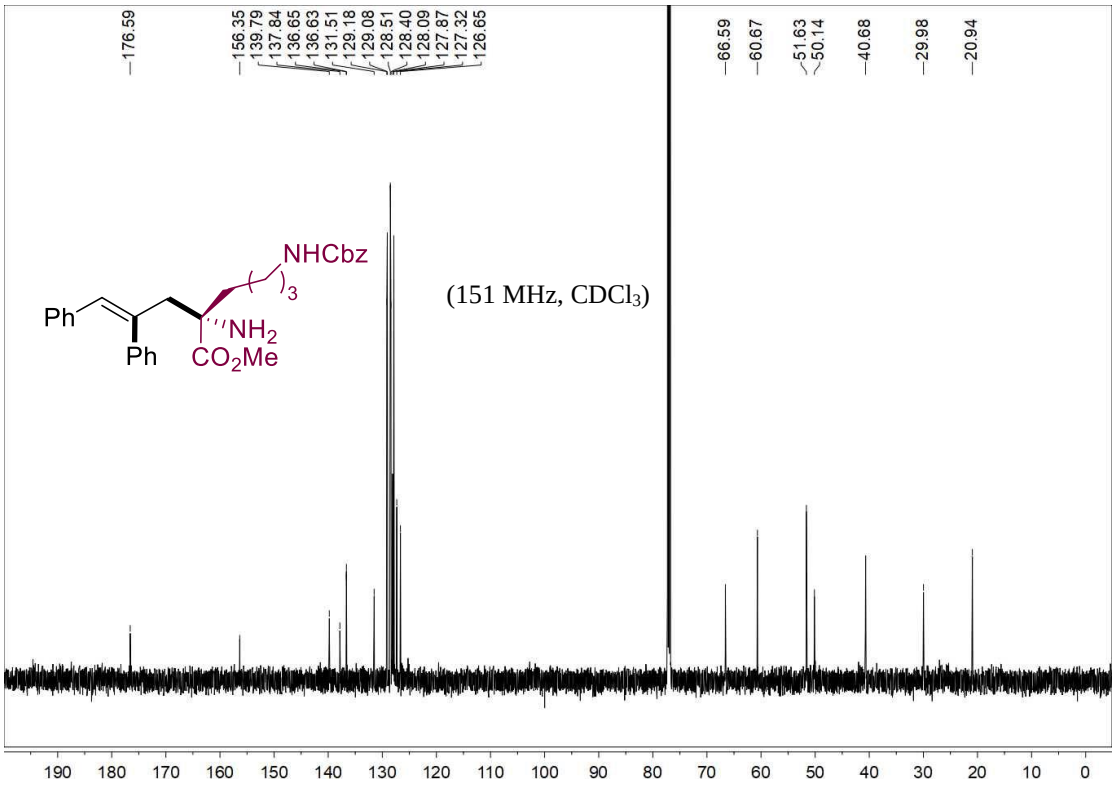


Diethyl (*S*, *Z*)-2-amino-2-(2,3-diphenylallyl)pentanedioate (4t):

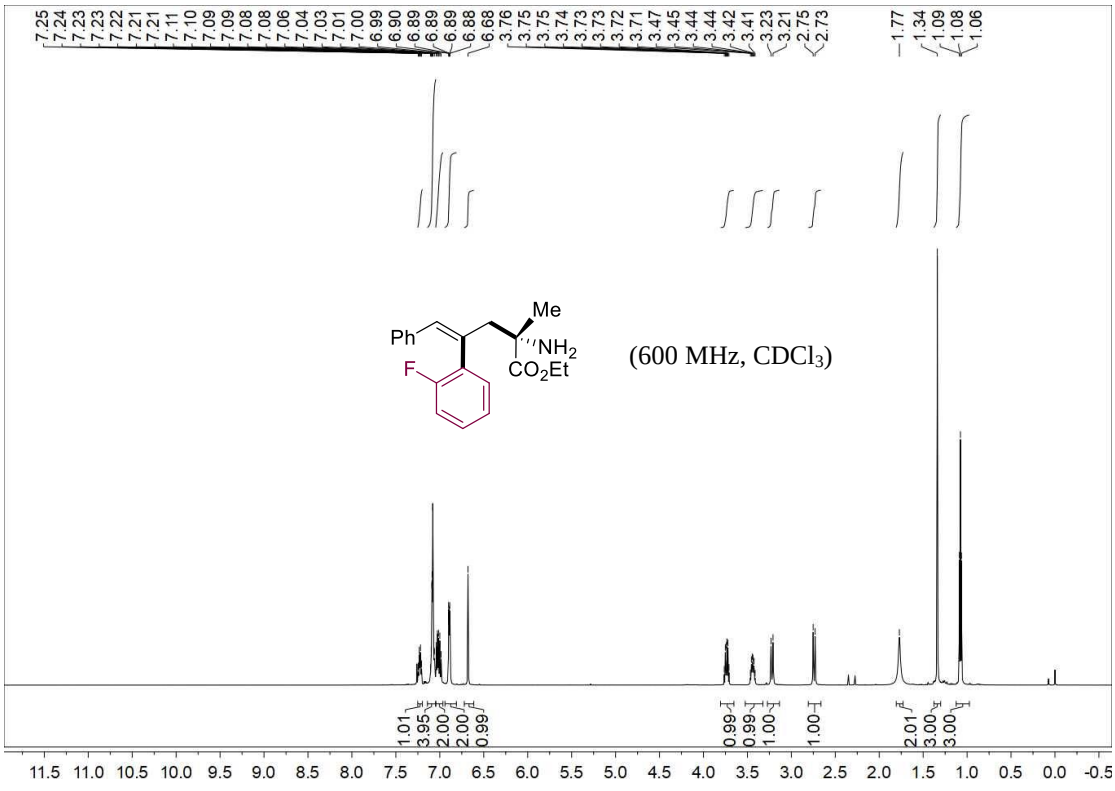


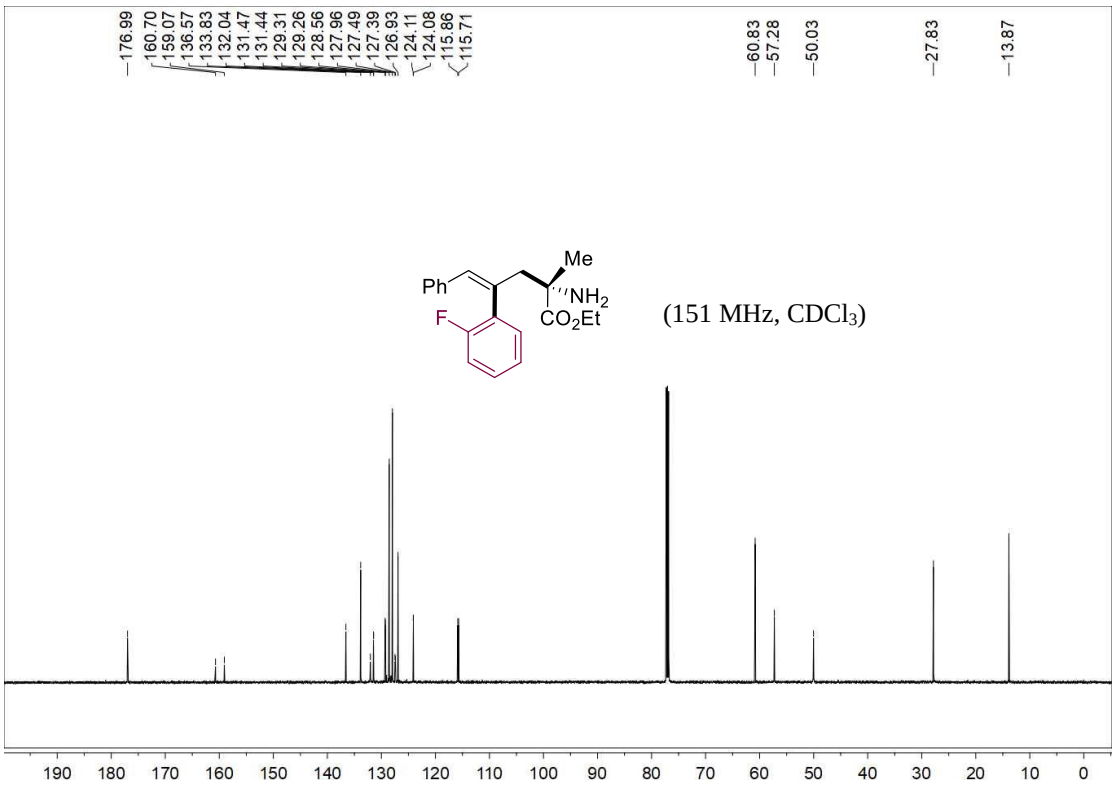
Methyl (*S*, *Z*)-2-amino-6-(((benzyloxy)carbonyl)amino)-2-(2,3-diphenylallyl)hexanoate (4u):



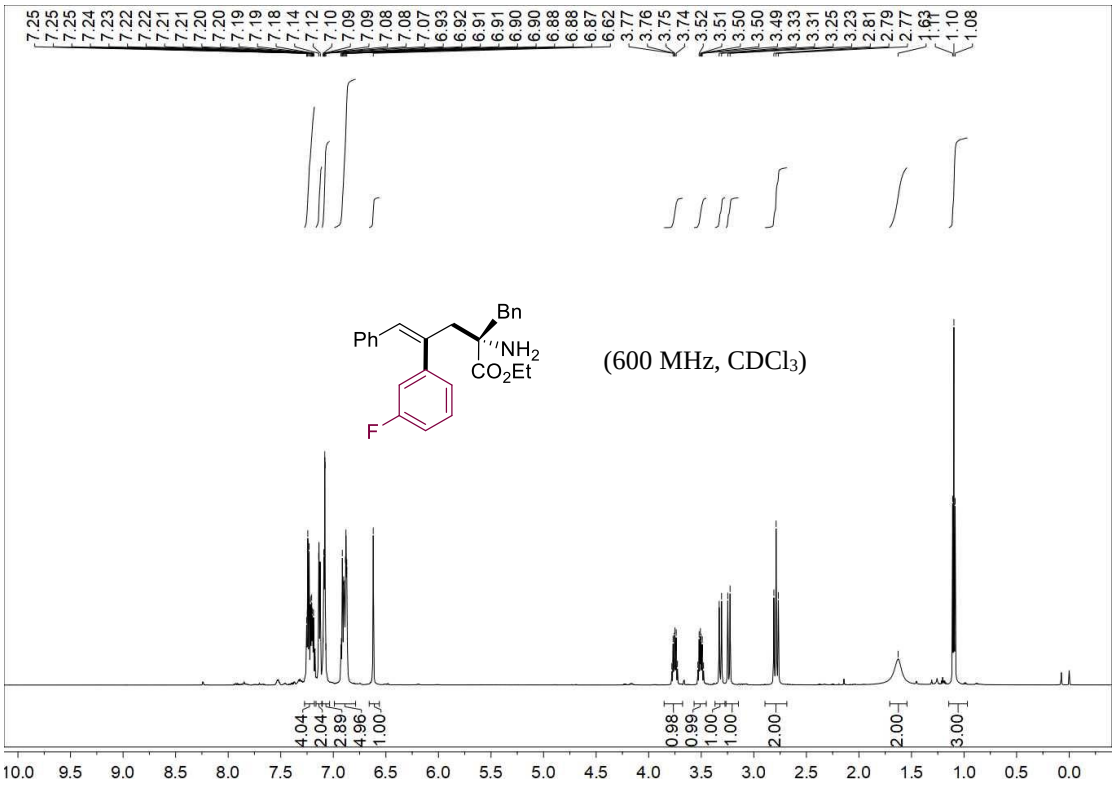


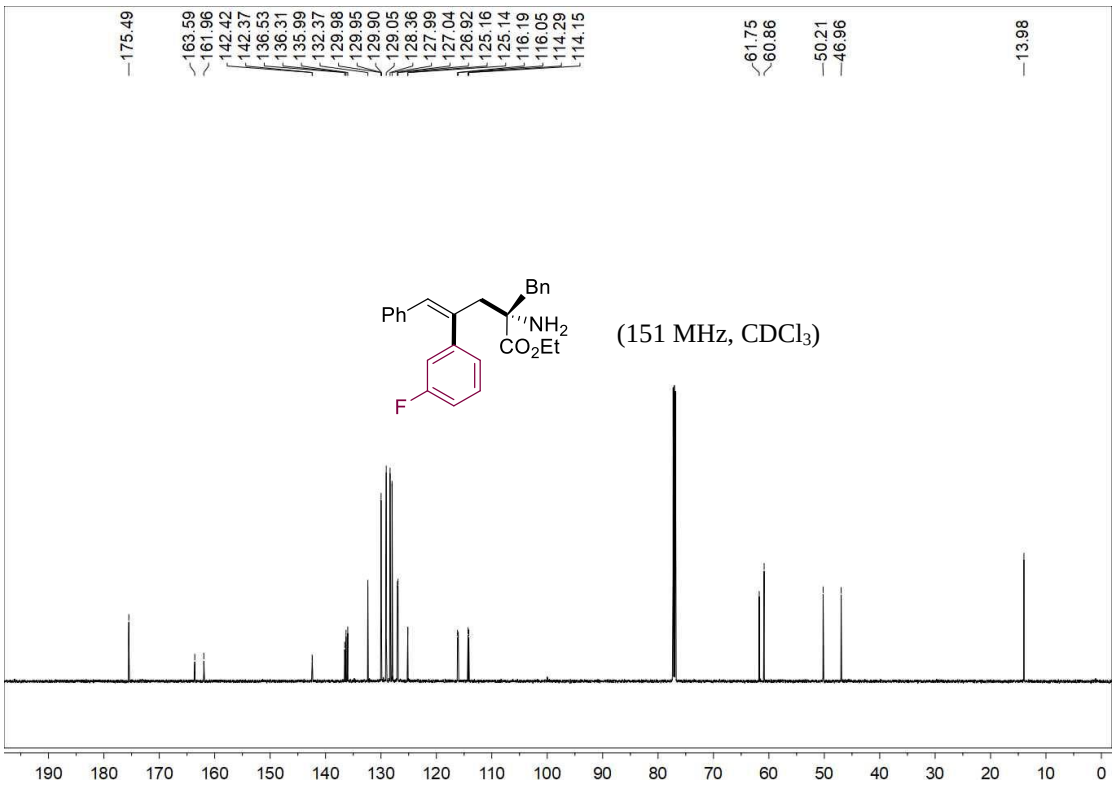
Ethyl (*S*, *Z*)-2-amino-4-(2-fluorophenyl)-2-methyl-5-phenylpent-4-enoate (5a):



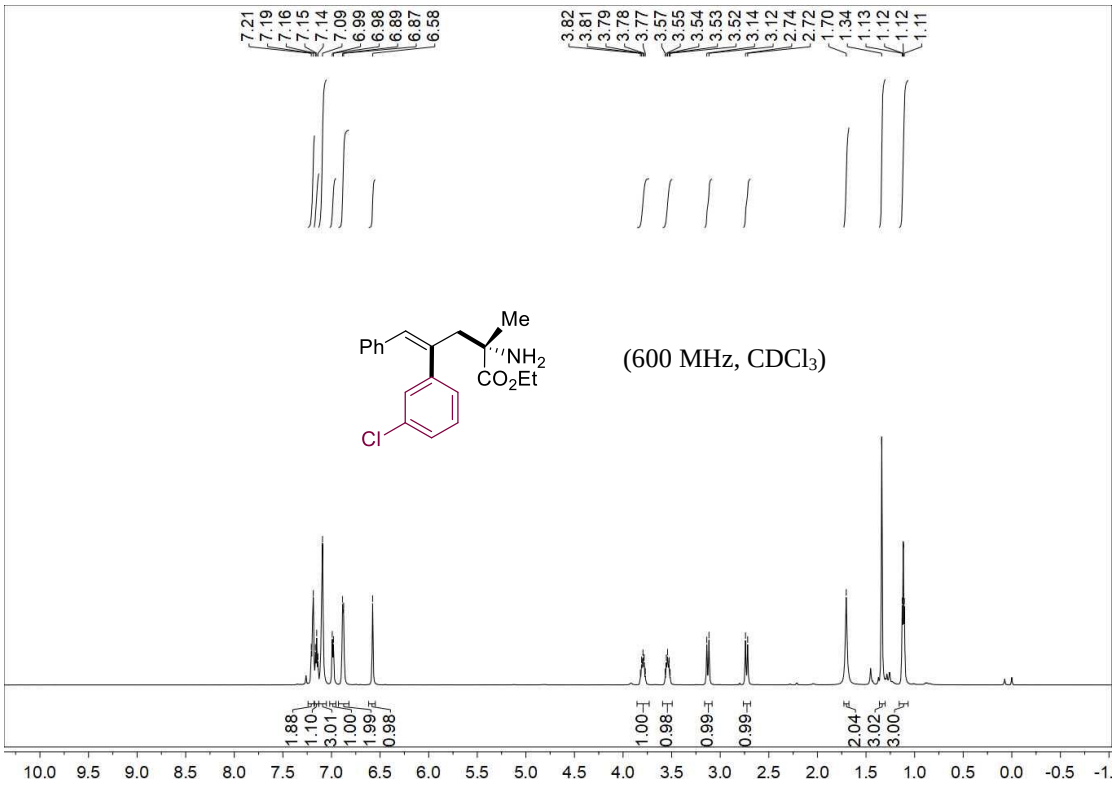


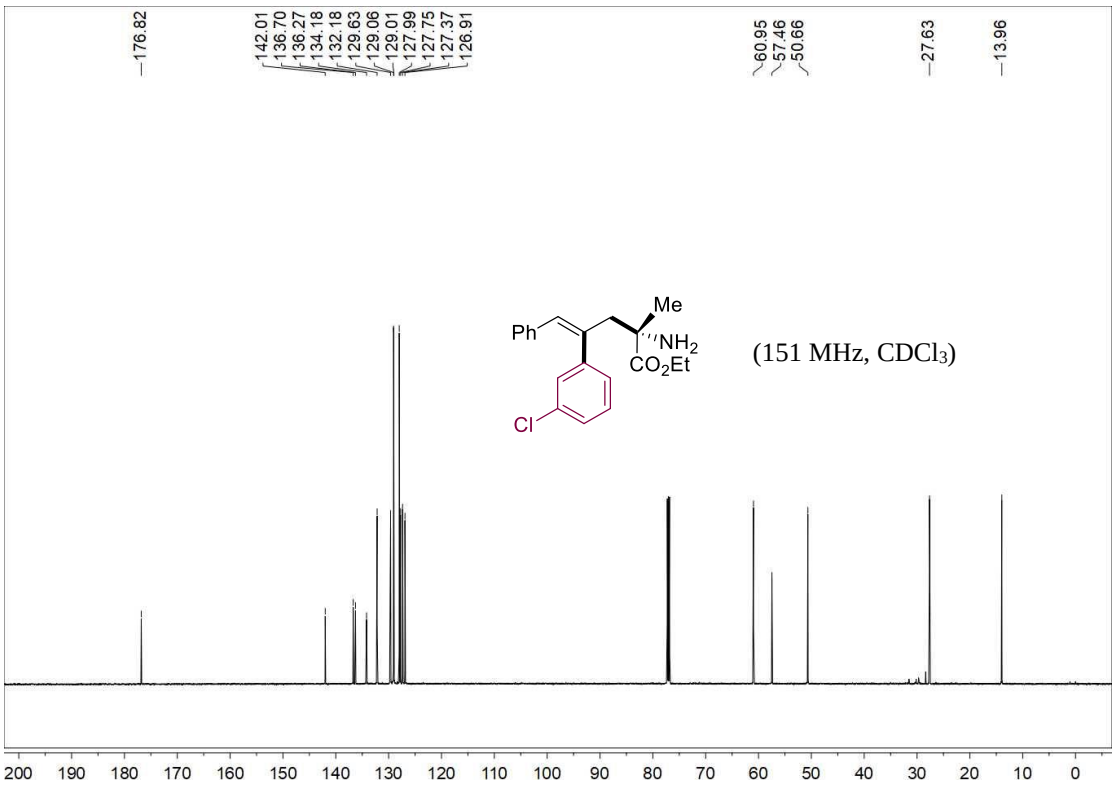
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(3-fluorophenyl)-5-phenylpent-4-enoate (5b):



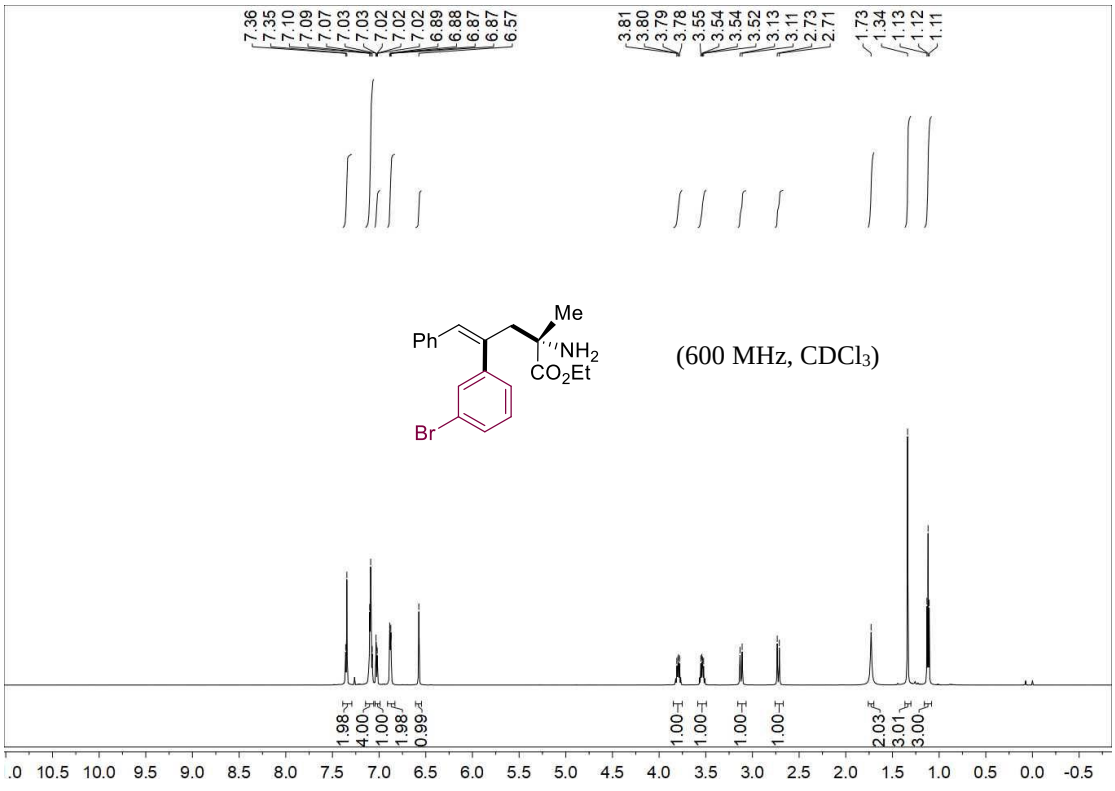


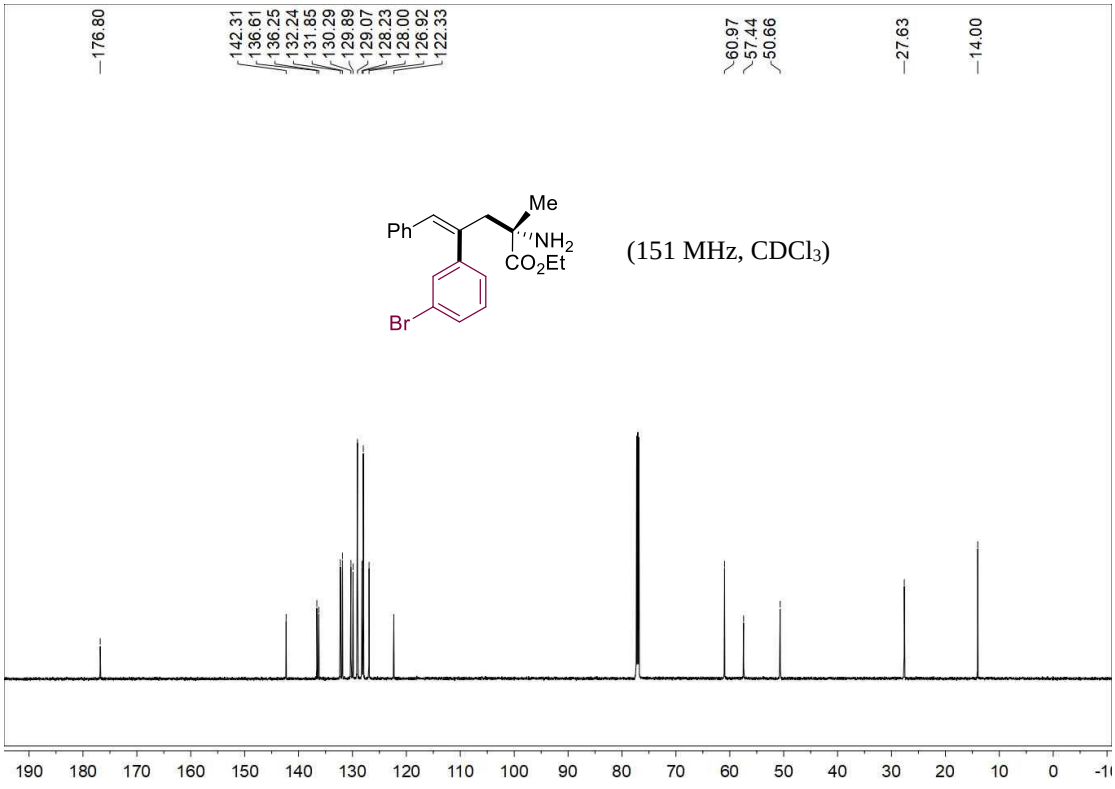
Ethyl (*S*, *Z*)-2-amino-4-(3-chlorophenyl)-2-methyl-5-phenylpent-4-enoate (5c):



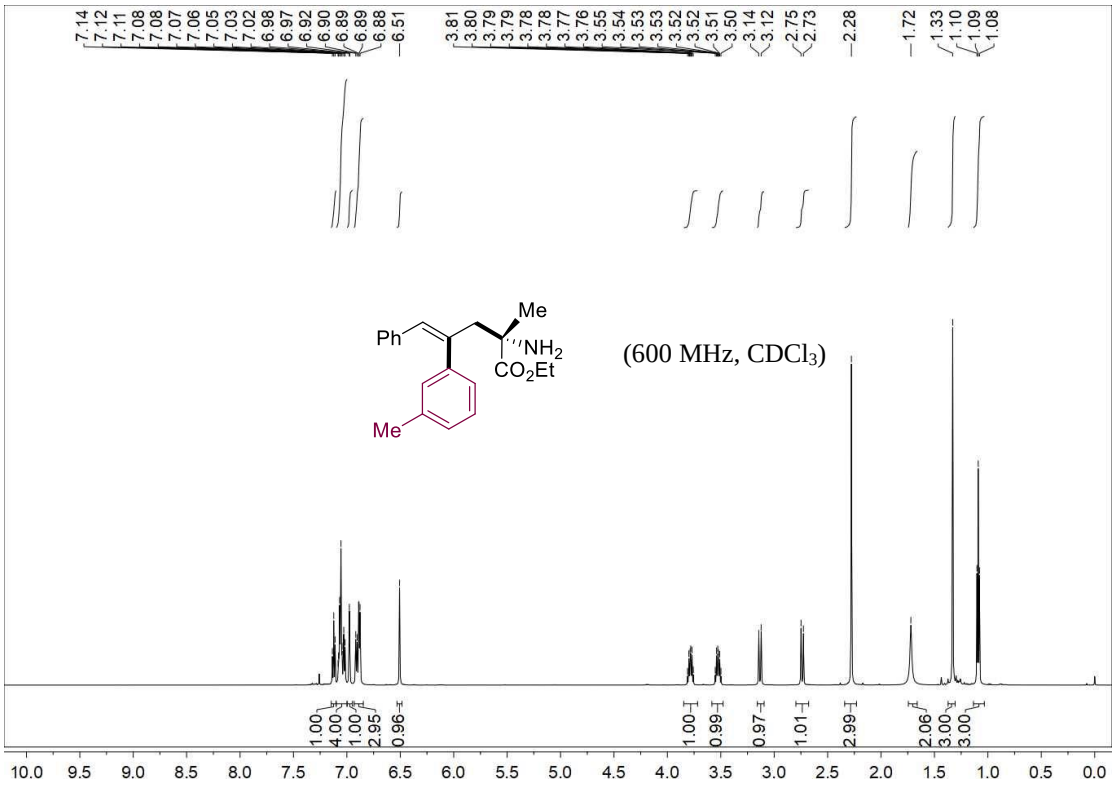


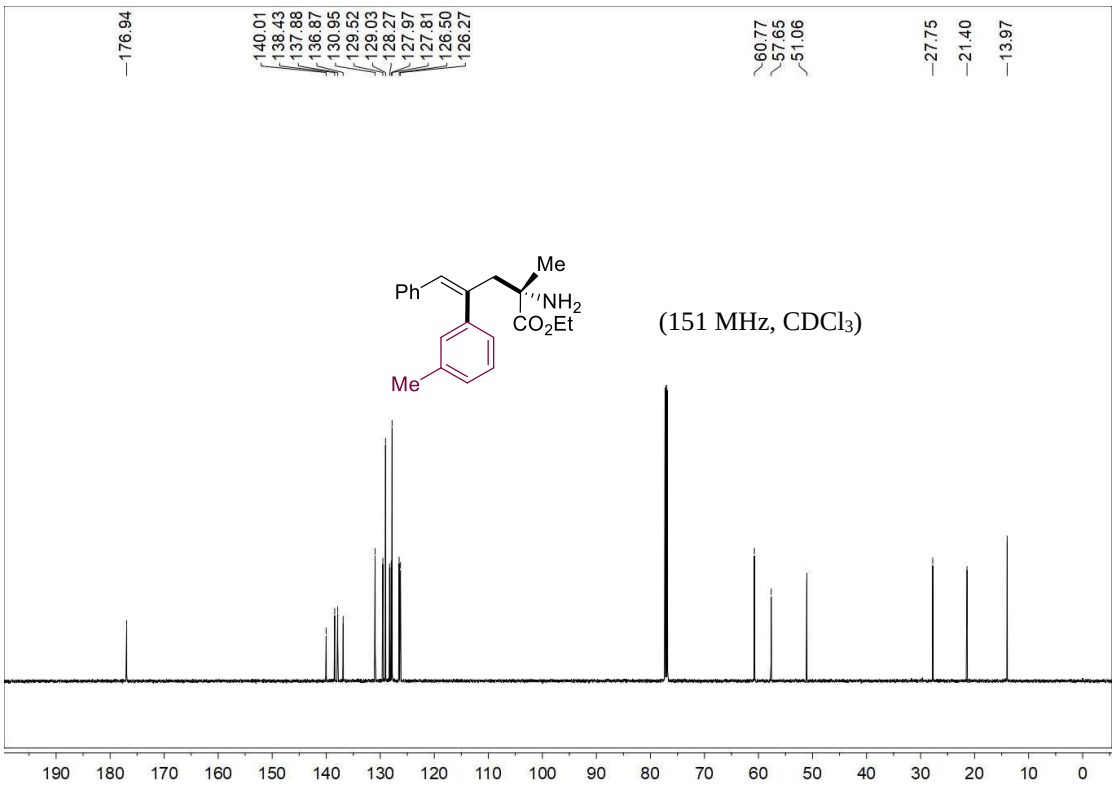
Ethyl (*S*, *Z*)-2-amino-4-(3-bromophenyl)-2-methyl-5-phenylpent-4-enoate (5d):



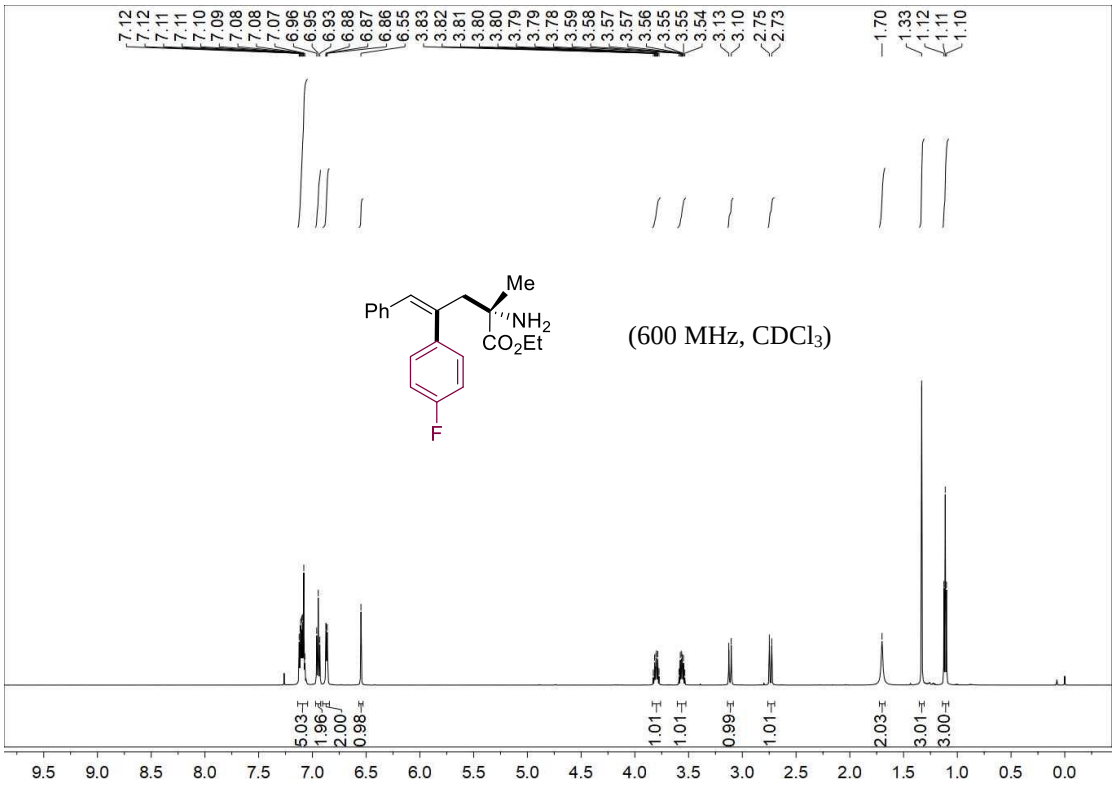


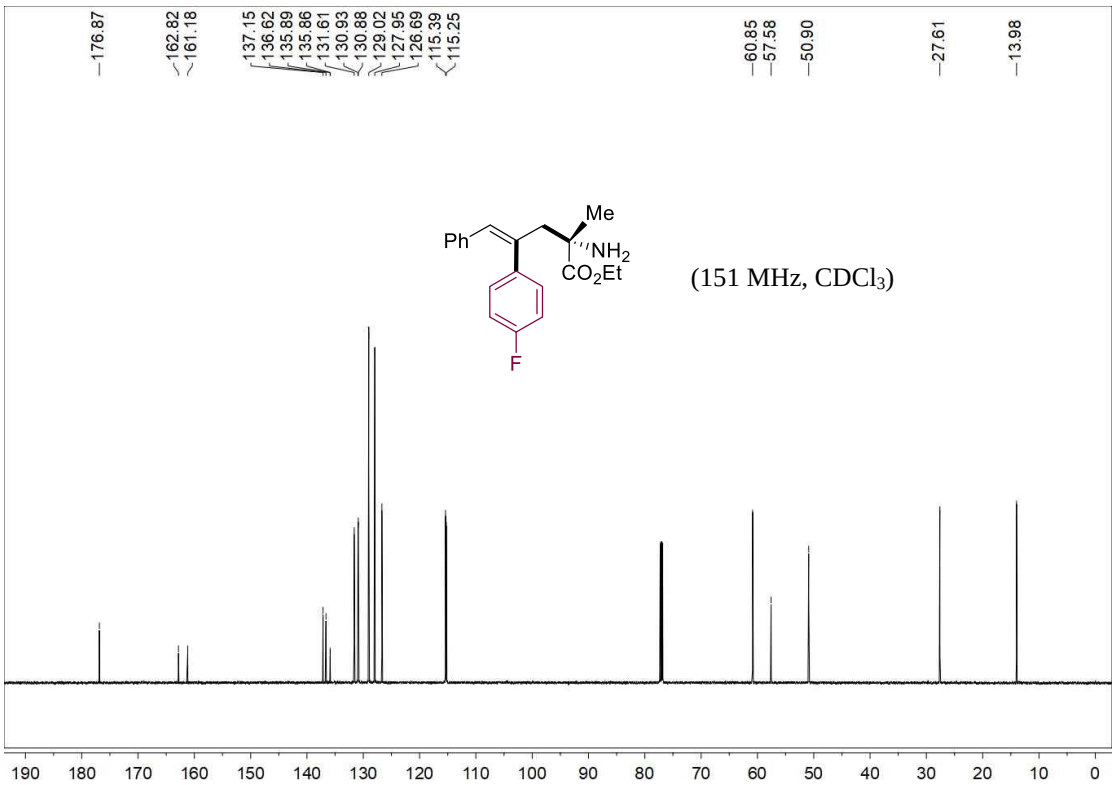
Ethyl (*S*, *Z*)-2-amino-2-methyl-5-phenyl-4-(m-tolyl)pent-4-enoate (5e):



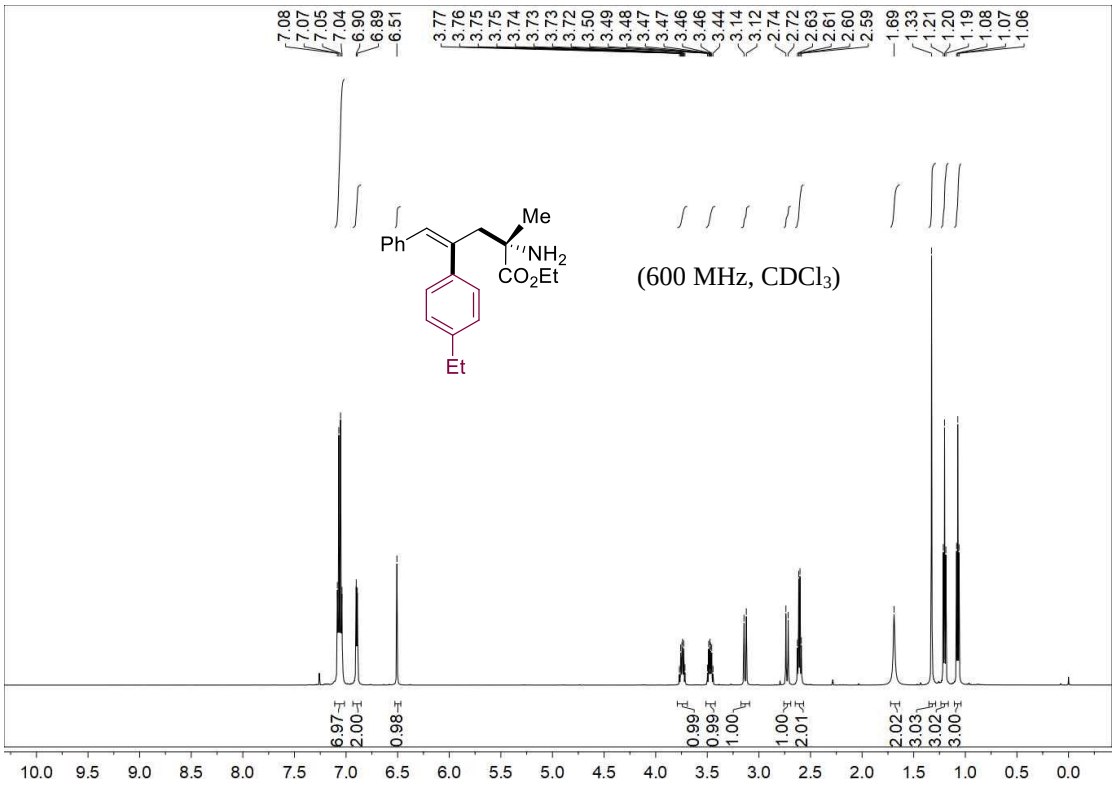


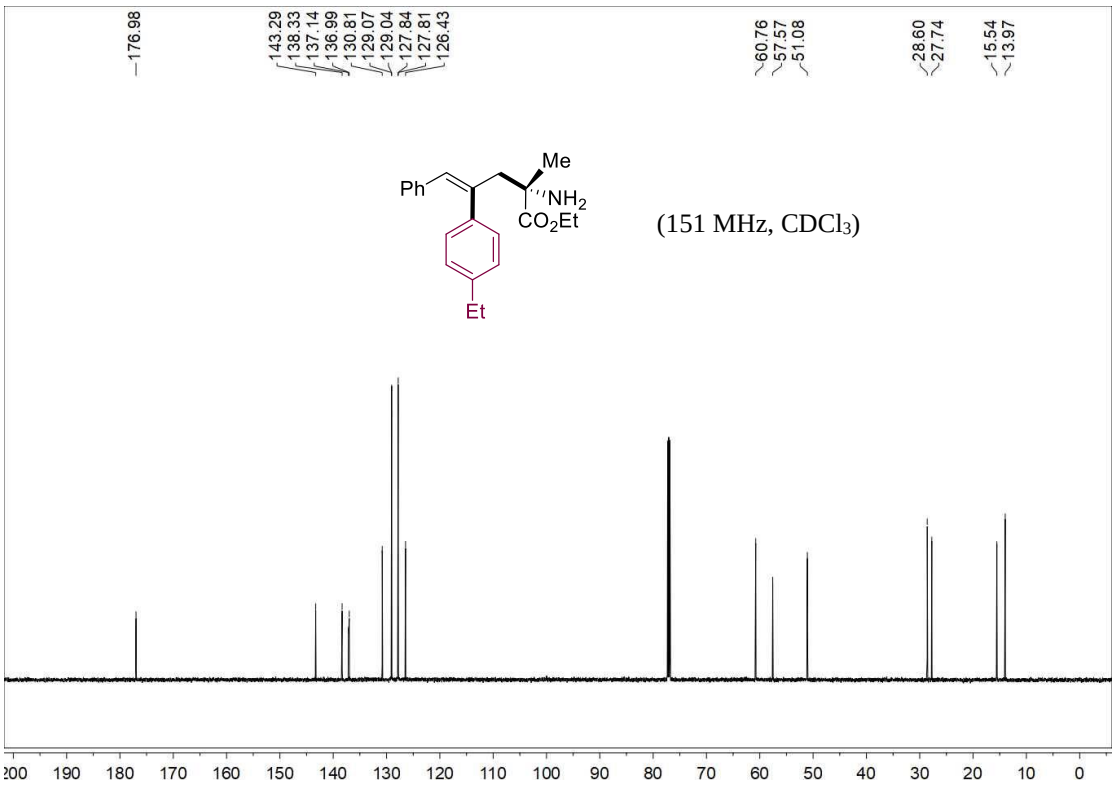
Ethyl (*S*, *Z*)-2-amino-4-(4-fluorophenyl)-2-methyl-5-phenylpent-4-enoate (5f):



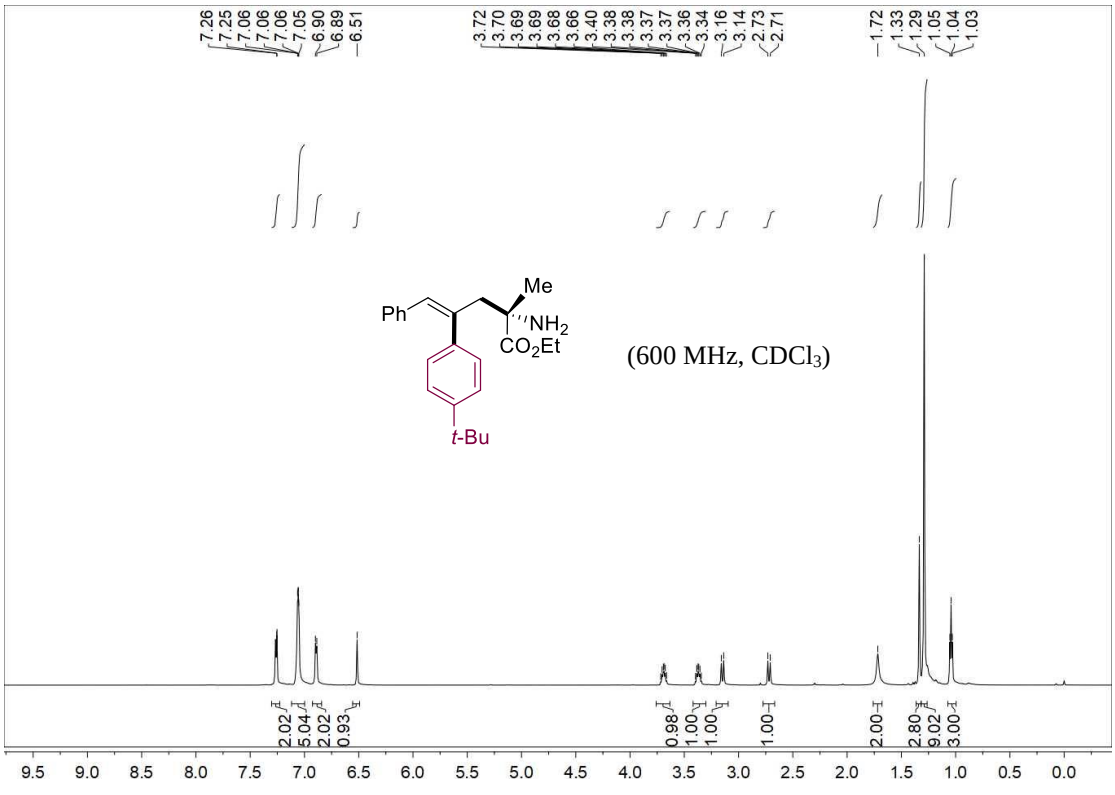


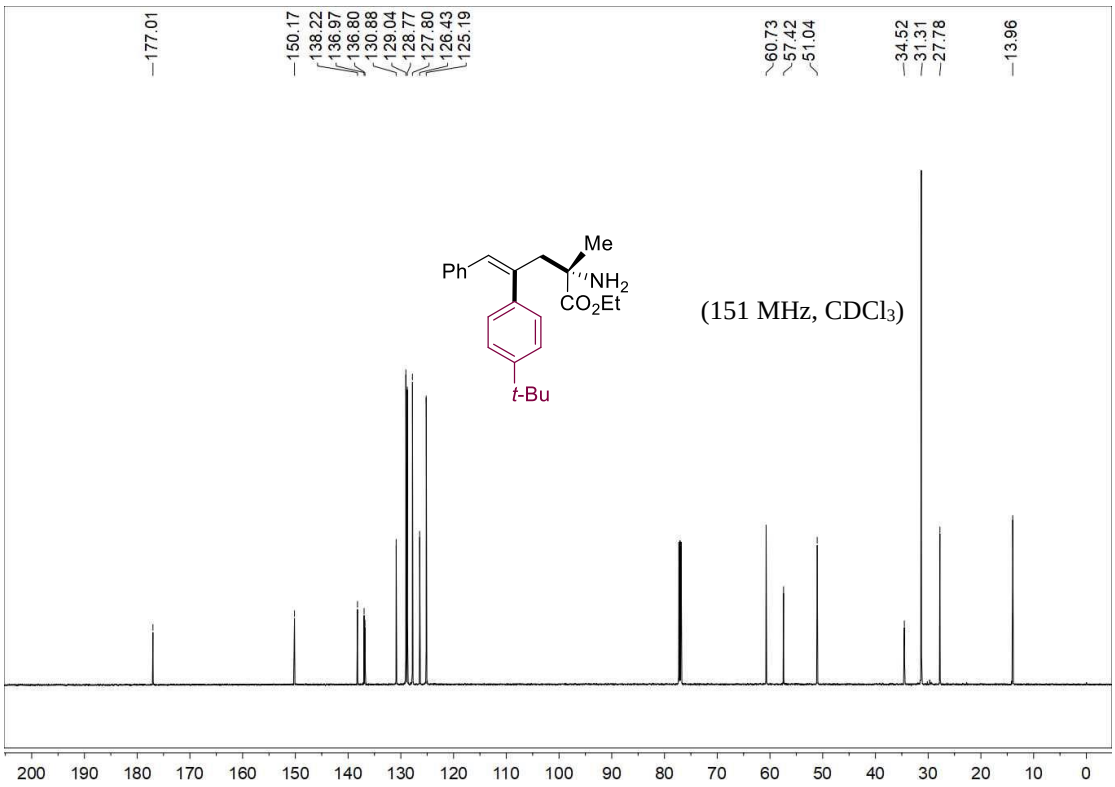
Ethyl (*S*, *Z*)-2-amino-4-(4-ethylphenyl)-2-methyl-5-phenylpent-4-enoate (5g):



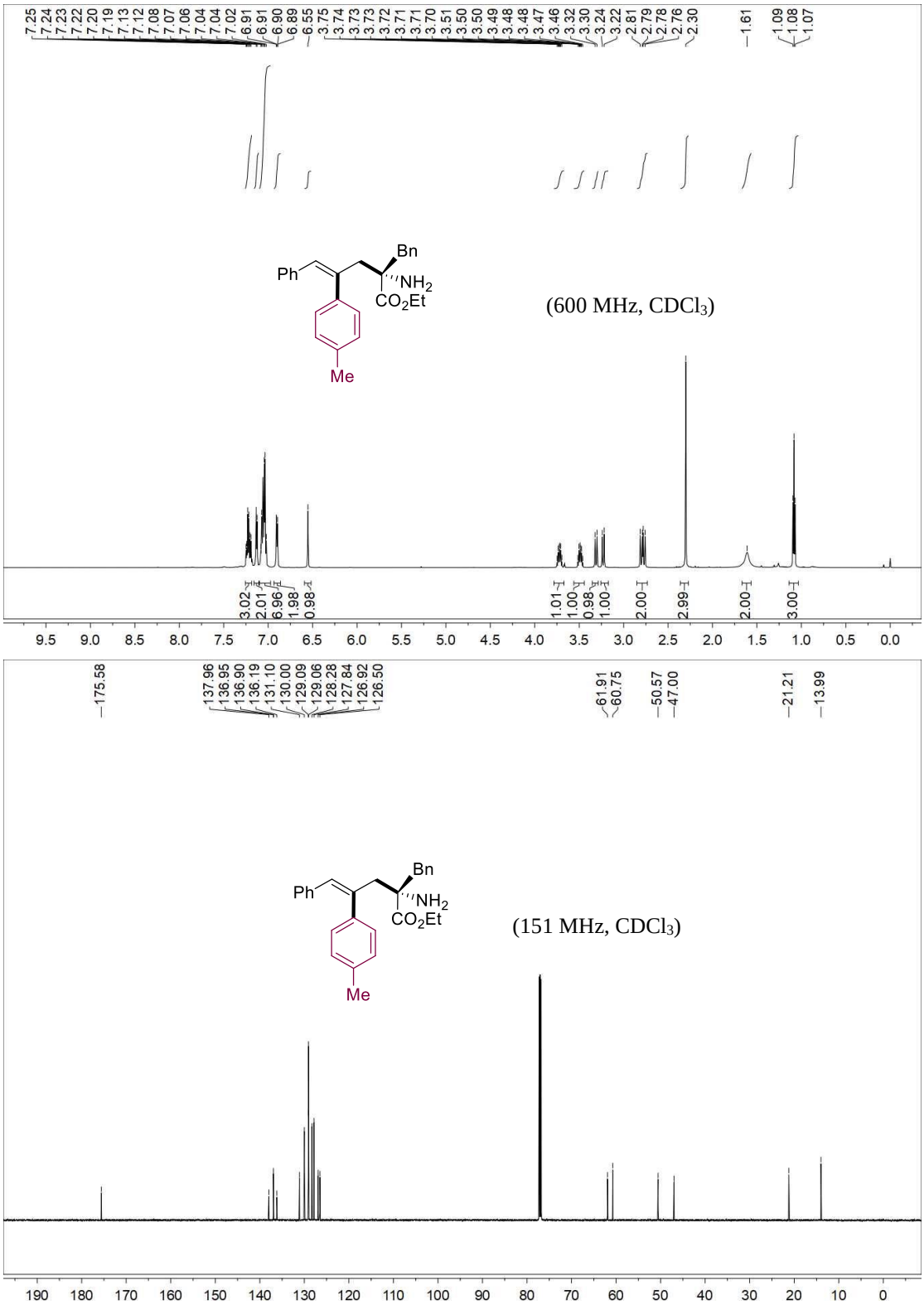


Ethyl (*S*, *Z*)-2-amino-4-(4-(tert-butyl)phenyl)-2-methyl-5-phenylpent-4-enoate (5h):

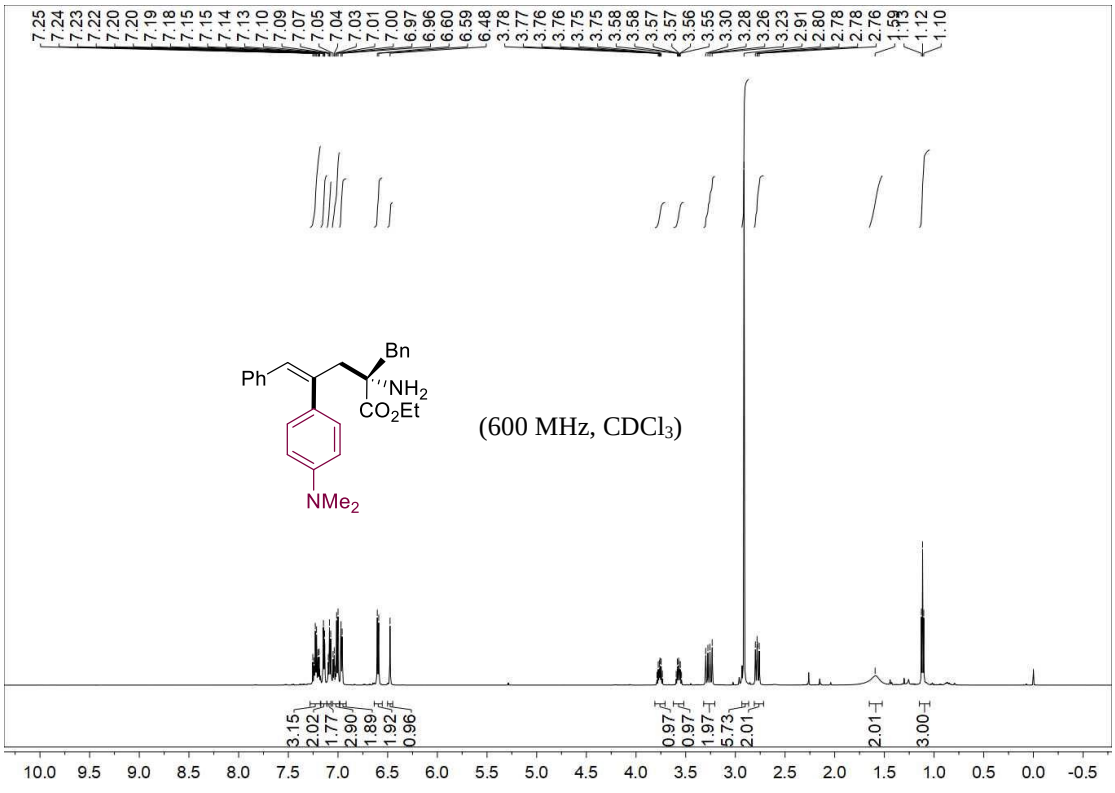


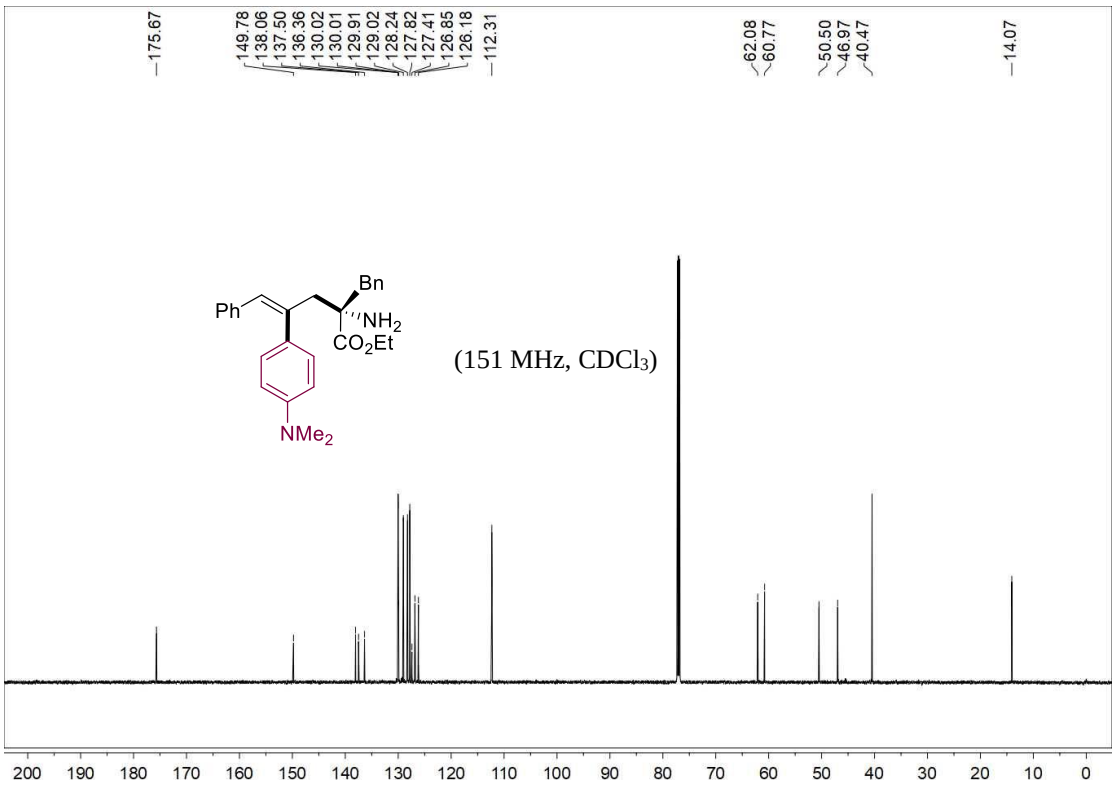


Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-phenyl-4-(p-tolyl)pent-4-enoate (5i):

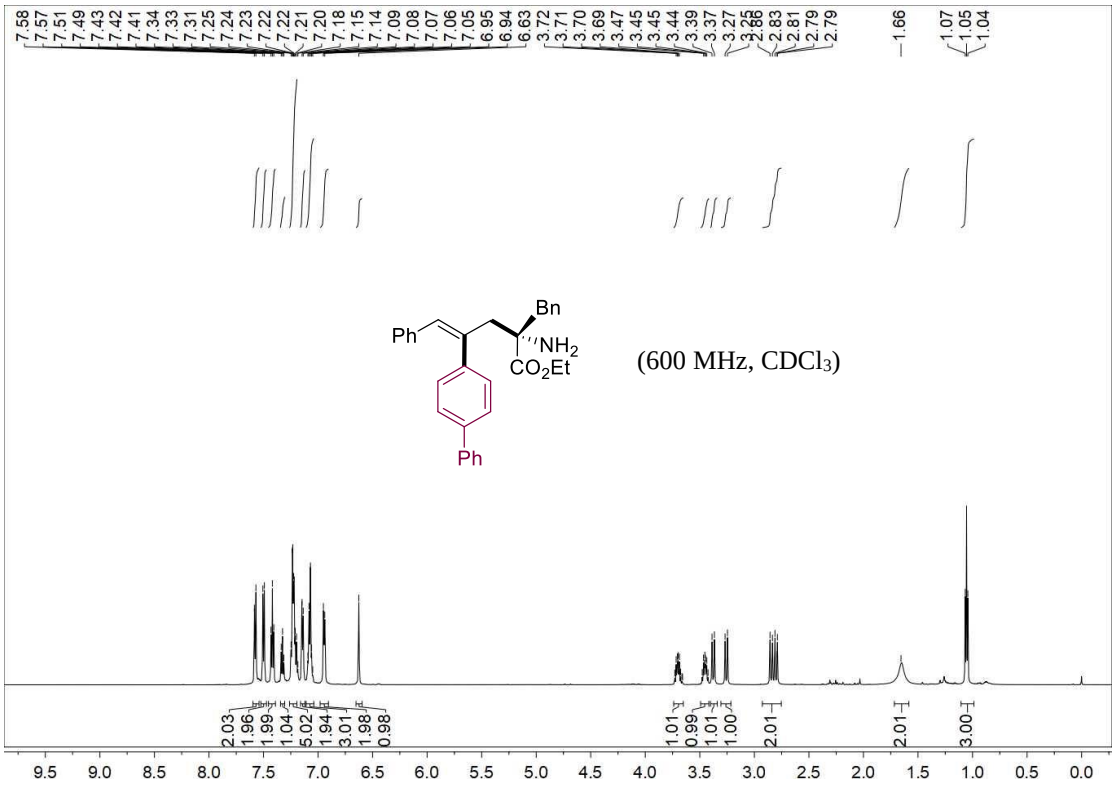


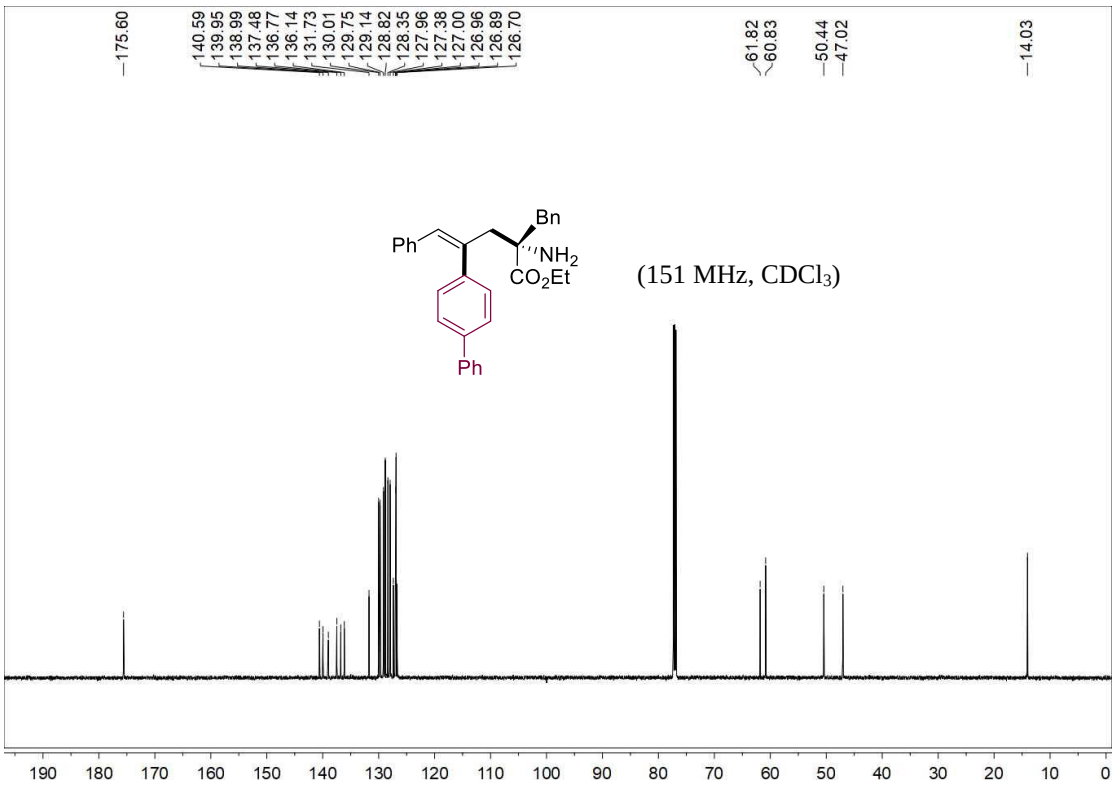
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-(dimethylamino)phenyl)-5-phenylpent-4-enoate (5j):



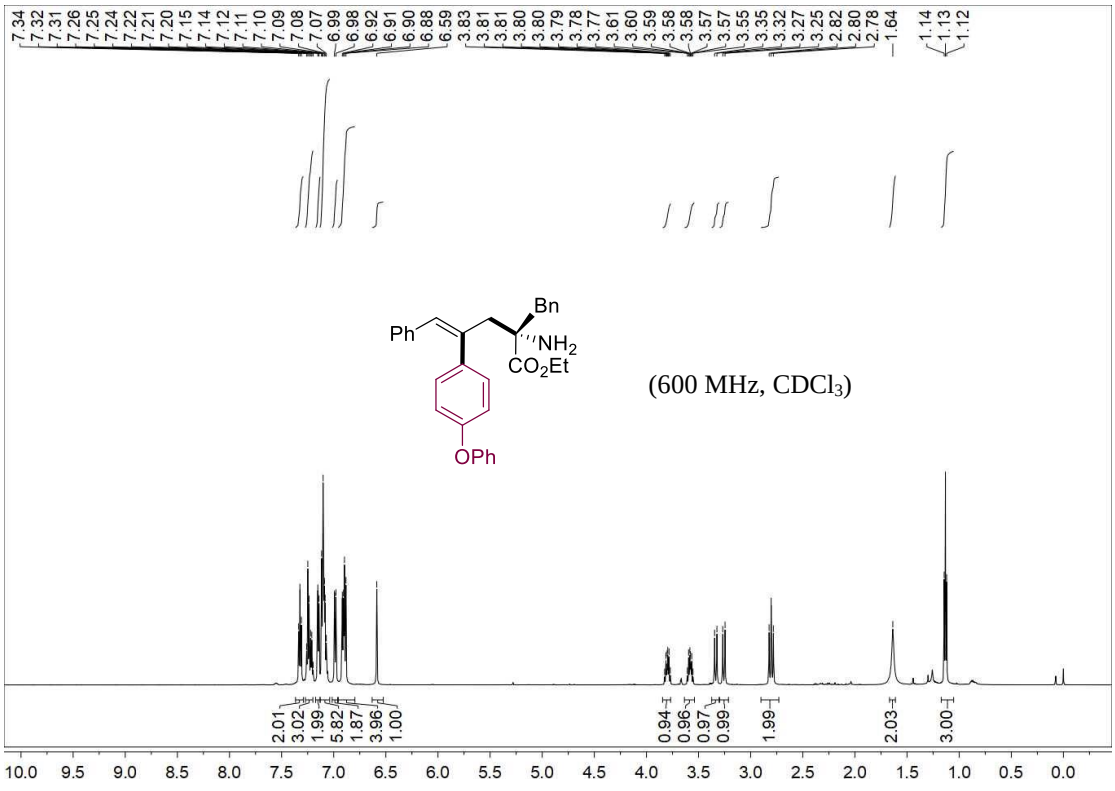


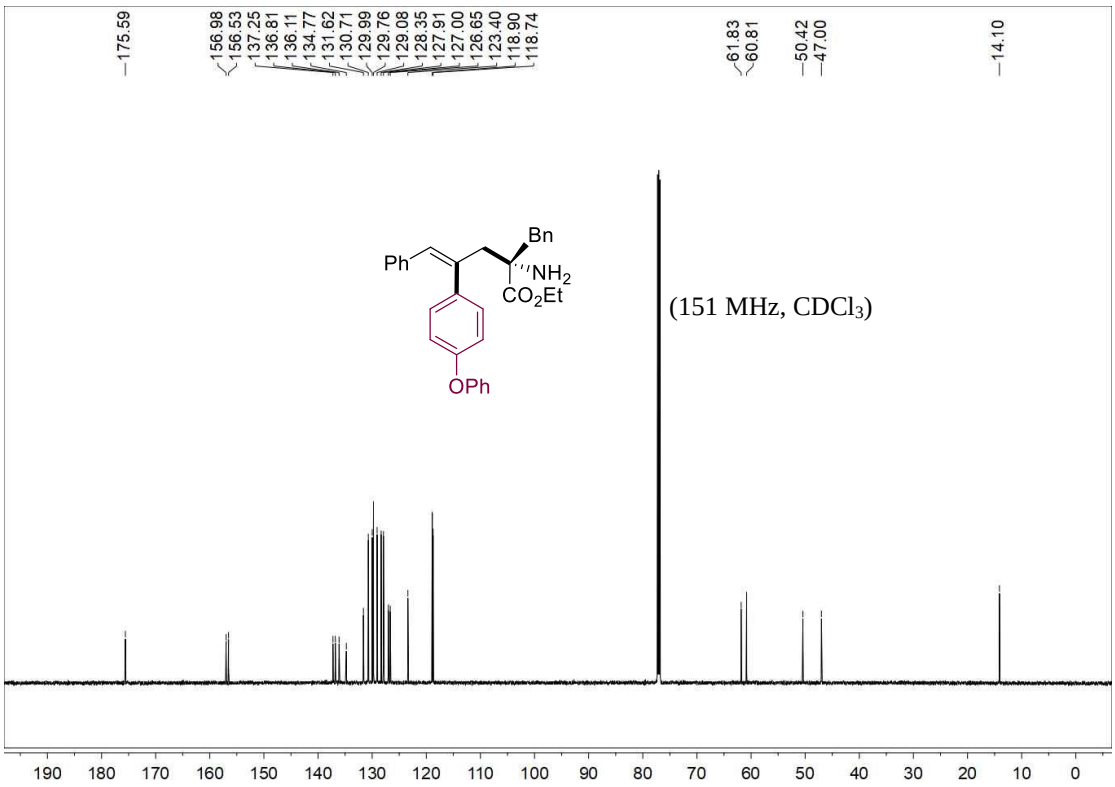
Ethyl (*S*, *Z*)-4-([1,1'-biphenyl]-4-yl)-2-amino-2-benzyl-5-phenylpent-4-enoate (5k):



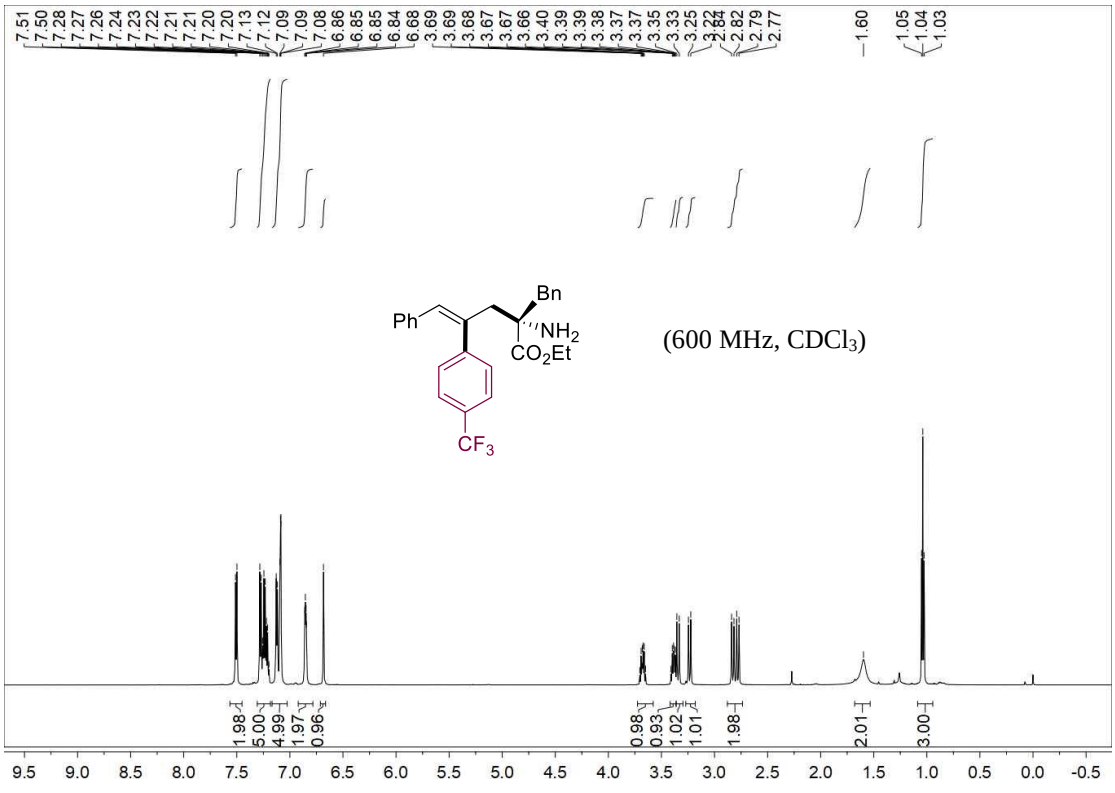


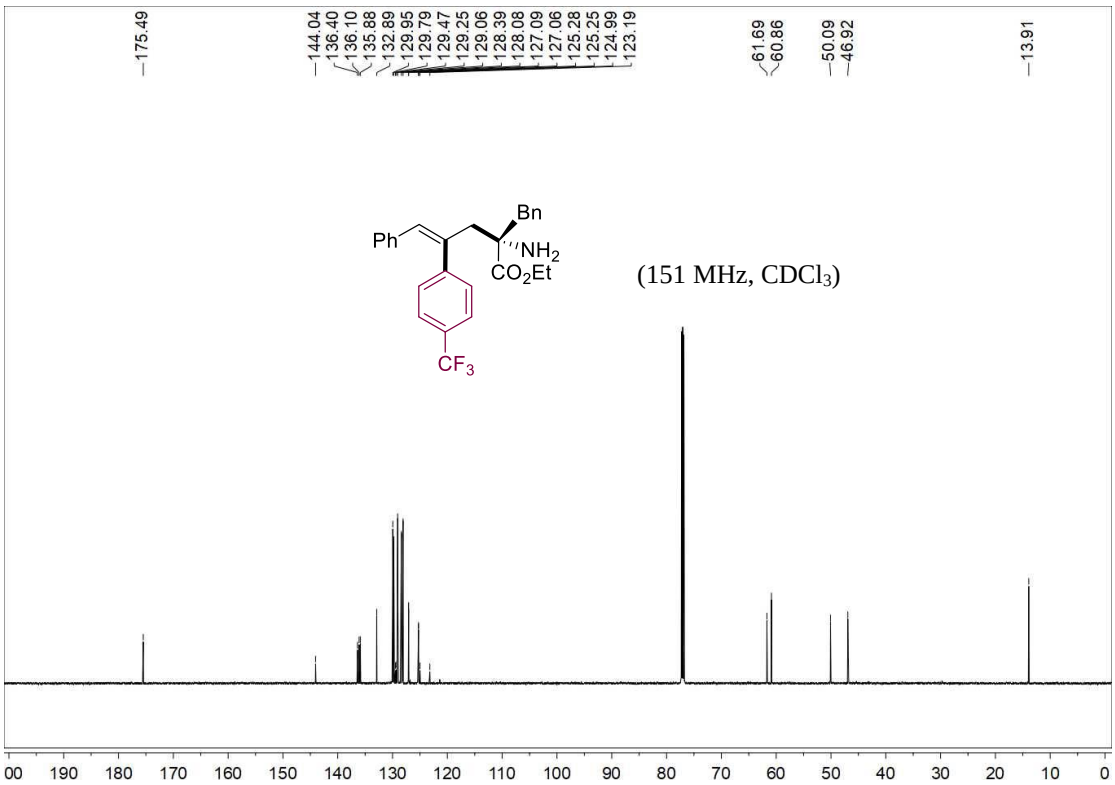
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-phenoxyphenyl)-5-phenylpent-4-enoate (5l):



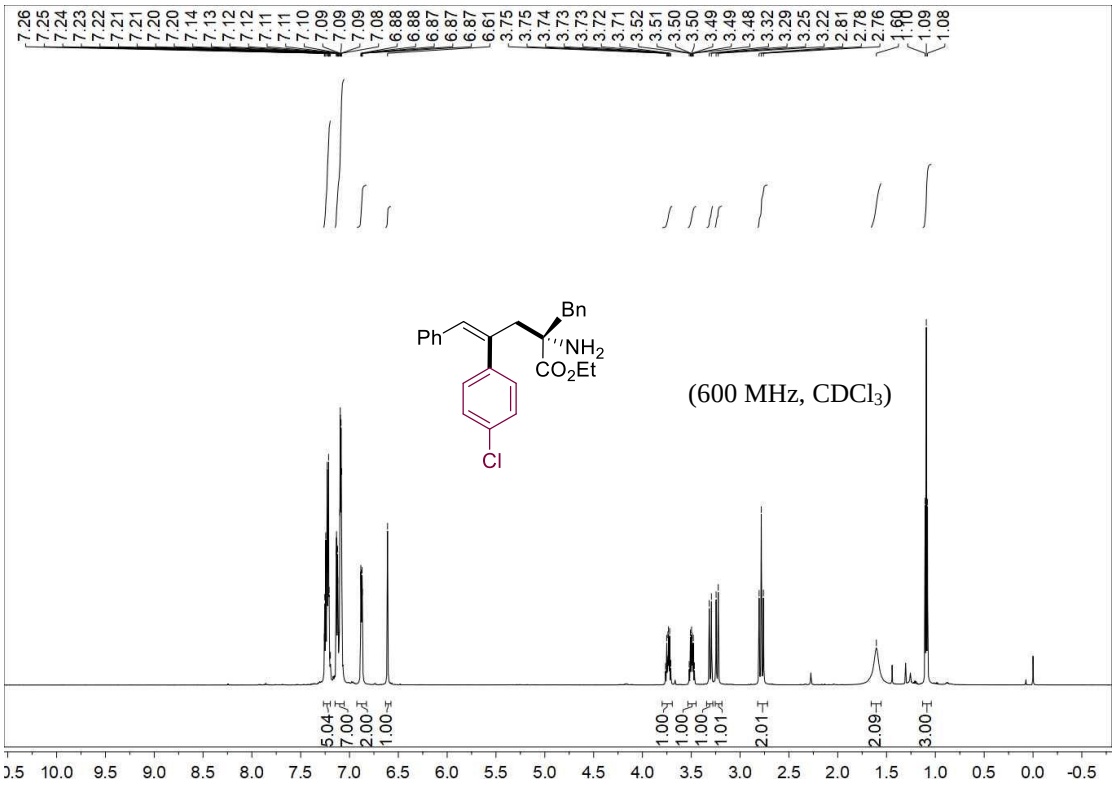


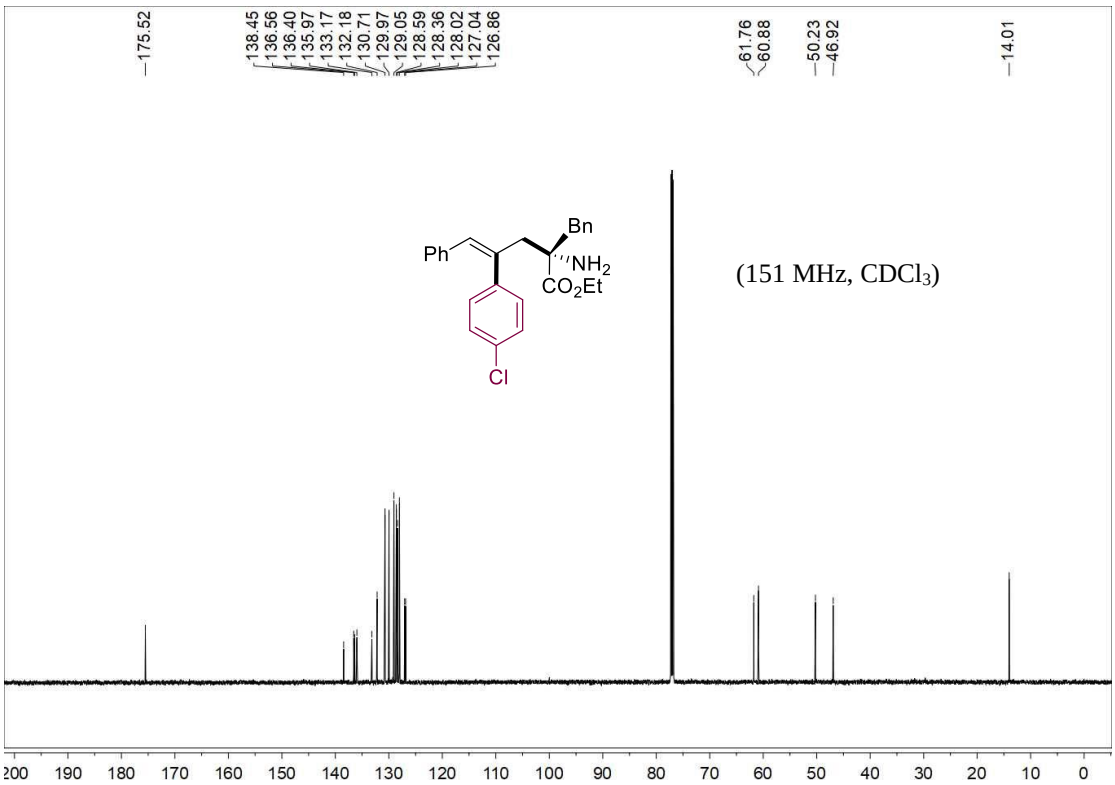
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-phenyl-4-(4-(trifluoromethyl)phenyl)pent-4-enoate (5m):



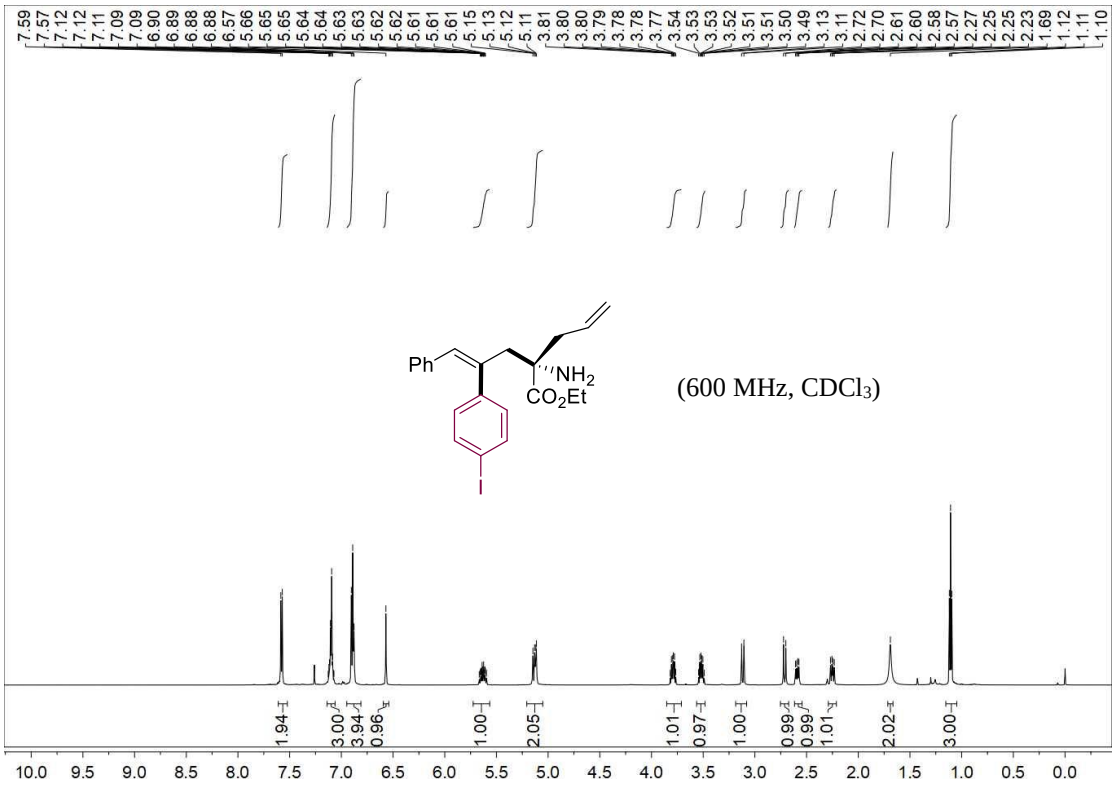


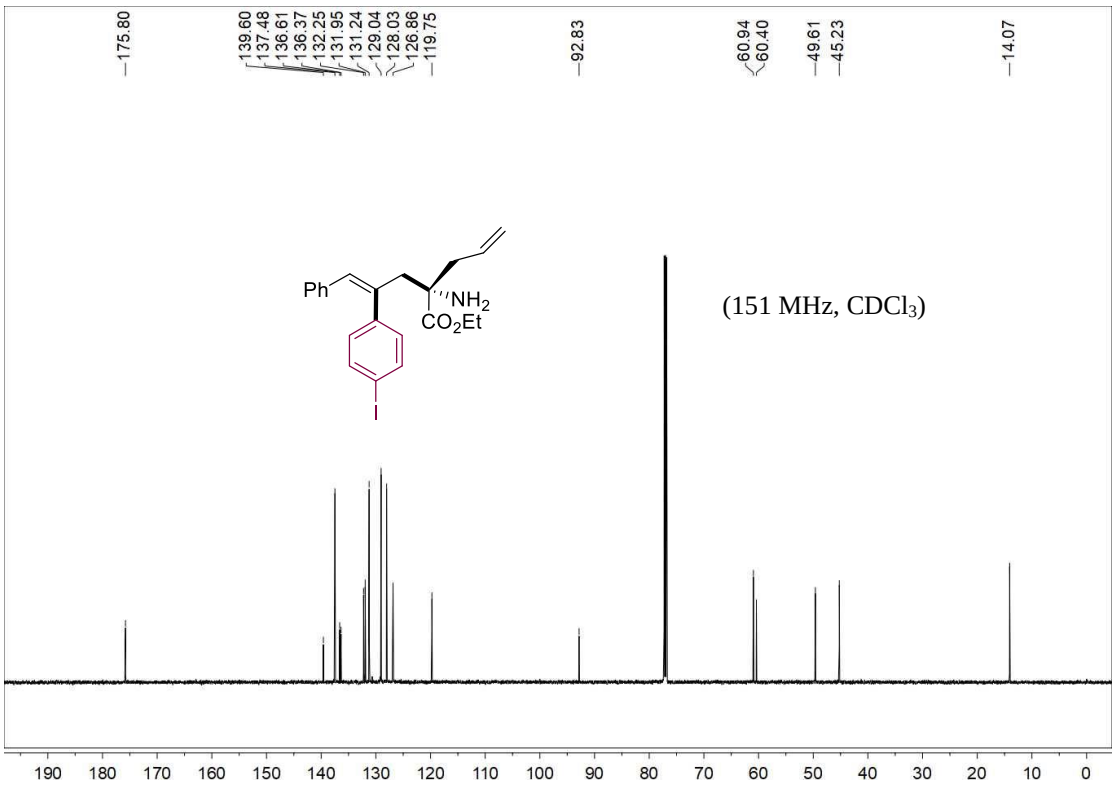
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-chlorophenyl)-5-phenylpent-4-enoate (5n):



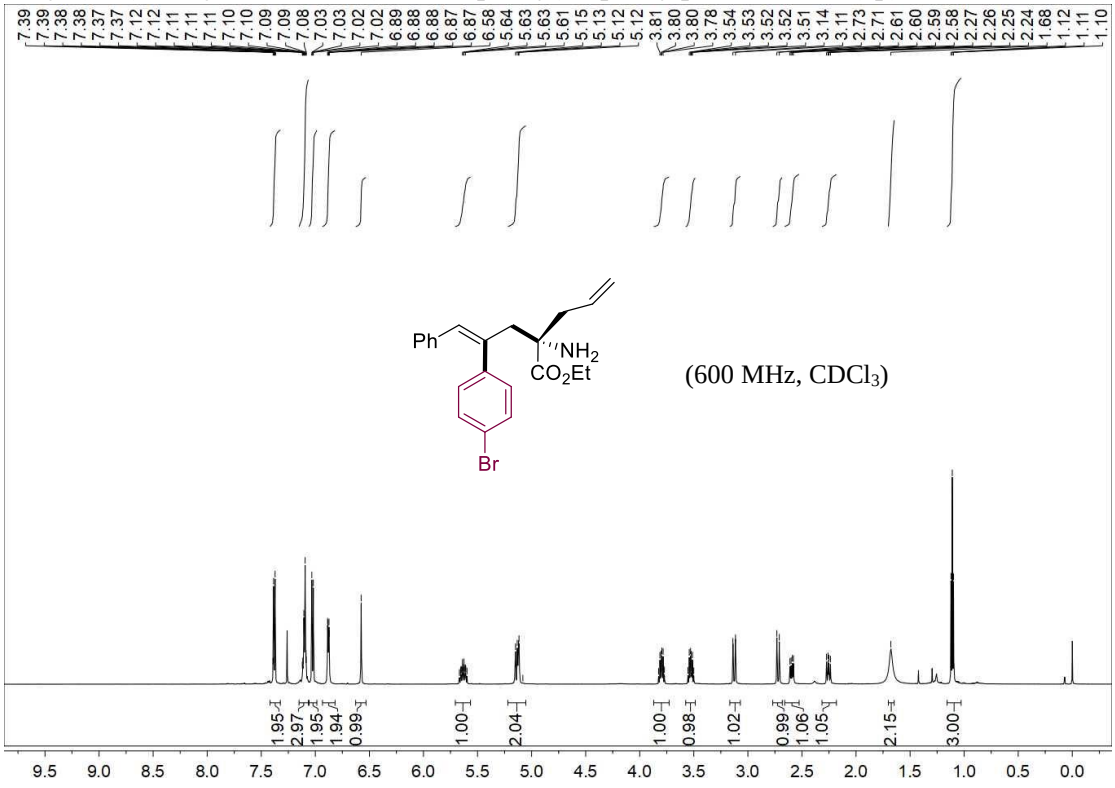


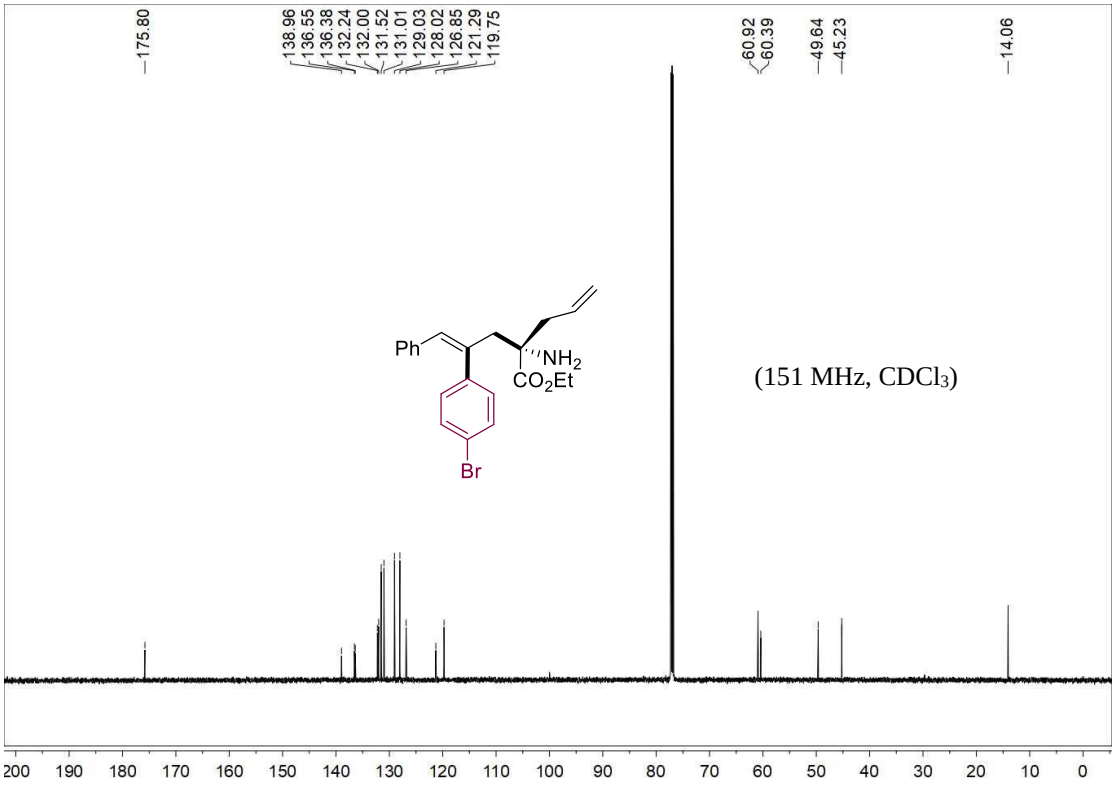
Ethyl (*S*, *Z*)-2-allyl-2-amino-4-(4-iodophenyl)-5-phenylpent-4-enoate (5o):



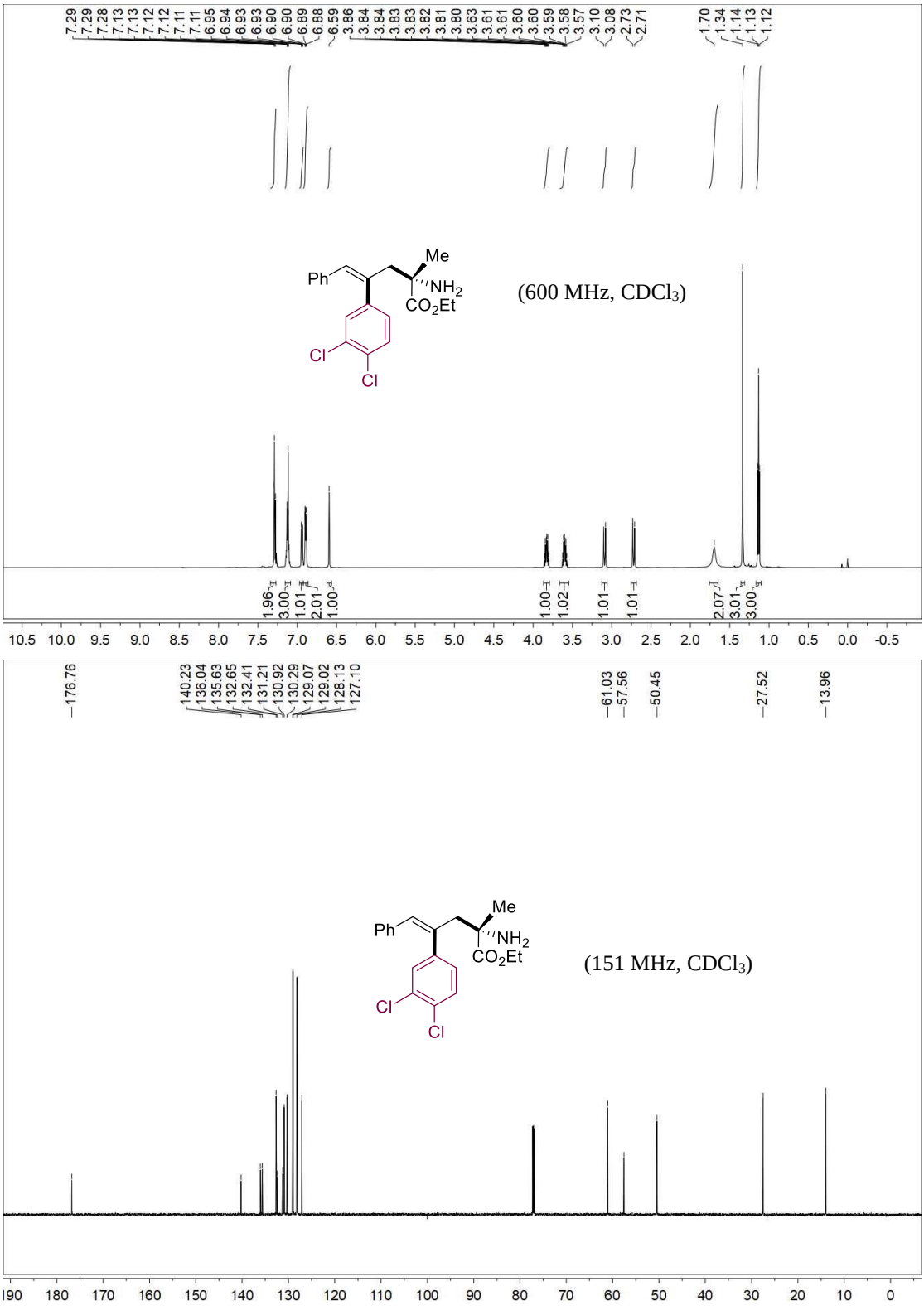


Ethyl (*S*, *Z*)-2-allyl-2-amino-4-(4-bromophenyl)-5-phenylpent-4-enoate (5p):

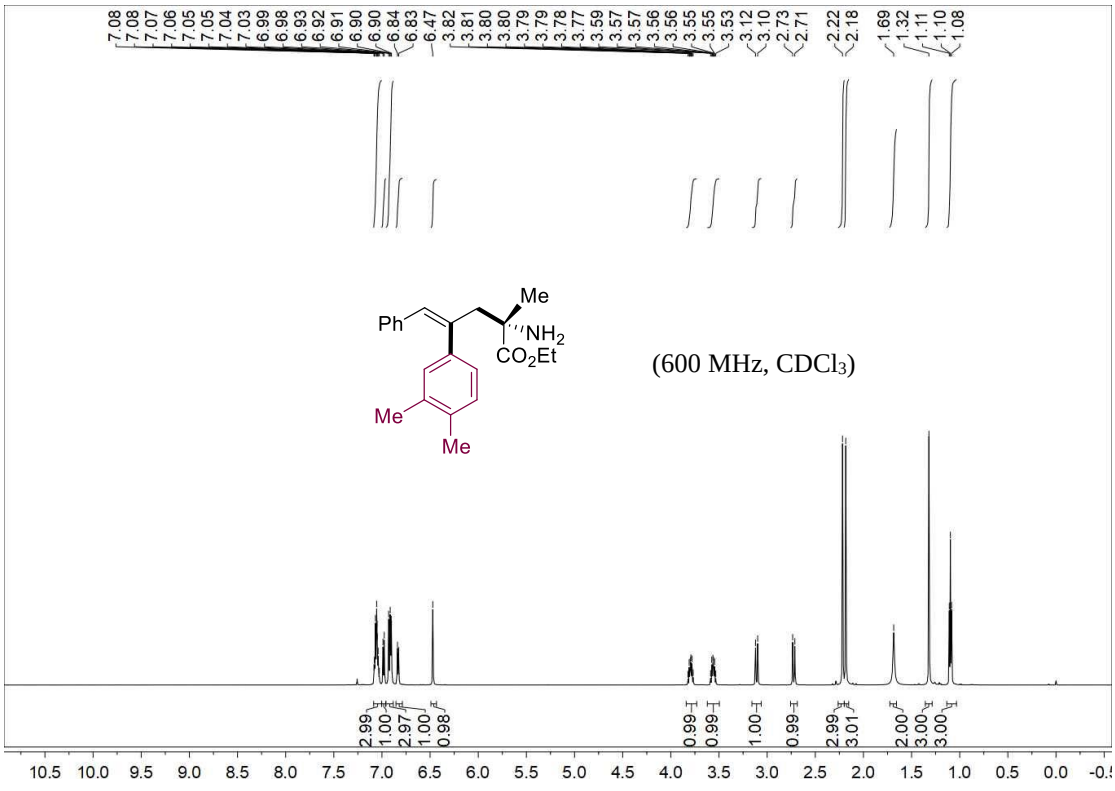


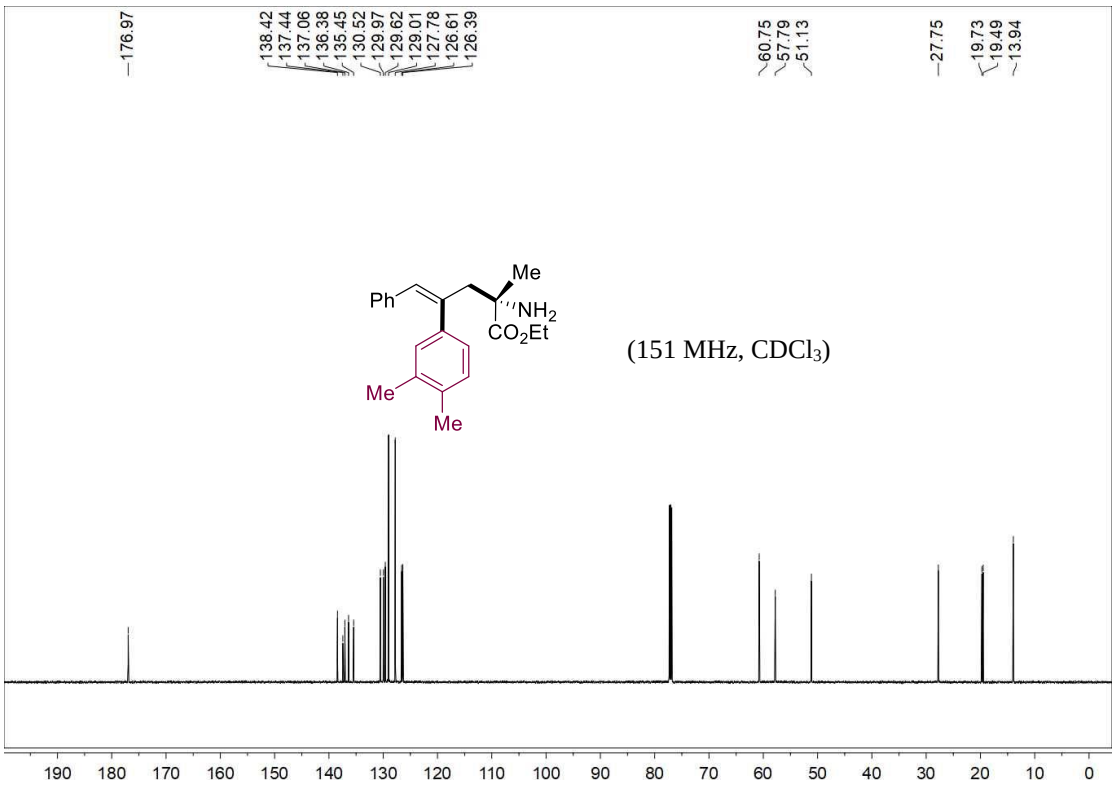


Ethyl (*S*, *Z*)-2-amino-4-(3, 4-dichlorophenyl)-2-methyl-5-phenylpent-4-enoate (5q):

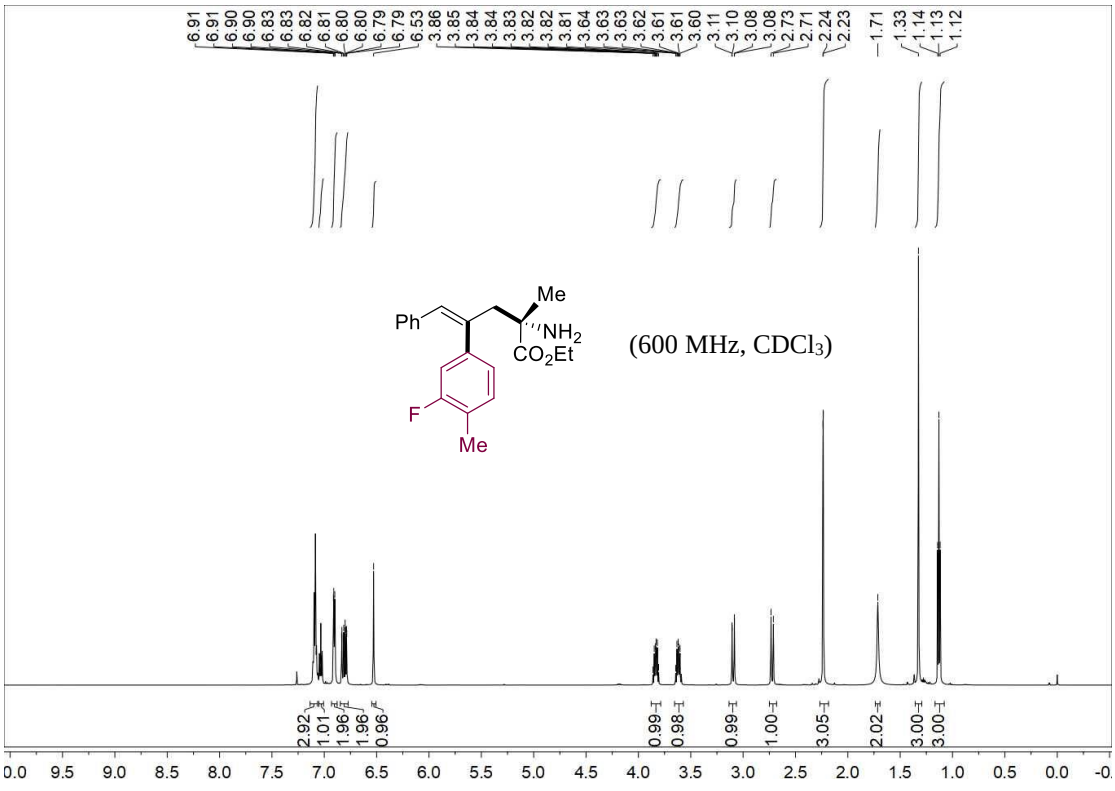


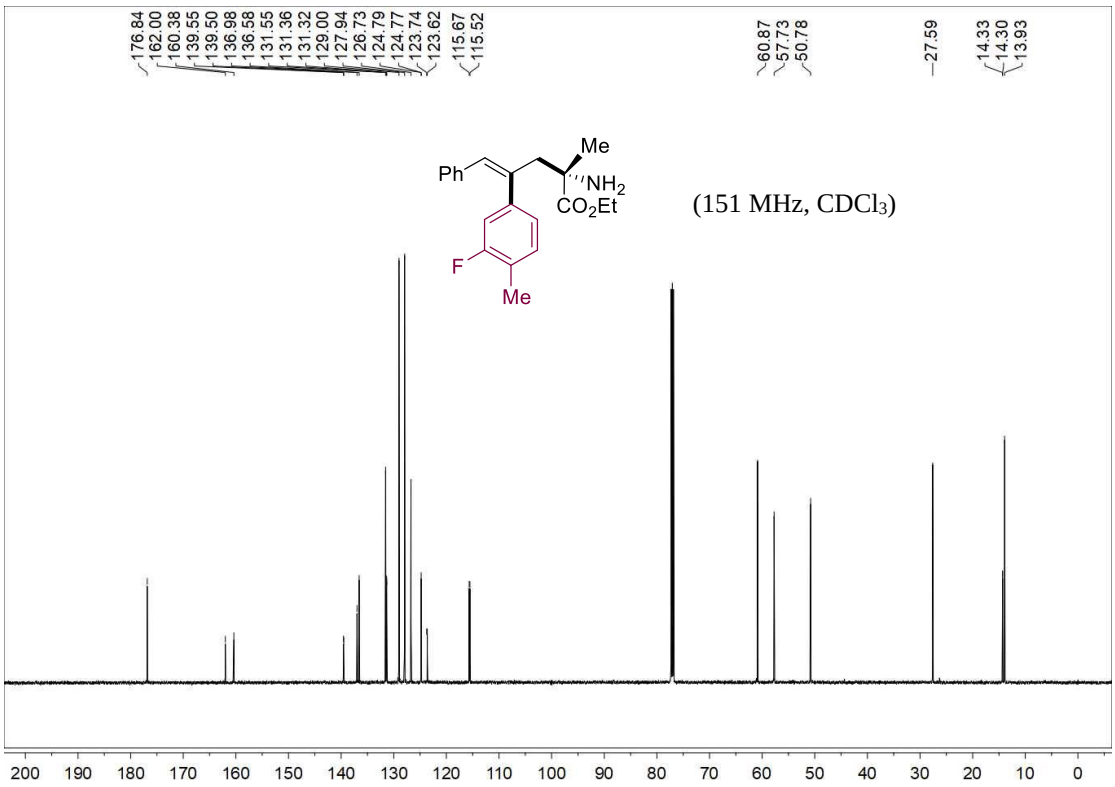
Ethyl (*S*, *Z*)-2-amino-4-(3, 4-dimethylphenyl)-2-methyl-5-phenylpent-4-enoate (5r):



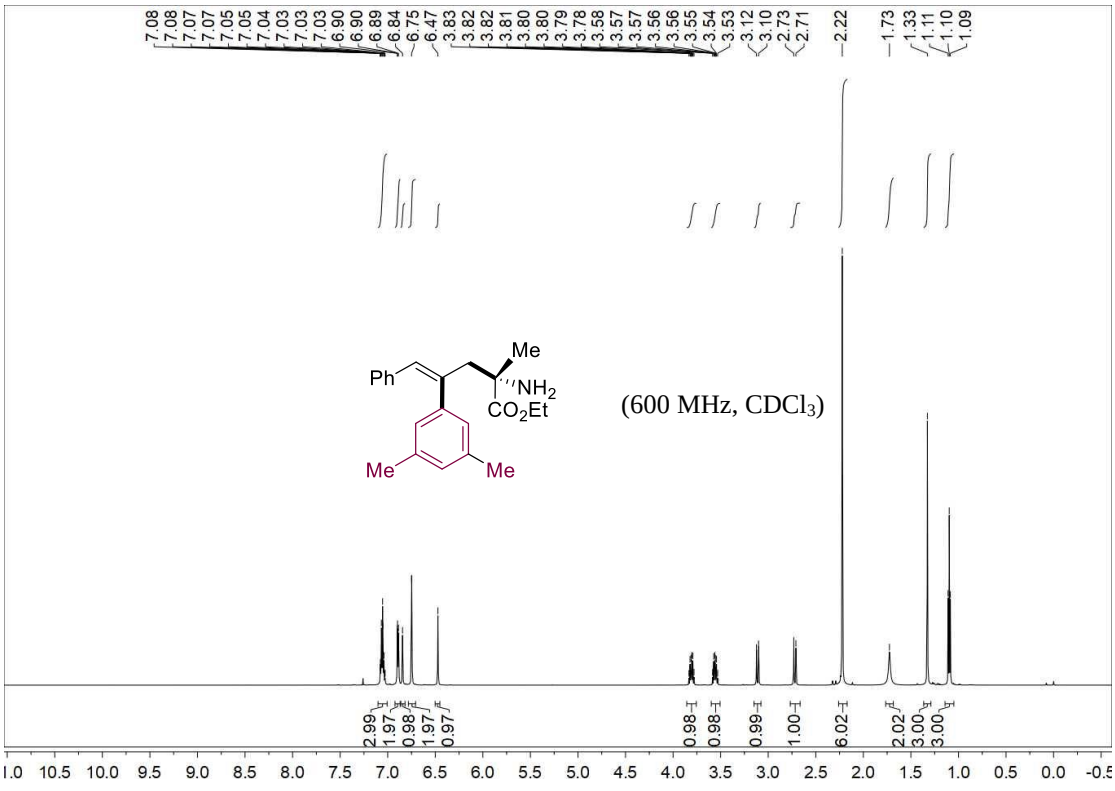


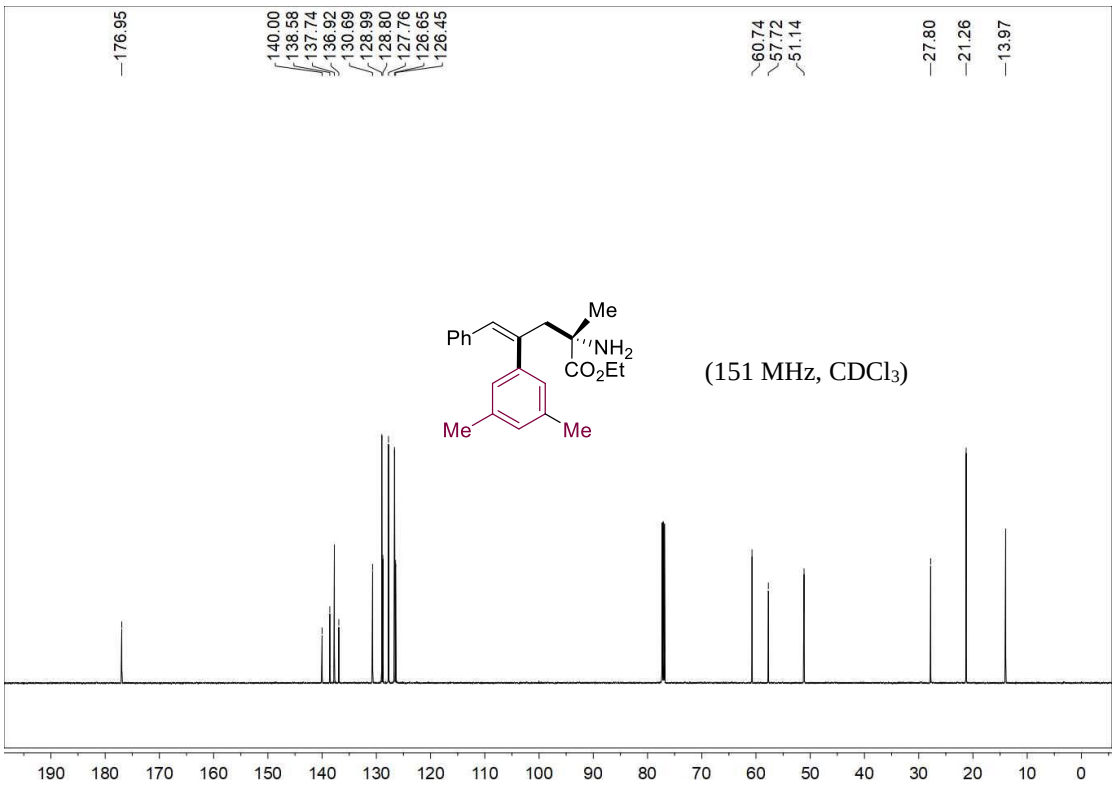
Ethyl (*S*, *Z*)-2-amino-4-(3-fluoro-4-methylphenyl)-2-methyl-5-phenylpent-4-enoate (5s):



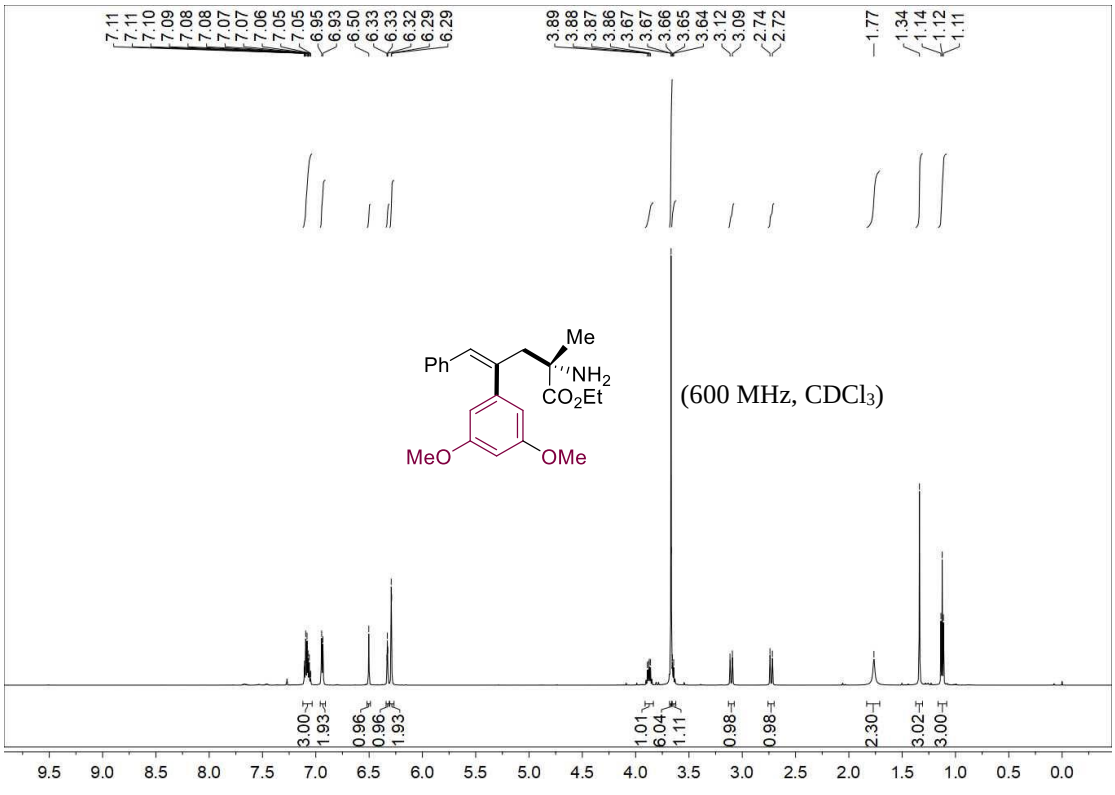


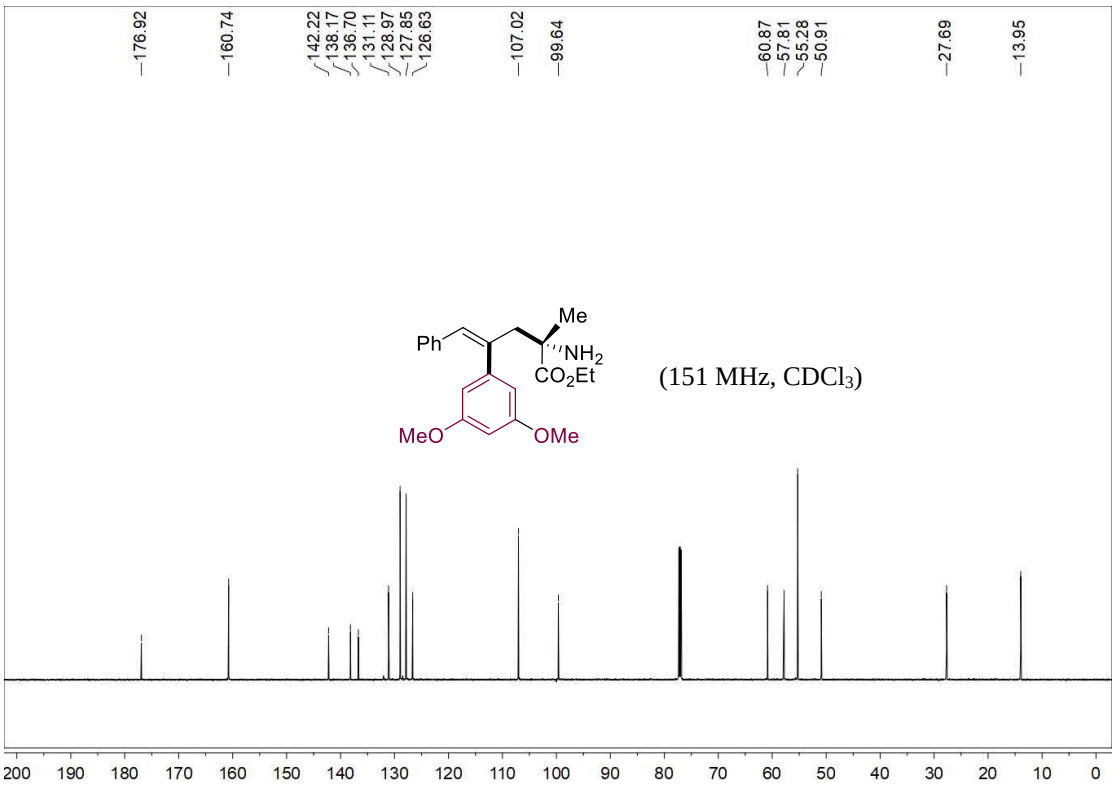
Ethyl (*S*, *Z*)-2-amino-4-(3, 5-dimethylphenyl)-2-methyl-5-phenylpent-4-enoate (5t):



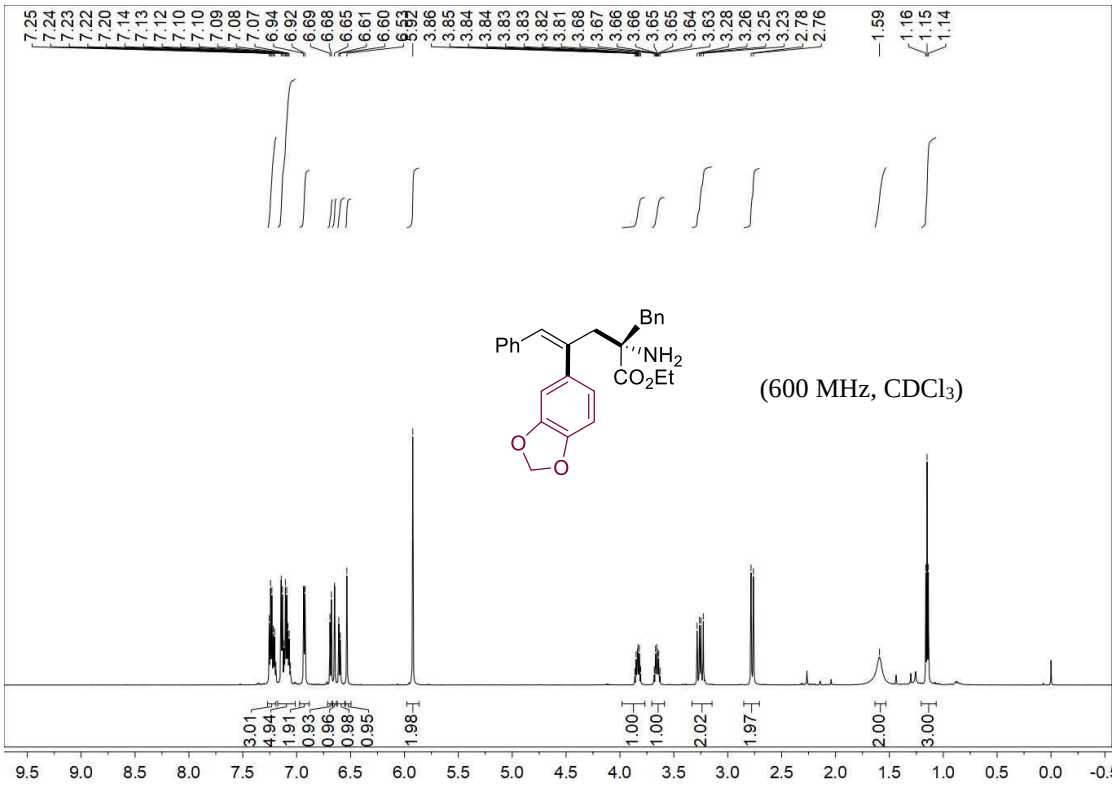


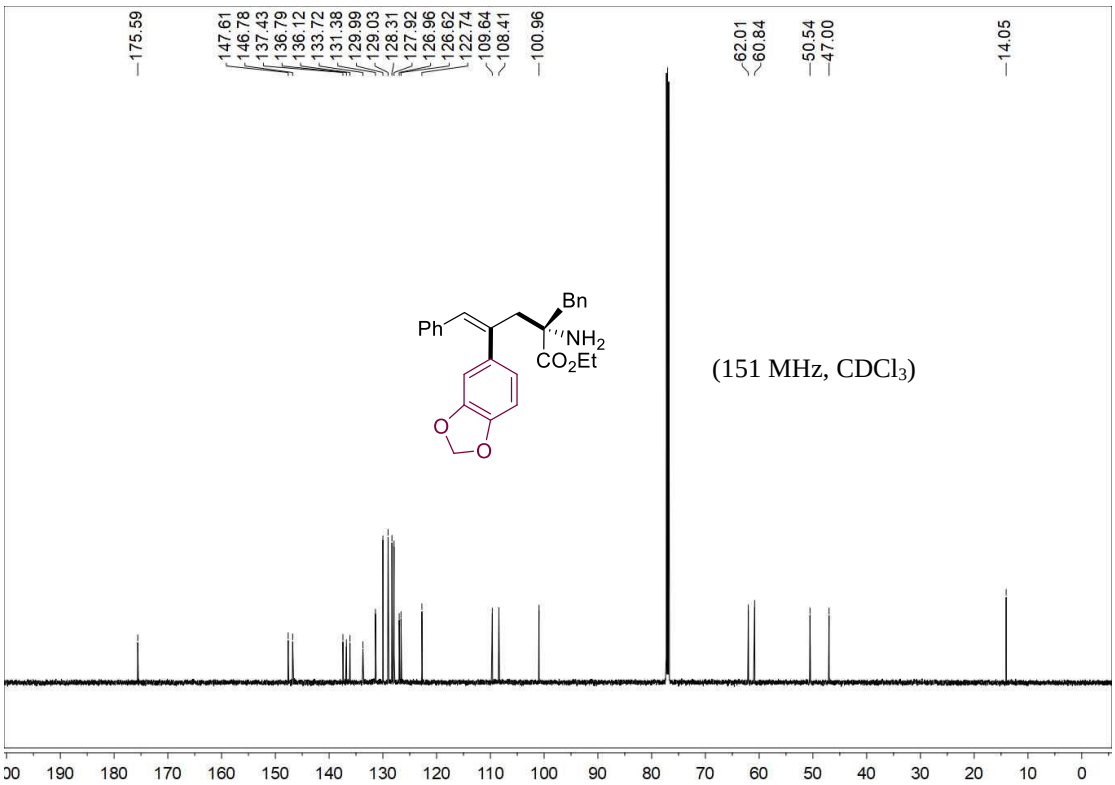
Ethyl (*S*, *Z*)-2-amino-4-(3, 5-dimethoxyphenyl)-2-methyl-5-phenylpent-4-enoate (5u):



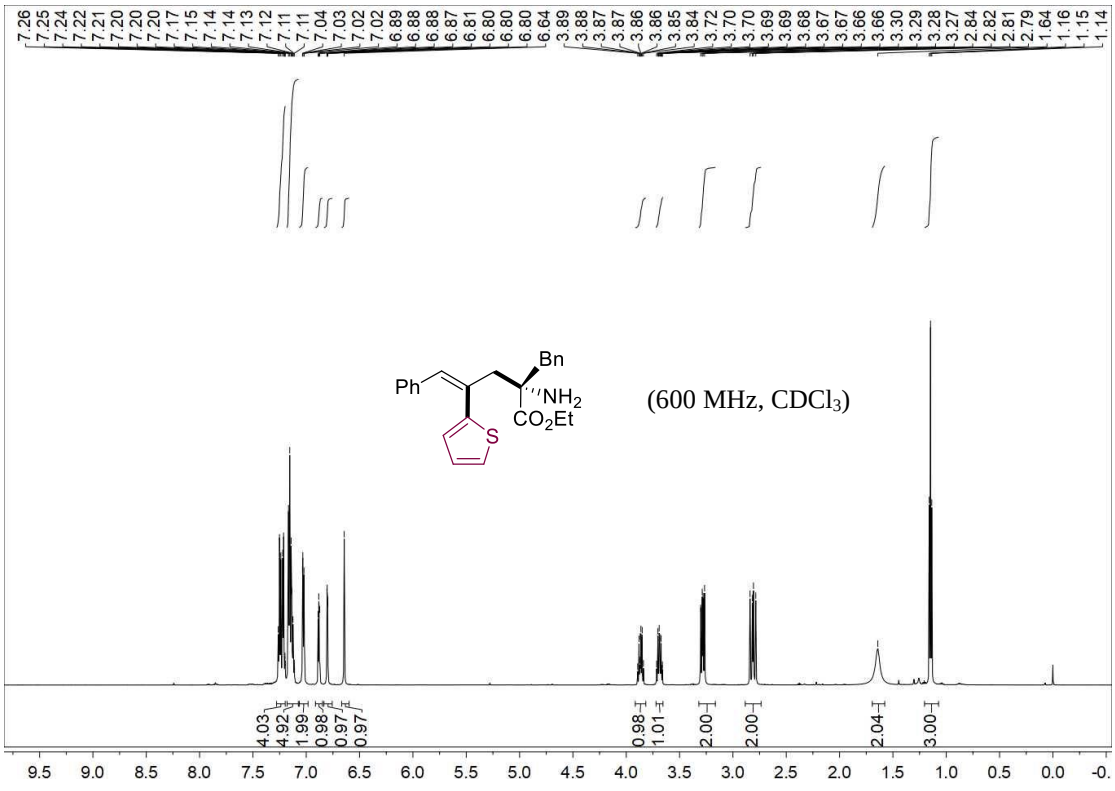


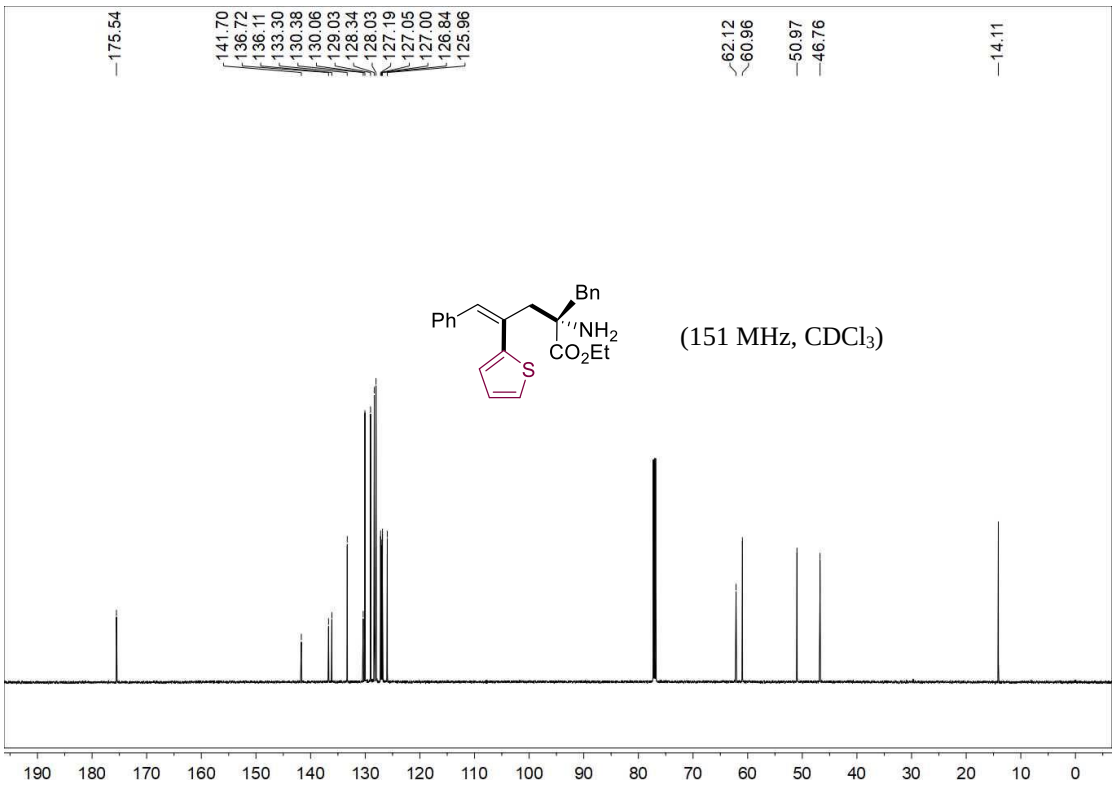
Ethyl (*S*, *Z*)-2-amino-4-(benzo[d][1, 3]dioxol-5-yl)-2-benzyl-5-phenylpent-4-enoate (5v):



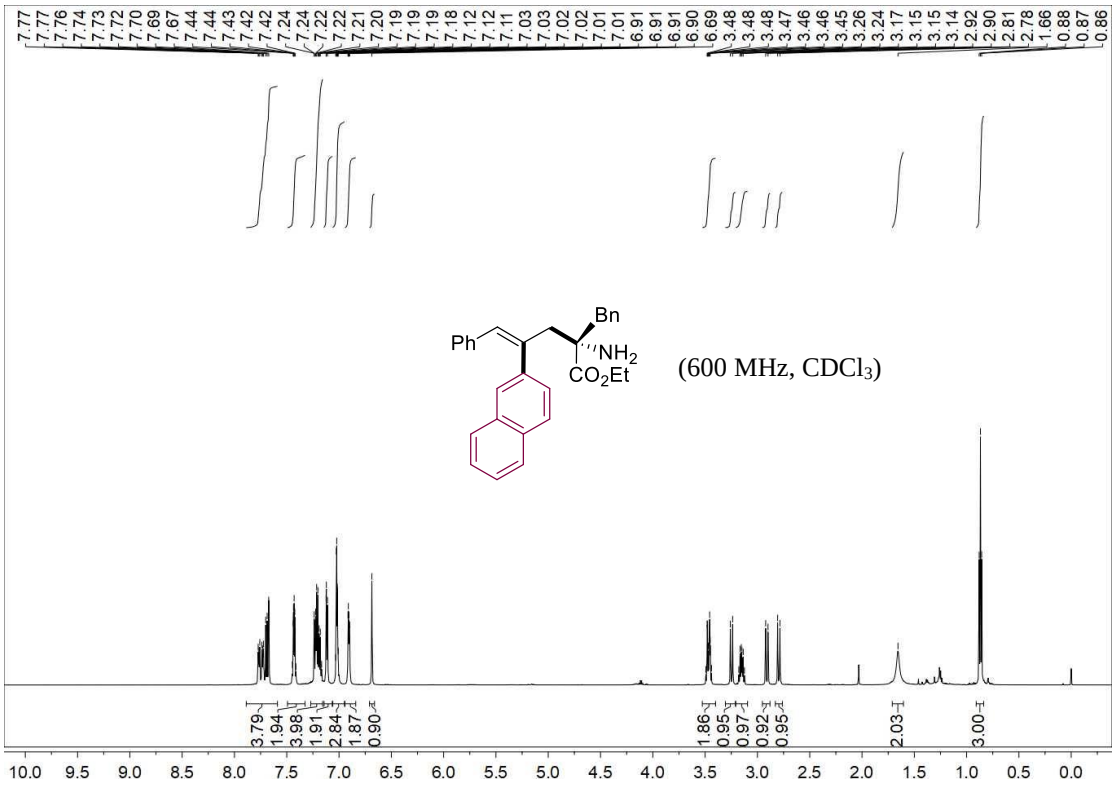


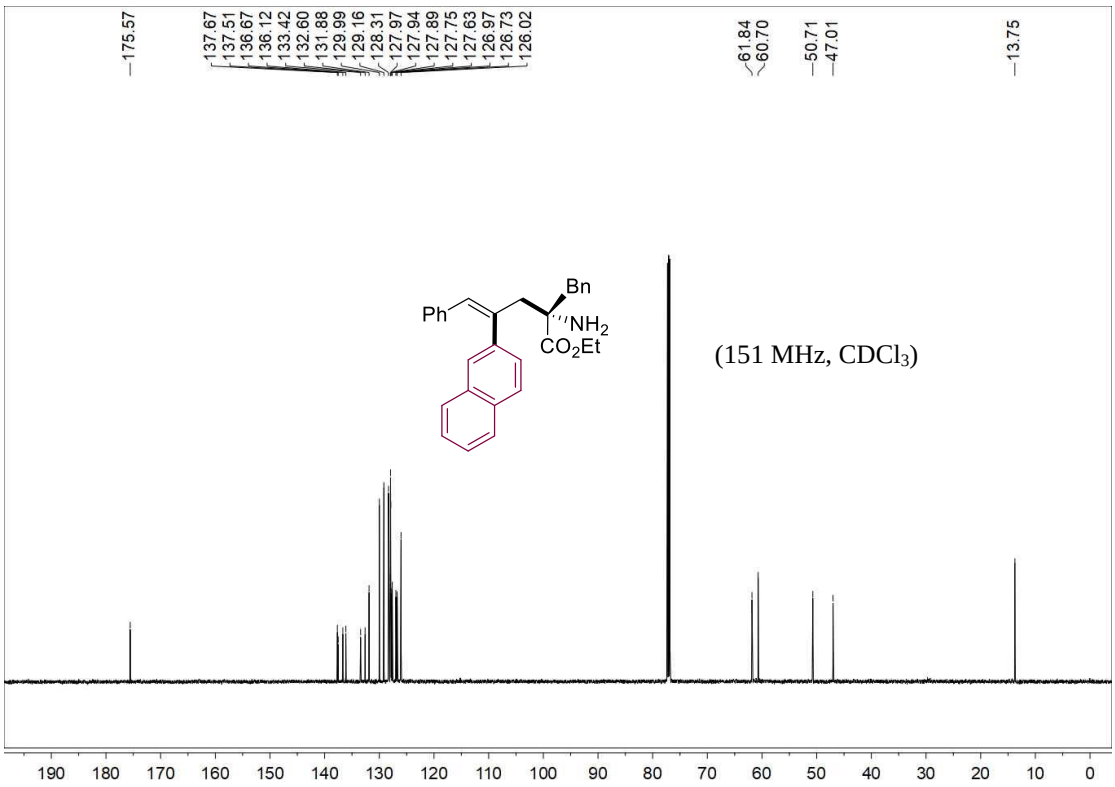
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-phenyl-4-(thiophen-2-yl)pent-4-enoate (5w):



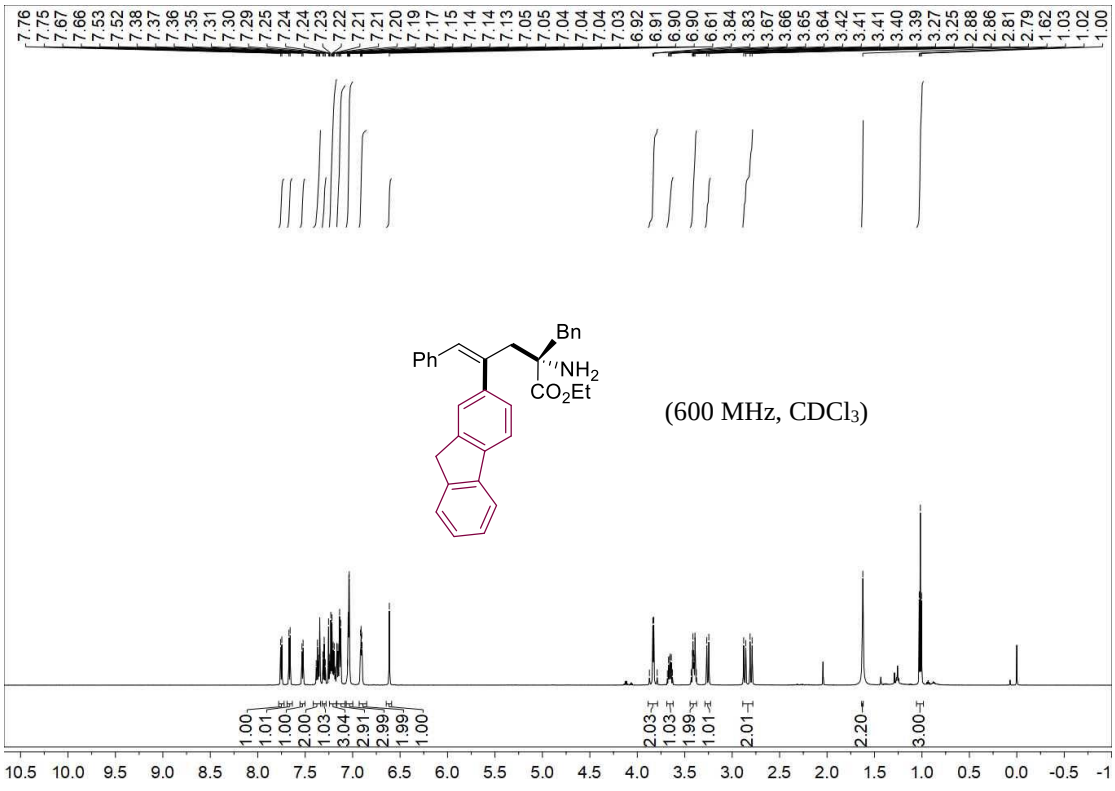


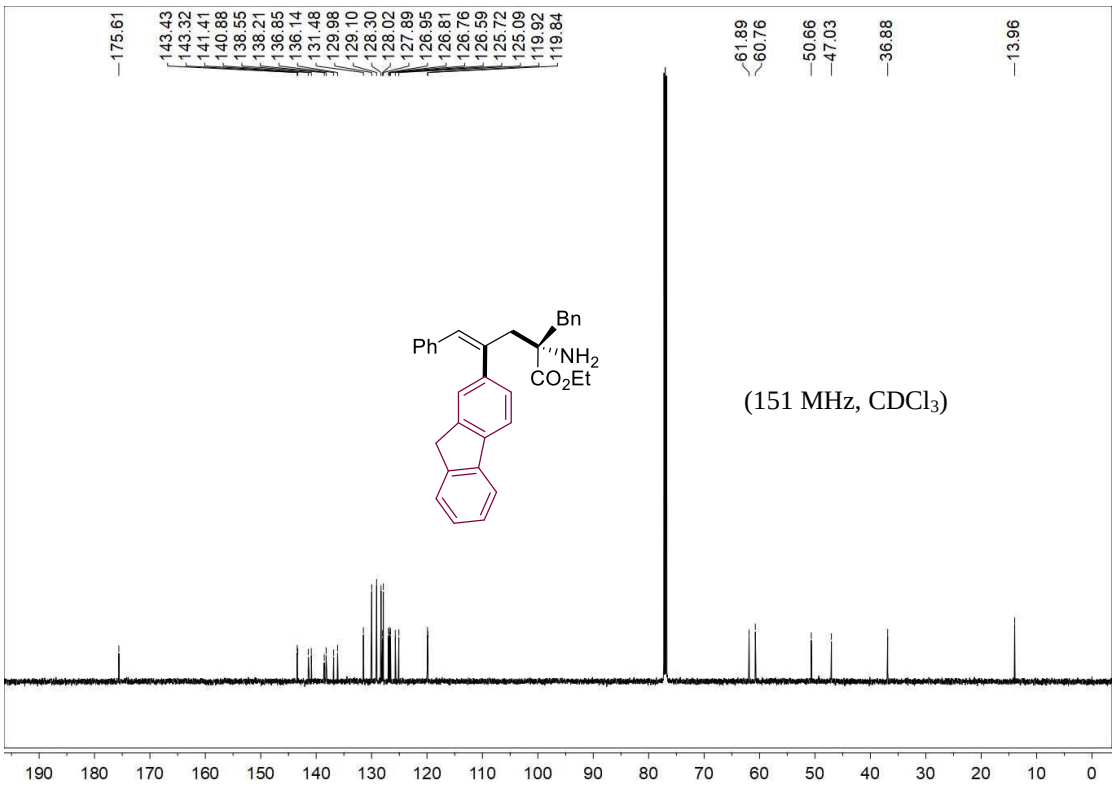
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(naphthalen-2-yl)-5-phenylpent-4-enoate (5x):



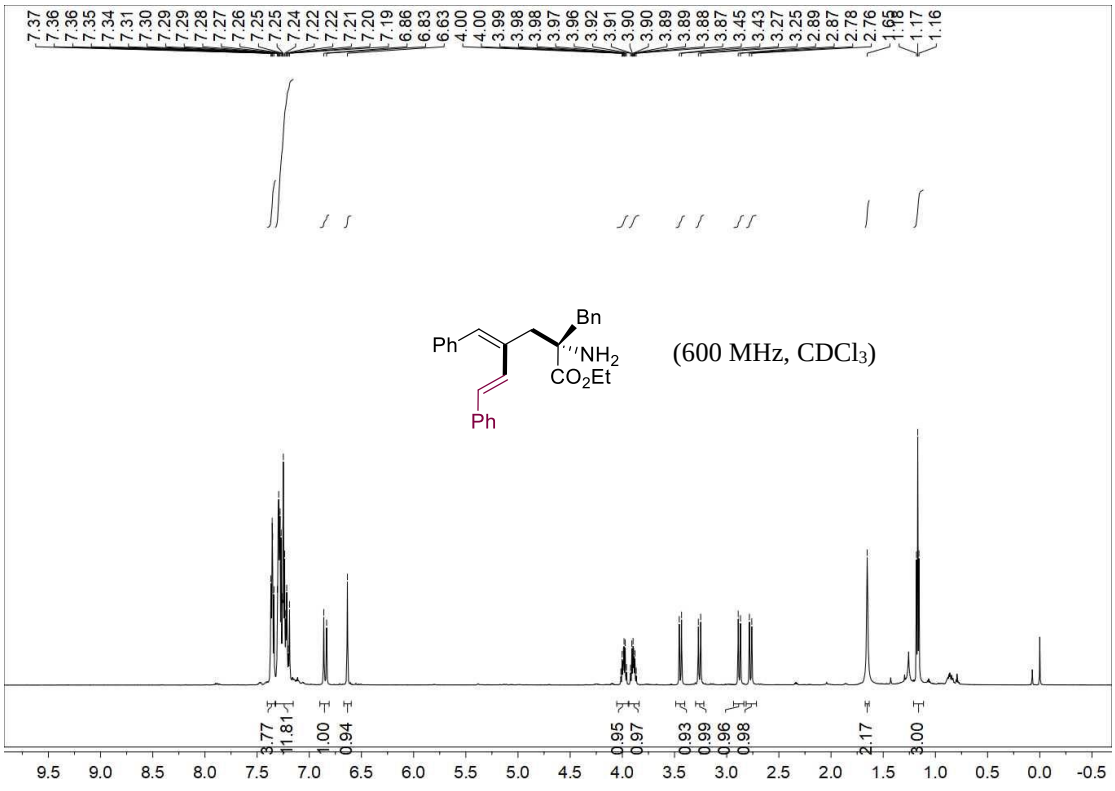


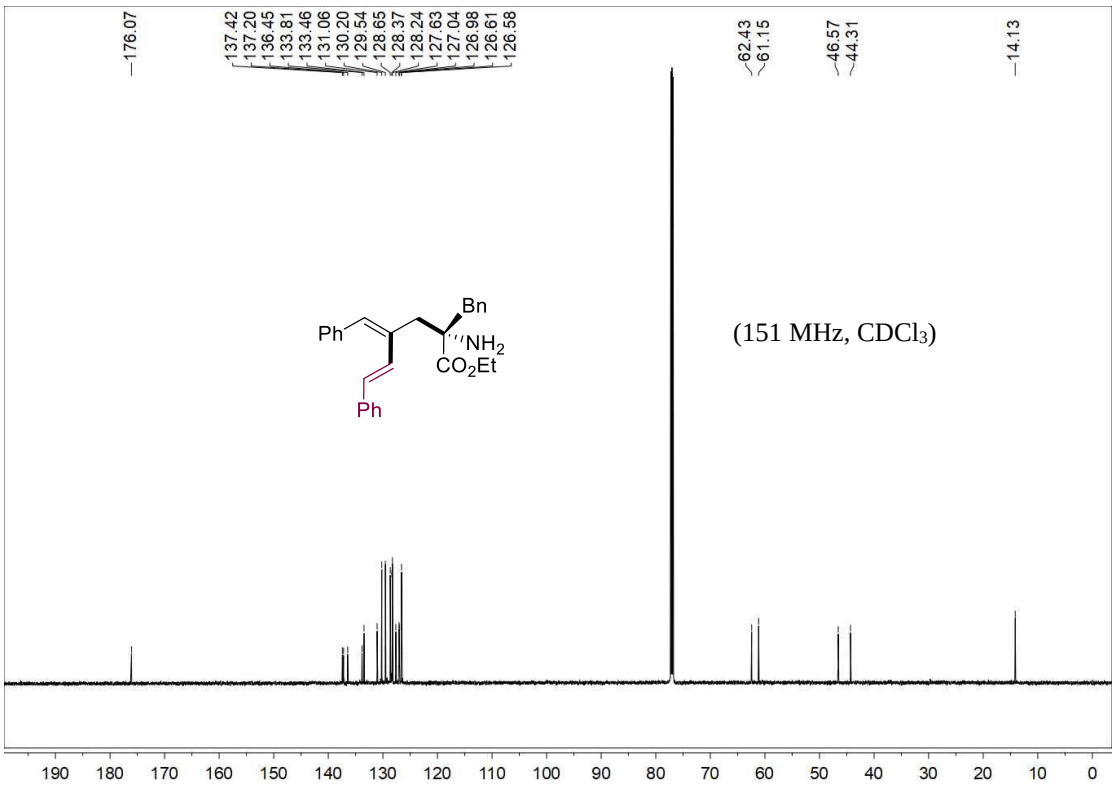
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(9H-fluoren-2-yl)-5-phenylpent-4-enoate (5y):



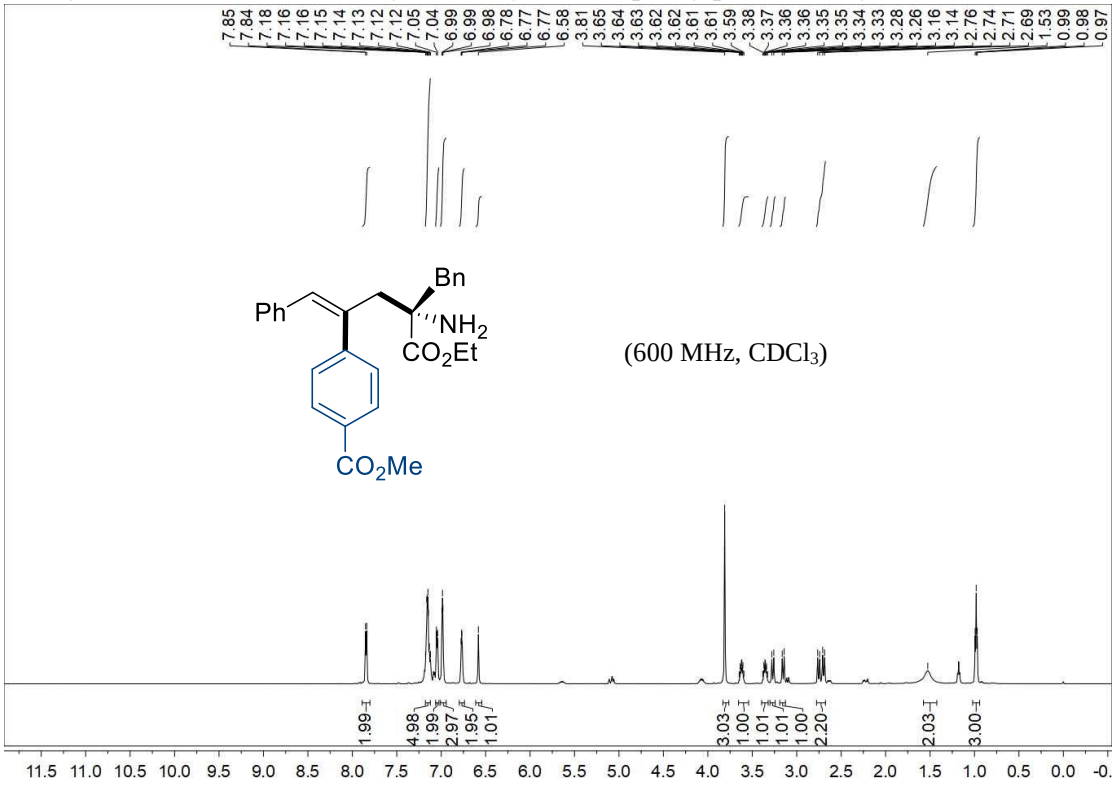


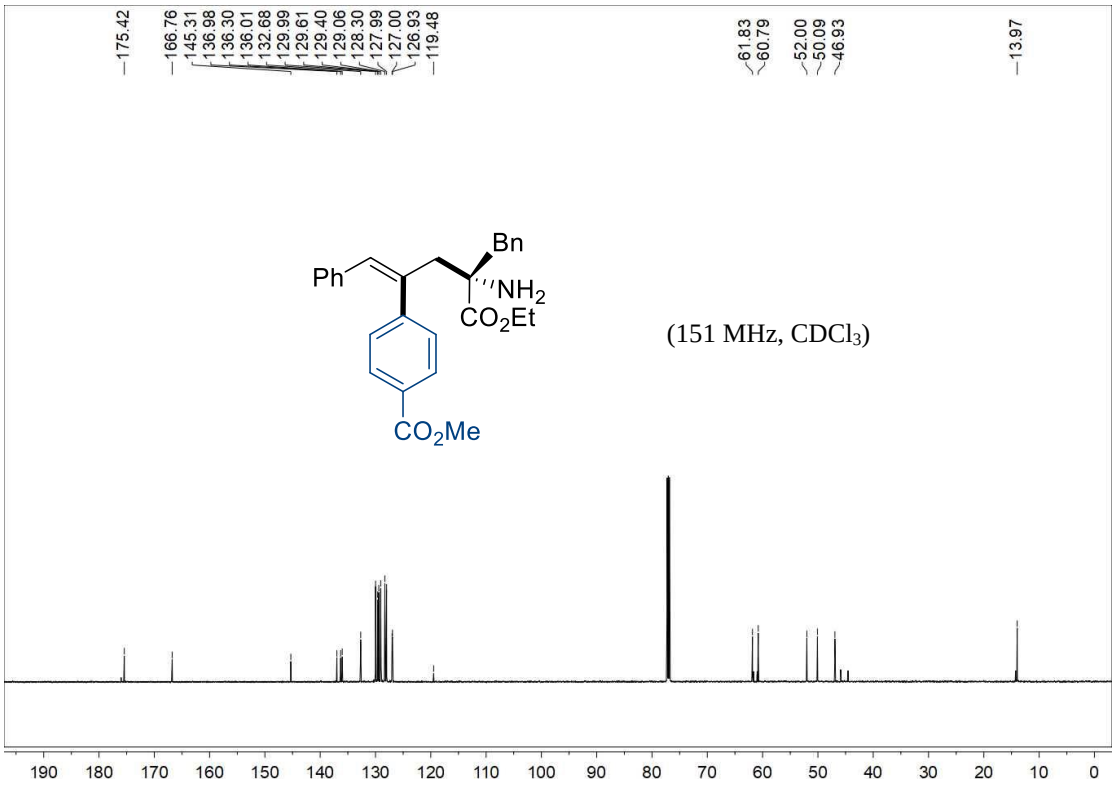
Ethyl (*S*, *E*)-2-amino-2-benzyl-4-((Z)-benzylidene)-6-phenylhex-5-enoate (5z):



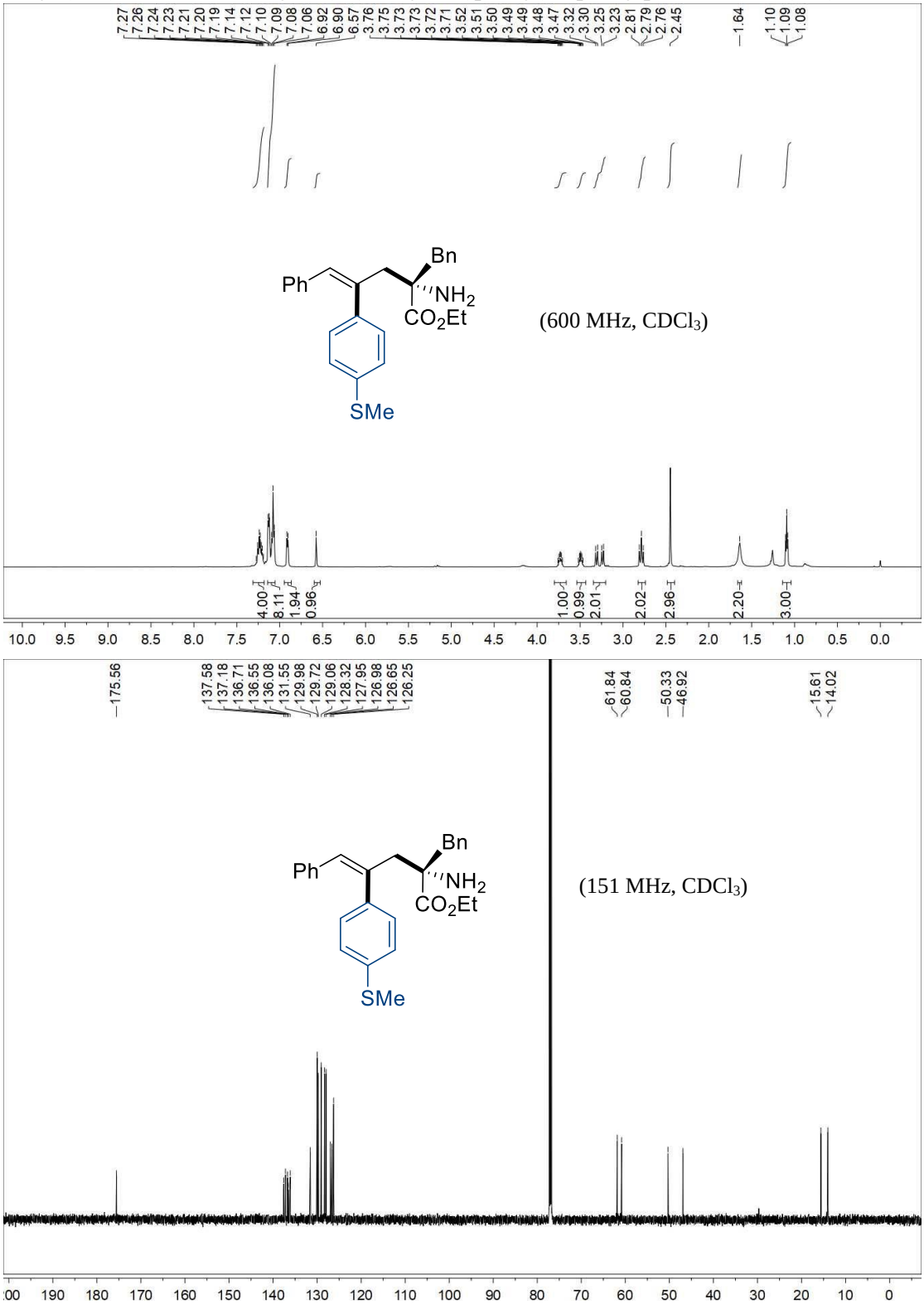


Methyl (*S*, *Z*)-4-(4-amino-4-benzyl-5-ethoxy-5-oxo-1-phenylpent-1-en-2-yl)benzoate (5aa):

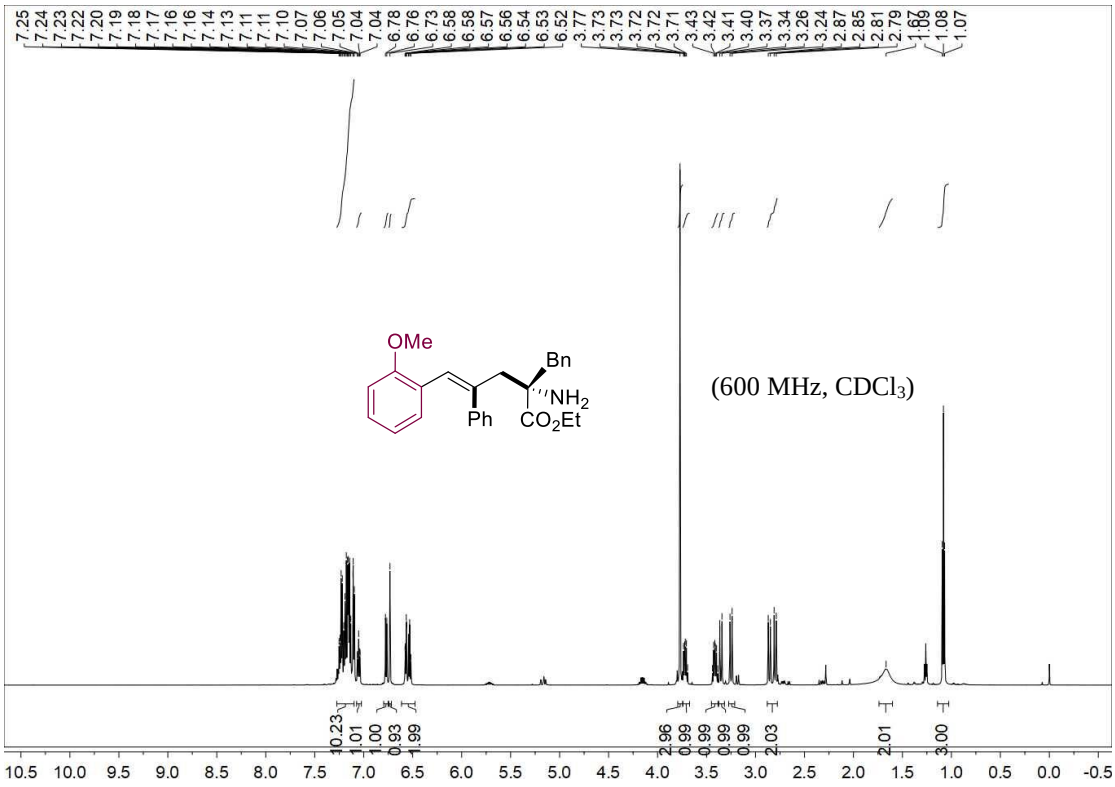


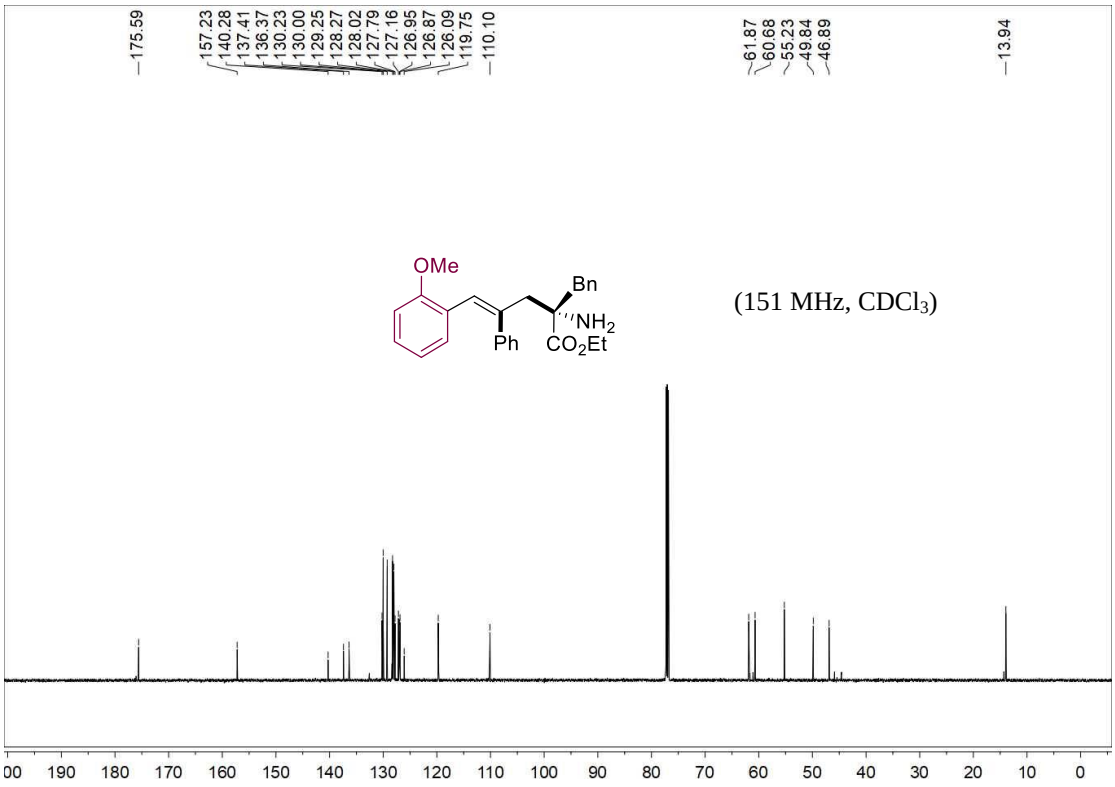


Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-(4-(methylthio)phenyl)-5-phenylpent-4-enoate (5ab):

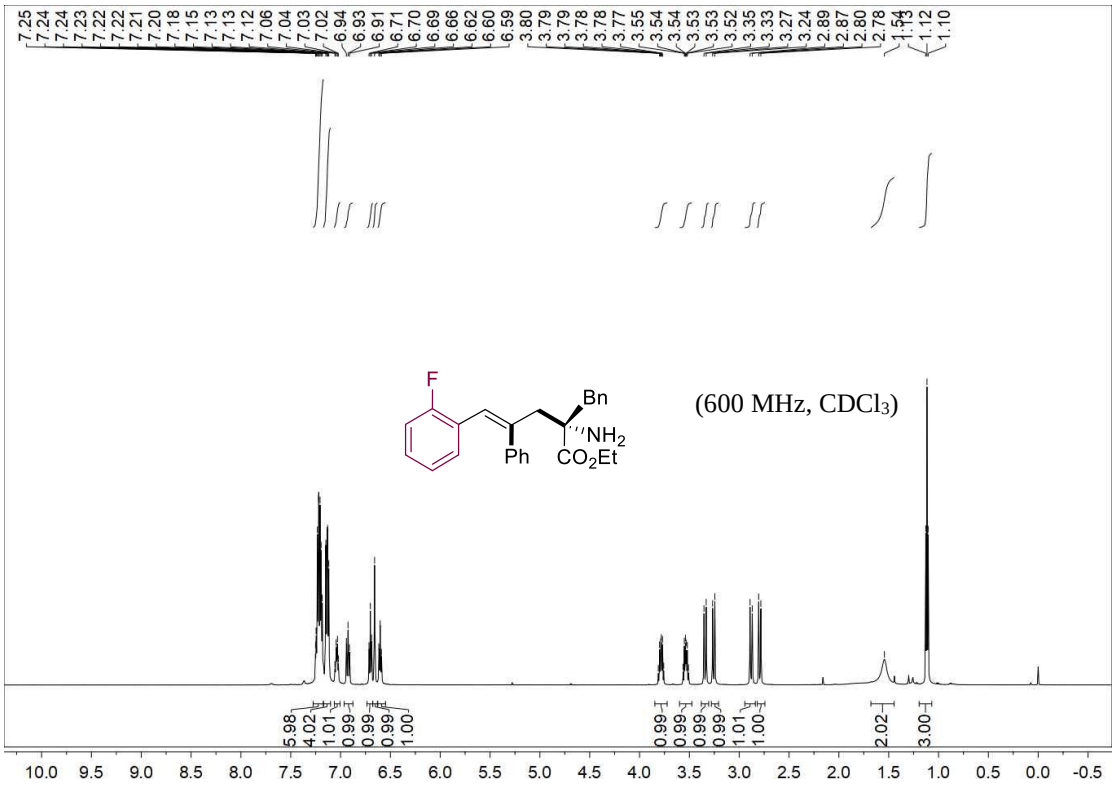


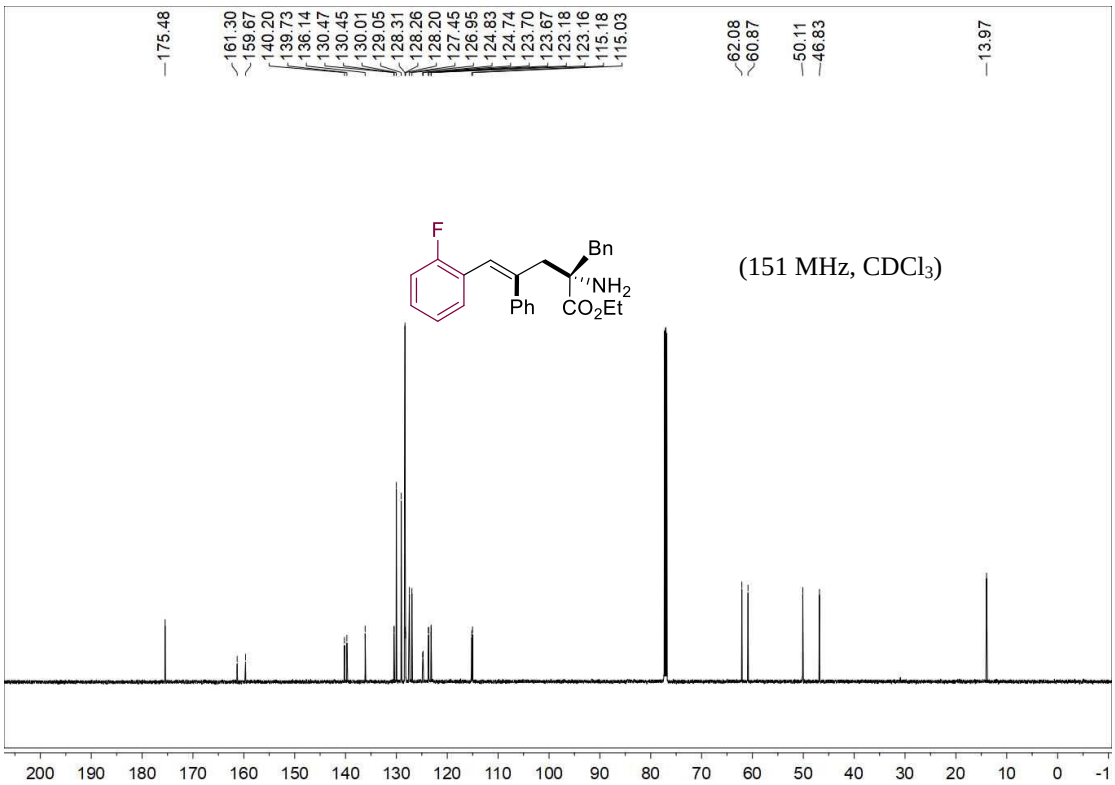
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(2-methoxyphenyl)-4-phenylpent-4-enoate (6a):



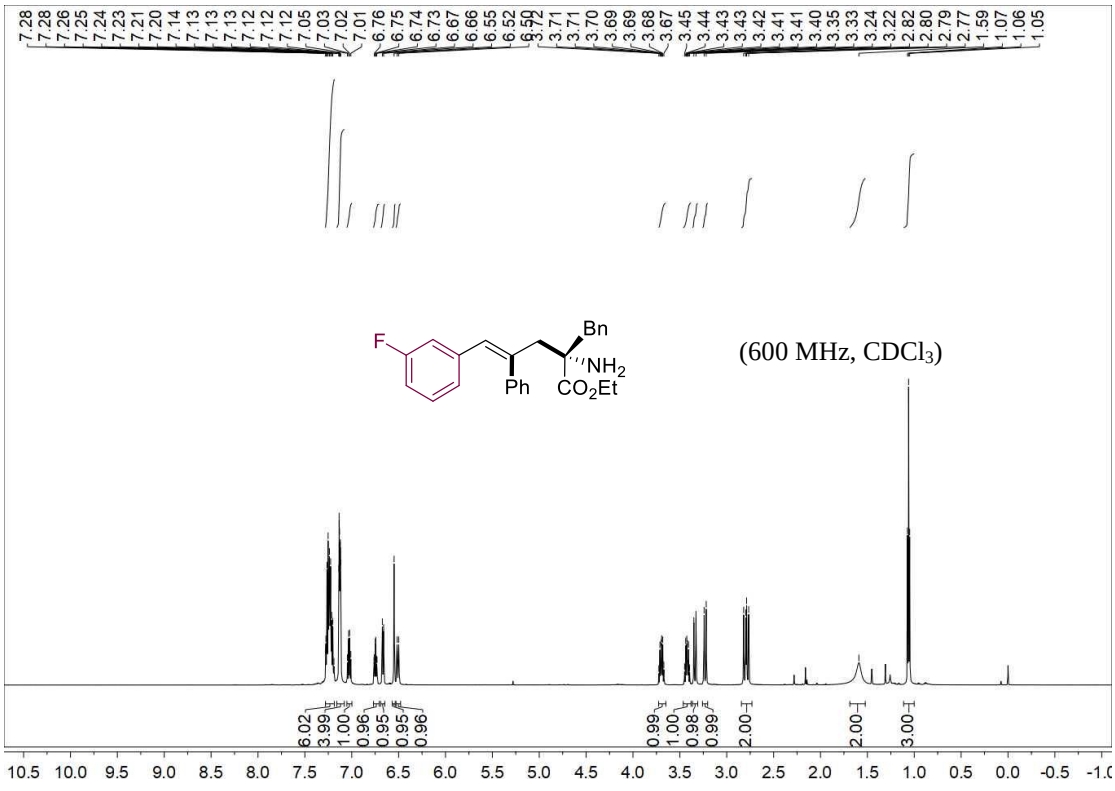


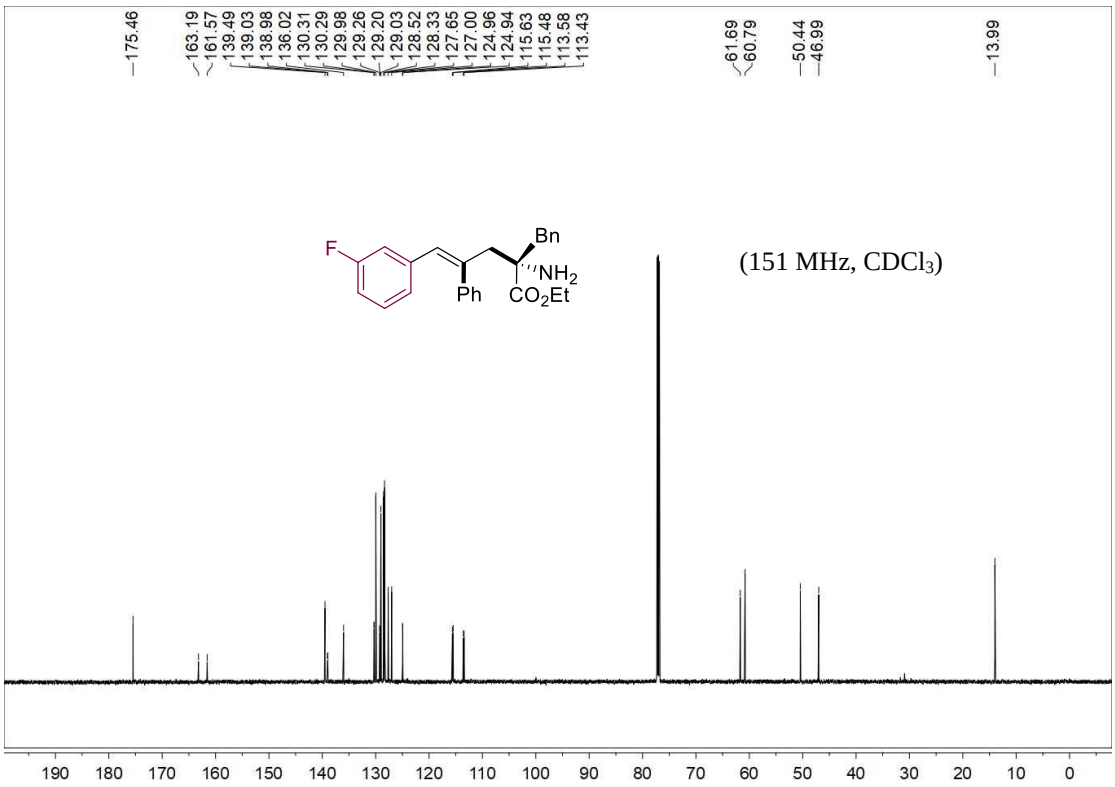
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(2-fluorophenyl)-4-phenylpent-4-enoate (6b):



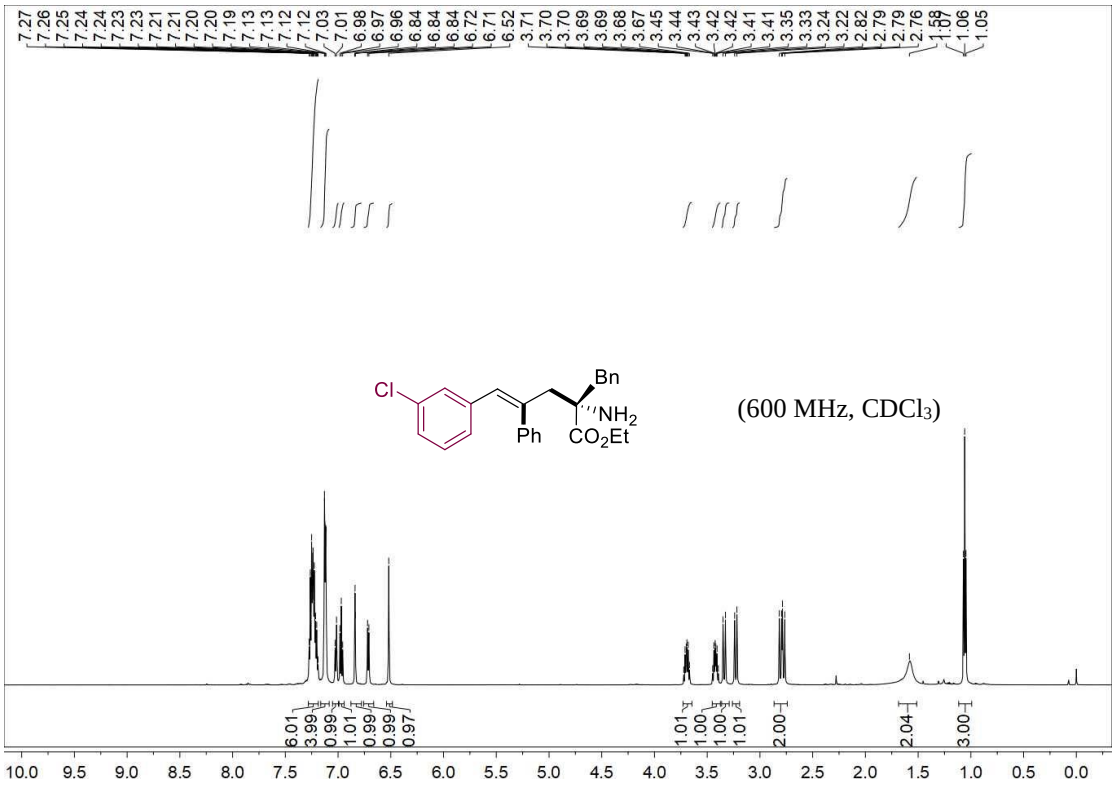


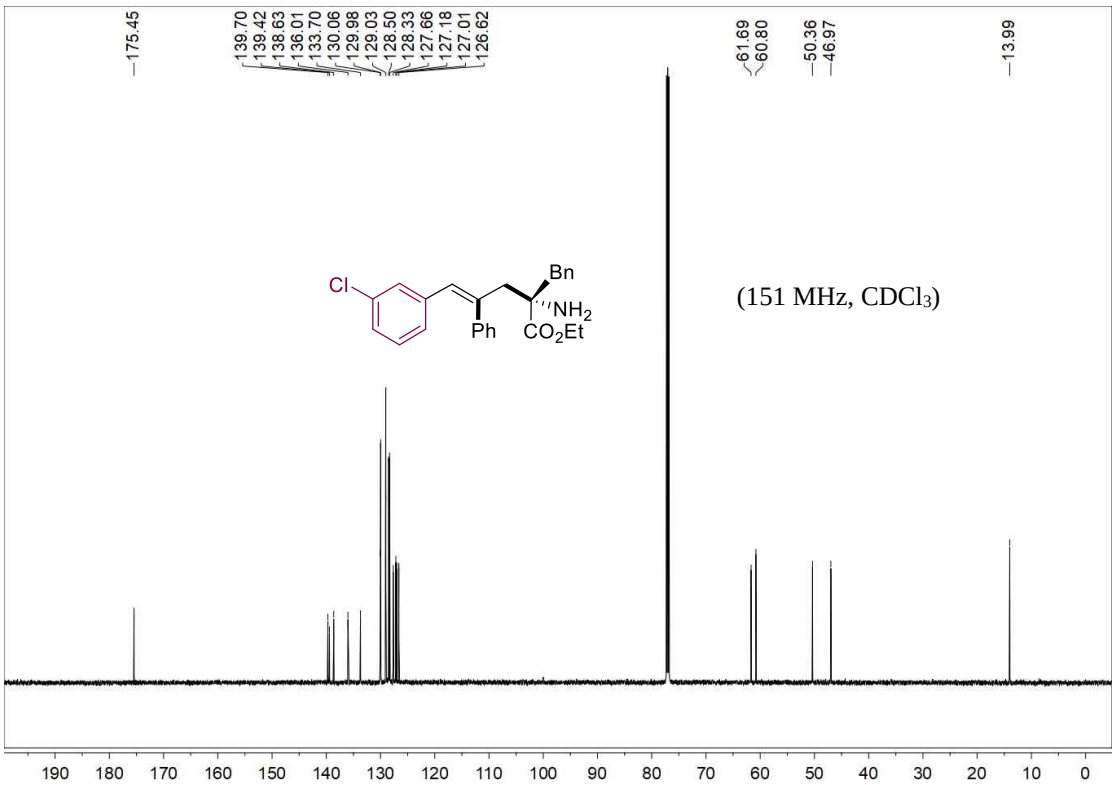
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3-fluorophenyl)-4-phenylpent-4-enoate (6c):



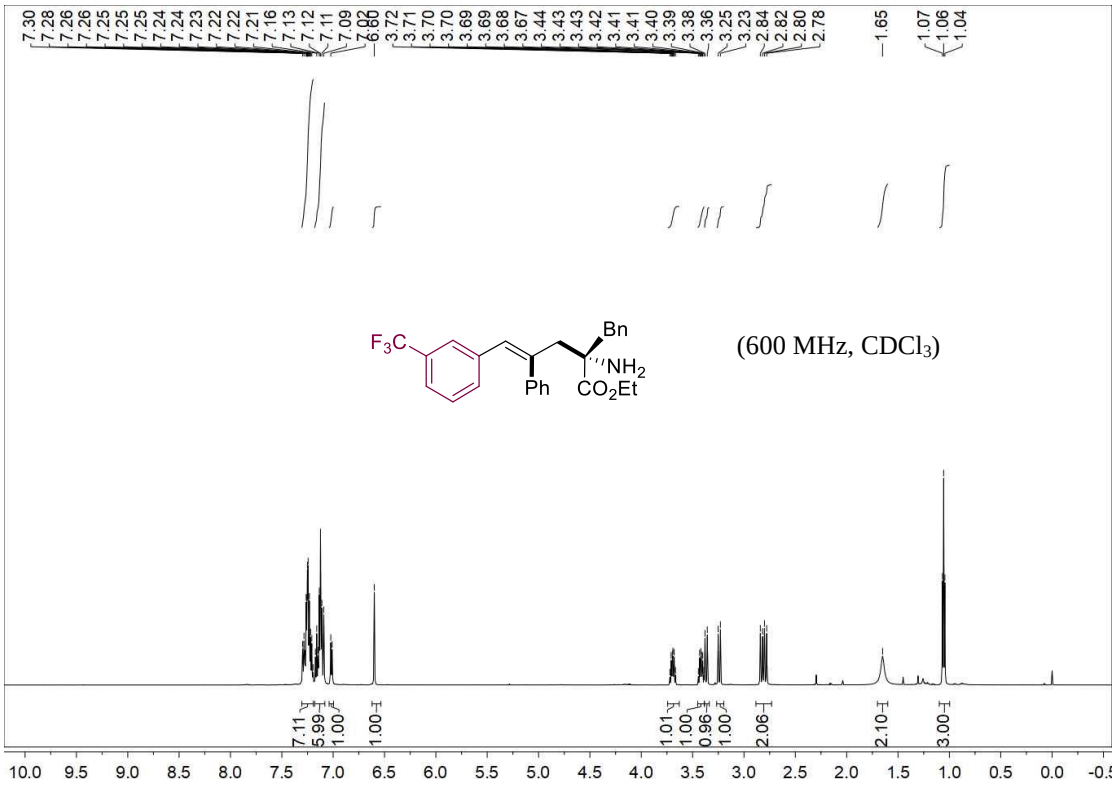


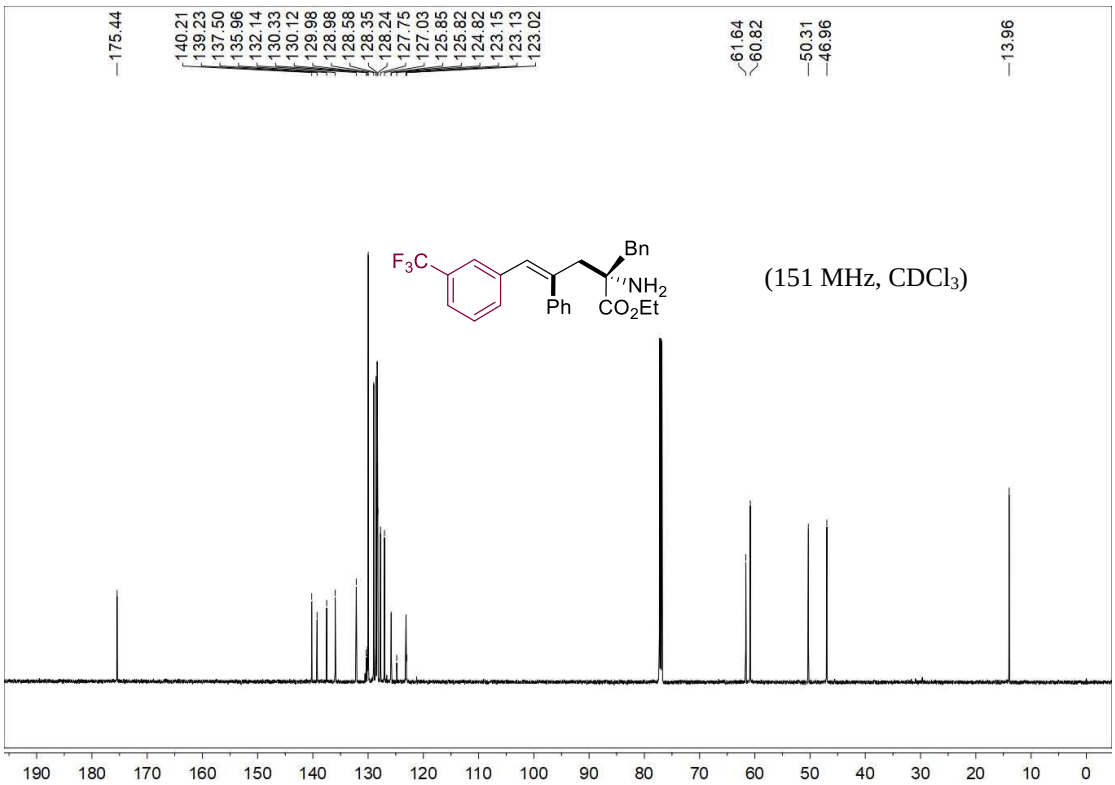
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3-chlorophenyl)-4-phenylpent-4-enoate (6d):



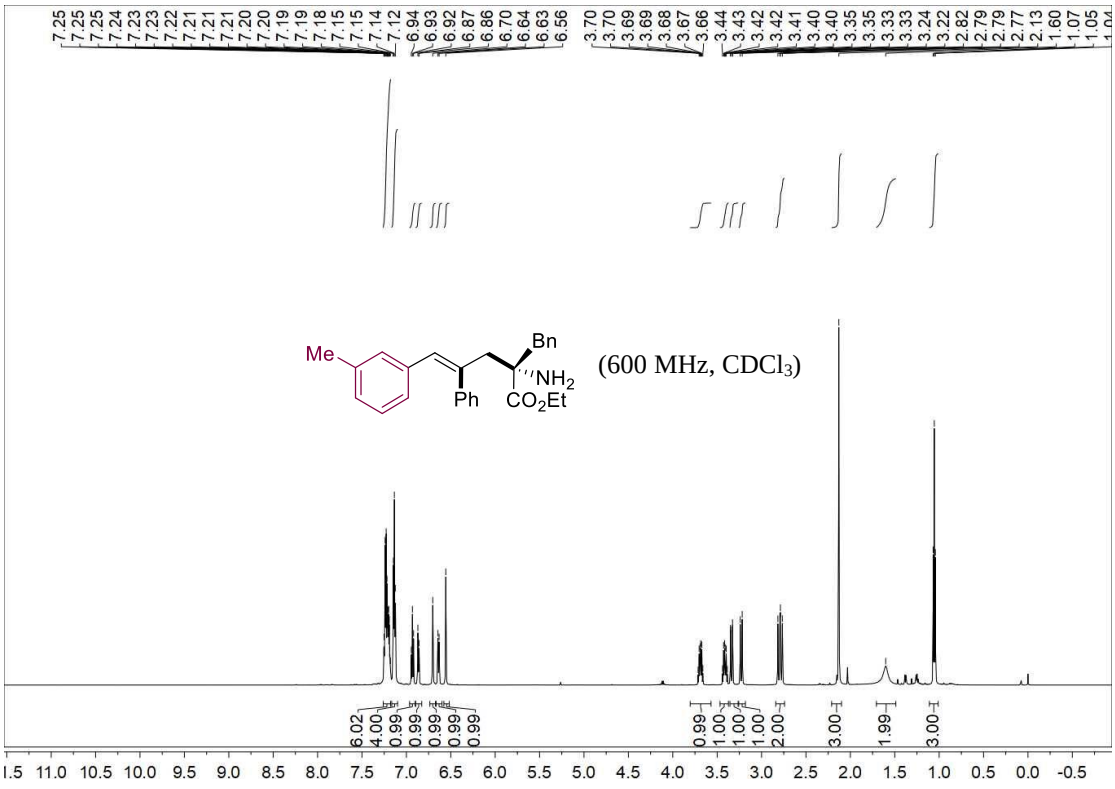


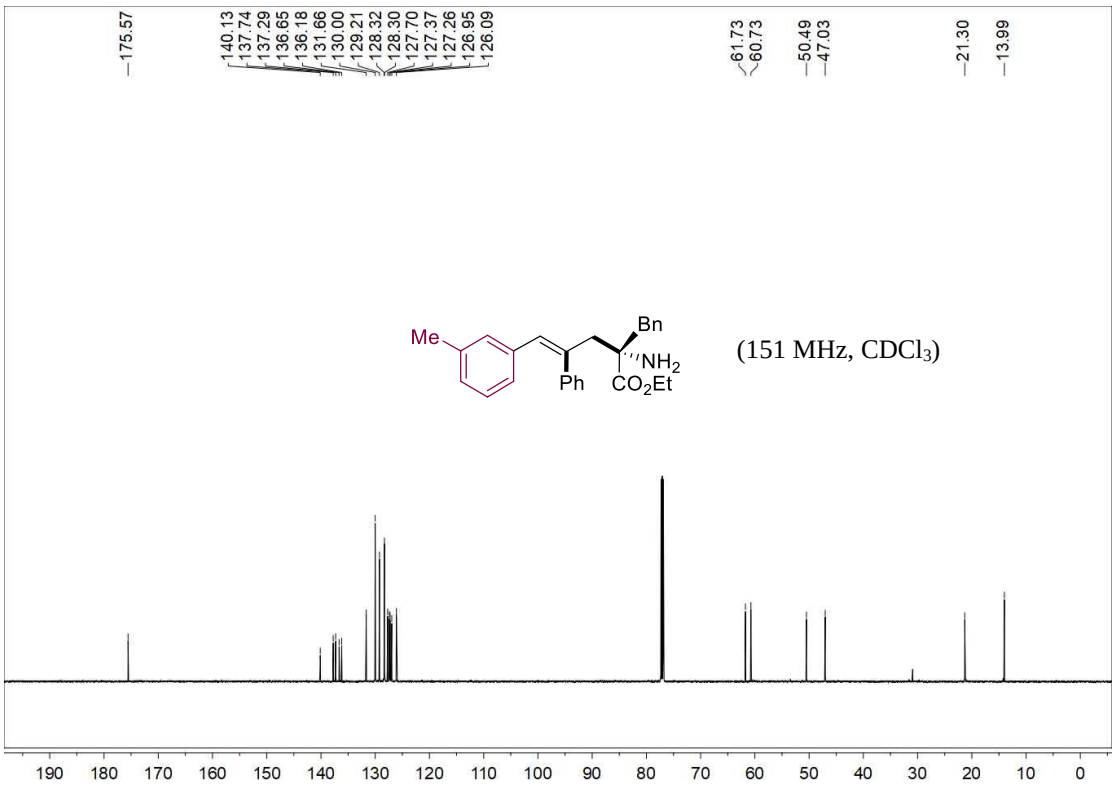
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(3-(trifluoromethyl)phenyl)pent-4-enoate (6e):



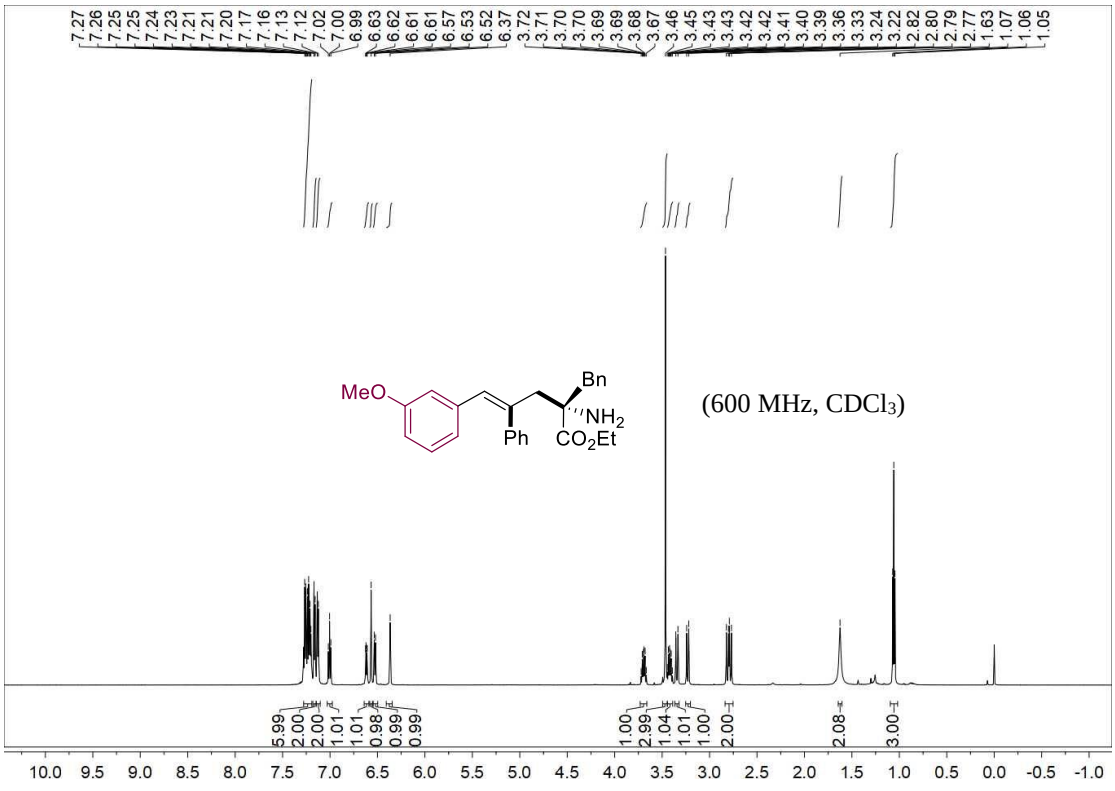


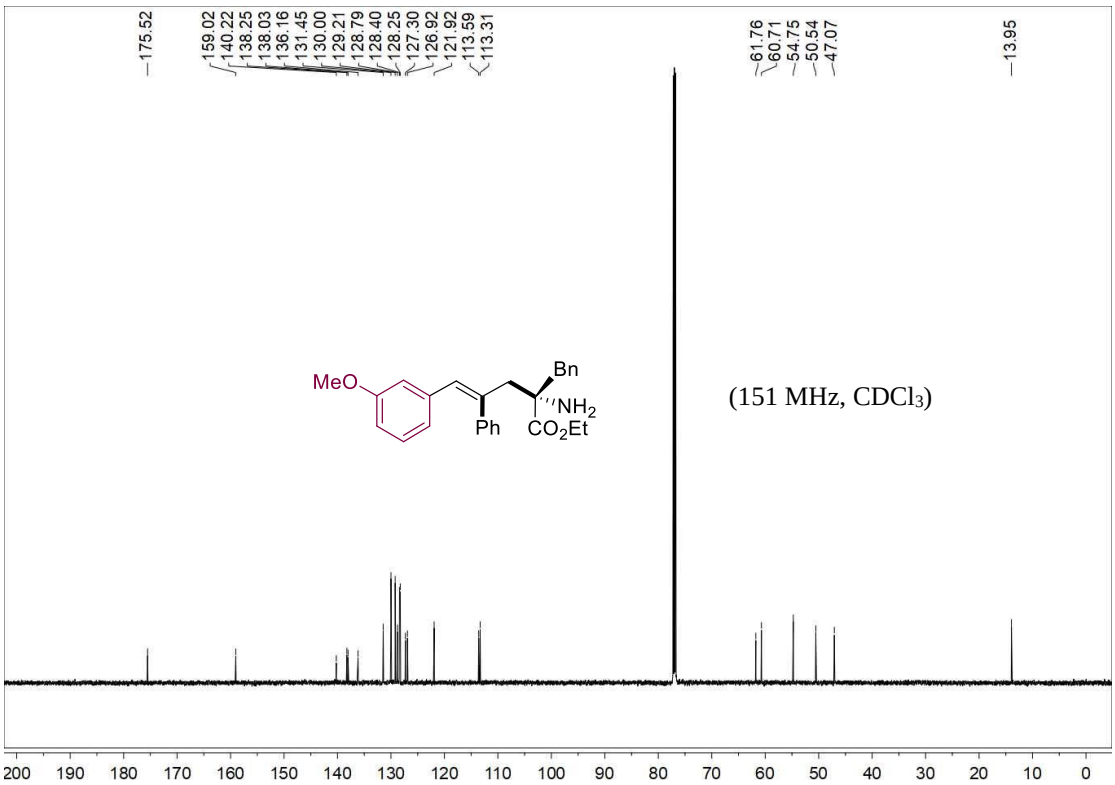
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(m-tolyl)pent-4-enoate (6f):



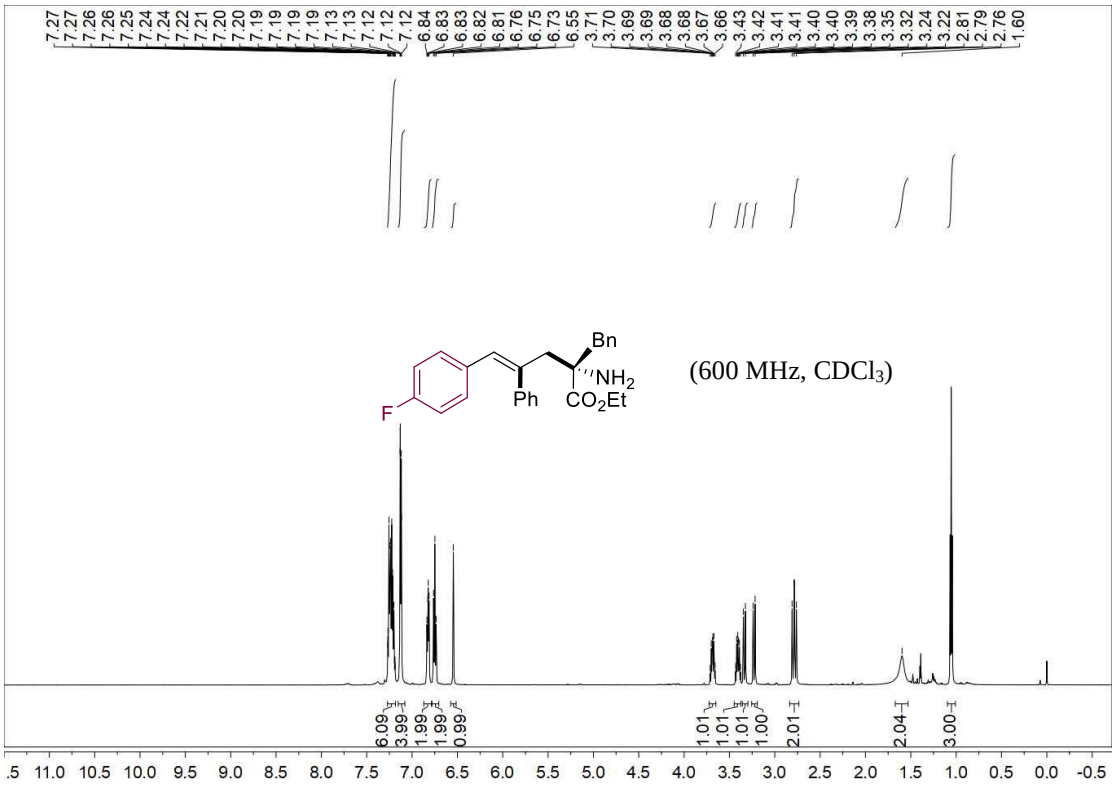


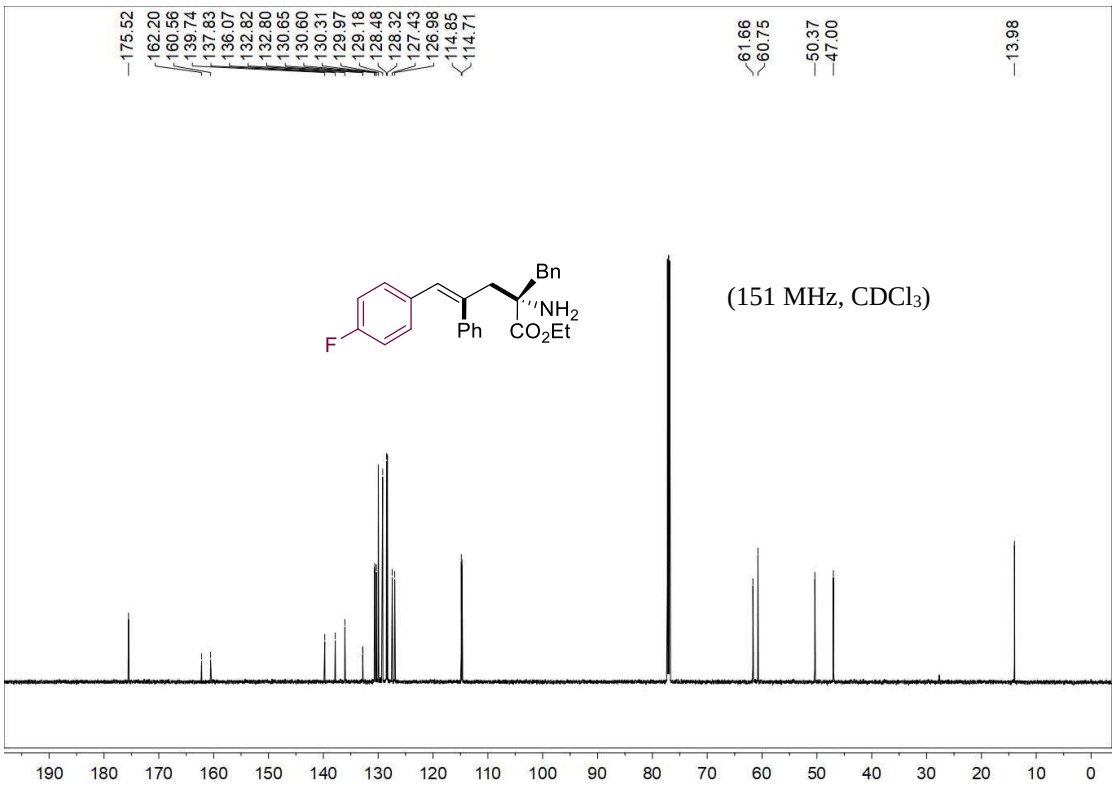
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3-methoxyphenyl)-4-phenylpent-4-enoate (6g):



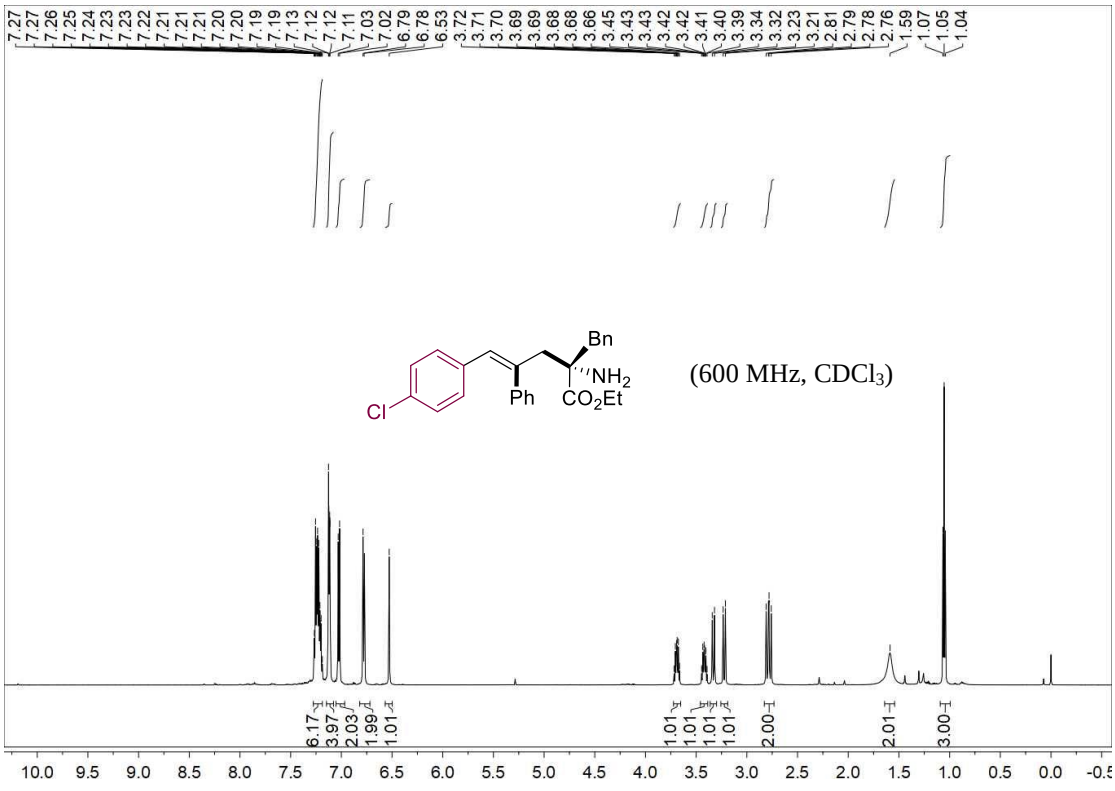


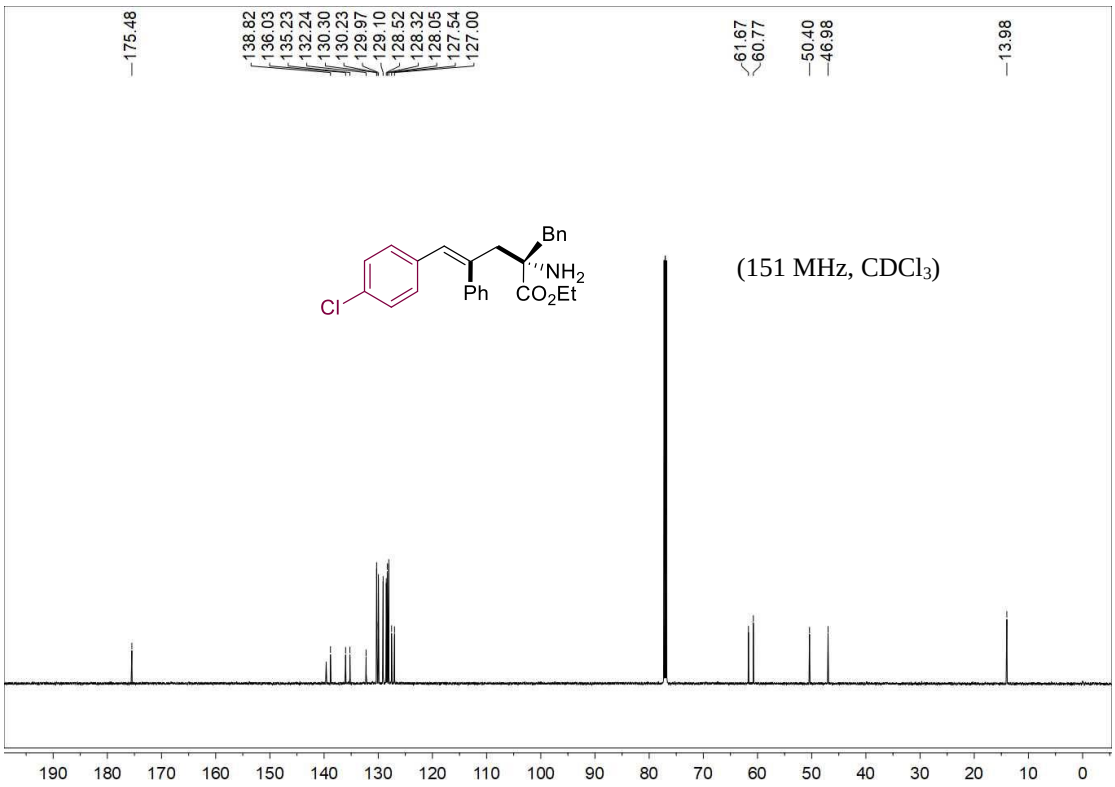
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-fluorophenyl)-4-phenylpent-4-enoate (6h):



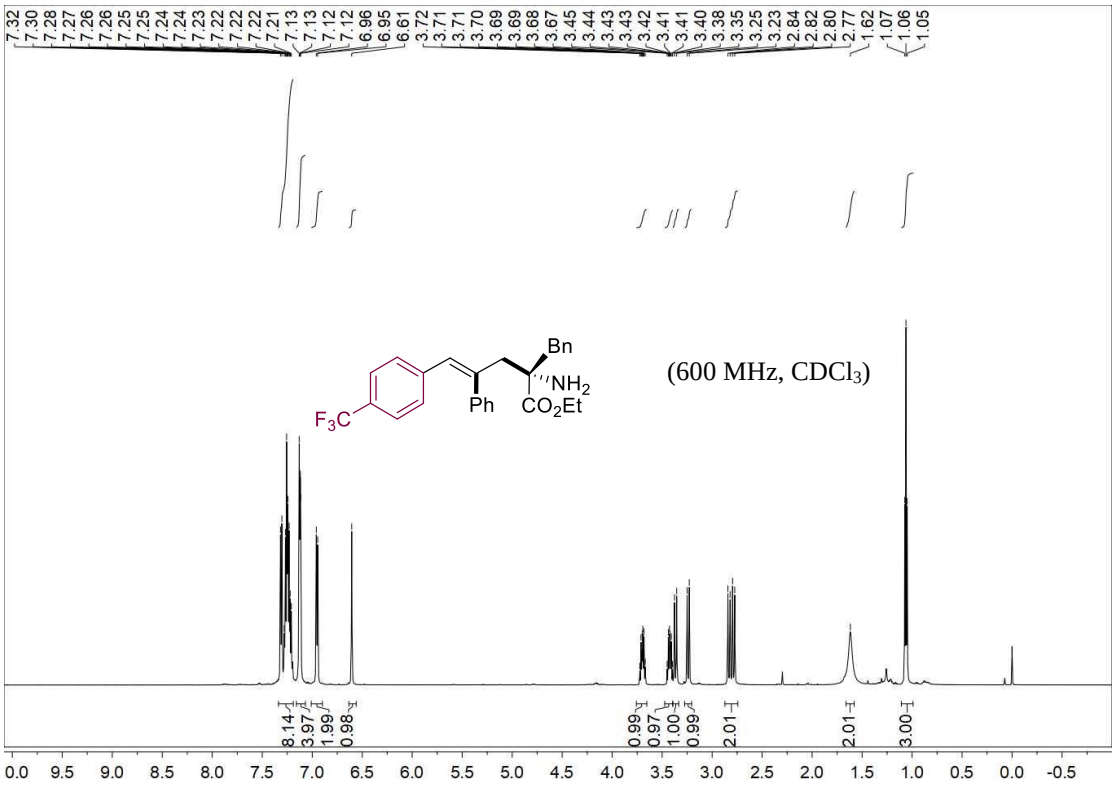


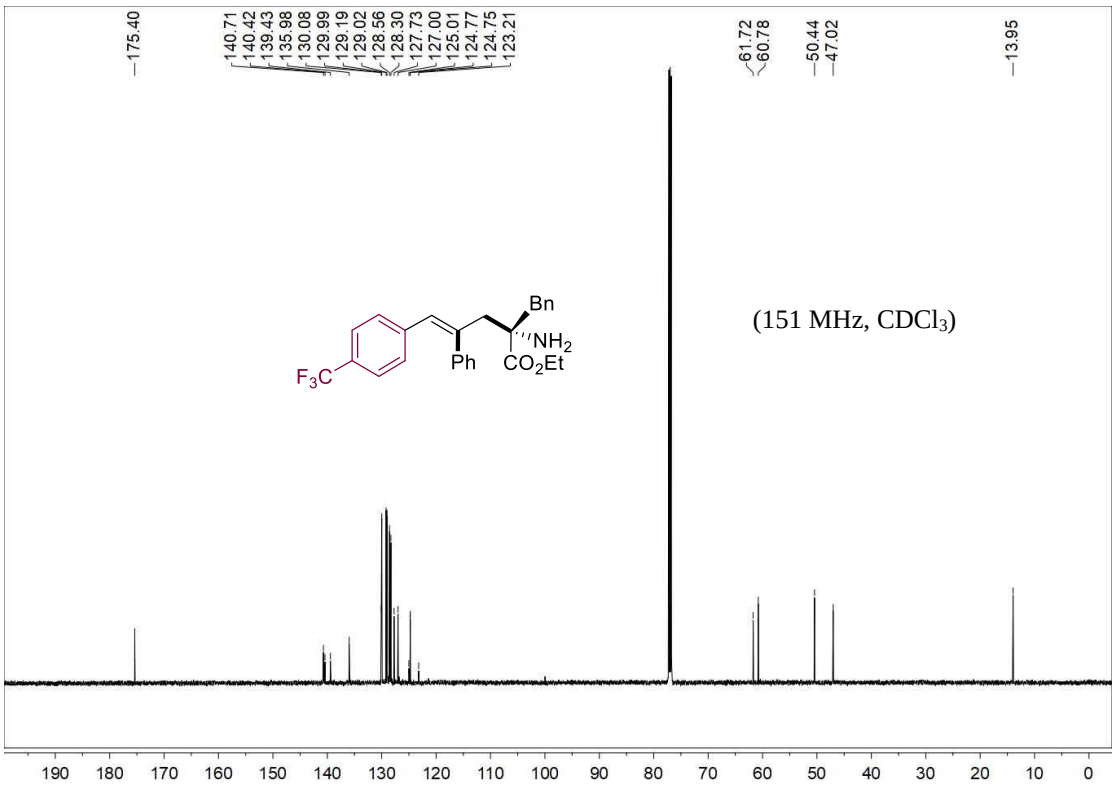
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-chlorophenyl)-4-phenylpent-4-enoate (6i):



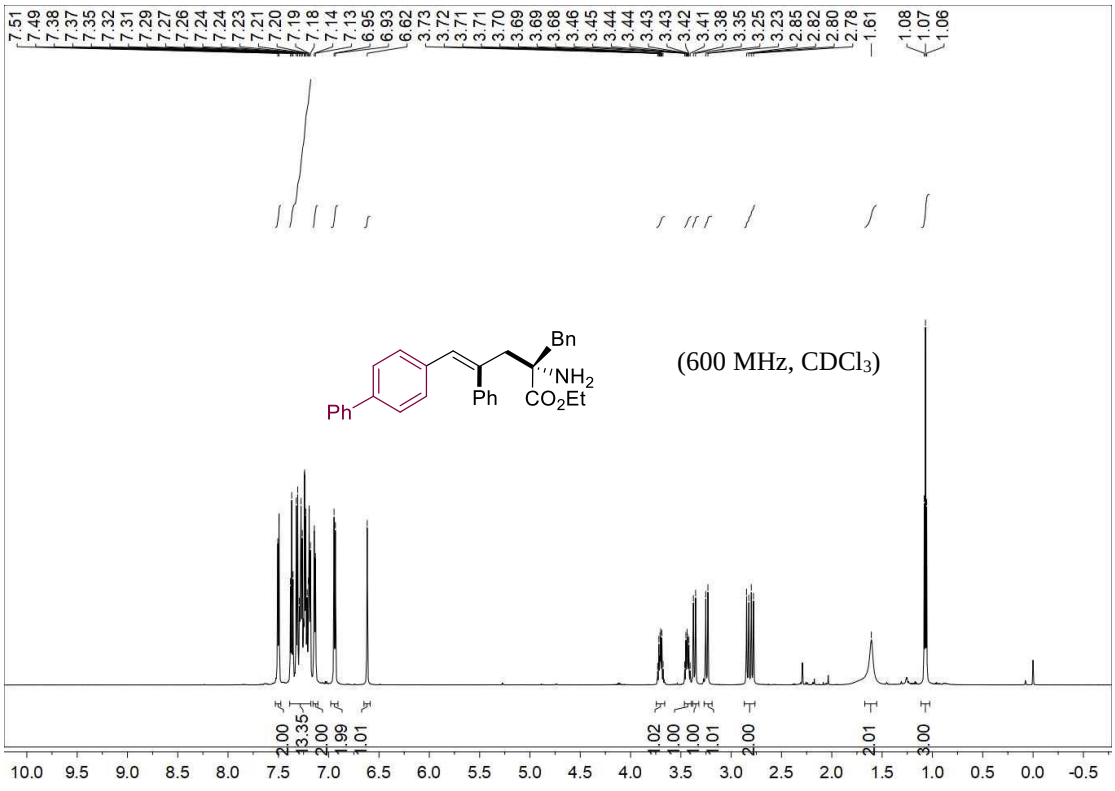


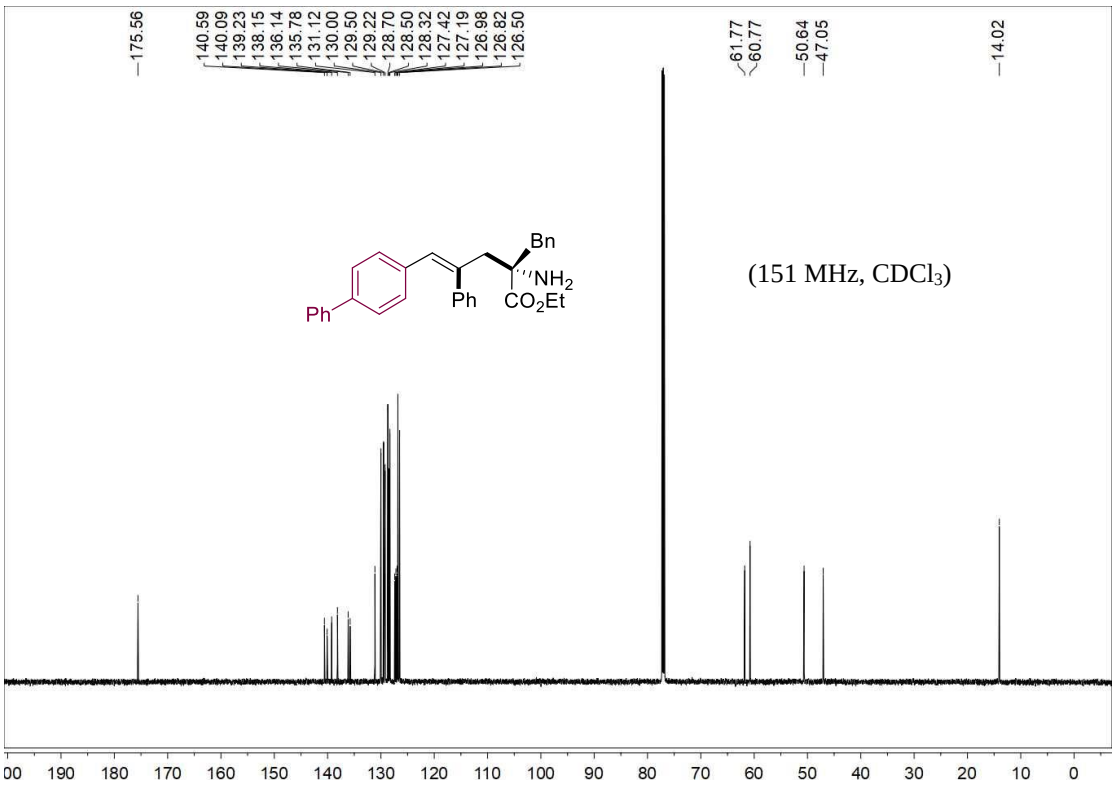
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(4-(trifluoromethyl)phenyl)pent-4-enoate (6j):



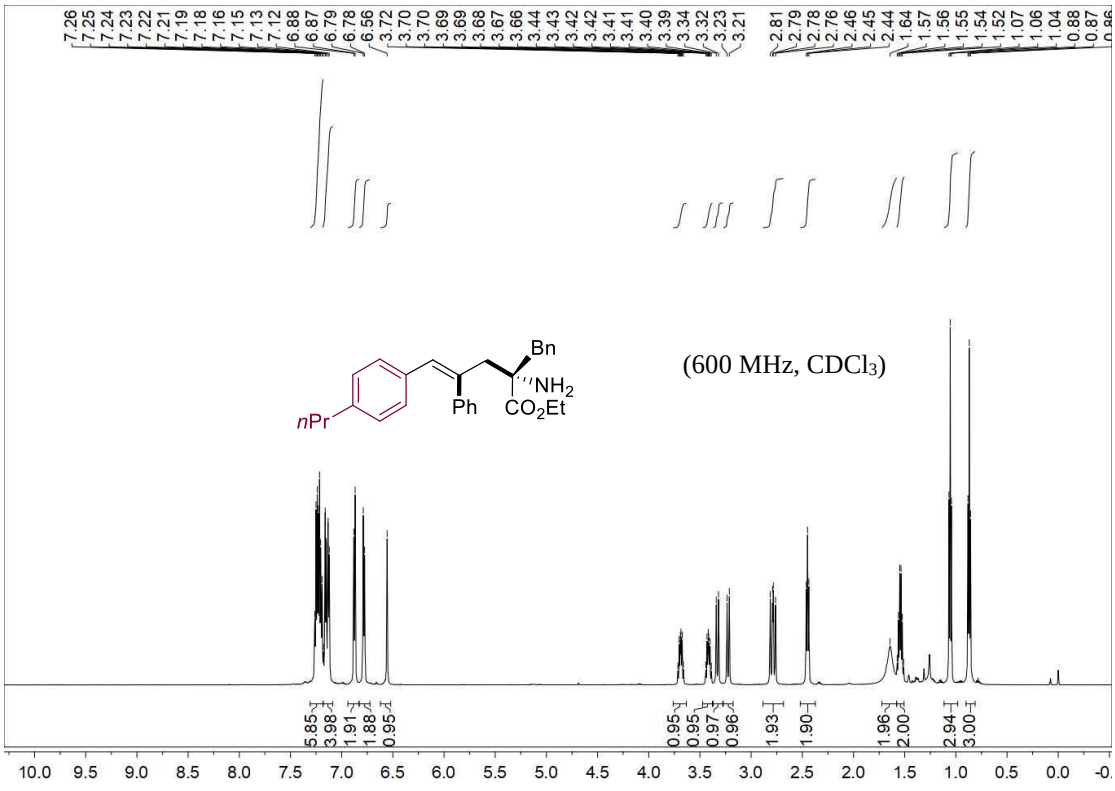


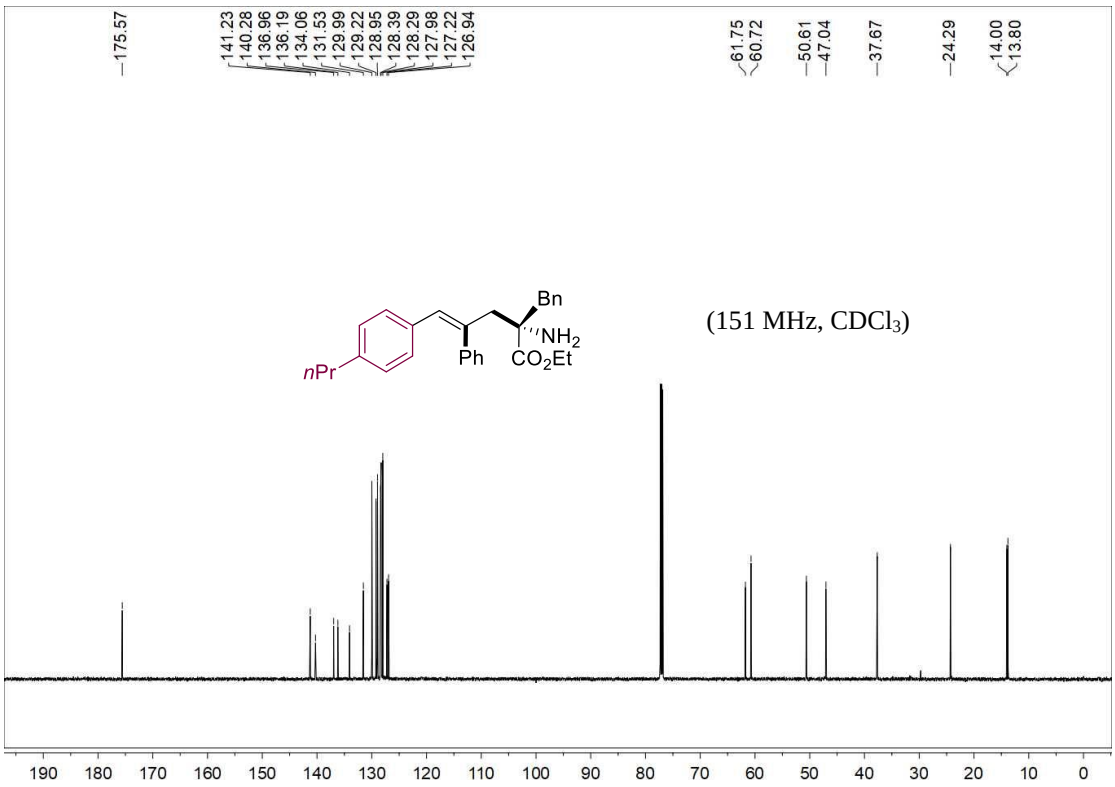
Ethyl (*S*, *Z*)-5-([1,1'-biphenyl]-4-yl)-2-amino-2-benzyl-4-phenylpent-4-enoate (6k):



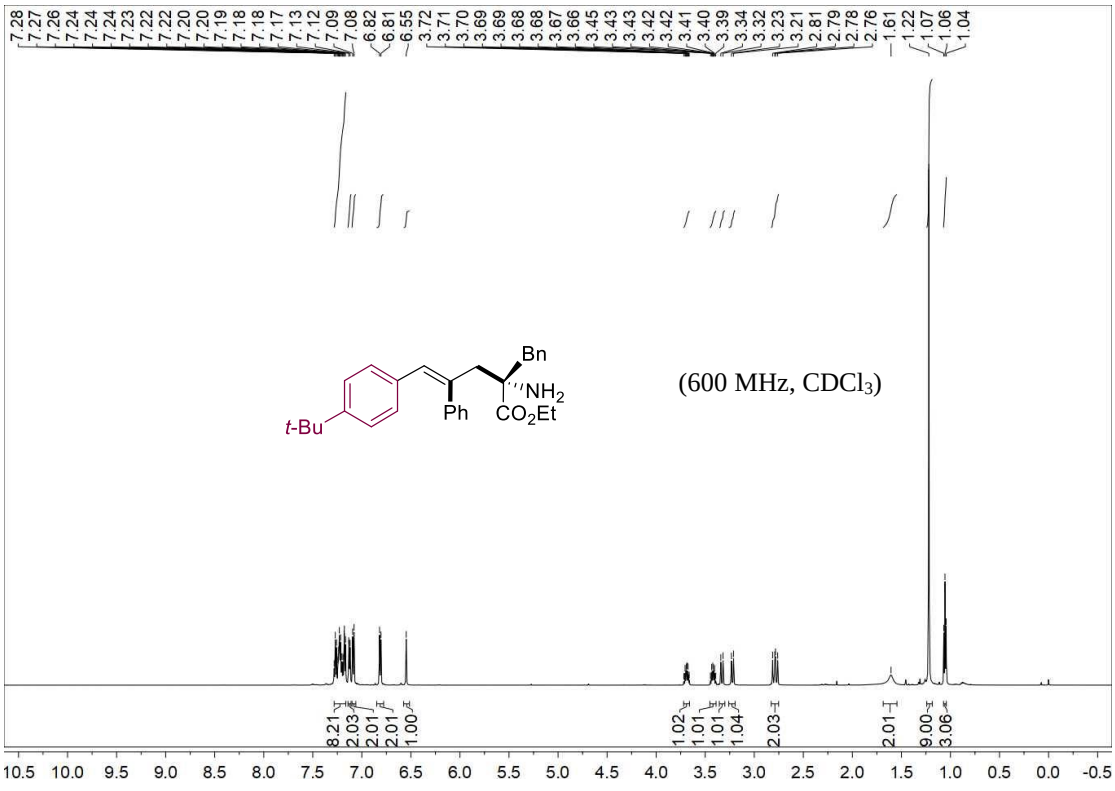


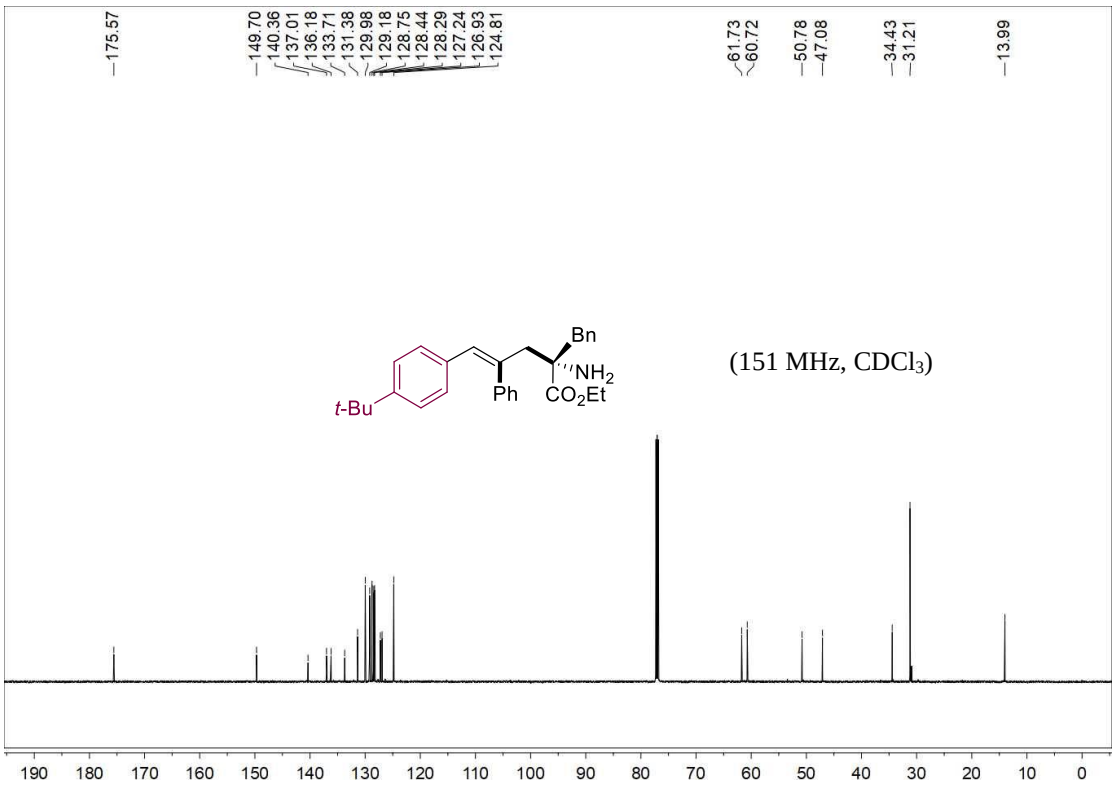
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(4-propylphenyl)pent-4-enoate (6l):



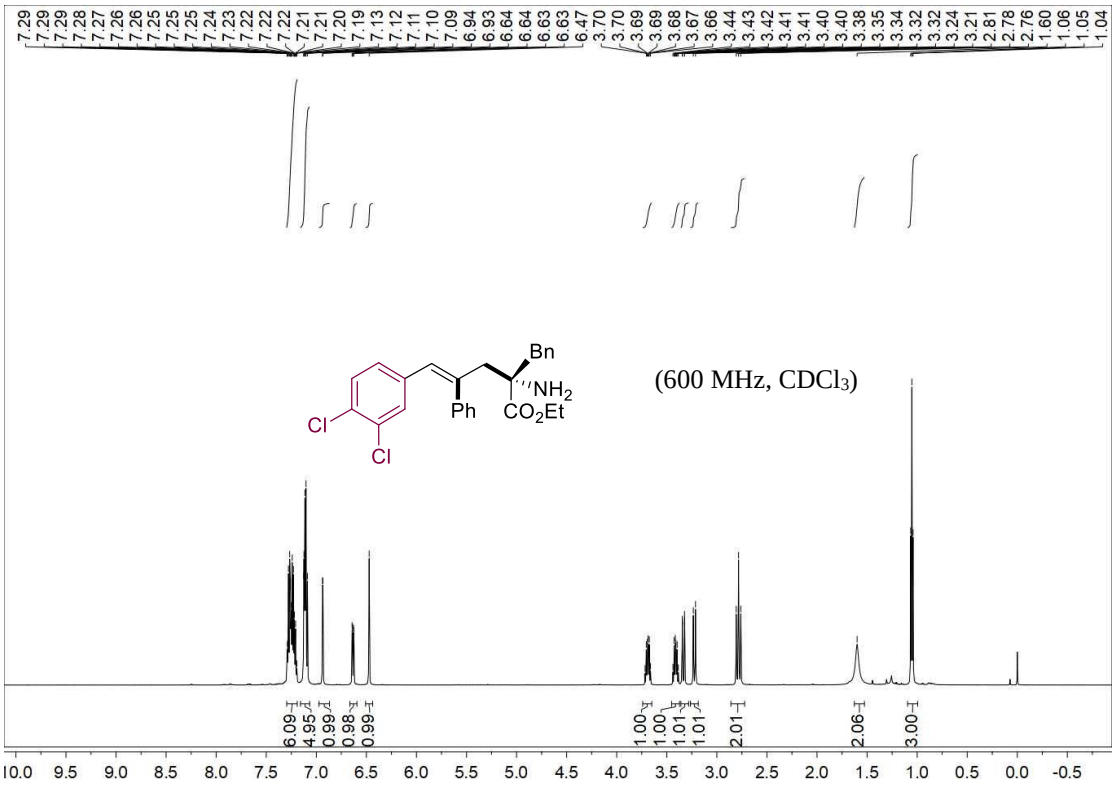


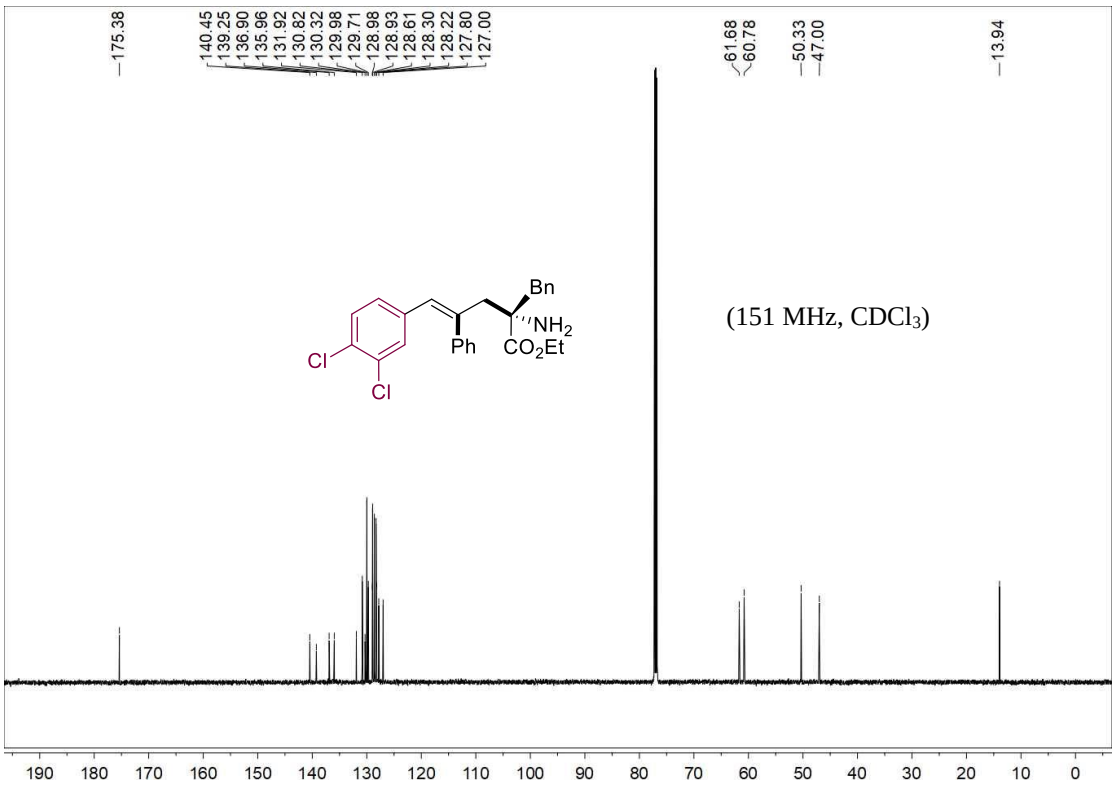
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-(tert-butyl)phenyl)-4-phenylpent-4-enoate (6m):



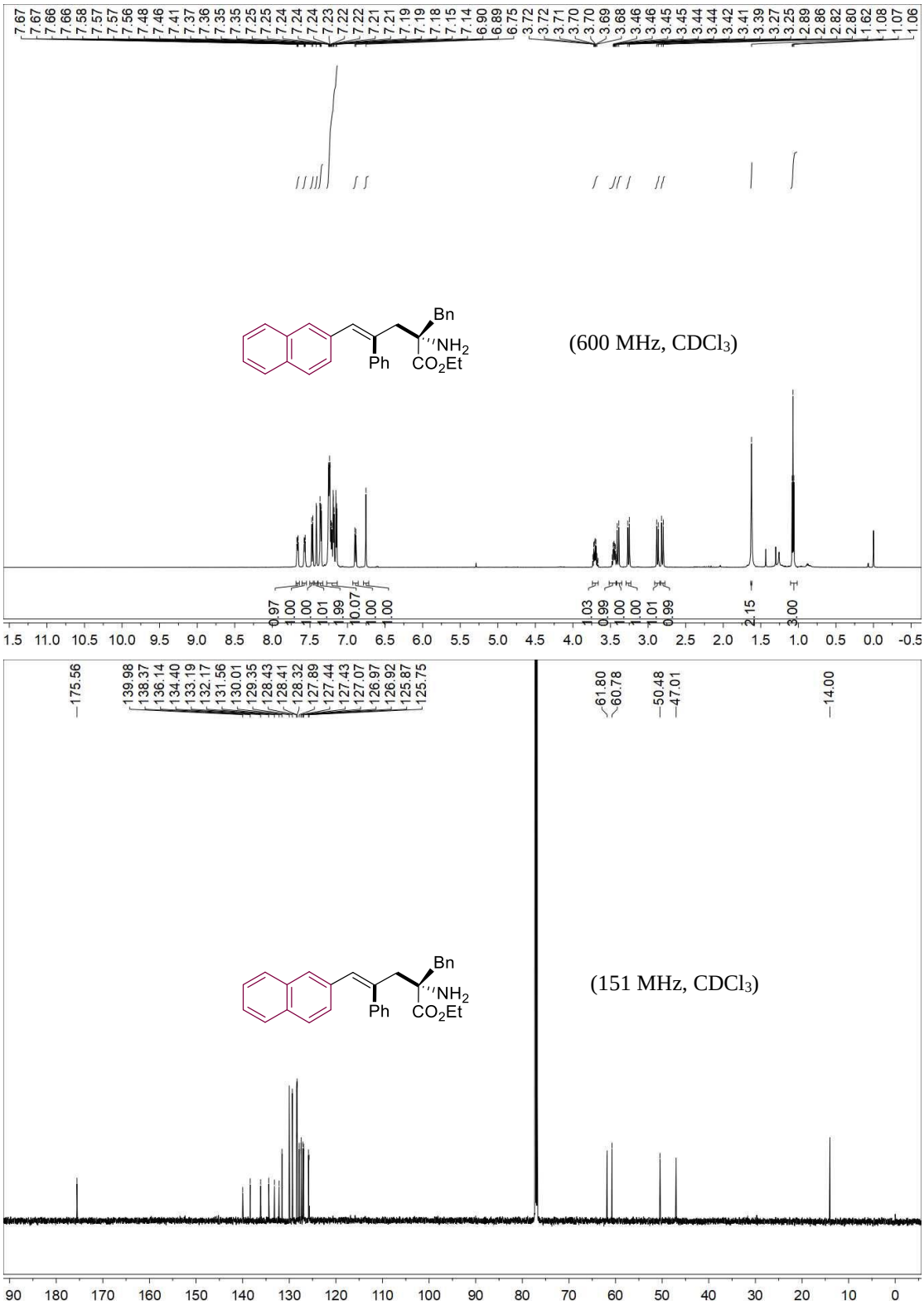


Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(3, 4-dichlorophenyl)-4-phenylpent-4-enoate (6n):

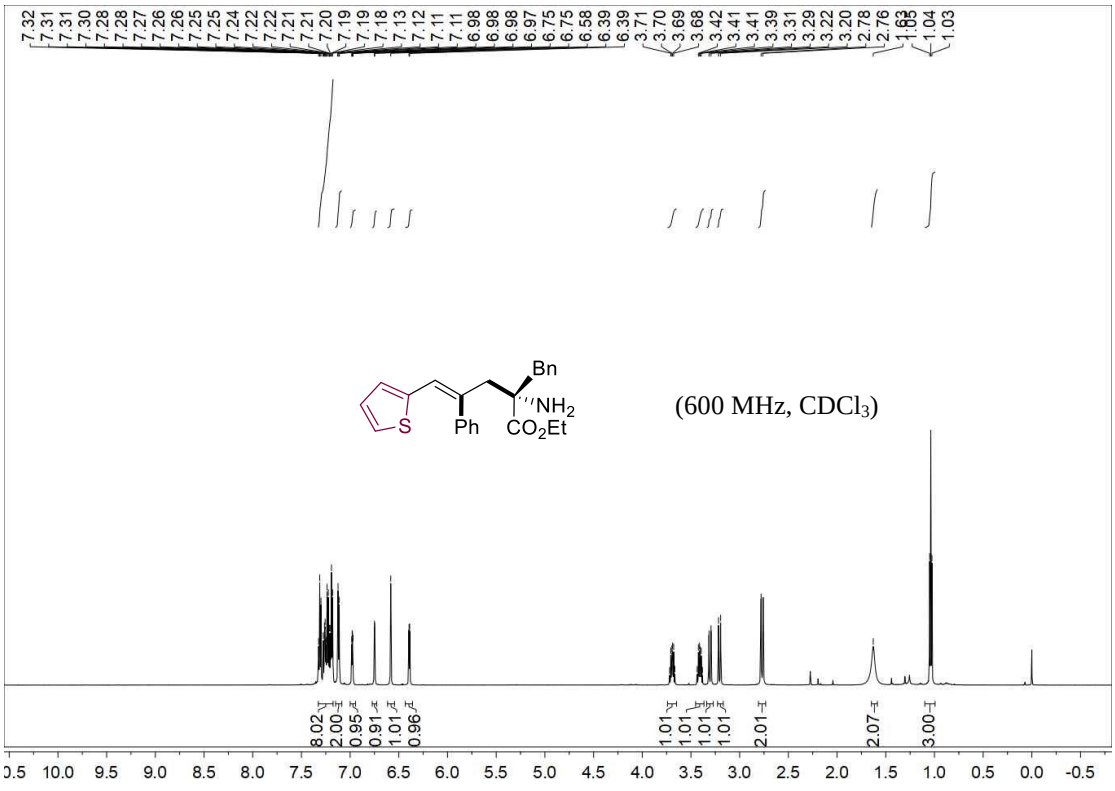


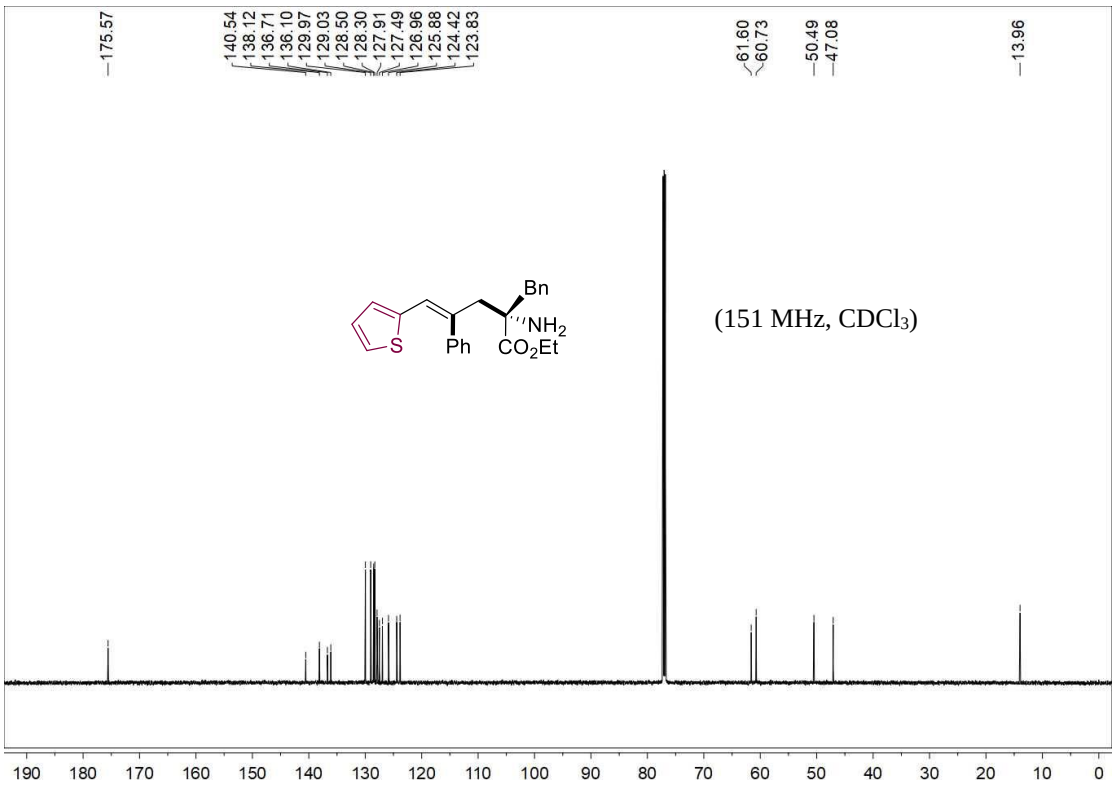


Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(naphthalen-2-yl)-4-phenylpent-4-enoate (6o):

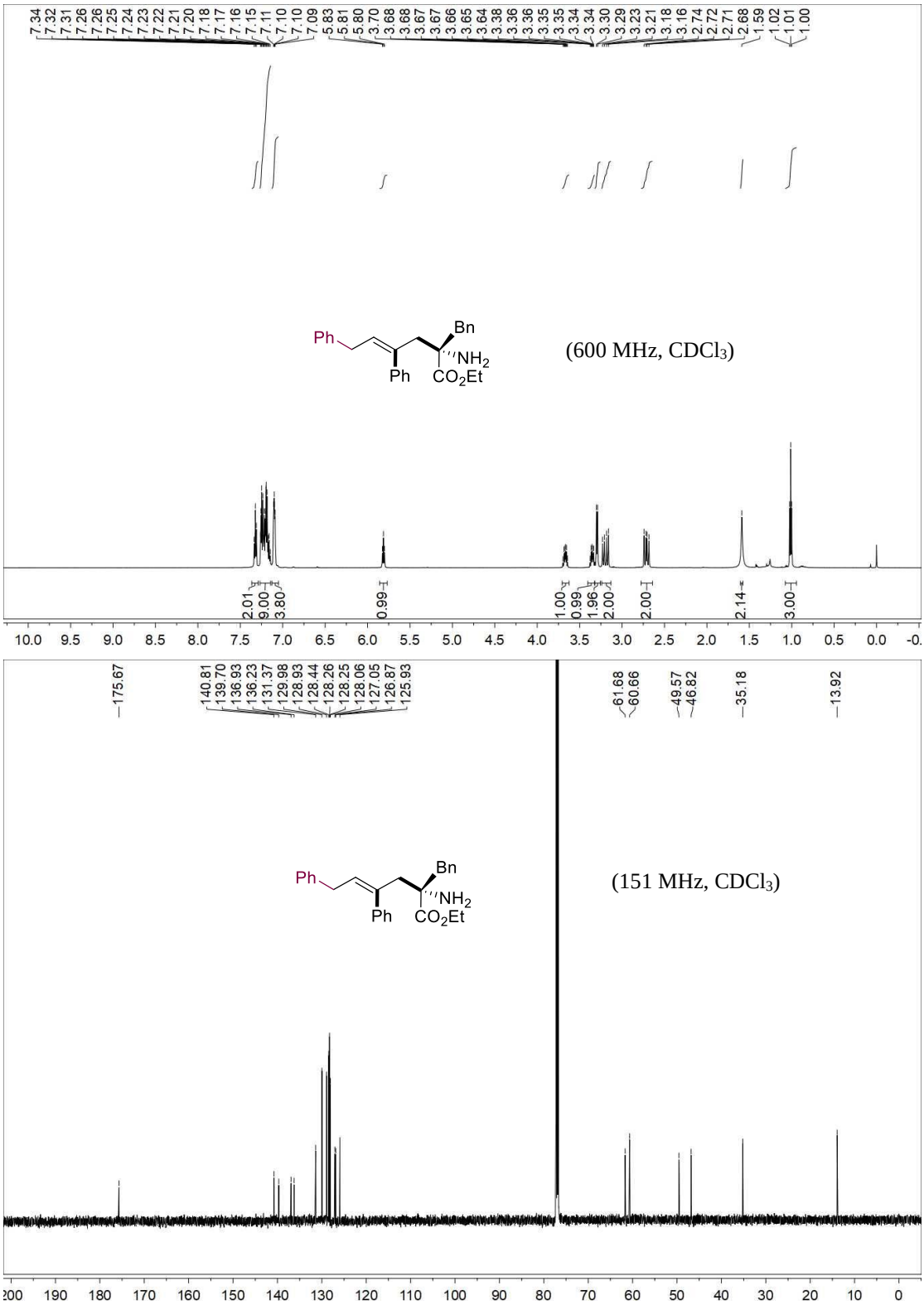


Ethyl (*S*, *Z*)-2-amino-2-benzyl-4-phenyl-5-(thiophen-2-yl)pent-4-enoate (6p):

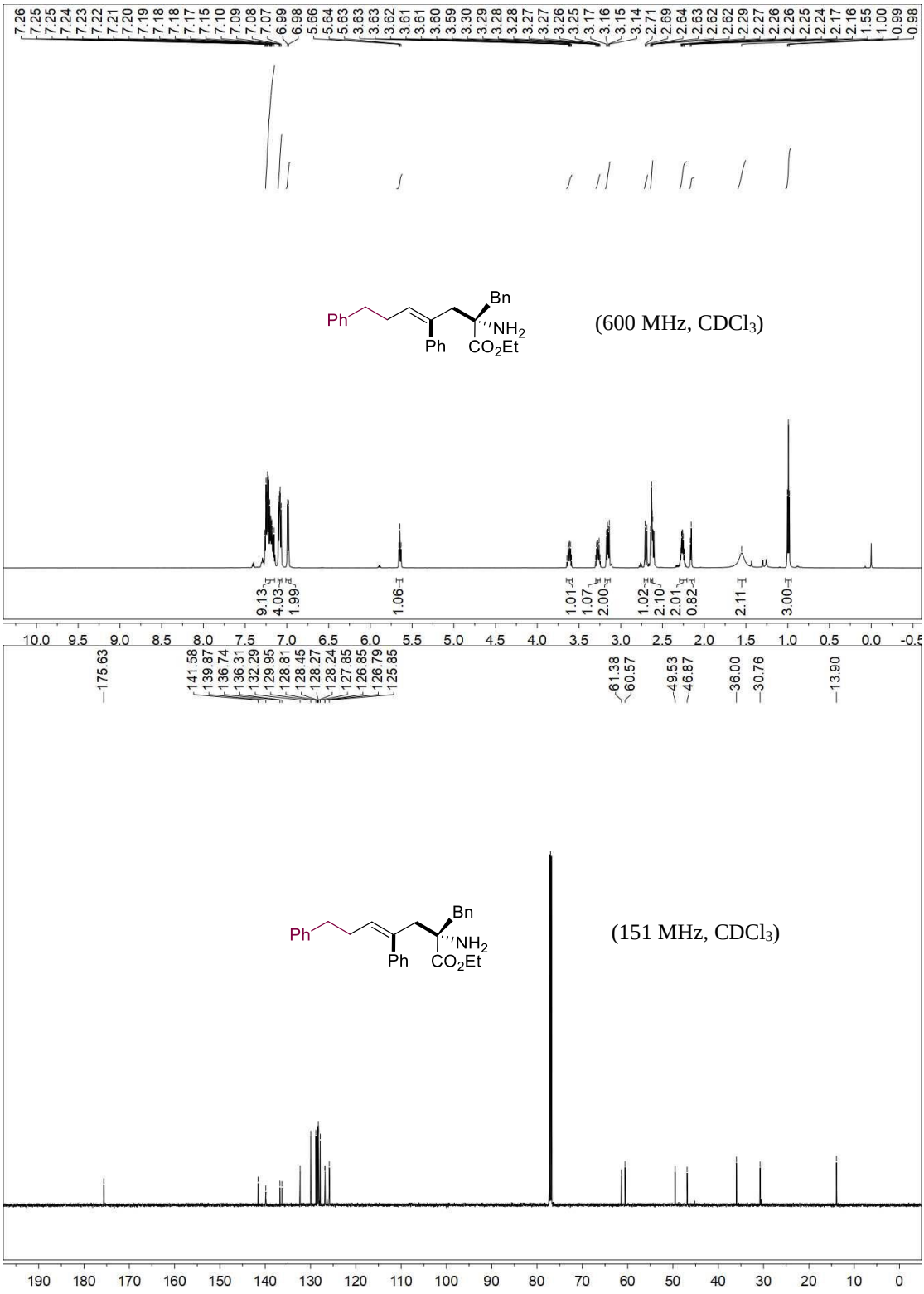




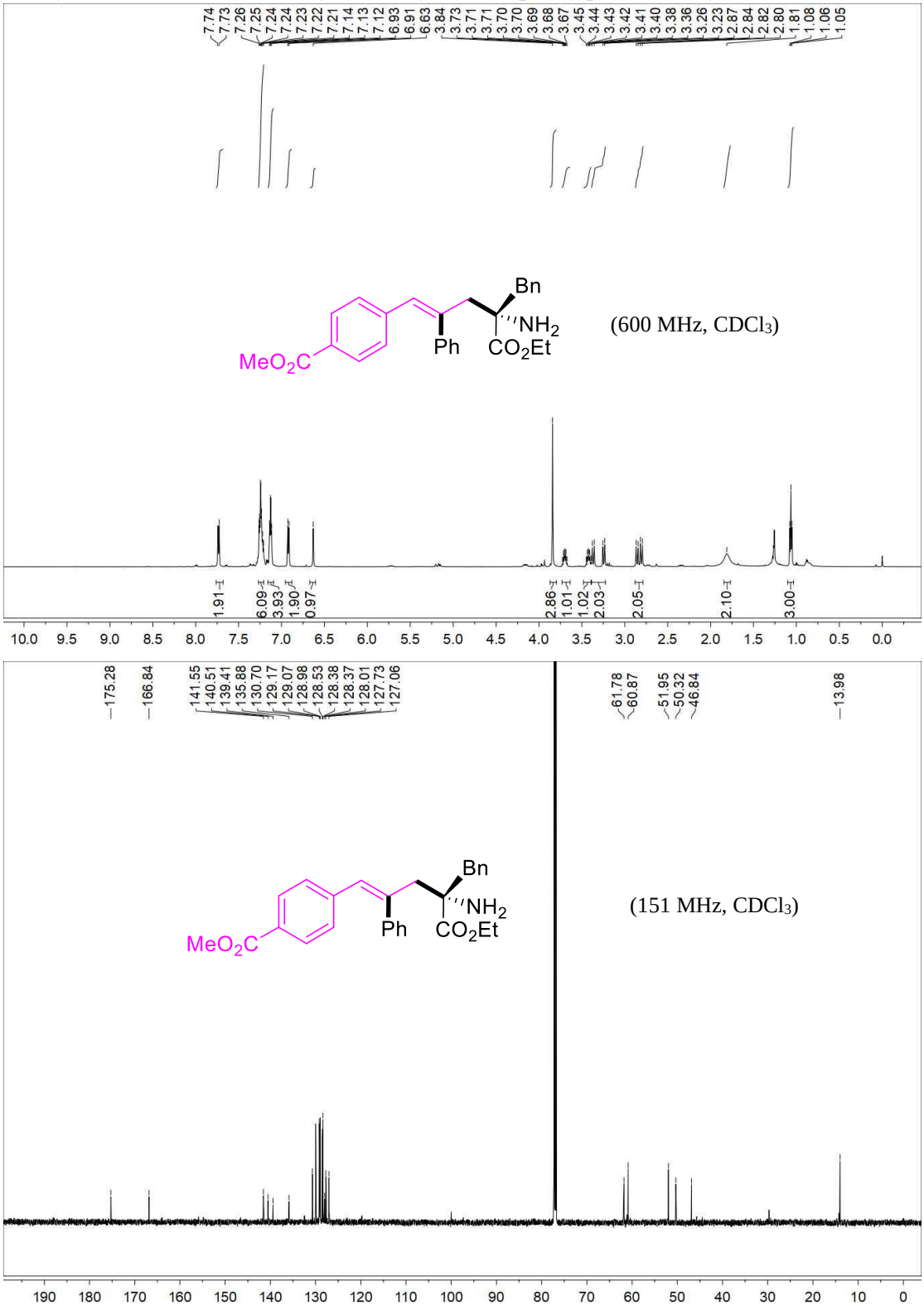
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4,6-diphenylhex-4-enoate (6q):



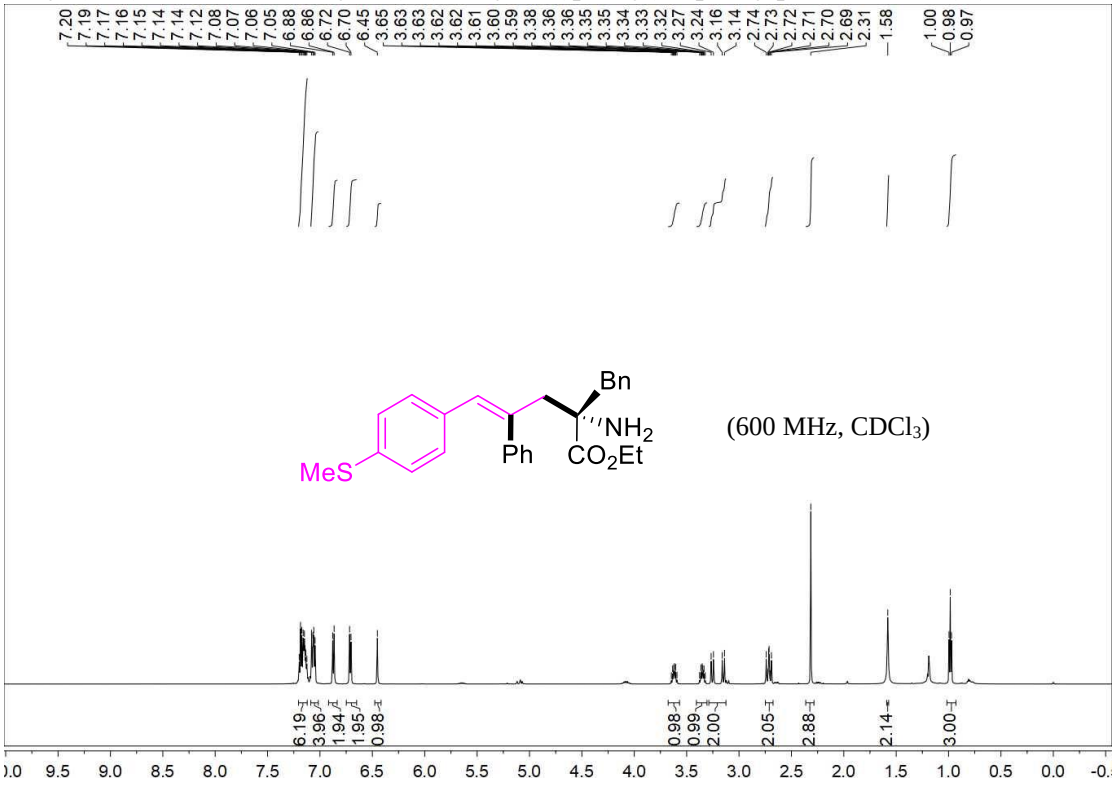
Ethyl (*S*, *Z*)-2-amino-2-benzyl-4, 7-diphenylhept-4-enoate (6r):

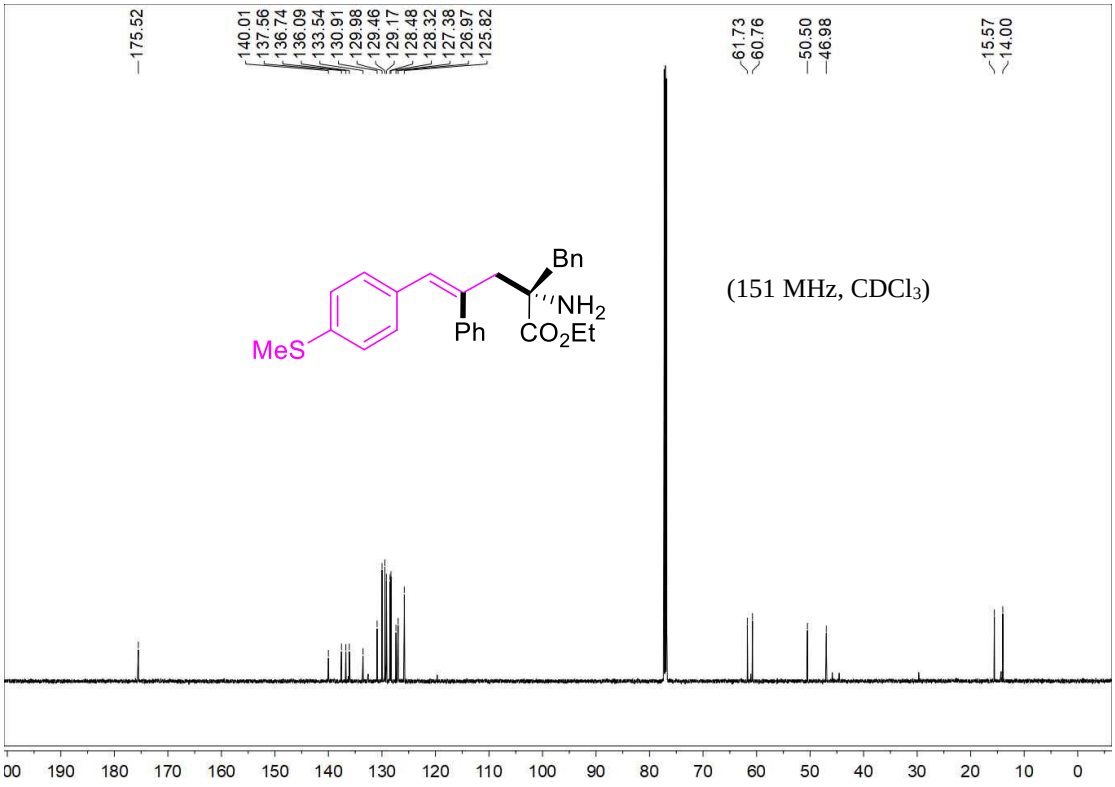


Methyl (S,Z)-4-(4-amino-4-benzyl-5-ethoxy-5-oxo-2-phenylpent-1-en-1-yl)benzoate (6s):

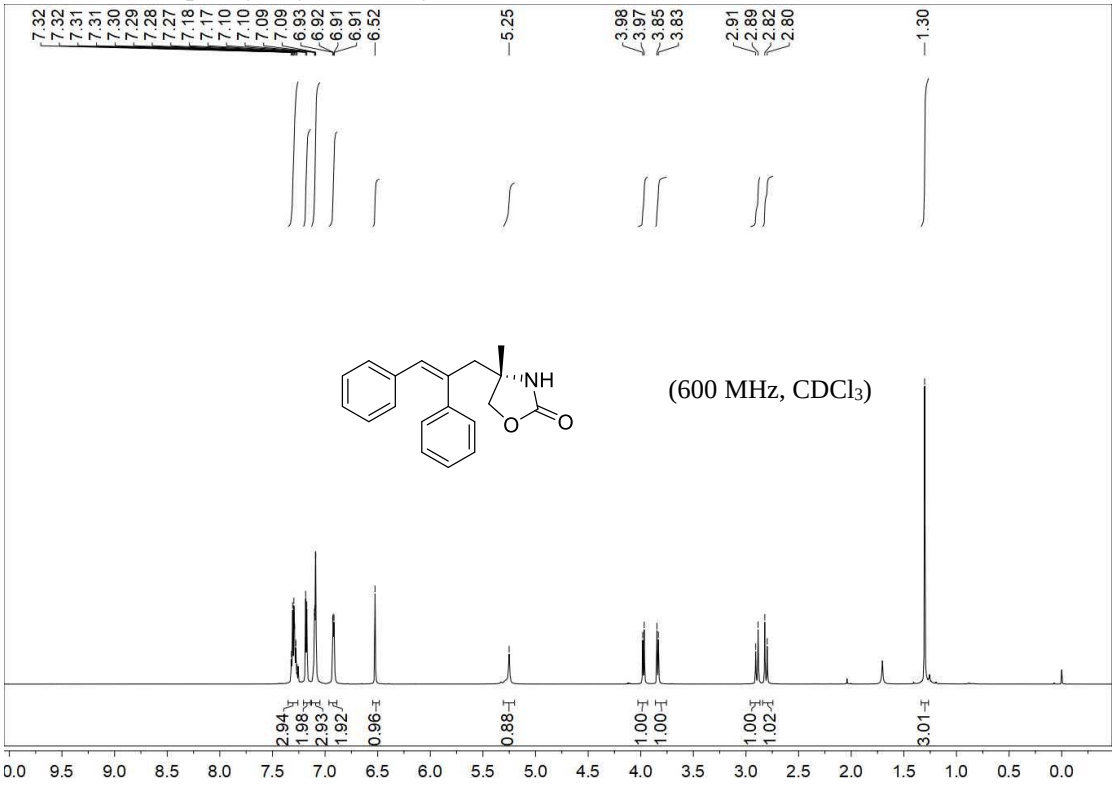


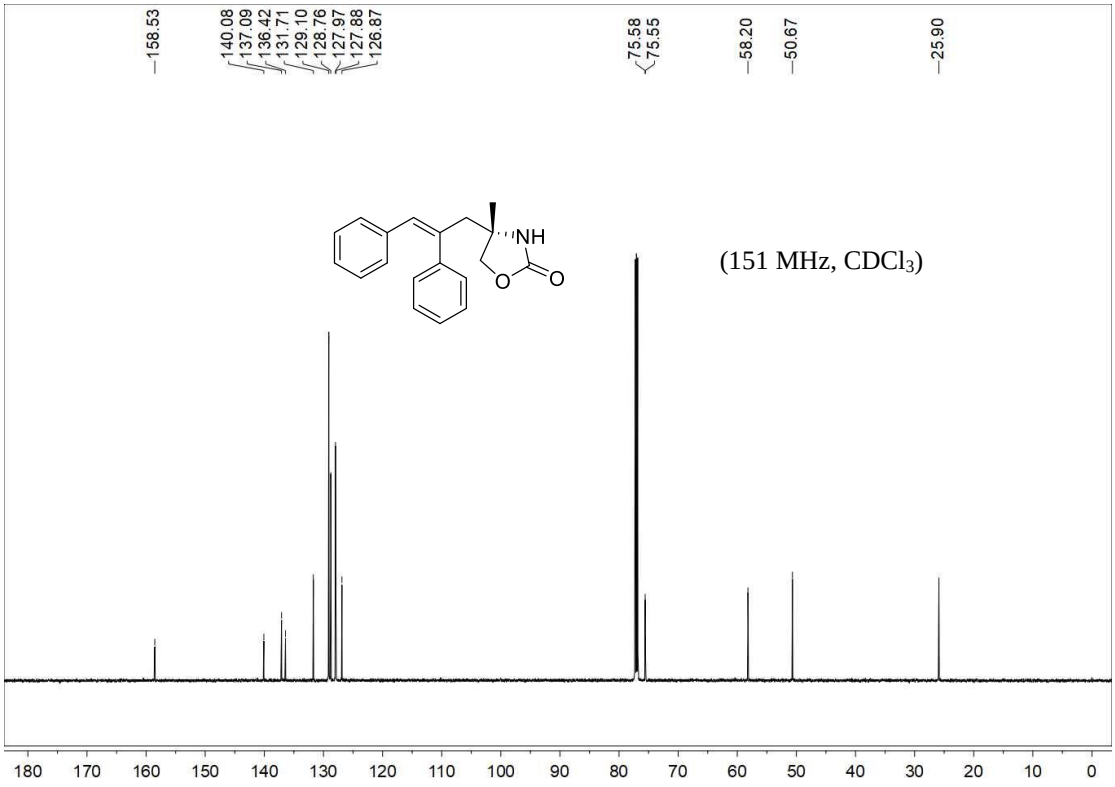
Ethyl (*S*, *Z*)-2-amino-2-benzyl-5-(4-(methylthio)phenyl)-4-phenylpent-4-enoate (6t):



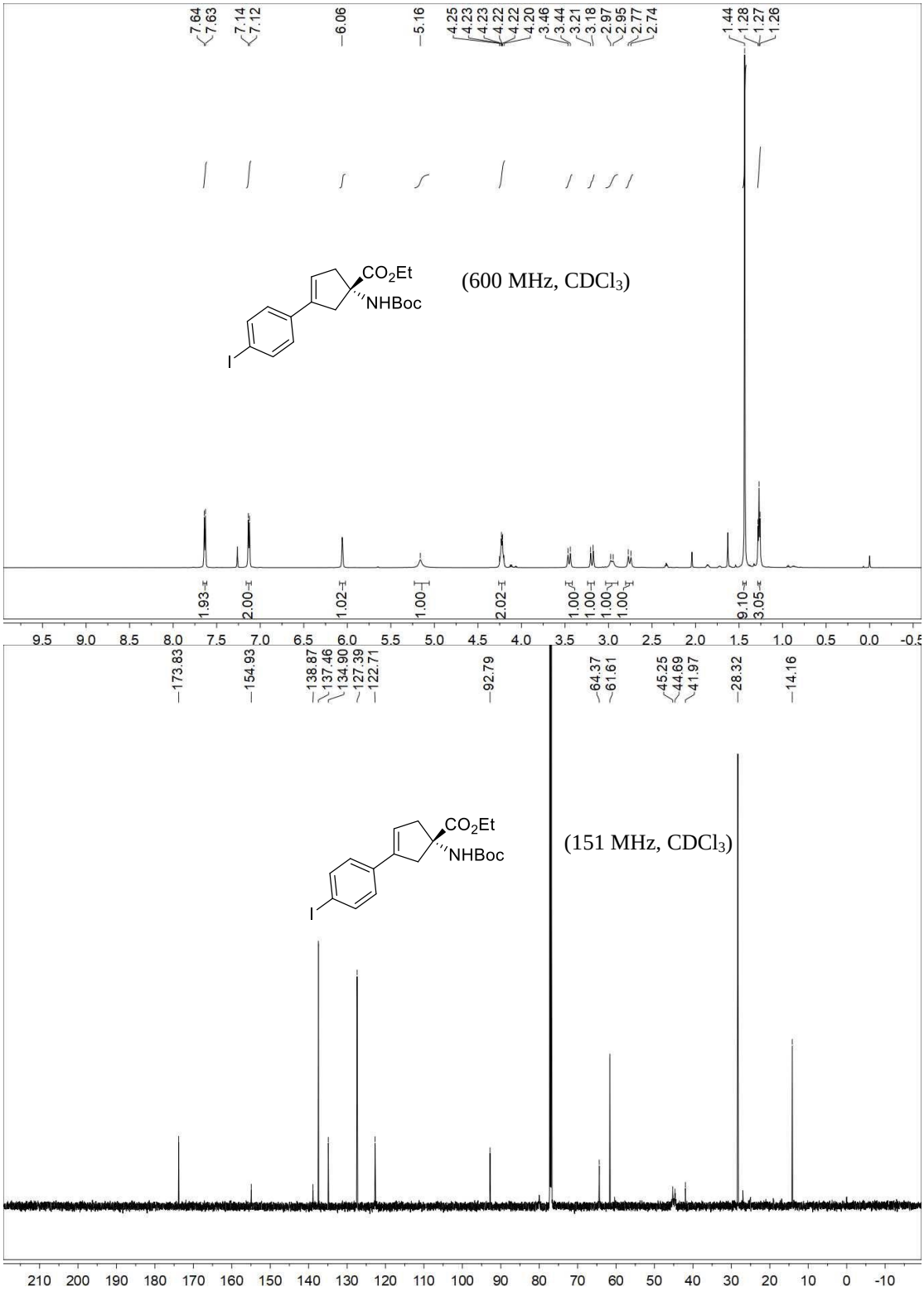


(*S*, *Z*)-4-(2, 3-diphenylallyl)-4-methyloxazolidin-2-one (8):

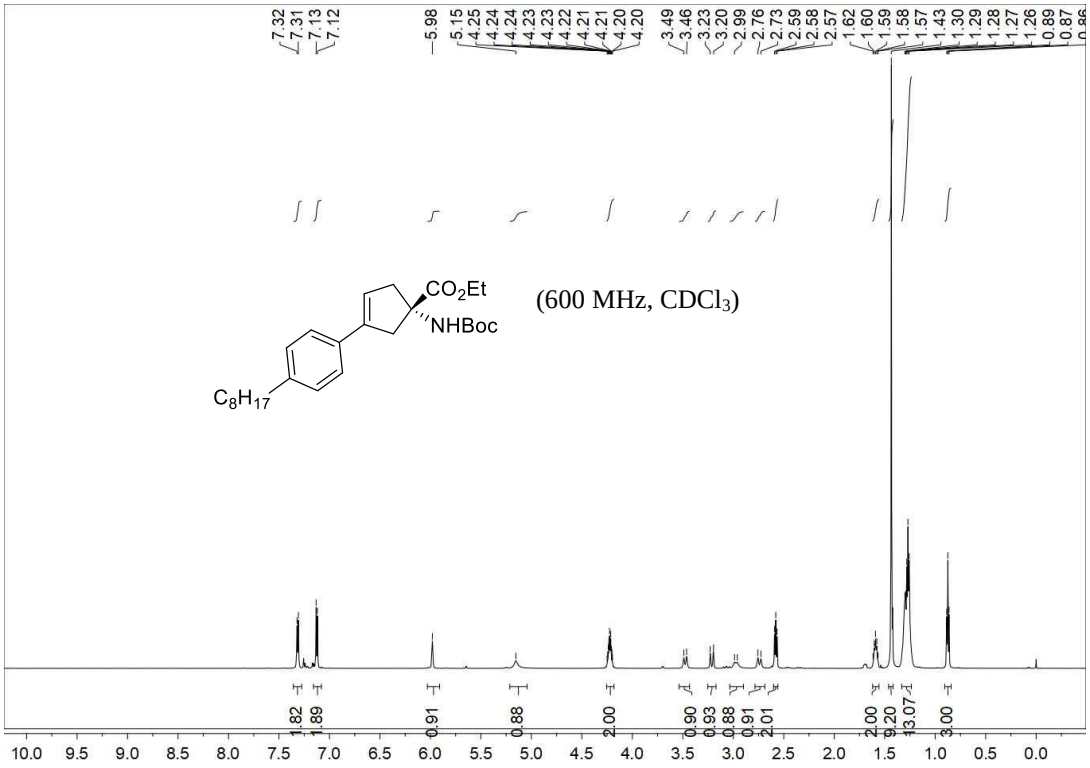


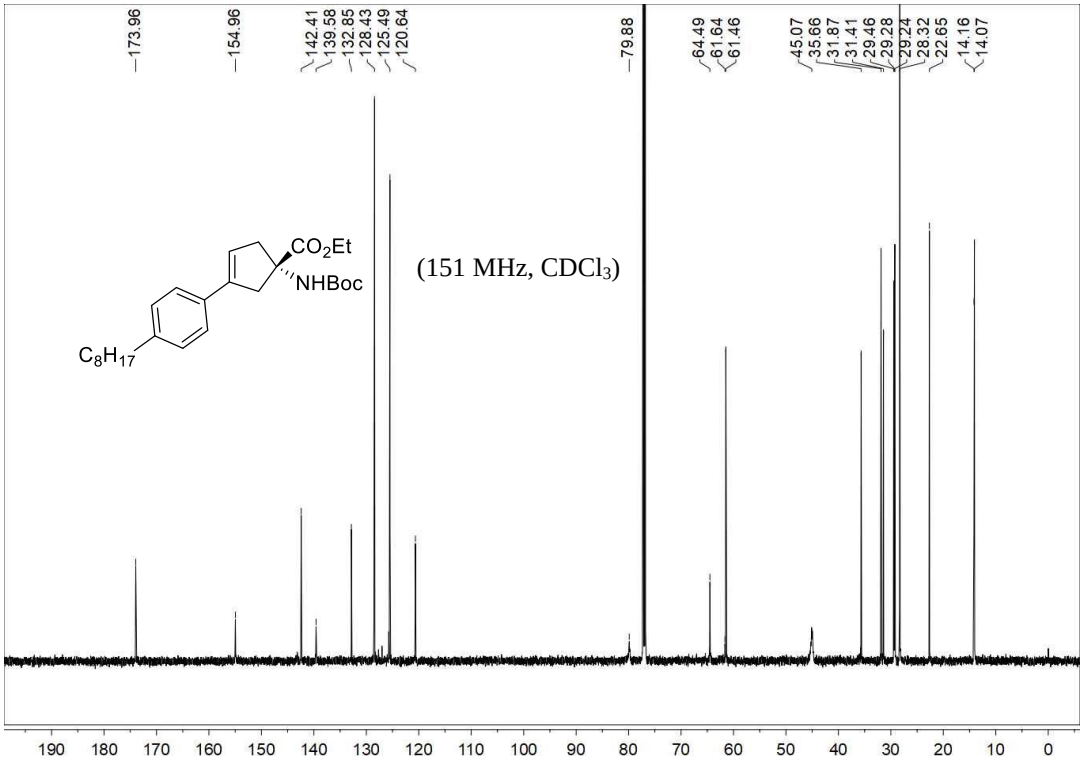


Ethyl (*S*)-1-((tert-butoxycarbonyl)amino)-3-(4-iodophenyl)cyclopent-3-ene-1-carboxylate (10):

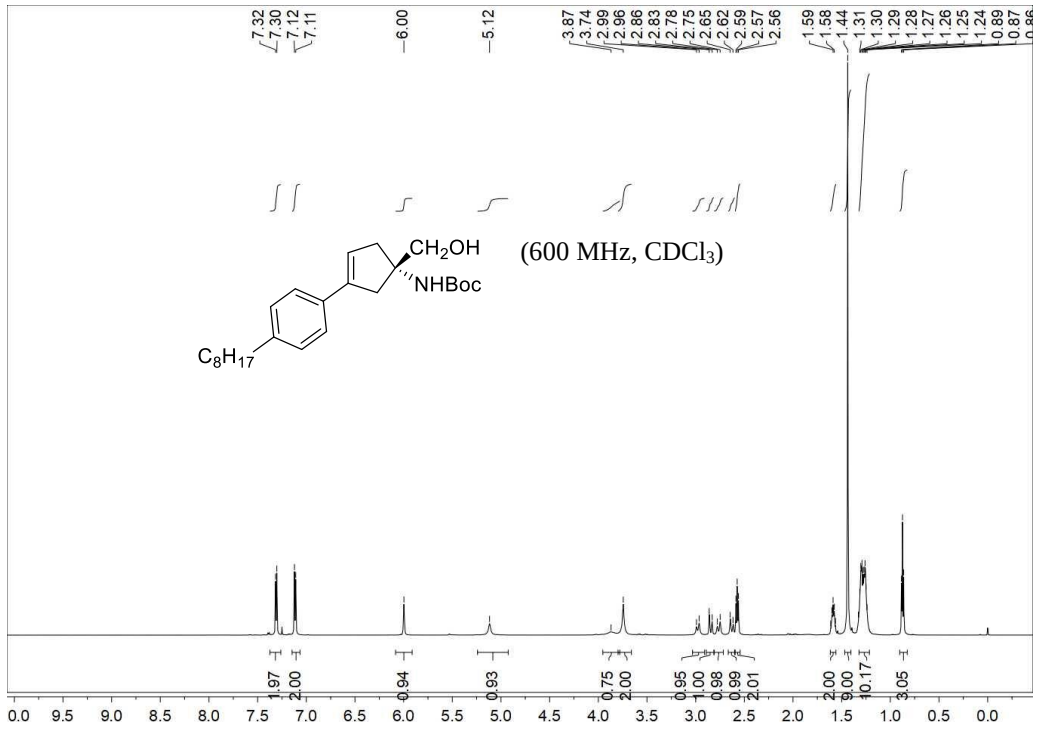


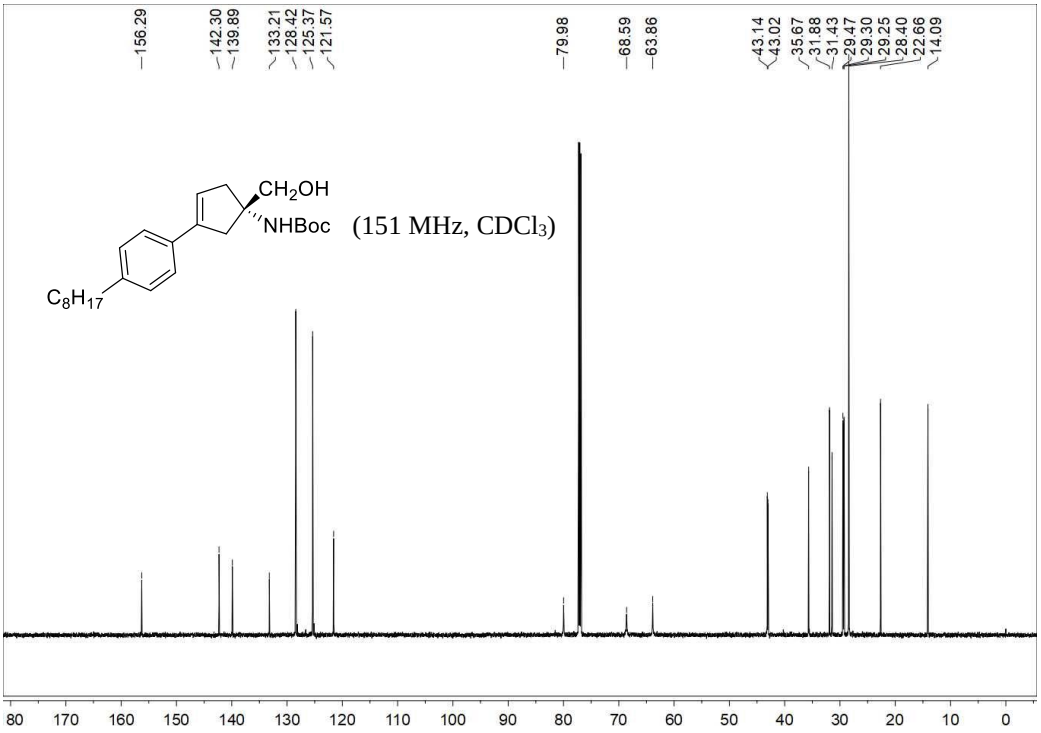
Ethyl (*S*)-1-((tert-butoxycarbonyl)amino)-3-(4-octylphenyl)cyclopent-3-ene-1-carboxylate (11):



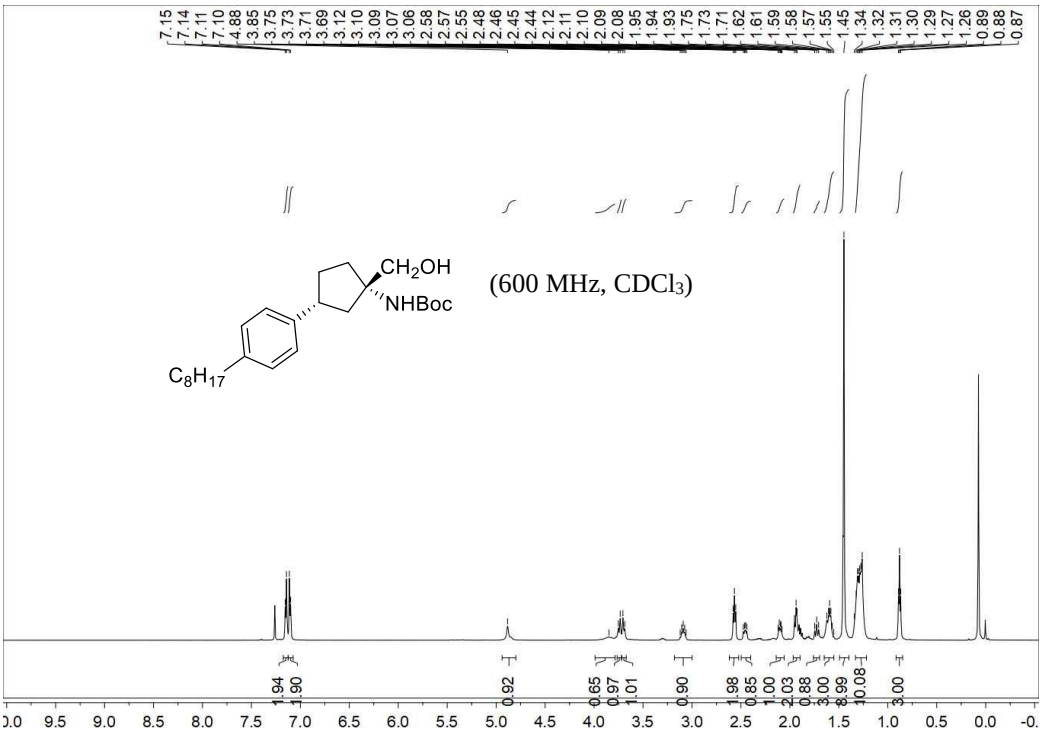


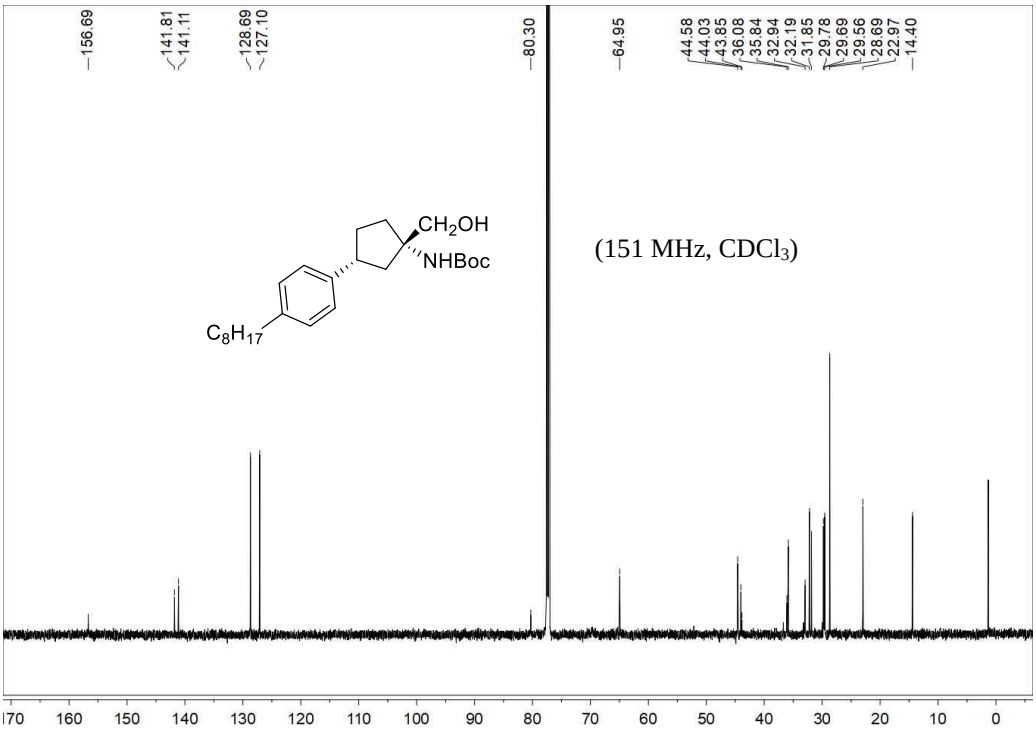
Tert-butyl (*S*)-(1-(hydroxymethyl)-3-(4-octylphenyl)cyclopent-3-en-1-yl)carbamate (12):





Tert-butyl ((*1S*, *3R*)-1-(hydroxymethyl)-3-(4-octylphenyl)cyclopentyl)carbamate (13):





((*1S, 3R*)-1-amino-3-(4-octylphenyl)cyclopentyl)methanol [(*S, R*)-VPC01091]: