

Supplementary Information

for

Asymmetric three-component Tsuji-Trost allylation reaction enabled by chiral aldehyde/palladium combined catalysis

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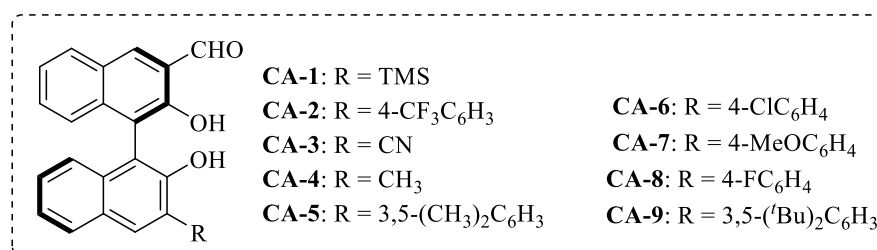
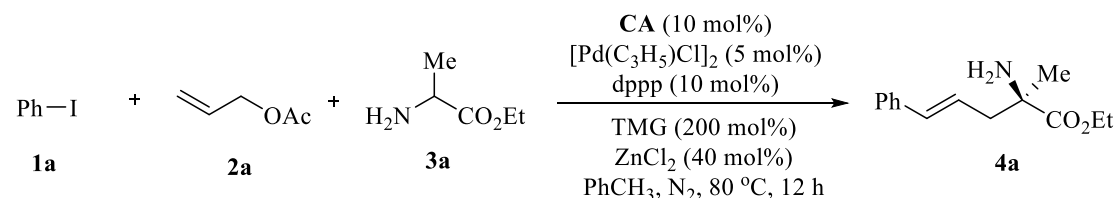
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1. General data

All non-aqueous reactions were carried out in a flame-dried glassware under nitrogen atmosphere or in a nitrogen-filled glove box unless otherwise noted. Solvents for reactions were dried appropriately before use: toluene, THF and Et₂O were dried by refluxing with sodium and benzophenone as indicator, CH₂Cl₂ and CHCl₃ were dried by refluxing with CaH₂. All other reagents were directly used as purchased from Aladdin, Adamas-beta[®] and Energy Chemical. ¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance 600 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 IF-H, IA-H, OD-H columns were purchased from Daicel Chemical Industries, LTD). Optical rotations were determined at $\lambda = 589$ nm (sodium D line) by using a Rudolph-API automatic polarimeter. alkenyl iodides,^[1] amino acid esters^[2,3] and chiral aldehydes catalysts^[4] were prepared according to the literature.

2. Reaction condition optimization

Table S1: Chiral aldehyde screening^a



Entry	CA	Time(h)	Yield(%) ^b	ee(%) ^c
1	CA-1	12	45	71
2	CA-2	12	29	50
3	CA-3	12	46	20
4	CA-4	12	49	65
5	CA-5	12	31	58
6	CA-6	12	32	65

7	CA-7	12	47	60
8	CA-8	12	51	64
9	CA-9	12	43	58

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA** (0.02 mmol), dppp (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.20 mmol) and ZnCl₂ (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S2: Transition-metal screening^a

Entry	[Pd]	Time(h)	Yield(%) ^b	ee(%) ^c
1	Pd(OAc) ₂	12	43	40
2	PdCl ₂	12	45	65
3	Pd ₂ (dba) ₃	12	NR	n.d. ^d
4	Pd(PPh ₃) ₂ Cl ₂	12	49	65
5	[(CH ₃)CyPd]	12	43	66
6	Pd(CO ₂ CF ₃) ₂	12	38	53
7	Pd(PPh ₃) ₄	12	Trace	n.d.
8	[Pd(C₃H₅)Cl]₂	12	45	71

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), dppp (0.02 mmol), [Pd] (0.01 mmol), TMG (0.20 mmol) and ZnCl₂ (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis. ^d n.d. = Not determined.

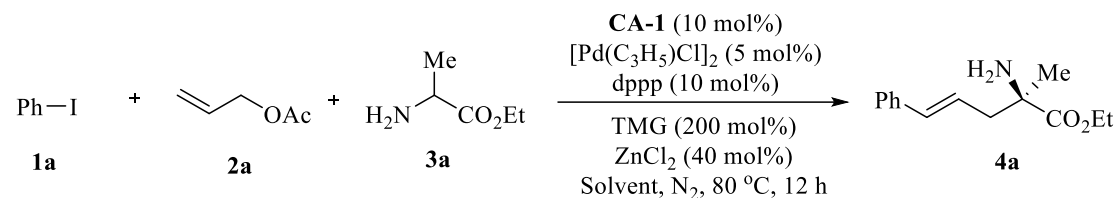
Table S3: Base screening^a

Entry	Base	Time(h)	Yield(%) ^b	ee(%) ^c
1	Et ₃ N	12	Trace	n.d. ^d
2	^t BuOK	12	Trace	n.d.
3	Metformin	12	NR	n.d.
4	2,2-Dimethylpyrrolidine	12	35	78
5	Quinuclidine	12	31	81
6	DABCO	12	29	81
7	TBD	12	23	64
8	^t Bu-TMG	12	45	58
9	DBN	12	32	52
10	DBU	12	36	67
11	Cs ₂ CO ₃	12	NR	n.d.
12	TMG	12	45	71
13	TDMAIP	12	41	61

14	^t Bu-TDMAIP	12	43	55
15		12	36	71

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), dppp (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), Base (0.20 mmol) and ZnCl₂ (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis. ^d n.d. = Not determined.

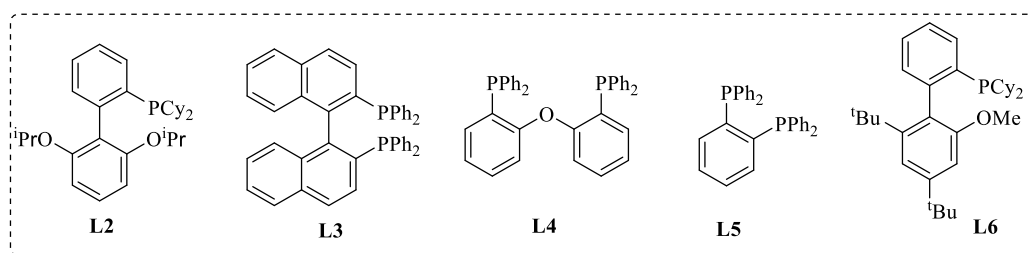
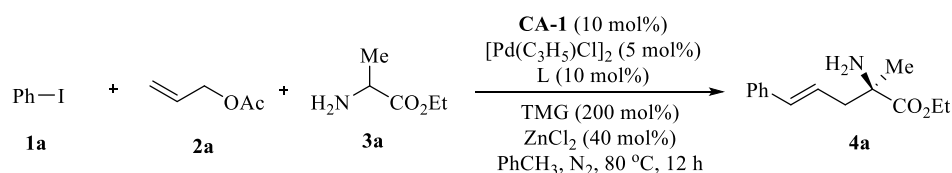
Table S4: Solvent screening^a



Entry	Solvent	Time(h)	Yield(%) ^b	ee(%) ^c
1	PhCH₃	12	45	71
2	PhCF ₃	12	55	51
3	Mesitylene	12	46	64
4	o-Xylene	12	52	65
5	m-Xylene	12	52	67
6	p-Xylene	12	53	67
7	PhCl	12	55	56
8	PhEt	12	47	66
9	Octane	12	56	26
10	1,2-dioxane	12	34	55

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), dppp (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.20 mmol) and ZnCl₂ (0.08 mmol) in Solvent (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S5: Achiral ligand screening^a



Entry	Ligand	Time(h)	Yield(%) ^b	ee(%) ^c
1	PPh ₃	12	NR	n.d. ^d
2	dpppe	12	trace	n.d.
3	dppf	12	31	60
4	dppe	12	52	67
5	dppb	12	25	76
6	dppp	12	45	71

7	L2	12	32	52
8	L3	12	25	65
9	L4	12	26	65
10	L5	12	NR	n.d.
11	L6	12	35	52

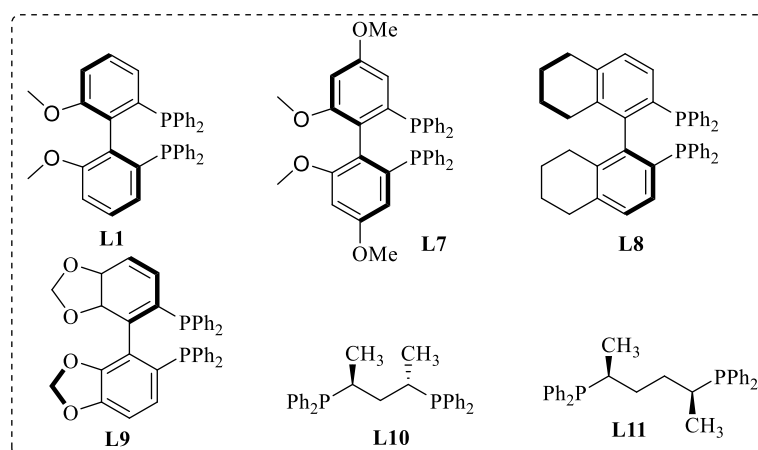
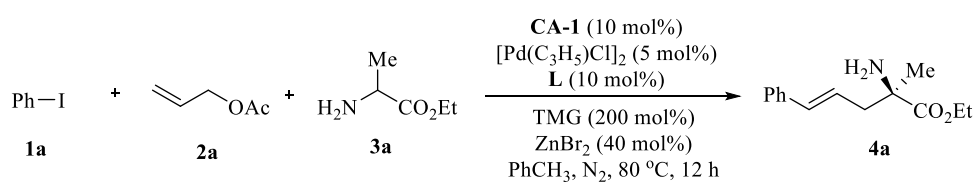
^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), L (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.20 mmol) and ZnCl₂ (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis. ^d n.d. = Not determined.

Table S6: Lewis acid screening^a

Entry	Lewis acid	Time(h)	Yield(%) ^b	ee(%) ^c
1	ZnF ₂	12	52	32
2	ZnCl ₂	12	45	71
3	ZnBr ₂	12	55	70
4	ZnI ₂	12	50	56
5	Zn(OAc) ₂	12	51	65
6	Zn(OTf) ₂	12	36	47
7	Zn(ClO ₄) ₂ ·6H ₂ O	12	45	61
8	LiCl	16	32	35
9	LiBr	17	15	30

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), dppp (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.20 mmol) and Lewis acid (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

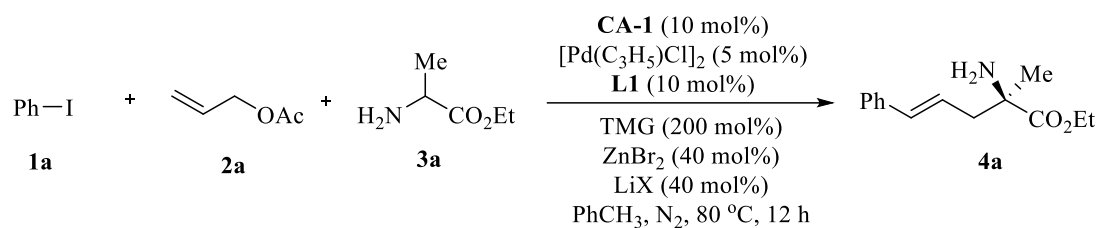
Table S7: Chiral ligand screening^a



entry	CA	ligand	time (h)	yield (%) ^b	ee (%) ^c
1	<i>ent</i> -CA-1	L1	12	32	16
2	CA-1	L1	12	30	88
3	<i>ent</i> -CA-1	L7	12	26	29
4	CA-1	L7	12	31	75
5	<i>ent</i> -CA-1	L8	12	30	21
6	CA-1	L8	12	34	75
7	<i>ent</i> -CA-1	L9	12	36	77
8	CA-1	L9	12	32	11
9	<i>ent</i> -CA-1	L10	12	53	63
10	CA-1	L10	12	50	63
11	<i>ent</i> -CA-1	L11	12	26	70
12	CA-1	L11	12	28	70

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), CA-1 (0.02 mmol), L (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01mmol), TMG (0.20 mmol) and ZnBr₂ (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

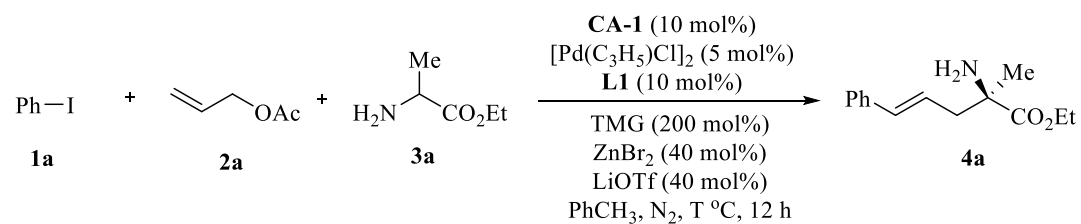
Table S8: Additive screening^a



Entry	LiX	Time(h)	Yield(%) ^b	ee(%) ^c
1	LiCl	12	49	88
2	LiBr	12	53	90
3	LiOTf	12	61	88
4	LiBF ₄	12	56	90
5	Li ₂ CO ₃	12	50	90
6	LiOAc	12	52	88
7	LiClO ₄	12	55	82
8	LiOH·H ₂ O	12	51	90

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), CA-1 (0.02 mmol), L1 (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01mmol), TMG (0.20 mmol), LiX (0.08 mmol) and ZnBr₂ (0.08 mmol) in PhCH₃ (0.5 mL) at 80 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S9: Reaction temperature screening^a



Entry	T(°C)	Time(h)	Yield(%) ^b	ee(%) ^c
1	90	12	64	86

2	80	12	61	88
3	70	12	56	92
4	60	12	45	93

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.20 mmol), LiOTf (0.08 mmol) and ZnBr₂ (0.08 mmol) in PhCH₃ (0.5 mL) at T °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S10: Lewis acid equivalents screening^a

Entry	X	Time(h)	Yield(%) ^b	ee(%) ^c
1	0	12	23	3
2	20	12	42	84
3	40	12	56	92
4	60	12	59	90
5	80	12	60	89
6	100	12	63	90
7	120	12	55	81

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.20 mmol), LiOTf (0.08 mmol) and ZnBr₂ (X mmol) in PhCH₃ (0.5 mL) at 70 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S11: Base equivalents screening^a

Entry	X	Time(h)	Yield(%) ^b	ee(%) ^c
1	180	12	48	88
2	200	12	63	90
3	220	12	67	89
4	240	12	71	87
5	260	12	66	85

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (X mmol), LiOTf (0.08 mmol) and ZnBr₂ (0.2 mmol) in PhCH₃ (0.5 mL) at 70 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S12: Leaving group screening^a

Entry	LG	Time(h)	Yield(%) ^b	ee(%) ^c
1	OAc	12	67	89
2	Br	12	49	81
3	OCO ₂ Ph	12	69	90
4	OBoc	12	56	84
5	O(CO ₂)Et	12	62	90

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.44 mmol), LiOTf (0.08 mmol) and ZnBr₂ (0.2 mmol) in PhCH₃ (0.5 mL) at 70 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S13: Alkoxy group screening^a

Entry	R	Time(h)	Yield(%) ^b	ee(%) ^c
1	Me	12	53	88
2	Et	12	69	90
3	^t Bu	12	71	96
4	Bn	12	47	85

^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01 mmol), TMG (0.44 mmol), LiOTf (0.08 mmol) and ZnBr₂ (0.2 mmol) in PhCH₃ (0.5 mL) at 70 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S14: Re-screening of the additives^a

Entry	LiX	Time(h)	Yield(%) ^b	ee(%) ^c
1	LiCl	12	63	95
2	LiBr	12	62	95
3	LiOTf	12	71	96
4	Li ₂ CO ₃	12	70	94
5	LiBF ₄	12	78	97

6	LiOAc	12	66	93
7	LiClO ₄	12	55	88
8	LiOH:H ₂ O	12	67	91

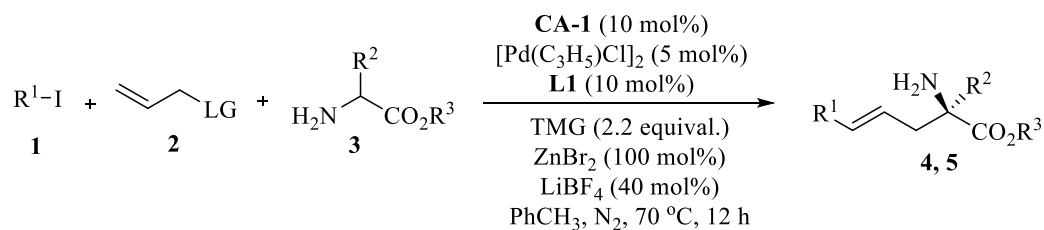
^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01mmol), TMG (0.44 mmol), LiX (0.08 mmol) and ZnBr₂ (0.2 mmol) in PhCH₃ (0.5 mL) at 70 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

Table S15: Reactant ratio screening^a

Entry	1b:2a:3b	Time(h)	Yield(%) ^b	ee(%) ^c
1	1.2:1:1.5	12	69	93
2	1.5:1:1.5	12	78	97
3	1.8:1:1.5	12	81	97
4	2:1:1.5	12	77	96

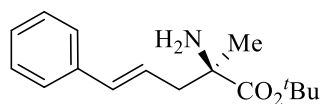
^a Unless noted otherwise, reactions were performed with **1a** (0.20 mmol), **2a** (0.30 mmol), **3a** (0.30 mmol), **CA-1** (0.02 mmol), **L1** (0.02 mmol), [Pd(C₃H₅)Cl]₂ (0.01mmol), TMG (0.44 mmol), LiBF₄ (0.08 mmol) and ZnBr₂ (0.2 mmol) in PhCH₃ (0.5 mL) at 70 °C. ^b Isolated yield. ^c Determined by chiral HPLC analysis.

3. General procedure

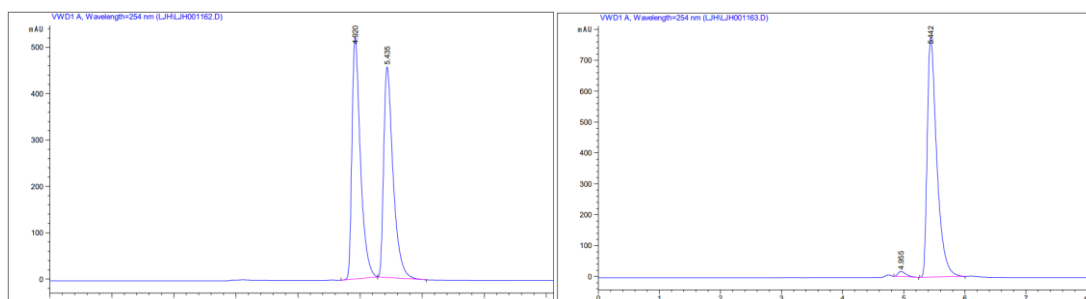


To a 10 mL vial charged with [Pd(C₃H₅)Cl]₂ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, aryl iodide **1** (0.2 mmol), allyl alcohol ester **2** (0.36 mmol), amino acid ester **3** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr₂ (45.0 mg, 0.2 mmol), LiBF₄ (7.5mg, 0.08 mmol) and TMG (56.2 uL, 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3).

***tert*-Butyl (*R, E*)-2-amino-2-methyl-5-phenylpent-4-enoate (**4b**):**

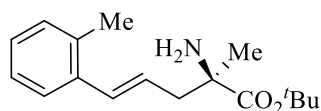


Colorless oil (42.1 mg, 81%); $R_f = 0.23$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 97% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 5.442 min, $t_R(\text{minor})$ 4.955 min; $[\alpha]_D^{20} = +16.25$ ($c = 0.88$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.36-7.29 (m, 4H), 7.23 (t, $J = 6.0$ Hz, 1H), 6.50 (d, $J = 18.0$ Hz, 1H), 6.25 – 5.93 (m, 1H), 2.67 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.42 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.79 (s, 2H), 1.50 (s, 9H), 1.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.39, 137.19, 134.02, 128.53, 127.34, 126.17, 124.71, 81.02, 58.11, 44.50, 28.04, 26.44; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{24}\text{NO}_2^+$ 262.1802; found 262.1809.

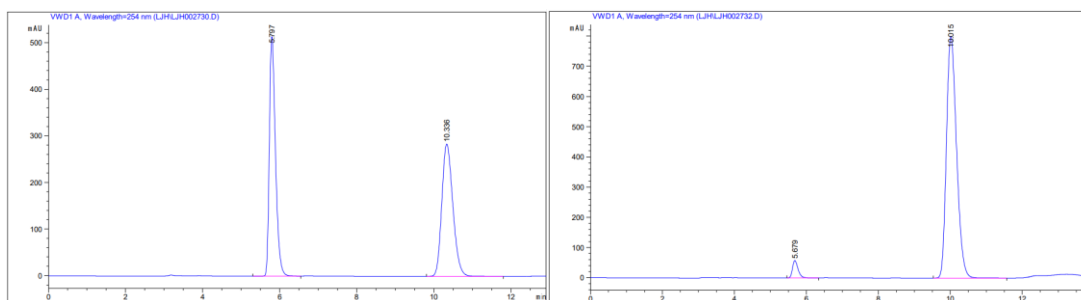


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1	4.920	BB	0.1423	4924.66504	521.26971	50.7793	1	4.955	BB	0.1348	148.11320	16.57980	1.7261
2	5.435	BB	0.1576	4773.50195	454.06982	49.2207	2	5.442	BB	0.1634	8432.45605	774.70374	98.2739

***tert*-Butyl (*R,E*)-2-amino-2-methyl-5-(*o*-tolyl)pent-4-enoate (**4c**):**

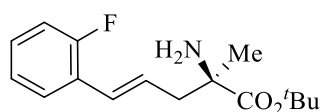


Colorless oil (17.1 mg, 31%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 92% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 10.015 min, $t_R(\text{minor})$ 5.679 min; $[\alpha]_D^{20} = +10.60$ ($c = 0.31$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.39 – 7.37 (m, 1H), 7.13 (d, $J = 6.0$ Hz, 3H), 6.68 (d, $J = 18.0$ Hz, 1H), 6.03 – 5.98 (m, 1H), 2.67 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.42 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.33 (s, 3H), 1.73 (s, 2H), 1.47 (s, 9H), 1.35 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.44, 136.39, 135.11, 131.95, 130.23, 127.27, 126.13, 126.06, 125.69, 80.98, 57.97, 44.76, 28.05, 26.47, 19.84.; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_2^+$ 276.1958; found 276.1957.

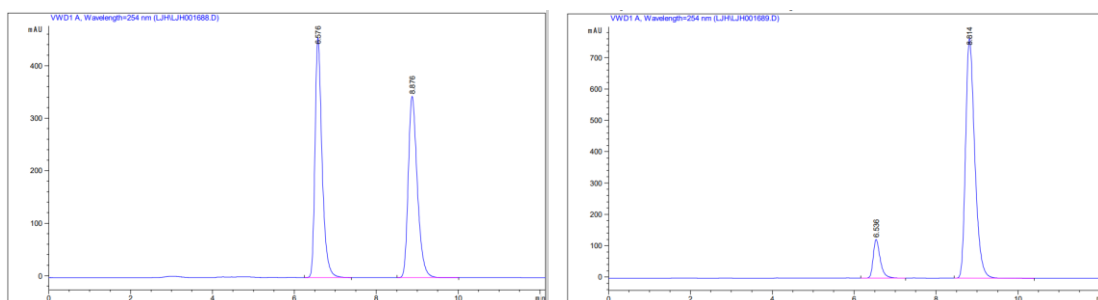


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.797	BB	0.1684	5683.67236	513.80054	50.1393	1	5.679	BB	0.1644	617.34601	57.59732	3.8128
2	10.336	BB	0.3095	5652.08594	283.93750	49.8607	2	10.015	BB	0.3030	1.55739e4	799.80554	96.1872

***tert*-Butyl (*R,E*)-2-amino-5-(2-fluorophenyl)-2-methylpent-4-enoate (4d):**

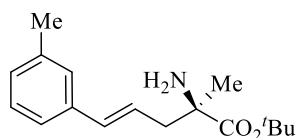


Colorless oil (32.2 mg, 58%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 78% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 8.814 min, $t_R(\text{minor})$ 6.536 min; $[\alpha]_D^{20} = +4.39$ ($c = 0.30$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.34 - 7.31 (m, 1H), 7.12 - 7.09 (m, 1H), 7.00 (t, $J = 7.3$ Hz, 1H), 6.94 (dd, $J = 12.0, 6.0$ Hz, 1H), 6.55 (d, $J = 12.0$ Hz, 1H), 6.19 - 6.14 (m, 1H), 2.59 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.35 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.67 (s, 2H), 1.40 (s, 9H), 1.28 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.29, 160.90(d, $J = 249.2$ Hz), 128.56(d, $J = 9.1$ Hz), 127.63(d, $J = 4.5$ Hz), 127.35(d, $J = 3.0$ Hz), 126.40(d, $J = 3.0$ Hz), 124.98(d, $J = 13.6$ Hz), 124.05(d, $J = 3.0$ Hz), 115.75(d, $J = 22.7$ Hz), 81.11, 58.12, 44.92, 28.00, 26.41; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{23}\text{FNO}_2^+$ 280.1707; found 280.1704.

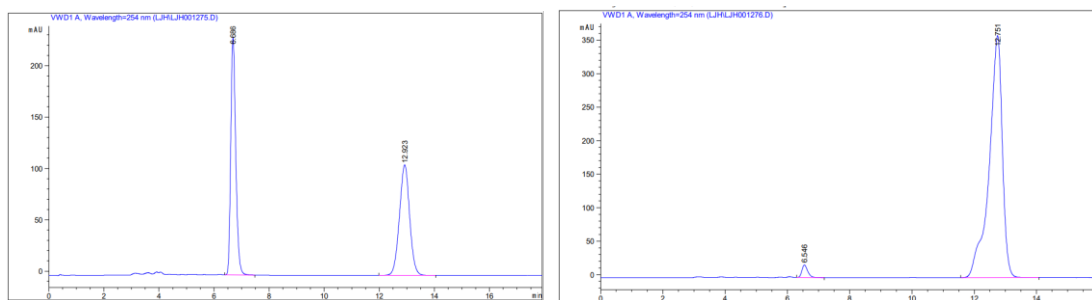


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.576	BB	0.1783	5435.41895	456.53137	50.5943	1	6.536	BB	0.1780	1466.90161	123.42873	10.9758
2	8.876	BB	0.2348	5307.73145	345.09726	49.4057	2	8.814	BB	0.2385	1.18979e4	764.05560	89.0242

***tert*-Butyl (*R,E*)-2-amino-2-methyl-5-(*m*-tolyl)pent-4-enoate (**4e**):**

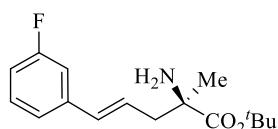


Colorless oil (32.5 mg, 59%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 12.751 min, $t_R(\text{minor})$ 6.546 min; $[\alpha]_D^{20} = +8.19$ ($c = 0.45$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.29 - 7.15 (m, 3H), 7.06 (d, $J = 6.0$ Hz, 1H), 6.47 (d, $J = 18.0$ Hz, 1H), 6.21 - 6.04 (m, 1H), 2.66 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.41 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.35 (s, 3H), 1.83 (s, 2H), 1.50 (s, 9H), 1.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.37, 138.07, 137.13, 134.13, 128.43, 128.14, 126.92, 124.42, 123.32, 81.03, 58.13, 44.46, 28.04, 26.39, 21.39; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_2^+$ 276.1958; found 276.1957.

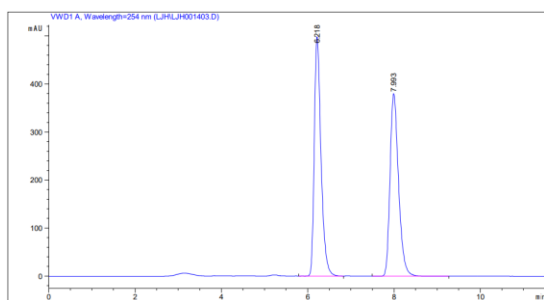


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.686	BB	0.1920	2903.70483	230.79671	51.2025	1	6.546	BB	0.1954	237.74306	18.65047	2.1837
2	12.923	BB	0.3936	2767.31738	107.50187	48.7975	2	12.751	BB	0.4301	1.06493e4	361.06296	97.8163

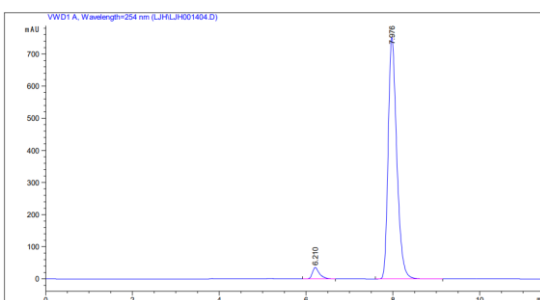
***tert*-Butyl (*R,E*)-2-amino-5-(3-fluorophenyl)-2-methylpent-4-enoate (**4f**):**



Colorless oil (35.2 mg, 63%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 93% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 7.976 min, $t_R(\text{minor})$ 6.210 min; $[\alpha]_D^{20} = +15.03$ ($c = 0.33$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.29 - 7.25 (m, 1H), 7.11 (d, $J = 7.7$ Hz, 1H), 7.04 (d, $J = 10.2$ Hz, 1H), 6.94 - 6.91 (m, 1H), 6.46 (d, $J = 12.0$ Hz, 1H), 6.25 - 6.01 (m, 1H), 2.66 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.42 (dd, $J = 13.5, 8.3$ Hz, 1H), 1.77 (s, 2H), 1.49 (s, 9H), 1.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.25, 163.92 (d, $J = 246.1$ Hz), 139.57 (d, $J = 7.6$ Hz), 132.87 (d, $J = 3.0$ Hz), 129.98 (d, $J = 9.1$ Hz), 126.32, 122.04 (d, $J = 3.0$ Hz), 114.18 (d, $J = 6.1$ Hz), 112.67 (d, $J = 7.6$ Hz), 81.11, 58.08, 44.38, 28.03, 26.39; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{23}\text{FNO}_2^+$ 280.1707; found 280.1704.

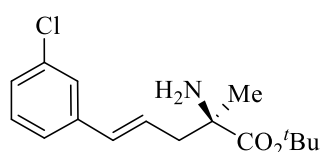


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.218	BB	0.1640	5383.00439	498.12210	50.8078
2	7.993	BB	0.2096	5211.83936	379.90634	49.1922

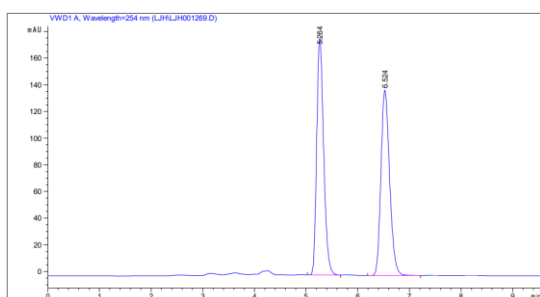


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.210	BB	0.1665	399.48621	35.44699	3.7255
2	7.976	BB	0.2099	1.03235e4	751.34546	96.2745

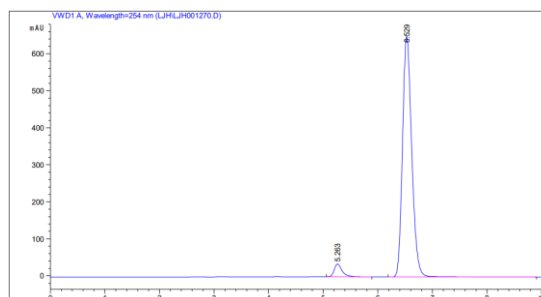
***tert*-Butyl (*R,E*)-2-amino-5-(3-chlorophenyl)-2-methylpent-4-enoate (4g):**



Colorless oil (35.9 mg, 61%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 6.529 min, t_R (minor) 5.263 min; $[\alpha]_D^{20} = +13.45$ ($c = 0.40$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.33-7.21 (m, 4H), 6.44 (d, $J = 18.0$ Hz, 1H), 6.20 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.66 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.43 (dd, $J = 18.0, 12.0$ Hz, 1H), 1.80 (s, 2H), 1.50 (s, 9H), 1.32 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.24, 139.06, 134.49, 132.61, 129.74, 127.27, 126.49, 126.12, 124.35, 81.12, 58.09, 44.40, 28.04, 26.37; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{23}\text{ClNO}_2^+$ 296.1412; found 296.1418.

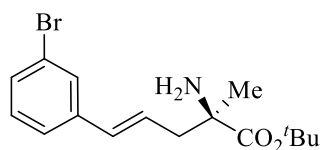


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.264	BB	0.1441	1662.89587	177.80638	50.6297
2	6.524	BB	0.1799	1621.53223	138.95844	49.3703



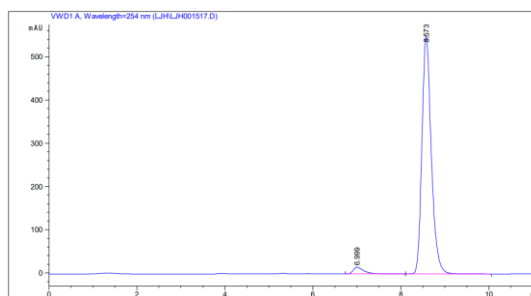
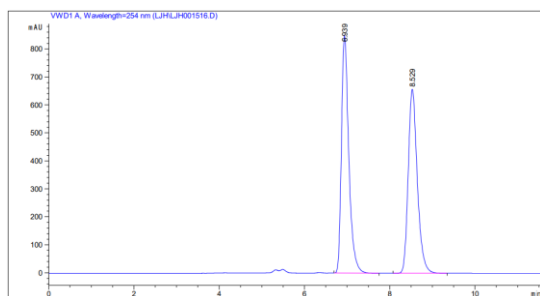
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.263	BB	0.1494	340.63361	34.29154	4.2525
2	6.529	BB	0.1812	7669.51416	650.66986	95.7475

***tert*-Butyl (*R,E*)-2-amino-5-(3-bromophenyl)-2-methylpent-4-enoate (4h):**



Colorless oil (40.6 mg, 60%); $R_f = 0.23$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 8.573 min,

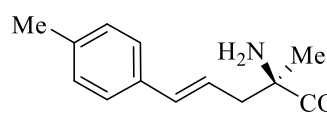
t_R (minor) 6.999 min; $[\alpha]_D^{20} = +7.94$ ($c = 0.77$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.47 (s, 1H), 7.33 (d, $J = 12.0$ Hz, 1H), 7.24 (d, $J = 6.0$ Hz, 1H), 7.15 (t, $J = 12.0$ Hz, 1H), 6.40 (d, $J = 12.0$ Hz, 1H), 6.19 – 6.13 (m, 1H), 2.63 (dd, $J = 12.6, 6.9$ Hz, 1H), 2.40 (dd, $J = 13.0, 8.3$ Hz, 1H), 1.71 (s, 2H), 1.47 (s, 9H), 1.34 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.25, 139.37, 132.47, 130.18, 130.03, 129.06, 126.59, 124.78, 122.74, 81.09, 58.08, 44.41, 28.04, 26.38; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{23}\text{BrNO}_2^+$ 340.0907; found 340.0904.



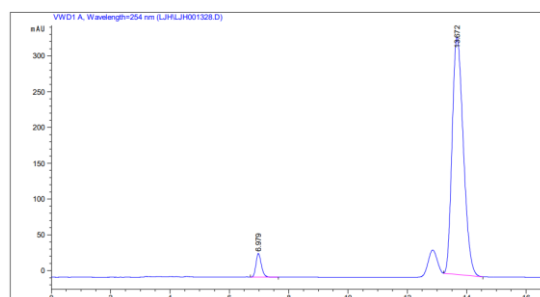
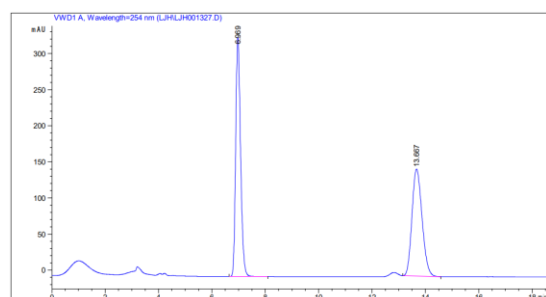
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.939	BB	0.1817	1.01396e4	848.68433	51.0080
2	8.529	BB	0.2252	9738.87402	657.90216	48.9920

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.999	BB	0.2524	257.91895	15.50596	3.0704
2	8.573	BB	0.2252	8142.35254	549.85730	96.9296

tert-Butyl (R,E)-2-amino-2-methyl-5-(p-tolyl)pent-4-enoate (4i):

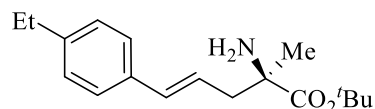


Colorless oil (39.9 mg, 73%); $R_f = 0.23$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 91% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30$ °C), UV 254 nm, t_R (major) 13.672 min, t_R (minor) 6.979 min; $[\alpha]_D^{20} = +12.88$ ($c = 0.50$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.25 (d, $J = 6.0$ Hz, 2H), 7.12 (d, $J = 6.0$ Hz, 2H), 6.47 (d, $J = 12.0$ Hz, 1H), 6.10 (ddd, $J = 15.4, 8.1, 7.0$ Hz, 1H), 2.66 (ddd, $J = 13.5, 6.8, 1.0$ Hz, 1H), 2.44 – 2.36 (m, 1H), 2.35 (s, 3H), 1.81 (s, 2H), 1.49 (s, 9H), 1.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.42, 137.11, 134.42, 133.90, 129.22, 126.07, 123.58, 80.97, 58.12, 44.52, 28.04, 26.42, 21.15; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_2^+$ 276.1958; found 276.1963.



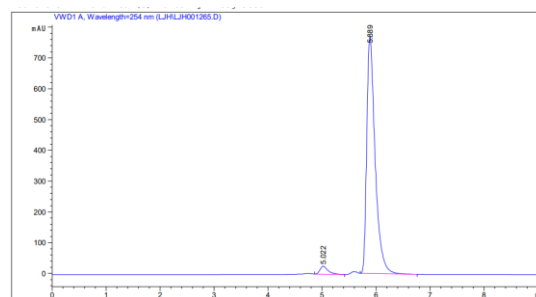
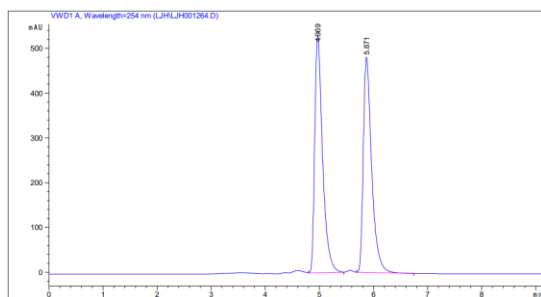
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.969	BB	0.1952	4209.73779	330.71246	51.9669	1	6.979	BB	0.1943	416.54797	32.90405	4.5690
2	13.667	BB	0.4112	3891.07324	148.24908	48.0331	2	13.672	BB	0.4112	8700.37598	331.46686	95.4310

***tert*-Butyl (*R,E*)-2-amino-5-(4-ethylphenyl)-2-methylpent-4-enoate (**4j**):**



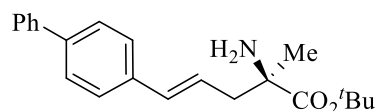
Colorless oil (42.1 mg, 73%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94%

by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 5.889 min, t_R (minor) 5.022 min; $[\alpha]_D^{20} = +15.06$ ($c = 0.43$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.28 (d, $J = 6.0$ Hz, 2H), 7.16(d, $J = 6.0$ Hz, 2H), 6.48 (d, $J = 12.0$ Hz, 1H), 6.13 – 6.08 (m, 1H), 2.68 – 2.63 (m, 3H), 2.40 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.80 (s, 2H), 1.50 (s, 9H), 1.36 (s, 3H), 1.25(t, $J = 6.0$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.42, 143.56, 134.68, 133.93, 128.04, 126.16, 123.66, 80.98, 58.11, 44.49, 28.58, 28.05, 26.43, 15.55; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{28}\text{NO}_2^+$ 290.2115; found 290.2114.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.969	BB	0.1525	5331.92139	529.26935	50.7627	1	5.022	BB	0.1515	258.91901	25.61263	3.0340
2	5.871	BB	0.1619	5171.69287	480.75259	49.2373	2	5.889	BB	0.1620	8275.11230	768.71417	96.9660

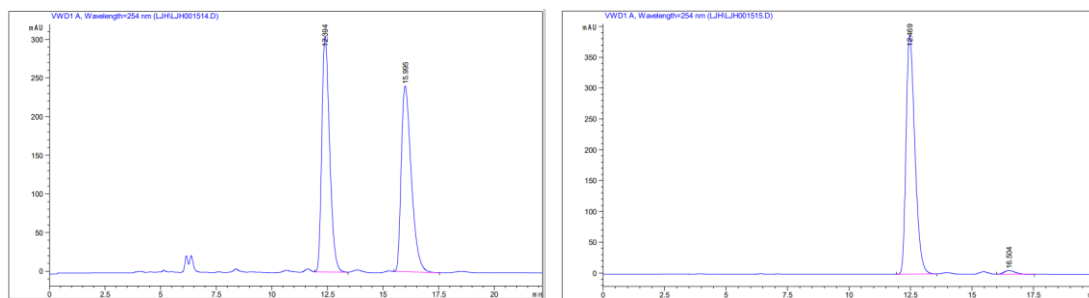
***tert*-Butyl (*R,E*)-5-([1,1'-biphenyl]-4-yl)-2-amino-2-methylpent-4-enoate (**4k**):**



White solid (45.1 mg, 67%); m.p. = 75-76 $^\circ\text{C}$; $R_f = 0.26$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess

was determined to be 96% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 12.469 min, t_R (minor) 16.504 min; $[\alpha]_D^{20} = +11.21$ ($c = 0.55$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.62 (d, $J = 12.0$ Hz, 2H), 7.57 (d, $J = 6.0$ Hz, 2H), 7.47 - 7.43 (m, 4H), 7.36 (t, $J = 6.0$ Hz, 1H), 6.55 (d, $J = 18.0$ Hz, 1H), 6.25 – 6.20 (m, 1H), 2.70 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.45 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.83 (s, 2H), 1.52 (s, 9H), 1.39 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.37, 140.75, 140.12, 136.24, 133.56, 128.78, 127.26, 127.25, 126.92, 126.60, 124.90, 81.05, 58.17, 44.58, 28.07, 26.44; **HRMS(ESI)** m/z :

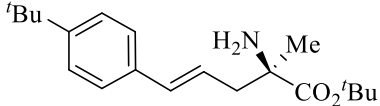
[M+H]⁺ Calculated for C₂₂H₂₈NO₂⁺ 338.2115; found 338.2112.

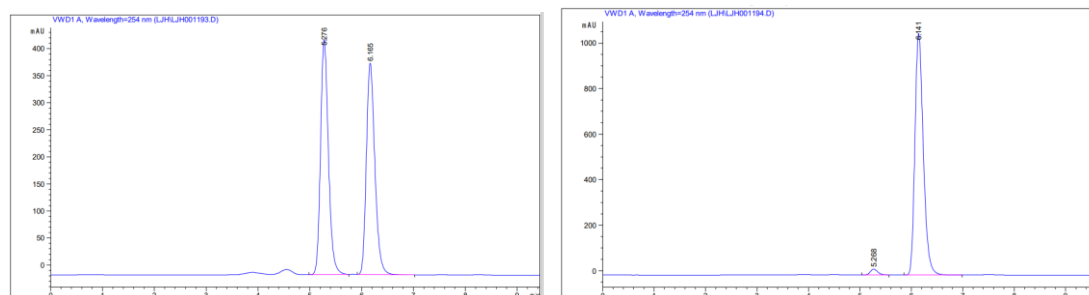


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.394	BB	0.3800	7461.24756	305.20517	49.7797
2	15.995	BB	0.4806	7527.29541	240.29253	50.2203

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.469	BB	0.3858	9652.33203	386.87268	98.0457
2	16.504	BB	0.5010	192.39676	5.97568	1.9543

tert-Butyl (R,E)-2-amino-5-(4-(tert-butyl)phenyl)-2-methylpent-4-enoate (4l):

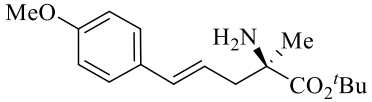
 Colorless oil (44.6 mg, 70%); R_f = 0.26 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R(major) 6.141 min, t_R(minor) 5.268 min; [α]_D²⁰ = +5.56 (c = 0.40, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.25 (d, J = 12.0 Hz, 2H), 7.20 (d, J = 12.0 Hz, 2H), 6.39 (d, J = 12.0 Hz, 1H), 6.02 (ddd, J = 15.5, 8.1, 7.0 Hz, 1H), 2.57 (dd, J = 18.0, 6.0 Hz, 1H), 2.31 (dd, J = 18.0, 6.0 Hz, 1H), 1.68 (s, 2H), 1.41 (s, 9H), 1.26 (s, 3H), 1.24 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 176.33, 150.42, 134.43, 133.82, 125.90, 125.44, 123.83, 80.99, 58.14, 44.45, 34.54, 31.30, 28.05, 26.40; HRMS(ESI) m/z: [M+H]⁺ Calculated for C₂₀H₃₂NO₂⁺ 318.2428; found 318.2427.



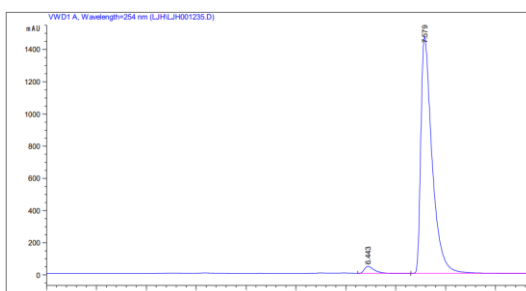
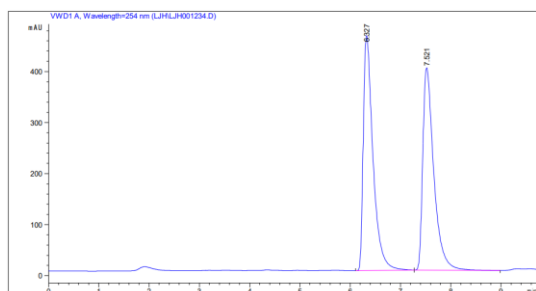
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.276	BB	0.1620	4570.98145	434.95544	50.6744
2	6.165	BB	0.1766	4449.31543	390.78174	49.3256

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.268	BB	0.1525	254.04808	25.53616	2.0678
2	6.141	BB	0.1747	1.20320e4	1060.27576	97.9322

tert-Butyl (R,E)-2-amino-5-(4-methoxyphenyl)-2-methylpent-4-enoate (4m):

 Colorless oil (41.2 mg, 72%); R_f = 0.21 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 1.0

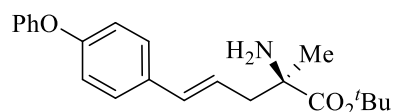
mL/min, T = 30 °C), UV 254 nm, t_R (major) 7.579 min, t_R (minor) 6.443 min; $[\alpha]_D^{20} = +17.54$ ($c = 0.80$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.19 (d, $J = 6.0$ Hz, 2H), 6.76 (d, $J = 6.0$ Hz, 2H), 6.34 (d, $J = 18.0$ Hz, 1H), 5.93-5.88 (m, 1H), 3.72 (s, 3H), 2.55 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.28 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.70 (s, 2H), 1.40 (s, 9H), 1.26 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.46, 159.03, 133.41, 130.04, 127.29, 122.38, 113.95, 80.92, 58.12, 55.28, 44.53, 28.04, 26.43; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_3^+$ 292.1907; found 292.1912.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.327	BB	0.2001	6167.70215	460.21545	50.5342
2	7.521	BB	0.2286	6037.30371	396.53659	49.4658

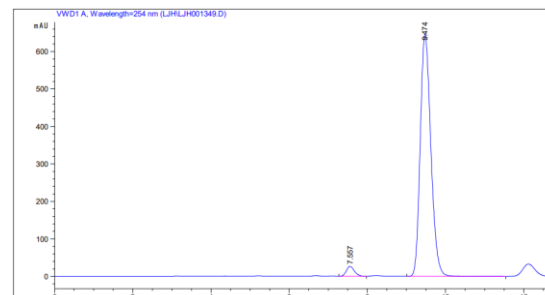
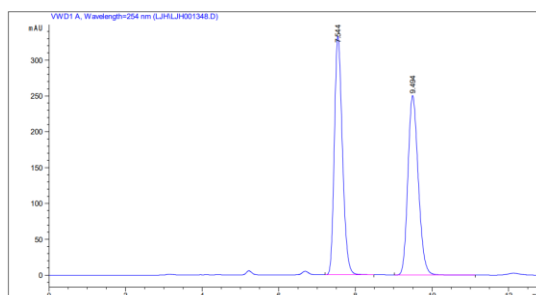
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.443	BB	0.2084	612.11133	43.75831	2.5880
2	7.579	BB	0.2340	2.30399e4	1469.36389	97.4120

tert-Butyl (R,E)-2-amino-2-methyl-5-(4-phenoxyphenyl)pent-4-enoate (4n):



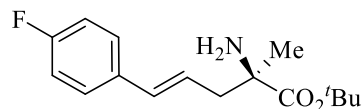
Colorless oil (53.1 mg, 75%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be

94% 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) 9.474 min, t_R (minor) 7.557 min; $[\alpha]_D^{20} = +17.36$ ($c = 0.53$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.36 - 7.29 (m, 4H), 7.12 (t, $J = 6.0$ Hz, 1H), 7.03 (d, $J = 6.0$ Hz, 2H), 6.96 (d, $J = 12.0$ Hz, 2H), 6.48 (d, $J = 18.0$ Hz, 1H), 6.10 - 6.05 (m, 1H), 2.66 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.41 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.80 (s, 2H), 1.50 (s, 9H), 1.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.42, 157.21, 156.59, 133.17, 132.50, 129.74, 127.48, 123.81, 123.27, 118.90, 80.99, 58.12, 44.50, 28.06, 26.43; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{22}\text{H}_{28}\text{NO}_3^+$ 354.2064; found 354.2069.



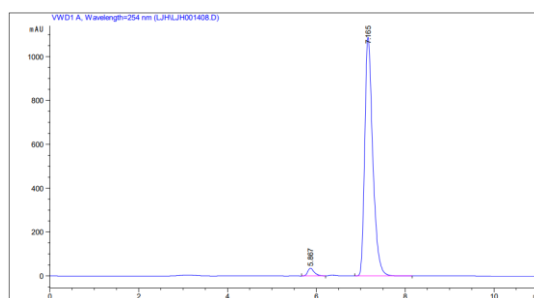
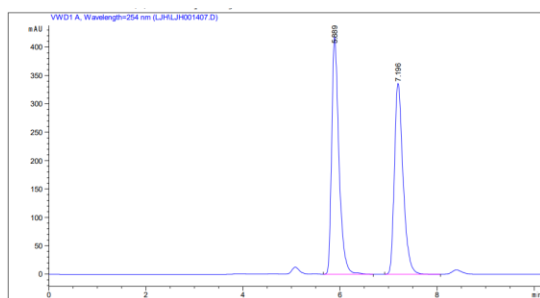
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.544	BB	0.2258	4859.06738	332.68939	50.7741	1	7.557	BB	0.2222	375.03467	26.23285	2.9848
2	9.494	BB	0.2924	4710.90137	250.41580	49.2259	2	9.474	BB	0.2915	1.21897e4	646.23926	97.0152

***tert*-Butyl (*R,E*)-2-amino-5-(4-fluorophenyl)-2-methylpent-4-enoate (**4o**):**



Colorless oil (36.3 mg, 65%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95%

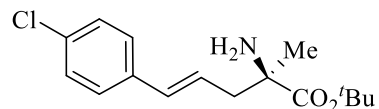
by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 7.165 min, t_R (minor) 5.867 min; $[\alpha]_D^{20} = +9.95$ ($c = 0.41$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.23 – 7.20 (m, 2H), 6.91 (t, $J = 6.0$ Hz, 2H), 6.36 (d, $J = 18.0$ Hz, 1H), 6.00 - 5.95 (m, 1H), 2.55 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.31 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.68 (s, 2H), 1.40 (s, 9H), 1.26 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.35, 162.98(d, $J = 246.1$ Hz), 133.37(d, $J = 3.0$ Hz), 132.77, 127.64(d, $J = 9.1$ Hz), 124.48, 115.48(d, $J = 22.7$ Hz), 81.04, 58.09, 44.43, 28.03, 26.40; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{23}\text{FNO}_2^+$ 280.1707; found 280.1704.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.889	BB	0.1566	4354.50000	417.58478	51.0983
2	7.196	BB	0.1884	4167.31201	336.10693	48.9017

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.867	BB	0.1529	351.32611	34.77355	2.5057
2	7.165	BB	0.1904	1.36698e4	1087.31055	97.4943

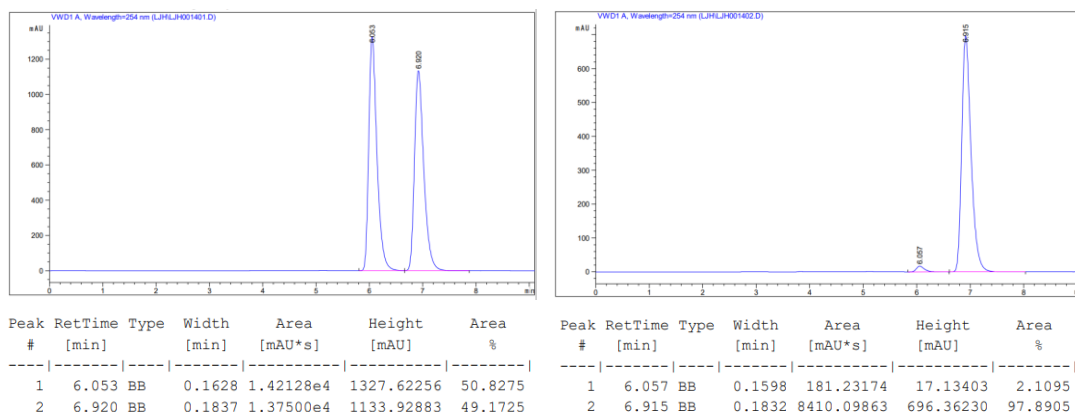
***tert*-Butyl (*R,E*)-2-amino-5-(4-chlorophenyl)-2-methylpent-4-enoate (**4p**):**



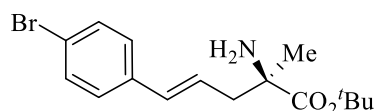
Colorless oil (39.1 mg, 66%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96%

by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 6.915 min, t_R (minor) 6.057 min; $[\alpha]_D^{20} = +8.02$ ($c = 0.58$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.27 (s, 4H), 6.44 (d, $J = 18.0$ Hz, 1H), 6.16 – 6.11 (m, 1H), 2.65 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.41 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.77 (s, 2H), 1.48 (s, 9H), 1.35 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.30, 135.67, 132.92, 132.72, 128.68, 127.35, 125.54, 81.08, 58.09, 44.46, 28.03, 26.40; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{16}\text{H}_{23}\text{ClNO}_2^+$ 296.1412; found

296.1409.

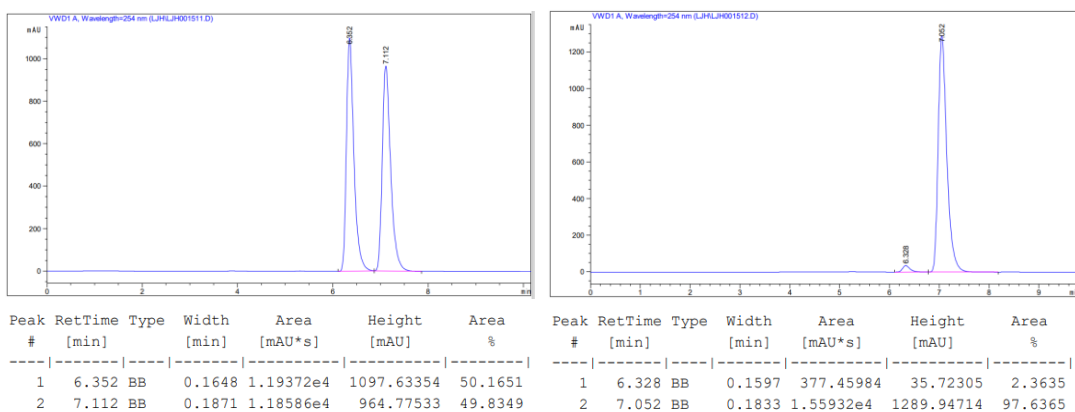


tert-Butyl (R,E)-2-amino-5-(4-bromophenyl)-2-methylpent-4-enoate (4q):

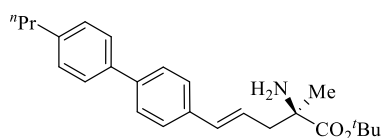


Colorless oil (43.7 mg, 64%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95%

by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 7.052 min, t_R (minor) 6.328 min; $[\alpha]_D^{20} = +12.63$ (c = 0.50, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.43 (d, J = 6.0 Hz, 2H), 7.21 (d, J = 6.0 Hz, 2H), 6.43 (d, J = 18.0 Hz, 1H), 6.18 – 6.13 (m, 1H), 2.64 (ddd, J = 13.6, 6.9, 1.2 Hz, 1H), 2.40 (ddd, J = 13.6, 8.2, 0.8 Hz, 1H), 1.79 (s, 2H), 1.48 (s, 9H), 1.35 (s, 3H); ¹³C NMR (151 MHz, CDCl₃) δ 176.26, 136.12, 132.76, 131.63, 127.68, 125.70, 121.04, 81.08, 58.07, 44.47, 28.03, 26.39; HRMS(ESI) m/z: [M+H]⁺ Calculated for C₁₆H₂₃BrNO₂⁺ 340.0907; found 340.0903.



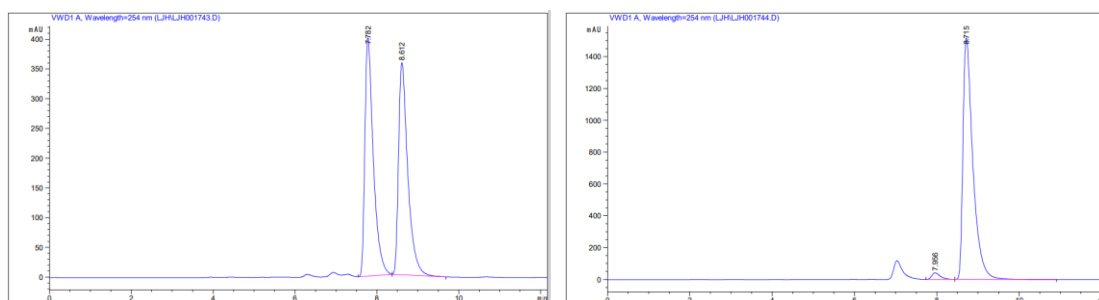
tert-Butyl (R,E)-2-amino-2-methyl-5-(4'-propyl-[1,1'-biphenyl]-4-yl)pent-4-enoate (4r):



Colorless oil (54.5 mg, 72%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IA-H column

(hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 8.715 min,

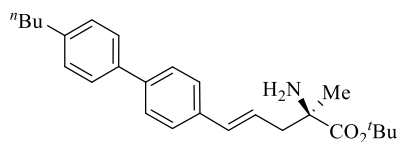
t_R (minor) 7.956 min; $[\alpha]_D^{20} = +16.09$ ($c = 0.86$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (d, $J = 6.0$ Hz, 2H), 7.54 (d, $J = 6.0$ Hz, 2H), 7.42 (d, $J = 12.0$ Hz, 2H), 7.27 (d, $J = 12.0$ Hz, 2H), 6.54 (d, $J = 18.0$ Hz, 1H), 6.23 - 6.18 (m, 1H), 2.70 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.68 - 2.64 (m, 2H), 2.45 (dd, $J = 18.0, 12.0$ Hz, 1H), 1.81 (s, 2H), 1.74 - 1.68 (m, 2H), 1.52 (s, 9H), 1.38 (s, 3H), 1.00 (t, $J = 7.3$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.38, 141.89, 140.10, 138.09, 135.93, 133.64, 128.91, 127.05, 126.72, 126.56, 124.64, 81.04, 58.16, 44.58, 37.71, 28.07, 26.44, 24.55, 13.88; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{25}\text{H}_{34}\text{NO}_2^+$ 380.2584; found 380.2585.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.782	BB	0.2145	5772.36963	401.09854	50.8520
2	8.612	BB	0.2334	5578.93408	356.87427	49.1480

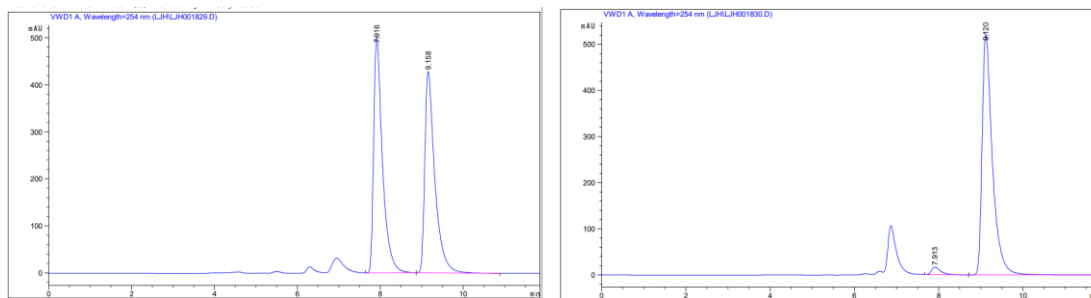
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.956	BB	0.2097	576.91602	41.28906	2.2276
2	8.715	BBA	0.2488	2.53211e4	1516.16333	97.7724

***tert*-Butyl (*R,E*)-2-amino-5-(4'-butyl-[1,1'-biphenyl]-4-yl)-2-methylpent-4-enoate (4s):**



Colorless oil (54.2 mg, 69%); $R_f = 0.27$ (petroleum ether/ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak IA-H

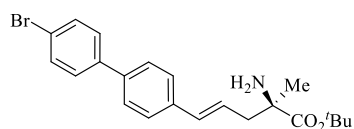
column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30$ °C), UV 254 nm, t_R (major) 9.120 min, t_R (minor) 7.913 min; $[\alpha]_D^{20} = +11.49$ ($c = 0.73$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.56 (d, $J = 12.0$ Hz, 2H), 7.54 (d, $J = 6.0$ Hz, 2H), 7.42 (d, $J = 6.0$ Hz, 2H), 7.27 (d, $J = 6.0$ Hz, 2H), 6.55 (d, $J = 18.0$ Hz, 1H), 6.21 (ddd, $J = 15.5, 8.1, 7.0$ Hz, 1H), 2.72 - 2.66 (m, 3H), 2.45 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.77 (s, 2H), 1.69 - 1.64 (m, 2H), 1.52 (s, 9H), 1.45 - 1.40 (m, 2H), 1.38 (s, 3H), 0.98 (t, $J = 7.4$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.42, 142.11, 140.11, 138.05, 135.94, 133.63, 128.86, 127.05, 126.74, 126.56, 124.67, 81.00, 58.15, 44.61, 35.31, 33.64, 28.07, 26.47, 22.41, 13.98; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{26}\text{H}_{36}\text{NO}_2^+$ 394.2741; found 394.2730.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.916	BB	0.2164	7369.56299	502.10611	50.6707
2	9.158	BBA	0.2466	7174.47949	427.95782	49.3293

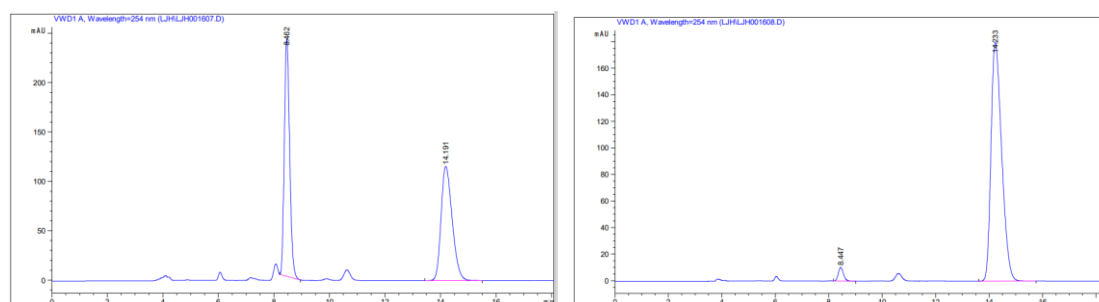
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.913	BB	0.2233	249.93297	16.50224	2.7485
2	9.120	BBA	0.2518	8843.65234	521.50635	97.2515

***tert*-Butyl (*R,E*)-2-amino-5-(4'-bromo-[1,1'-biphenyl]-4-yl)-2-methylpent-4-enoate (4t):**



White solid (49.2 mg, 59%); m.p. = 79-80 °C; R_f = 0.25 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak OD-

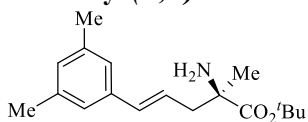
H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 14.233 min, t_R (minor) 8.447 min; $[\alpha]_D^{20}$ = +12.65 (c = 0.71, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.57 (d, J = 6.0 Hz, 2H), 7.51 (d, J = 6.0 Hz, 2H), 7.47 (d, J = 6.0 Hz, 2H), 7.42 (d, J = 6.0 Hz, 2H), 6.53 (d, J = 18.0 Hz, 1H), 6.25 – 6.20 (m, 1H), 2.69 (dd, J = 12.0, 6.0 Hz, 1H), 2.44 (dd, J = 12.0, 6.0 Hz, 1H), 1.78 (s, 2H), 1.51 (s, 9H), 1.38 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.37, 139.65, 138.81, 136.65, 133.36, 131.88, 128.47, 127.02, 126.71, 125.31, 121.49, 81.04, 58.14, 44.59, 28.07, 26.45; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{22}\text{H}_{27}\text{BrNO}_2^+$ 416.1220; found 416.1227.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.462	BB	0.2079	3201.81689	240.32304	49.9222
2	14.191	BB	0.4303	3211.79443	115.70697	50.0778

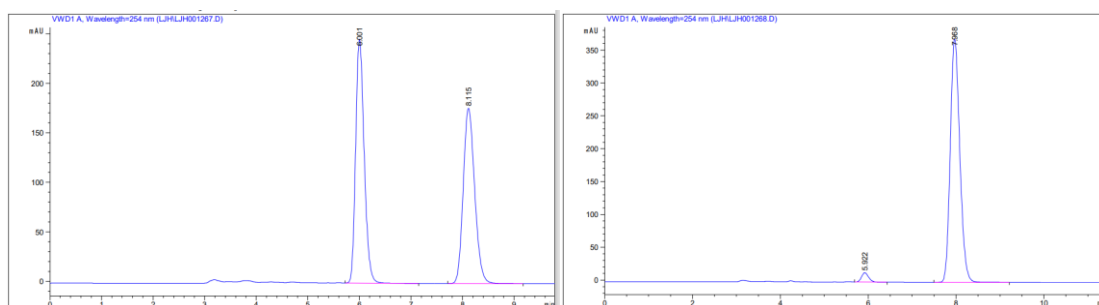
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.447	BB	0.2055	136.65524	10.22416	2.6684
2	14.233	BB	0.4282	4984.49316	179.89030	97.3316

***tert*-Butyl (*R,E*)-2-amino-5-(3,5-dimethylphenyl)-2-methylpent-4-enoate (4u):**



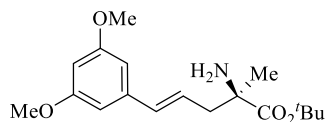
Colorless oil (40.3 mg, 71%); R_f = 0.23 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC

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) 7.968 min, t_R (minor) 5.922 min; $[\alpha]_D^{20} = +10.86$ ($c = 0.40$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.98 (s, 2H), 6.89 (s, 1H), 6.44 (d, $J = 12.0$ Hz, 1H), 6.26 – 5.99 (m, 1H), 2.65 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.41 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.32 (s, 6H), 1.82 (s, 2H), 1.50 (s, 9H), 1.36 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.38, 137.95, 137.12, 134.17, 129.06, 124.23, 124.09, 80.98, 58.13, 44.48, 28.04, 26.38, 21.25; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{28}\text{NO}_2^+$ 290.2115; found 290.2118.

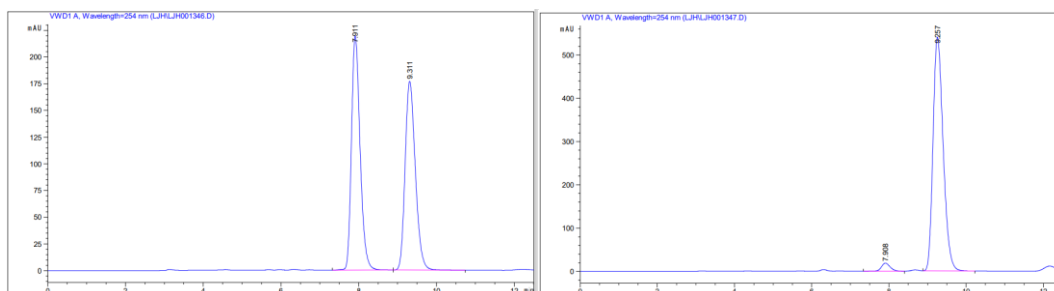


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.001	BB	0.1794	2830.98486	246.00703	50.9080	1	5.922	BB	0.1739	160.72661	14.24538	2.7997
2	8.115	BB	0.2396	2729.99268	177.09204	49.0920	2	7.968	BB	0.2342	5580.07520	370.04404	97.2003

***tert*-Butyl (*R,E*)-2-amino-5-(3,5-dimethoxyphenyl)-2-methylpent-4-enoate (4v):**

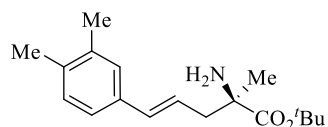


Colorless oil (41.7 mg, 65%); $R_f = 0.21$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R (major) 9.257 min, t_R (minor) 7.908 min; $[\alpha]_D^{20} = +11.20$ ($c = 0.73$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 6.42 (d, $J = 6.0$ Hz, 2H), 6.33 (d, $J = 12.0$ Hz, 1H), 6.28 (s, 1H), 6.08 -6.03 (m, 1H), 3.71 (s, 6H), 2.56 (dd, $J = 13.5, 6.9$ Hz, 1H), 2.31 (dd, $J = 13.5, 8.2$ Hz, 1H), 1.70 (s, 2H), 1.40 (s, 9H), 1.26 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.33, 160.89, 139.23, 133.95, 125.31, 104.31, 99.60, 81.02, 58.09, 55.30, 44.41, 28.03, 26.42; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{28}\text{NO}_4^+$ 322.2013; found 322.2019.



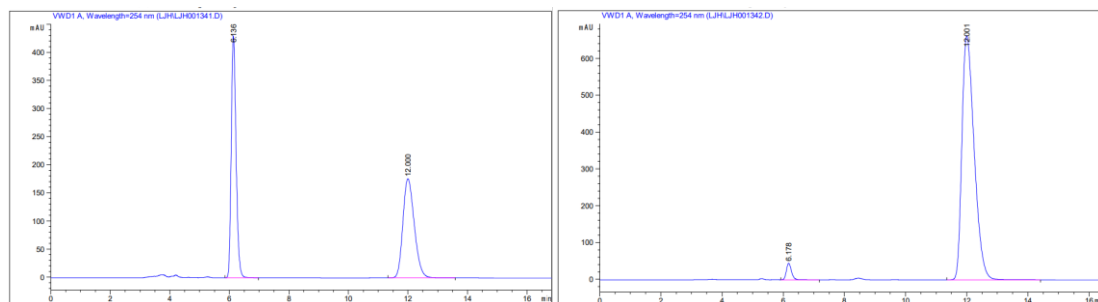
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.911	BB	0.2374	3392.70923	219.28722	51.2158	1	7.908	BB	0.2405	289.80240	18.55972	2.8608
2	9.311	BB	0.2831	3231.62842	176.93367	48.7842	2	9.257	BB	0.2824	9840.42676	540.32935	97.1392

***tert*-Butyl (*R,E*)-2-amino-5-(3,4-dimethylphenyl)-2-methylpent-4-enoate (4w):**



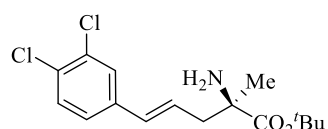
Colorless oil (39.7 mg, 69%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC analysis on Daicel Chirapak OD-H column

(hexane/isopropanol = 80/20, flow rate 1.0 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 12.001 min, t_R (minor) 6.178 min; $[\alpha]_D^{20} = +15.99$ ($c = 0.55$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.04 (s, 1H), 6.98 (q, $J = 8.0$ Hz, 2H), 6.35 (d, $J = 18.0$ Hz, 1H), 6.00 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.55 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.30 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.16 (s, 3H), 2.16 (s, 3H), 1.67 (s, 2H), 1.40 (s, 9H), 1.26 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.46, 136.58, 135.81, 134.88, 133.98, 129.79, 127.46, 123.63, 123.42, 80.94, 58.12, 44.53, 28.05, 26.43, 19.76, 19.48; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{28}\text{NO}_2^+$ 290.2115; found 290.2120.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.136	BB	0.1739	4849.01611	429.66846	50.9066	1	6.178	BB	0.1776	516.89404	45.03924	2.7274
2	12.000	BB	0.4116	4676.30566	176.25706	49.0934	2	12.001	BB	0.4310	1.84353e4	662.63470	97.2726

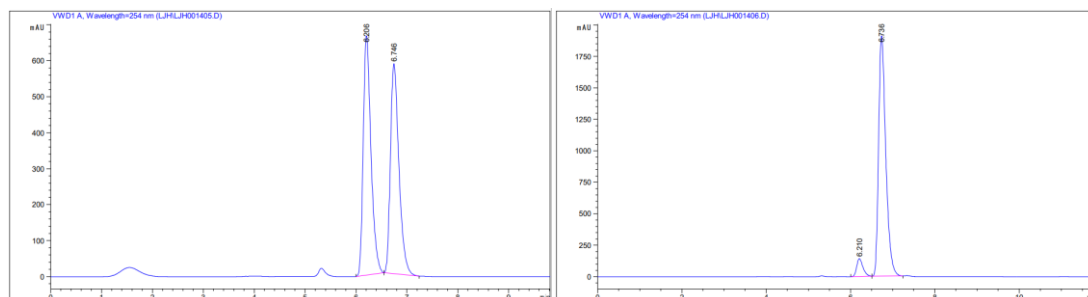
***tert*-Butyl (*R,E*)-2-amino-5-(3,4-dichlorophenyl)-2-methylpent-4-enoate (4x):**



Colorless oil (37.2 mg, 56%); $R_f = 0.22$ (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 = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 6.736 min, t_R (minor) 6.210 min; $[\alpha]_D^{20} = +6.15$ ($c = 0.48$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.39 - 7.34 (m, 2H), 7.14 (dd, $J = 12.0, 6.0$ Hz, 1H), 6.37 (d, $J = 12.0$ Hz, 1H), 6.19 - 6.14 (m, 1H), 2.61 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.40 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.69 (s, 2H), 1.47 (s, 9H), 1.33 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.18, 137.32, 132.63, 131.51, 130.91, 130.41, 127.87, 127.19, 125.31, 81.12,

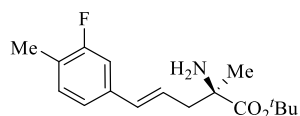
58.05, 44.39, 28.03, 26.37; **HRMS(ESI) m/z:** $[M+H]^+$ Calculated for $C_{16}H_{22}Cl_2NO_2^+$ 330.1022; found 330.1020.



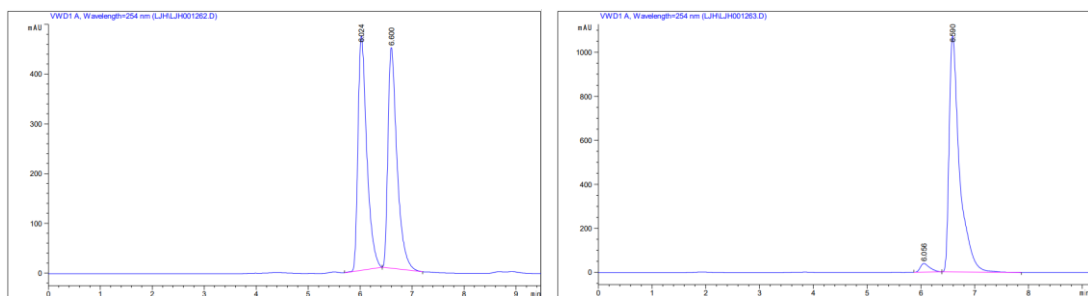
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.206	BB	0.1599	7036.67236	664.87317	50.9770
2	6.746	BB	0.1761	6766.93994	583.77429	49.0230

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.210	BB	0.1568	1462.01611	141.75027	6.0911
2	6.736	BB	0.1800	2.25406e4	1909.01563	93.9089

***tert*-Butyl (*R,E*)-2-amino-5-(3-fluoro-4-methylphenyl)-2-methylpent-4-enoate (**4y**):**



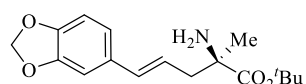
Colorless oil (39.1 mg, 66%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30$ °C), UV 254 nm, t_R (major) 6.590 min, t_R (minor) 6.056 min; $[\alpha]_D^{20} = +15.79$ ($c = 0.42$, $CHCl_3$); **1H NMR (600 MHz, $CDCl_3$)** δ 7.01 (t, $J = 6.0$ Hz, 1H), 6.90 (d, $J = 12.0$ Hz, 2H), 6.33 (d, $J = 18.0$ Hz, 1H), 6.03 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.55 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.31 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.17 (s, 3H), 1.66 (s, 2H), 1.40 (s, 9H), 1.26 (s, 3H); **^{13}C NMR (151 MHz, $CDCl_3$)** δ 176.32, 162.28(d, $J = 244.6$ Hz), 136.98(d, $J = 7.6$ Hz), 132.89, 131.41(d, $J = 6.1$ Hz), 125.09, 123.82(d, $J = 9.1$ Hz), 121.74(d, $J = 3.0$ Hz), 112.29(d, $J = 22.7$ Hz), 81.04, 58.09, 44.42, 28.03, 26.41, 14.32; **HRMS(ESI) m/z:** $[M+H]^+$ Calculated for $C_{17}H_{25}FNO_2^+$ 294.1864; found 294.1869.



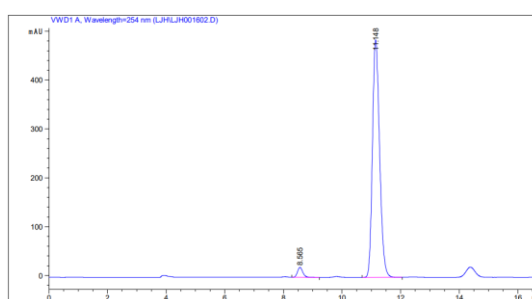
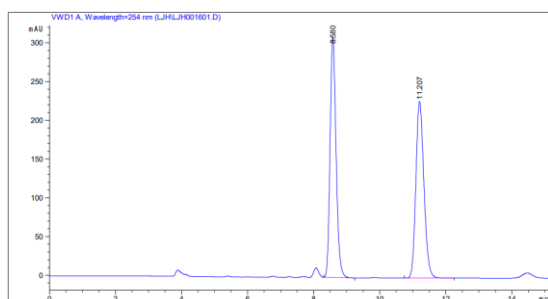
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.024	BB	0.1783	5553.04102	471.07623	50.7317
2	6.600	BB	0.1826	5392.85254	443.67047	49.2683

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.056	BB	0.1798	480.87225	39.52296	3.2266
2	6.590	BB	0.1962	1.44227e4	1072.67810	96.7734

***tert*-Butyl (*R,E*)-2-amino-5-(benzo[d][1,3]dioxol-5-yl)-2-methylpent-4-enoate (4z):**

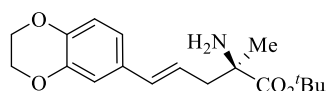


Colorless oil (37.2 mg, 61%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 11.148 min, $t_R(\text{minor})$ 8.565 min; $[\alpha]_D^{20} = +13.00$ ($c = 0.60$, CHCl_3); **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ 6.88 (s, 1H), 6.76 (q, $J = 8.0$ Hz, 2H), 6.40 (d, $J = 18.0$ Hz, 1H), 5.99 – 5.97 (m, 1H), 5.95 (s, 2H), 2.62 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.37 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.81 (s, 2H), 1.48 (s, 9H), 1.34 (s, 3H); **$^{13}\text{C NMR}$ (151 MHz, CDCl_3)** δ 176.38, 147.97, 146.99, 133.56, 131.72, 122.84, 120.67, 108.24, 105.54, 100.99, 80.98, 58.11, 44.40, 28.04, 26.38; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{24}\text{NO}_4^+$ 306.1700; found 306.1701.

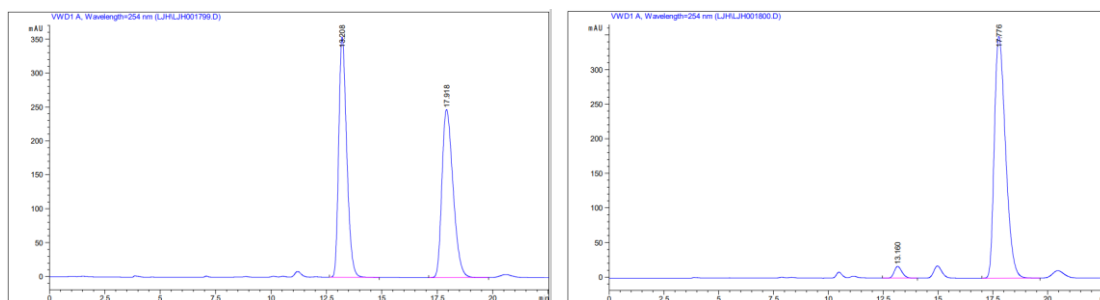


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.580	BB	0.1953	3907.31104	309.79144	50.3951	1	8.565	BB	0.1938	257.72379	20.42818	3.0269
2	11.207	BB	0.2610	3846.03882	227.97629	49.6049	2	11.148	BB	0.2637	8256.65137	486.23410	96.9731

***tert*-Butyl(*R,E*)-2-amino-5-(2,3-dihydrobenzo[b][1,4]dioxin-6-yl)-2-methylpent-4-enoate (4aa):**



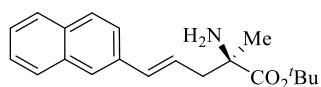
Colorless oil (38.4 mg, 60%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 93% by HPLC analysis on Daicel Chirapak OD-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 17.776 min, $t_R(\text{minor})$ 13.160 min; $[\alpha]_D^{20} = +10.39$ ($c = 0.74$, CHCl_3); **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ 6.78 - 6.70 (m, 3H), 6.28 (d, $J = 12.0$ Hz, 1H), 5.89 (ddd, $J = 15.5, 8.2, 7.0$ Hz, 1H), 4.17 (s, 4H), 2.54 (ddd, $J = 13.5, 6.8, 1.1$ Hz, 1H), 2.28 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.67 (s, 2H), 1.40 (s, 9H), 1.25 (s, 3H); **$^{13}\text{C NMR}$ (151 MHz, CDCl_3)** δ 176.40, 143.47, 143.07, 133.32, 131.07, 123.00, 119.56, 117.24, 114.69, 80.95, 64.43, 64.37, 58.10, 44.44, 28.05, 26.41; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{26}\text{NO}_4^+$ 320.1856; found 320.1852.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.208	BB	0.3864	8900.60547	354.29892	50.6869
2	17.918	BB	0.5464	8659.37500	247.66812	49.3131

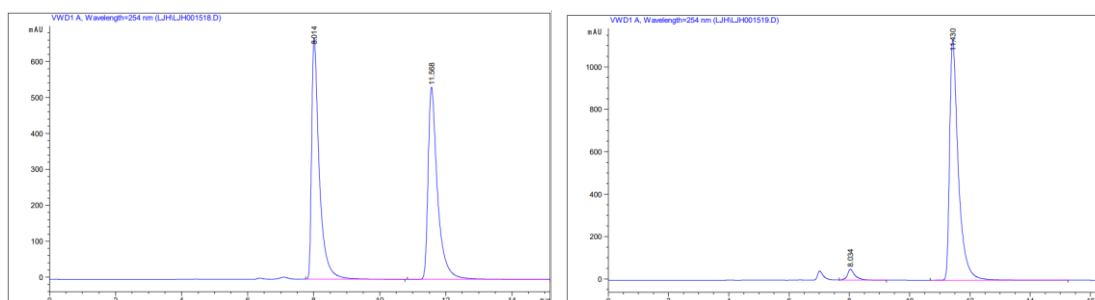
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.160	BB	0.3791	417.01700	16.93716	3.2531
2	17.776	BB	0.5543	1.24019e4	349.21277	96.7469

***tert*-Butyl (*R,E*)-2-amino-2-methyl-5-(naphthalen-2-yl)pent-4-enoate (4ab):**



White solid (47.2 mg, 76%); m.p. = 76-77 °C R_f = 0.23 (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined

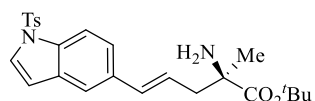
to be 92% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30 °C), UV 254 nm, t_R (major) 11.430 min, t_R (minor) 8.034 min; $[\alpha]_D^{20} = +16.06$ ($c = 0.60$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.80 (dd, $J = 12.7, 8.5$ Hz, 3H), 7.70 (s, 1H), 7.59 - 7.57 (m, 1H), 7.49 - 7.43 (m, 2H), 6.67 (d, $J = 12.0$ Hz, 1H), 6.33 - 6.28 (m, 1H), 2.73 (ddd, $J = 13.5, 6.8, 0.9$ Hz, 1H), 2.49 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.83 (s, 2H), 1.51 (s, 9H), 1.40 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.40, 134.66, 134.08, 133.64, 132.90, 128.17, 127.93, 127.66, 126.23, 125.90, 125.73, 125.19, 123.51, 81.05, 58.19, 44.69, 28.07, 26.46; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{20}\text{H}_{26}\text{NO}_2^+$ 312.1958; found 312.1956.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.014	BB	0.2362	1.08207e4	671.12646	50.4418
2	11.568	BBA	0.2932	1.06312e4	534.68170	49.5582

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.034	BB	0.2505	889.48541	50.89672	3.7592
2	11.430	BB	0.2973	2.27723e4	1132.24475	96.2408

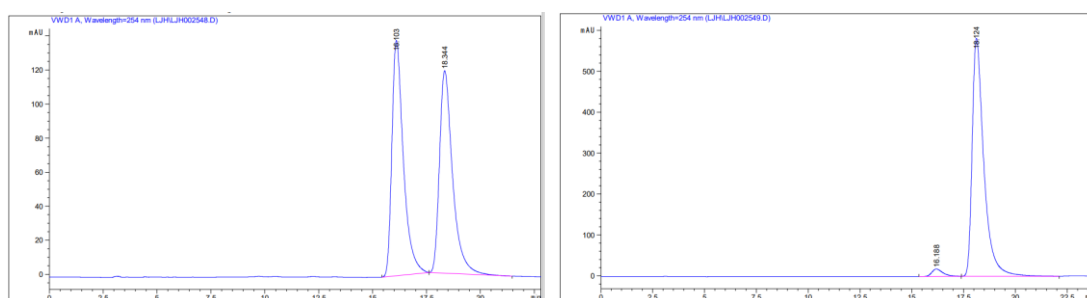
***tert*-Butyl (*R,E*)-2-amino-2-methyl-5-(1-tosyl-1H-indol-5-yl)pent-4-enoate (4ac):**



Colorless oil (46.3 mg, 51%); R_f = 0.24 (petroleum ether/ ethyl acetate = 1:1); the enantiomeric excess was determined to be 94% by HPLC

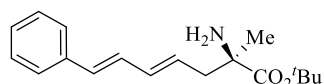
analysis on Daicel Chirapak IF-H column (hexane/isopropanol = 80/20, flow rate 1.0 mL/min, T =

30 °C), UV 254 nm, $t_{R}(\text{major})$ 18.124 min, $t_{R}(\text{minor})$ 16.188 min; $[\alpha]_{D}^{20} = +16.47$ ($c = 0.51$, CHCl_3); **^1H NMR (600 MHz, CDCl_3)** δ 7.90 (d, $J = 6.0$ Hz, 1H), 7.74 (d, $J = 6.0$ Hz, 2H), 7.52 (d, $J = 6.0$ Hz, 1H), 7.43 (s, 1H), 7.32 (d, $J = 6.0$ Hz, 1H), 7.20 (d, $J = 6.0$ Hz, 2H), 6.60 (d, $J = 3.2$ Hz, 1H), 6.52 (d, $J = 18.0$ Hz, 1H), 6.13-6.07(m, 1H), 2.64 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.43 – 2.35 (m, 1H), 2.33 (s, 3H), 1.75 (s, 2H), 1.47 (s, 9H), 1.33 (s, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ 176.39, 144.93, 135.29, 134.23, 133.86, 132.80, 131.13, 129.87, 126.81, 124.13, 122.85, 119.06, 113.59, 109.20, 80.99, 58.12, 44.50, 28.05, 26.41, 21.54; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{25}\text{H}_{31}\text{N}_2\text{O}_4\text{S}^+$ 455.1999; found 455.2000.

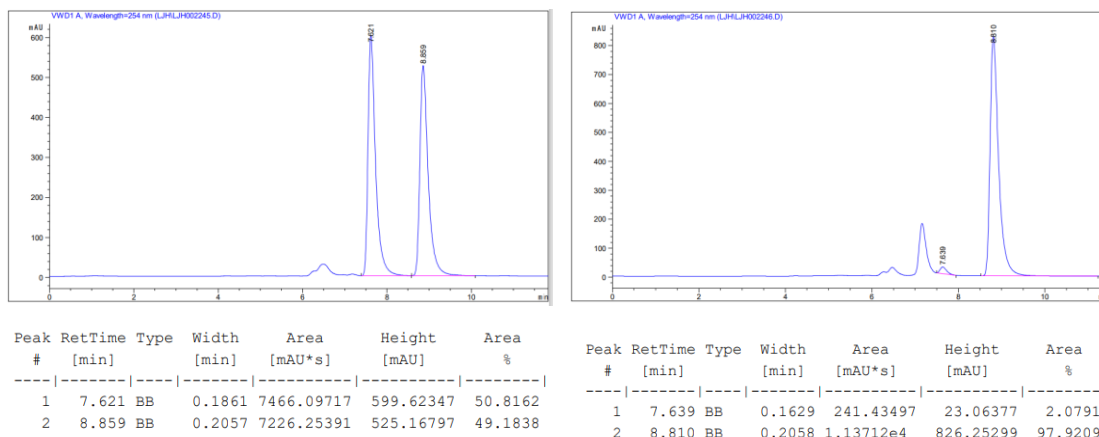


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.103	BB	0.5569	5108.42334	138.09941	50.4489	1	16.188	BB	0.5620	676.27881	18.12844	2.8870
2	18.344	BB	0.6340	5017.51172	118.83975	49.5511	2	18.124	BB	0.5834	2.27486e4	581.23383	97.1130

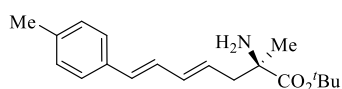
***tert*-Butyl (*R,4E,6E*)-2-amino-2-methyl-7-phenylhepta-4,6-dienoate (4ad):**



Colorless oil (35.6 mg, 62%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 1.0 mL/min, $T = 30$ °C), UV 254 nm, $t_{R}(\text{major})$ 8.810 min, $t_{R}(\text{minor})$ 7.639 min; $[\alpha]_{D}^{20} = +7.85$ ($c = 0.76$, CHCl_3); **^1H NMR (600 MHz, CDCl_3)** δ 7.37 (d, $J = 12.0$ Hz, 2H), 7.33 – 7.26 (m, 2H), 7.20 (t, $J = 7.3$ Hz, 1H), 6.74 (dd, $J = 18.0, 12.0$ Hz, 1H), 6.47 (d, $J = 12.0$ Hz, 1H), 6.28 (dd, $J = 12.0, 6.0$ Hz, 1H), 5.75 – 5.70 (m, 1H), 2.57 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.32 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.68 (s, 2H), 1.47 (s, 9H), 1.31 (s, 3H); **^{13}C NMR (151 MHz, CDCl_3)** δ 176.38, 137.36, 134.61, 131.45, 129.05, 128.75, 128.58, 127.39, 126.28, 80.97, 58.13, 44.39, 28.04, 26.43; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{18}\text{H}_{26}\text{NO}_2^+$ 288.1958; found 288.1960.

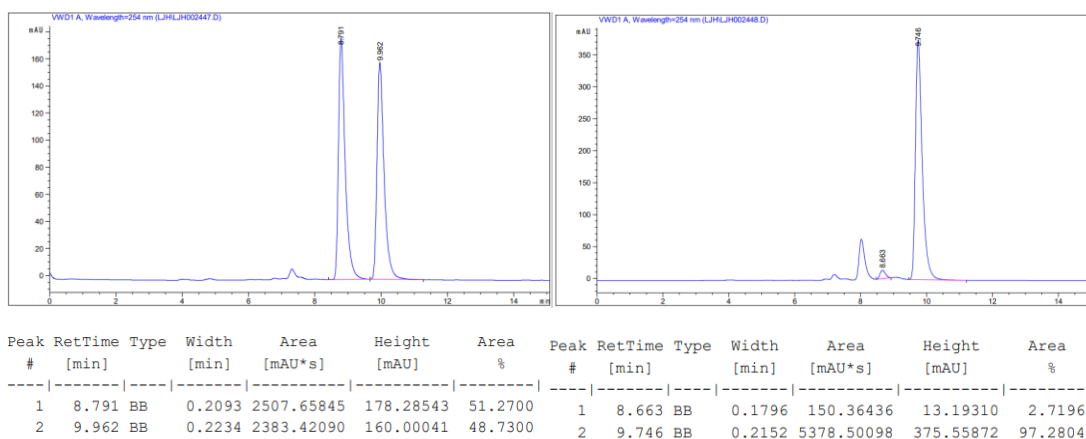


***tert*-Butyl (*R*,*4E*,*6E*)-2-amino-2-methyl-7-(*p*-tolyl)hepta-4,6-dienoate (**4ae**):**

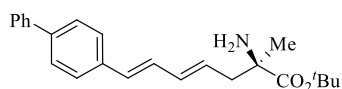


Colorless oil (37.9 mg, 64%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95%

by HPLC analysis on Daicel Chirapak IF-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 9.746 min, t_R (minor) 8.663 min; $[\alpha]_D^{20} = +12.40$ ($c = 0.72$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.27 (d, $J = 12.0$ Hz, 2H), 7.11 (d, $J = 6.0$ Hz, 2H), 6.69 (dd, $J = 12.0, 6.0$ Hz, 1H), 6.44 (d, $J = 18.0$ Hz, 1H), 6.27 (dd, $J = 12.0, 12.0$ Hz, 1H), 5.71-5.66 (m, 1H), 2.57 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.33 (s, 3H), 2.30 (d, $J = 6.0$ Hz, 1H), 1.70 (s, 2H), 1.47 (s, 9H), 1.31 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.40, 137.26, 134.78, 134.57, 131.44, 129.30, 128.36, 127.80, 126.20, 80.96, 58.13, 44.39, 28.04, 26.41, 21.20; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{19}\text{H}_{28}\text{NO}_2^+$ 302.2115; found 302.2119.



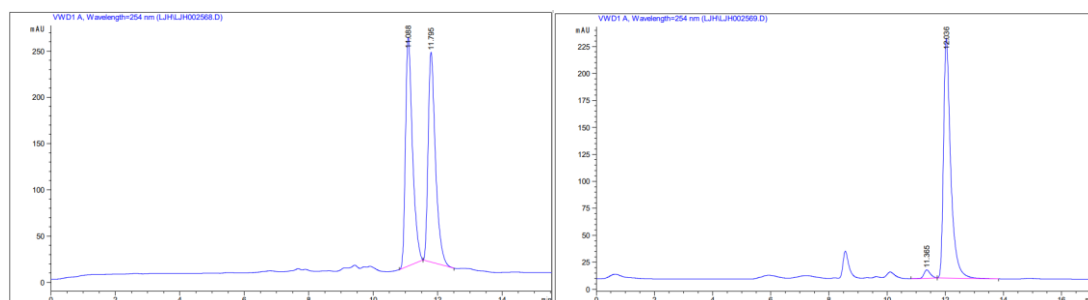
***tert*-Butyl (*R*,*4E*,*6E*)-7-([1,1'-biphenyl]-4-yl)-2-amino-2-methylhepta-4,6-dienoate (**4af**):**



White solid (35.5 mg, 49%); m.p. = 109-110 $^\circ\text{C}$; $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was

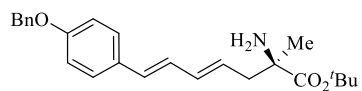
determined to be 94% by HPLC analysis on Daicel Chirapak IF-H column (hexane/isopropanol =

90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 12.036 min, t_R (minor) 11.365 min; $[\alpha]_D^{20} = +28.42$ ($c = 0.40$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.59 (d, $J = 12.0$ Hz, 2H), 7.54 (d, $J = 6.0$ Hz, 2H), 7.45-7.41 (m, 4H), 7.33 (t, $J = 6.0$ Hz, 1H), 6.78 (m, 1H), 6.51 (d, $J = 18.0$ Hz, 1H), 6.31 (d, $J = 6.0$ Hz, 1H), 5.77-5.72 (m, 1H), 2.59 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.34 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.71 (s, 2H), 1.48 (s, 9H), 1.32 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.38, 140.70, 140.13, 136.43, 134.68, 131.00, 129.18, 128.85, 128.79, 127.27, 126.89, 126.72, 81.01, 58.16, 44.43, 28.06, 26.44; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{24}\text{H}_{30}\text{NO}_2^+$ 364.2271; found 364.2276.



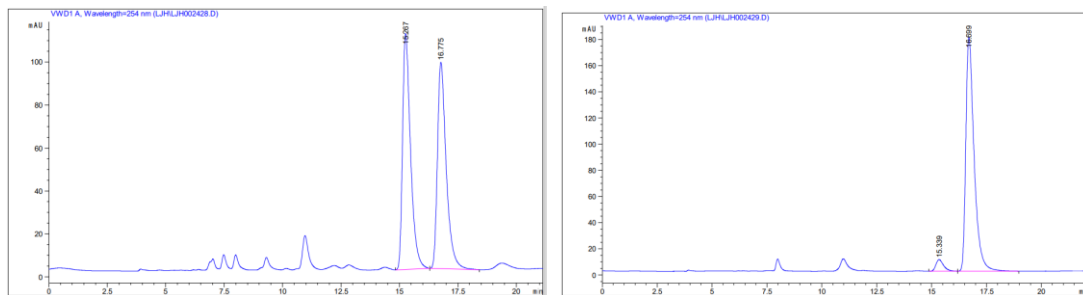
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.088	BB	0.2256	3727.83984	247.05945	50.9610	1	11.365	BB	0.2292	116.06969	7.72519	2.9569
2	11.795	BB	0.2383	3587.24585	227.01712	49.0390	2	12.036	BB	0.2556	3809.27783	221.92734	97.0431

***tert*-Butyl (*R,4E,6E*)-2-amino-7-(4-(benzyloxy)phenyl)-2-methylhepta-4,6-dienoate (4ag):**



White solid (36.2 mg, 46%); m.p. = 78-79 °C; $R_f = 0.24$ (petroleum ether/ ethyl acetate = 1:1); the enantiomeric excess

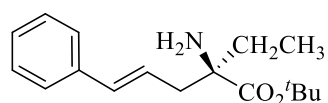
was determined to be 91% by HPLC analysis on Daicel Chirapak IF-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 16.699 min, t_R (minor) 15.339 min; $[\alpha]_D^{20} = +14.21$ ($c = 0.57$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.42 (d, $J = 6.0$ Hz, 2H), 7.38 (t, $J = 6.0$ Hz, 2H), 7.34 - 7.25 (m, 3H), 6.91 (d, $J = 6.0$ Hz, 2H), 6.61 (dd, $J = 12.0, 6.0$ Hz, 1H), 6.42 (d, $J = 12.0$ Hz, 1H), 6.26 (dd, $J = 18.0, 12.0$ Hz, 1H), 5.69-5.64 (m, 1H), 5.06 (s, 2H), 2.57 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.31 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.72 (s, 2H), 1.47 (s, 9H), 1.31 (s, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.39, 158.37, 136.96, 134.83, 130.99, 130.47, 128.59, 127.98, 127.82, 127.47, 126.92, 115.06, 80.97, 70.08, 58.15, 44.38, 28.05, 26.40; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{25}\text{H}_{32}\text{NO}_3^+$ 394.2377; found 394.2382.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.267	BB	0.3581	2601.28076	109.77973	50.8470
2	16.775	BB	0.3942	2514.61450	96.10860	49.1530

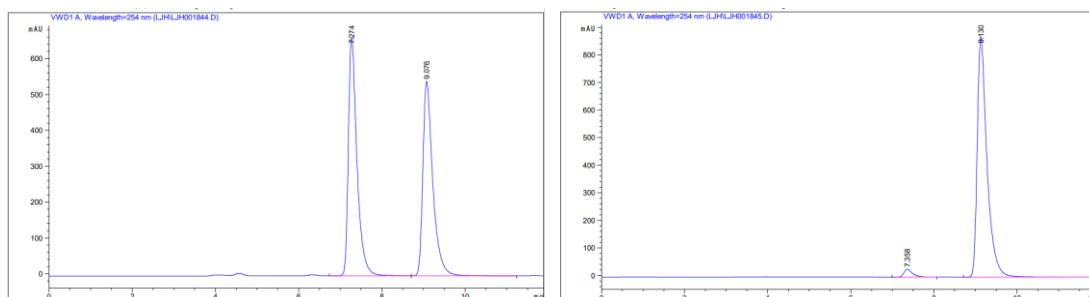
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	15.339	BB	0.3662	215.64597	8.93388	4.3969
2	16.699	BB	0.3933	4688.85938	178.84898	95.6031

tert-Butyl (*R,E*)-2-amino-2-ethyl-5-phenylpent-4-enoate (5a):



Colorless oil (34.7 mg, 63%); $R_f = 0.22$ (petroleum ether/ ethyl acetate = 5:1); the enantiomeric excess was determined to be 94%

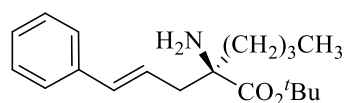
by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 95/5, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 9.130 min, t_R (minor) 7.358 min; $[\alpha]_D^{20} = +22.34$ ($c = 0.48$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.26 – 7.19 (m, 4H), 7.14 (t, $J = 7.2$ Hz, 1H), 6.41 (d, $J = 12.0$ Hz, 1H), 6.05 (ddd, $J = 15.5, 8.3, 6.8$ Hz, 1H), 2.60 (ddd, $J = 13.5, 6.7, 1.0$ Hz, 1H), 2.29 (dd, $J = 13.5, 8.5$ Hz, 1H), 1.78 - 1.72 (m, 1H), 1.61 (s, 2H), 1.54 – 1.48 (m, 1H), 1.41 (s, 9H), 0.83 (t, $J = 6.0$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 175.86, 137.20, 134.01, 128.52, 127.32, 126.16, 124.66, 81.01, 61.53, 43.42, 32.99, 28.10, 8.20; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{17}\text{H}_{26}\text{NO}_2^+$ 276.1958; found 276.1954.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.274	BB	0.2157	9550.26465	664.84900	51.4850
2	9.076	BB	0.2477	8999.33691	541.83380	48.5150

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.358	BB	0.2143	416.89499	28.76424	2.8414
2	9.130	BB	0.2418	1.42551e4	871.68939	97.1586

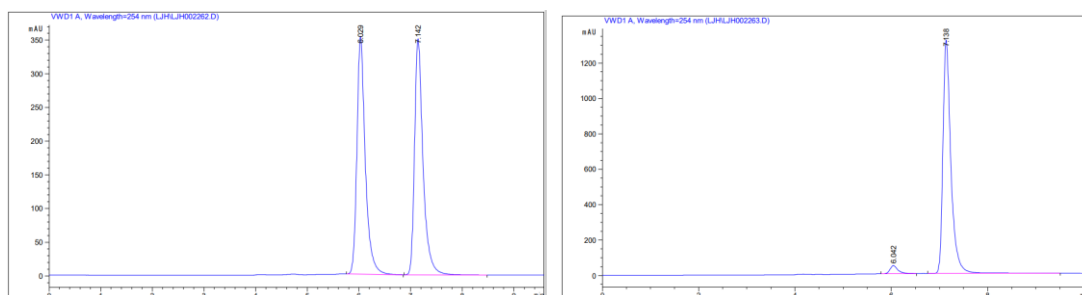
tert-Butyl (*R*)-2-amino-2-cinnamylhexanoate (5b):



Colorless oil (35.1 mg, 57%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 5:1); the enantiomeric excess was determined to be 93%

by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8

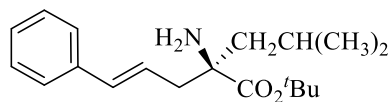
mL/min, T = 30 °C), UV 254 nm, t_R (major) 7.138 min, t_R (minor) 6.042 min; $[\alpha]_D^{20} = +15.38$ ($c = 0.31$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.33 – 7.26 (m, 4H), 7.21 (t, $J = 6.0$ Hz, 1H), 6.48 (d, $J = 12.0$ Hz, 1H), 6.11 (ddd, $J = 15.5, 8.4, 6.7$ Hz, 1H), 2.67 (ddd, $J = 13.5, 6.6, 1.0$ Hz, 1H), 2.36 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.80 – 1.75 (m, 1H), 1.68 (s, 2H), 1.57 – 1.52 (m, 1H), 1.48 (s, 9H), 1.40 – 1.28 (m, 3H), 1.22 – 1.12 (m, 1H), 0.91 (t, $J = 6.0$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.02, 137.20, 134.04, 128.52, 127.32, 126.17, 124.60, 80.99, 61.21, 43.78, 39.86, 28.10, 26.06, 23.00, 13.96; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{19}\text{H}_{30}\text{NO}_2^+$ 304.2271; found 304.2268.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.029	BB	0.1680	3969.00195	352.06573	49.8332
2	7.142	BB	0.1711	3995.56738	350.09576	50.1668

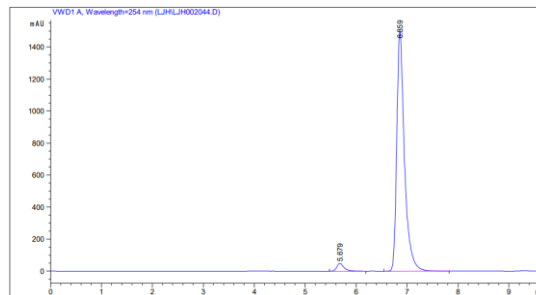
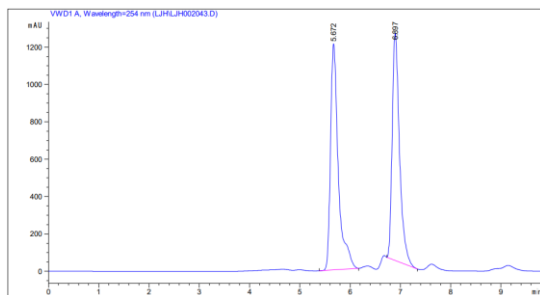
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.042	BB	0.1692	520.57434	45.74467	3.3365
2	7.138	BB	0.1715	1.50819e4	1316.65442	96.6635

***tert*-Butyl (*R,E*)-2-amino-2-isobutyl-5-phenylpent-4-enoate (**5c**):**



Colorless oil (38.9 mg, 64%); $R_f = 0.26$ (petroleum ether/ ethyl acetate = 5:1); the enantiomeric excess was determined to be

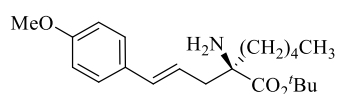
94% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 6.859 min, t_R (minor) 5.679 min; $[\alpha]_D^{20} = +18.44$ ($c = 0.30$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.33 – 7.26 (m, 4H), 7.21 (t, $J = 7.1$ Hz, 1H), 6.47 (d, $J = 18.0$ Hz, 1H), 6.09 (ddd, $J = 15.4, 8.5, 6.7$ Hz, 1H), 2.66 (ddd, $J = 13.5, 6.6, 1.1$ Hz, 1H), 2.33 (dd, $J = 13.4, 8.6$ Hz, 1H), 1.85 – 1.73 (m, 2H), 1.68 (s, 2H), 1.53 (q, $J = 8.1$ Hz, 1H), 1.48 (s, 9H), 0.97 (d, $J = 6.0$ Hz, 3H), 0.90 (d, $J = 6.0$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.51, 137.17, 134.22, 128.53, 127.34, 126.18, 124.33, 81.14, 60.98, 48.42, 45.36, 28.08, 24.69, 24.50, 23.41; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{19}\text{H}_{30}\text{NO}_2^+$ 304.2271; found 304.2268.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.672	BB	0.1596	1.30817e4	1210.39148	51.5057
2	6.897	BB	0.1532	1.23169e4	1215.31604	48.4943

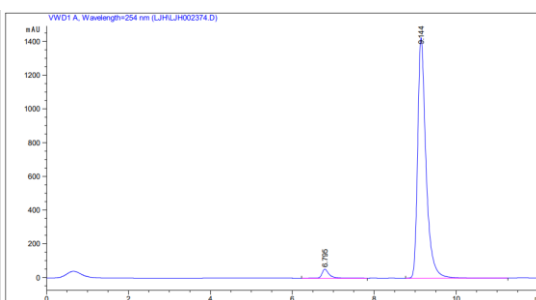
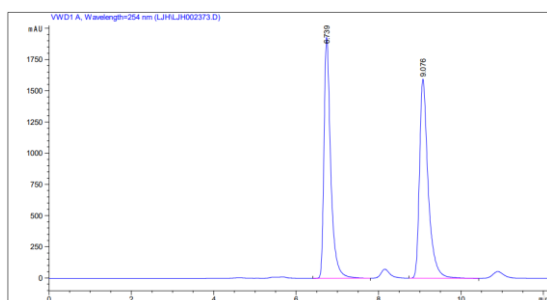
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.679	BB	0.1476	477.93964	48.24855	2.9397
2	6.859	BB	0.1567	1.57802e4	1494.67444	97.0603

***tert*-Butyl (*R,E*)-2-amino-2-(3-(4-methoxyphenyl)allyl)heptanoate (**5d**):**



Colorless oil (41.6 mg, 60%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94%

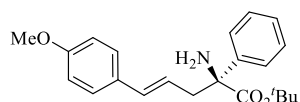
by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 9.144 min, $t_R(\text{minor})$ 6.795 min; $[\alpha]_D^{20} = +17.74$ ($c = 0.62$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.25 (d, $J = 6.0$ Hz, 2H), 6.83 (d, $J = 12.0$ Hz, 2H), 6.42 (d, $J = 18.0$ Hz, 1H), 5.98 – 5.93 (m, 1H), 3.79 (s, 3H), 2.65 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.33 (dd, $J = 13.5, 8.5$ Hz, 1H), 1.78 – 1.73 (m, 1H), 1.72 (s, 2H), 1.55 – 1.50 (m, 1H), 1.47 (s, 9H), 1.40 – 1.36 (m, 1H), 1.33 – 1.26 (m, 4H), 1.21 – 1.16 (m, 1H), 0.89 (t, $J = 7.0$ Hz, 3H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 176.09, 159.03, 133.44, 130.06, 127.29, 122.25, 113.95, 80.90, 61.26, 55.27, 43.80, 40.14, 32.10, 28.10, 23.52, 22.46, 13.96; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{21}\text{H}_{34}\text{NO}_3^+$ 348.2533; found 348.2535.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.739	BB	0.1699	2.18336e4	1929.86108	48.5026
2	9.076	BB	0.2162	2.31817e4	1594.78406	51.4974

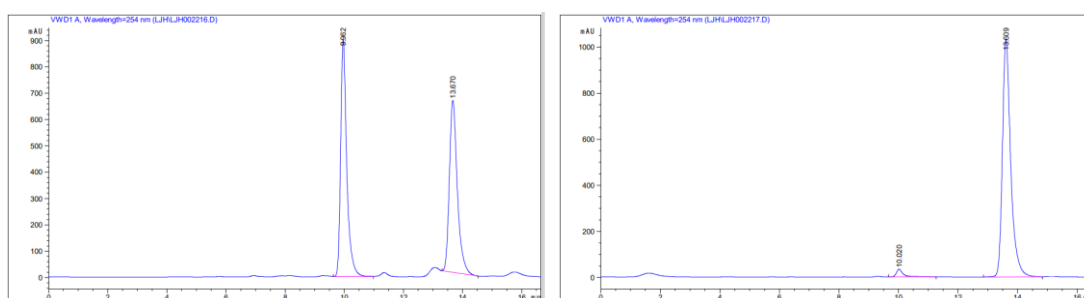
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.795	BB	0.1763	645.71362	53.87347	3.1069
2	9.144	BB	0.2115	2.01375e4	1425.53528	96.8931

***tert*-Butyl (*S,E*)-2-amino-5-(4-methoxyphenyl)-2-phenylpent-4-enoate (**5e**):**



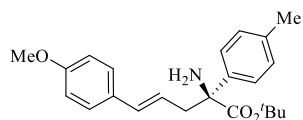
Colorless oil (45.1 mg, 64%); $R_f = 0.26$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95% by HPLC

analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 13.609 min, t_R (minor) 10.020 min; $[\alpha]_D^{20} = -19.11$ ($c = 0.59$, CHCl_3); **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ 7.57 (d, $J = 6.0$ Hz, 2H), 7.35 (t, $J = 7.7$ Hz, 2H), 7.29 – 7.24 (m, 3H), 6.83 (d, $J = 12.0$ Hz, 2H), 6.49 (d, $J = 18.0$ Hz, 1H), 6.01 – 5.96 (m, 1H), 3.79 (s, 3H), 3.09 (dd, $J = 12.0$, 6.0 Hz, 1H), 2.71 (dd, $J = 18.0$, 12.0 Hz, 1H), 1.98 (s, 2H), 1.45 (s, 9H); **$^{13}\text{C NMR}$ (151 MHz, CDCl_3)** δ 174.35, 159.11, 143.52, 134.13, 130.01, 128.31, 127.35, 127.28, 125.43, 122.37, 113.98, 81.66, 63.78, 55.30, 43.94, 27.92; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{22}\text{H}_{28}\text{NO}_3^+$ 354.2064; found 354.2057.

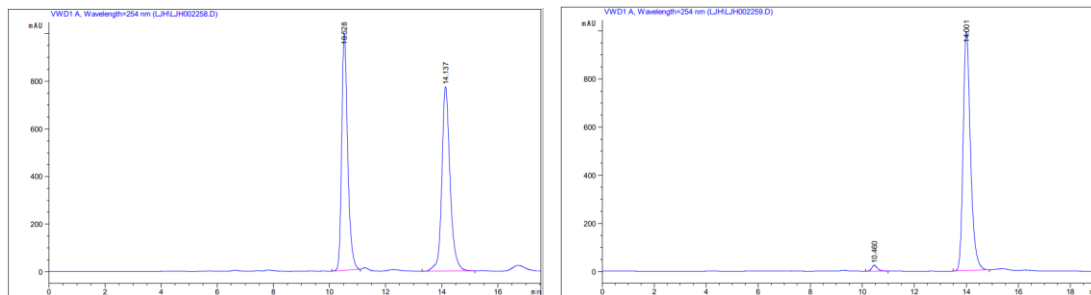


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.962	BB	0.2136	1.28701e4	899.45239	51.2938	1	10.020	BB	0.2370	545.73926	33.44857	2.6634
2	13.670	BB	0.2839	1.22209e4	653.01886	48.7062	2	13.609	BB	0.2901	1.99443e4	1029.91016	97.3366

***tert*-Butyl (*S,E*)-2-amino-5-(4-methoxyphenyl)-2-(*p*-tolyl)pent-4-enoate (**5f**):**



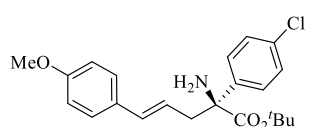
Colorless oil (44.7 mg, 61%); $R_f = 0.23$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 14.001 min, t_R (minor) 10.460 min; $[\alpha]_D^{20} = -25.77$ ($c = 0.59$, CHCl_3); **$^1\text{H NMR}$ (600 MHz, CDCl_3)** δ 7.45 (d, $J = 6.0$ Hz, 2H), 7.25 (d, $J = 12.0$ Hz, 2H), 7.16 (d, $J = 6.0$ Hz, 2H), 6.83 (d, $J = 6.0$ Hz, 2H), 6.48 (d, $J = 18.0$ Hz, 1H), 6.01 – 5.96 (m, 1H), 3.79 (s, 3H), 3.07 (dd, $J = 13.6$, 6.8 Hz, 1H), 2.69 (dd, $J = 13.5$, 8.0 Hz, 1H), 2.34 (s, 3H), 1.95 (s, 2H), 1.44 (s, 9H); **$^{13}\text{C NMR}$ (151 MHz, CDCl_3)** δ 174.48, 159.09, 140.58, 136.87, 134.03, 130.05, 129.01, 127.34, 125.31, 122.50, 113.97, 81.56, 63.56, 55.29, 43.98, 27.96, 20.99; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{23}\text{H}_{30}\text{NO}_3^+$ 368.2220; found 368.2223.



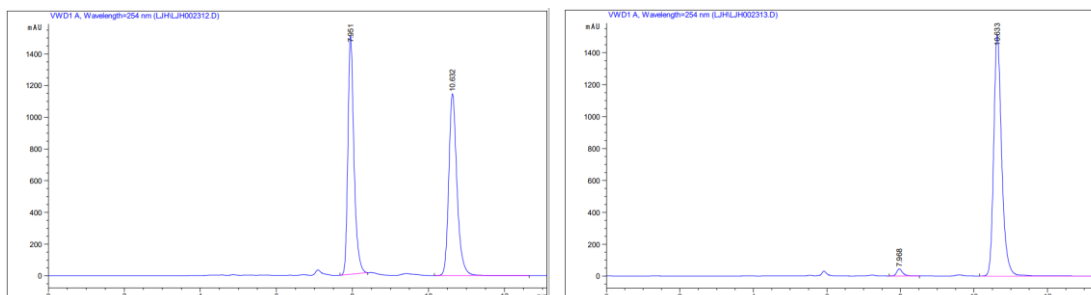
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.528	BB	0.2256	1.47435e4	993.37024	48.2203
2	14.137	BB	0.3082	1.58318e4	775.26245	51.7797

Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.460	BB	0.2254	367.70737	24.59619	1.8547
2	14.001	BB	0.2972	1.94579e4	992.65302	98.1453

***tert*-Butyl (*S,E*)-2-amino-2-(4-chlorophenyl)-5-(4-methoxyphenyl)pent-4-enoate (**5g**):**



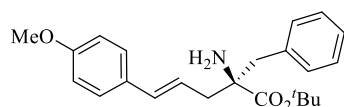
Colorless oil (44.9 mg, 58%); $R_f = 0.21$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 80/20, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, t_R (major) 10.633 min, t_R (minor) 7.968 min; $[\alpha]_D^{20} = -37.78$ ($c = 0.51$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.53 (d, $J = 6.0$ Hz, 2H), 7.32 (d, $J = 12.0$ Hz, 2H), 7.25 (d, $J = 6.0$ Hz, 2H), 6.83 (d, $J = 12.0$ Hz, 2H), 6.47 (d, $J = 15.8$ Hz, 1H), 5.97 – 5.92 (m, 1H), 3.79 (s, 3H), 3.04 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.66 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.92 (s, 2H), 1.44 (s, 9H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 173.95, 159.19, 142.03, 134.40, 133.17, 129.83, 128.39, 127.37, 127.07, 121.86, 114.00, 81.97, 63.43, 55.30, 44.05, 27.92; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{22}\text{H}_{27}\text{ClNO}_3^+$ 388.1674; found 388.1676.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.951	BB	0.1688	1.66900e4	1504.07629	49.2703
2	10.632	BB	0.2274	1.71844e4	1146.46521	50.7297

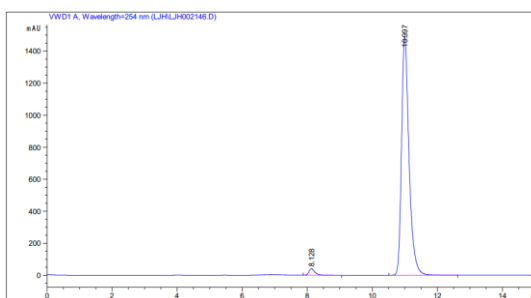
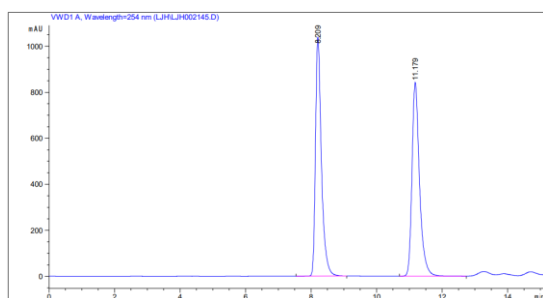
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.968	BB	0.1683	493.05054	44.12591	2.1240
2	10.633	BBA	0.2280	2.27206e4	1510.63049	97.8760

***tert*-Butyl (*S,E*)-2-amino-2-benzyl-5-(4-methoxyphenyl)pent-4-enoate (**5h**):**



Colorless oil (44.7 mg, 60%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96% by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8

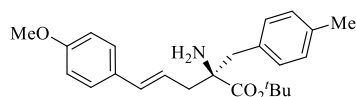
mL/min, T = 30 °C), UV 254 nm, $t_R(\text{major})$ 10.997 min, $t_R(\text{minor})$ 8.128 min; $[\alpha]_D^{20} = +9.49$ ($c = 0.69$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.29 – 7.23 (m, 7H), 6.83 (d, $J = 12.0$ Hz, 2H), 6.46 (d, $J = 12.0$ Hz, 1H), 5.97 (ddd, $J = 15.5, 8.4, 6.8$ Hz, 1H), 3.79 (s, 3H), 3.21 (d, $J = 12.0$ Hz, 1H), 2.92 – 2.70 (m, 2H), 2.40 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.63 (s, 2H), 1.46 (s, 9H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 175.31, 159.09, 136.56, 133.78, 130.26, 129.97, 128.25, 127.33, 126.89, 121.81, 113.98, 81.43, 62.03, 55.29, 45.75, 44.36, 28.14; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{23}\text{H}_{30}\text{NO}_3^+$ 368.2220; found 368.2218.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.209	BB	0.1889	1.30559e4	1038.84351	49.2939
2	11.179	BB	0.2401	1.34300e4	841.77106	50.7061

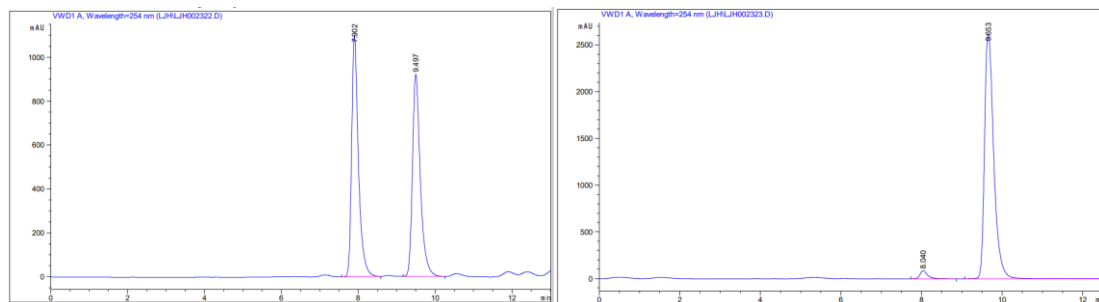
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.128	BB	0.1908	528.64502	41.11035	2.1668
2	10.997	BB	0.2408	2.38684e4	1490.17078	97.8332

***tert*-Butyl (*S,E*)-2-amino-5-(4-methoxyphenyl)-2-(4-methylbenzyl)pent-4-enoate (**5i**):**



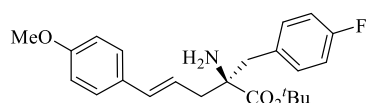
Colorless oil (47.2 mg, 62%); $R_f = 0.25$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 95%

by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, $t_R(\text{major})$ 9.653 min, $t_R(\text{minor})$ 8.040 min; $[\alpha]_D^{20} = +9.64$ ($c = 0.57$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.25 (d, $J = 6.0$ Hz, 2H), 7.12 (d, $J = 12.0$ Hz, 2H), 7.08 (d, $J = 6.0$ Hz, 2H), 6.83 (d, $J = 6.0$ Hz, 2H), 6.45 (d, $J = 12.0$ Hz, 1H), 5.97 (ddd, $J = 15.5, 8.3, 6.9$ Hz, 1H), 3.79 (s, 3H), 3.17 (d, $J = 12.0$ Hz, 1H), 2.79 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.75 (d, $J = 12.0$ Hz, 1H), 2.40 – 2.37 (m, 1H), 2.31 (s, 3H), 1.64 (s, 2H), 1.47 (s, 9H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 175.41, 159.08, 136.40, 133.69, 133.38, 130.10, 130.01, 128.96, 127.32, 121.92, 113.98, 81.36, 62.04, 55.29, 45.28, 44.34, 28.16, 21.04; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{24}\text{H}_{32}\text{NO}_3^+$ 382.2377; found 382.2377.



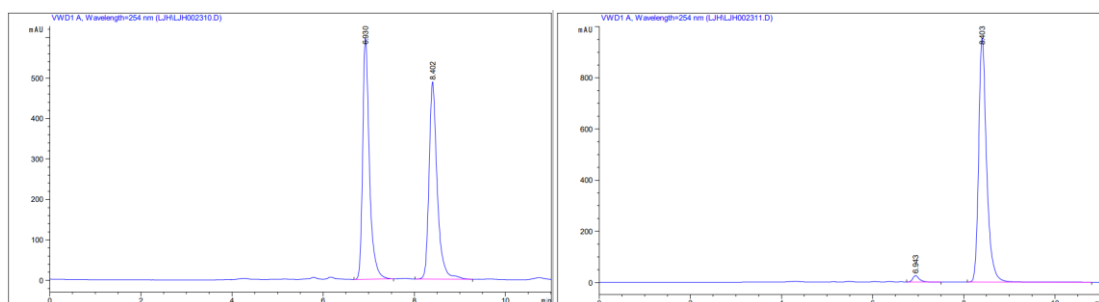
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.902	BB	0.1823	1.34223e4	1095.83569	50.7613	1	8.040	BB	0.1903	1091.96704	86.04393	2.5645
2	9.497	BB	0.2131	1.30197e4	920.33545	49.2387	2	9.653	BBA	0.2422	4.14877e4	2611.04785	97.4355

tert-Butyl (*S,E*)-2-amino-2-(4-fluorobenzyl)-5-(4-methoxyphenyl)pent-4-enoate (5j):



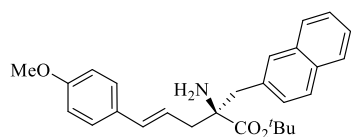
Colorless oil (43.9 mg, 57%); $R_f = 0.23$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 96%

by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 80/20, flow rate 0.8 mL/min, $T = 30\text{ }^\circ\text{C}$), UV 254 nm, $t_R(\text{major})$ 8.403 min, $t_R(\text{minor})$ 6.943 min; $[\alpha]_D^{20} = +12.71$ ($c = 0.44$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.26 (d, $J = 6.0$ Hz, 2H), 7.21 (dd, $J = 12.0, 6.0$ Hz, 2H), 6.97 (t, $J = 8.6$ Hz, 2H), 6.83 (d, $J = 8.6$ Hz, 2H), 6.45 (d, $J = 18.0$ Hz, 1H), 5.98 – 5.93 (m, 1H), 3.79 (s, 3H), 3.17 (d, $J = 18.0$ Hz, 1H), 2.81 - 2.75 (m, 2H), 2.38 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.65 (s, 2H), 1.45 (s, 9H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 175.17, 162.82, 161.20, 159.15, 133.93 (d, $J = 252.2$ Hz), 131.71 (d, $J = 7.6$ Hz), 129.88, 127.34, 121.58, 115.11, 114.97 (d, $J = 146.5$ Hz), 81.57, 62.01, 55.29, 44.87, 44.19, 28.13; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{23}\text{H}_{29}\text{FNO}_3^+$ 386.2126; found 386.2129.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.930	BB	0.1533	6118.66504	595.90686	50.1918	1	6.943	BB	0.1548	256.38004	24.95638	2.1705
2	8.402	BB	0.1862	6071.90137	487.38828	49.8082	2	8.403	BB	0.1837	1.15554e4	952.96722	97.8295

***tert*-Butyl (*S,E*)-2-amino-5-(4-methoxyphenyl)-2-(naphthalen-2-ylmethyl)pent-4-enoate (**5k**):**



White solid (45.9 mg, 55%); m.p. = 100-101 °C; R_f = 0.26

(petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was

determined to be 95% by HPLC analysis on Daicel Chirapak IA-

H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major)

13.663 min, t_R (minor) 17.602 min; $[\alpha]_D^{20}$ = -10.78 (c = 0.58, CHCl_3); **^1H NMR (600 MHz, CDCl_3)**

δ 7.81 – 7.71 (m, 4H), 7.46 – 7.37 (m, 3H), 7.26 (d, J = 6.0 Hz, 2H), 6.83 (d, J = 12.0 Hz, 2H), 6.48 (d,

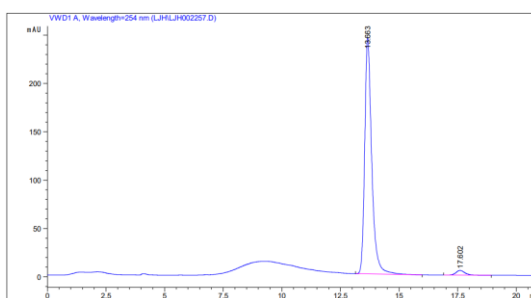
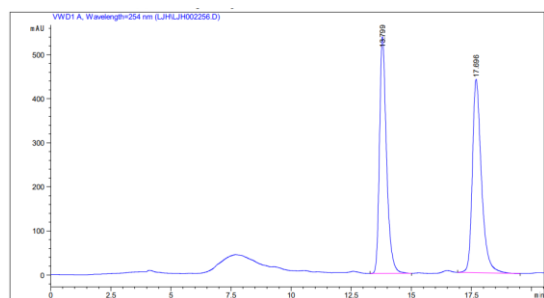
J = 18.0 Hz, 1H), 6.00 (ddd, J = 15.4, 8.4, 6.8 Hz, 1H), 3.78 (s, 3H), 3.39 (d, J = 12.0 Hz, 1H), 2.95 (d,

J = 18.0 Hz, 1H), 2.88 – 2.85 (m, 1H), 2.45 (dd, J = 12.0, 6.0 Hz, 1H), 1.64 (s, 2H), 1.47 (s, 9H); **^{13}C**

NMR (151 MHz, CDCl_3) δ 175.37, 159.13, 134.21, 133.87, 133.37, 132.49, 129.96, 128.92, 128.58,

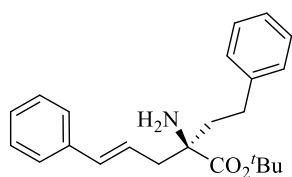
127.78, 127.63, 127.36, 126.02, 125.59, 121.77, 114.01, 81.51, 62.27, 55.30, 45.86, 44.52, 28.18;

HRMS(ESI) m/z : $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{27}\text{H}_{32}\text{NO}_3^+$ 418.2377; found 418.2376.



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.799	BB	0.3058	1.09267e4	537.21375	48.6164	1	13.663	BB	0.3139	5105.08887	244.17932	97.4970
2	17.696	BB	0.3942	1.15486e4	439.26151	51.3836	2	17.602	BB	0.3974	131.06105	4.93404	2.5030

***tert*-Butyl (*R,E*)-2-amino-2-phenethyl-5-phenylpent-4-enoate (**5l**):**



Colorless oil (44.2 mg, 57%); R_f = 0.23 (petroleum ether/ ethyl acetate

= 5:1); the enantiomeric excess was determined to be 93% by HPLC

analysis on Daicel Chirapak IA-H column (hexane/isopropanol =

90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 9.695 min, t_R (minor) 7.830 min;

$[\alpha]_D^{20}$ = +9.25 (c = 0.33, CHCl_3); **^1H NMR (600 MHz, CDCl_3)** δ 7.33 – 7.27 (m, 6H), 7.23 – 7.18 (m,

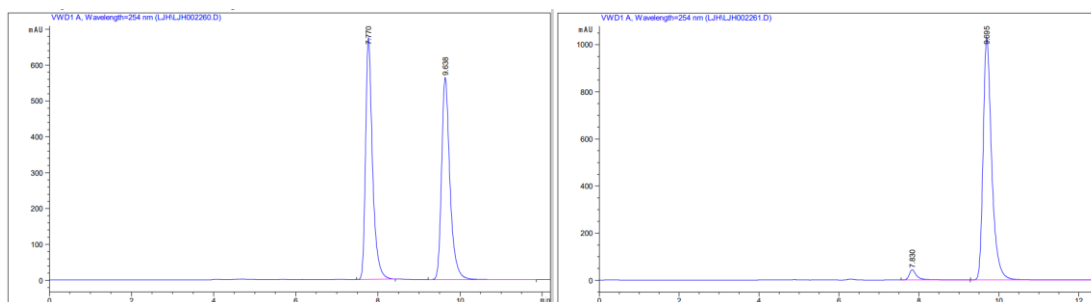
4H), 6.50 (d, J = 18.0 Hz, 1H), 6.22 – 6.04 (m, 1H), 2.75 - 2.69 (m, 2H), 2.54 – 2.49 (m, 1H), 2.43 (dd,

J = 12.0, 6.0 Hz, 1H), 2.08 (td, J = 13.1, 4.3 Hz, 1H), 1.87 (td, J = 13.1, 5.2 Hz, 1H), 1.74 (s, 2H), 1.52

(s, 9H); **^{13}C NMR (151 MHz, CDCl_3)** δ 175.68, 141.87, 137.09, 134.34, 128.56, 128.51, 128.36,

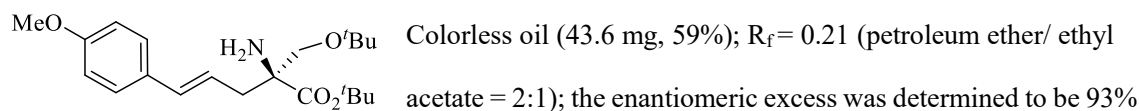
127.42, 126.21, 125.98, 124.23, 81.33, 61.27, 43.81, 42.27, 30.61, 28.18; **HRMS(ESI)** m/z : $[\text{M}+\text{H}]^+$

Calculated for C₂₃H₃₀NO₂⁺ 352.2271; found 352.2268.

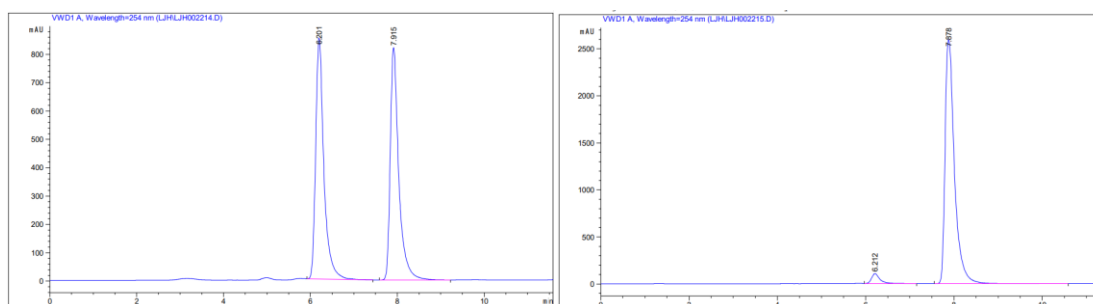


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.770	BB	0.1750	7909.64551	673.00439	49.7574	1	7.830	BB	0.1938	576.13379	43.52164	3.6086
2	9.638	BB	0.2134	7986.78662	563.59399	50.2426	2	9.695	BBA	0.2258	1.53892e4	1027.03503	96.3914

***tert*-Butyl (*S,E*)-2-amino-2-(*tert*-butoxymethyl)-5-(4-methoxyphenyl)pen (5m):**

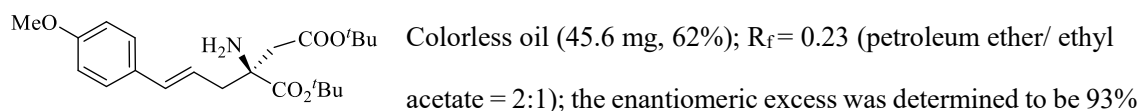


by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R(major) 7.878 min, t_R(minor) 6.212 min; [α]_D²⁰ = +12.52 (c = 0.65, CHCl₃); ¹H NMR (600 MHz, CDCl₃) δ 7.26 (d, J = 6.0 Hz, 2H), 6.83 (d, J = 12.0 Hz, 2H), 6.42 (d, J = 18.0 Hz, 1H), 5.98 – 5.93 (m, 1H), 3.79 (s, 3H), 3.65 (d, J = 6.0 Hz, 1H), 3.28 (d, J = 6.0 Hz, 1H), 2.56 (dd, J = 12.0, 6.0 Hz, 1H), 2.31 (dd, J = 12.0, 6.0 Hz, 1H), 1.93 (s, 2H), 1.47 (s, 9H), 1.16 (s, 9H); ¹³C NMR (151 MHz, CDCl₃) δ 174.89, 159.01, 133.32, 130.06, 127.31, 121.50, 113.93, 80.75, 72.74, 67.95, 61.97, 55.27, 40.29, 28.10, 27.45; HRMS(ESI) m/z: [M+H]⁺ Calculated for C₂₁H₃₄NO₄⁺ 364.2482; found 364.2482.

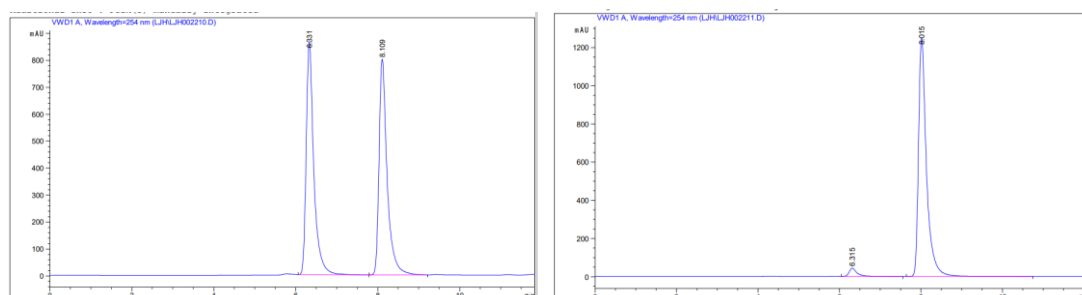


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %	Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.201	BB	0.1957	1.11737e4	849.84833	50.1954	1	6.212	BB	0.1957	1402.06152	105.58316	3.5428
2	7.915	BB	0.2015	1.10867e4	819.62274	49.8046	2	7.878	BB	0.2228	3.81729e4	2593.00684	96.4572

***di-tert*-Butyl (*S,E*)-2-amino-2-(3-(4-methoxyphenyl)allyl)succinate (5n):**



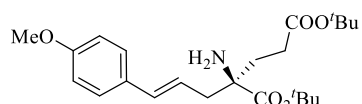
by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 8.015 min, t_R (minor) 6.315 min; $[\alpha]_D^{20} = +7.54$ ($c = 0.42$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.26 (d, $J = 6.0$ Hz, 2H), 6.83 (d, $J = 12.0$ Hz, 2H), 6.42 (d, $J = 18.0$ Hz, 1H), 5.98 - 5.93 (m, 1H), 3.80 (s, 3H), 3.64 (d, $J = 6.0$ Hz, 1H), 3.28 (d, $J = 6.0$ Hz, 1H), 2.56 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.31 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.93 (s, 2H), 1.47 (s, 9H), 1.16 (s, 9H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 174.90, 159.01, 133.32, 130.07, 127.32, 121.51, 113.93, 80.76, 72.75, 67.96, 61.98, 55.28, 40.30, 28.10, 27.46; **HRMS(ESI) m/z: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{22}\text{H}_{34}\text{NO}_5^+$ 364.2482; found 364.2482.**



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.331	BB	0.1913	1.11408e4	863.54626	50.4213
2	8.109	BB	0.2035	1.09546e4	800.10468	49.5787

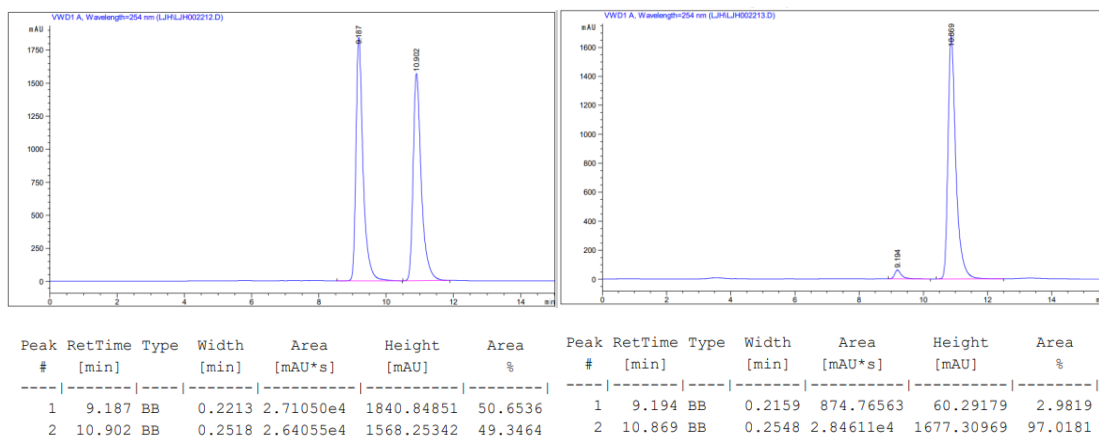
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.315	BB	0.1948	569.22485	42.73330	3.2579
2	8.015	BB	0.2018	1.69028e4	1247.39673	96.7421

di-tert-Butyl (R,E)-2-amino-2-(3-(4-methoxyphenyl)allyl)pentanedioate (5o):



Colorless oil (42.1 mg, 52%); $R_f = 0.24$ (petroleum ether/ ethyl acetate = 2:1); the enantiomeric excess was determined to be 94%

by HPLC analysis on Daicel Chirapak IA-H column (hexane/isopropanol = 90/10, flow rate 0.8 mL/min, T = 30 °C), UV 254 nm, t_R (major) 10.869 min, t_R (minor) 9.194 min; $[\alpha]_D^{20} = +9.44$ ($c = 0.82$, CHCl_3); $^1\text{H NMR}$ (600 MHz, CDCl_3) δ 7.25 (d, $J = 12.0$ Hz, 2H), 6.83 (d, $J = 12.0$ Hz, 2H), 6.42 (d, $J = 18.0$ Hz, 1H), 5.95 (ddd, $J = 15.3, 8.2, 6.9$ Hz, 1H), 3.79 (s, 3H), 2.64 (dd, $J = 12.0, 6.0$ Hz, 1H), 2.39 - 2.33 (m, 2H), 2.22 - 2.17 (m, 1H), 2.07 - 2.02 (m, 1H), 1.89 - 1.84 (m, 1H), 1.62 (s, 2H), 1.48 (s, 9H), 1.44 (s, 9H); $^{13}\text{C NMR}$ (151 MHz, CDCl_3) δ 175.33, 172.73, 159.09, 133.76, 129.90, 127.32, 121.78, 113.96, 81.34, 80.31, 60.66, 55.27, 43.49, 34.82, 30.42, 28.10, 28.07; **HRMS(ESI) m/z: $[\text{M}+\text{H}]^+$ Calculated for $\text{C}_{23}\text{H}_{36}\text{NO}_5^+$ 406.2588; found 406.2586.**



4. Determination of the absolute configuration of **4b**

The absolute configuration of compound **4b** was established by comparing its optical rotation value with the literature data:

(<i>R</i>)-product (4b) in this work	(<i>S</i>)-product in literature ^[5]
<p><i>tert</i>-butyl (<i>R,E</i>)-2-amino-2-methyl-5-phenylpent-4-enoate</p>	<p><i>tert</i>-butyl (<i>S,E</i>)-2-amino-2-methyl-5-phenylpent-4-enoate</p>
$[\alpha]_{\text{D}}^{20} = +16.25$ ($c = 0.90$, CHCl_3)	$[\alpha]_{\text{D}}^{20} = -7.4$ ($c = 1.00$, CHCl_3)

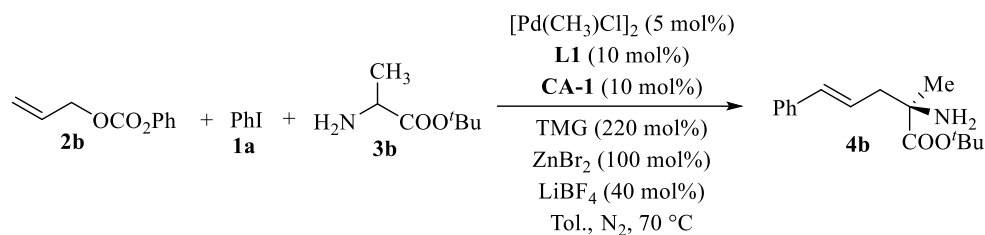
Literature:

¹H NMR (400 MHz, CDCl₃) δ = 7.35 -7.26 (m, 4H), 7.24 -7.18 (m, 1H), 6.48 (d, $J = 15.8$ Hz, 1H), 6.23 - 5.96 (m, 1H), 2.65 (ddd, $J = 13.5, 6.8, 1.4$ Hz, 1H), 2.38 (ddd, $J = 13.5, 8.3, 1.1$ Hz, 1H), 1.82 (s, 2H), 1.47 (s, 9H), 1.34 (s, 3H).

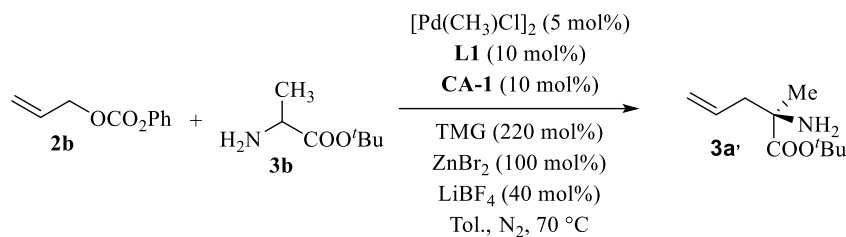
This work:

¹H NMR (600 MHz, CDCl₃) δ 7.36-7.29 (m, 4H), 7.25-7.22 (m, 1H), 6.50 (d, $J = 18.0$ Hz, 1H), 6.25 - 5.93 (m, 1H), 2.67 (dd, $J = 18.0, 6.0$ Hz, 1H), 2.42 (dd, $J = 12.0, 6.0$ Hz, 1H), 1.79 (s, 2H), 1.50 (s, 9H), 1.36 (s, 3H).

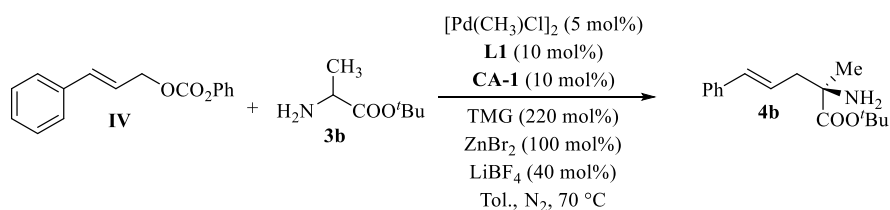
5. Mechanistic Studies



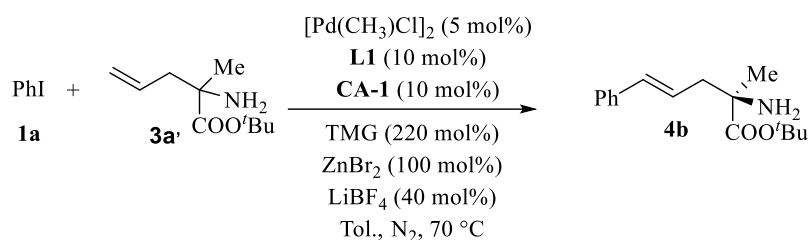
To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **1a** (0.2 mmol), **2b** (0.36 mmol), **3b** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5 mg, 0.08 mmol) and TMG (56.2 μL , 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3). The reaction yielded **4b** in 81% yield and 96% ee.



To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **2b** (0.36 mmol), **3b** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5 mg, 0.08 mmol) and TMG (56.2 μL , 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =300/100/3). The reaction yielded **3a'** in 79% yield and 97% ee.

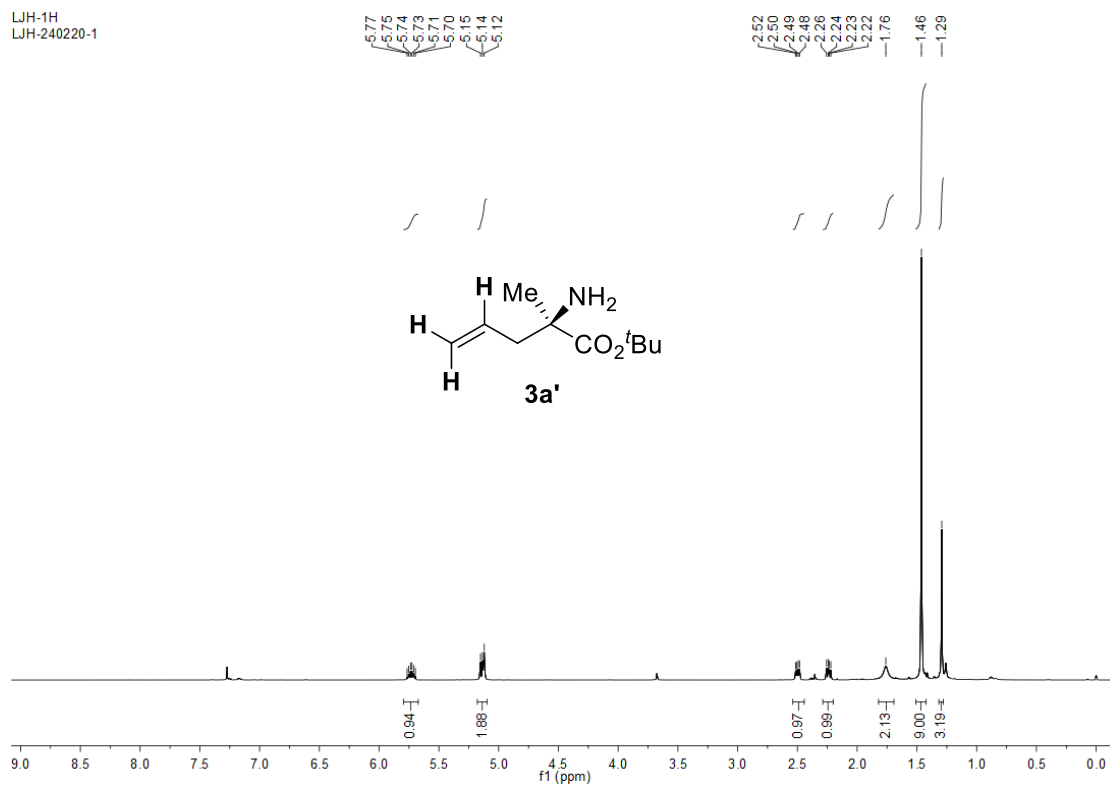


To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **IV** (0.2 mmol), **3b** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5mg, 0.08 mmol) and TMG (56.2 uL, 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3). The reaction yielded **4b** in 90% yield and 92% ee.

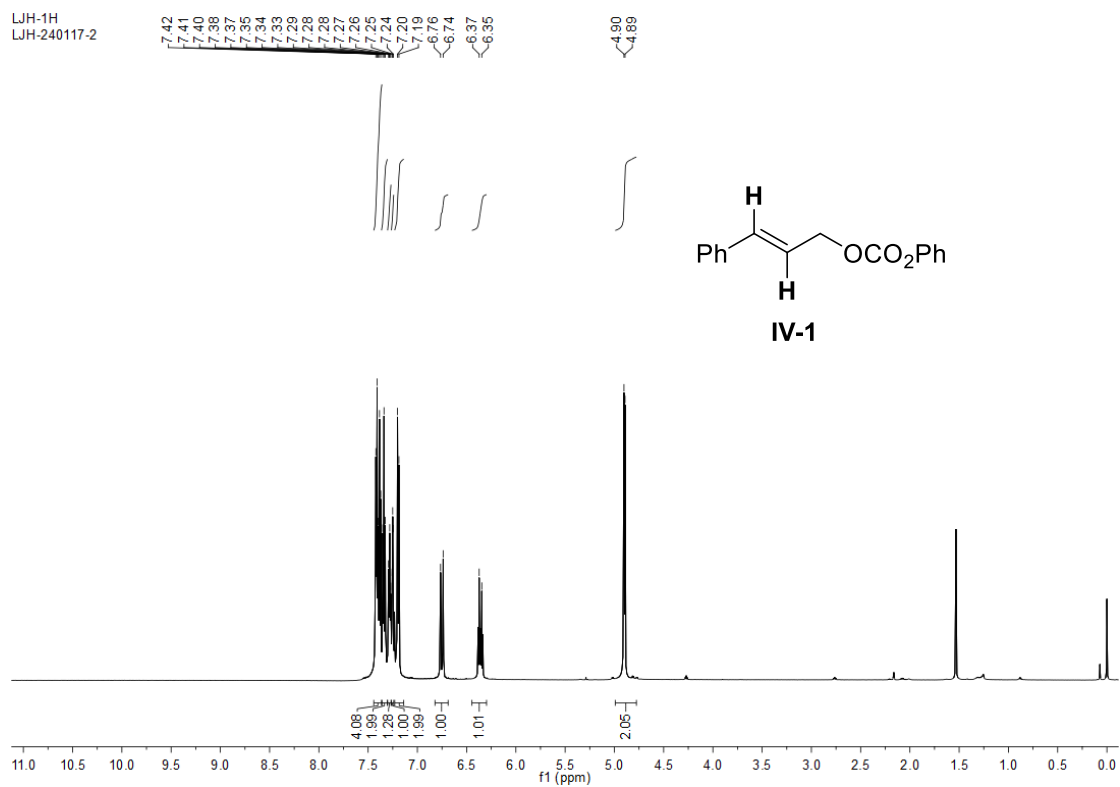


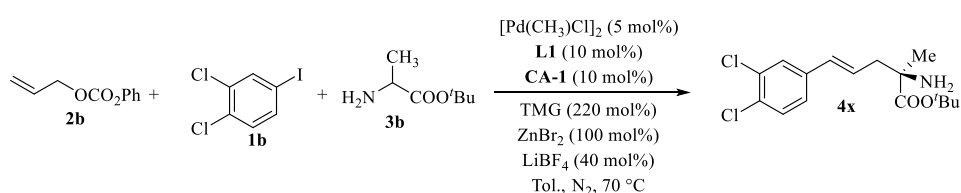
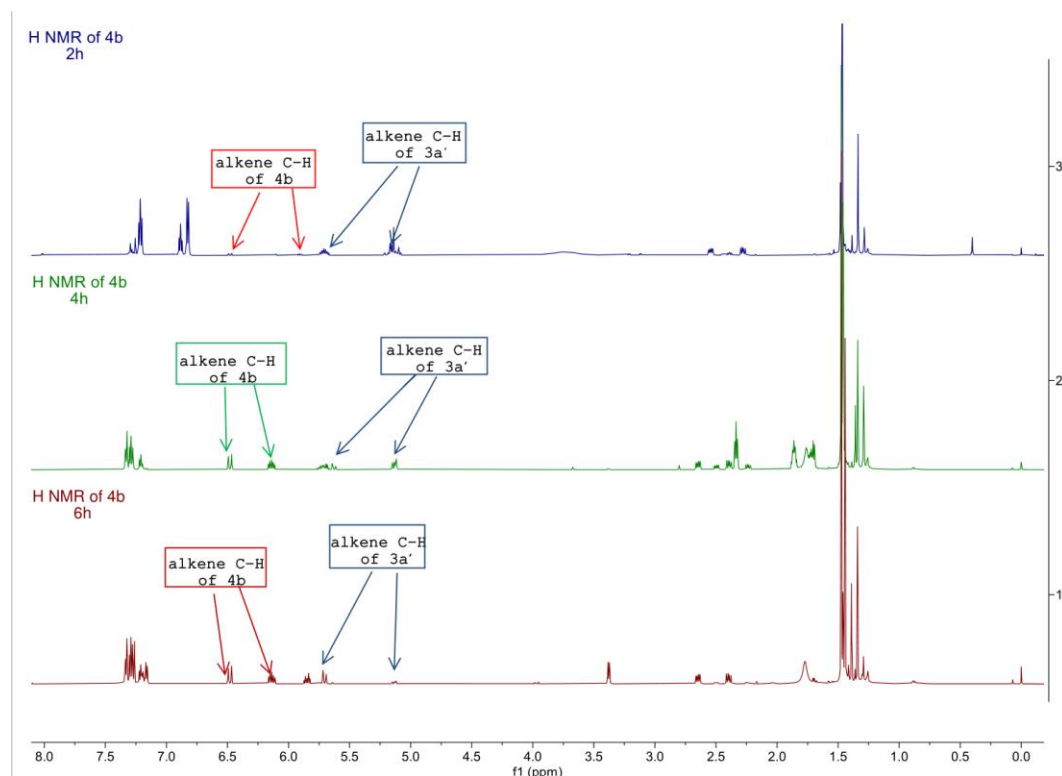
To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **1a** (0.2 mmol), **3a'** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5mg, 0.08 mmol) and TMG (56.2 uL, 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3). The reaction yielded **4b** in 65% yield and 96% ee.

LJH-1H
LJH-240220-1

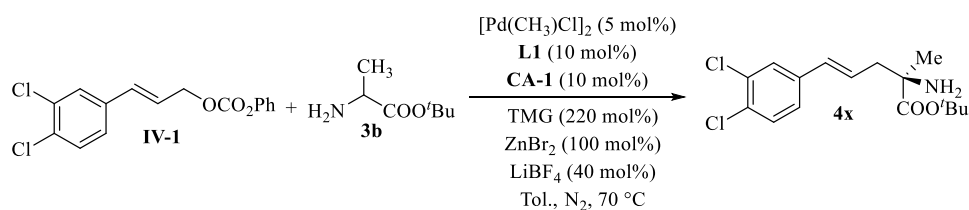


LJH-1H
LJH-240117-2

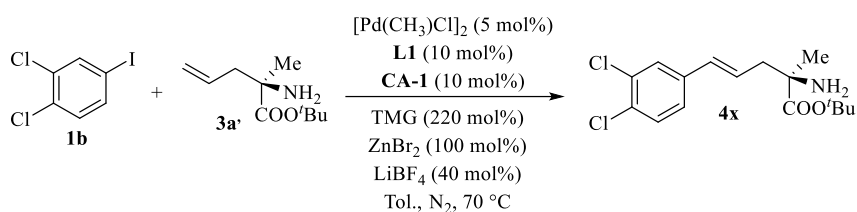




To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **1b** (0.2 mmol), **2b** (0.36 mmol), **3b** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5 mg, 0.08 mmol) and TMG (56.2 μL , 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3). The reaction yielded **4x** in 56% yield and 88% ee.

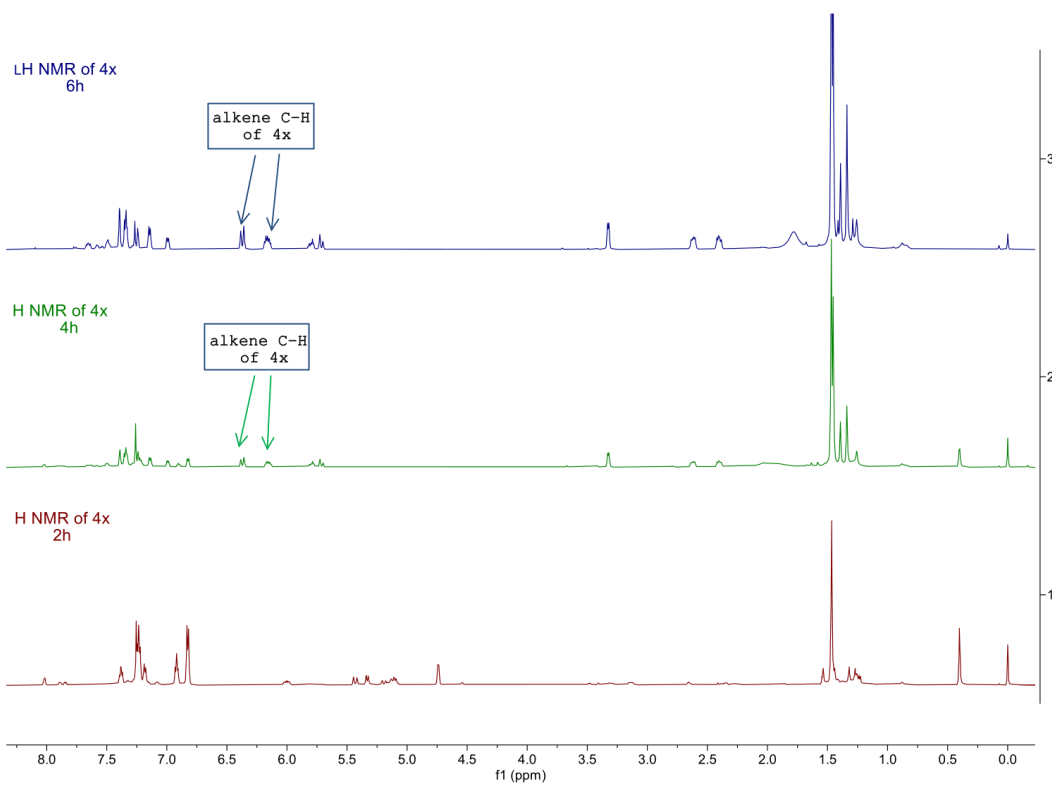
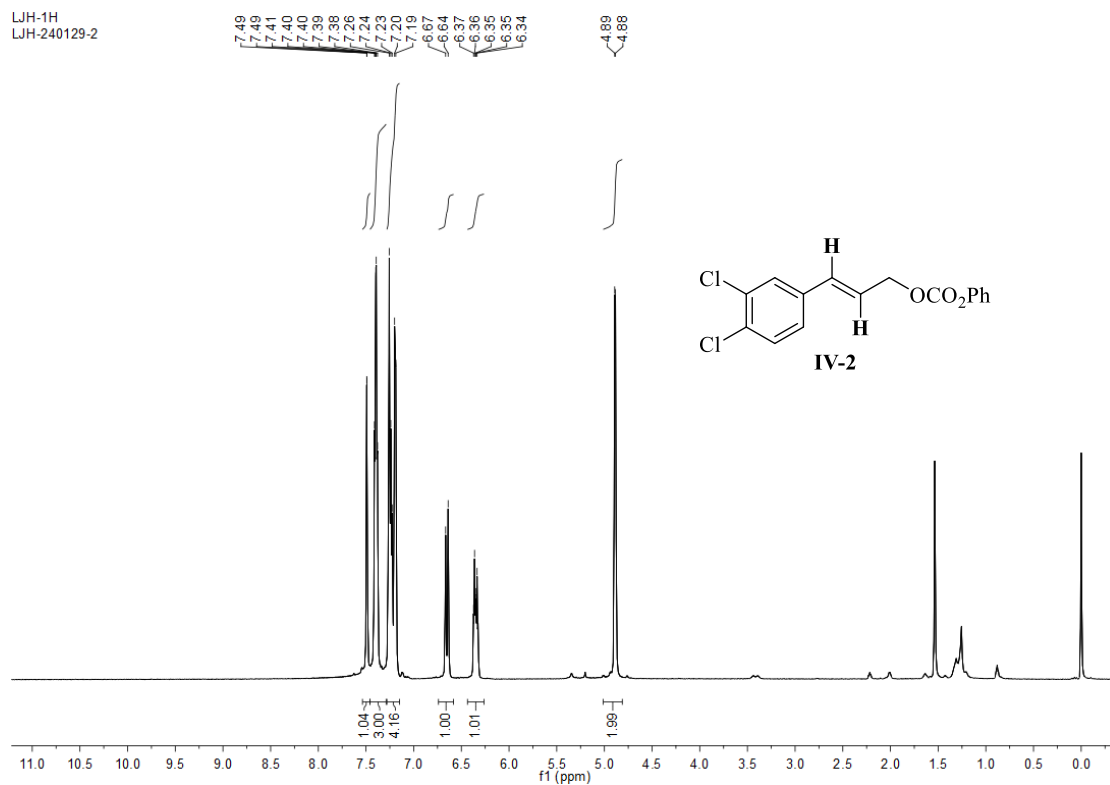


To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **IV-1** (0.2 mmol), **3b** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5mg, 0.08 mmol) and TMG (56.2 uL, 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3). The reaction yielded **4x** in 83% yield and 89% ee.



To a 10 mL vial charged with $[\text{Pd}(\text{C}_3\text{H}_5)\text{Cl}]_2$ (3.6 mg, 0.01 mmol) and **L1** (11.7 mg, 0.02 mmol) was added 0.5 mL toluene, and the mixture was stirred under nitrogen atmosphere at room temperature for 30 min. Then, **1a** (0.2 mmol), **3a'** (0.3 mmol), chiral aldehyde **CA-1** (7.7 mg, 0.02 mmol), ZnBr_2 (45.0 mg, 0.2 mmol), LiBF_4 (7.5mg, 0.08 mmol) and TMG (56.2 uL, 0.44 mmol) were added. The mixture was continuously stirred at indicated reaction temperature under nitrogen atmosphere. After the reaction completed, the solvent was removed by rotary evaporation, and the residue was purified by flash chromatography column on silica gel (eluent: petroleum ether/ ethyl acetate/ triethylamine =200/100/3). No desired product **4x** was generated in this reaction.

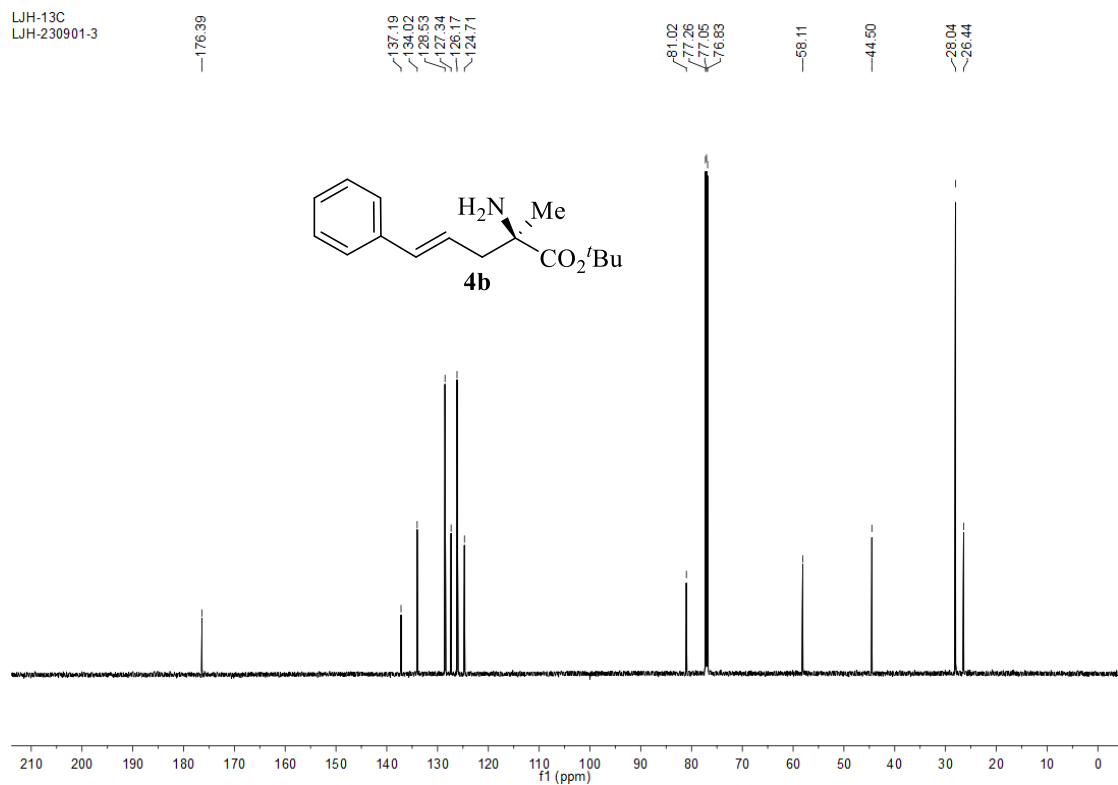
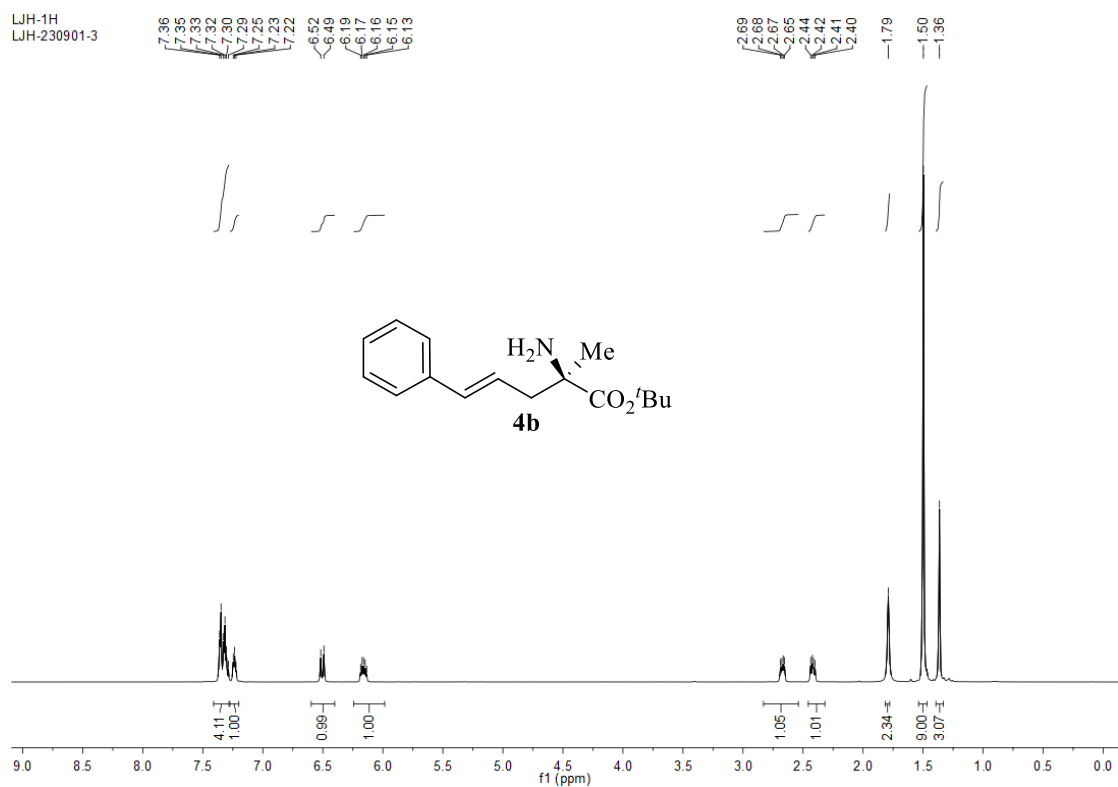
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LJH-240129-2



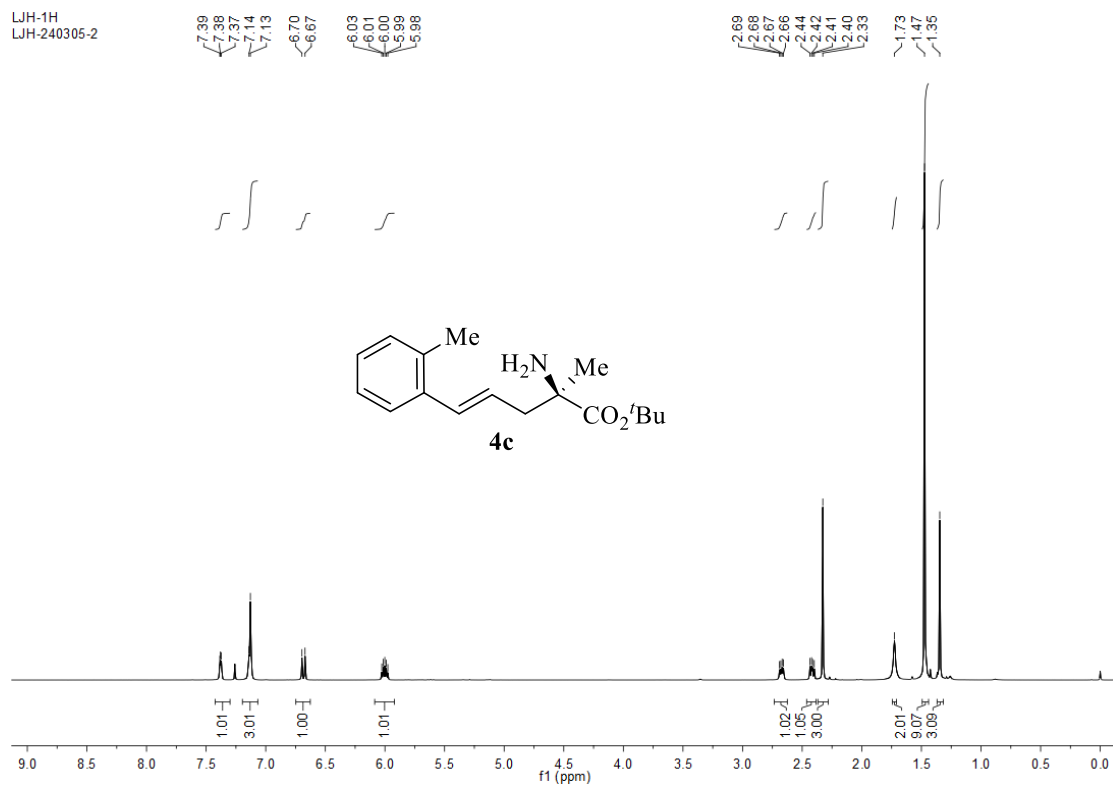
6. References

- [1] a) Urvashi, S. Mishra, N. T. Patil, Gold-catalyzed alkenylation and arylation of phosphorothioates. *Chem. Sci.* **2023**, *14*, 13134. b) J. A. Cadge, H. A. Sparkes, J. F. Bower, C. A. Russell, *Angew. Chem. Int. Ed.* **2020**, *59*, 6617–6621.
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- [3] K. Manna, H. M. Begam, K. Samanta, R. Jana, Overcoming the deallylation problem: palladium(II)-catalyzed chemo-, regio-, and stereoselective allylic oxidation of aryl allyl ether, amine, and amino acids. *Org. Lett.* **2020**, *22*, 7443-7449.
- [4] B. Xu, et al. Catalytic asymmetric direct α -alkylation of amino esters by aldehydes via imine activation. *Chem. Sci.* **2014**, *5*, 1988-1991.
- [5] X.-H. Huo, R. He, J. -K. Fu, J.-C. Zhang, G.-Q. Yang, W.-B. Zhang, Stereoselective and Site-Specific Allylic Alkylation of Amino Acids and Small Peptides via a Pd/Cu Dual Catalysis. *J. Am. Chem. Soc.* **2017**, *139*, 9819–9822.

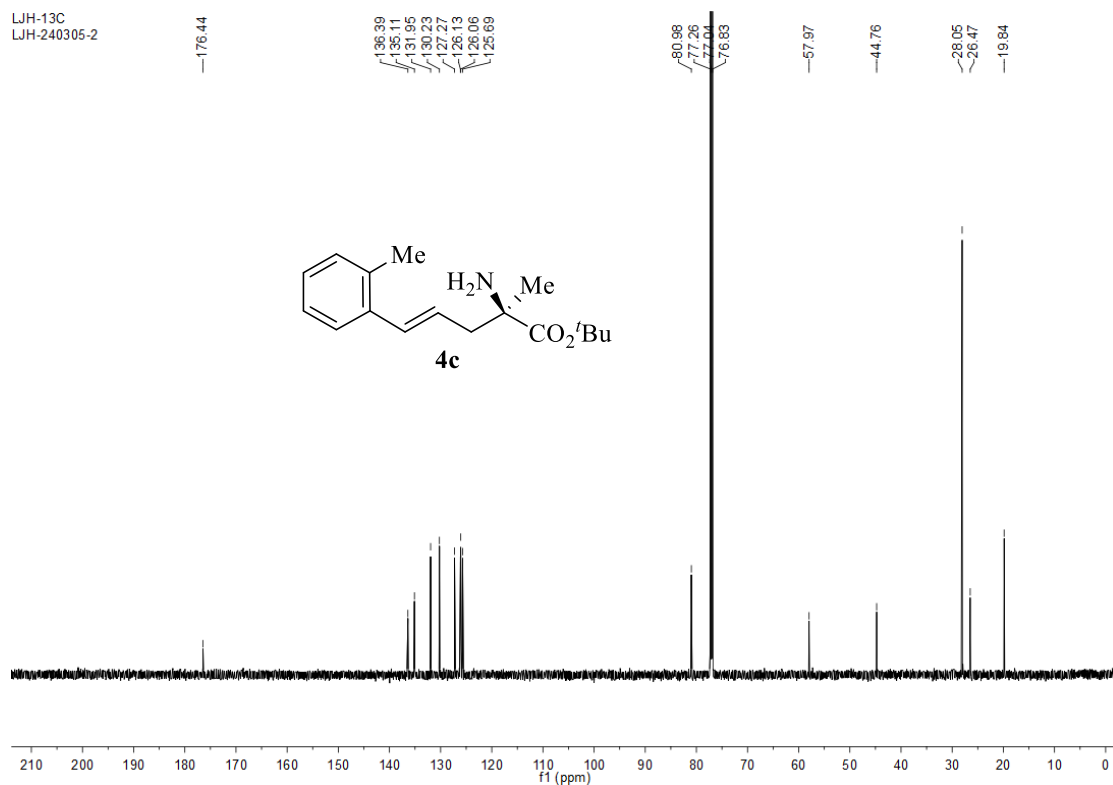
7. Copies of ^1H NMR and ^{13}C NMR spectra

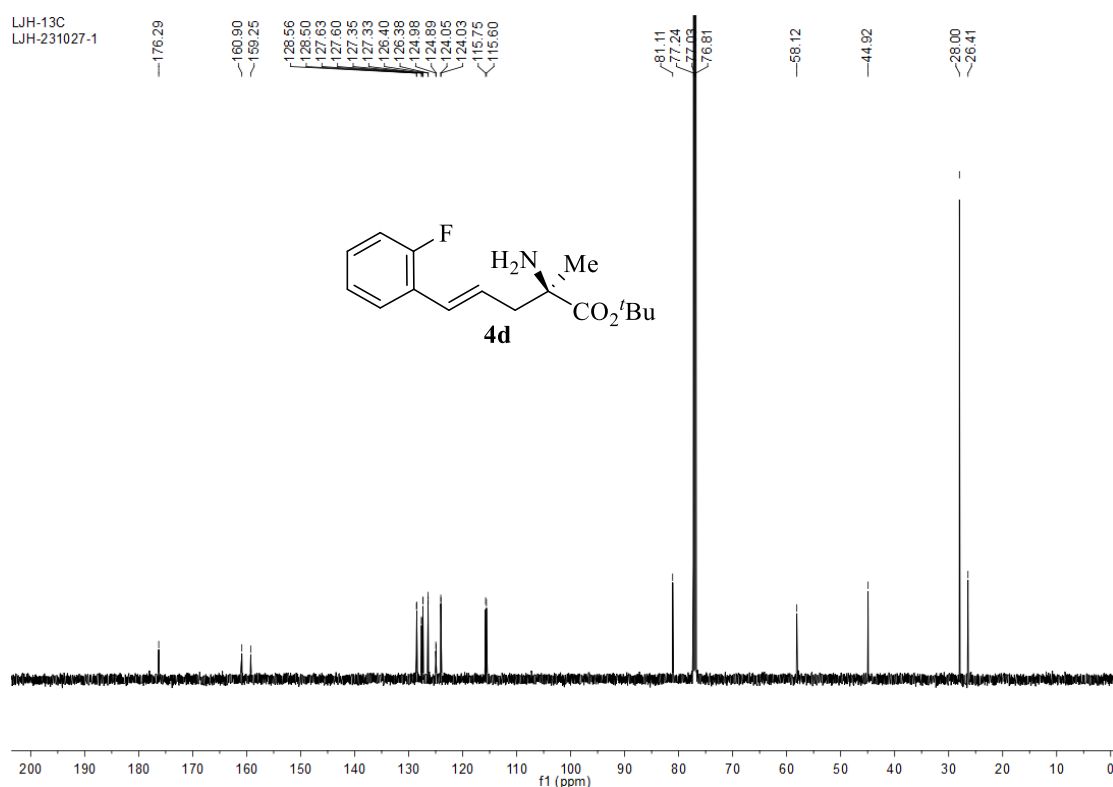
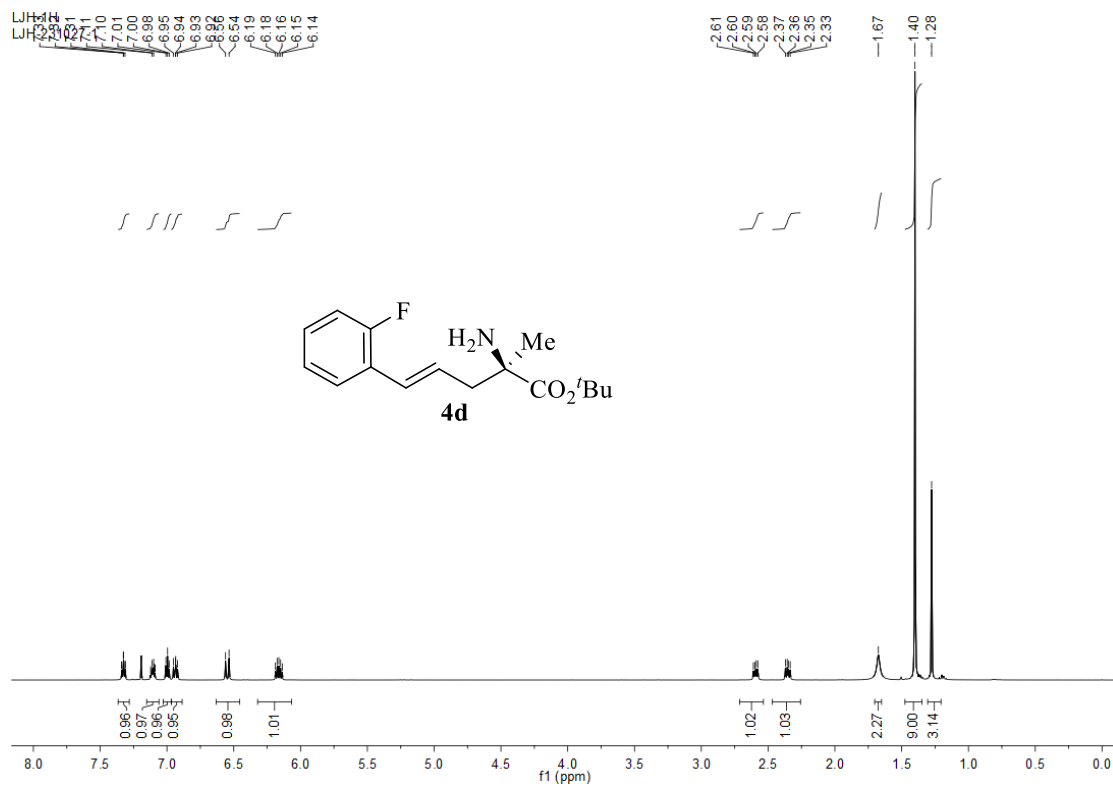


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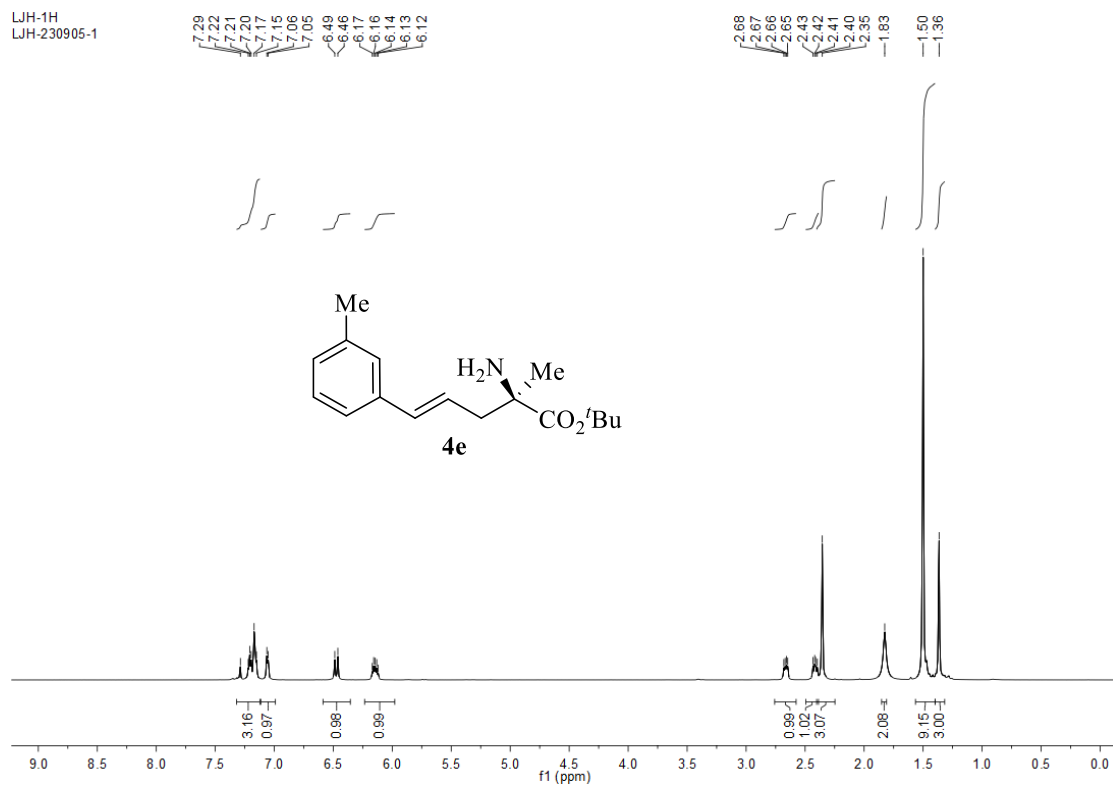


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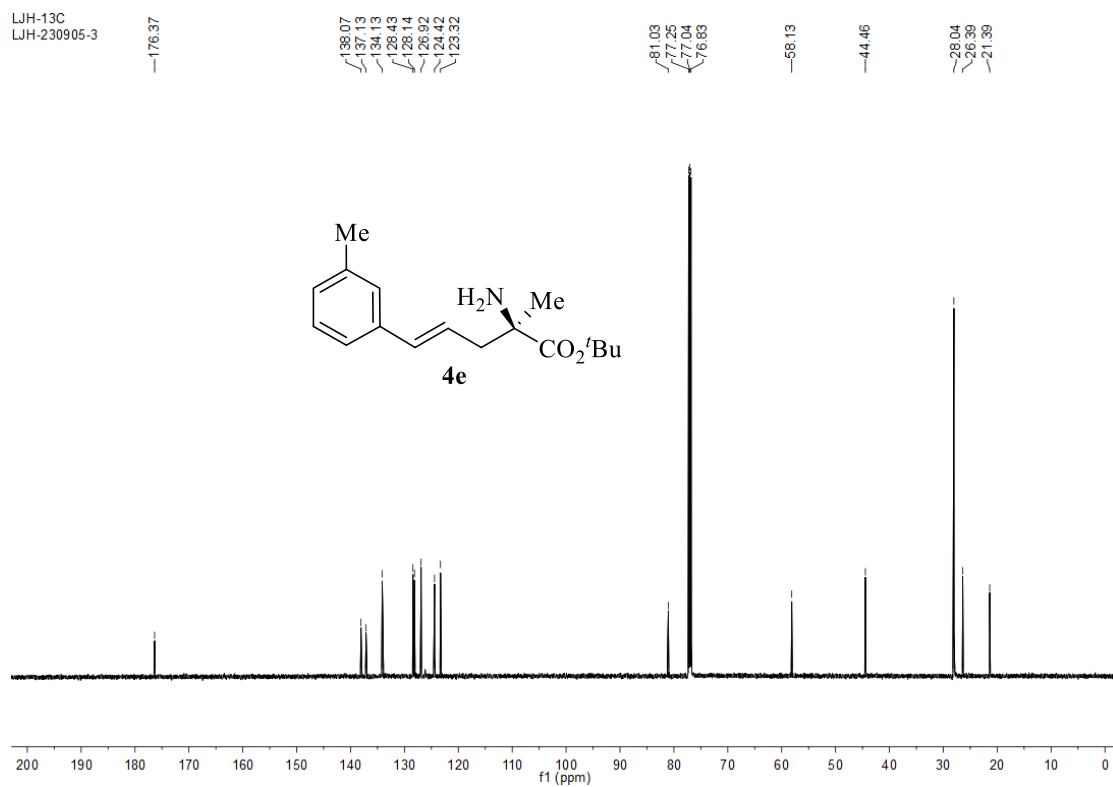


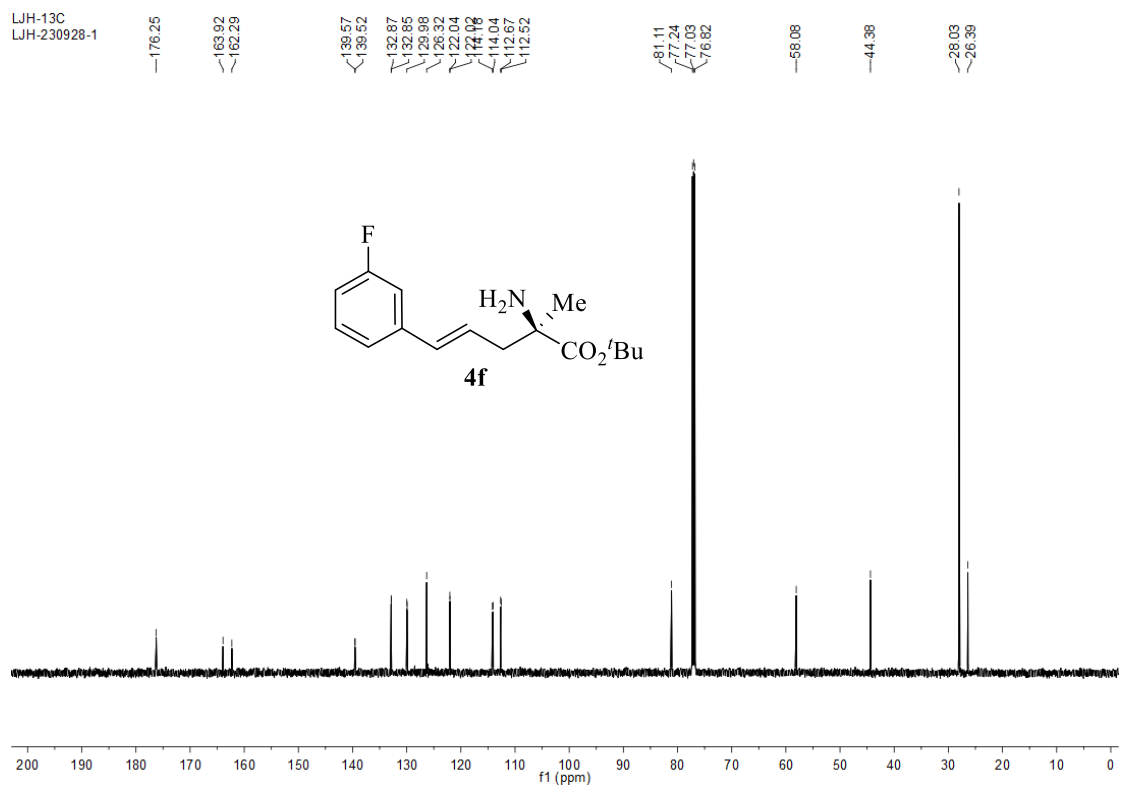
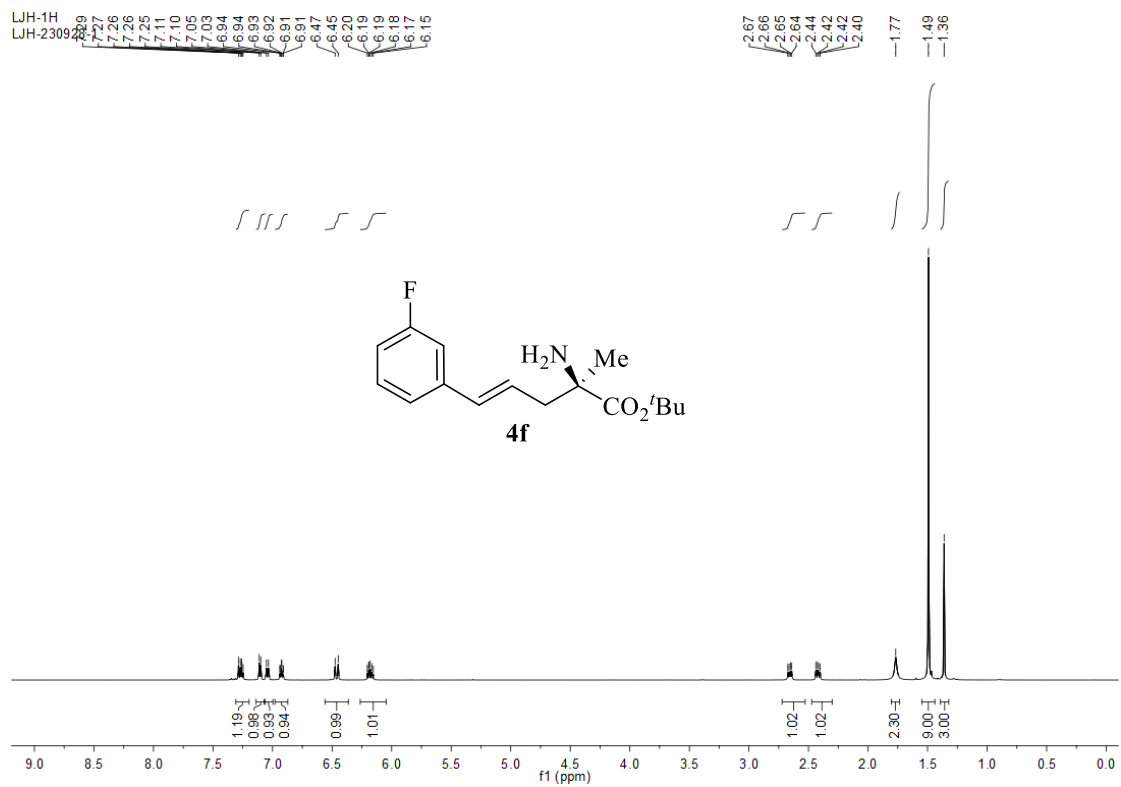


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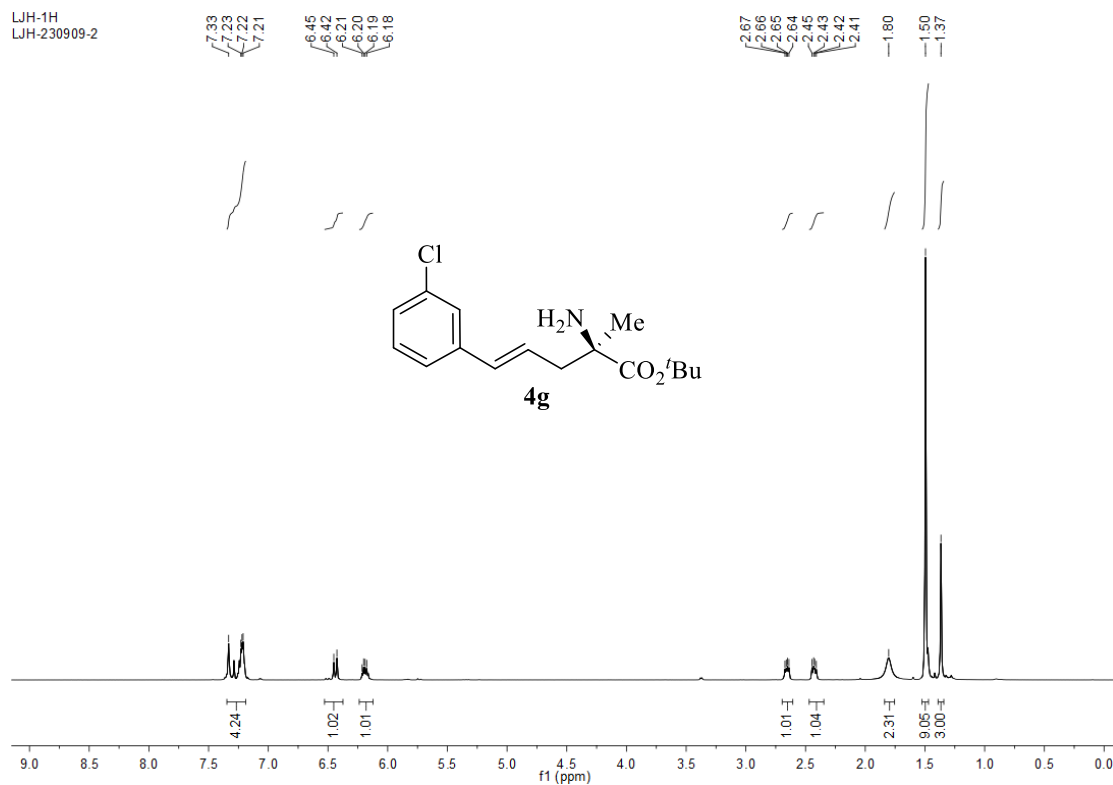


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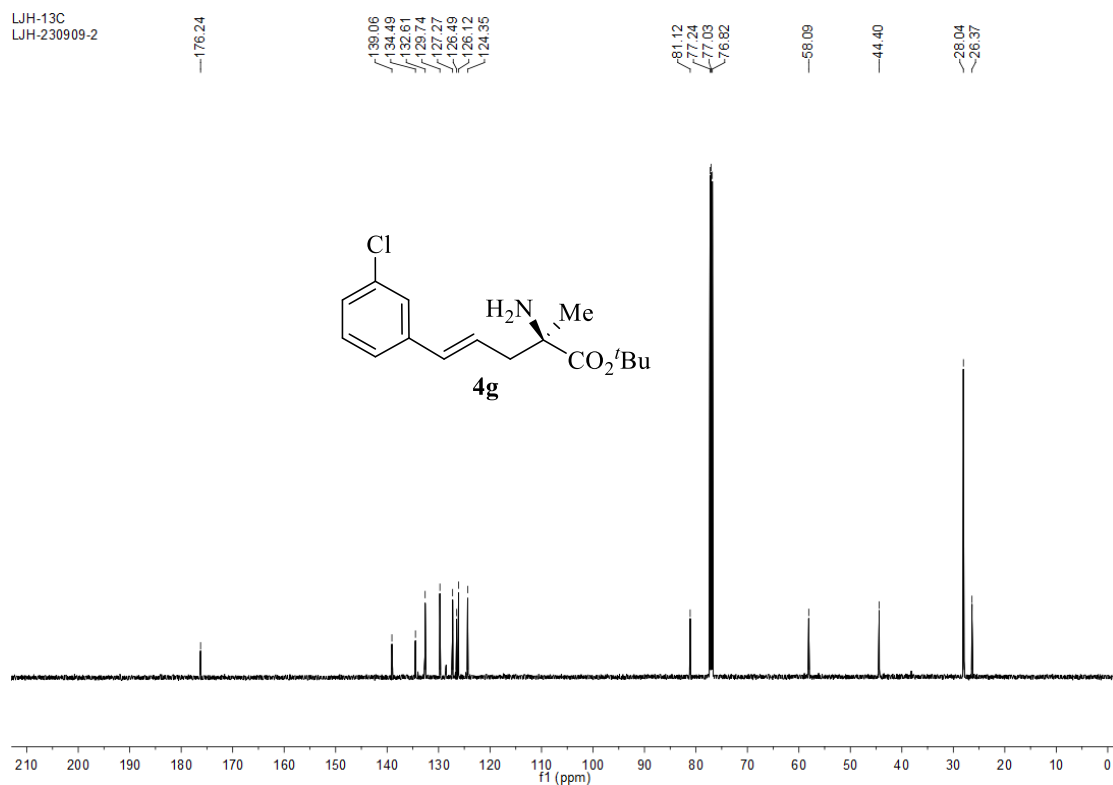




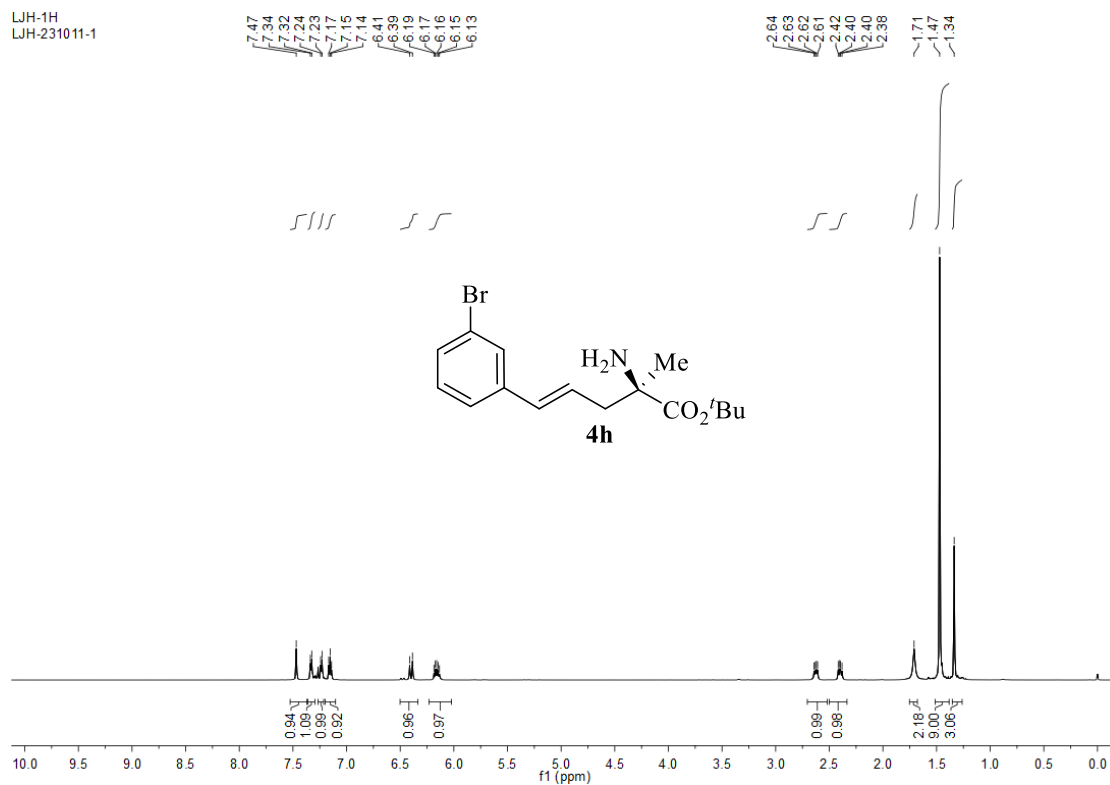
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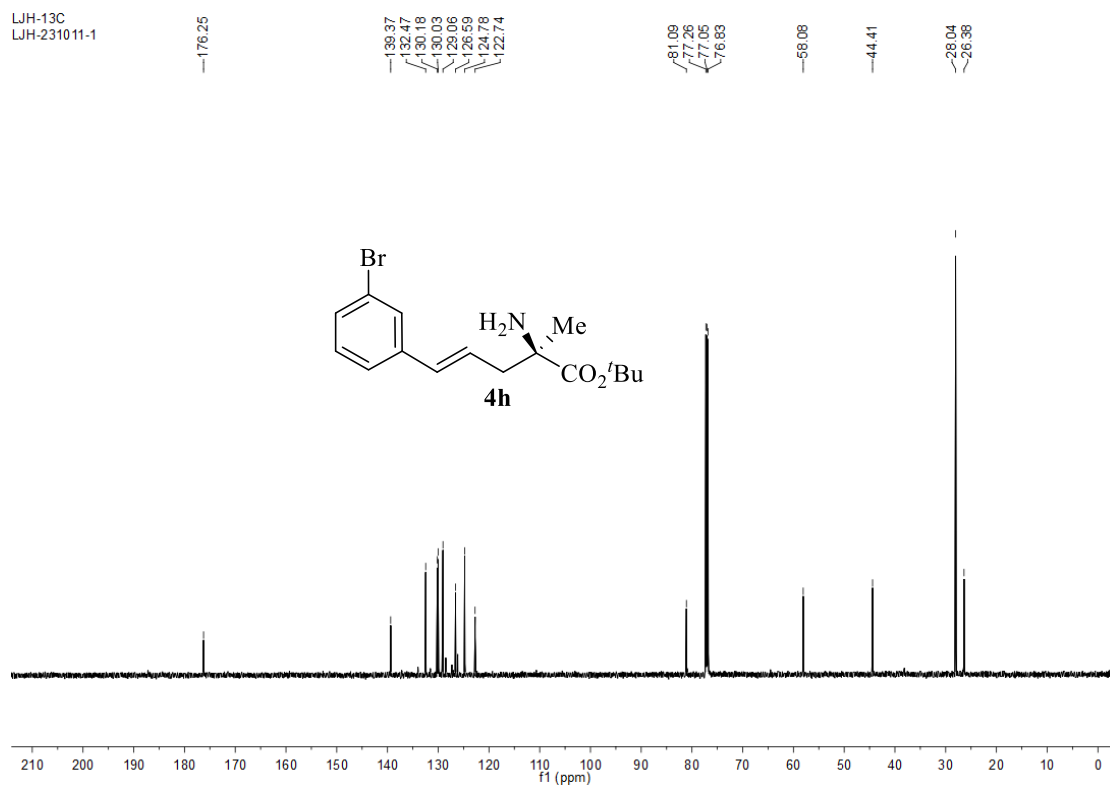
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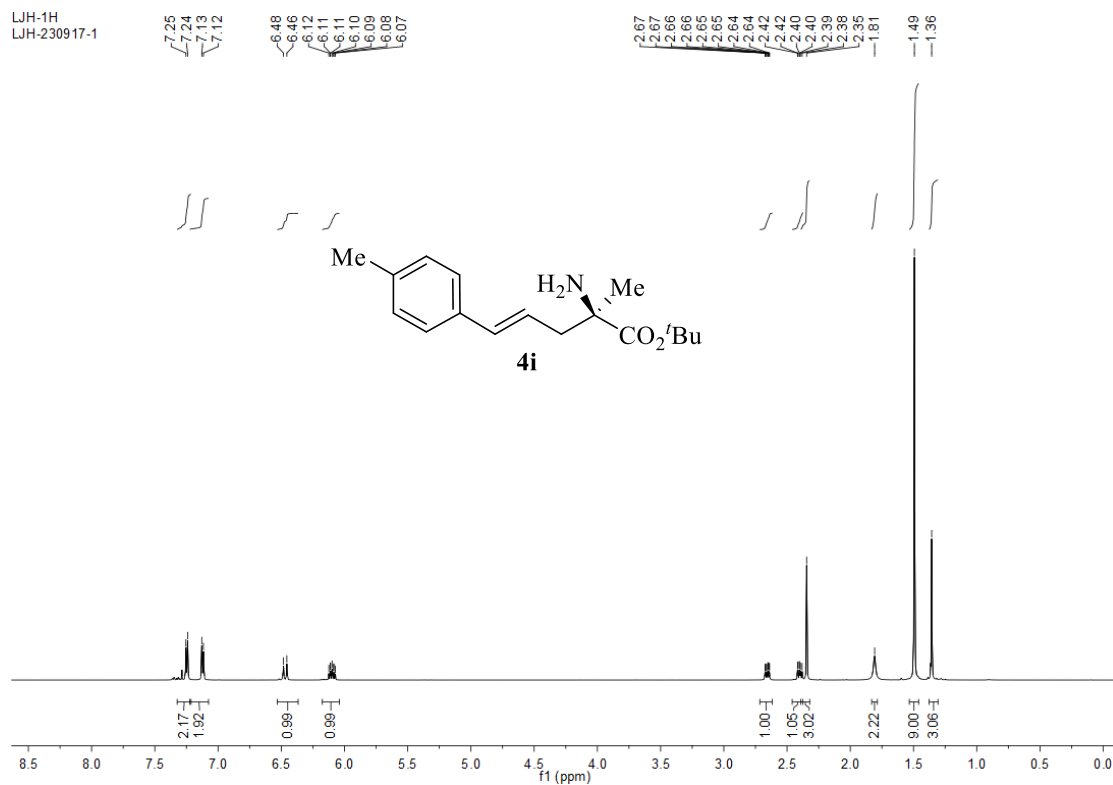
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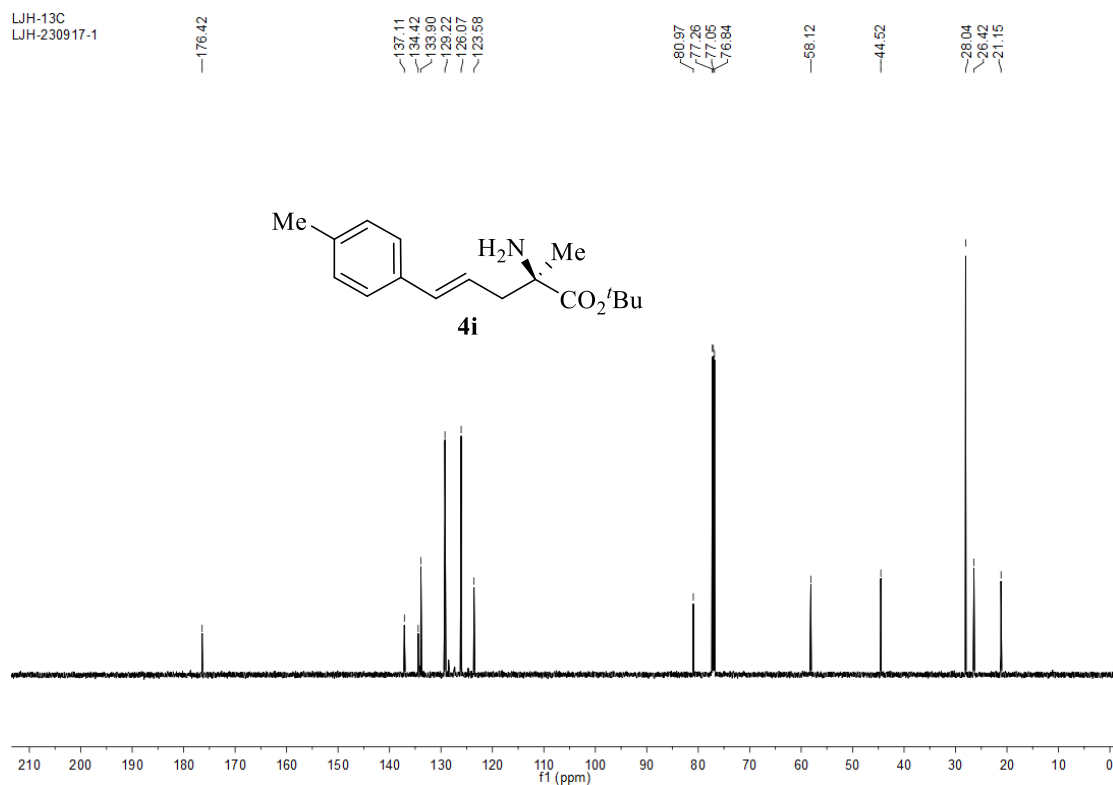
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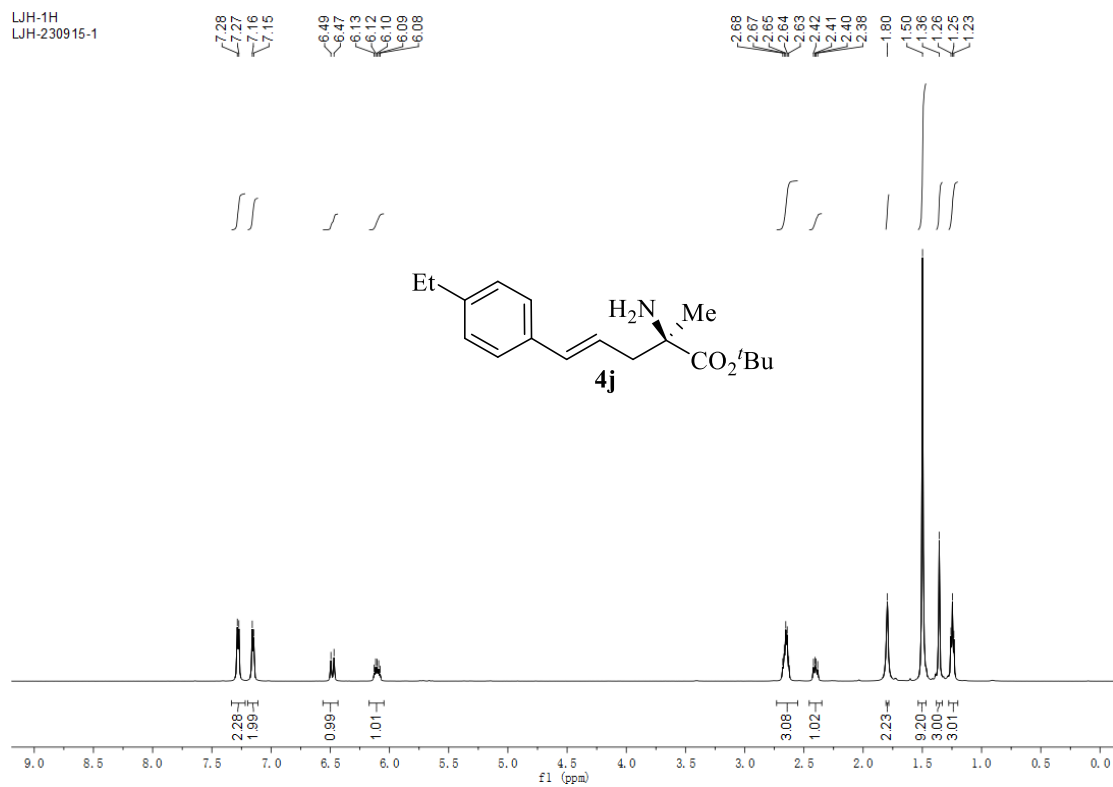
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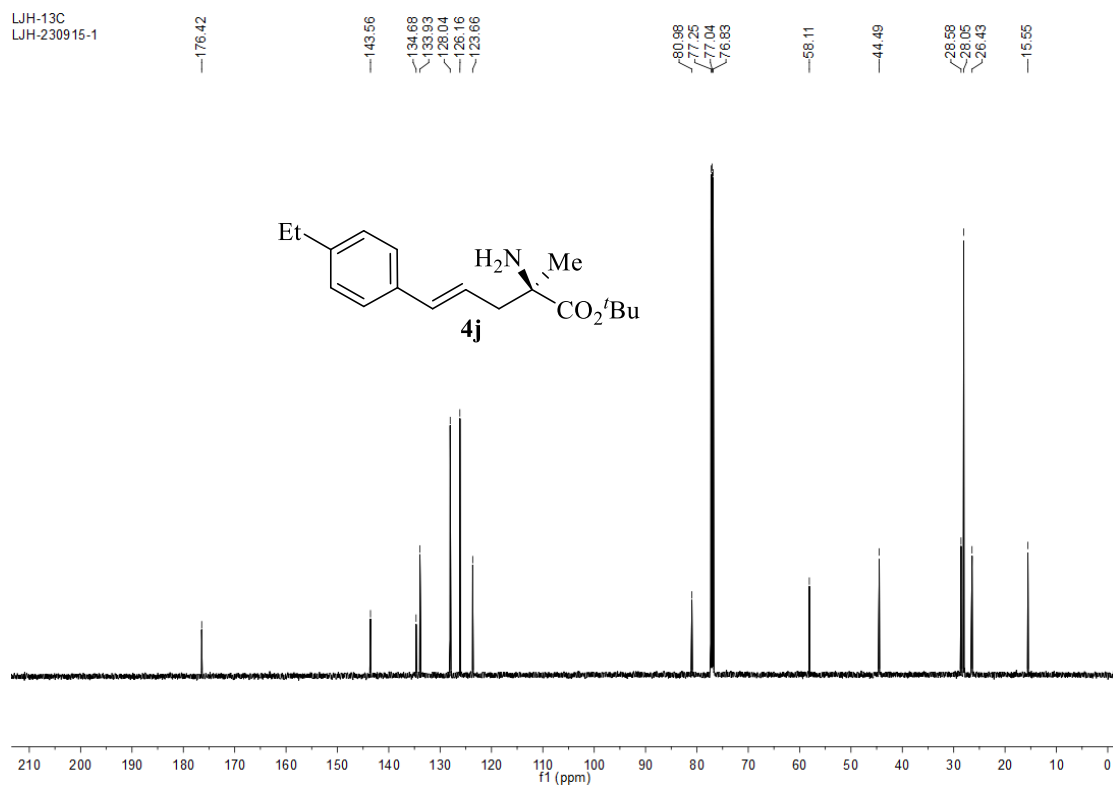
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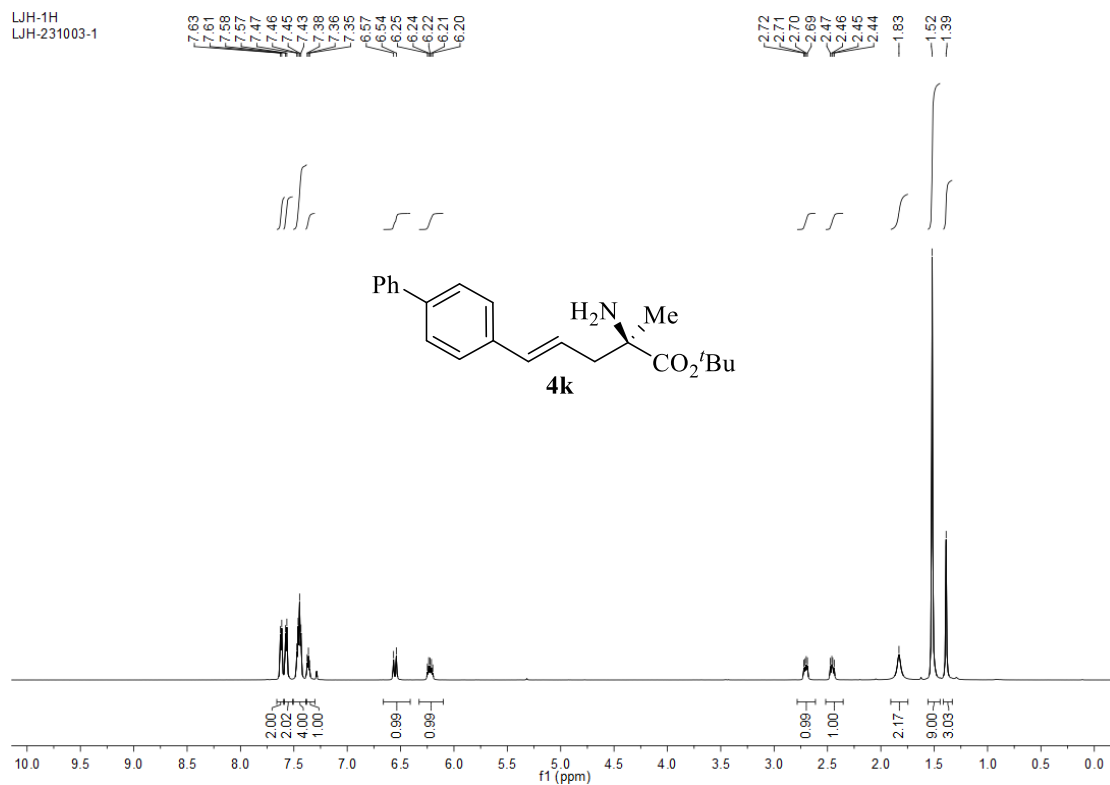
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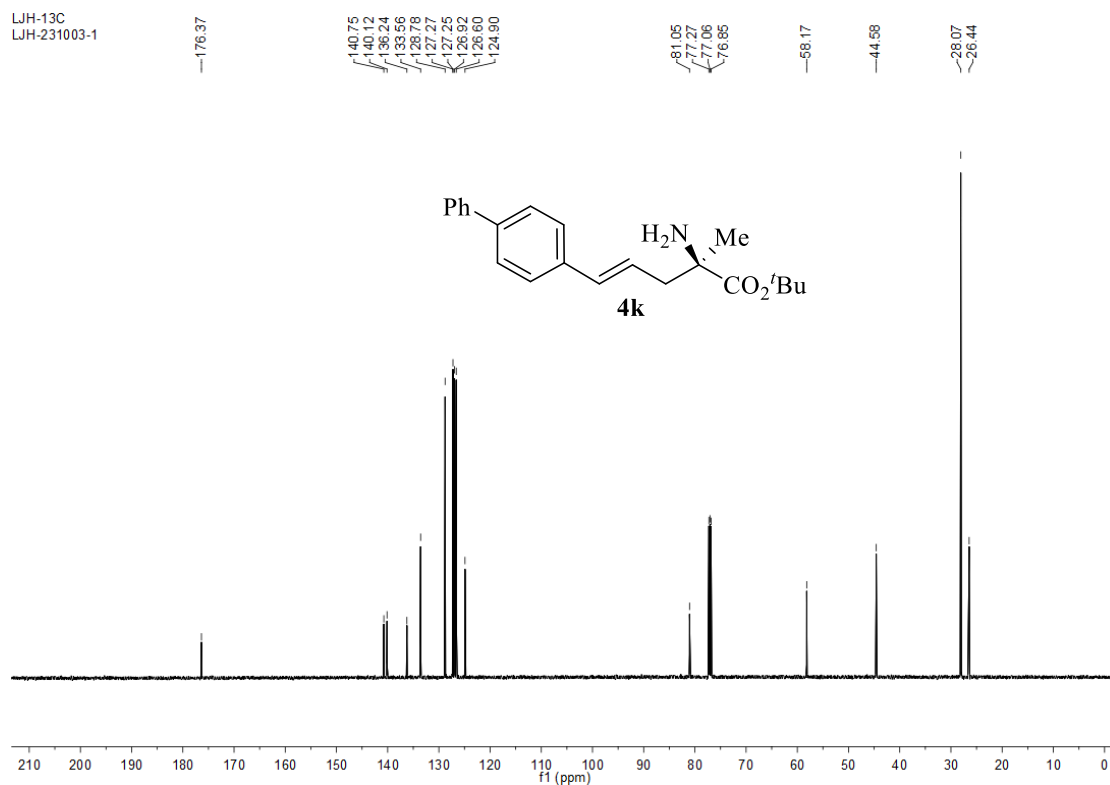
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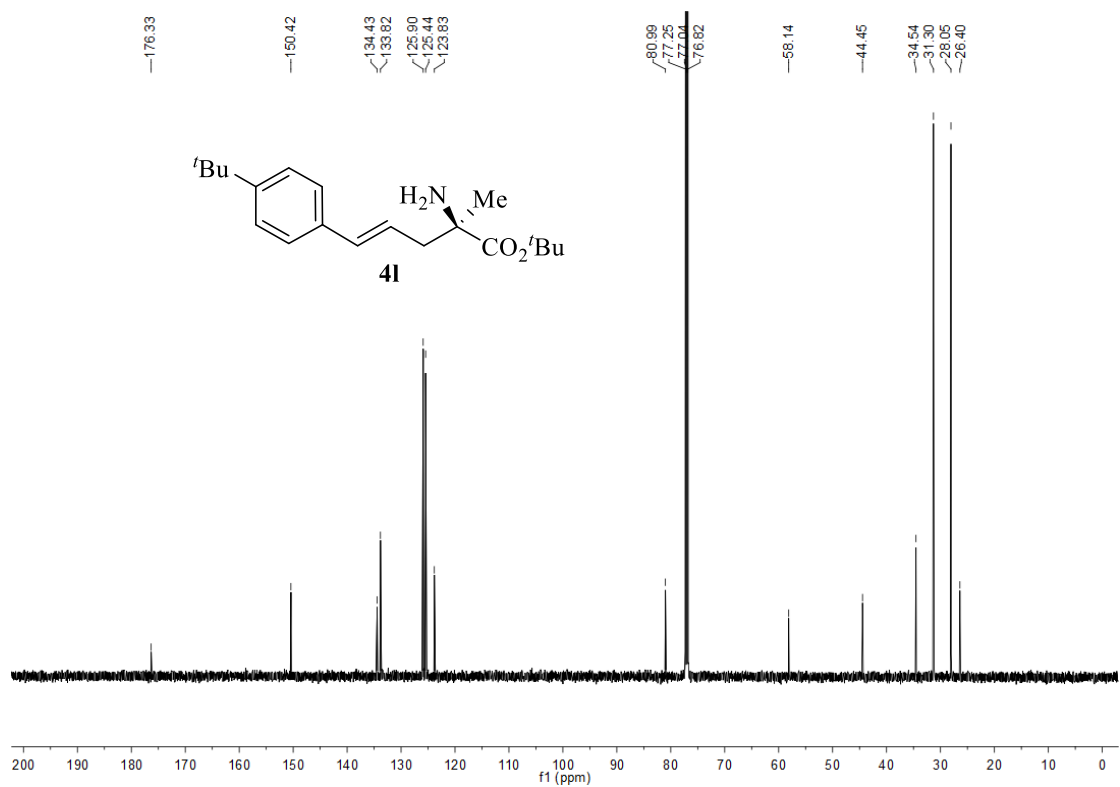
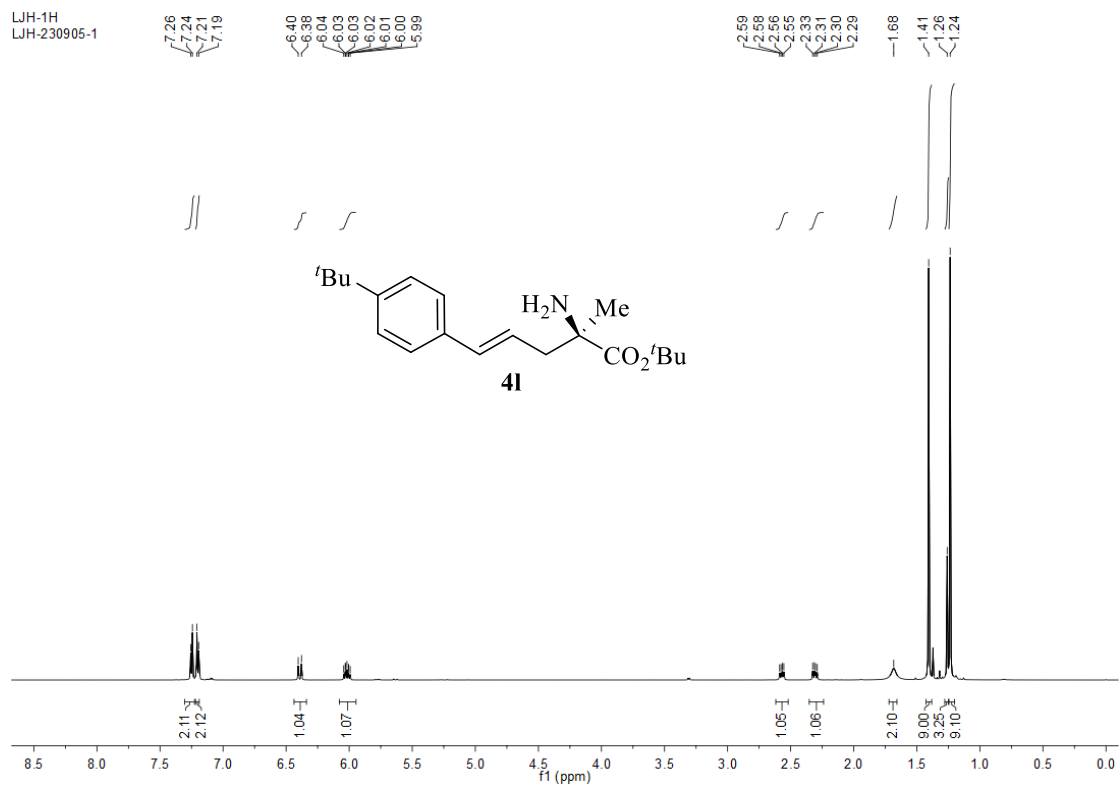
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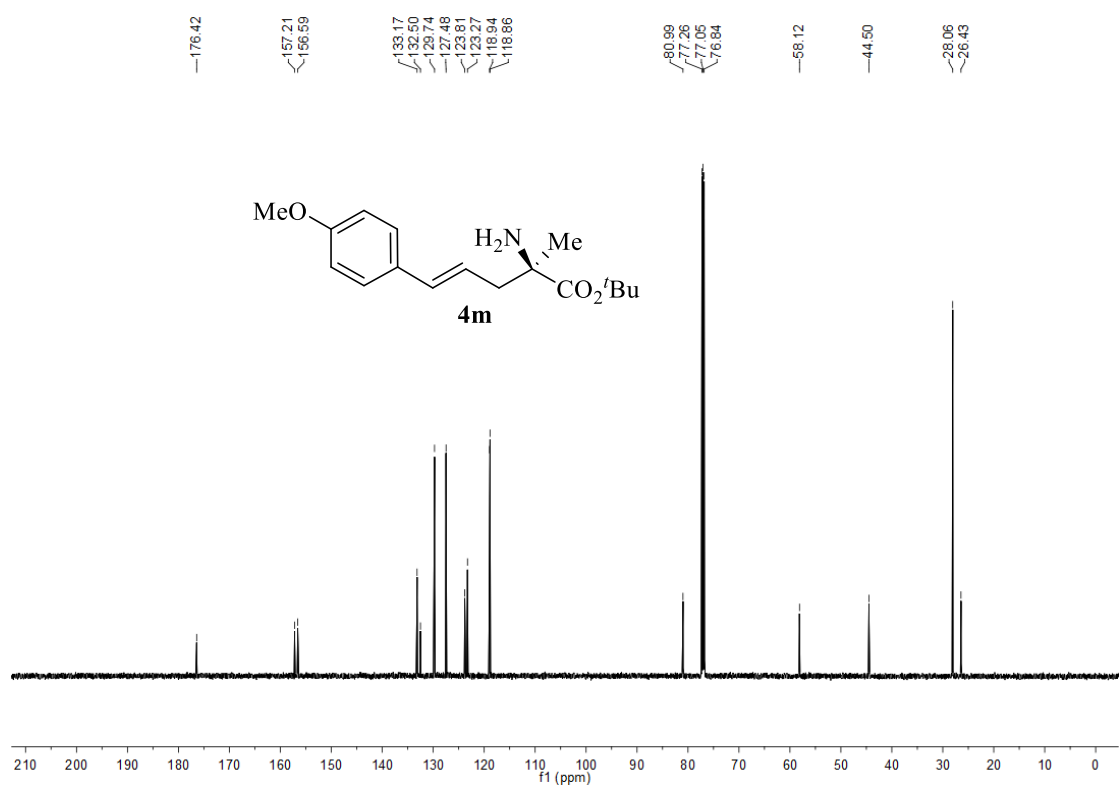
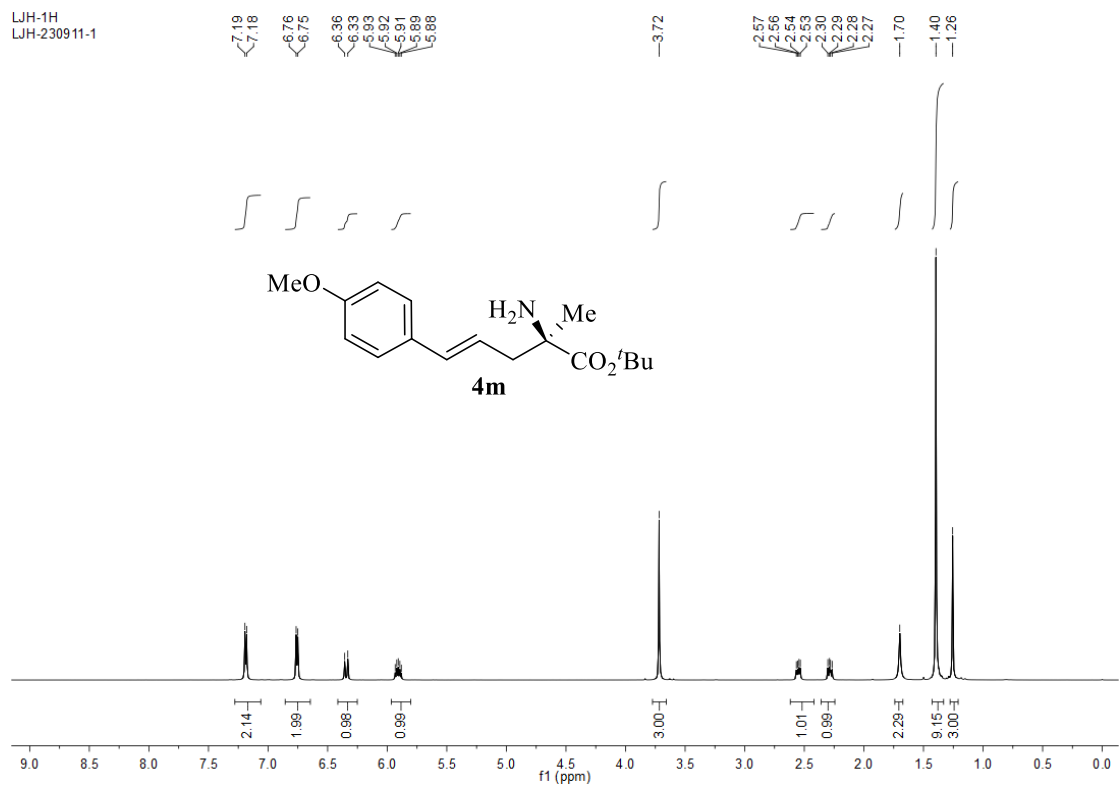
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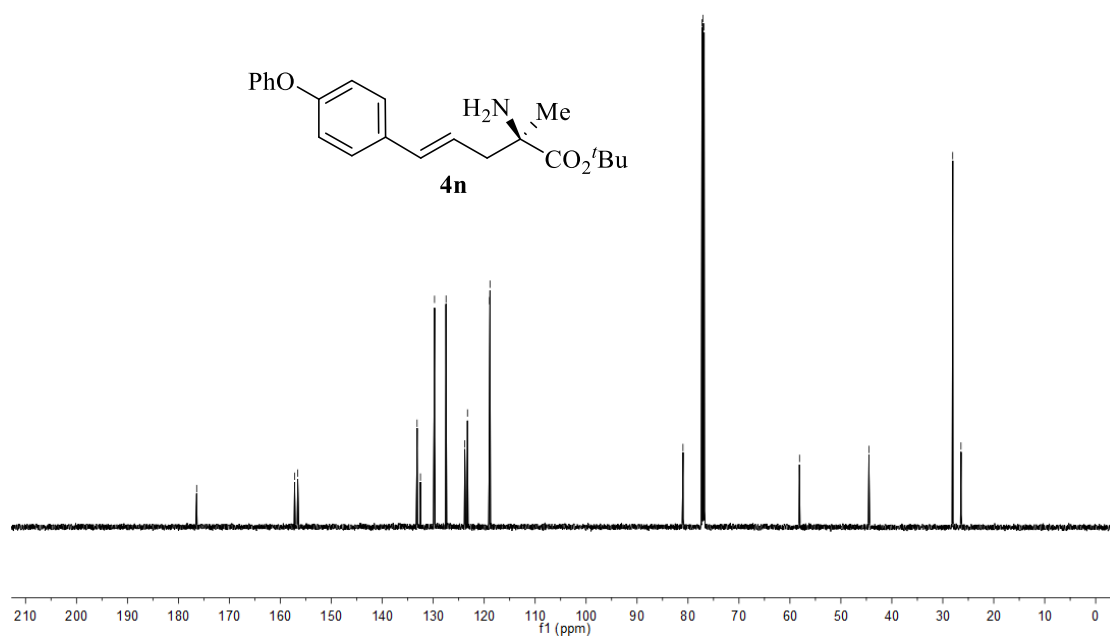
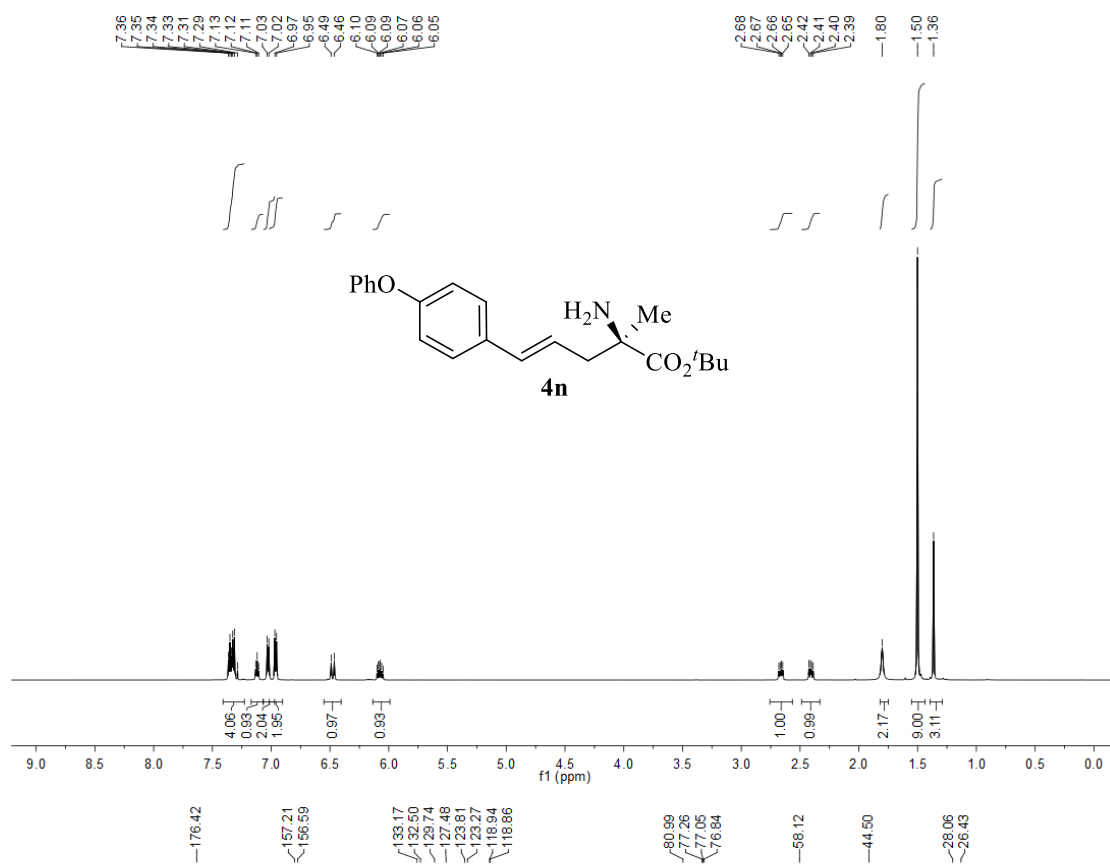


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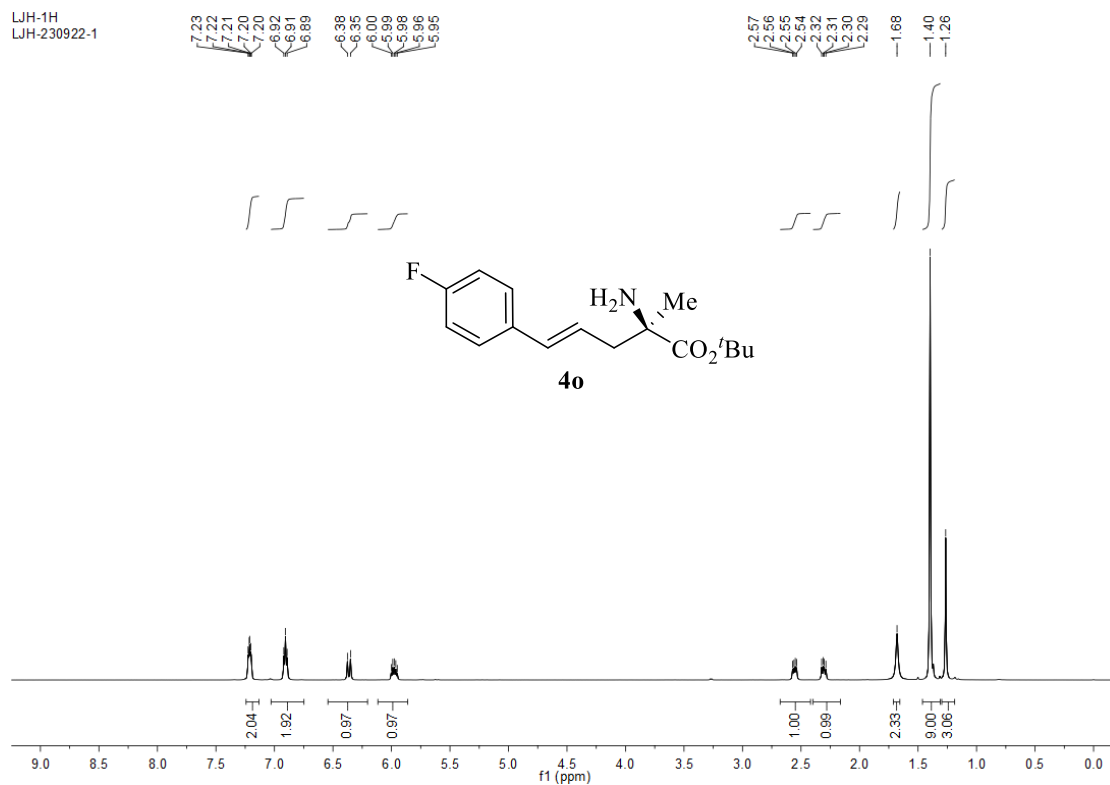


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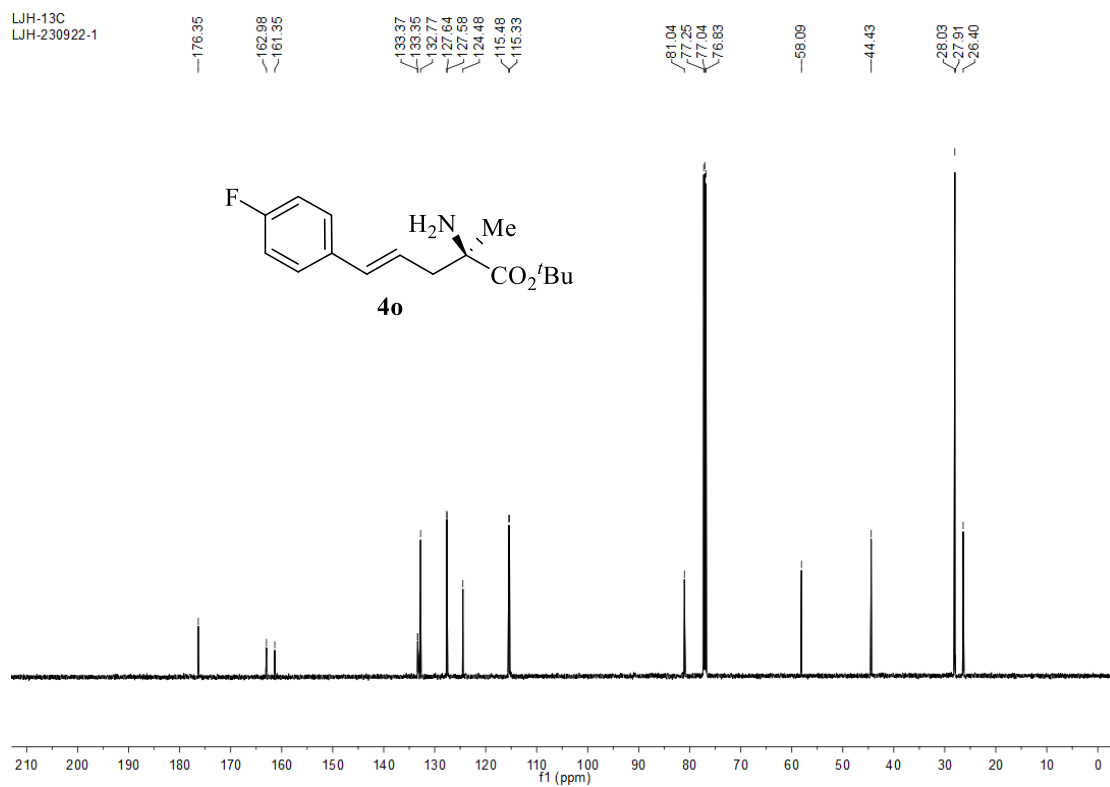




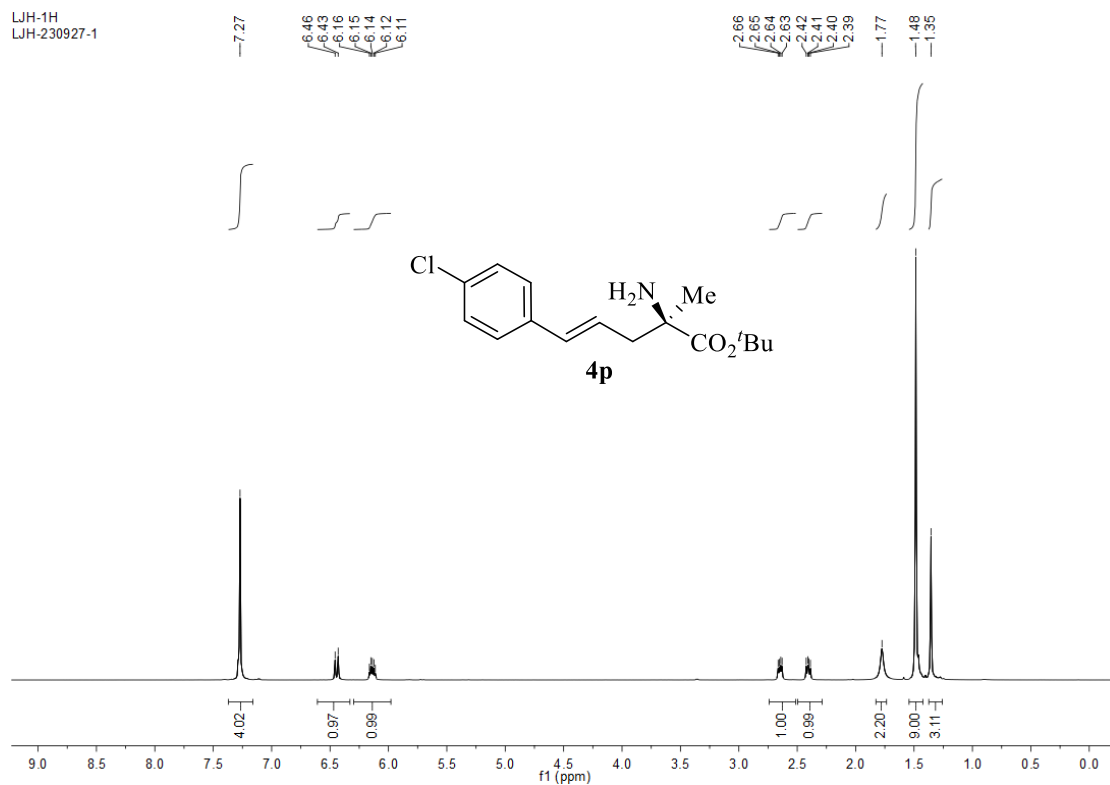
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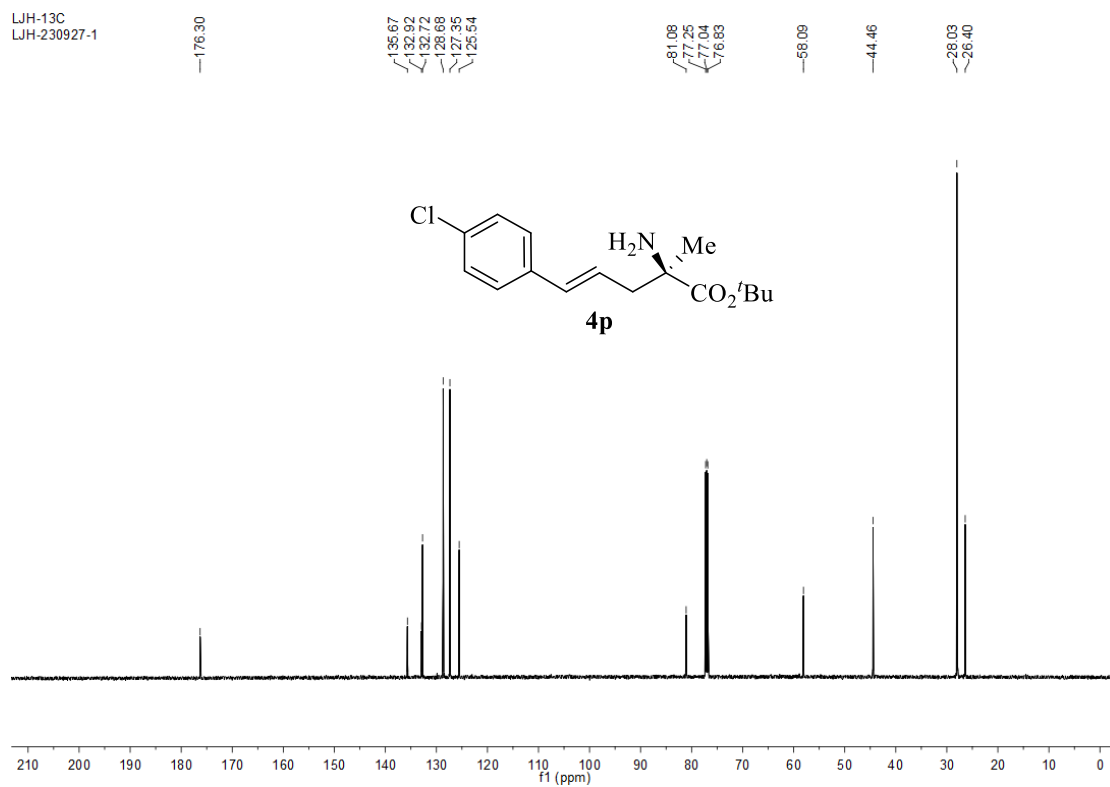
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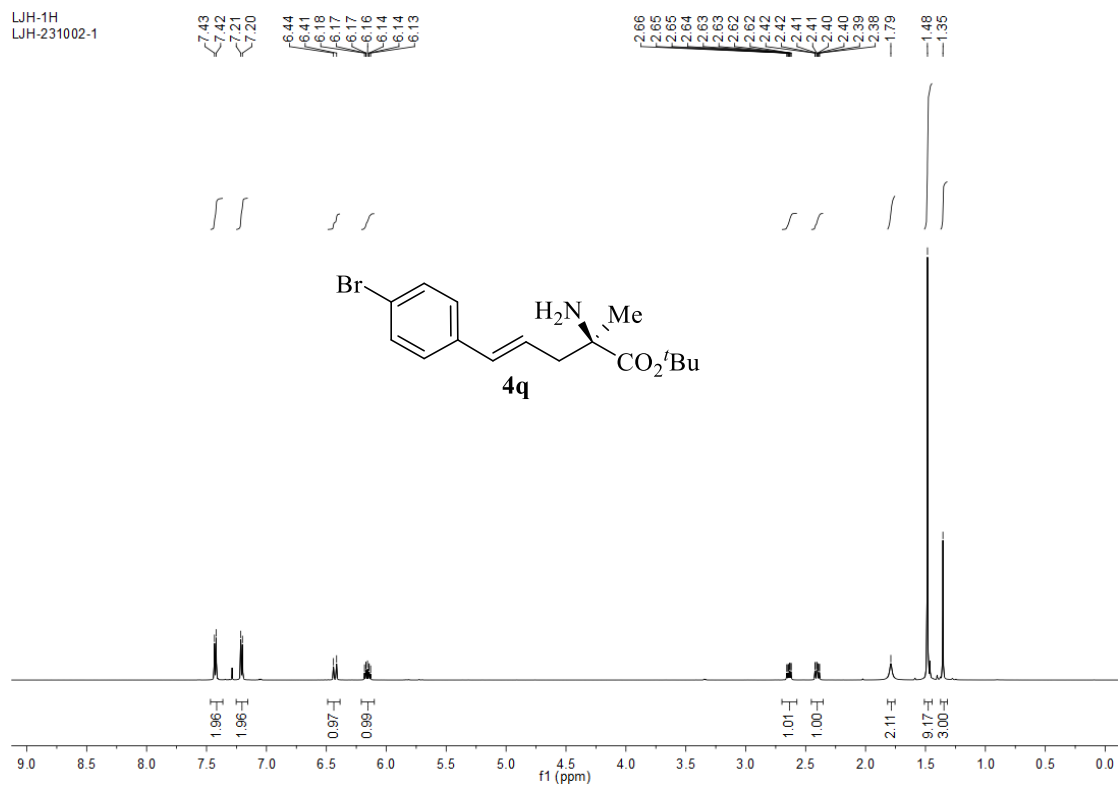
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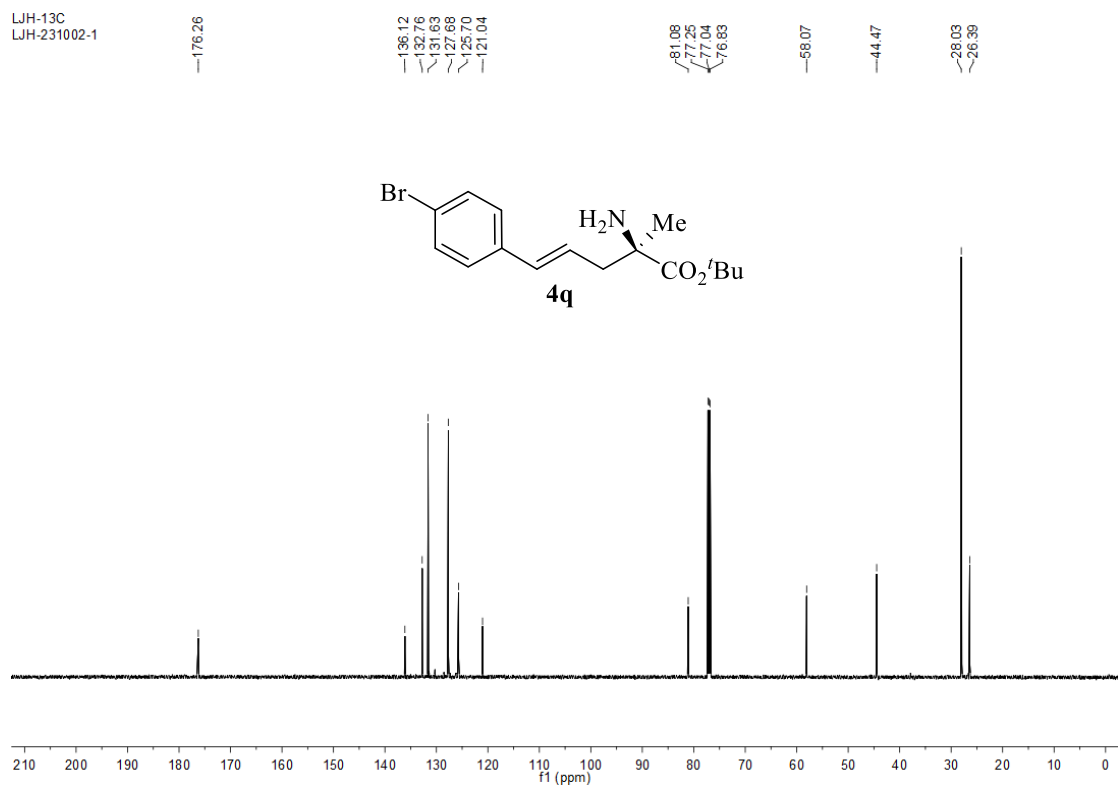
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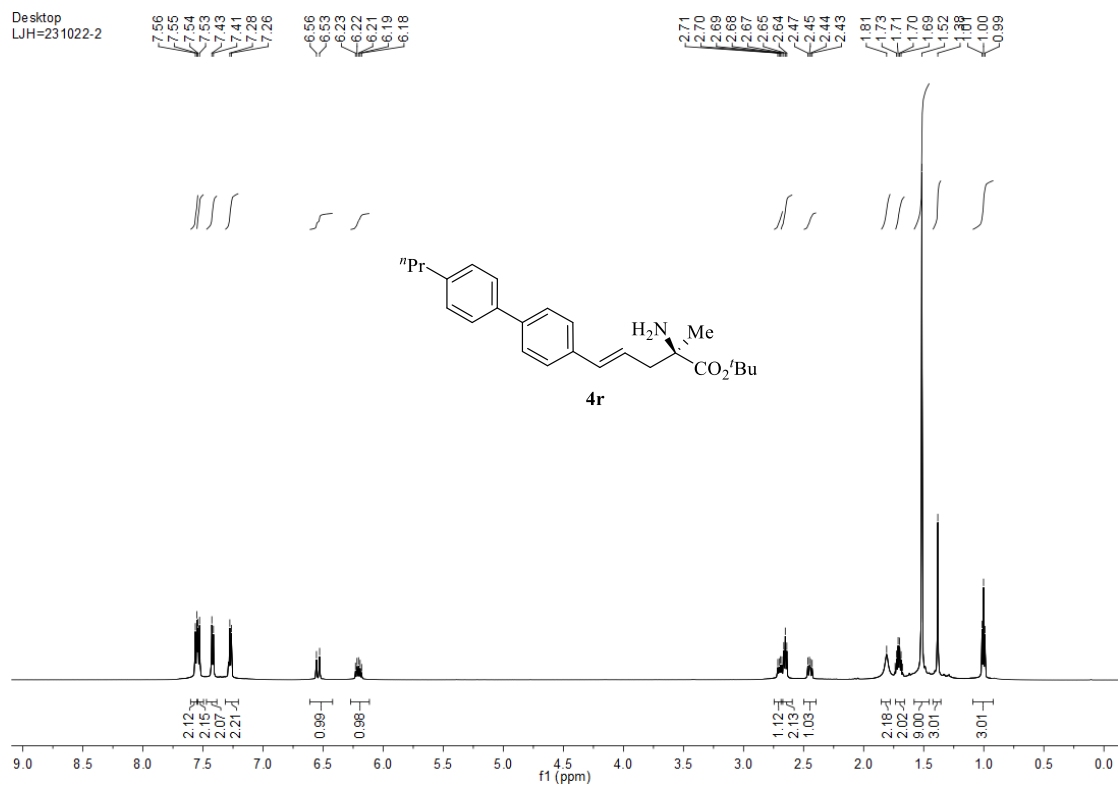
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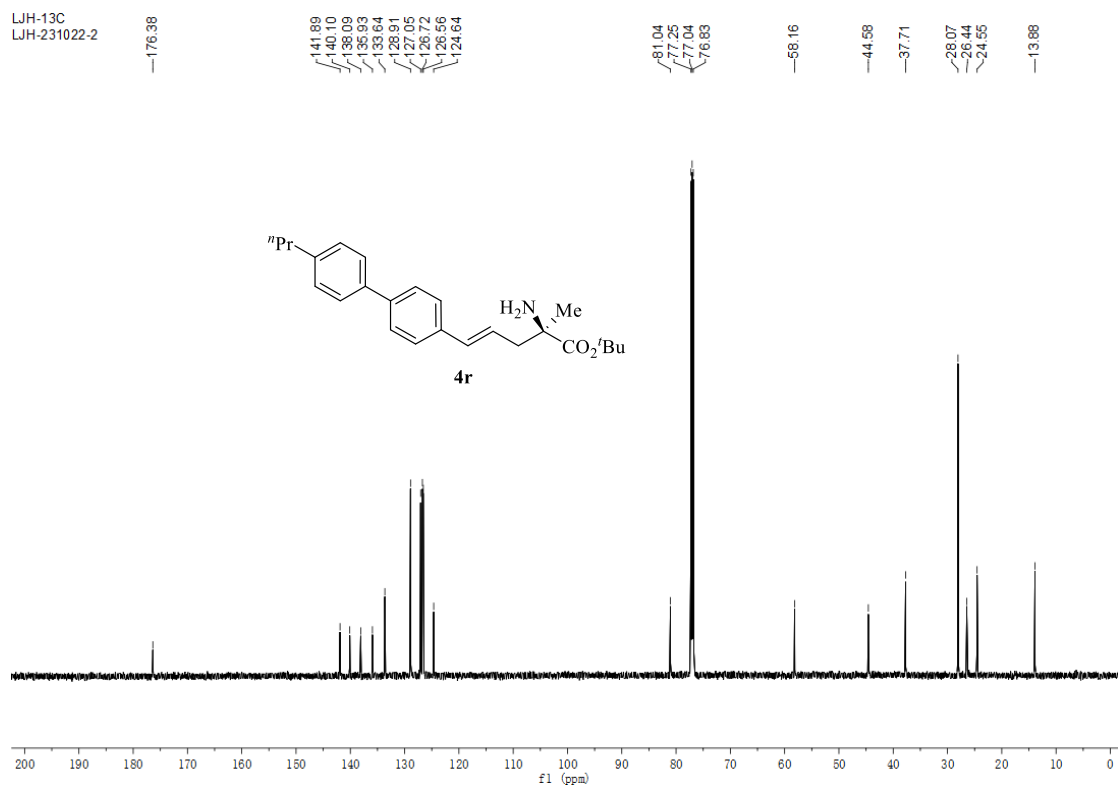
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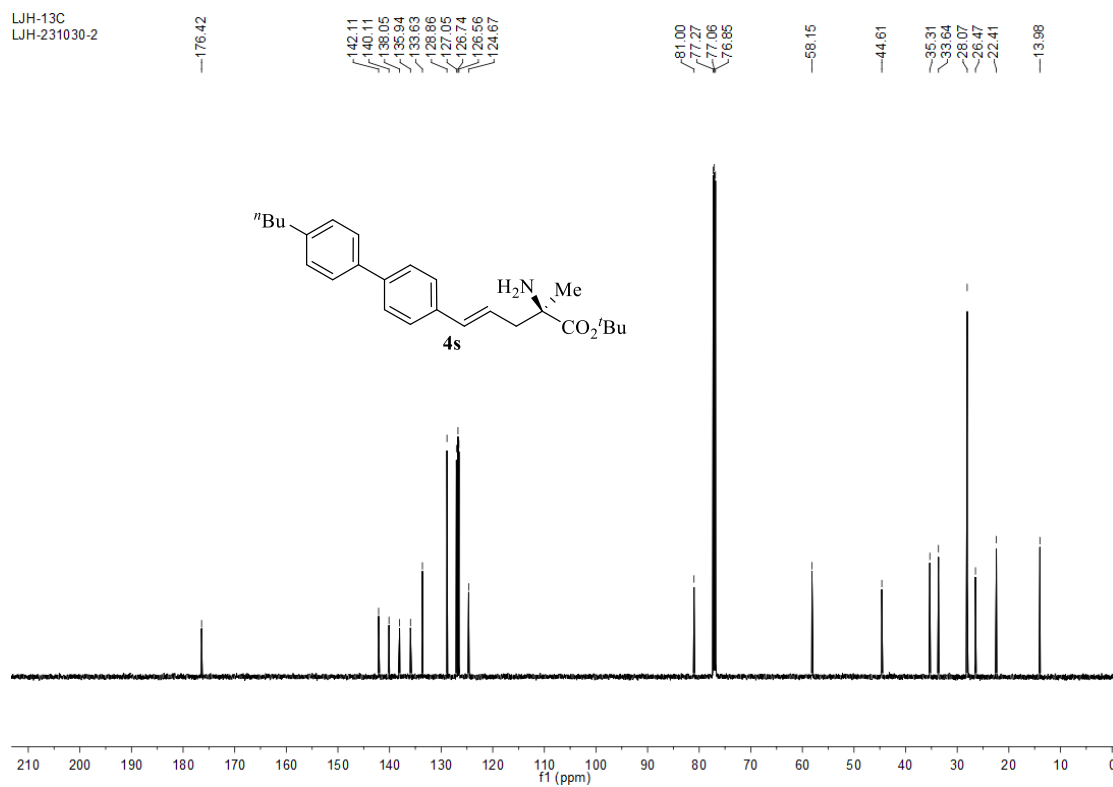
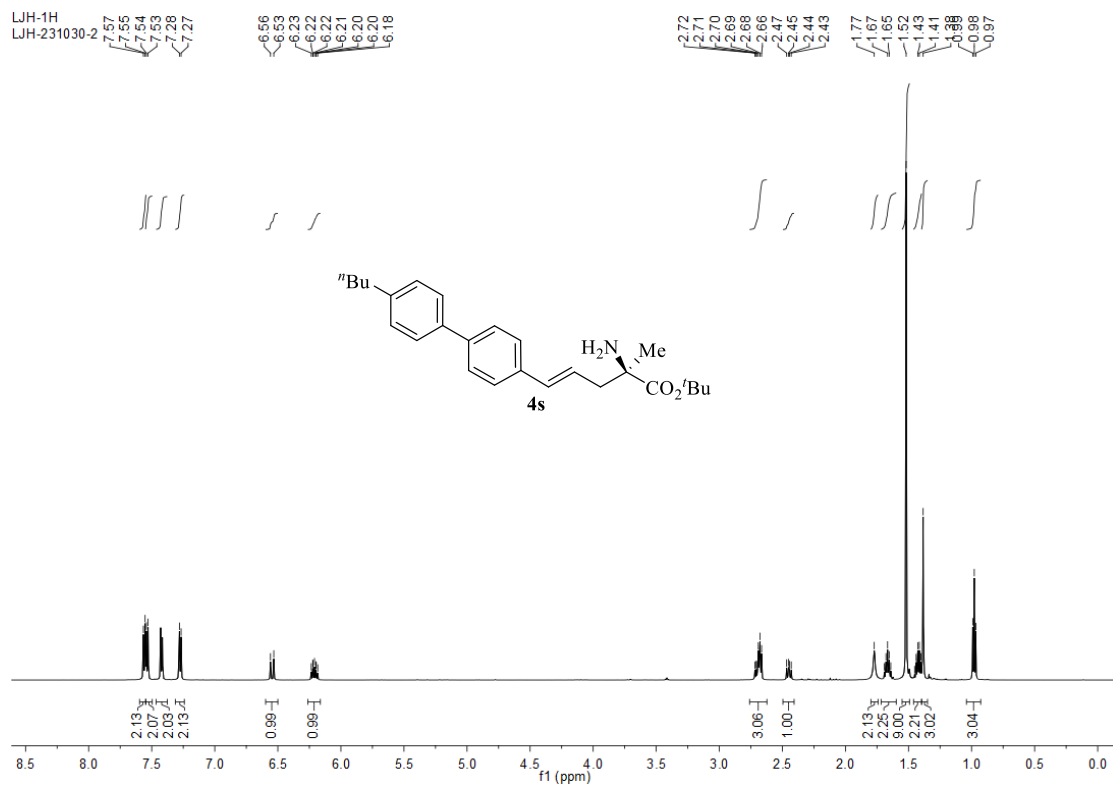


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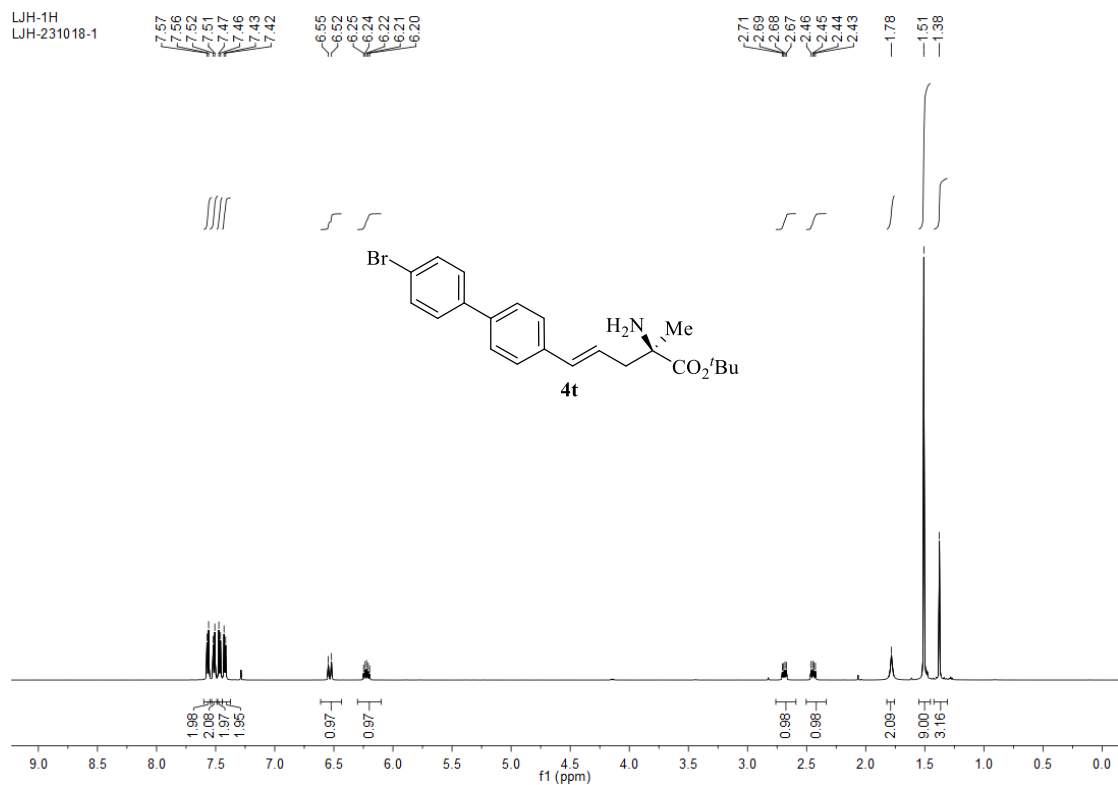


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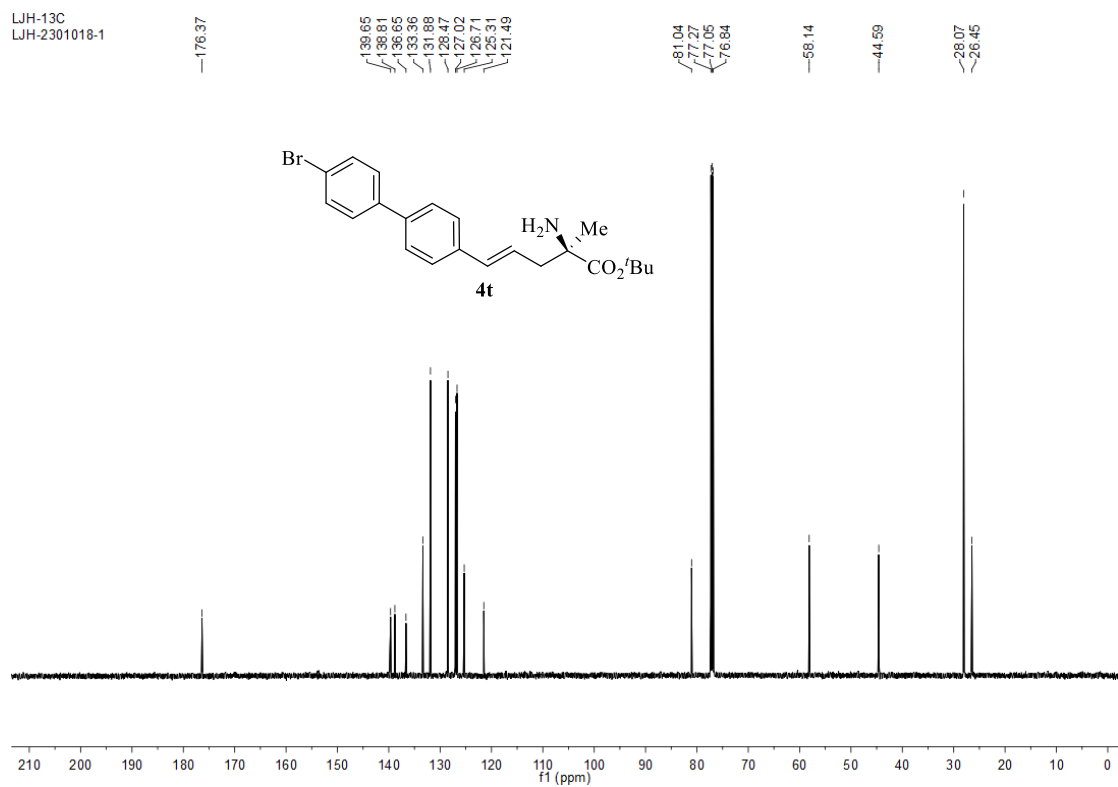




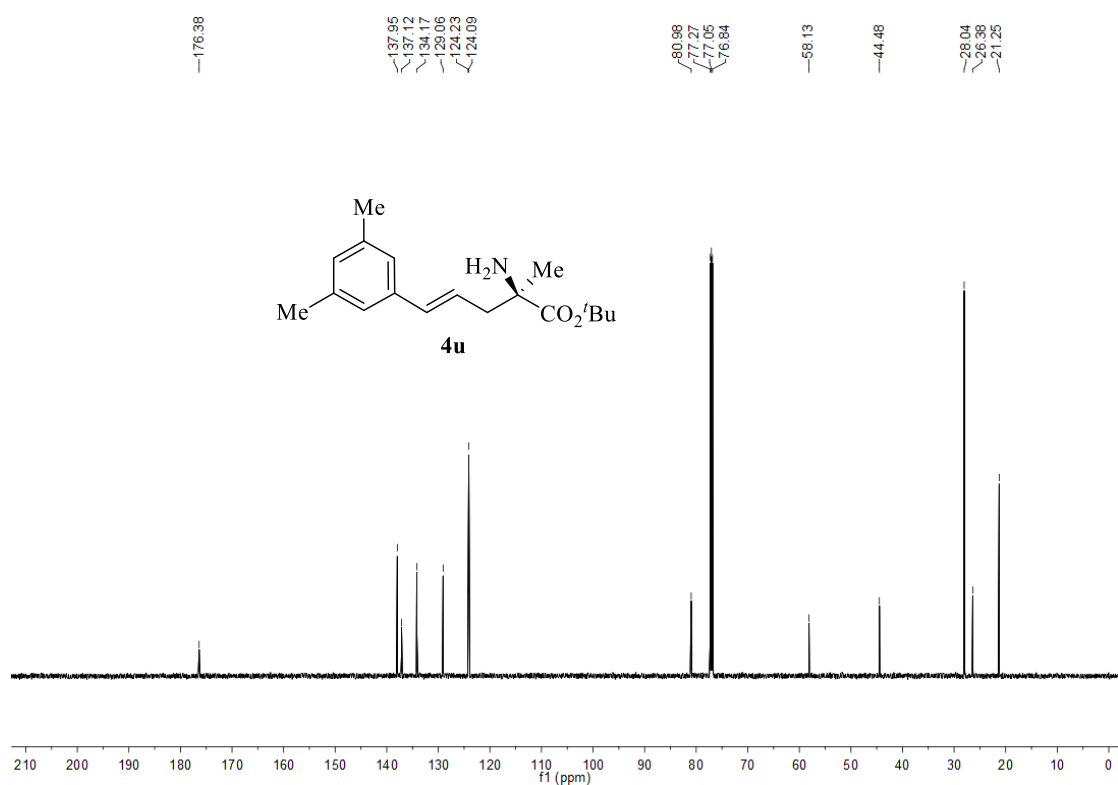
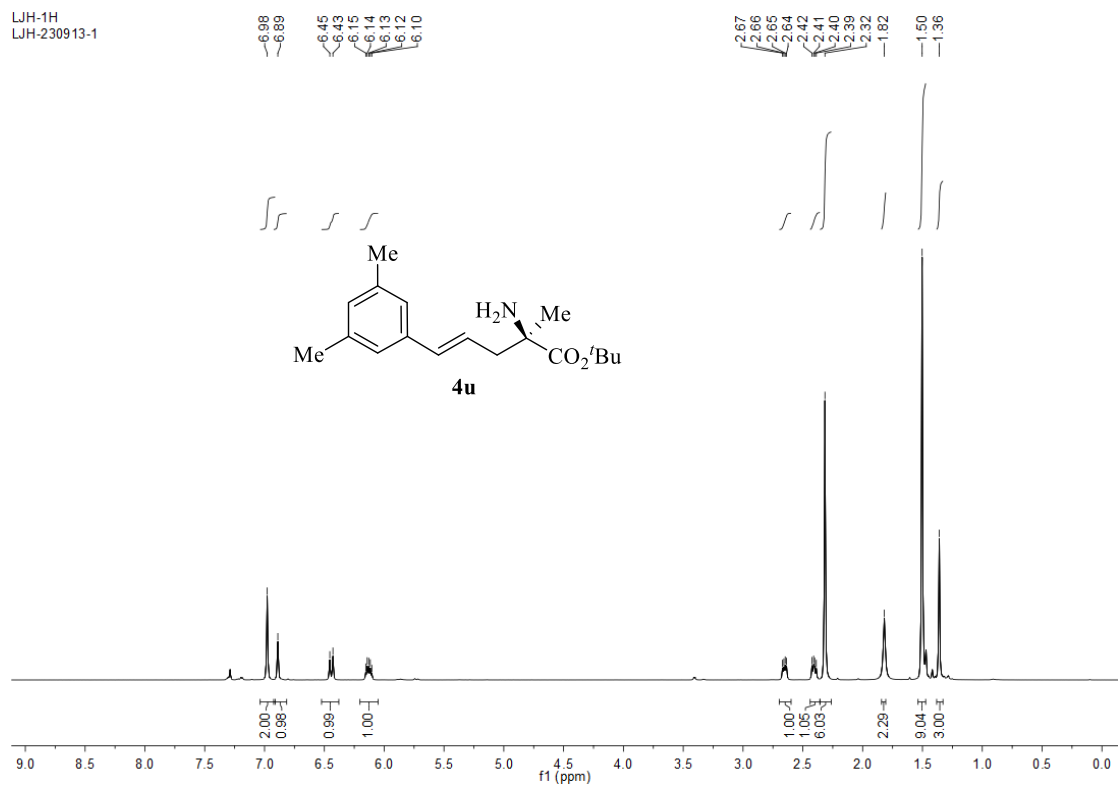
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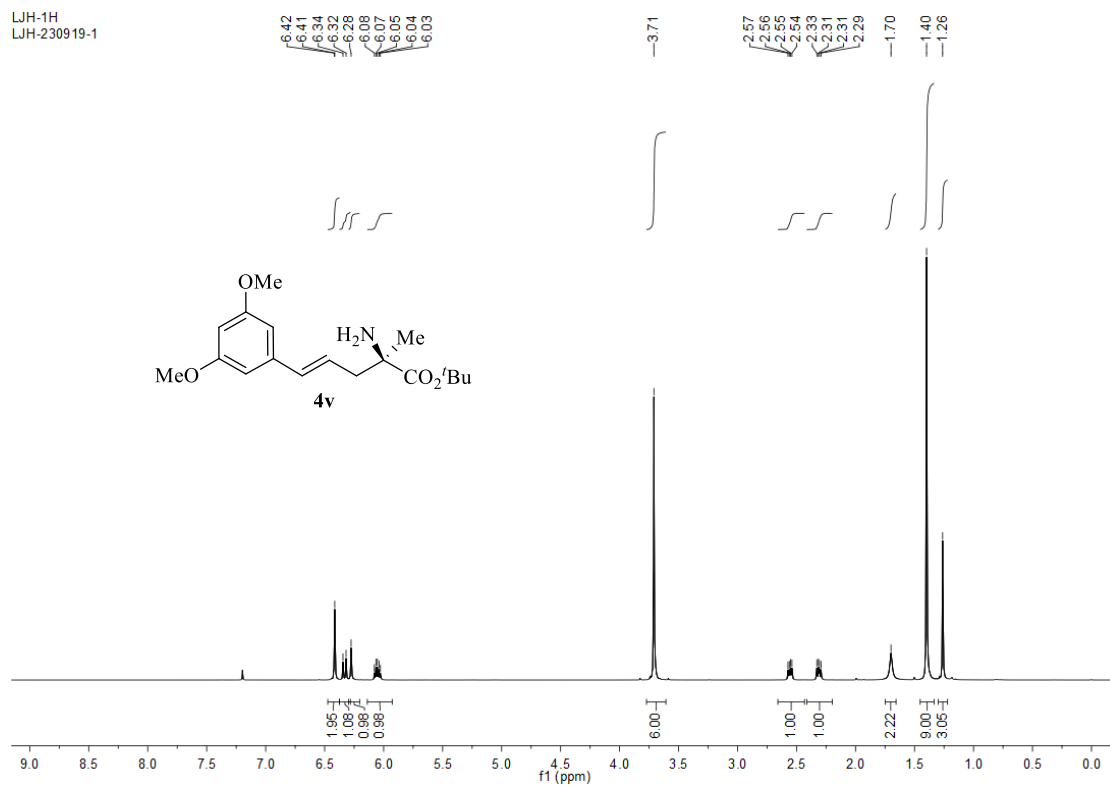
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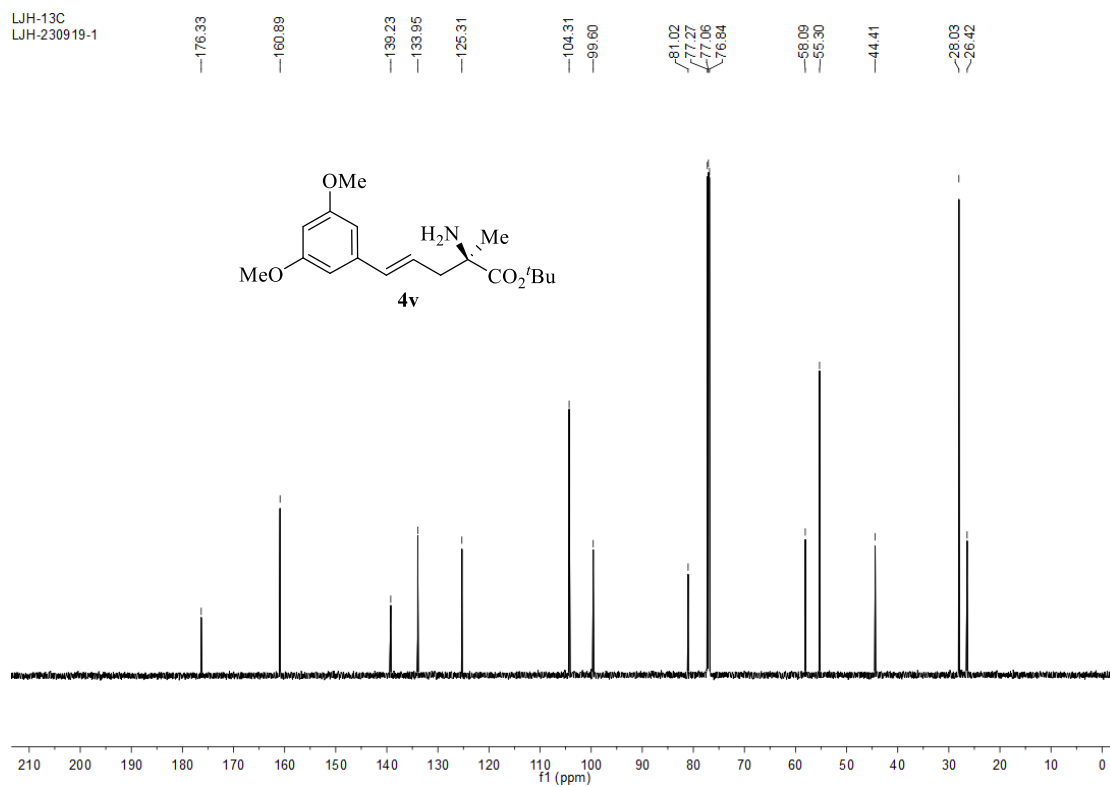
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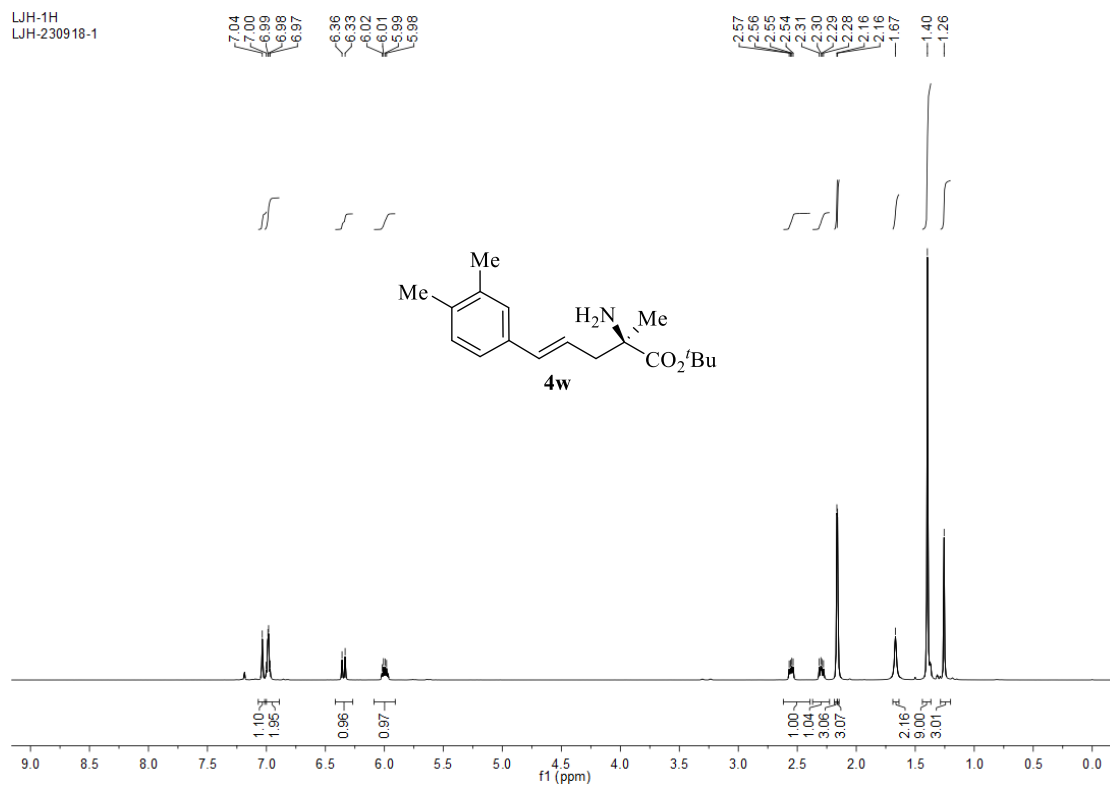
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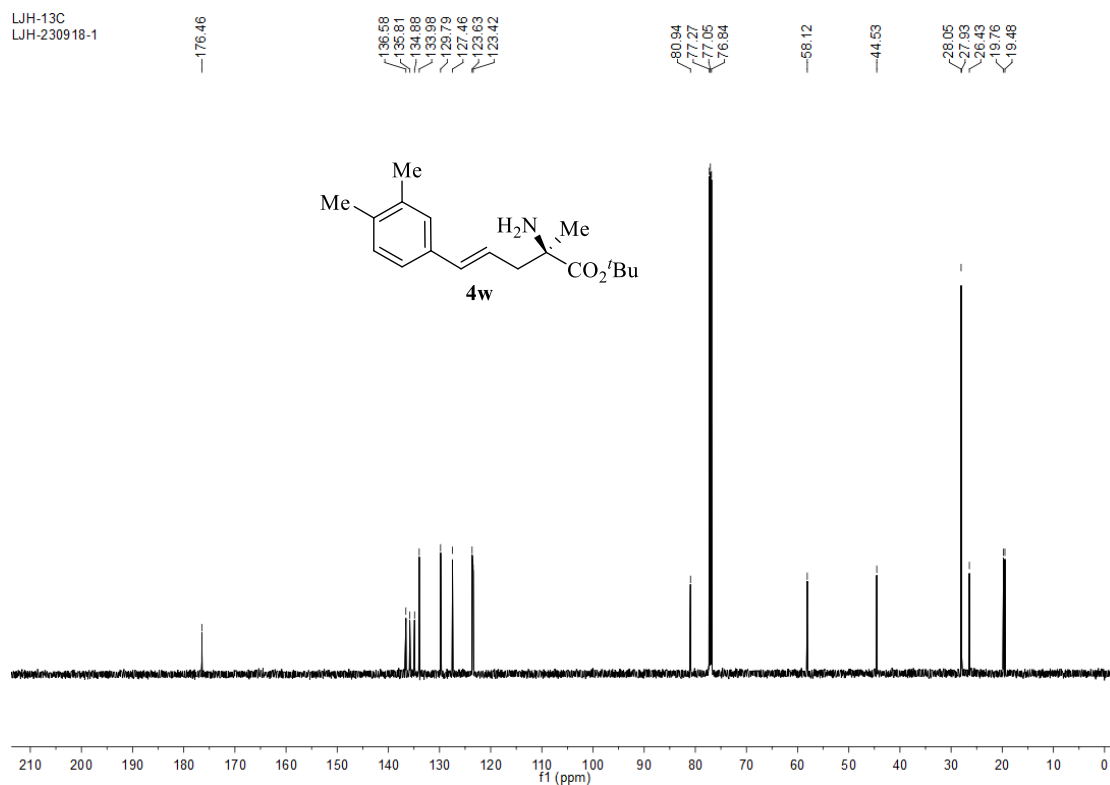
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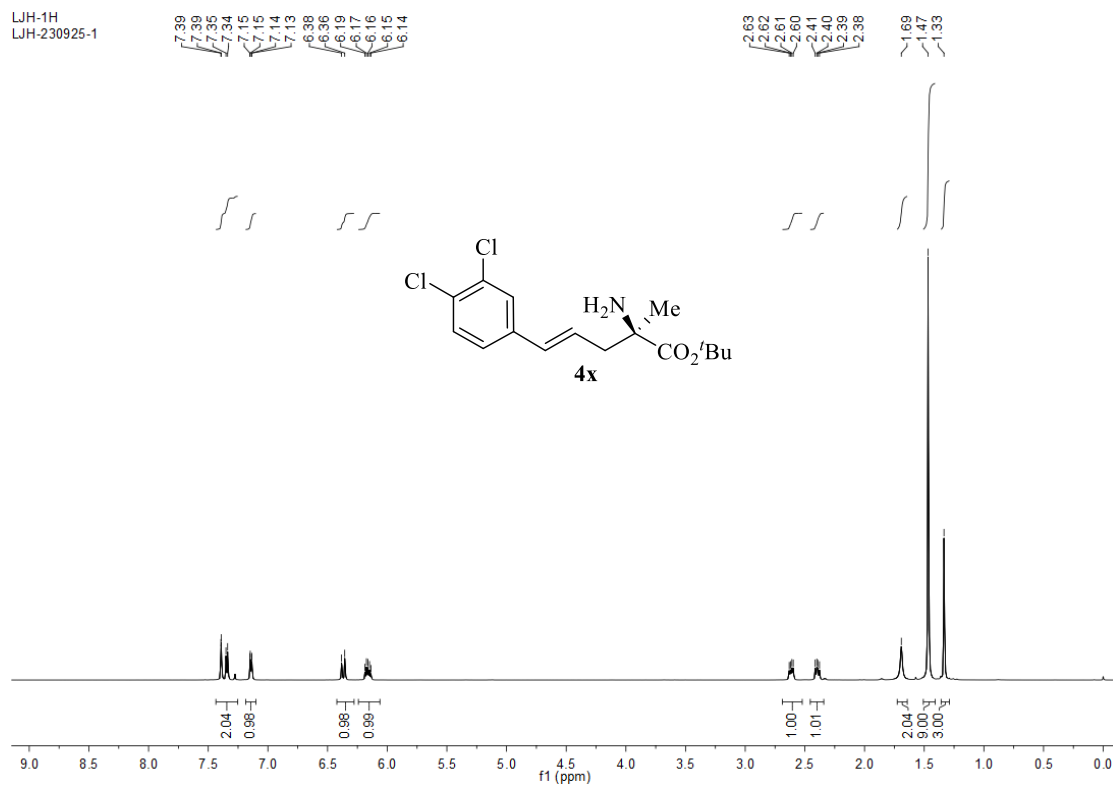
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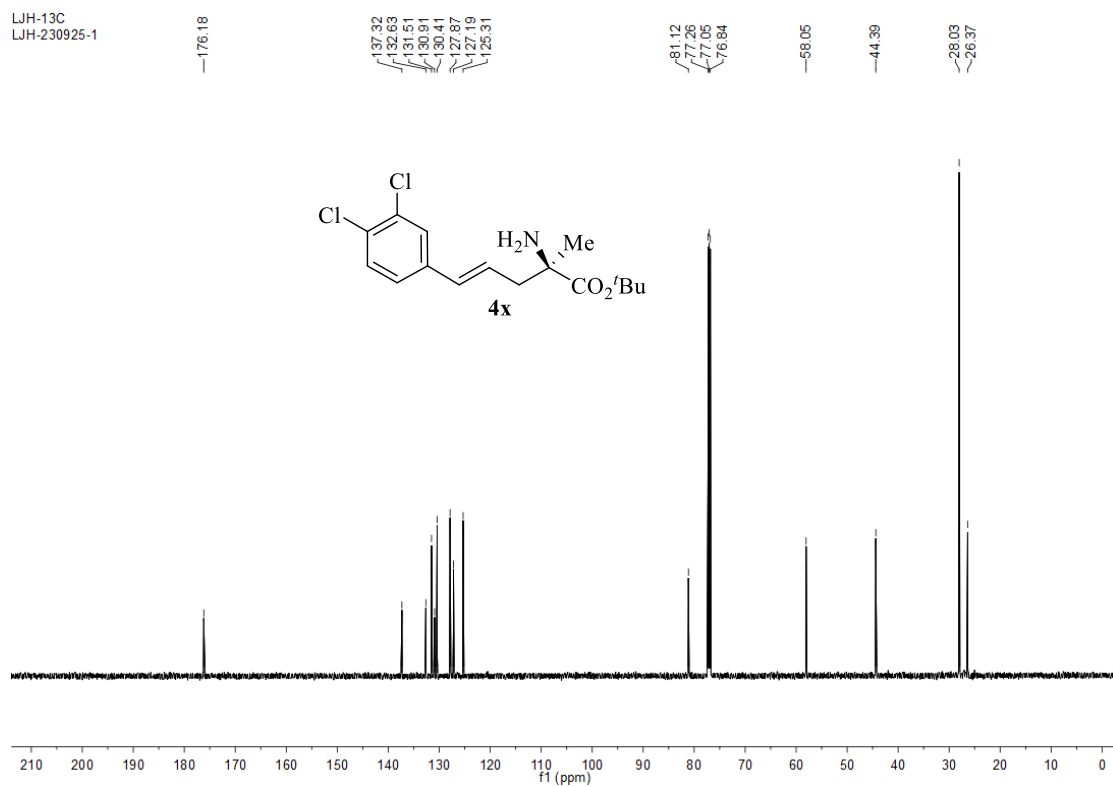
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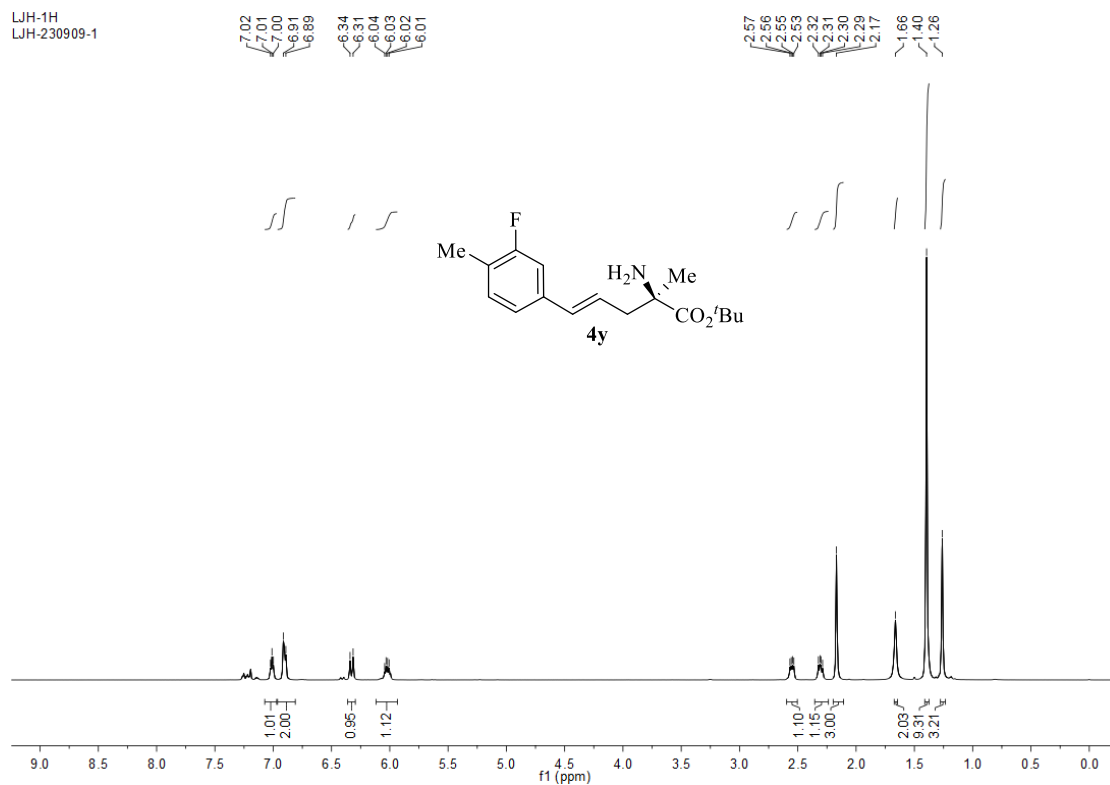
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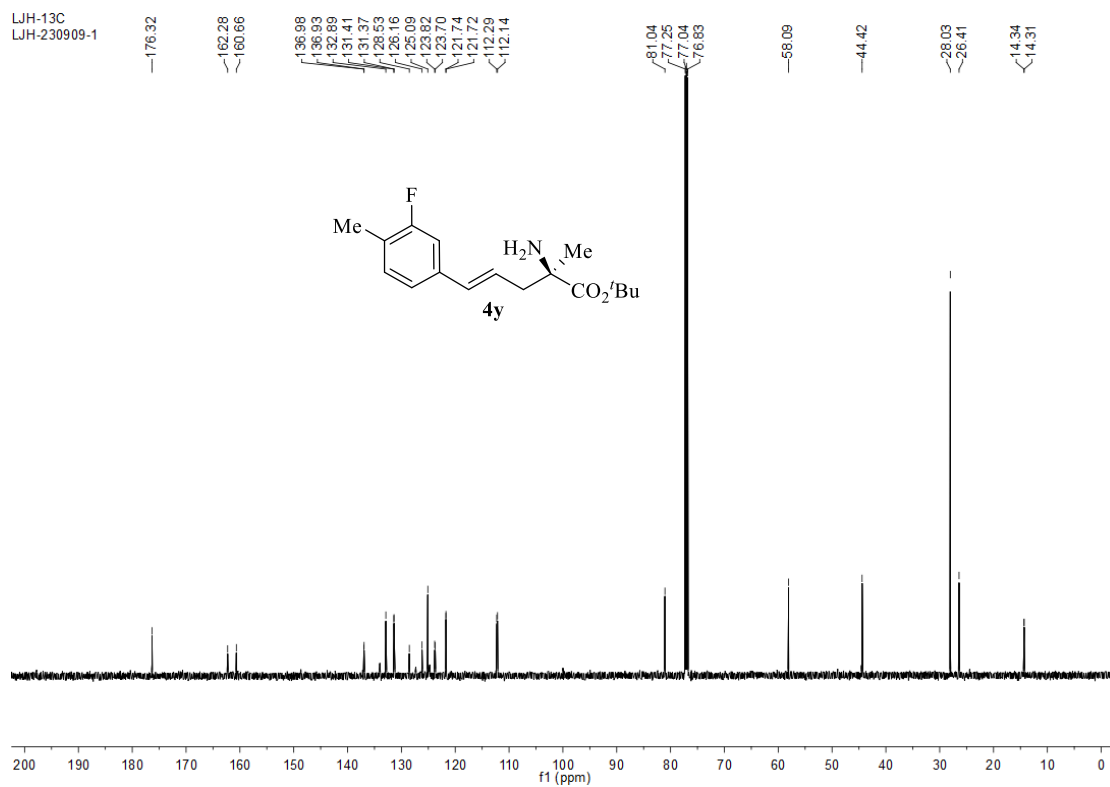
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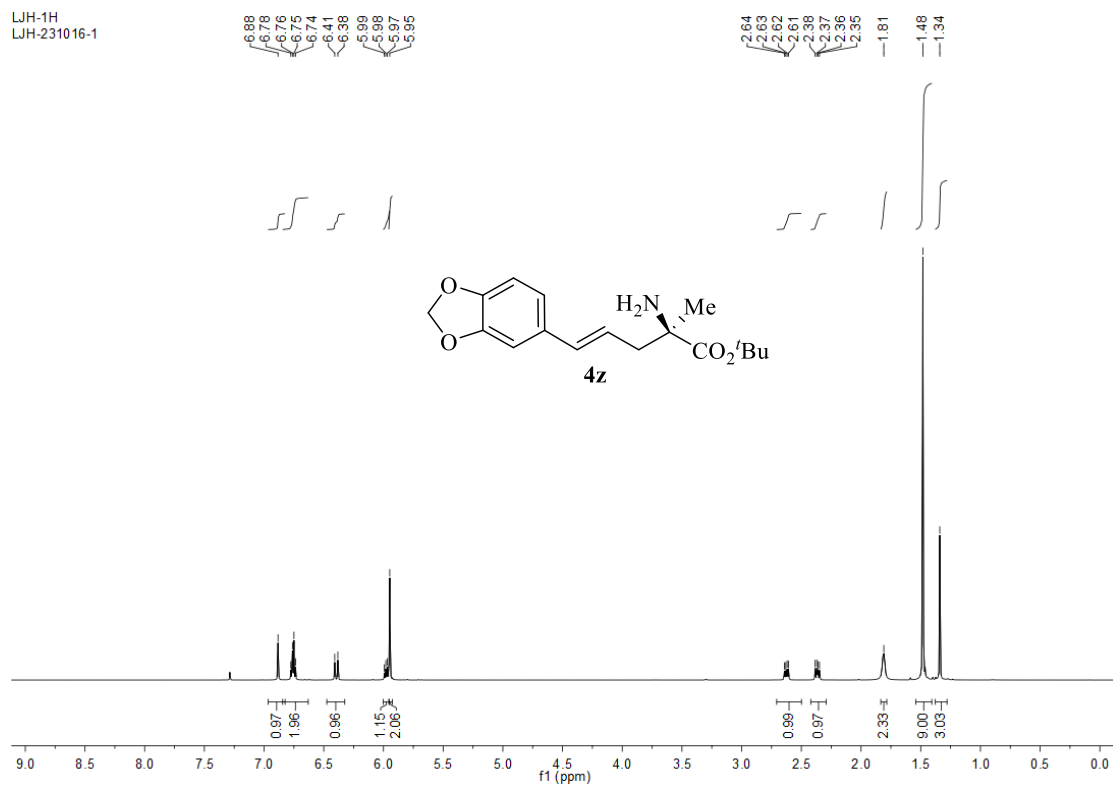
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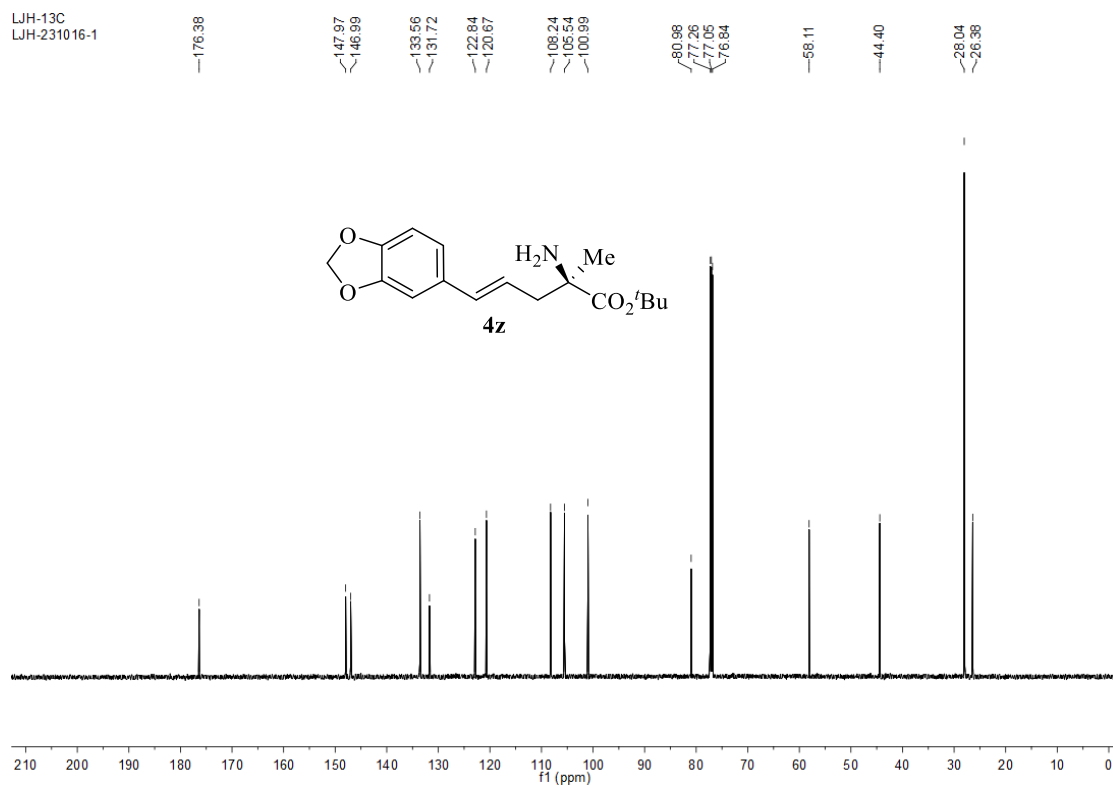
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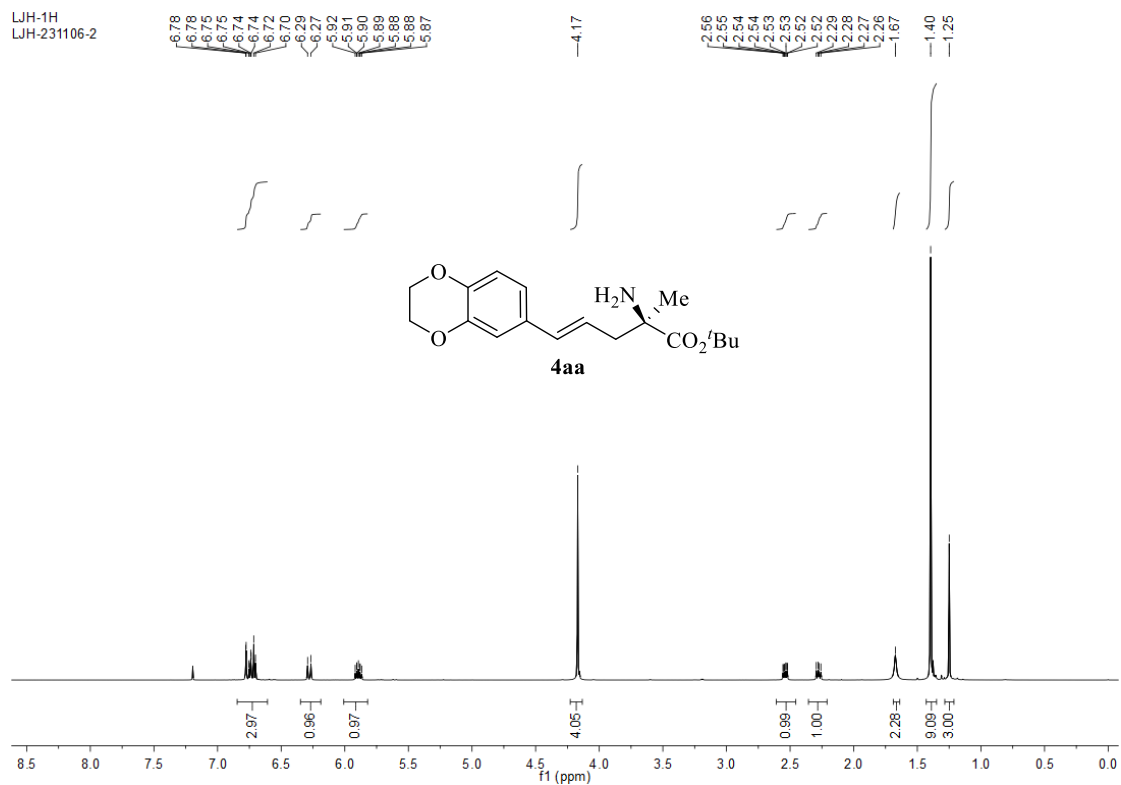
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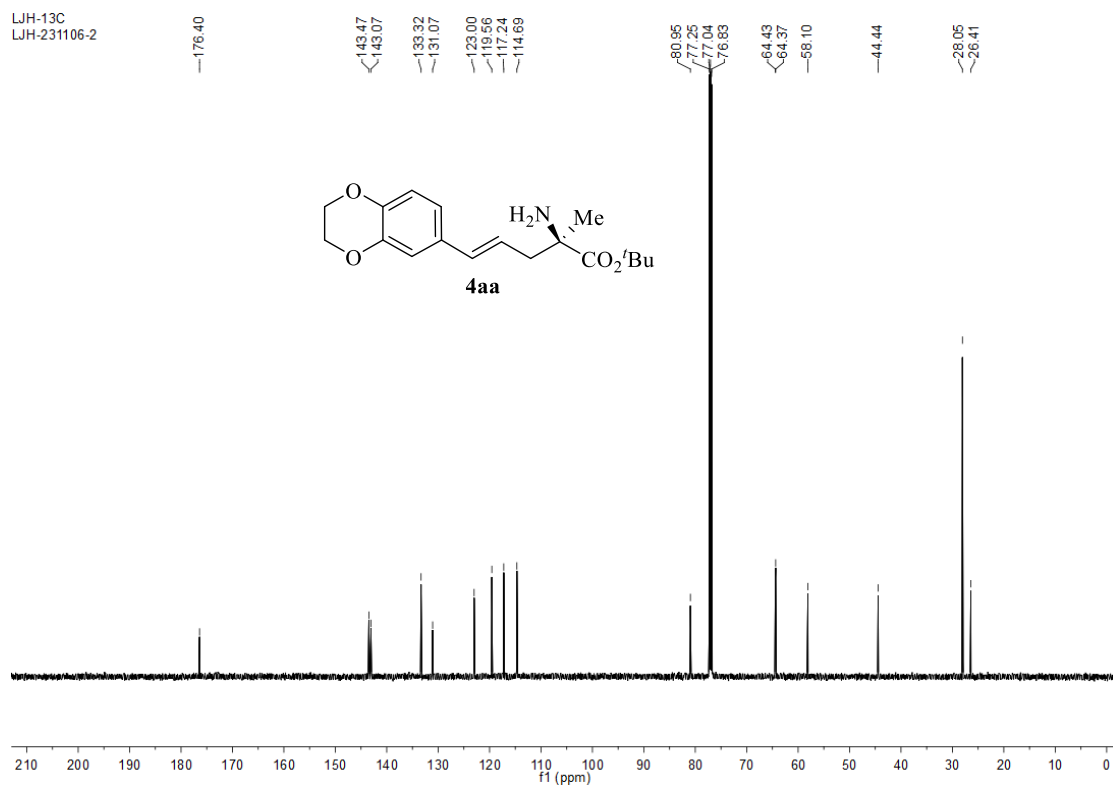
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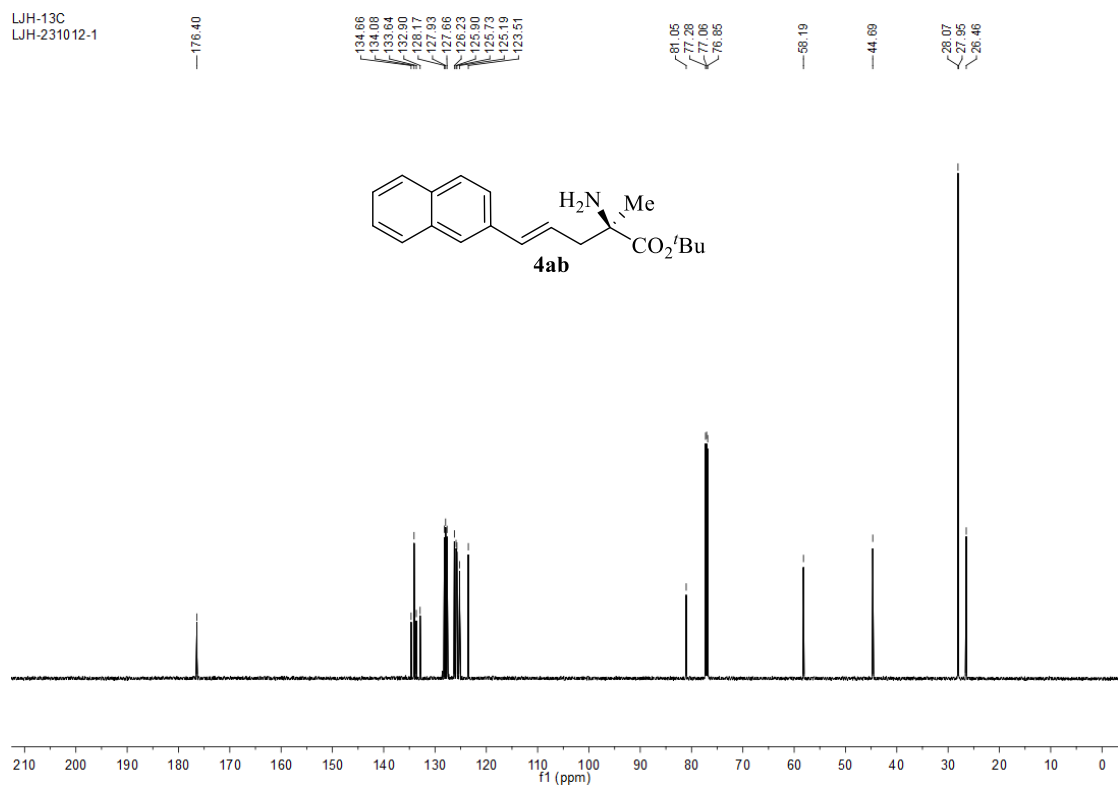
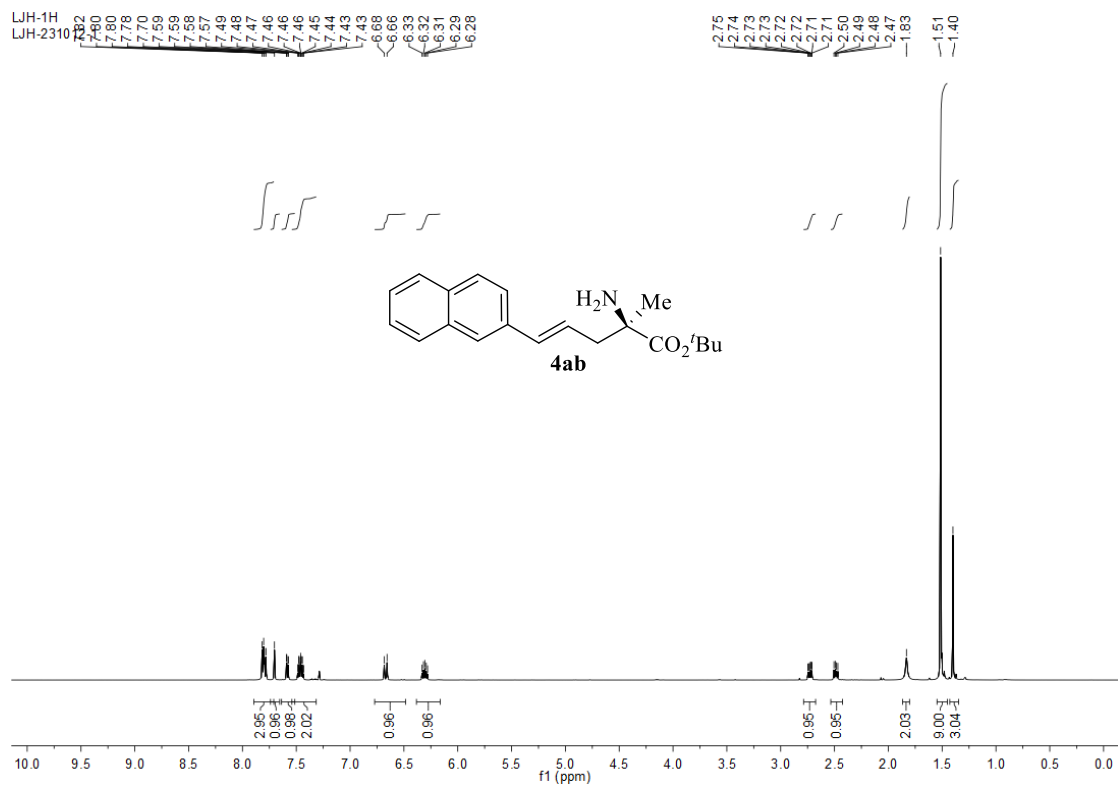


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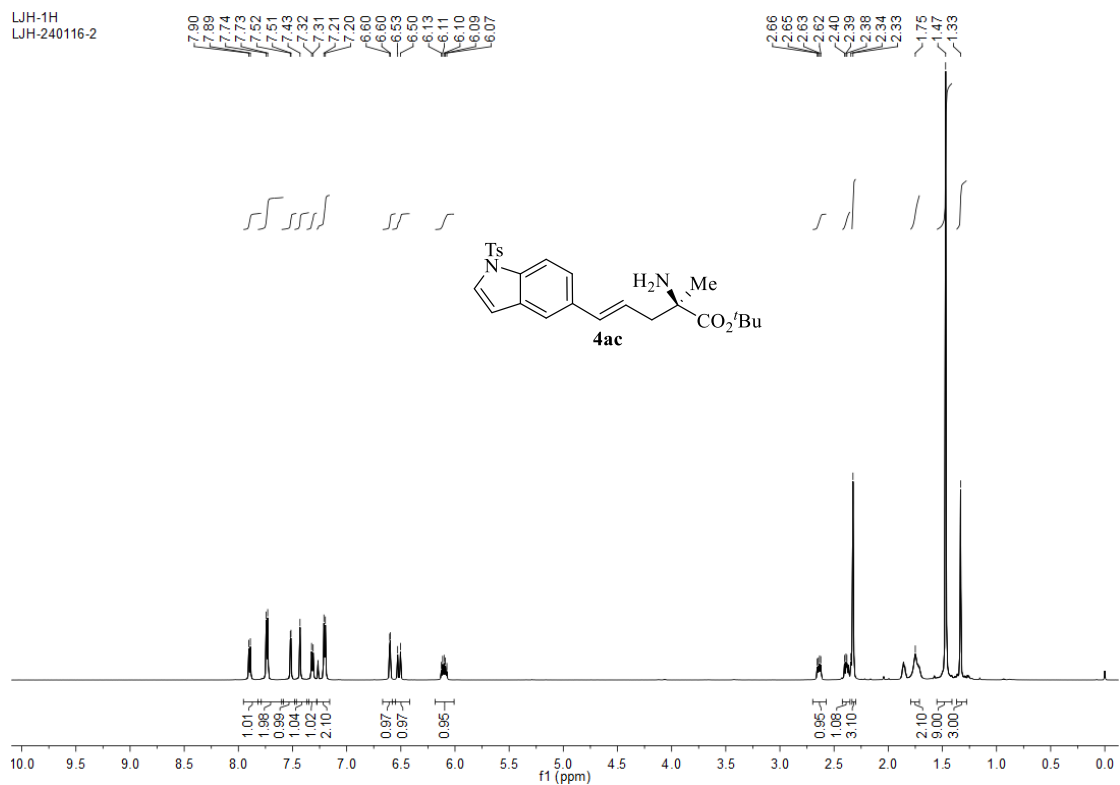


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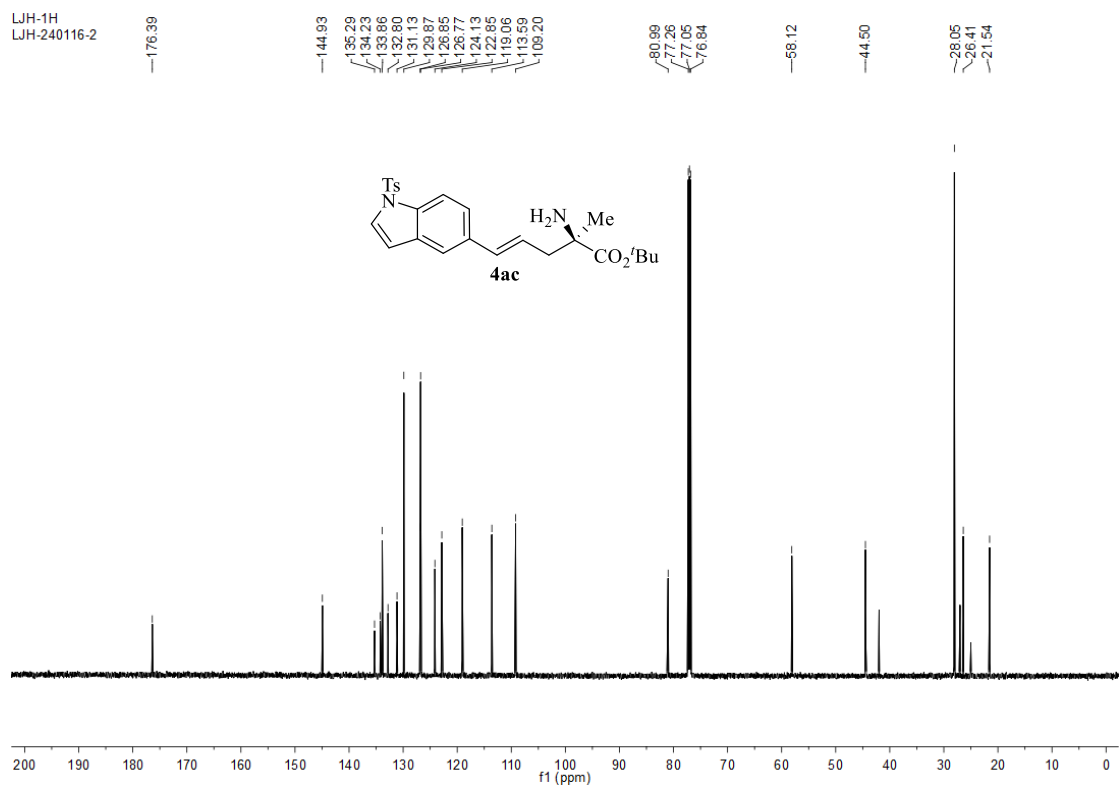


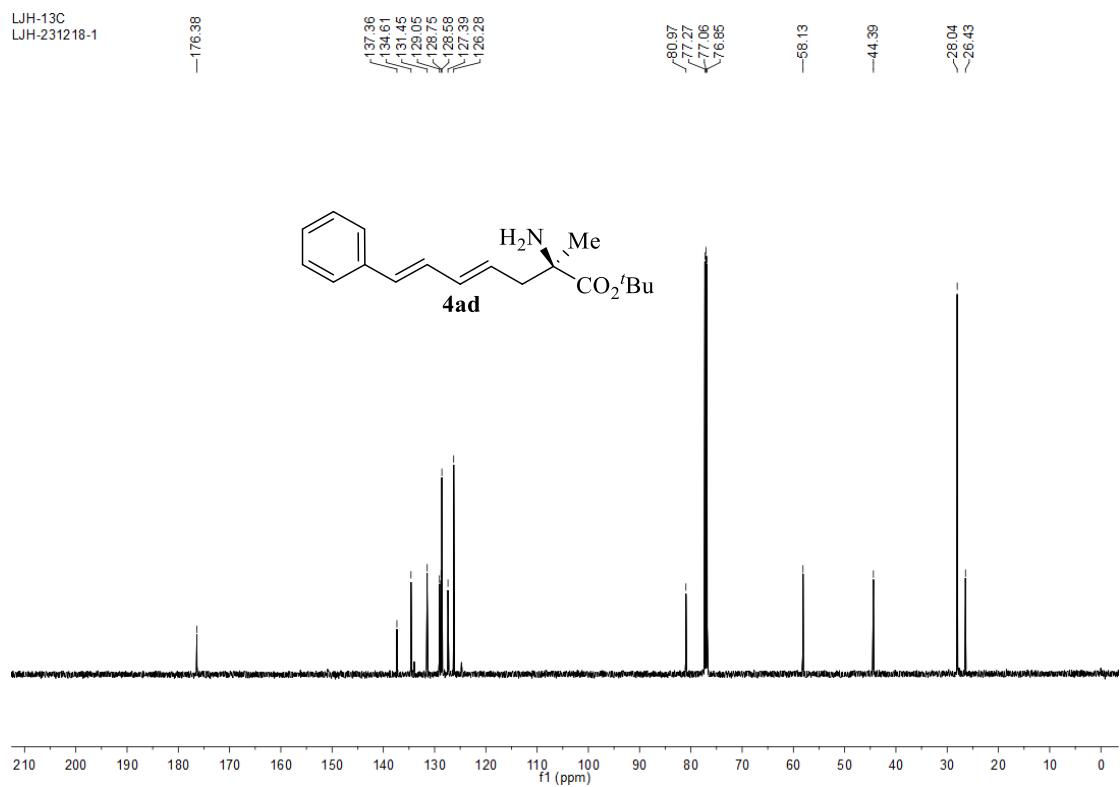
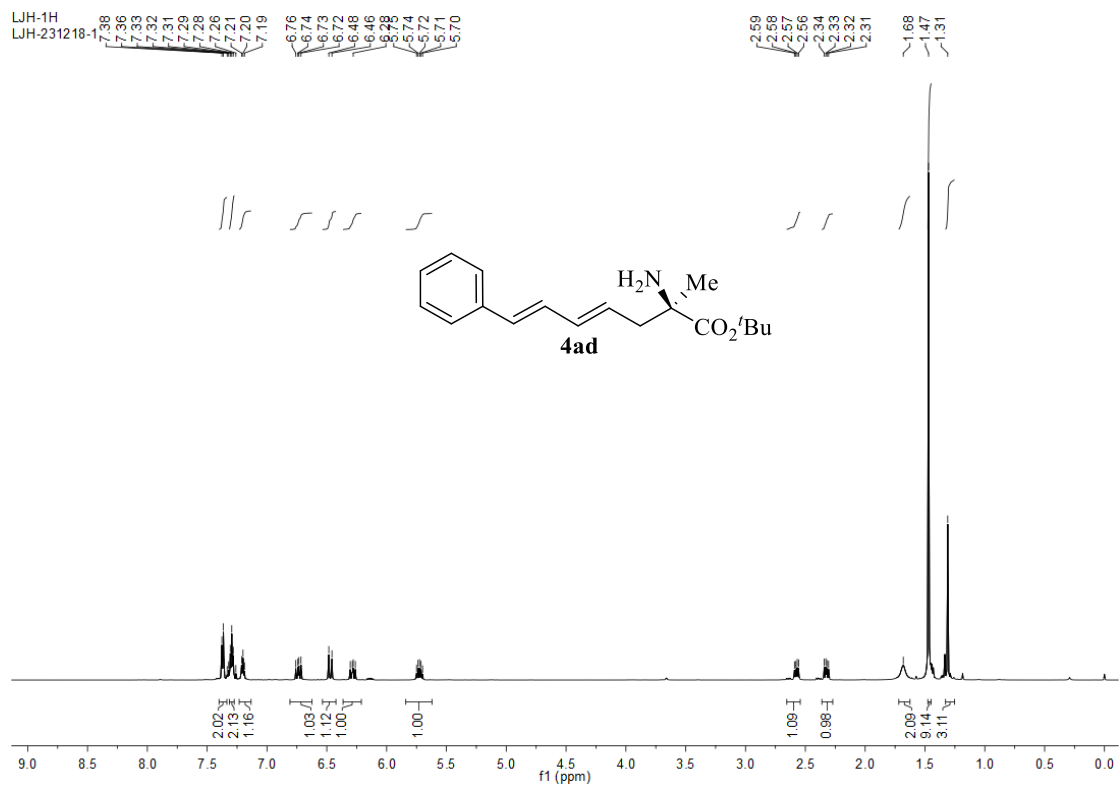


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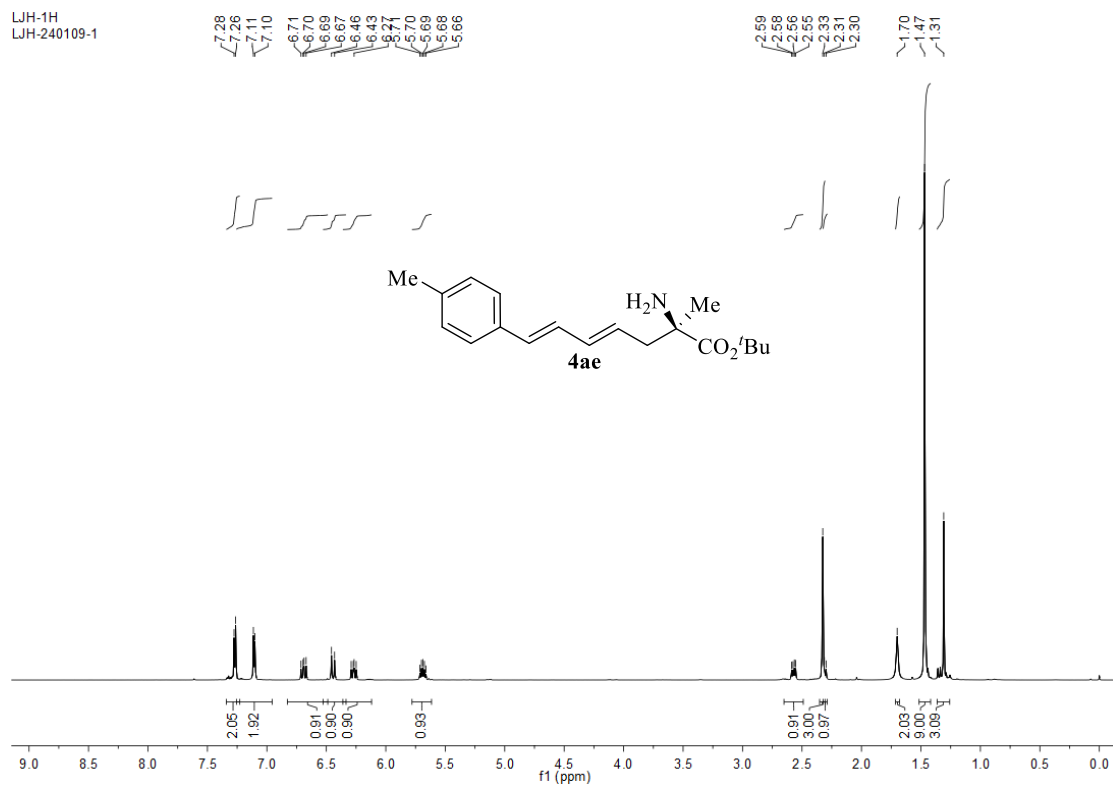


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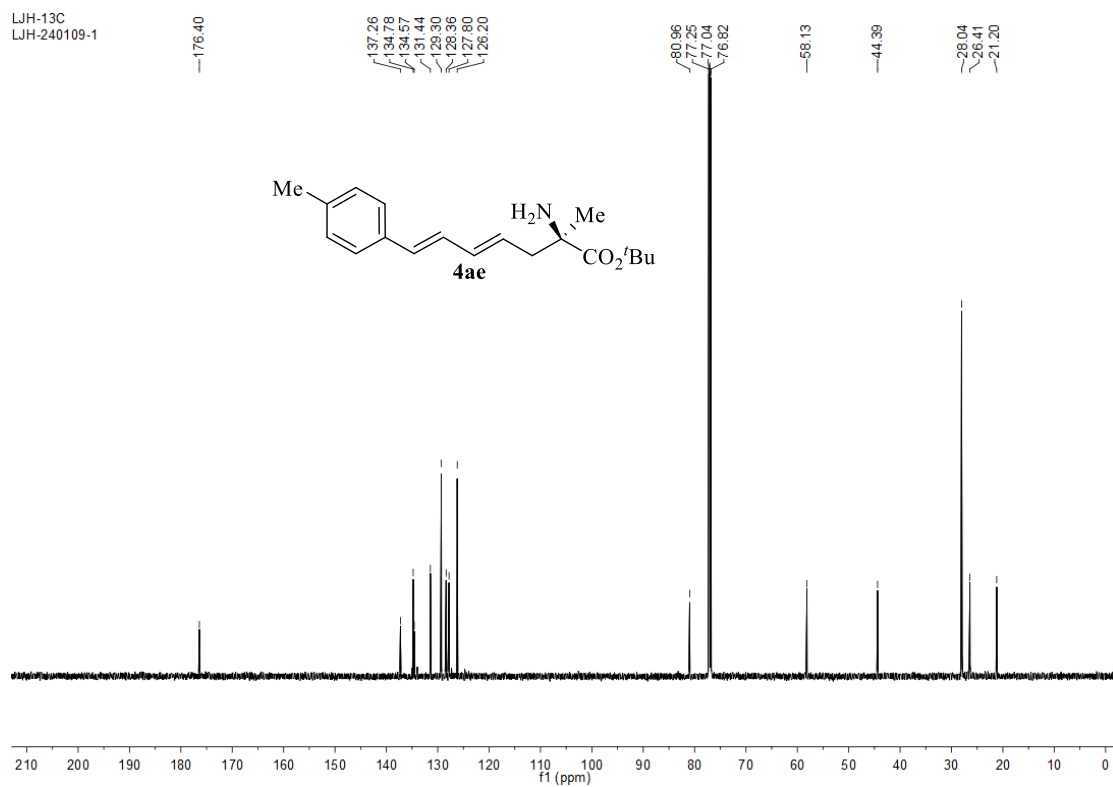




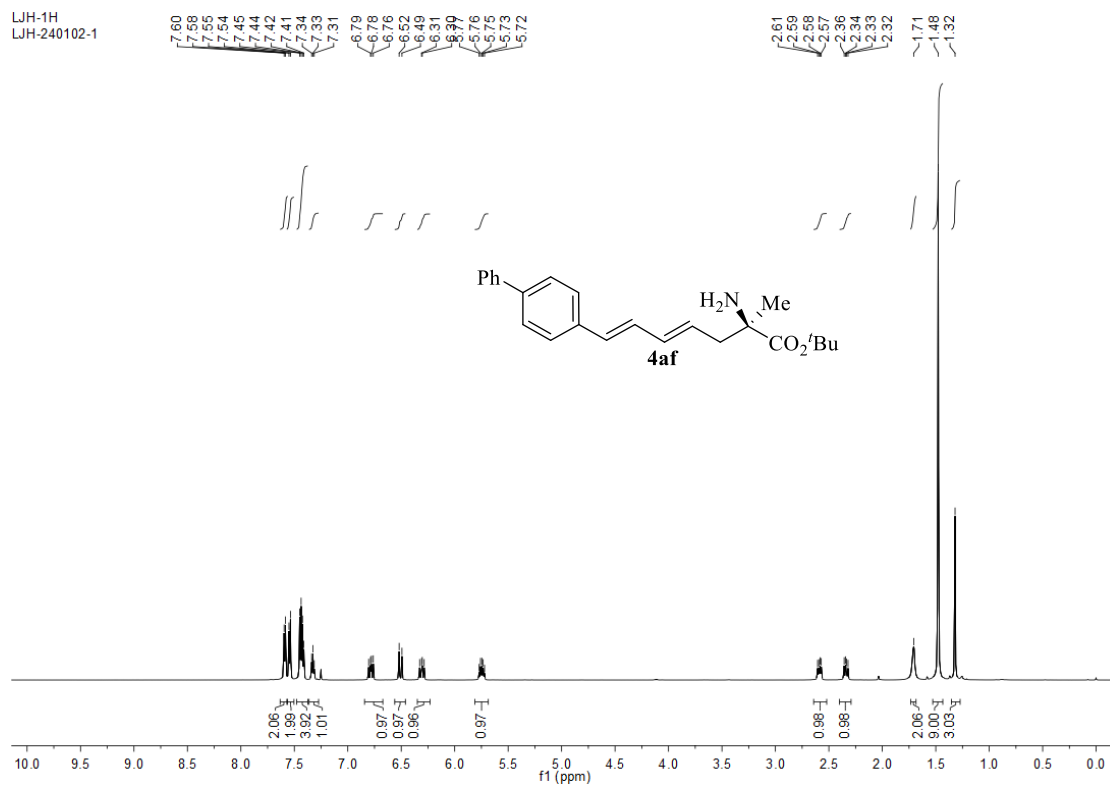
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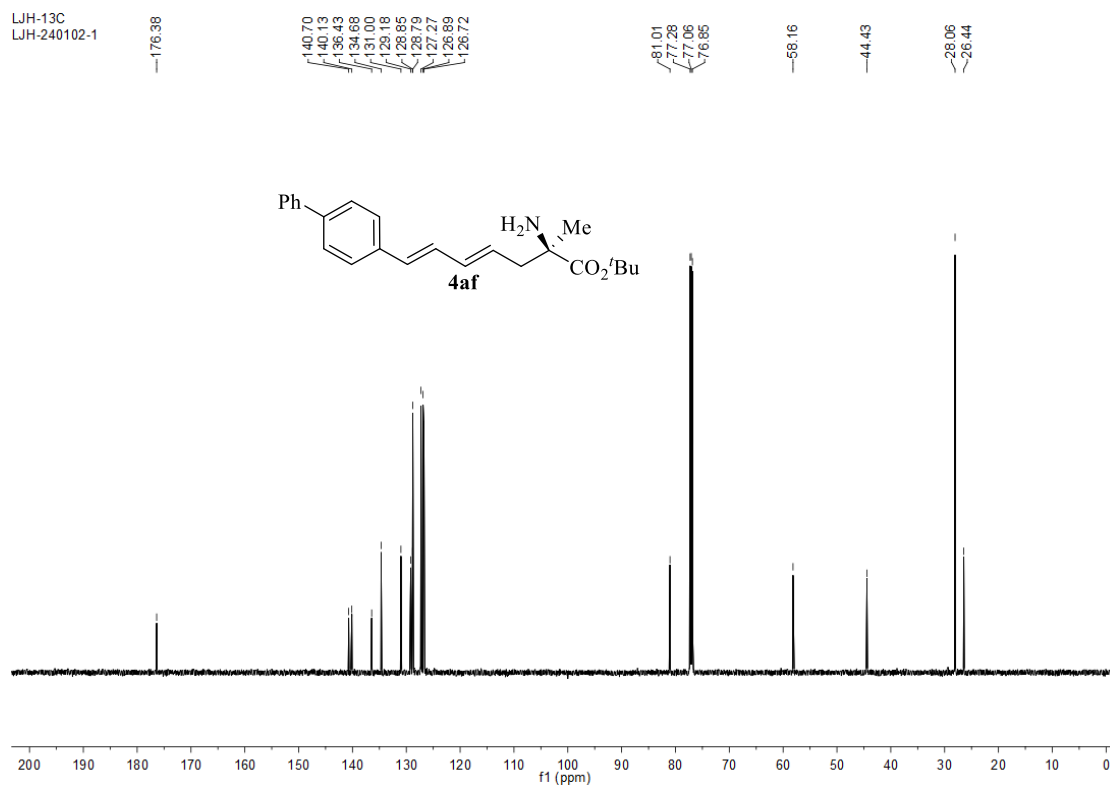
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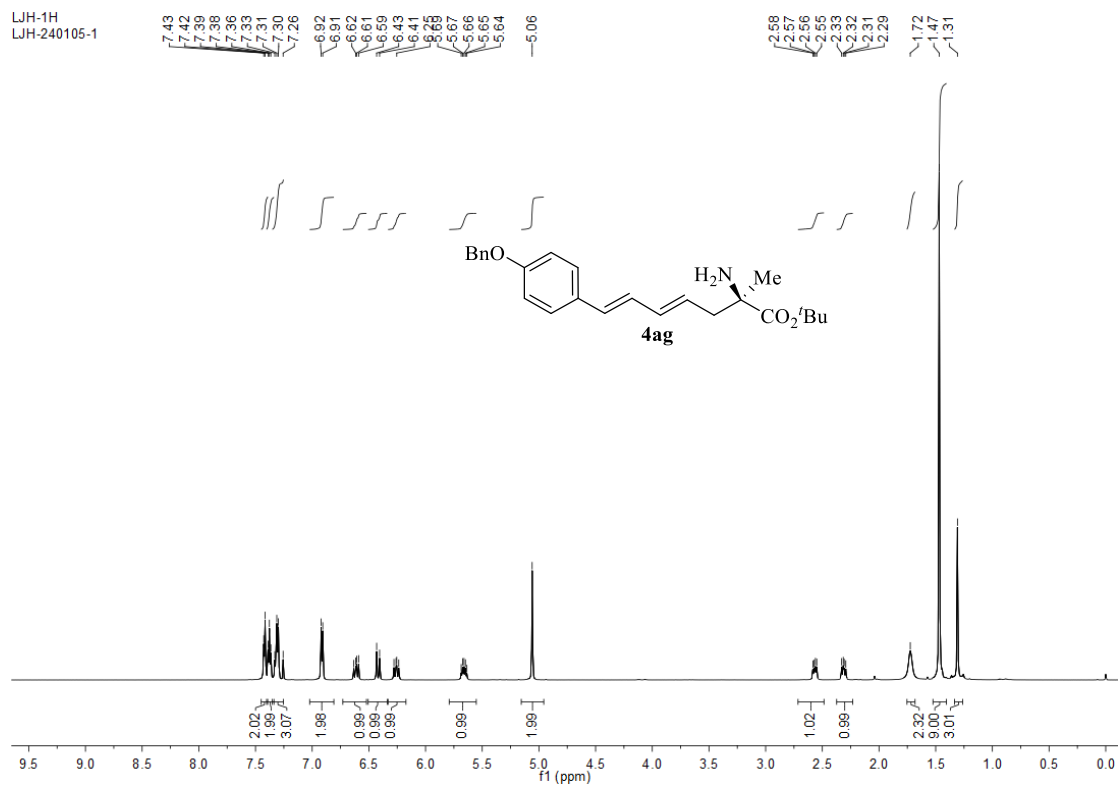
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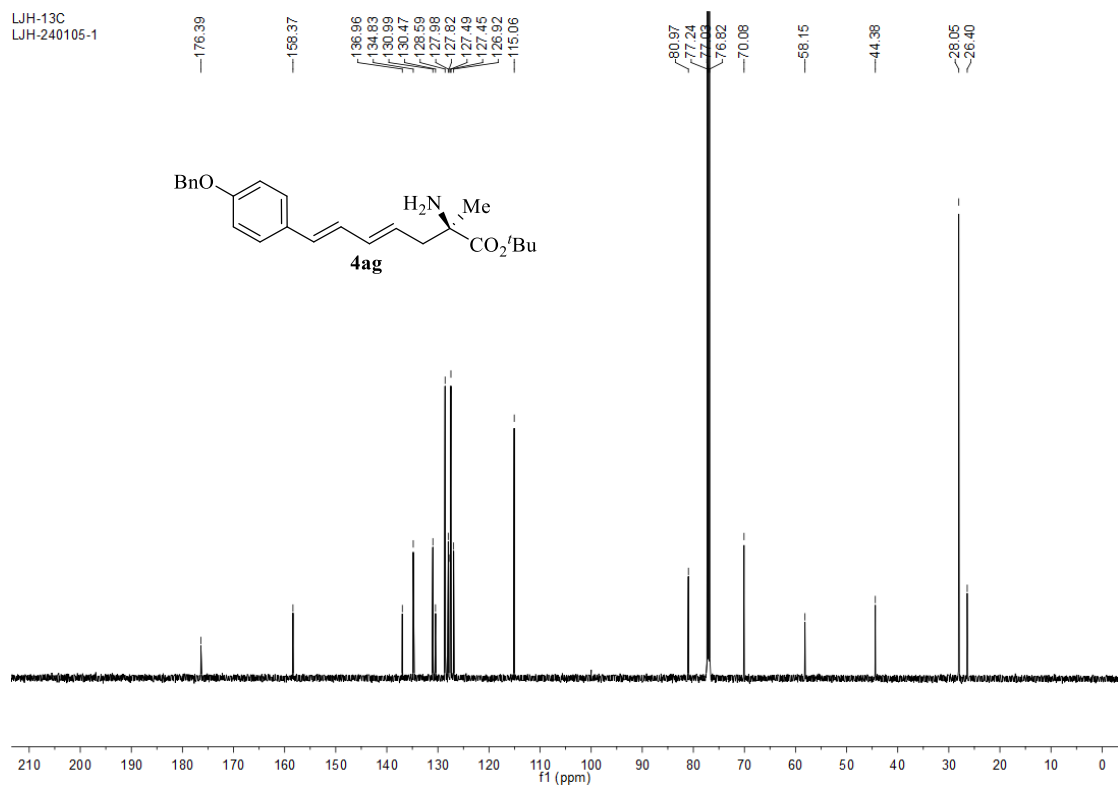
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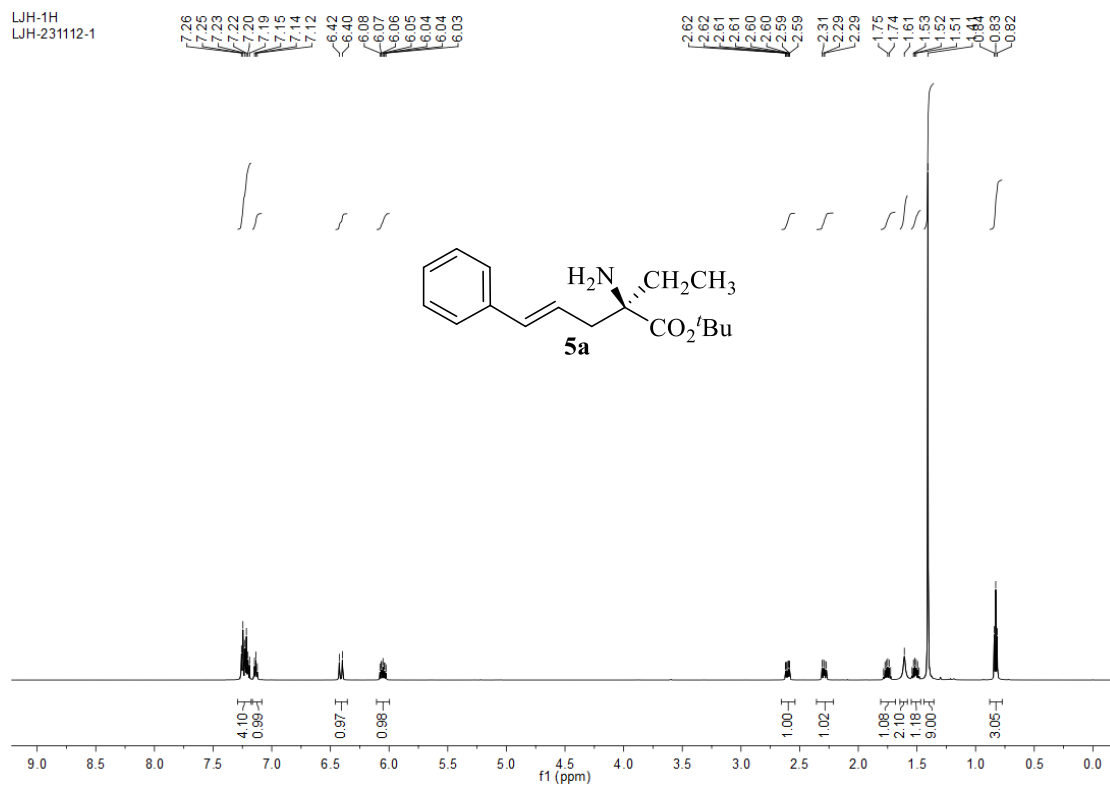
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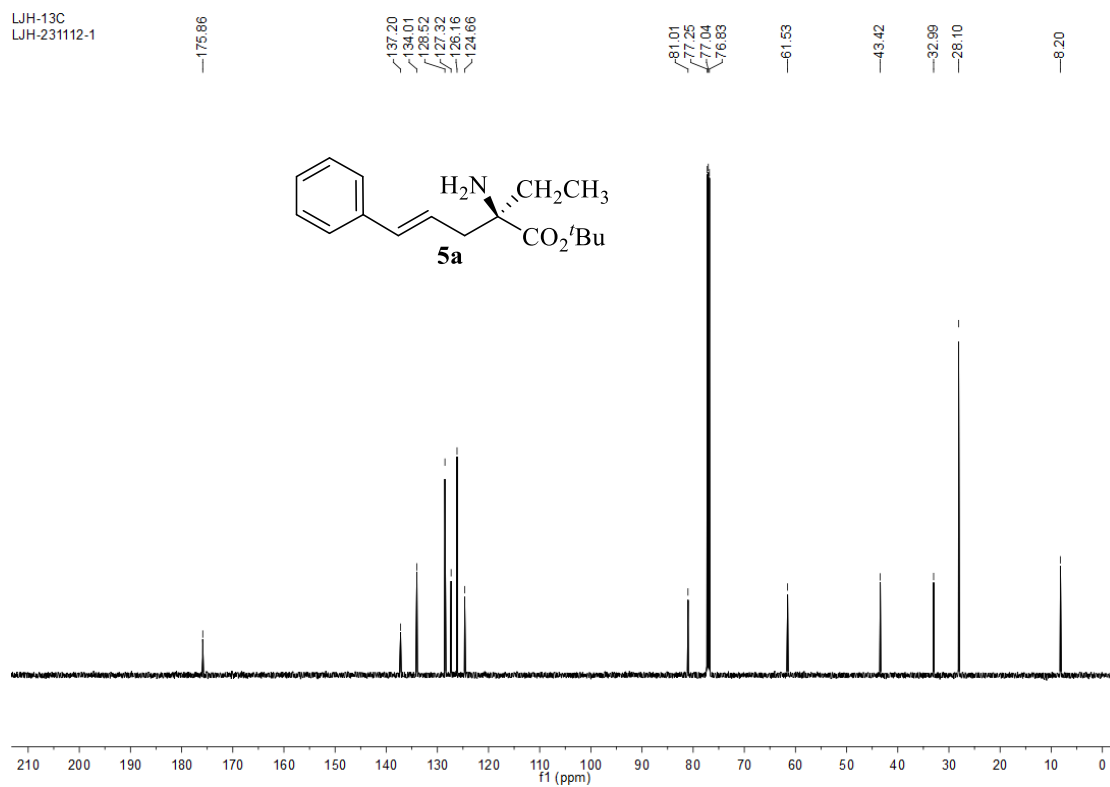
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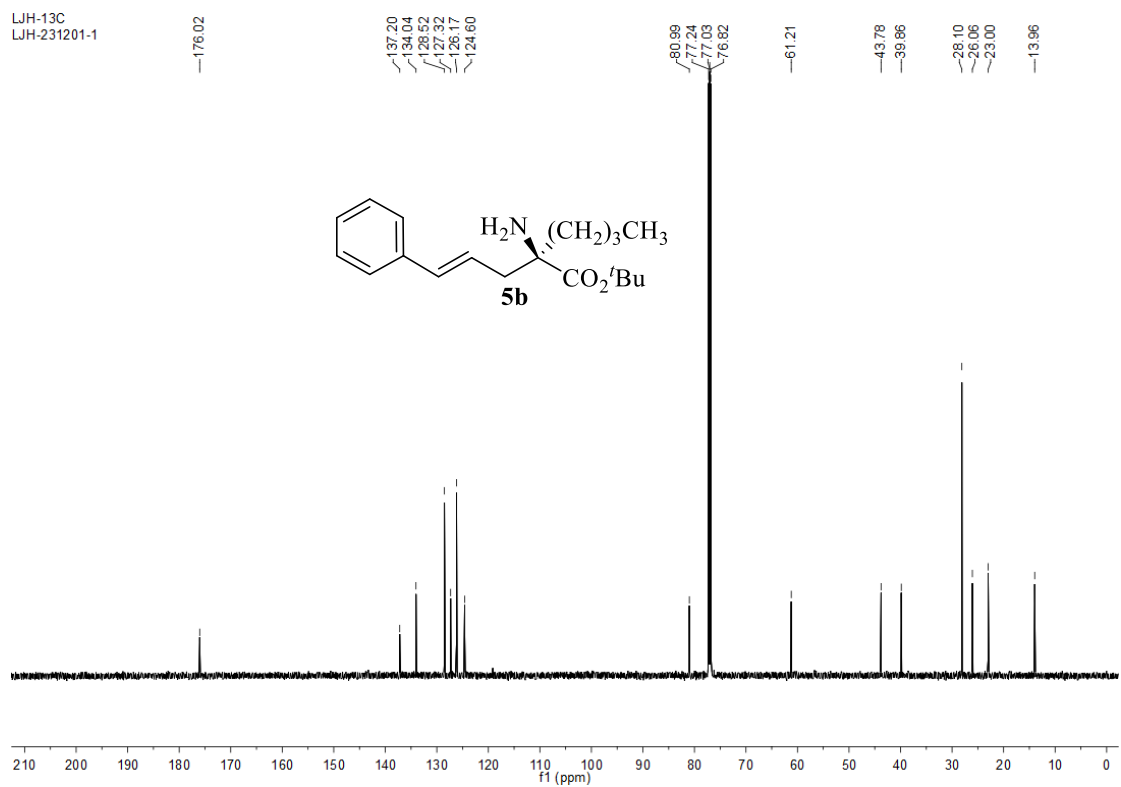
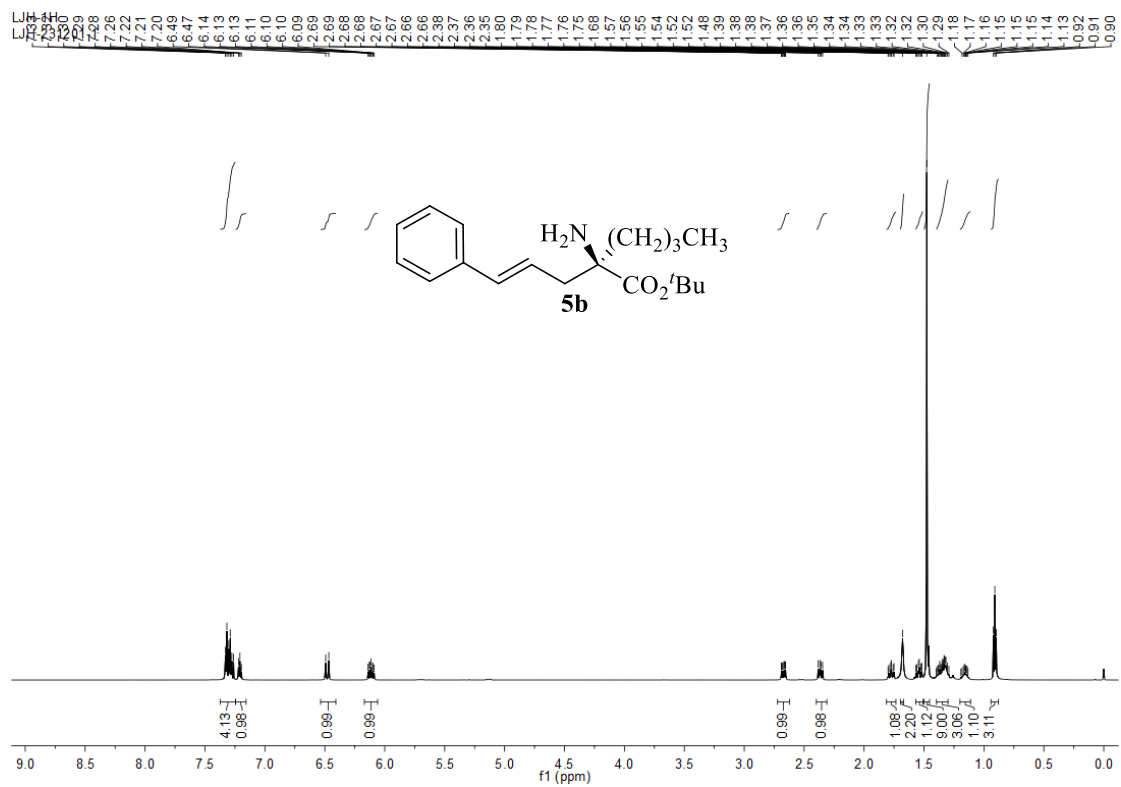


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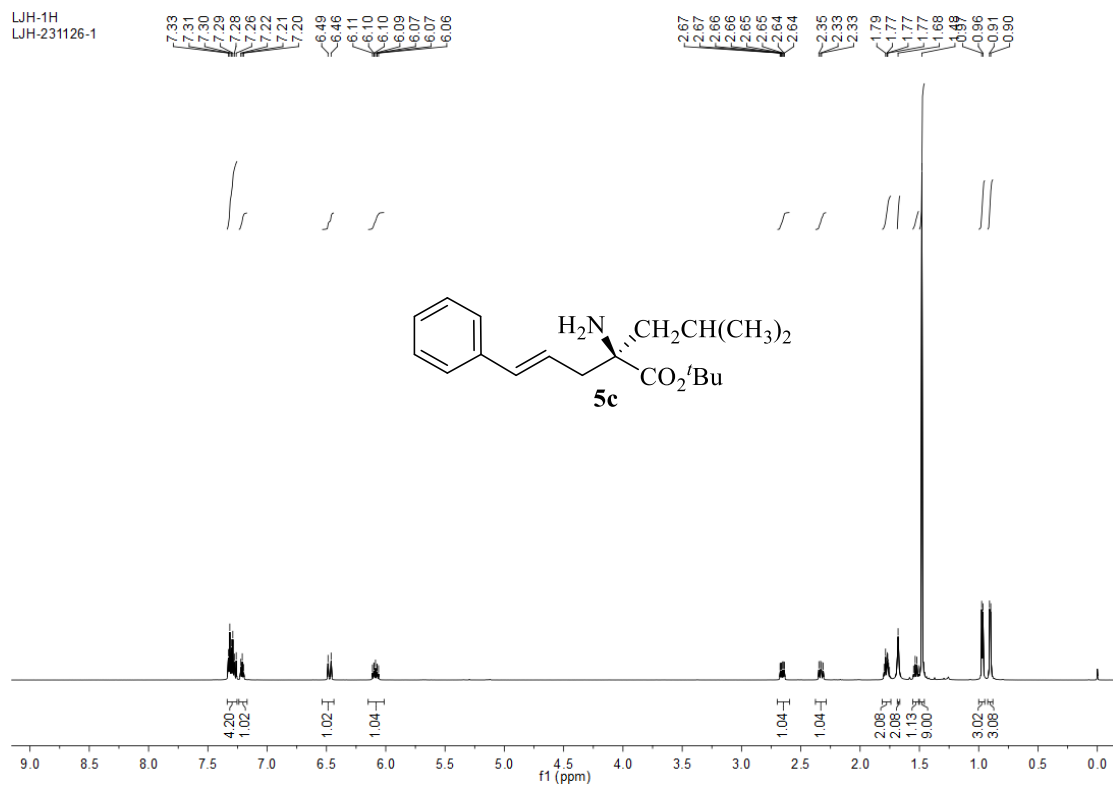


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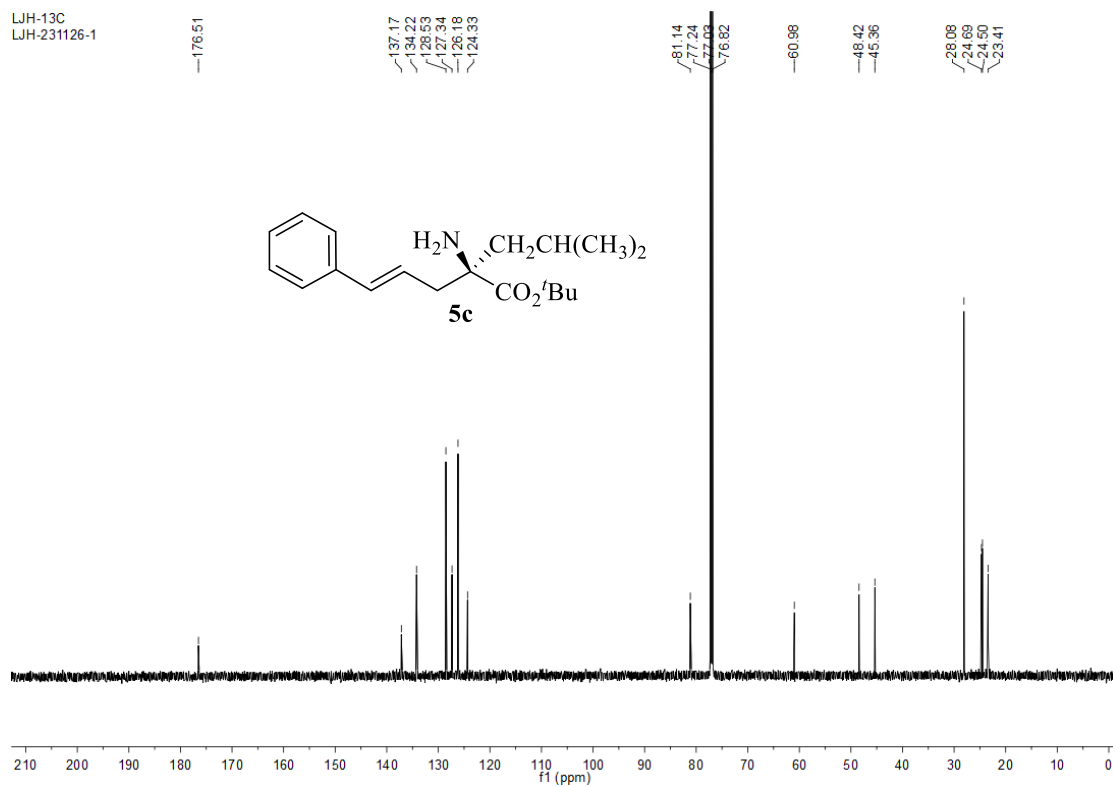




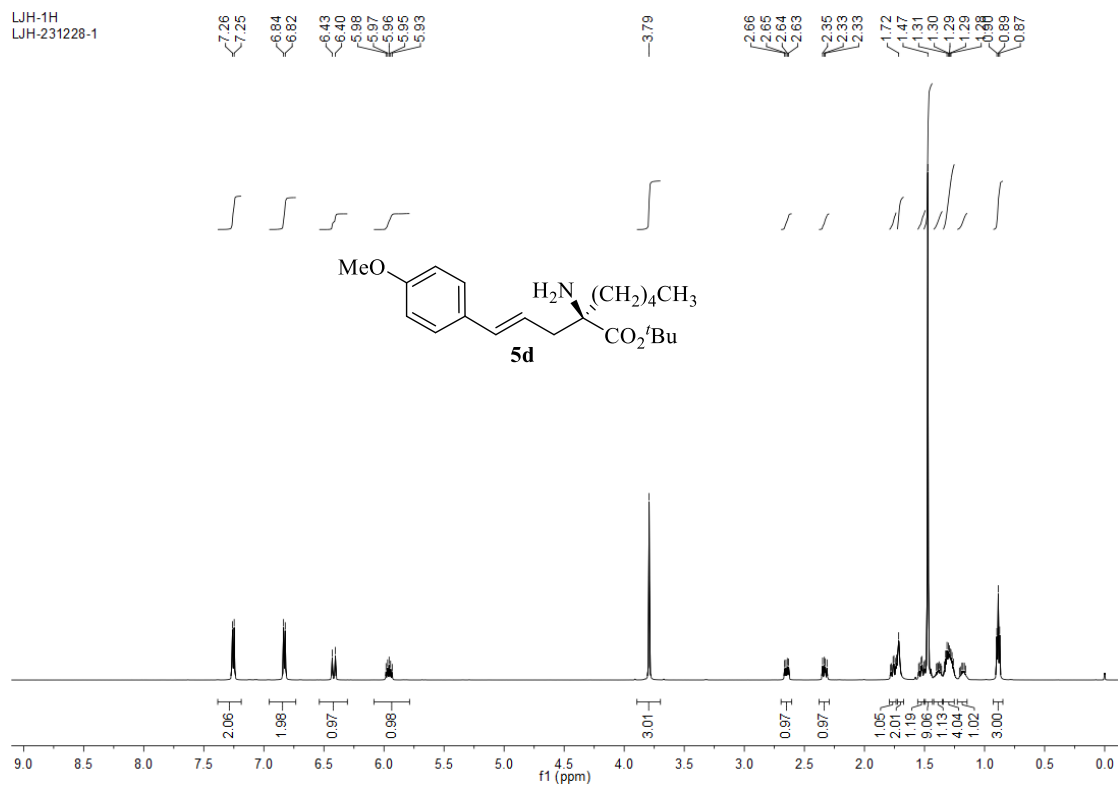
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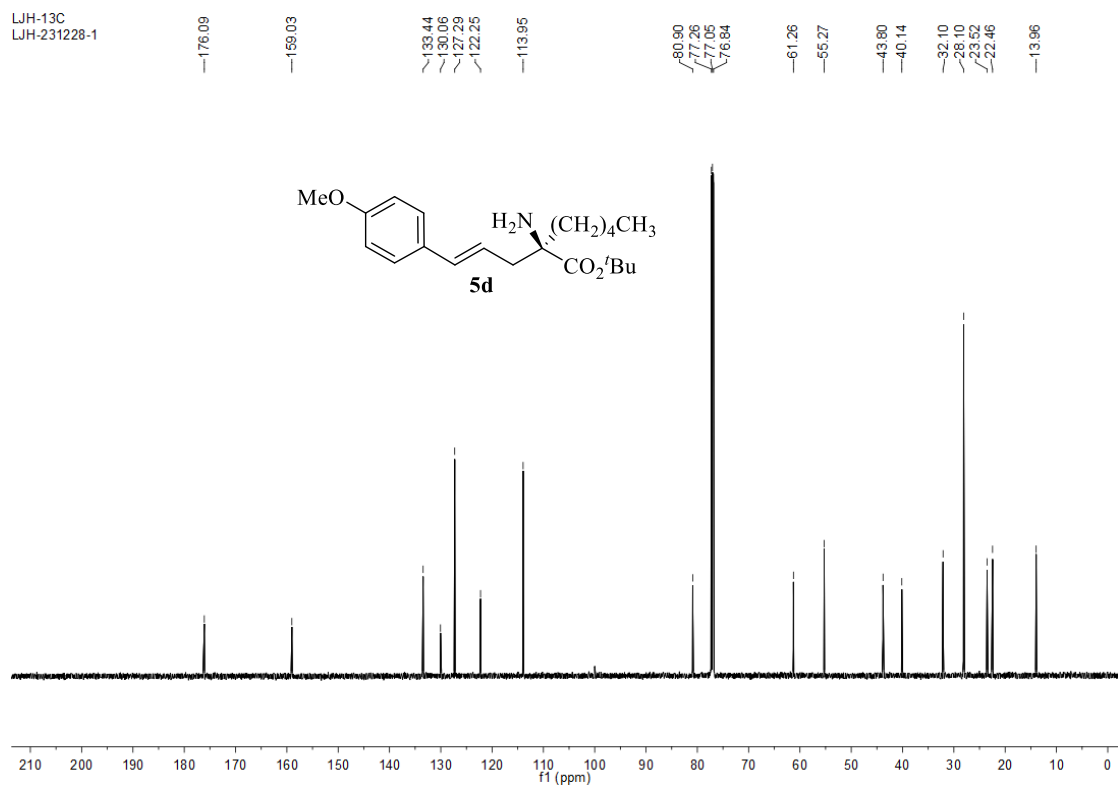
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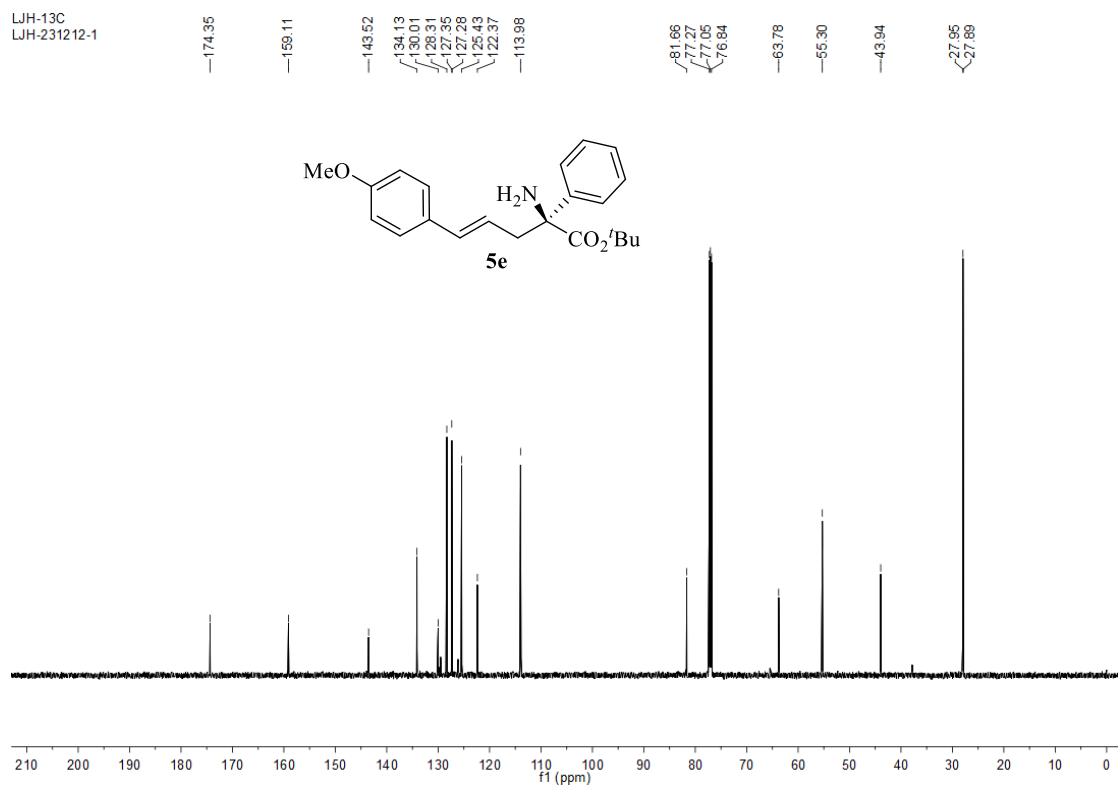
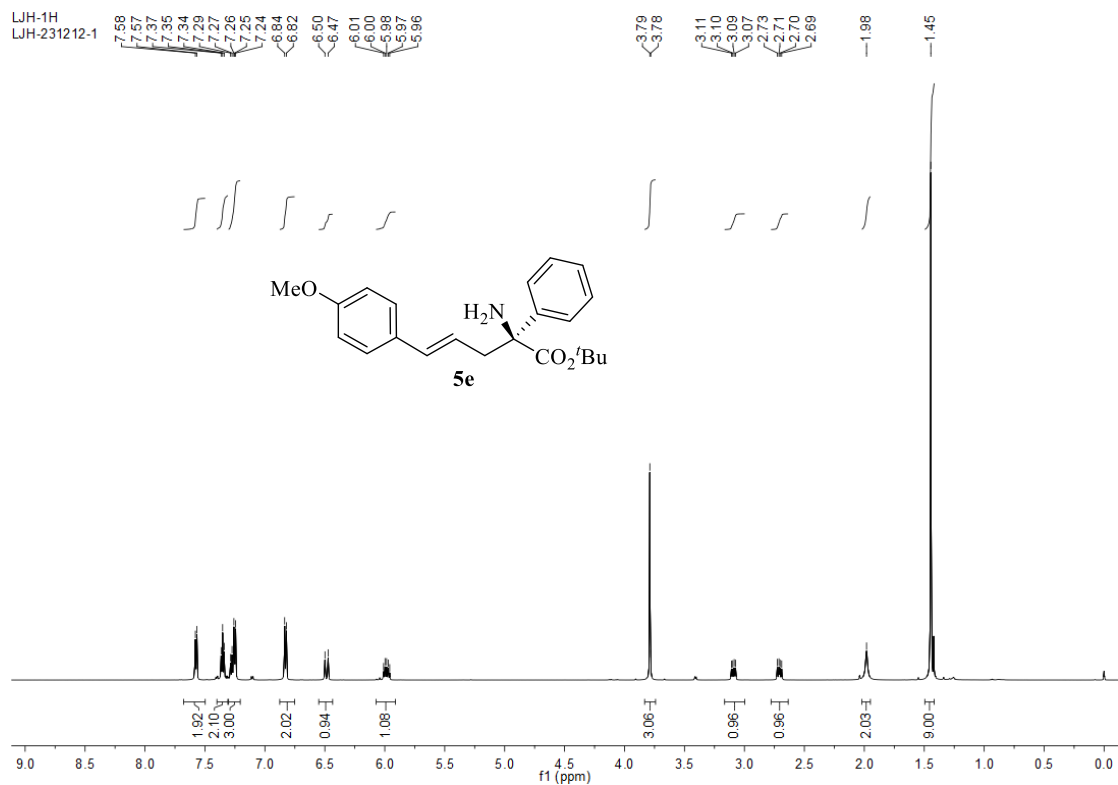


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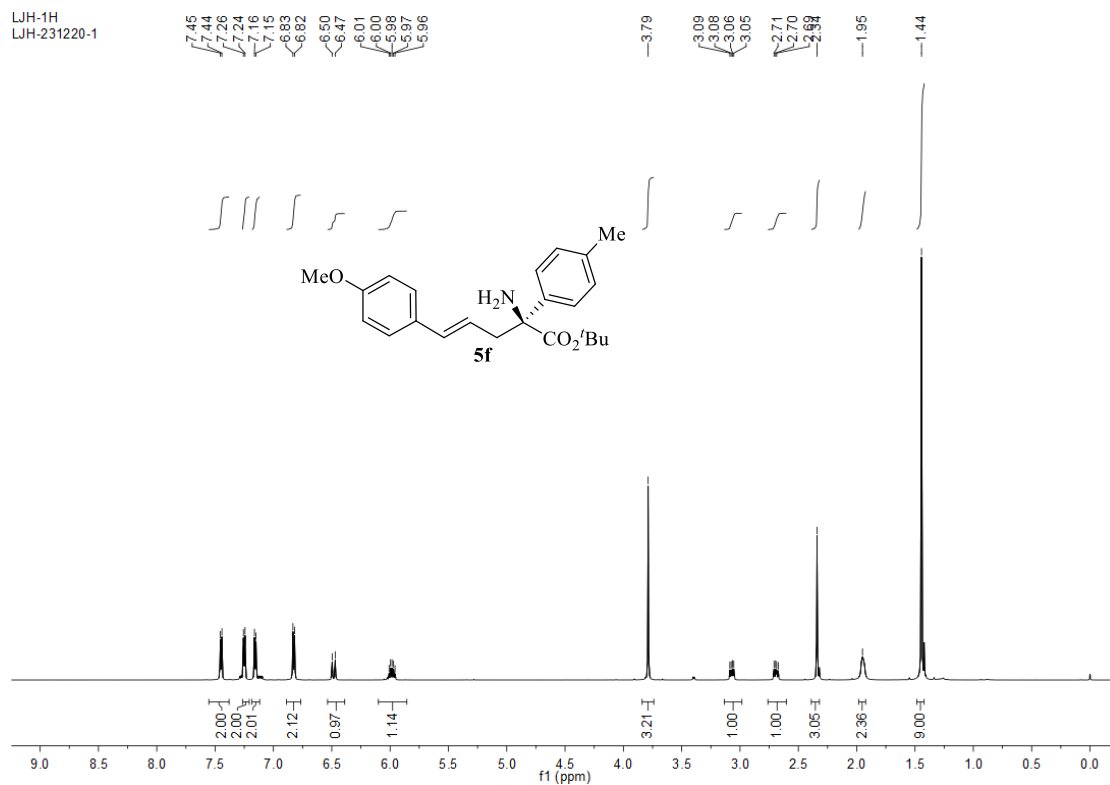


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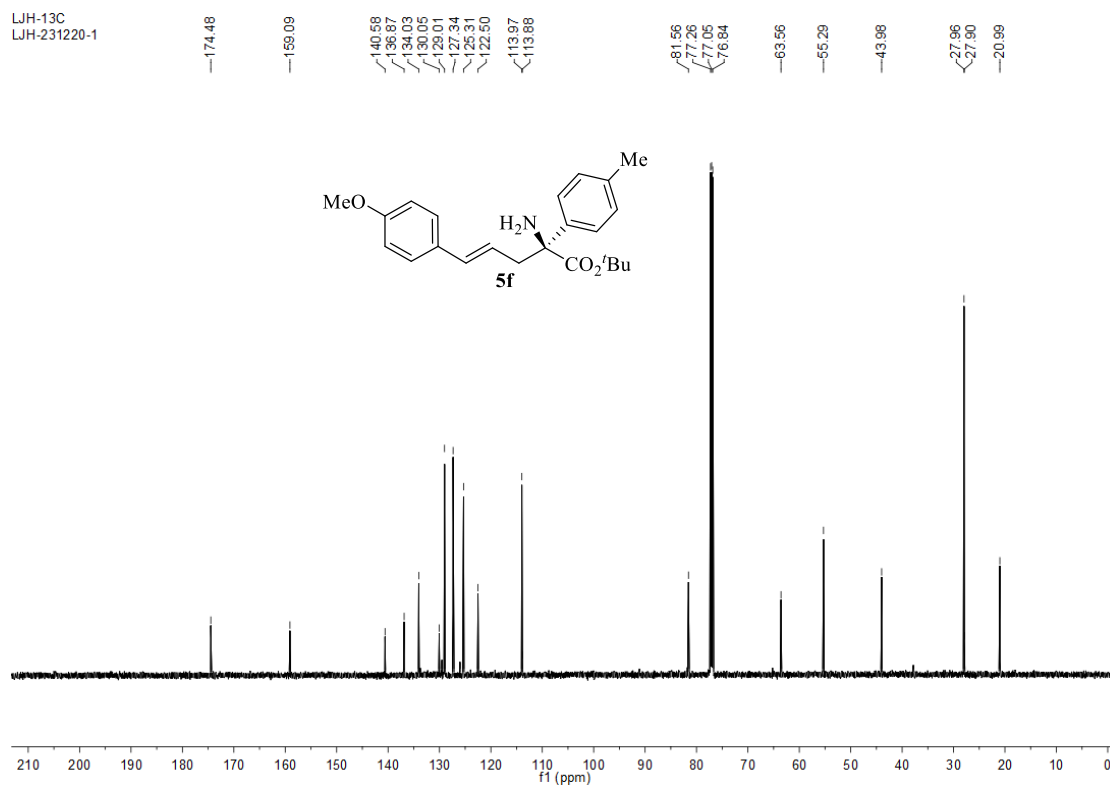




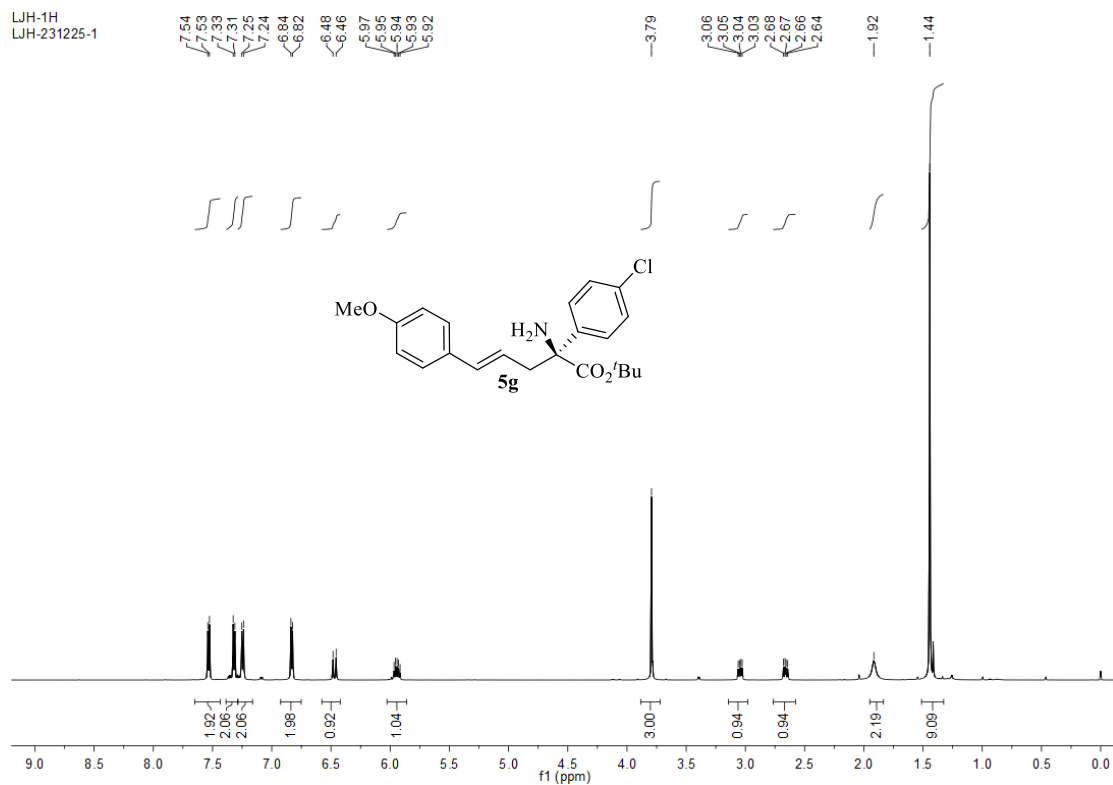
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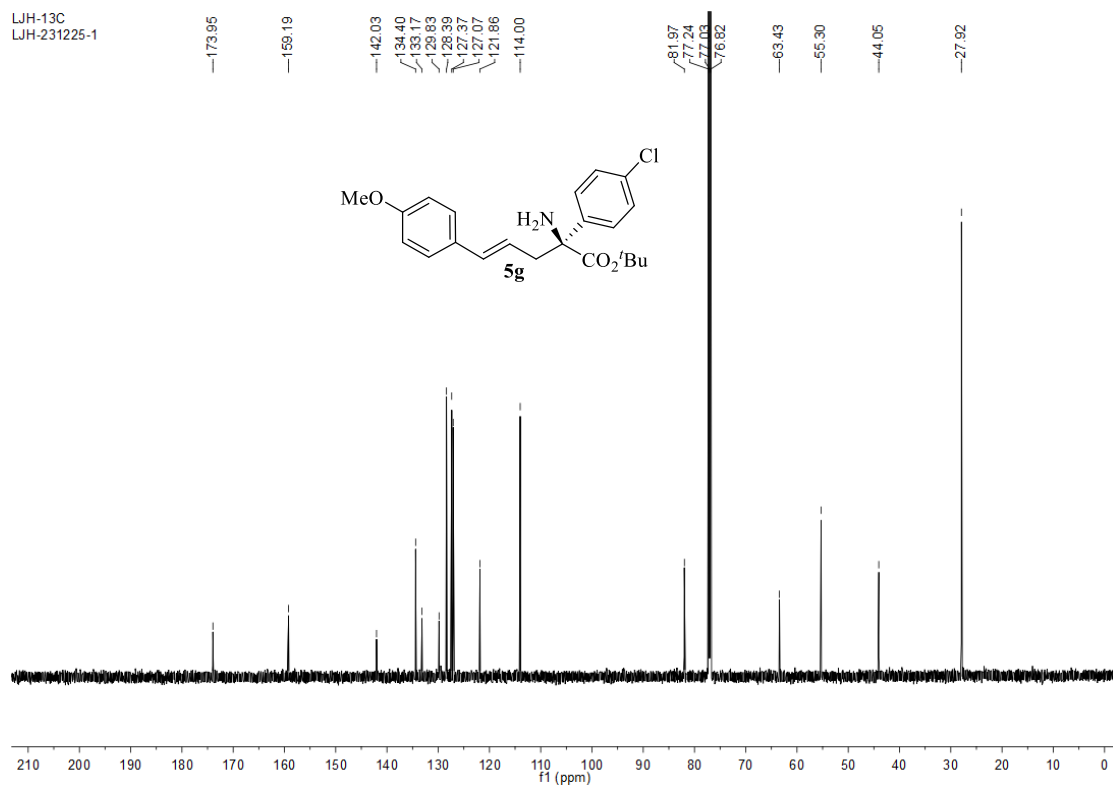
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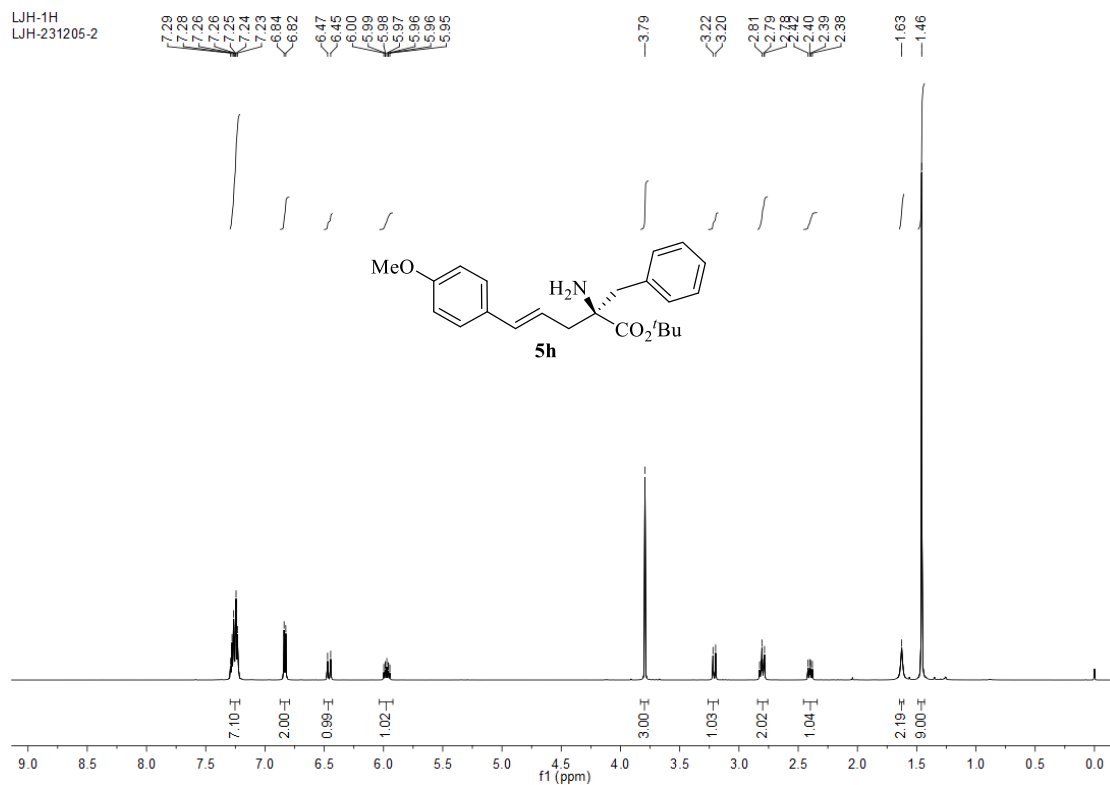
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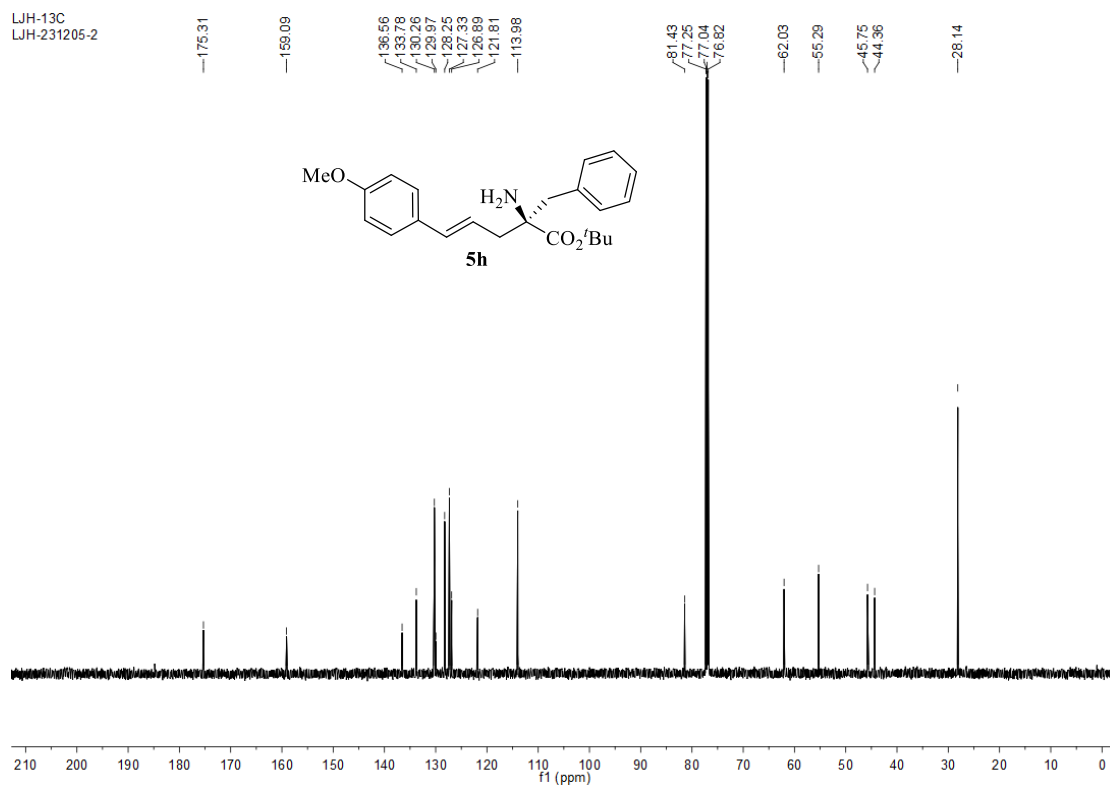
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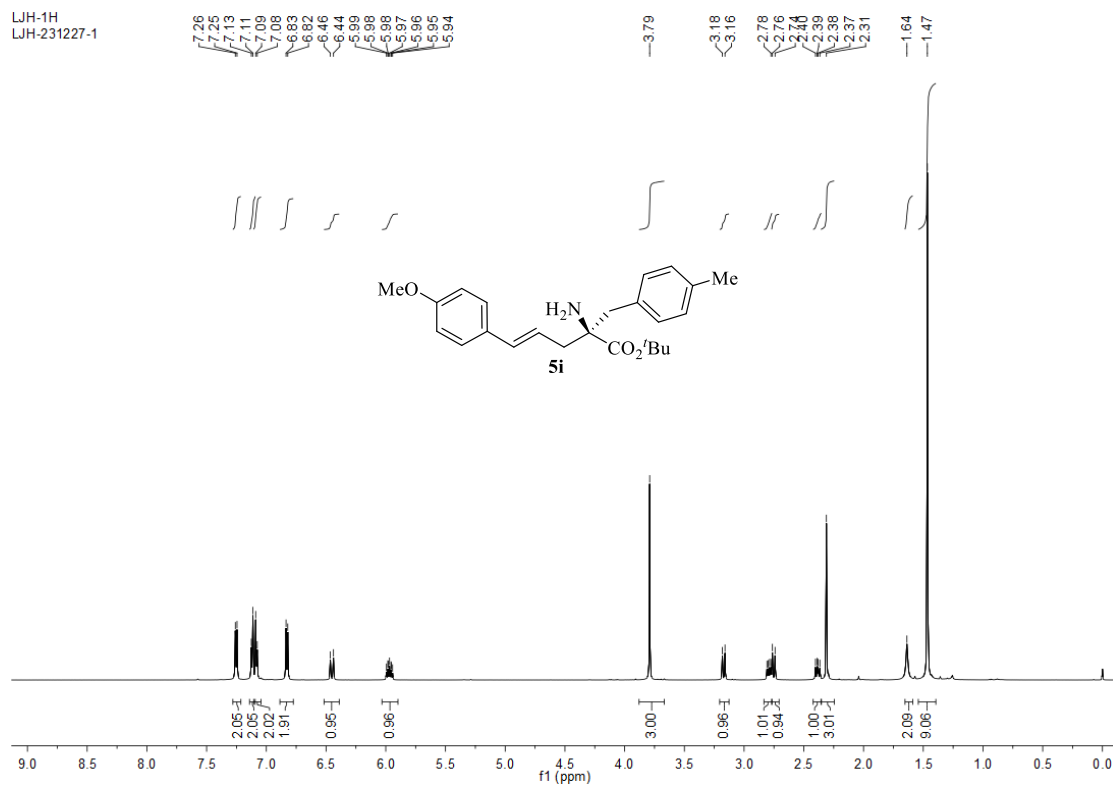
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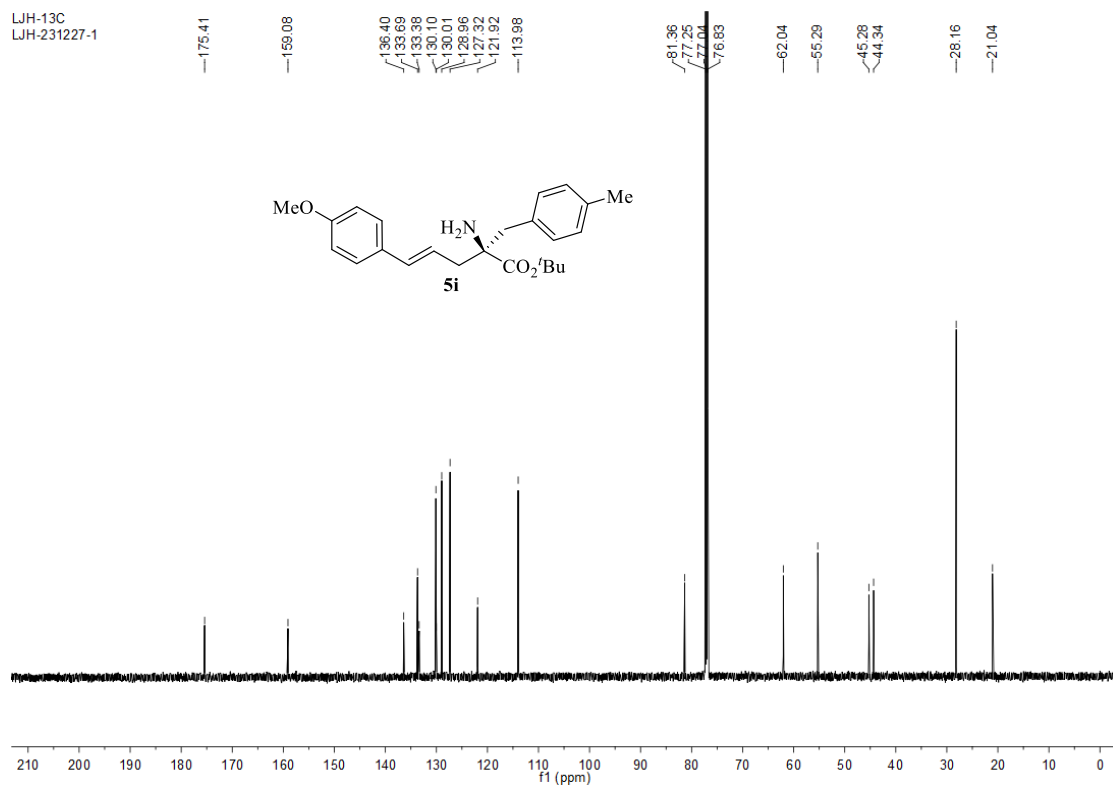
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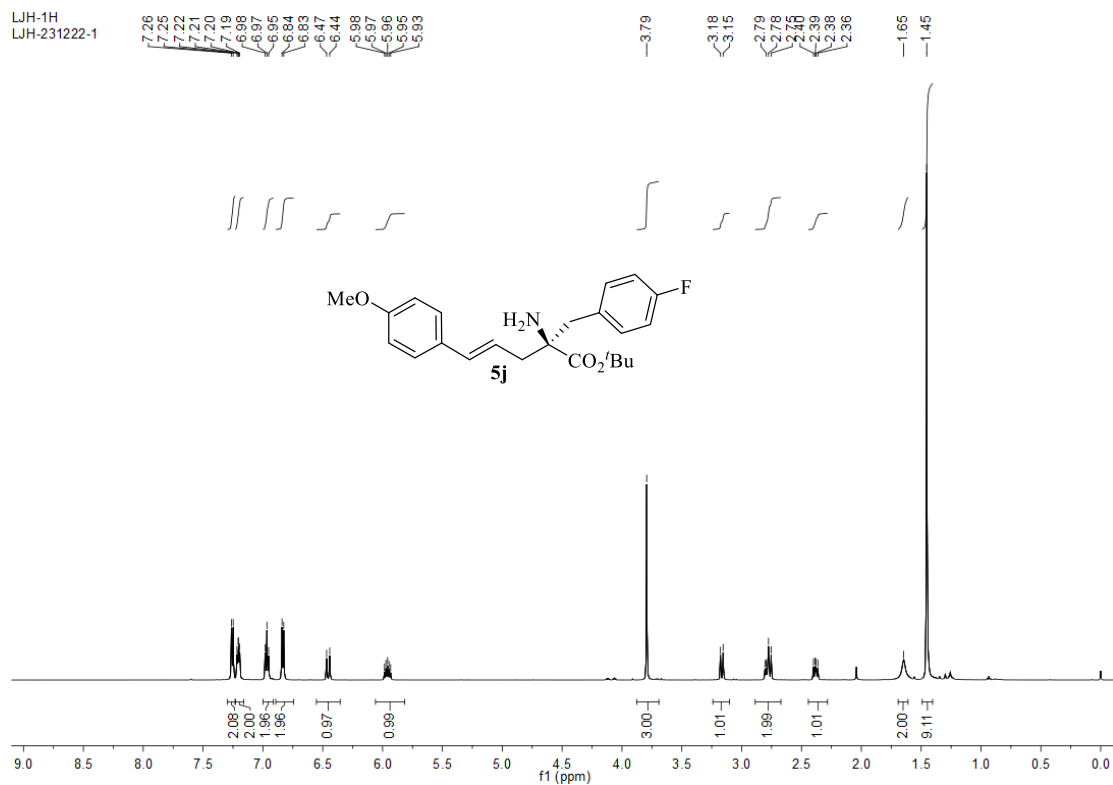
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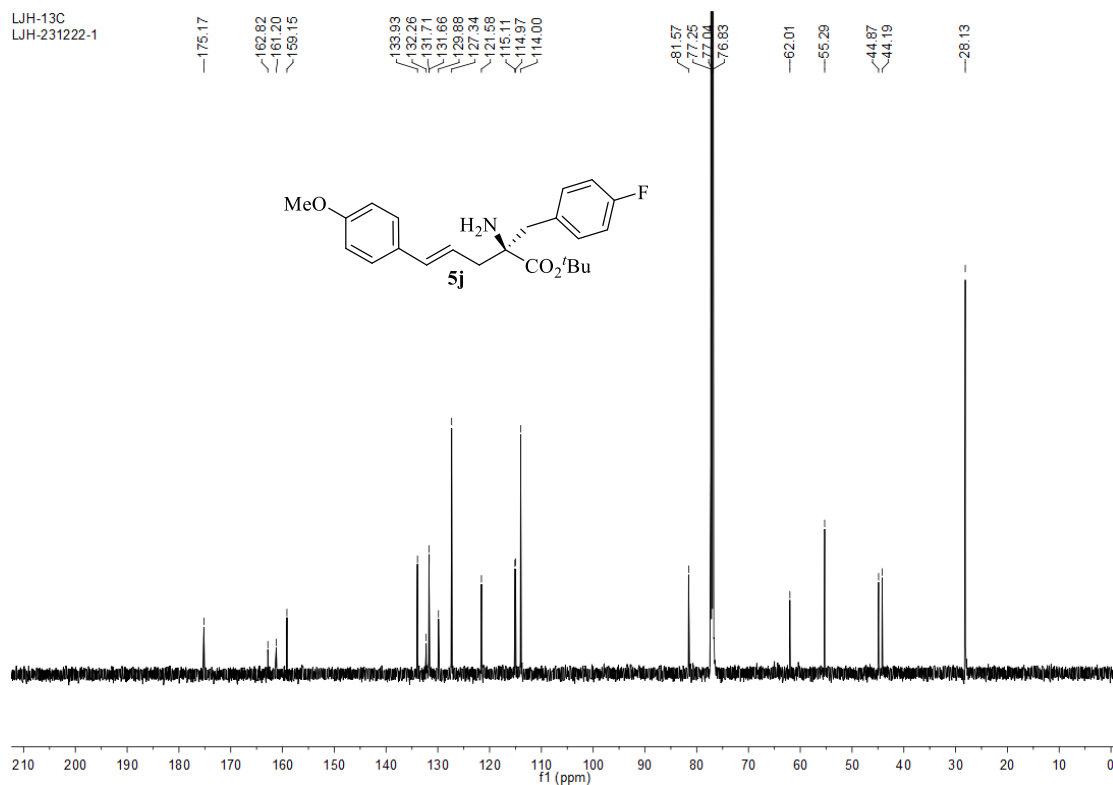
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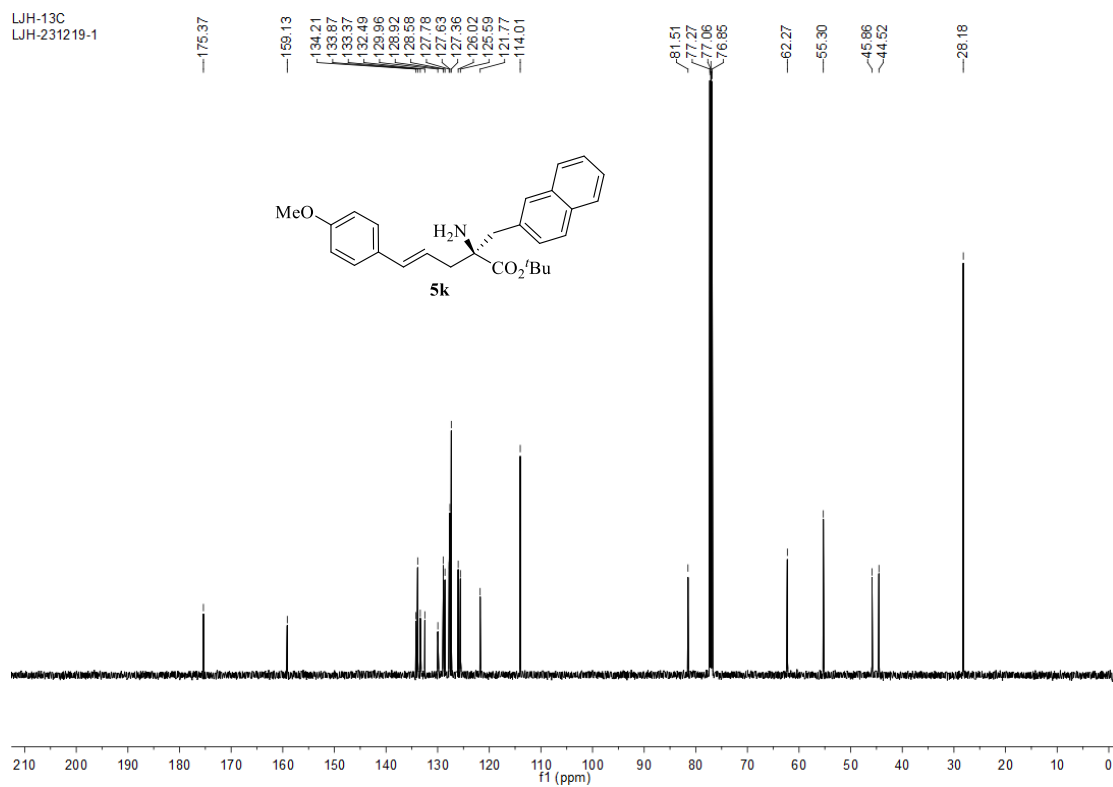
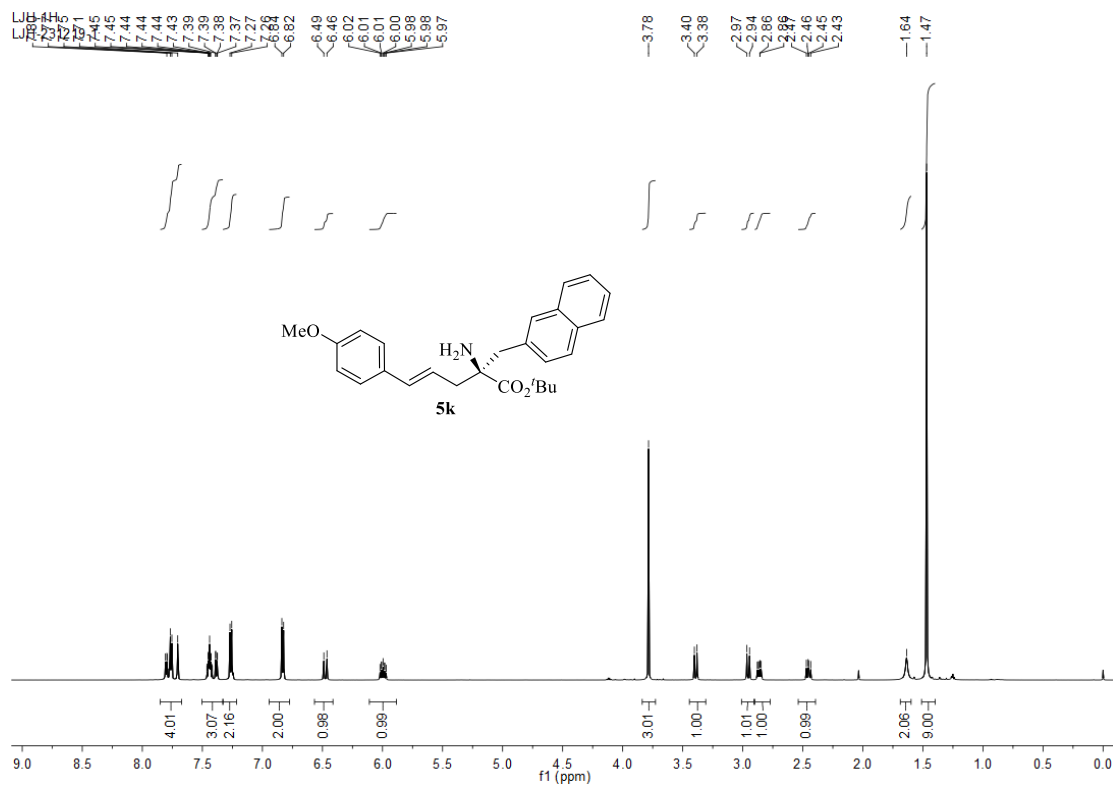


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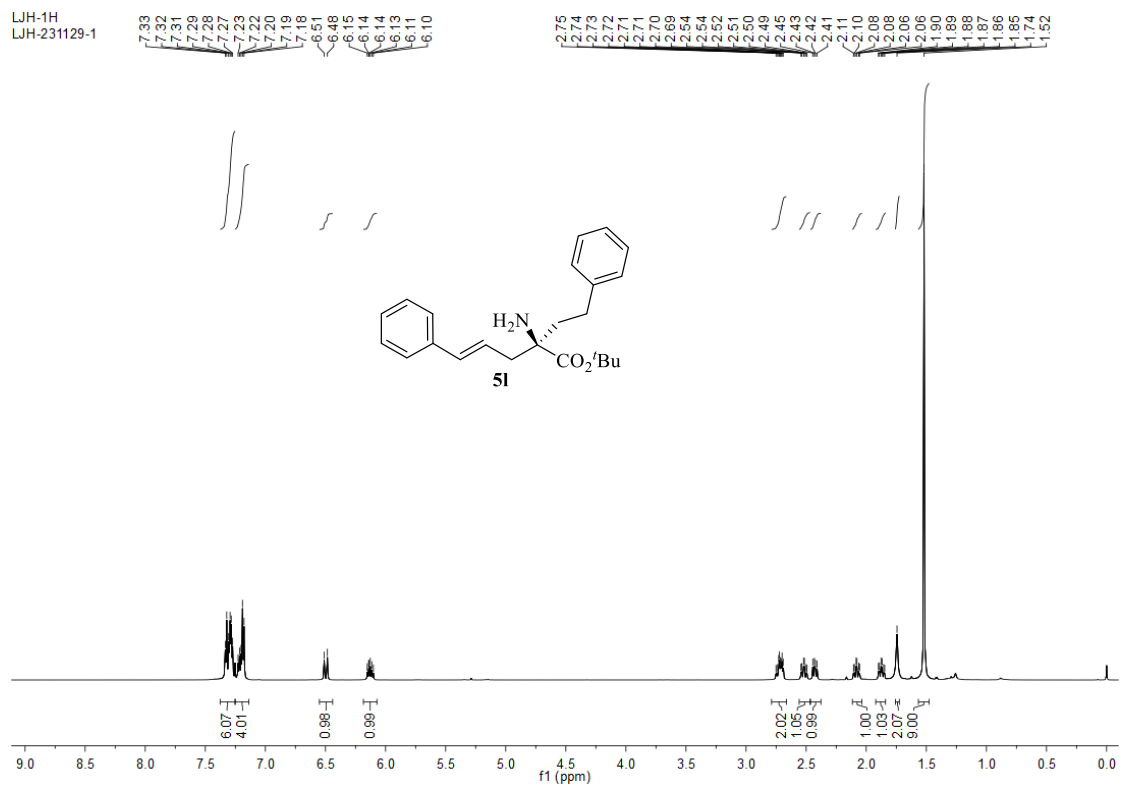


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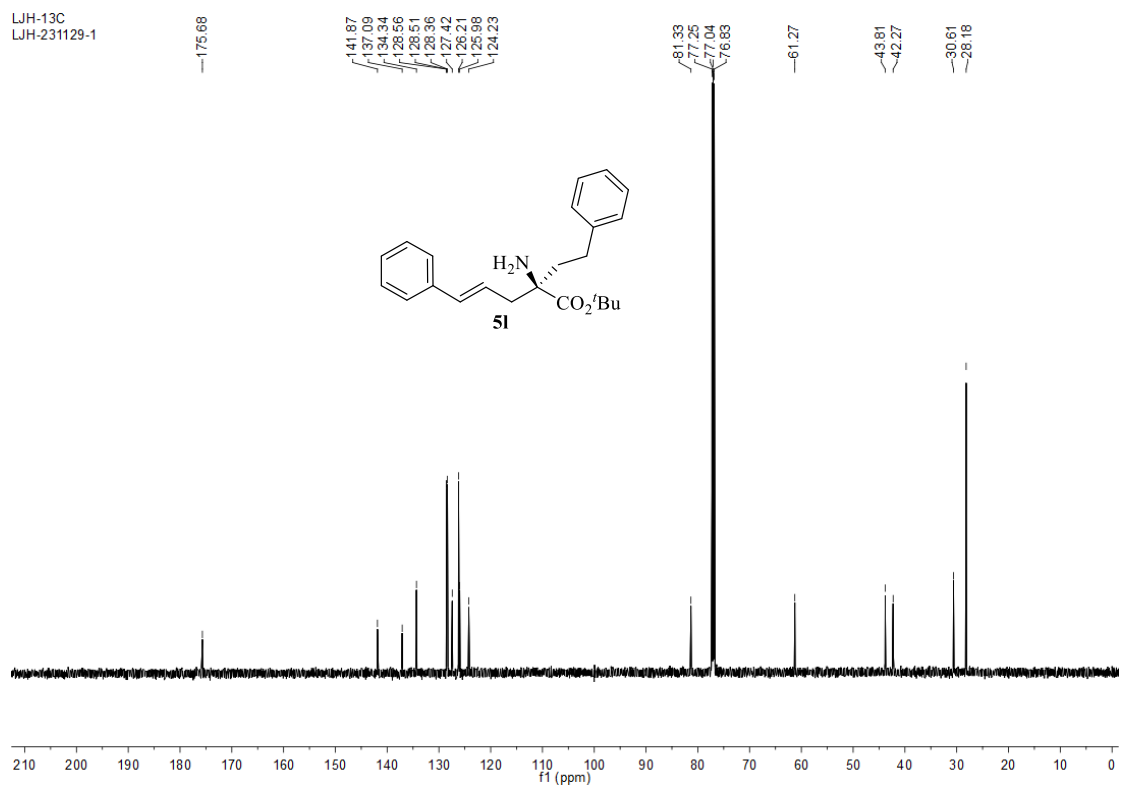




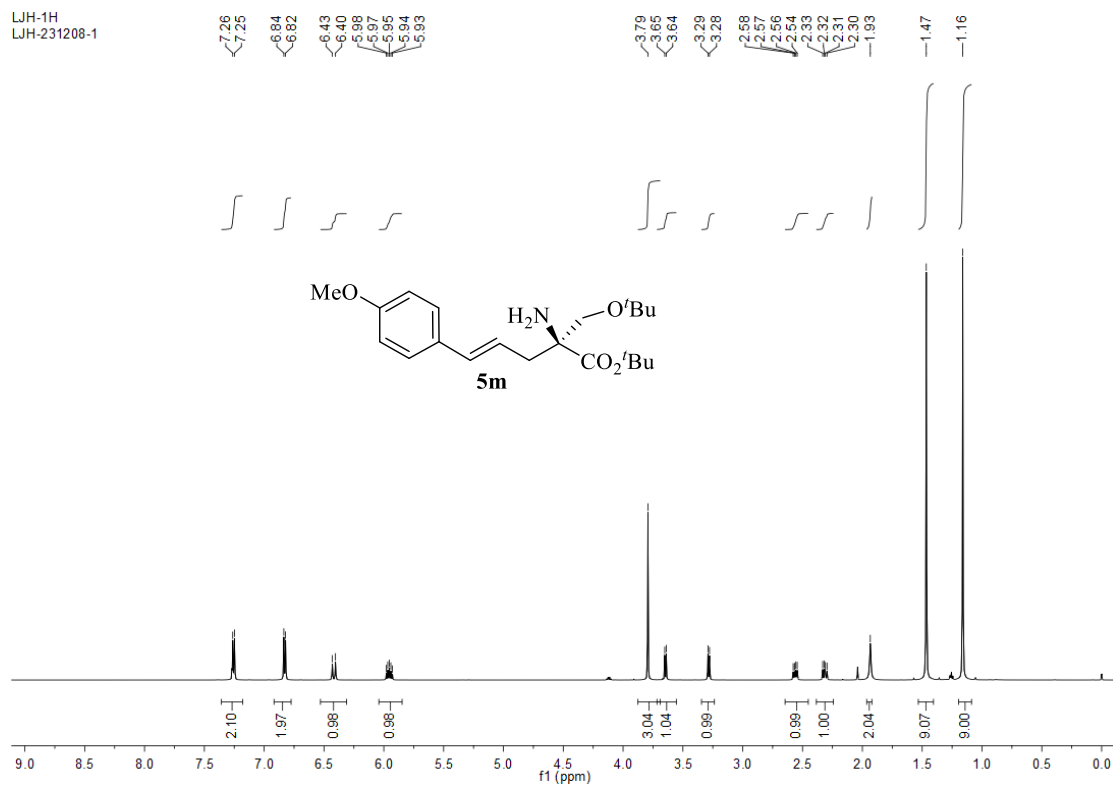
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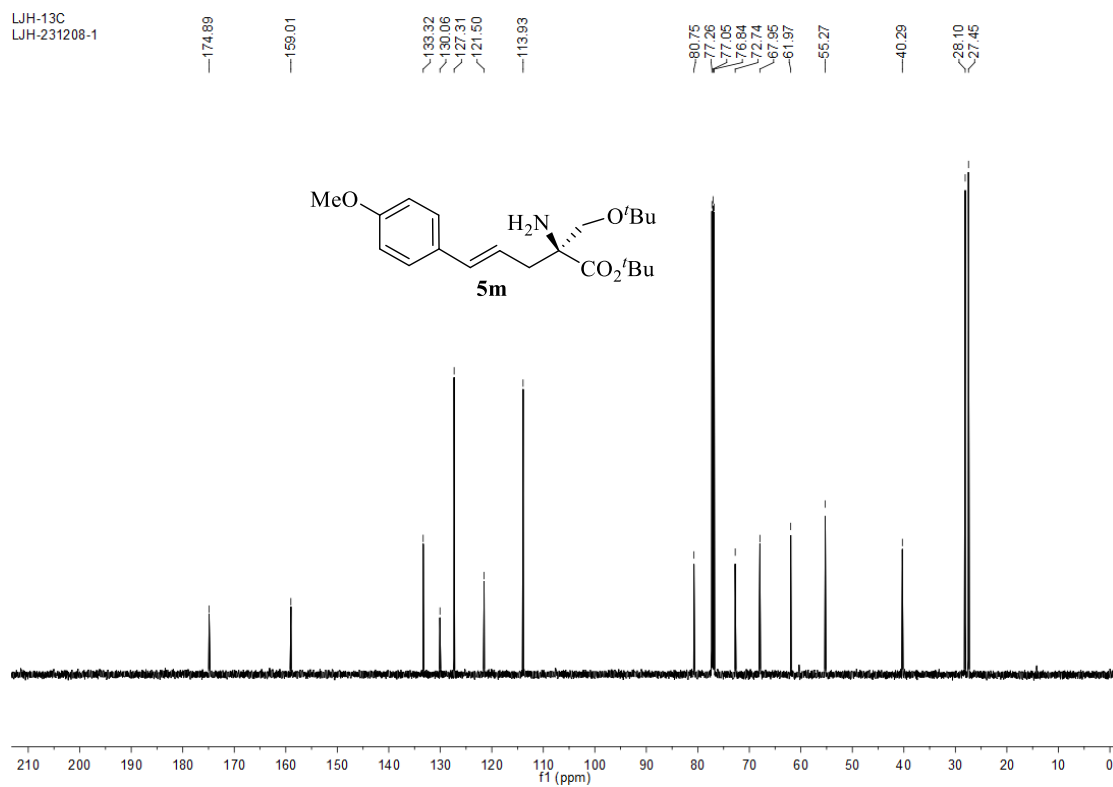
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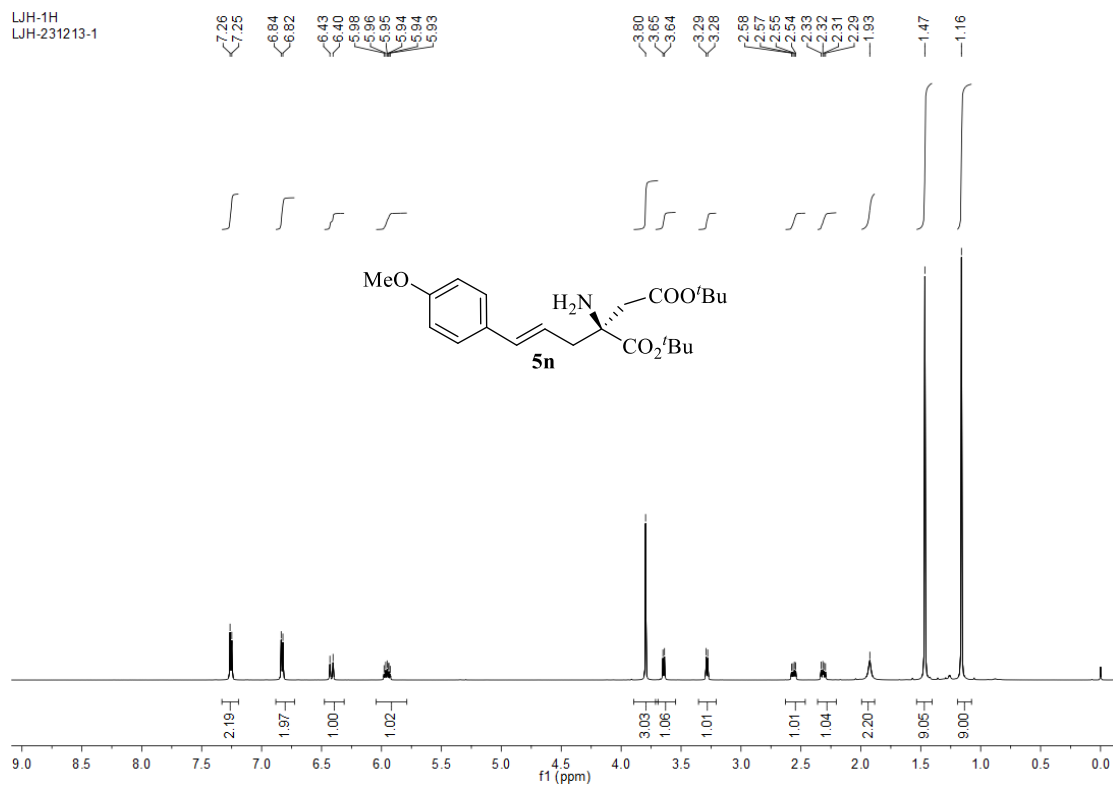
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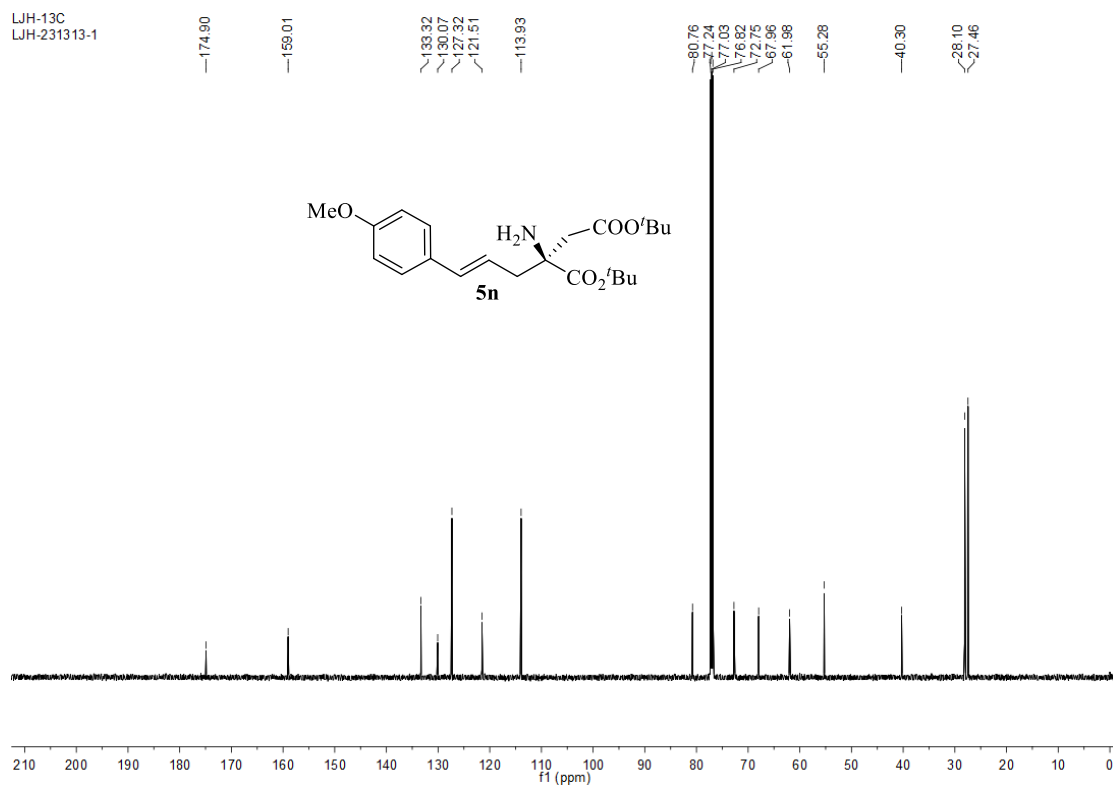
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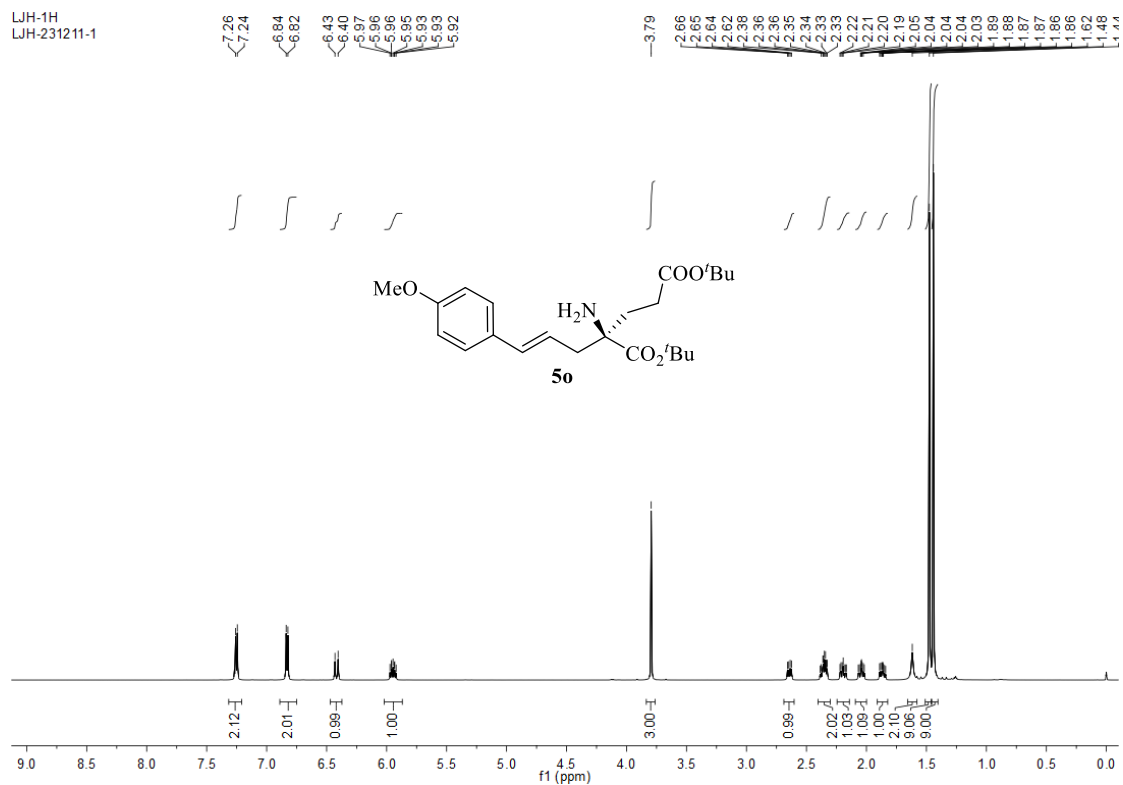
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LJH-1H
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