Electronic Supplementary Material (ESI) for ChemComm.

Ir/PTC Cooperatively Catalyzed Asymmetric Umpolung Allylation of α-Imino Esters Enabled Synthesis of α-Quaternary Amino Acid Derivatives Bearing Two Vicinal stereocenters

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Supporting Information

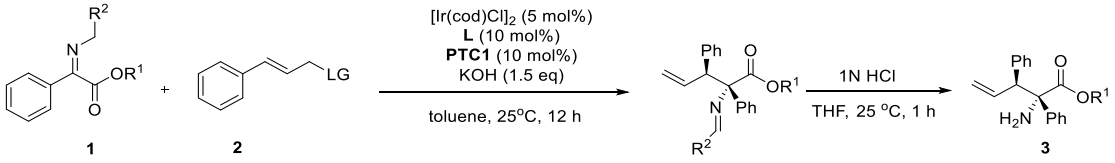
Contents:

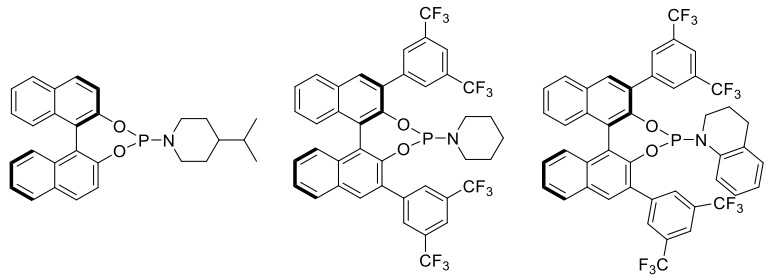
1. General Data

NMR spectra were recorded on a Brucker-400 MHz spectrometer. The high resolution mass spectra (HRMS) were recorded on a Thermo LTQ Orbitrap XL (ESI+) or a P-SIMS-Gly of Brucker DaltonicsInc (EI+). Infrared spectra were recorded on a Nicolet MX-1E FT-IR spectrometer. Enantiomeric excesses were performed on Agilent 1200 (UV detection monitored at 220 nm) Chiralpak OD-H, IB, IA, IC columns were purchased from Daicel Chemical Industries, LTD. Optical rotations were measured on Anton Paar MCP 200.

Materials: Starting materials were purchased from commercial suppliers (Aldrich, Acros, TCI, J&K, etc) and used as supplied unless otherwise stated. Allylic acetates were prepared by following the literature report.[1] Imino esters were prepared as described below. All solvents were purified and dried according to standard methods prior to use, unless stated otherwise.

Table S1. Optimization of catalysts and reaction conditions[a]

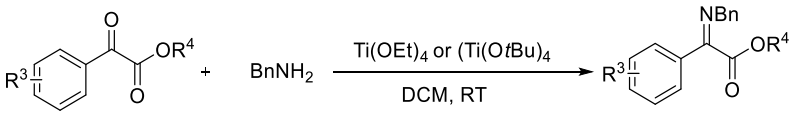




entry	R^1	R^2	LG	L	PTC	yield (%)[b]	d.r.[c]	ee (%)[d]
1	Et	Ph	OAc	**LS1**	**PTC1**	59	4:1	70 (56)
2	Et	Ph	OAc	**LS2**	**PTC1**	N.P.	N.D.	N.D.
3	Et	Ph	OAc	**LS3**	**PTC1**	40	15:1	4 (8)
4	Et	Ph	OAc	**LS4**	**PTC1**	46	2:1	53 (3)
5	*t*Bu	3,4-Cl_2Ph	OAc	**L6**	**PTC1**	21	N.D.	83 (N.D.)
6	*t*Bu	Ph	$OPO(OEt)_2$	**L6**	**PTC1**	40	3:1	78 (50)
7	*t*Bu	Ph	OCO_2Me	**L6**	**PTC1**	29	4:1	85 (50)
8	*t*Bu	Ph	OAc	**L6**	**PTC9**	trace	N.D.	N.D.
9	*t*Bu	Ph	OAc	**L6**	**PTC10**	19	2:1.	81 (53)
10	*t*Bu	Ph	OAc[e]	**L6**	**PTC1**	48	3:1	50 (11)

[a] Reaction conditions: unless indicated otherwise, reactions of **1** (0.20 mmol), **2** (0.10 mmol), $[Ir(cod)Cl]_2$ (0.005 mmol), **L** (0.010 mmol), TBAB (0.01 mmol) and KOH (0.15 mmol) were carried out in toluene (1 mL) for 12 h. Then workup with 1N HCl at rt. [b] Isolated yield. [c] The d.r. was determined by 1H NMR analysis of the crude reaction mixture. [d] Determined by chiral HPLC analysis. [e] The reaction was conducted with branched allylic ester.

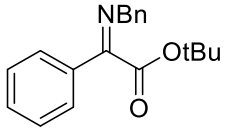
2. General Procedures for the Preparation of Imino Esters



A flame-dried round-bottom flask was equipped with vacuum/argon stopcock and a magnetic stirring bar. The round-bottom flask was charged with α-keto ester (10.0 mmol, 1 equiv), $BnNH_2$ (12.0 mmol, 1.2 equiv), $Ti(OEt)_4$ or $Ti(OtBu)_4$ and DCM (30 mL). The resulting mixture was stirred at room temperature, monitored by crude ^1H NMR until the full conversion of the α-keto ester. The resulting mixture was quenched with water (20 mL), then filtered through celite. The aqueous phase was extracted with DCM (3×20 mL) and the combined organic layers were washed with brine. The organic phase was dried over anhydrous Na_2SO_4, filtered and concentrated. The products were used without further purification.

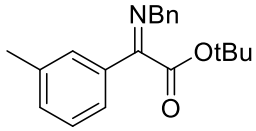
3. Characterization Data for the Imino Esters

tert-butyl (E)-2-(benzylimino)-2-phenylacetate (1a)



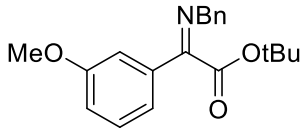
Pale yellow oil. Yield: 77%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.76 (m, 2H), 7.48 – 7.37 (m, 5H), 7.37 – 7.32 (m, 2H), 7.30 – 7.26 (m, 1H), 4.79 (s, 2H), 1.62 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.12, 160.97, 138.98, 134.52, 130.89, 128.53, 128.44, 128.02, 127.36, 127.00, 84.18, 57.93, 28.33. **IR (KBr)** γ 3063, 3029, 2979, 2932, 1724, 1633, 1495, 1450, 1369, 1299, 1235, 1151, 691 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{19}H_{21}NO_2Na$: 318.1470, observed: 318.1477.

tert-butyl (E)-2-(benzylimino)-2-(m-tolyl)acetate (1b)



Pale yellow oil. Yield: 72%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.67 – 7.63 (m, 1H), 7.58 – 7.51 (m, 1H), 7.43 – 7.36 (m, 3H), 7.36 – 7.31 (m, 2H), 7.29 – 7.26 (m, 2H), 4.78 (s, 2H), 2.37 (s, 3H), 1.62 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.27, 161.25, 138.94, 138.33, 134.37, 131.77, 128.46, 128.41, 128.06, 127.74, 127.02, 124.68, 84.15, 57.99, 28.33, 21.43. **IR (KBr)** γ 3062, 3029, 2979, 2930, 2869, 1724, 1633, 1369, 1246, 1147, 695 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{20}H_{23}NO_2Na$: 332.1626, observed: 332.1634.

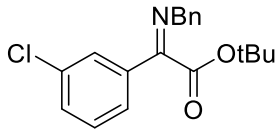
tert-butyl (E)-2-(benzylimino)-2-(3-methoxyphenyl)acetate (1c)



Pale yellow oil. Yield: 92%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.40 (m, 2H), 7.39 – 7.36 (m, 2H), 7.35 – 7.30 (m, 2H), 7.29 – 7.22 (m, 2H), 7.02 – 6.96 (m, 1H), 4.78 (s, 2H), 3.82 (s, 3H), 1.62 (s, 9H). **^{13}C NMR** (101 MHz, CDCl3) δ 165.12, 160.91, 159.76, 138.90, 135.84, 129.54, 128.46, 128.05, 127.04, 120.18, 117.46, 111.66, 84.22, 57.96, 55.37, 28.33. **IR (KBr)** γ 3063, 3029, 2978, 2932, 1724, 1255, 1147, 1041, 695 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{20}H_{23}NO_3Na$: 348.1576, observed: 348.1591.

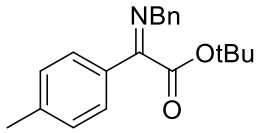
tert-butyl (E)-2-(benzylimino)-2-(3-chlorophenyl)acetate (1d)

Pale yellow oil. Yield: 51%.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.86 – 7.81 (m, 1H), 7.64 – 7.58 (m, 1H), 7.44 – 7.39 (m, 2H), 7.39 – 7.37 (m, 2H), 7.37 – 7.33 (m, 2H), 7.30 –



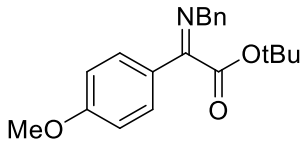
7.26 (m, 1H), 4.78 (s, 2H), 1.63 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.55, 159.62, 138.60, 136.24, 134.77, 130.91, 129.77, 128.53, 128.04, 127.31, 127.17, 125.60, 84.63, 58.07, 28.32. **IR (KBr)** γ3065, 3029, 2979, 2930, 1725, 1632, 1369, 1297, 1151, 696 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{19}H_{20}NO_2NaCl$: 352.1080, observed: 352.1094.

tert-butyl (E)-2-(benzylimino)-2-(p-tolyl)acetate (1e)



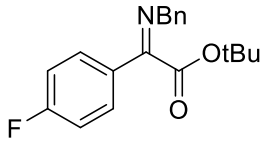
Pale yellow solid. Yield: 74%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.69 (d, *J* = 8.2 Hz, 2H), 7.42 – 7.30 (m, 5H), 7.21 (d, *J* = 8.1 Hz, 2H), 4.77 (s, 2H), 2.38 (s, 3H), 1.61 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 165.32, 160.95, 141.28, 139.09, 131.80, 129.27, 128.43, 128.02, 127.32, 126.96, 84.06, 57.85, 28.33, 21.50. **IR (KBr)** γ3028, 3002, 2979, 2930, 1724, 1368, 1300, 1243, 1151, 697 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{20}H_{23}NO_2Na$: 332.1626, observed: 332.1638.

tert-butyl (E)-2-(benzylimino)-2-(4-methoxyphenyl)acetate (1f)



Pale yellow solid. Yield: 89%.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.44 – 7.37 (m, 3H), 7.37 – 7.29 (m, 4H), 7.29 – 7.26 (m, 1H), 7.05 – 6.95 (m, 1H), 4.78 (s, 2H), 3.83 (s, 3H), 1.62 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.36, 160.76, 159.34, 138.17, 127.95, 127.37, 126.95, 126.17, 125.88, 112.87, 82.98, 56.70, 54.34, 27.28. **IR (KBr)** γ3029, 3003, 2978, 2934, 1723, 1604, 1512, 1257, 1173, 1151, 1029 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{20}H_{23}NO_3Na$: 348.1576, observed: 348.1592

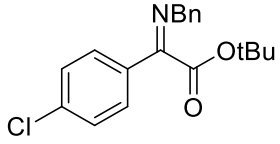
tert-butyl (E)-2-(benzylimino)-2-(4-fluorophenyl)acetate (1g)



Pale yellow solid. Yield: 76%. **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.84 – 7.74 (m, 2H), 7.43 – 7.32 (m, 4H), 7.31 – 7.26 (m, 1H), 7.13 – 7.03 (m, 2H), 4.76 (s, 2H), 1.62 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.94, δ 164.47 (d, *J* = 251.4 Hz), 159.69, 138.86, 130.74 (d, *J* = 3.1 Hz), 129.45 (d, *J* = 8.7 Hz), 128.50, 128.02, 127.09, 115.66 (d, *J* = 21.9 Hz), 84.42, 57.92, 28.33. **IR (KBr)** γ3064, 3030, 2980, 2933, 1724, 1508, 1370, 1231, 1150, 835 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{19}H_{20}NO_2NaF$: 336.1376, observed:

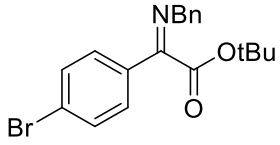
336.1391.

tert-butyl (E)-2-(benzylimino)-2-(4-chlorophenyl)acetate (1h)



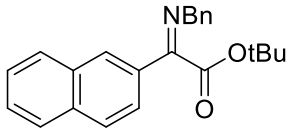
Pale yellow oil. Yield: 85%.**^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.76 – 7.65 (m, 2H), 7.40 – 7.32 (m, 6H), 7.30 – 7.27 (m, 1H), 4.77 (s, 2H), 1.62 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 164.74, 159.78, 138.73, 137.06, 132.96, 128.82, 128.66, 128.51, 128.02, 127.12, 84.51, 58.01, 28.32. **IR (KBr)** γ3063, 3029, 2979, 2929, 2854, 1724, 1490, 1369, 1151, 1091, 1014 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{19}H_{20}NO_2NaCl$: 352.1080, observed: 352.1098.

tert-butyl (E)-2-(benzylimino)-2-(4-bromophenyl)acetate (1i)



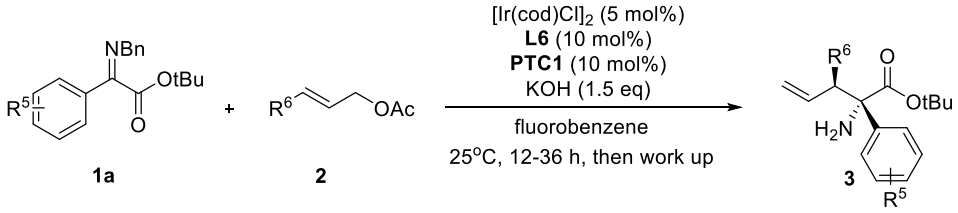
Pale yellow oil. Yield: 82%.^{1}H NMR (400 MHz, $CDCl_3$) δ 7.68 – 7.62 (m, 2H), 7.56 – 7.51 (m, 2H), 7.40 – 7.33 (m, 4H), 7.31 – 7.26 (m, 1H), 4.76 (s, 2H), 1.61 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 164.68, 159.90, 138.70, 133.41, 131.78, 128.87, 128.51, 128.02, 127.13, 125.55, 84.52, 58.04, 28.33. **IR (KBr)** γ3063, 3029, 2979, 2932, 1728, 1487, 1369, 1154, 1010, 697 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{19}H_{20}NO_2NaBr$: 396.0575, observed: 396.0586.

tert-butyl (E)-2-(benzylimino)-2-(naphthalen-2-yl)acetate (1j)



Pale yellow solid. Yield: 65%. ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.11 (s, 1H), 8.05 (dd, *J* = 8.7, 1.7 Hz, 1H), 7.86 (m, 3H), 7.56 – 7.49 (m, 2H), 7.44 (m, 2H), 7.40 – 7.35 (m, 2H), 7.31 – 7.27 (m, 1H), 4.85 (s, 2H), 1.66 (s, 9H). ^{13}C NMR (101 MHz, $CDCl_3$) δ 165.25, 161.09, 139.00, 134.63, 132.82, 131.94, 128.95, 128.49, 128.42, 128.40, 128.07, 127.78, 127.42, 127.06, 126.50, 123.74, 84.30, 58.10, 28.38. **IR (KBr)** γ3061, 3029, 2978, 2932, 1732, 1624, 1369, 1250, 1151, 1132 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{23}H_{23}NO_2Na$: 368.1626, observed: 368.1642.

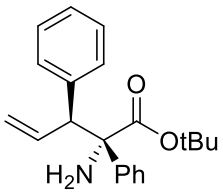
4. General Experimental Procedures



To a flame-dried and Ar-purged schlenk tube (25 mL) was added $[Ir(cod)Cl]_2$(3.4 mg, 0.005 mmol), **L6** (0.010 mmol), **PTC1** (3.2 mg, 0.010 mmol), KOH (8.4 mg, 0.15 mmol) and a stir bar. The schlenk tube was then evacuated and filled with argon. This cycle was repeated three times and followed by addition of imino ester (0.20 mmol), allylic acetate (0.1 mmol) in fluorobenzene (1 mL) via syringe. The mixture was stirred at 25 °C until the full conversion of the allylic acetate (monitored by TLC). Then the reaction mixture was added 2 ml THF and 2 ml 1N HCl and stirred at 25 °C for 1 h. The mixture was brought to pH 10 with Na_2CO_3 (aq), extracted with Et_2O (4 x 15 mL), dried over Na_2SO_4, filtered, concentrated, and purified by column chromatography on silica gel (petroleum/ethyl acetate = 30/1 to 15/1).

5. Characterization Data for the Products

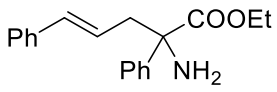
tert-butyl (2S,3S)-2-amino-2,3-diphenylpent-4-enoate (3aa)



Colorless oil. Yield: 61%. dr: 4:1. Enantiomeric excess: **major**: 93%, **minor**: 71%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 92/8, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 4.756 min, t_R= 6.299 min (major); **minor**: t_R= 4.974 min, t_R= 5.334 min (major). $[\alpha]_D^{20}$ = -15.2 (c 0.29, $CHCl_3$) (major); $[\alpha]_D^{20}$ = -387.2 (c 0.07, $CHCl_3$)(minor) . **^{1}H NMR** (400 MHz, $CDCl_3$) δ **major**: 7.51 – 7.43 (m, 2H), 7.22 – 7.12 (m, 3H), 7.07 (s, 5H), 6.36 (ddd, *J* = 17.1, 10.4, 8.0 Hz, 1H), 5.21 (ddd, *J* = 10.4, 1.7, 0.9 Hz, 1H), 5.18 – 5.09 (m, 1H), 4.31 (d, *J* = 8.0 Hz, 1H), 1.87 (brs, 2H), 1.47 (s, 9H); **minor :** 7.76 – 7.71 (m, 2H), 7.52 – 7.44 (m, 2H), 7.38 – 7.27 (m, 5H),

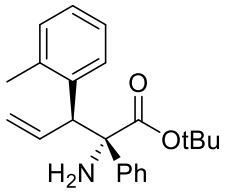
7.25 – 7.21 (m, 1H), 5.98 (ddd, *J* = 17.2, 10.4, 7.9 Hz, 1H), 5.00 – 4.87 (m, 1H), 4.85 – 4.73 (m, 1H), 4.40 (d, *J* = 7.9 Hz, 1H), 1.73 (brs, 2H), 1.27 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ **major**: 173.35, 141.83, 139.14, 137.56, 129.89, 127.74, 127.60, 127.08, 126.45, 126.17, 118.17, 82.06, 67.59, 57.51, 27.93. **minor:** 173.28, 141.90, 140.36, 136.95, 129.98, 128.13, 128.00, 127.24, 126.95, 126.42, 117.94, 81.90, 67.11, 56.55, 27.68. **IR (KBr)** γ (major) 3061, 3028, 2976, 2926, 2853, 1724, 1682, 1368, 1247, 1153, 701 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{21}H_{25}NO_2Na$: 346.1783, observed: 346.1799.

ethyl (E)-2-amino-2,5-diphenylpent-4-enoate (3aa'')



Colorless oil. Yield: 41%. Enantiomeric excess: 6%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 33.3/66.7, flow rate 1.0 mL/min, T = 30°C, 254 nm): t_R= 6.990min, t_R= 8.683 min (major). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (d, *J* = 7.5 Hz, 1H), 7.37 (m, 1H), 7.29 (m, 1H), 7.21 (m, 1H), 6.54 (d, *J* = 15.8 Hz, 1H), 6.20 – 6.04 (m, 1H), 4.21 (m, 1H), 3.23 – 3.09 (m, 1H), 2.78 (dd, *J* = 13.9, 7.8 Hz, 1H), 2.04 (br, 1H), 1.25 (t, *J* = 7.1 Hz, 1H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 175.11, 142.90, 137.03, 134.95, 128.54, 128.47, 128.41, 127.56, 127.49, 126.26, 125.39, 124.38, 63.51, 61.57, 44.01, 14.18. **HRMS (ESI)** m/z $(M+H)^+$ calculated for $C_{19}H_{22}NO_2$: 296.1645, observed: 296.1651.

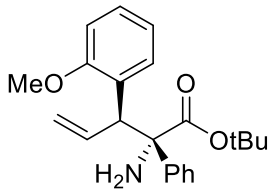
tert-butyl (2S,3S)-2-amino-2-phenyl-3-(o-tolyl)pent-4-enoate (3ab)



Colorless oil. Yield: 74%. dr: >20:1. Enantiomeric excess: 90%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 4.615min, t_R= 7.837 min (major). $[\alpha]_D^{20}$ = 23.7 (c 0.21, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.68 (dd, *J* = 7.8, 1.2 Hz, 1H), 7.50 – 7.29 (m, 2H), 7.11 – 7.02 (m, 3H), 6.99 – 6.79 (m, 3H), 6.11 (ddd, *J* = 17.3, 10.3, 7.1 Hz, 1H), 5.09 (ddd, *J* = 10.3, 1.8, 1.2 Hz, 1H), 4.95 – 4.83 (m, 1H), 4.65 (d, *J* = 7.1 Hz, 1H), 1.99 (s, 3H), 1.79 (brs, 2H), 1.43 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.41, 140.54, 136.80, 136.45, 135.89, 128.88, 128.49, 126.58, 125.98, 125.15, 124.93, 124.31, 117.17, 81.03, 66.84, 50.12, 26.90, 18.84. **IR (KBr)** γ 3371, 3057, 3004, 2972, 2926, 2853, 1720, 1263, 1154, 735 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{27}NO_2Na$: 360.1939, observed:

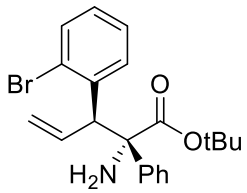
360.1954.

tert-butyl (2S,3S)-2-amino-3-(2-methoxyphenyl)-2-phenylpent-4-enoate (3ac)



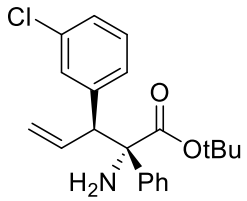
Colorless oil. Yield: 81%. dr: 17:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 6.656 min, t_R= 13.004 min (major). $[\alpha]_D^{20}$ = 20.7 (c 0.51, $CHCl_3$). **^{1}H NMR** (400 MHz, CDCl3) δ 7.49 (m, 1H), 7.43 – 7.33 (m, 2H), 7.10 – 6.92 (m, 4H), 6.72 (m, 1H), 6.53 – 6.45 (m, 1H), 6.22 – 6.12 (m, 1H), 5.10 (ddd, *J* = 2.9, 1.9, 1.4 Hz, 1H), 5.06 – 4.95 (m, 2H), 3.43 (s, 3H), 1.86 (brs, 2H), 1.40 (s, 9H). **^{13}C NMR** (101 MHz, CDCl3) δ 173.01, 155.99, 140.73, 136.77, 129.51, 126.70, 126.35, 126.12, 125.68, 125.06, 118.83, 116.82, 109.25, 80.84, 66.71, 54.18, 46.31, 26.89. **IR (KBr)** γ 3390, 3059, 2976, 2930, 2853, 2835, 1720, 1490, 1240, 1151, 754 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{27}NO_3Na$: 376.1889, observed: 376.1905.

tert-butyl (2S,3S)-2-amino-3-(2-bromophenyl)-2-phenylpent-4-enoate (3ad)



Colorless oil. Yield: 68%. dr: 6:1. Enantiomeric excess: **major**: 95%, **minor**: 83%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 98/2, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 4.517 min, t_R= 6.367 min (major); **minor**: t_R= 5.044 min (major), t_R= 5.538 min. $[\alpha]_D^{20}$ = 92.5 (c 0.22, $CHCl_3$). **^{1}H NMR** (400 MHz, CDCl3) δ 8.01 (m, 1H), 7.57 – 7.45 (m, 2H), 7.33 (m, 1H), 7.17 – 7.04 (m, 4H), 6.92 – 6.81 (m, 1H), 6.07 (ddd, *J* = 17.1, 10.3, 6.6 Hz, 1H), 5.31 (d, *J* = 6.6 Hz, 1H), 5.25 (dt, *J* = 10.3, 1.4 Hz, 1H), 4.98 (dt, J = 17.1, 1.5 Hz, 1H), 2.10 (brs, 2H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.54, 140.57, 138.36, 136.55, 132.39, 131.44, 127.79, 127.66, 127.00, 126.70, 126.30, 125.95, 119.26, 82.23, 67.46, 53.40, 27.87. **IR (KBr)** γ 3056, 3004, 2980, 2927, 2854, 1720, 1265, 1155, 738, 703 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{21}H_{24}NO_2NaBr$: 424.0888, observed: 424.0891.

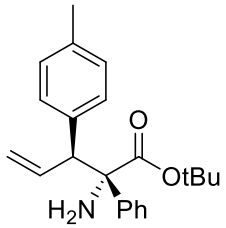
tert-butyl (2S,3S)-2-amino-3-(3-chlorophenyl)-2-phenylpent-4-enoate (3ae)



Colorless oil. Yield: 50%. dr: 5:1. Enantiomeric excess: **major**: 90%, **minor**: 69%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 98.5/1.5, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 5.872 min, t_R= 7.280 min (major); **minor**:

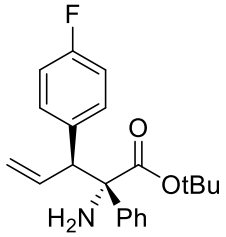
t_R= 6.921 min, t_R= 7.704 min (major). $[\alpha]_D^{20}$ = -25.2 (c 0.10, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.24 – 7.12 (m, 4H), 6.99 (m, 3H), 6.33 – 6.19 (m, 1H), 5.23 (dd, *J* = 10.3, 1.0 Hz, 1H), 5.12 (dd, *J* = 17.1, 1.2 Hz, 1H), 4.29 (d, *J* = 7.9 Hz, 1H), 1.75 (brs, 3H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.32, 141.28, 136.96, 133.35, 130.00, 128.71, 128.18, 127.89, 127.28, 126.58, 125.99, 118.76, 82.27, 67.45, 57.08, 27.91. **IR (KBr)** γ 3360, 3057, 2979, 2924, 2852, 1722, 1265, 1154, 739, 702 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{21}H_{24}NO_2NaCl$: 380.1393, observed: 380.1411.

tert-butyl (2S,3S)-2-amino-2-phenyl-3-(p-tolyl)pent-4-enoate (3af)



Colorless solid. Yield: 56%. dr: 8:1. Enantiomeric excess: **major**: 91%, **minor**: 59%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 96/4, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 5.257 min, t_R= 6.102 min (major); **minor**: t_R= 5.759 min, t_R= 6.466 min (major). $[\alpha]_D^{20}$ = -28.4 (c 0.16, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 – 7.44 (m, 2H), 7.25 – 7.11 (m, 3H), 7.00 – 6.83 (m, 4H), 6.35 (ddd, *J* = 17.1, 10.3, 8.1 Hz, 1H), 5.24 – 5.06 (m, 2H), 4.28 (d, *J* = 8.1 Hz, 1H), 2.20 (s, 3H), 1.85 (s, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.28, 141.93, 137.72, 136.03, 135.95, 129.68, 128.39, 127.73, 127.05, 126.29, 117.91, 82.03, 67.55, 57.14, 27.92, 20.94. **IR (KBr)** γ 3408, 3056, 2980, 2926, 2854, 1716, 1368, 1264, 1156, 742, 700 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{27}NO_2Na$: 360.1939, observed: 360.1956.

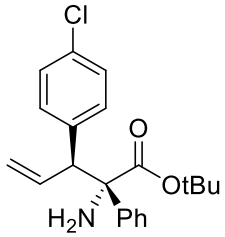
tert-butyl (2S,3S)-2-amino-3-(4-fluorophenyl)-2-phenylpent-4-enoate (3ag)



Colorless solid. Yield: 56%. dr: 4:1. Enantiomeric excess: **major**: 91%, **minor**: 70%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 98.5/1.5, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 5.465 min, t_R=6.850 min (major); **minor**: t_R= 5.720 min (major), t_R= 6.426 min.$[\alpha]_D^{20}$ = -33.2 (c 0.10, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.48 – 7.42 (m, 2H), 7.22 – 7.12 (m, 3H), 7.08 – 6.99 (m, 2H), 6.80 – 6.72 (m, 2H), 6.29 (ddd, *J* = 17.2, 10.4, 7.7 Hz, 1H), 5.28 – 5.19 (m, 1H), 5.17 – 5.06 (m, 1H), 4.32 (d, *J* = 7.7 Hz, 1H), 1.77 (brs, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$)

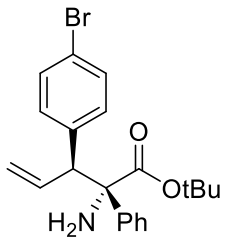
δ 173.43, 161.53 (d, *J* = 244.7 Hz), 141.48, 137.41, 134.79(d, *J* = 3.29 Hz), 131.35 (d, *J* = 7.8 Hz), 127.83, 127.17, 126.00, 118.44, 114.33 (d, *J* = 21.0 Hz), 82.16, 67.50, 56.53, 27.91. **IR (KBr)** γ 3360, 3057, 2962, 2923, 2851, 1277, 1508, 1264, 1155, 1016, 802, 739 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{21}H_{24}NO_2NaF$: 364.1689, observed: 364.1707.

tert-butyl (2S,3S)-2-amino-3-(4-chlorophenyl)-2-phenylpent-4-enoate (3ah)



Colorless solid. Yield: 57%. dr: 8:1. Enantiomeric excess: **major**: 90%, **minor**: 67%, determined by HPLC (CHIRALPAK IB, hexane/isopropanol = 99.55/0.45, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 6.699 min, t_R= 7.184 min (major); **minor**: t_R= 5.879 min, t_R= 6.148 min (major). $[\alpha]_D^{20}$ = -22.4(c 0.12, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.50 – 7.40 (m, 2H), 7.24 – 7.12 (m, 3H), 7.05 – 6.99 (m, 4H), 6.28 (ddd, *J* = 17.2, 10.4, 7.7 Hz, 1H), 5.29 – 5.17 (m, 1H), 5.17 – 5.07 (m, 1H), 4.32 (d, *J* = 7.7 Hz, 1H), 1.72 (brs, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.36, 141.34, 137.66, 137.16, 132.25, 131.27, 127.88, 127.68, 127.23, 125.98, 118.64, 82.21, 67.39, 56.63, 27.90. **IR (KBr)** γ 3359, 2962, 2922, 2851, 1724, 1260, 1154, 1092, 1016, 800 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{21}H_{24}NO_2NaCl$: 380.1393, observed: 380.1407.

tert-butyl (2S,3S)-2-amino-3-(4-bromophenyl)-2-phenylpent-4-enoate (3ai)

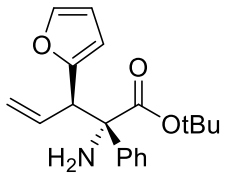


3ai

Colorless solid. Yield: 62%. dr: 4:1. Enantiomeric excess: **major**: 91%, **minor**: 71%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 98.5/1.5, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 5.390 min, t_R= 6.026 min (major); **minor**: t_R= 5.720 min (major), t_R= 6.482 min. $[\alpha]_D^{20}$ = 19.7(c 0.12, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 – 7.38 (m, 2H), 7.23 – 7.13 (m, 5H), 7.01 – 6.89 (m, 2H), 6.27 (ddd, *J* = 17.2, 10.4, 7.7 Hz, 1H), 5.23 (ddd, *J* = 10.4, 1.6, 1.1 Hz, 1H), 5.17 – 5.06 (m, 1H), 4.30 (d, *J* = 7.7 Hz, 1H), 1.75 (brs, 2H), 1.46 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.34, 141.31, 138.20, 137.09, 131.66, 130.63, 127.90, 127.25, 125.98, 120.47, 118.68, 82.22, 67.33, 56.68, 27.90. **IR (KBr)** γ 3395, 3053, 2962, 2926, 2853, 1721, 1264, 1011, 805, 741, 704 cm^{-1}. **HRMS (ESI)** m/z

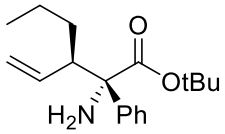
$(M+Na)^+$ calculated for $C_{21}H_{24}NO_2NaBr$: 424.0888, observed: 424.0898.

tert-butyl (2S,3R)-2-amino-3-(furan-2-yl)-2-phenylpent-4-enoate (3aj)



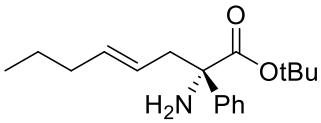
Colorless solid. Yield: 47%. dr: 5:1. Enantiomeric excess: **major**: 81%, **minor**: 36%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 97/3, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 7.340 min, t_R= 13.103 min (major); **minor**: t_R= 6.288 min(major), t_R=8.938 min. $[\alpha]_D^{20}$ = 37.7(c 0.12, $CHCl_3$). **^{1}H NMR** (400 MHz, CDCl3) δ 7.62 – 7.49 (m, 2H), 7.29 – 7.23 (m, 2H), 7.23 – 7.16 (m, 2H), 6.24 – 6.15 (m, 1H), 6.15 – 6.12 (m, 1H), 5.92 (d, *J* = 3.2 Hz, 1H), 5.31 – 5.20 (m, 1H), 5.19 – 5.08 (m, 1H), 4.52 (d, *J* = 7.6 Hz, 1H), 2.09 (brs, 2H), 1.44 (s, 9H).**^{13}C NMR** (101 MHz, $CDCl_3$) δ 172.41, 152.79, 141.53, 141.34, 134.97, 127.87, 127.27, 126.07, 118.82, 110.00, 108.41, 82.33, 67.20, 51.46, 27.84. **IR (KBr)** γ 3359, 3060, 2978, 2922, 2852, 1728, 1369, 1252, 1154, 736 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{19}H_{23}NO_3Na$: 336.1576, observed: 336.1591.

tert-butyl (2S,3R)-2-amino-2-phenyl-3-vinylhexanoate (3ak-b)



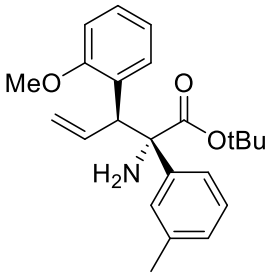
Colorless oil. Yield: 50%. dr: 2:1. Enantiomeric excess: **major**: 81%, **minor**: 70%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 98.5/1.5, flow rate 1.0 mL/min, T = 30°C, 220 nm), **major**: t_R= 6.664 min, t_R= 8.403 min (major); **minor**: t_R= 5.986 min (major), t_R=9.726 min. $[\alpha]_D^{20}$ = -85.4(c 0.07, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.65 – 7.60 (m, 2H), 7.57 (m, 1H), 7.36 – 7.30 (m, 3H), 7.30– 7.20 (m, 1.5H), 5.78 (ddd, *J* = 16.7, 10.8, 8.7 Hz, 1H), 5.45 (ddd, *J* = 17.2, 10.4, 8.9 Hz, 0.5H), 5.24 (m, 1H), 5.22 – 5.18 (m, 1H), 4.93 (m, 0.5H), 4.87 – 4.80 (m, 0.5H)., 3.07 – 2.98 (m, 1H), 2.93 (m, 0.5H), 1.74 (brs, 3H),1.45 (s, 4.5H), 1.37 (s, 9H), 1.34 – 1.14 (m, 4H), 1.12 – 0.99 (m, 12H), 0.91 (t, *J* = 7.2 Hz, 1.5H), 0.75 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.18, 173.89, 142.37, 142.03, 137.61, 137.06, 128.02, 127.90, 127.04, 127.00, 126.26, 126.16, 118.45, 117.93, 81.71, 81.52, 67.27, 66.91, 51.40, 50.38, 32.11, 29.66, 27.89, 27.83, 21.01, 20.66, 14.02, 13.88. **IR (KBr)** γ 3359, 3059, 2958, 2926, 2856, 1726, 1265, 1248, 1153, 740 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{18}H_{27}NO_2Na$: 312.1939, observed: 312.1956.

tert-butyl (S,E)-2-amino-2-phenyloct-4-enoate (3ak-l)



Colorless oil. Yield: 24%. Enantiomeric excess: 8%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 98.5/1.5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 9.750 min (major), t_R= 14.007 min. $[\alpha]_D^{20}$ = 2.2(c 0.20, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 – 7.52 (m, 2H), 7.36 – 7.30 (m, 2H), 7.28 – 7.22 (m, 1H), 5.61 (dt, *J* = 14.9, 6.8 Hz, 1H), 5.50 – 5.24 (m, 1H), 2.92 (ddd, *J* = 13.5, 6.4, 1.0 Hz, 1H), 2.52 (dd, *J* = 13.5, 8.0 Hz, 1H), 1.98 (q, *J* = 7.1 Hz, 2H), 1.89 (brs, 2H), 1.43 (s, 9H), 1.41 – 1.30 (m, 2H), 0.88 (t, *J* = 7.4 Hz, 3H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.53, 143.56, 136.15, 128.20, 127.14, 125.47, 124.32, 81.51, 63.40, 43.32, 34.80, 27.90, 22.48, 13.65. **IR (KBr)** γ 3377, 3059, 3026, 2960, 2928, 2872, 1724, 1368, 1157, 738, 699 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{18}H_{27}NO_2Na$: 312.1939, observed: 312.1954.

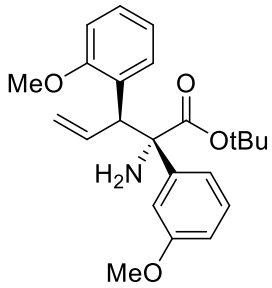
tert-butyl (2S,3S)-2-amino-3-(2-methoxyphenyl)-2-(m-tolyl)pent-4-enoate (3bc)



Colorless oil. Yield: 88%. dr: >20:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 5.837 min, t_R= 10.844 min (major). $[\alpha]_D^{20}$ = -198.9(c 0.37, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.55 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.26 (s, 1H), 7.22 (dd, *J* = 7.9, 0.5 Hz, 1H), 7.09 – 6.96 (m, 2H), 6.89 (d, *J* = 7.5 Hz, 1H), 6.80 (m, 1H), 6.59 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.25 (ddd, *J* = 17.4, 10.3, 7.2 Hz, 1H), 5.16 (ddd, *J* = 10.2, 1.7, 1.1 Hz, 1H), 5.08 (dtd, *J* = 4.5, 3.2, 1.4 Hz, 2H), 3.51 (s, 3H), 2.22 (s, 3H), 2.08 (brs, 2H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.01, 157.08, 141.63, 137.87, 136.52, 130.51, 127.83, 127.42, 127.38, 127.03, 126.96, 123.13, 119.90, 117.76, 110.28, 81.84, 67.78, 55.22, 47.35, 27.93, 21.52. **IR (KBr)** γ 3390, 3325, 2976, 2928, 2855, 1720, 1491, 1368, 1243, 1154, 755 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{23}H_{29}NO_3Na$: 390.2045, observed: 390.2061.

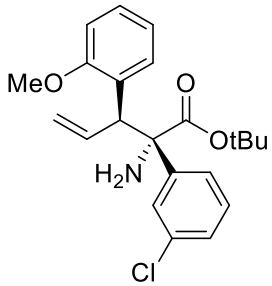
tert-butyl (2S,3S)-2-amino-3-(2-methoxyphenyl)-2-(3-methoxyphenyl)pent-4-enoate (3cc)

Colorless oil. Yield: 85%. dr: >20:1. Enantiomeric excess: 91%, determined by HPLC (CHIRALPAK OD, hexane/isopropanol = 97/3, flow rate 0.8 mL/min, T = 30°C, 220



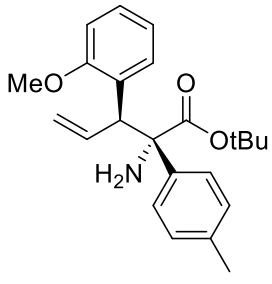
nm): t_R= 6.769 min, t_R= 8.282 min (major). $[\alpha]_D^{20}$ = 20.6(c 0.43, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.57 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.09 – 6.99 (m, 4H), 6.80 (td, *J* = 7.5, 1.1 Hz, 1H), 6.68 – 6.55 (m, 2H), 6.34 – 6.19 (m, 1H), 5.23 – 5.14 (m, 1H), 5.13 – 5.04 (m, 2H), 3.67 (s, 3H), 3.51 (s, 3H), 2.02 (brs, 2H), 1.49 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.94, 158.78, 157.08, 143.43, 137.71, 130.56, 128.01, 127.75, 127.41, 119.89, 118.52, 117.92, 112.84, 111.78, 110.33, 81.92, 67.81, 55.27, 55.07, 47.36, 27.94. **IR (KBr)** γ 3388, 3324, 3077, 2975, 2931, 1720, 1599, 1491, 1463, 1246, 1154 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{23}H_{29}NO_4Na$: 406.1994, observed: 406.2006.

tert-butyl (2S,3S)-2-amino-2-(3-chlorophenyl)-3-(2-methoxyphenyl)pent-4-enoate (3dc)



Colorless oil. Yield: 82%. dr: >20:1. Enantiomeric excess: 83%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 4.859 min, t_R= 11.481 min (major). $[\alpha]_D^{20}$ = 9.1(c 0.47, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.59 (t, *J* = 1.8 Hz, 1H), 7.52 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.38 – 7.27 (m, 1H), 7.13 – 6.95 (m, 3H), 6.80 (td, *J* = 7.5, 1.0 Hz, 1H), 6.59 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.22 (ddd, *J* = 17.1, 10.3, 7.5 Hz, 1H), 5.30 – 5.03 (m, 3H), 3.55 (s, 3H), 1.95 (brs, 2H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.48, 156.81, 143.92, 137.25, 133.10, 130.40, 128.28, 127.63, 127.13, 127.02, 126.85, 124.22, 119.91, 118.28, 110.21, 82.30, 67.62, 55.19, 47.18, 27.90. **IR (KBr)** γ 3388, 3325, 3074, 2977, 2931, 2854, 2836, 1724, 1491, 1243, 1154, 755 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{26}NO_3NaCl$: 410.1499, observed: 410.1513.

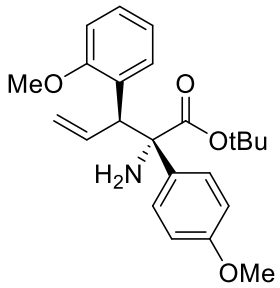
tert-butyl (2S,3S)-2-amino-3-(2-methoxyphenyl)-2-(p-tolyl)pent-4-enoate(3ec)



Colorless oil. Yield: 84%. dr: >20:1. Enantiomeric excess: 93%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 6.144 min, t_R= 23.511 min (major). $[\alpha]_D^{20}$ = 21.0(c 0.41, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.56 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.39 – 7.29 (m, 2H), 7.04 (ddd, *J* = 8.2, 7.4, 1.7 Hz, 1H), 6.92 (d, *J* = 8.0 Hz, 2H), 6.79 (m, 1H),

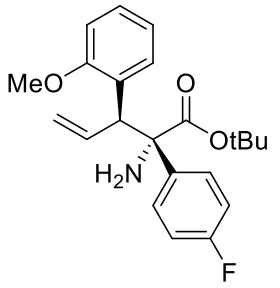
6.60 (dd, *J* = 8.2, 1.0 Hz, 1H), 6.24 (ddd, *J* = 10.3, 9.4, 7.1 Hz, 1H), 5.15 (ddd, *J* = 10.6, 1.7, 1.1 Hz, 1H), 5.10 – 5.01 (m, 2H), 3.52 (s, 3H), 2.36 – 2.16 (s, 3H), 2.16 – 2.01 (brs, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.08, 157.10, 138.73, 137.91, 136.18, 130.56, 127.94, 127.90, 127.35, 125.99, 119.92, 117.73, 110.39, 81.82, 67.56, 55.27, 47.42, 27.92, 20.87. **IR (KBr)** γ 3391, 3325, 3076, 2976, 2929, 2855, 1720, 1491, 1368, 1246, 1154, 755 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{23}H_{29}NO_3Na$: 390.2045, observed: 390.2062.

tert-butyl (2S,3S)-2-amino-3-(2-methoxyphenyl)-2-(4-methoxyphenyl)pent-4-enoate (3fc)



Colorless oil. Yield: 80%. dr: >20:1. Enantiomeric excess: 96%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 5.661 min, t_R= 10.279 min (major). $[\alpha]_D^{20}$ = 12.5(c 0.39, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.7, 1.6 Hz, 1H), 7.41 – 7.34 (m, 2H), 7.09 – 7.01 (m, 1H), 6.79 (td, *J* = 7.6, 0.9 Hz, 1H), 6.70 – 6.57 (m, 3H), 6.32 – 6.17 (m, 1H), 5.16 (dt, *J* = 4.0, 1.7 Hz, 1H), 5.12 – 5.02 (m, 2H), 3.70 (s, 3H), 3.55 (s, 3H), 2.21 (brs, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 174.06, 158.32, 157.03, 137.76, 133.72, 130.55, 127.77, 127.40, 127.33, 119.93, 117.85, 112.52, 110.39, 81.90, 67.32, 55.29, 55.09, 47.49, 27.93. **IR (KBr)** γ 3385, 3076, 2975, 2930, 2853, 2836, 1720, 1509, 1491, 1246, 1155, 1033 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{23}H_{29}NO_4Na$: 406.1994, observed: 406.2009.

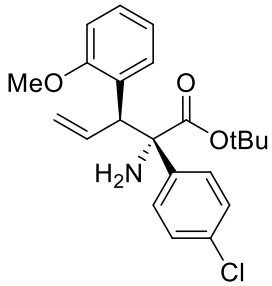
tert-butyl (2S,3S)-2-amino-2-(4-fluorophenyl)-3-(2-methoxyphenyl)pent-4-enoate (3gc)



Colorless oil. Yield: 77%. dr: >20:1. Enantiomeric excess: 88%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 4.872 min, t_R= 5.705 min (major). $[\alpha]_D^{20}$ = 19.3(c 0.42, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.54 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.47 – 7.39 (m, 2H), 7.09 – 7.01 (m, 1H), 6.84 – 6.74 (m, 3H), 6.59 (d, *J* = 8.1 Hz, 1H), 6.29 – 6.15 (m, 1H), 5.19 (dd, *J* = 6.4, 5.2 Hz, 1H), 5.09 (ddd, *J* = 3.6, 3.0, 1.6 Hz, 2H), 3.53 (s, 3H), 2.00 (brs, 2H), 1.48 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.95, 161.73 (d, *J*

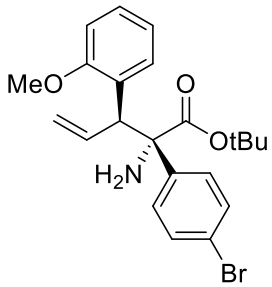
= 245.2 Hz), 156.88, 137.42, 130.52, 127.92 (d, *J* = 8.0 Hz), 127.52, 127.37, 119.89, 118.18, 114.36, 113.78 (d, *J* = 21.1 Hz), 110.25, 82.08, 67.34, 55.16, 47.34, 27.91. **IR (KBr)** γ 3389, 3326, 3077, 2977, 2930, 2854 2837, 1724, 1507, 1491, 1243, 1154 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{26}NO_3NaF$: 394.1794, observed: 394.1808.

tert-butyl (2S,3S)-2-amino-2-(4-chlorophenyl)-3-(2-methoxyphenyl)pent-4-enoate (3hc)



Colorless oil. Yield: 77%. dr: >20:1. Enantiomeric excess: 84%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 4.831 min, t_R= 6.071 min (major). $[\alpha]_D^{20}$ = 18.3(c 0.21, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.45 – 7.36 (m, 2H), 7.11 – 7.01 (m, 3H), 6.79 (m, 1H), 6.59 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.21 (ddd, *J* = 17.1, 10.3, 7.5 Hz, 1H), 5.22 – 5.15 (m, 1H), 5.08 (ddd, *J* = 7.3, 4.5, 2.8 Hz, 2H), 3.53 (s, 3H), 1.99 (brs, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.73, 156.86, 140.34, 137.32, 132.59, 130.50, 127.72, 127.59, 127.23, 127.19, 119.92, 118.27, 110.29, 82.19, 67.41, 55.15, 47.26, 27.90. **IR (KBr)** γ 3362, 3052, 2979, 2927, 2851, 1720, 1491, 1265, 1244, 1155, 739 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{26}NO_3NaCl$: 410.1499, observed: 410.1519.

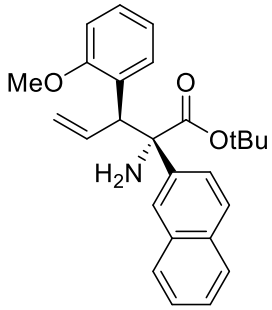
tert-butyl (2S,3S)-2-amino-2-(4-bromophenyl)-3-(2-methoxyphenyl)pent-4-enoate(3ic)



Colorless oil. Yield: 81%. dr: >20:1. Enantiomeric excess: 85%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 95/5, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 4.890 min, t_R= 6.306 min (major). $[\alpha]_D^{20}$ = 9.3(c 0.48, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.53 (dd, *J* = 7.7, 1.7 Hz, 1H), 7.39 – 7.31 (m, 2H), 7.29 – 7.18 (m, 2H), 7.05 (m, 1H), 6.79 (m, 1H), 6.59 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.21 (ddd, *J* = 17.1, 10.3, 7.4 Hz, 1H), 5.19 (ddd, *J* = 10.3, 1.7, 1.2 Hz, 1H), 5.14 – 5.03 (m, 2H), 3.52 (s, 3H), 1.97 (brs, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.64, 156.86, 140.90, 137.29, 130.50, 130.14, 128.11, 127.61, 127.20, 120.87,

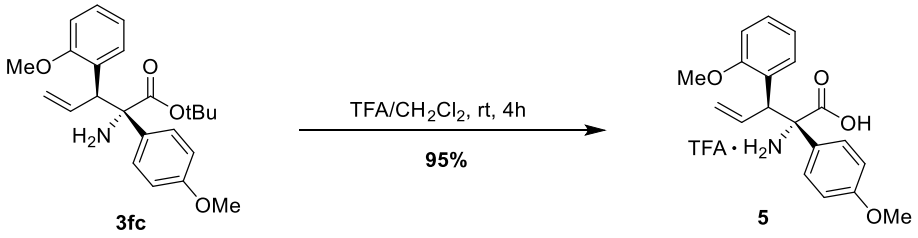
119.93, 118.29, 110.30, 82.21, 67.47, 55.15, 47.23, 27.90. **IR (KBr)** γ 3387, 3076, 2976, 2930, 2853, 1726, 1490, 1244, 1155, 1009, 754 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{22}H_{26}NO_3NaBr$: 454.0994, observed: 454.1004.

tert-butyl (2S,3S)-2-amino-3-(2-methoxyphenyl)-2-(naphthalen-2-yl)pent-4-enoate(3jc)



Colorless oil. Yield: 82%. dr: >20:1. Enantiomeric excess: 82%, determined by HPLC (CHIRALPAK IA, hexane/isopropanol = 90/10, flow rate 1.0 mL/min, T = 30°C, 220 nm): t_R= 5.727 min (major), t_R= 7.552 min. $[\alpha]_D^{20}$ = 9.0(c 0.29, $CHCl_3$). **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.89 (d, *J* = 1.7 Hz, 1H), 7.69 (m, 3H), 7.64 – 7.57 (m, 2H), 7.37 (dd, *J* = 6.2, 3.2 Hz, 2H), 6.97 (ddd, *J* = 8.2, 7.5, 1.7 Hz, 1H), 6.77 (td, *J* = 7.5, 1.1 Hz, 1H), 6.49 (dd, *J* = 8.2, 0.9 Hz, 1H), 6.30 (ddd, *J* = 17.5, 10.3, 7.4 Hz, 1H), 5.21 (ddd, *J* = 11.5, 5.9, 4.3 Hz, 2H), 5.16 – 5.08 (m, 1H), 3.41 (s, 3H), 2.06 (brs, 2H), 1.47 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ 173.87, 156.96, 139.35, 137.74, 132.77, 132.36, 130.51, 128.28, 127.57, 127.46, 127.16, 126.41, 125.62, 125.50, 125.11, 124.81, 119.94, 118.00, 110.32, 82.08, 67.94, 55.16, 47.29, 27.94. **IR (KBr)** γ 3369, 3057, 2977, 2929, 2853, 1720, 1491, 1368, 1253, 1153, 741 cm^{-1}. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{26}H_{29}NO_3Na$: 426.2045, observed: 426.2058.

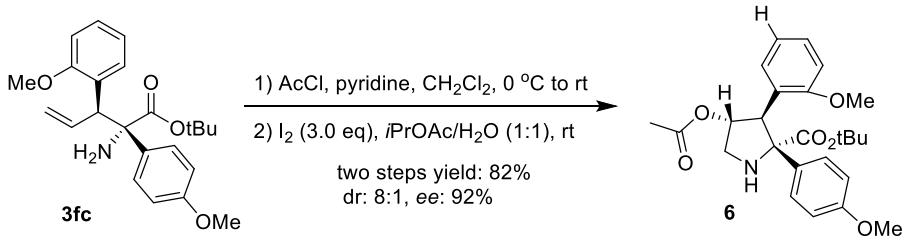
6. Synthesis and Characterization of 5



To a solution of **3fc** (38.3 mg, 0.1 mmol) in DCM (1 mL) was added TFA (1 mL), and the mixture was stirred at room temperature for 4 h. After evaporation, pure **5** was

obtained. Colorless solid. Yield: 95% $[\alpha]_D^{20}$ = -115.4(c 0.63, $CHCl_3$)**^{1}H NMR** (400 MHz, MeOD) δ 7.55 – 7.45 (m, 2H), 7.32 – 7.14 (m, 2H), 7.06 – 6.95 (m, 1H), 6.95 – 6.81 (m, 3H), 6.53 – 6.35 (m, 1H), 5.19 – 4.85 (m, 6H), 3.84 (s, 3H), 3.79 (s, 3H). **^{13}C NMR** (101 MHz, MeOD) δ 170.35, 159.99, 156.96, 135.48, 130.53, 128.91, 128.20, 126.79, 125.10, 120.66, 118.20, 113.34, 111.00, 54.55, 54.39, 49.16, 26.74. **HRMS (ESI)** m/z $(M\text{-}CF_3COOH+Na)^+$calculated for $C_{19}H_{21}NNaO_4$: 350.1363, observed: 350.1345.

7. Synthesis and Characterization of 6

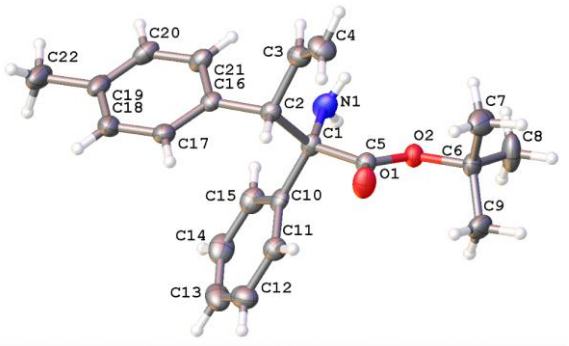


To a solution of **3fc** (114.9 mg, 0.3 mmol) and pyridine (242μL, 1.5 mmol) in DCM (3 mL) was added slowly the acetyl chloride (107 μL, 1.5 mmol) at 0 °C. The reaction was continued for 2 h. Water (10 mL) was added to the reaction mixture and this solution was extracted with DCM (10 mL × 3).The organic layer was washed with 1N HCl , $NaHCO_3$ solution and brine .After drying of the organic layer over Na_2SO_4, the mixture was concentrated in vacuo and the obtained residue was purified by column chromatography (AcOEt/Hexane = 1/10).To a solution of tert-butyl (2S,3S)-2-acetamido-3-(2-methoxyphenyl)-2-(4-methoxyphenyl)pent-4-enoate in *i*PrOAc/H_2O (5 ml) was added I_2 (228.4 mg, 0.9 mmol), and the mixture was stirred at room temperature for 1 h . Na_2SO_3 saturated solution (3 ml) was added to the reaction mixture and this solution was extracted with DCM (10 ml×3). The combined organic layers were dried over anhydrous Na_2SO_4, and concentrated in vacuo. The residue was subjected to a flash column chromatography on silica gel (ethyl acetate/petroleum ether) to afford product **6** as colorless oil. Yield: 82%. dr: 8:1. Enantiomeric excess: 92%, determined by HPLC (CHIRALPAK IC, hexane/isopropanol = 94/6, flow rate 1.0

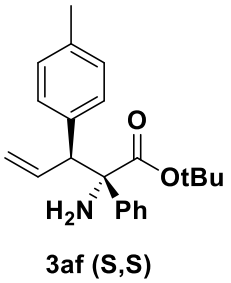
mL/min, T = 30°C, 220 nm): t_R= 13.192 min (major), t_R= 14.434 min. $[\alpha]_D^{20}$ = 85.4(c 0.63, $CHCl_3$) **^{1}H NMR** (400 MHz, $CDCl_3$) δ**major:** 7.31 – 7.17 (m, 2H), 7.03 – 6.88 (m, 2H), 6.68 – 6.61 (m, 2H), 6.60 – 6.53 (m, 2H), 5.19 – 5.13 (m, 1H), 4.86 (s, 1H), 3.73 (s, 3H), 3.69 (dd, *J* = 10.6, 4.8 Hz, 1H), 3.68 – 3.60 (s, 3H), 3.17 (dd, *J* = 12.0, 2.5 Hz, 1H), 2.05 (s, 3H), 1.43 (s, 9H). **minor:** 7.25 – 7.17 (m, 2H), 7.07 (d, *J* = 6.8 Hz, 1H), 7.02 – 6.93 (m, 1H), 6.68 (d, *J* = 8.2 Hz, 1H), 6.65 – 6.53 (m, 3H), 5.46 (dd, *J* = 13.8, 7.5 Hz, 1H), 5.21 (d, *J* = 7.4 Hz, 1H), 3.77 (s, 3H), 3.68 (m, 4H), 3.53 (dd, *J* = 10.7, 8.1 Hz, 1H), 3.13 (dd, *J* = 10.6, 5.8 Hz, 1H), 1.70 (s, 3H), 1.42 (s, 9H). **^{13}C NMR** (101 MHz, $CDCl_3$) δ**major:** 174.48, 170.36, 158.15, 156.81, 131.55, 130.06, 128.21, 127.61, 126.95, 120.18, 112.40, 110.07, 81.76, 81.11, 75.32, 55.42, 55.00, 51.37, 27.82, 21.33. **minor:** 174.90, 170.19, 158.15, 158.04, 132.31, 131.60, 127.98, 127.17, 123.99, 119.49, 112.64, 109.76, 82.14, 74.94, 73.61, 55.60, 55.01, 48.57, 44.05, 29.71, 27.83, 27.73, 20.69. **HRMS (ESI)** m/z $(M+Na)^+$ calculated for $C_{25}H_{31}NO_6Na$: 464.2049, observed: 464.2056

8. X-ray Single Crystal Data - Determination of the Absolute Configuration

Determination of the Absolute Configuration of product 3af



≡



3af (S,S)

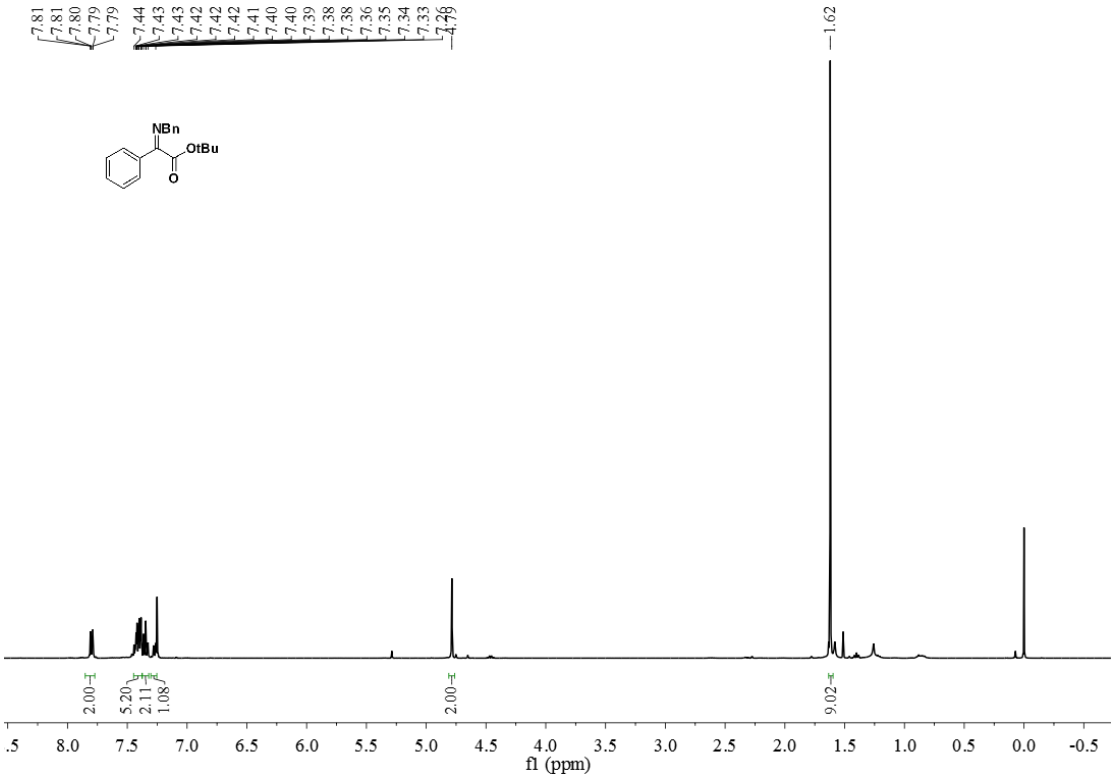
Empirical formula	C_{22} H_{27} NO_2
Formula weight	337.44
Space group	P 1 21 1

Z	2
a/Å	11.8823(2)
b/Å	99.1510(10)
c/Å	13.2198(2)
α/°	90
β/°	107.684(7)
γ/°	90
Volume/Å^3	955.40(3)
Temperature/K	130
ρ_{calc}mg/mm^3	1.173

9. References

[1] S. D. Paget, C. M. Boggs, B. D. Foleno, R. M. Goldschmidt, D. J. Hlasta, M. A. Weidner-Wells, H. M. Werblood, K. Bush, M. J. Macielag, *Bioorg. Med. Chem. Lett.* **2006**, *16*, 4537-4542.

10. NMR Data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7.81
7.80
7.79
7.79
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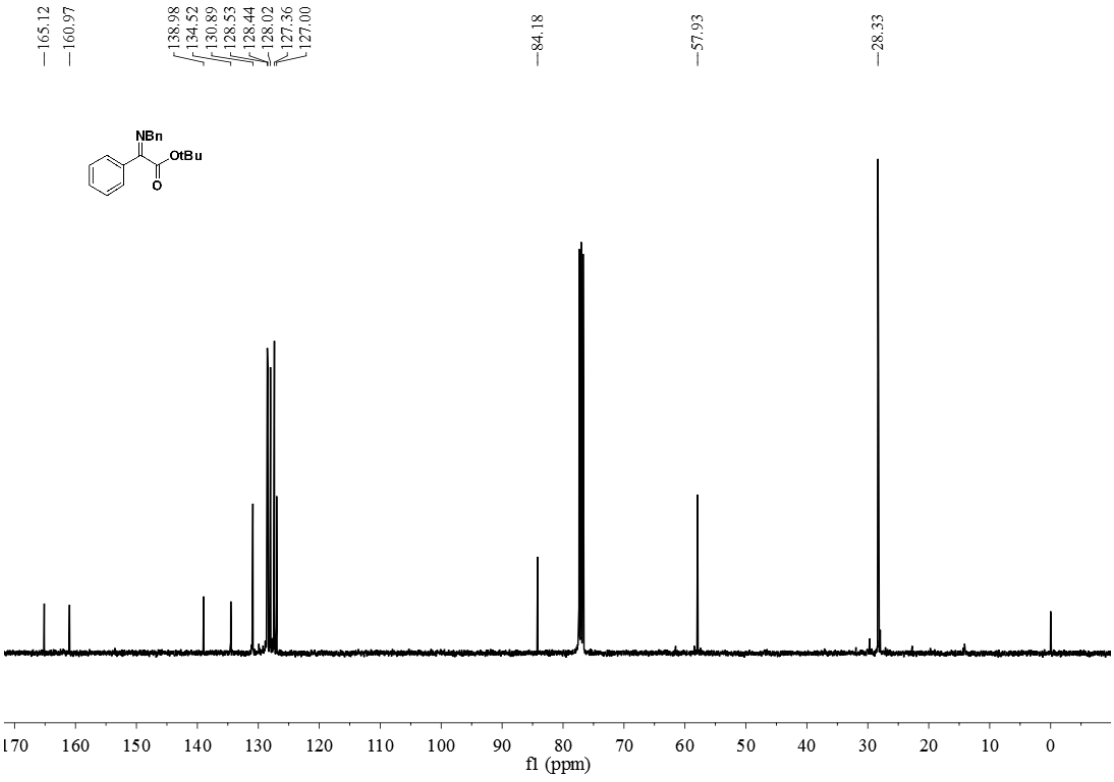
7.43
7.43
7.42
7.42
7.42
7.41
7.40
7.40
7.39
7.38
7.38
7.36
7.35
7.34
7.33
7.26
4.79
1.62
NBn
OtBu
O
2.00
5.20
2.11
1.08
2.00
9.02
.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0 -0.5
f1 (ppm)


165.12
160.97
138.98
134.52
130.89
128.53
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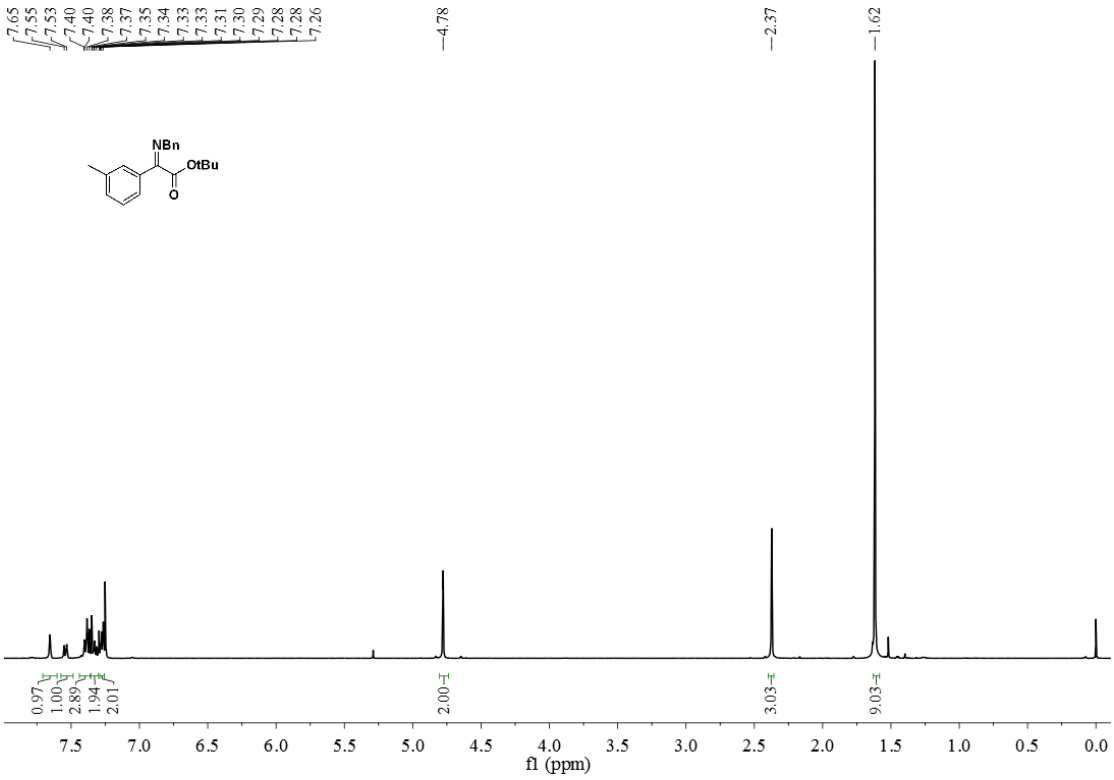
128.02
127.36
127.00
84.18
57.93
28.33
NBn
OtBu
O
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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7.33
7.33
7.31
7.30
7.29
7.28
7.28
7.26
4.78
2.37
1.62
NBn
OtBu
O
0.97
1.00
2.89
1.94
2.01
2.00
3.03
9.03
7.5
7.0
6.5
6.0
5.5
5.0
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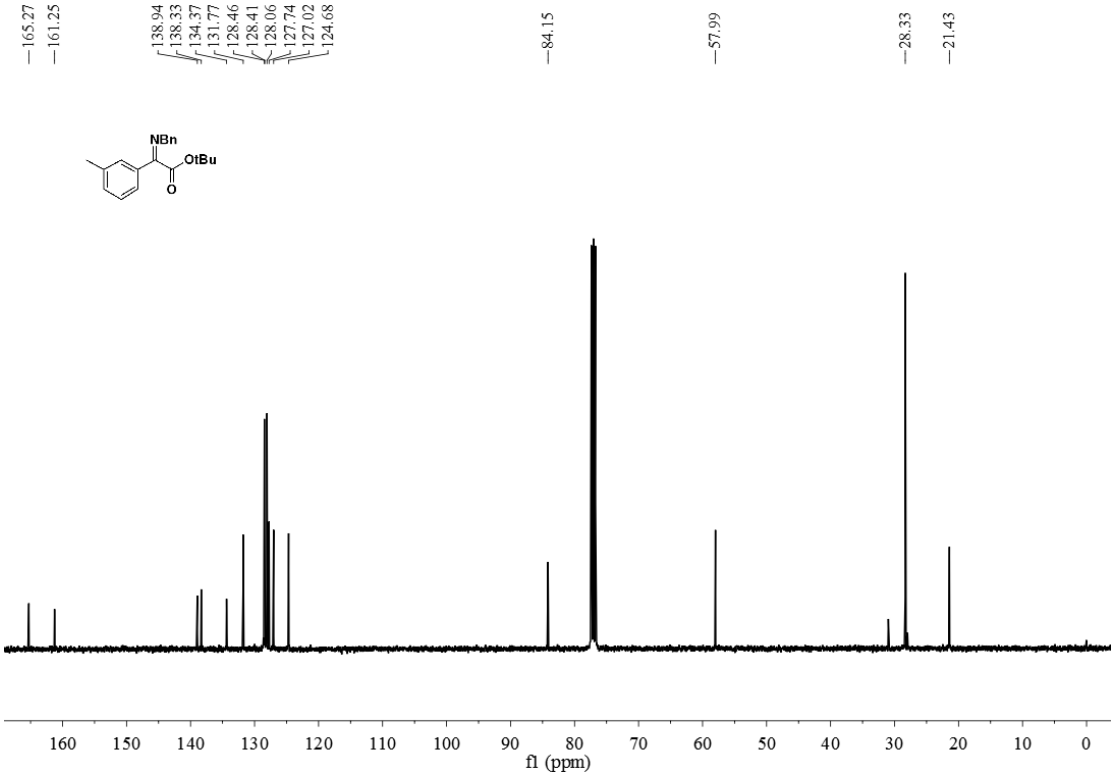
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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134.37
131.77
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128.41
128.06
127.74
127.02
124.68
84.15
57.99
28.33
21.43
NBn
OtBu
O
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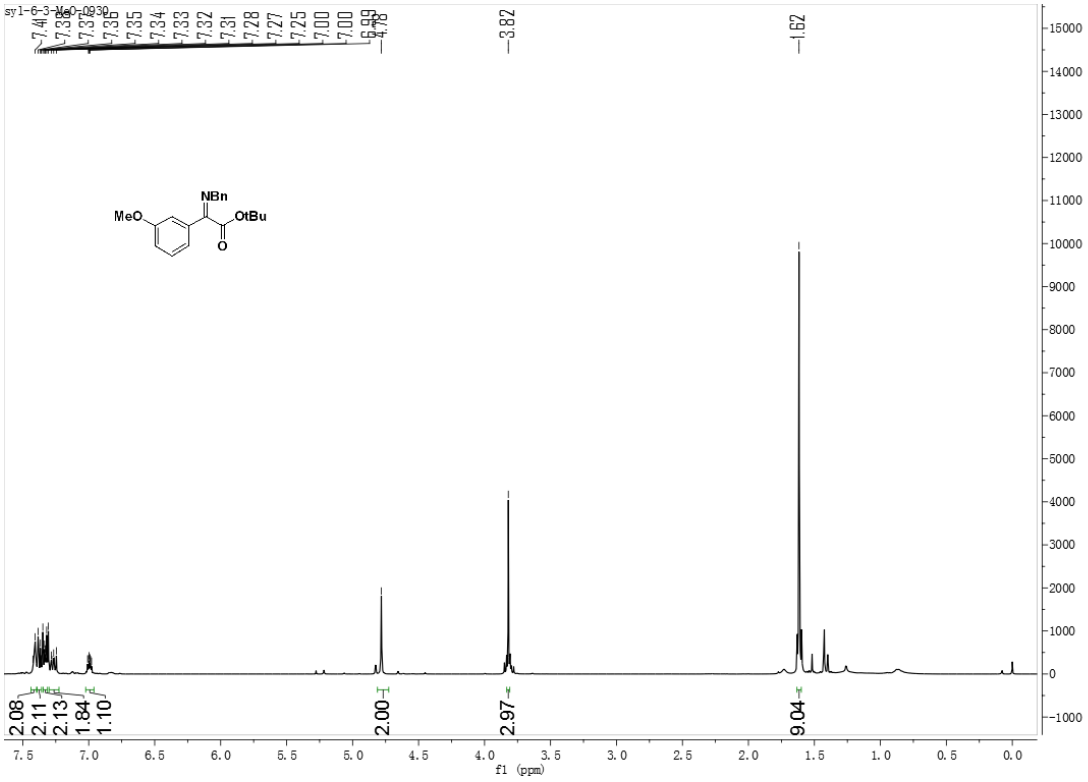
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


sy1-6-3-MeO-0930
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7.36
7.35
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7.33
7.32
7.31
7.28
7.27
7.25
7.00
7.00
6.99
4.78
3.82
1.62
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MeO
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O
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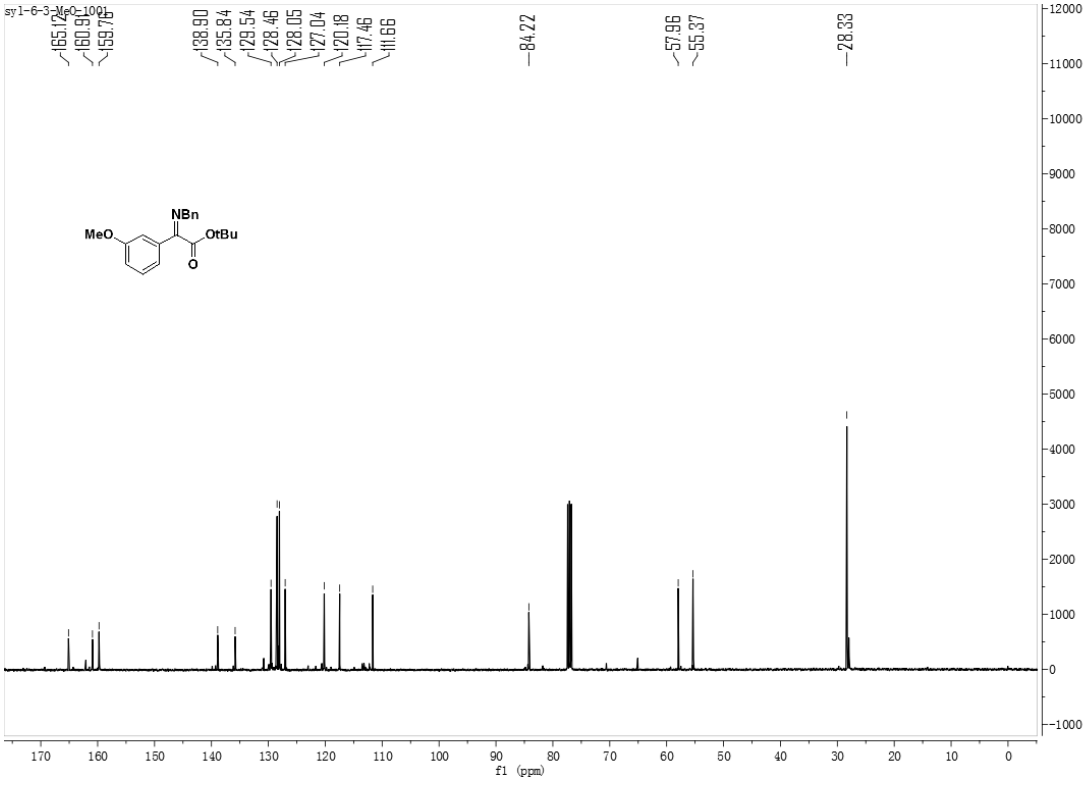
2.11
2.13
1.84
1.10
2.00
2.97
9.04
f1 (ppm)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129.54
128.46
128.05
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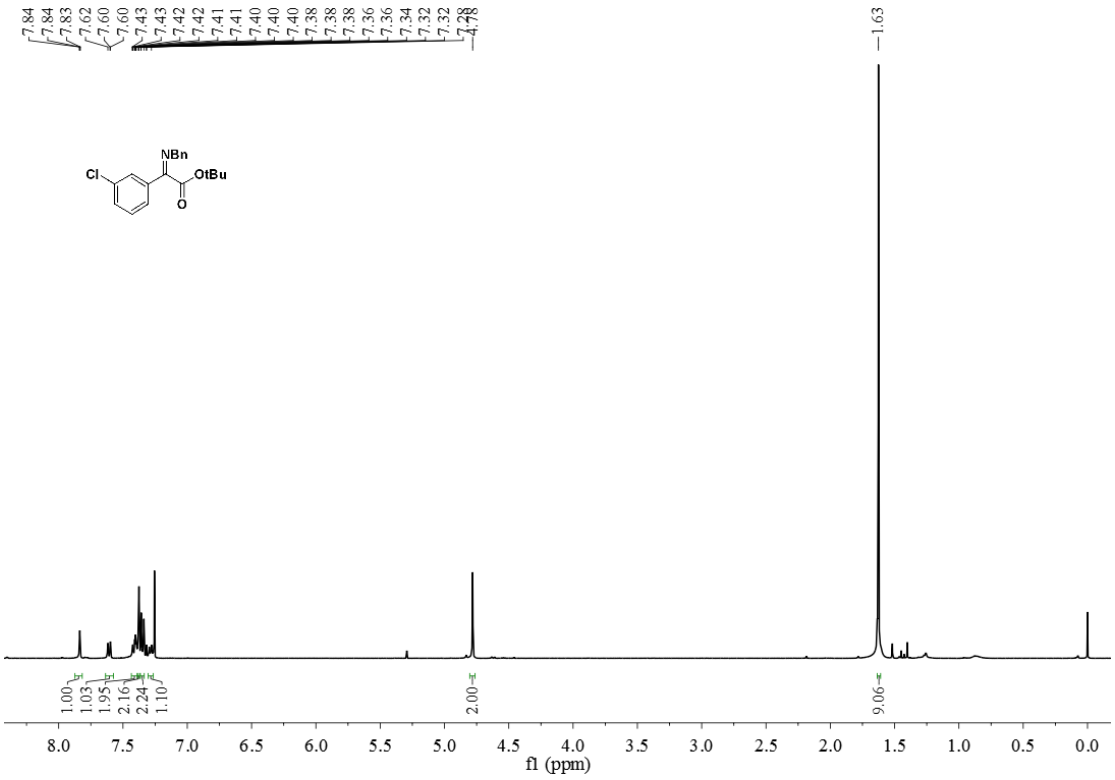
111.66
84.22
57.96
55.37
28.33
NBn
MeO
OtBu
O
f1 (ppm)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7.84
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7.60
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7.43
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7.42
7.41
7.41
7.40
7.40
7.40
7.38
7.38
7.36
7.36
7.34
7.32
7.28
4.78
1.63
NBn
Cl
OtBu
O
1.00
1.03
1.95
2.16
2.24
1.10
2.00
9.06
8.0
7.5
7.0
6.5
6.0
5.5
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3.5
3.0
2.5
2.0
1.5
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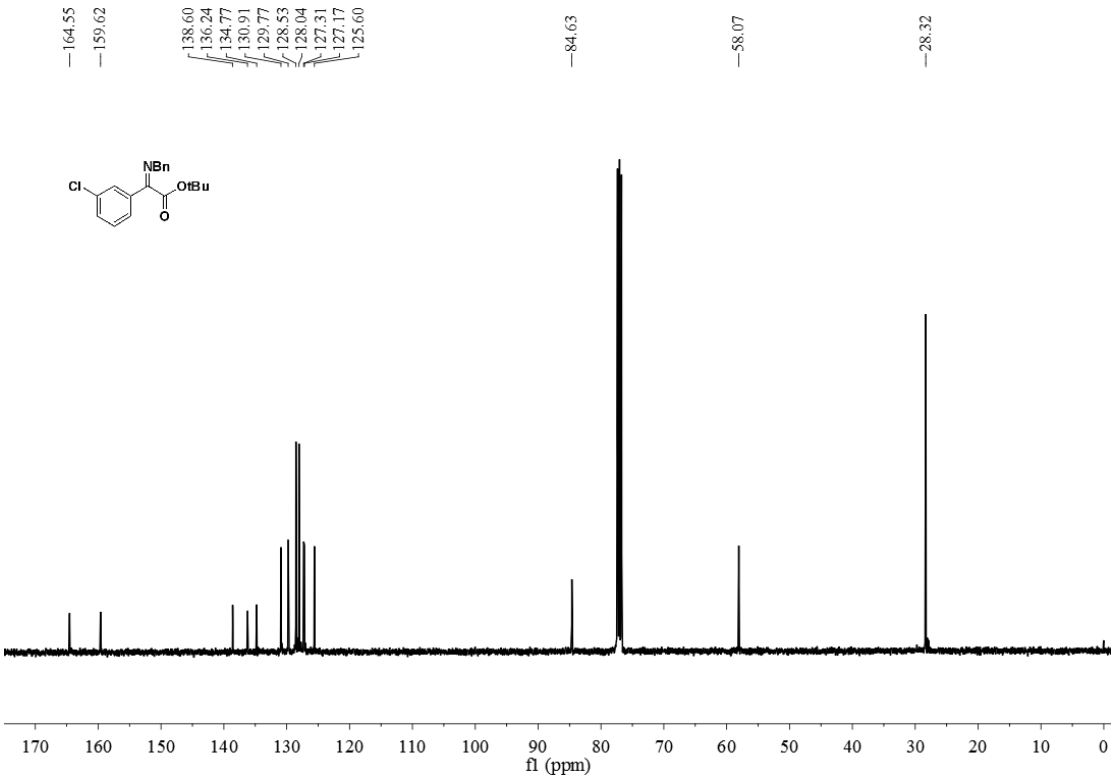
0.0
f1 (ppm)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128.53
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127.31
127.17
125.60
84.63
58.07
28.32
NBn
Cl
OtBu
O
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120
110
100
90
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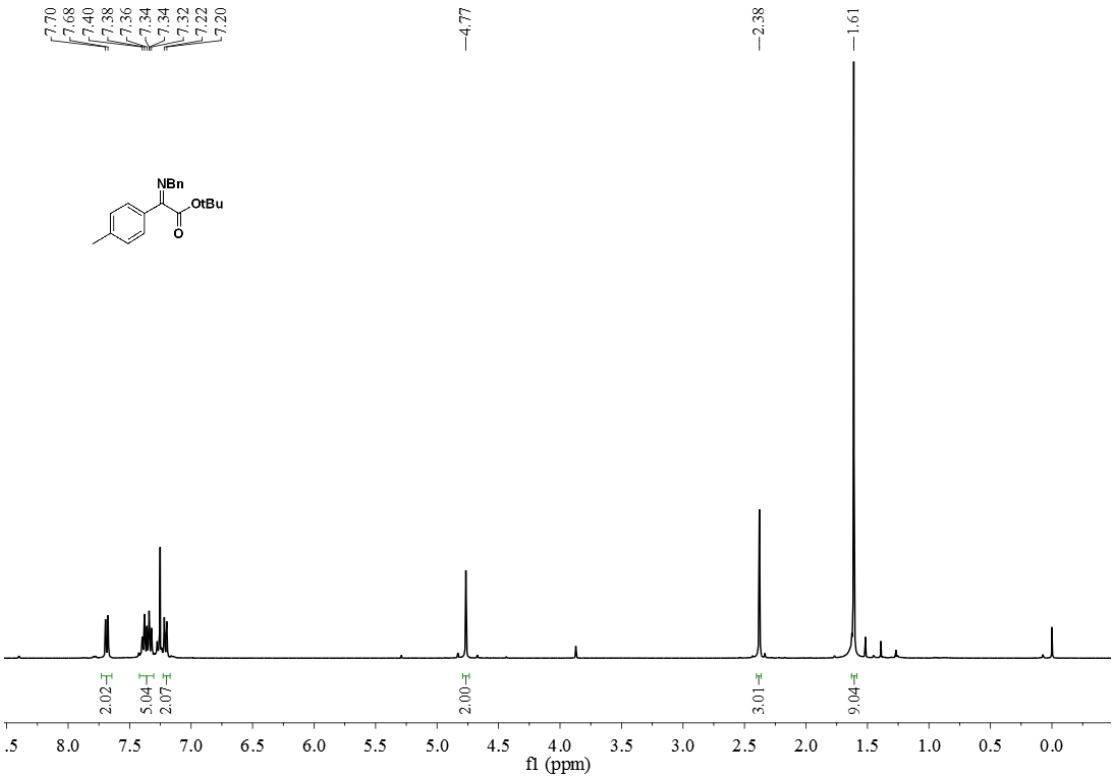
50
40
30
20
10
0
f1 (ppm)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7.32
7.22
7.20
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O
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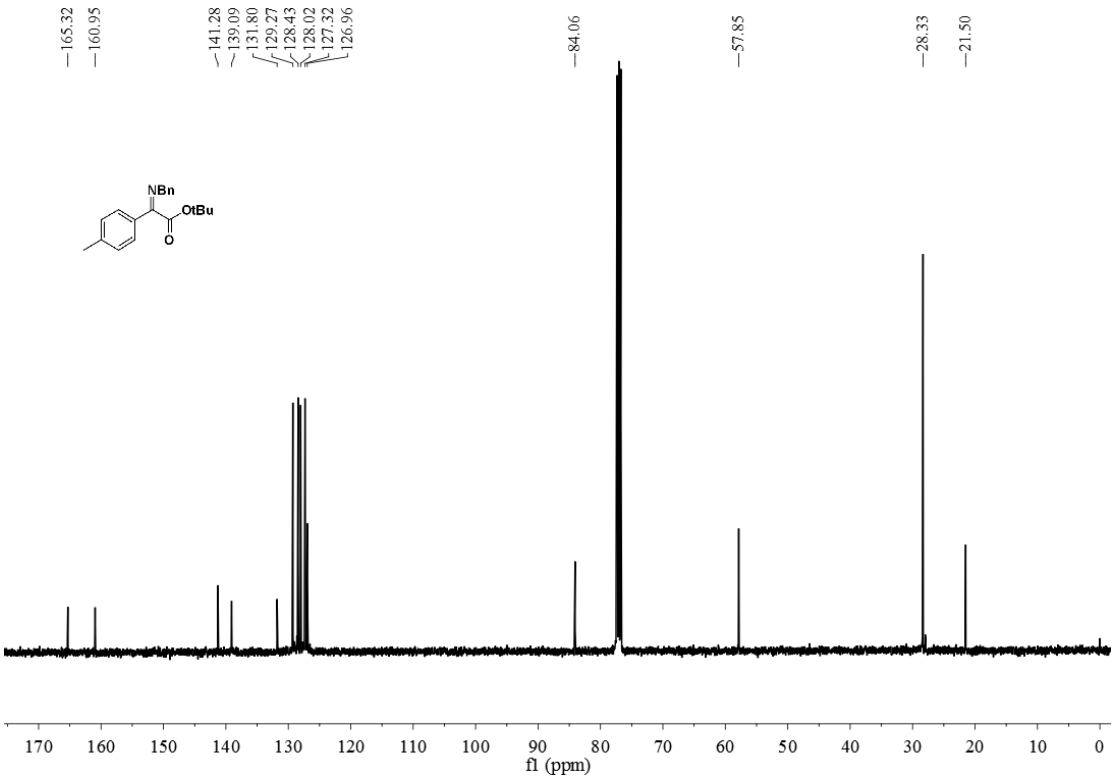
5.04
2.07
2.00
3.01
9.04
fl (ppm)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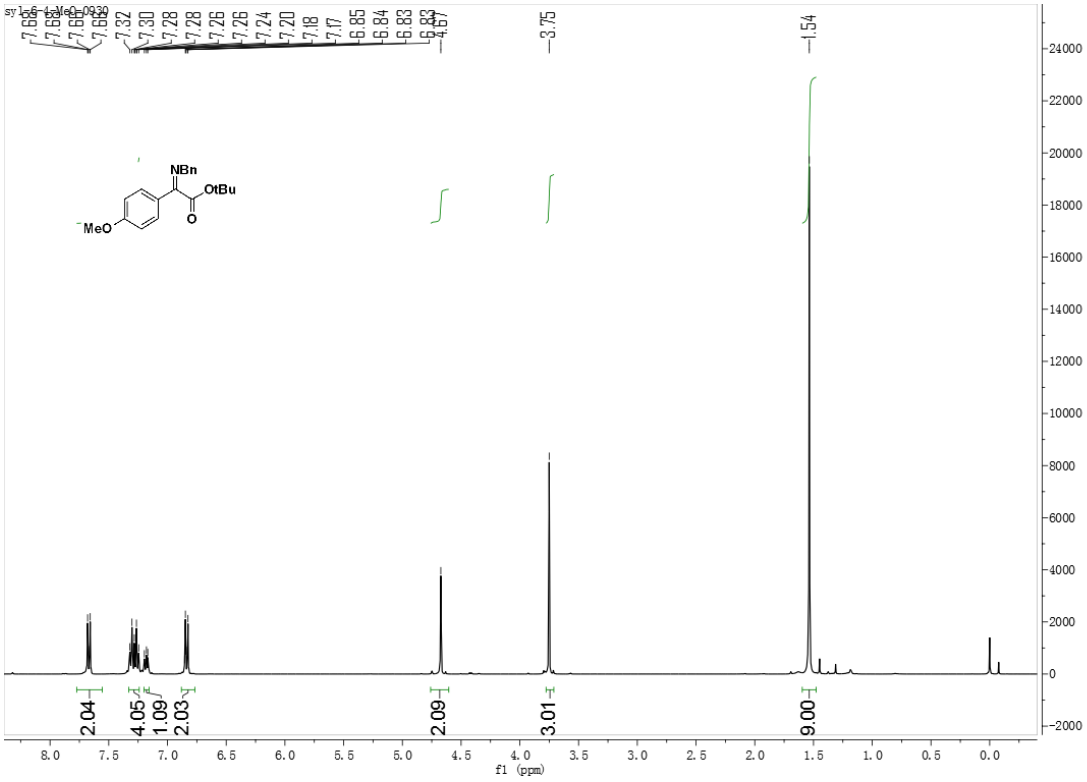
127.32
126.96
84.06
57.85
28.33
21.50
NBn
OtBu
O
fl (ppm)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OtBu
O
MeO
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7.32
7.30
7.28
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7.24
7.20
7.18
7.17
6.85
6.84
6.83
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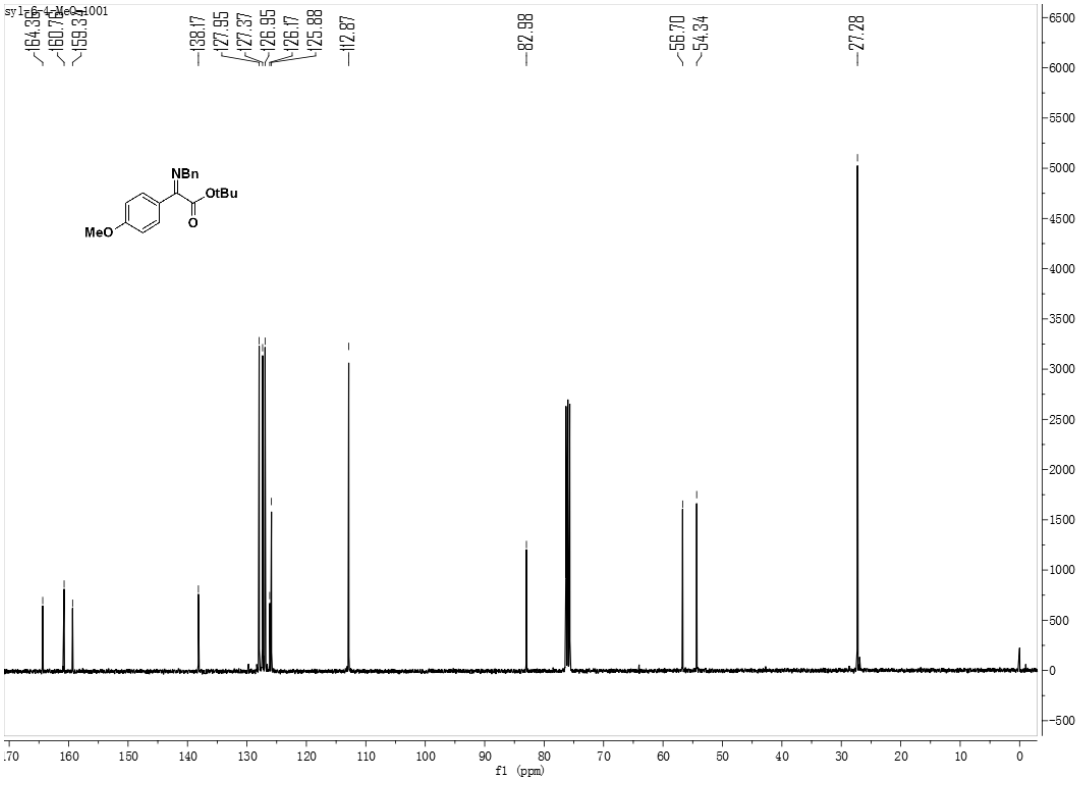
4.05
1.09
2.03
2.09
3.01
9.00
f1 (ppm)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OtBu
O
MeO
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125.88
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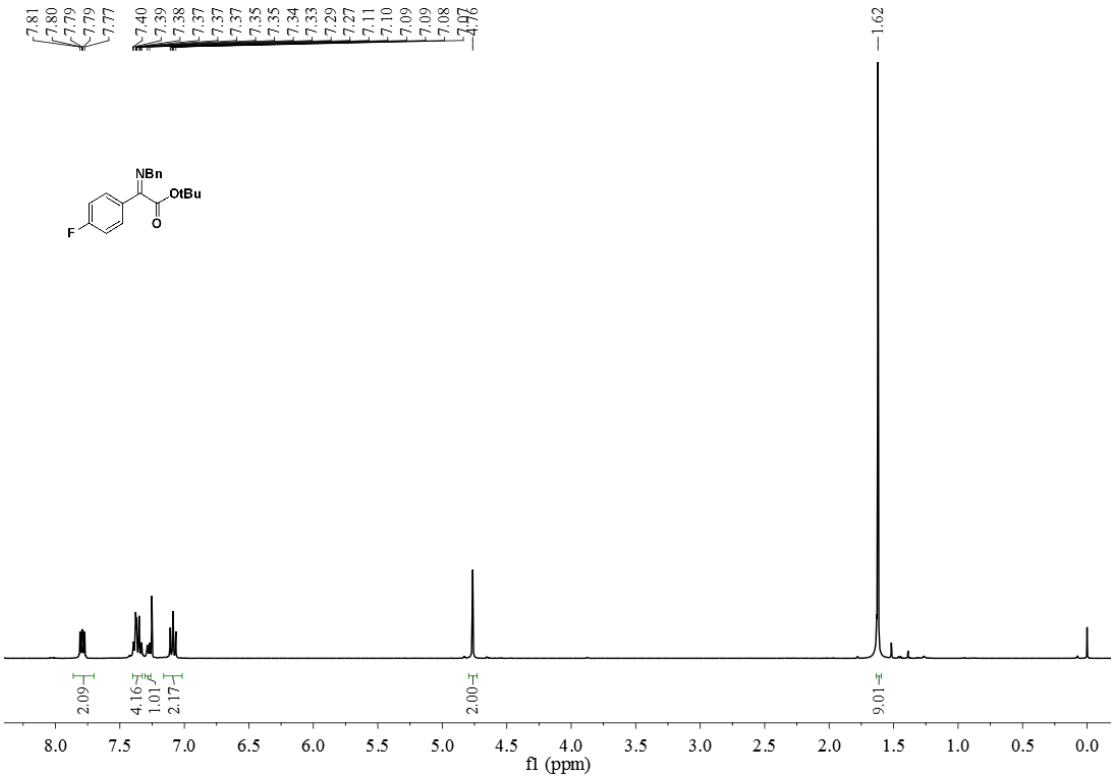
82.98
56.70
54.34
27.28
f1 (ppm)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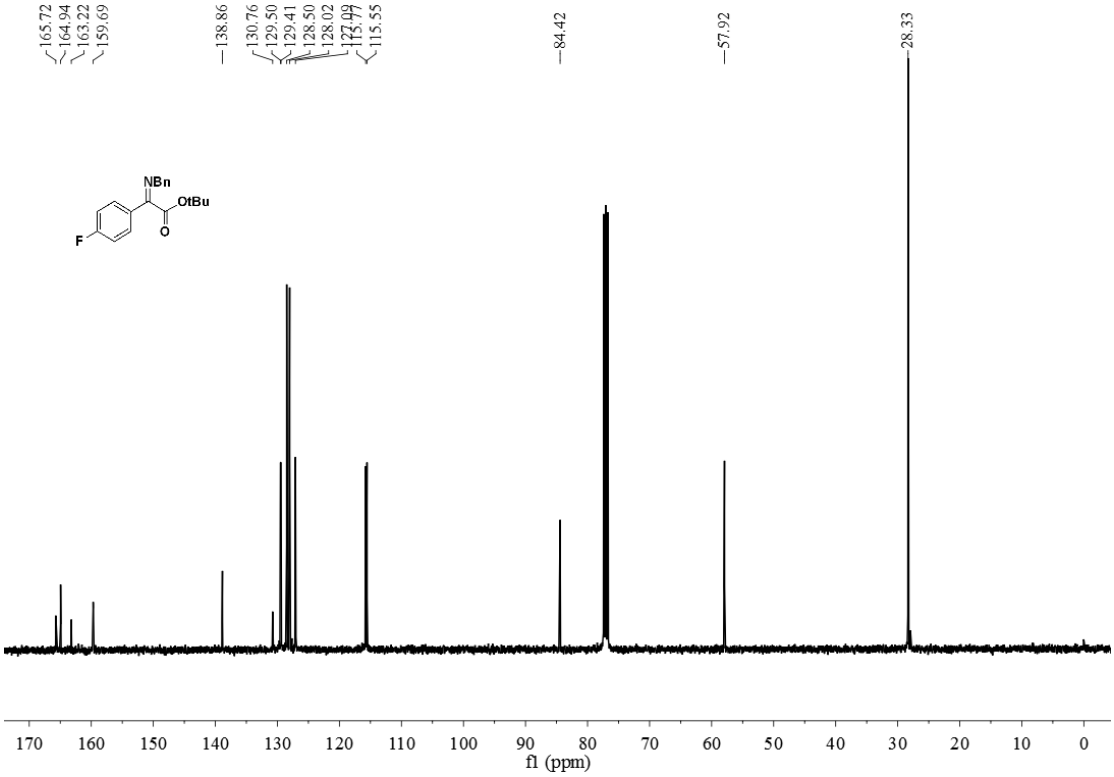
7.34
7.33
7.29
7.27
7.11
7.10
7.09
7.09
7.08
7.07
4.76
1.62
NBn
OtBu
O
F
2.09
4.16
1.01
2.17
2.00
9.01
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
0.0
f1 (ppm)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129.50
129.41
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128.02
127.09
115.77
115.55
84.42
57.92
28.33
NBn
OtBu
O
F
170
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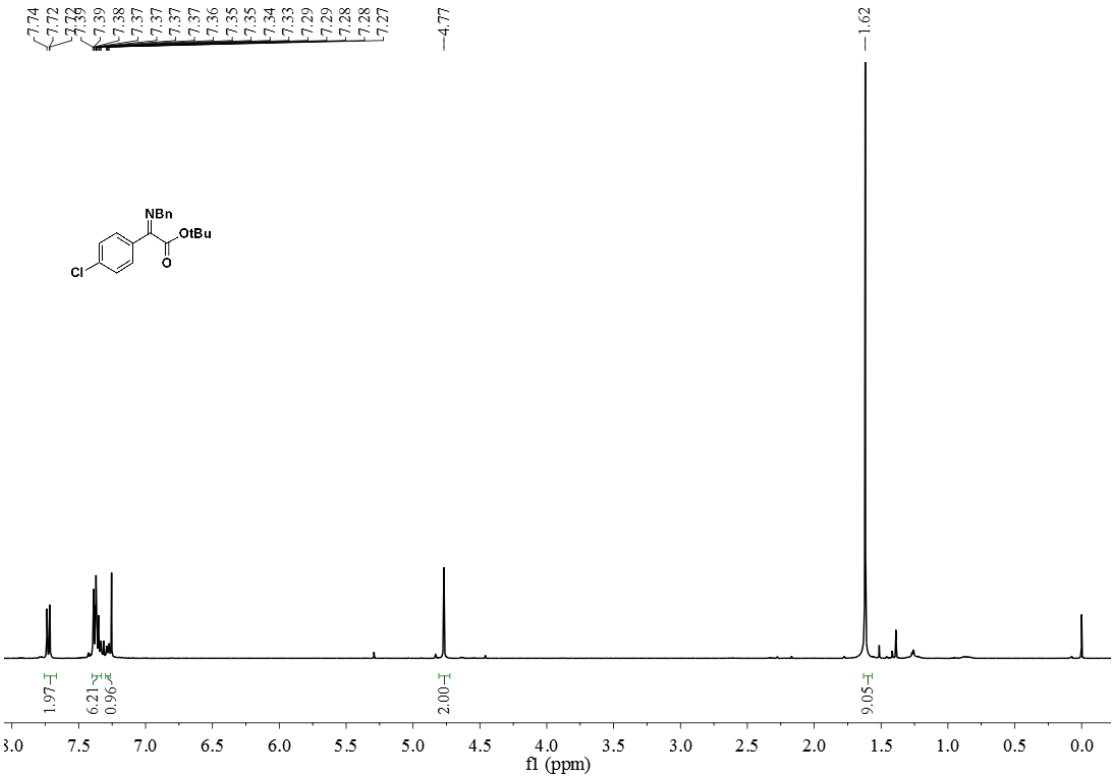
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)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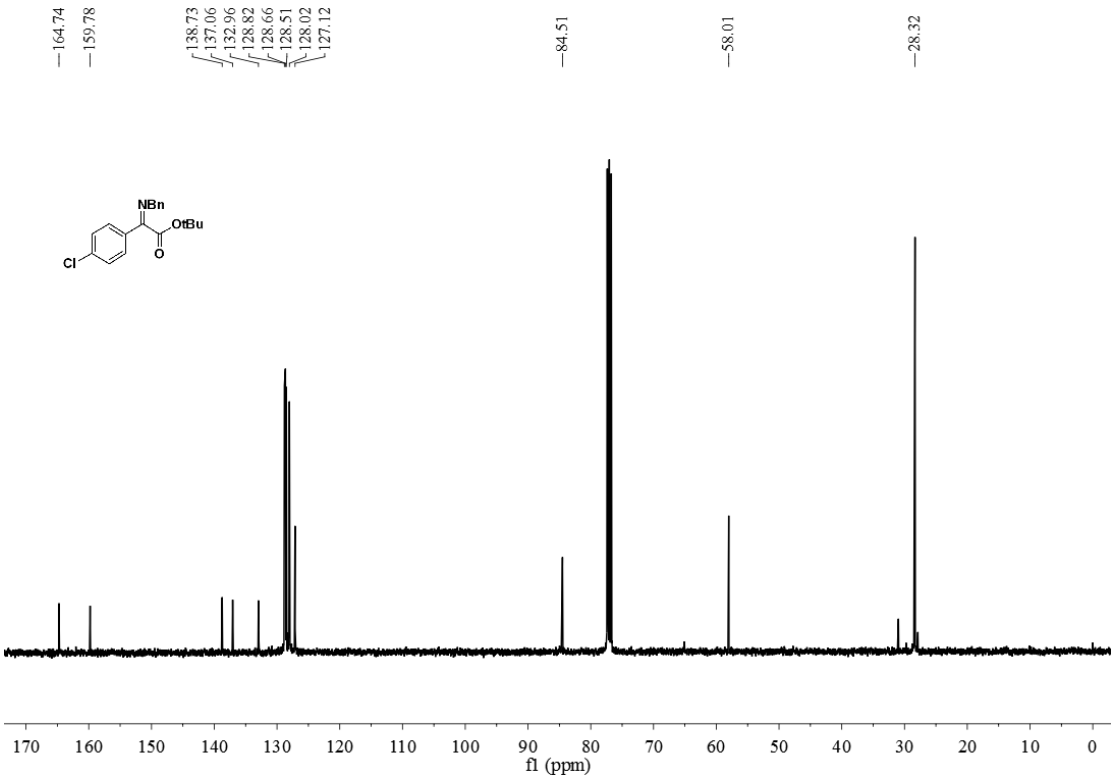
7.35
7.34
7.33
7.29
7.28
7.28
7.27
4.77
1.62
NBn
OtBu
O
Cl
1.97
6.21
0.96
2.00
9.05
fl (ppm)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84.51
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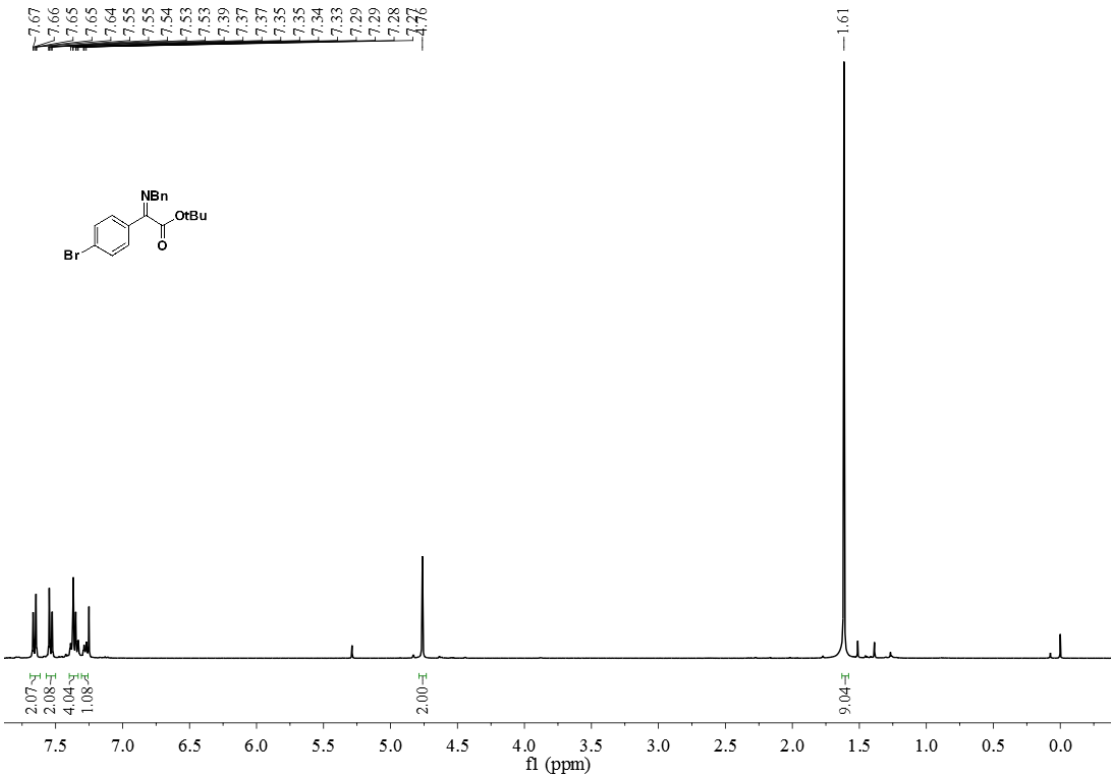
28.32
NBn
OtBu
O
Cl
fl (ppm)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7.55
7.54
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7.53
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7.37
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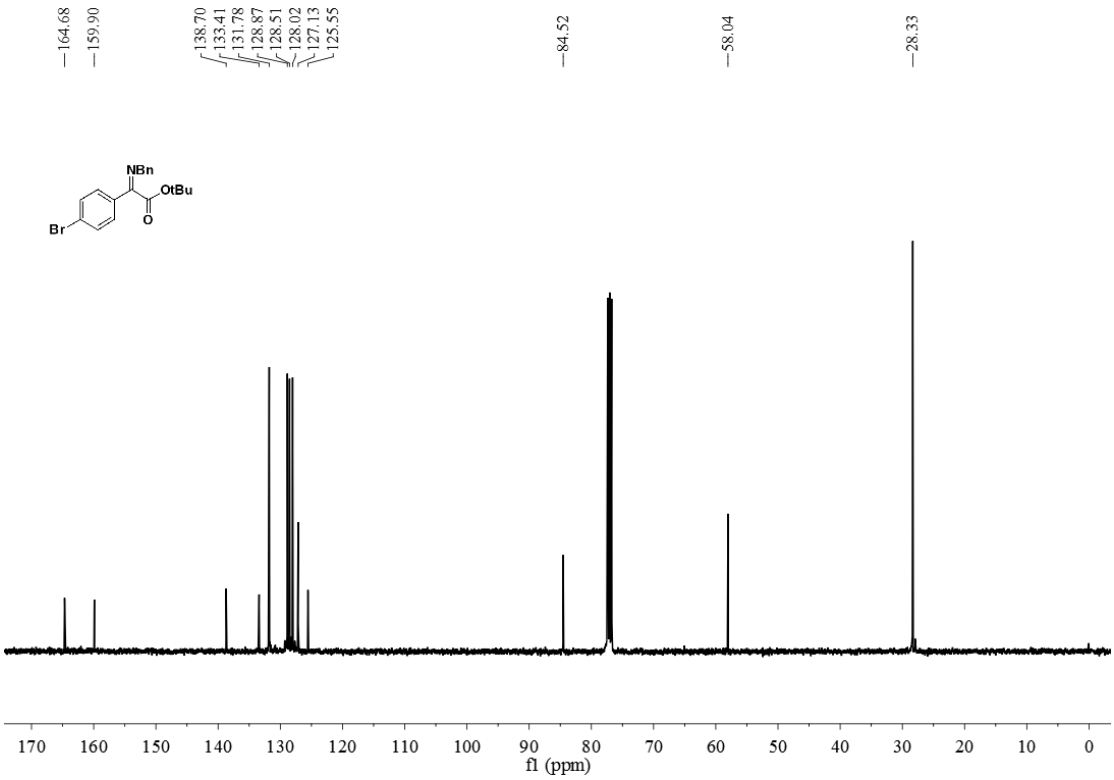
7.35
7.35
7.34
7.33
7.29
7.29
7.28
7.27
7.26
1.61
NBn
OtBu
O
Br
2.07
2.08
4.04
1.08
2.00
9.04
fl (ppm)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131.78
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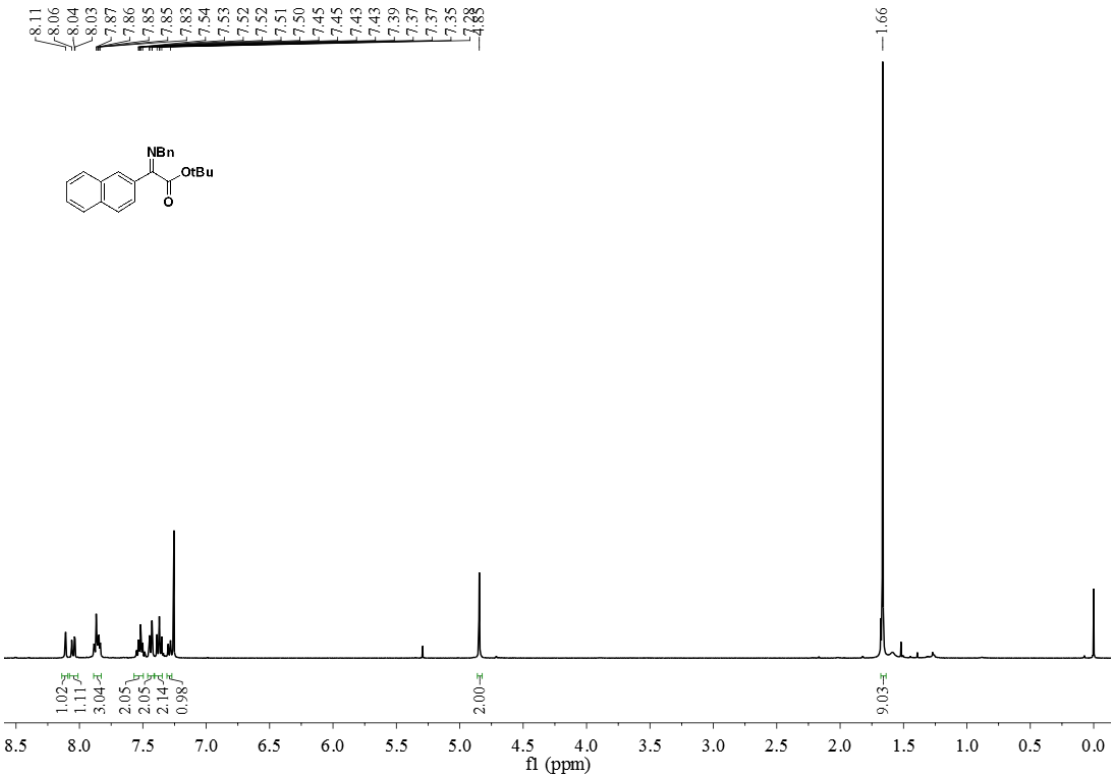
128.02
127.13
125.55
84.52
58.04
28.33
NBn
OtBu
O
Br
fl (ppm)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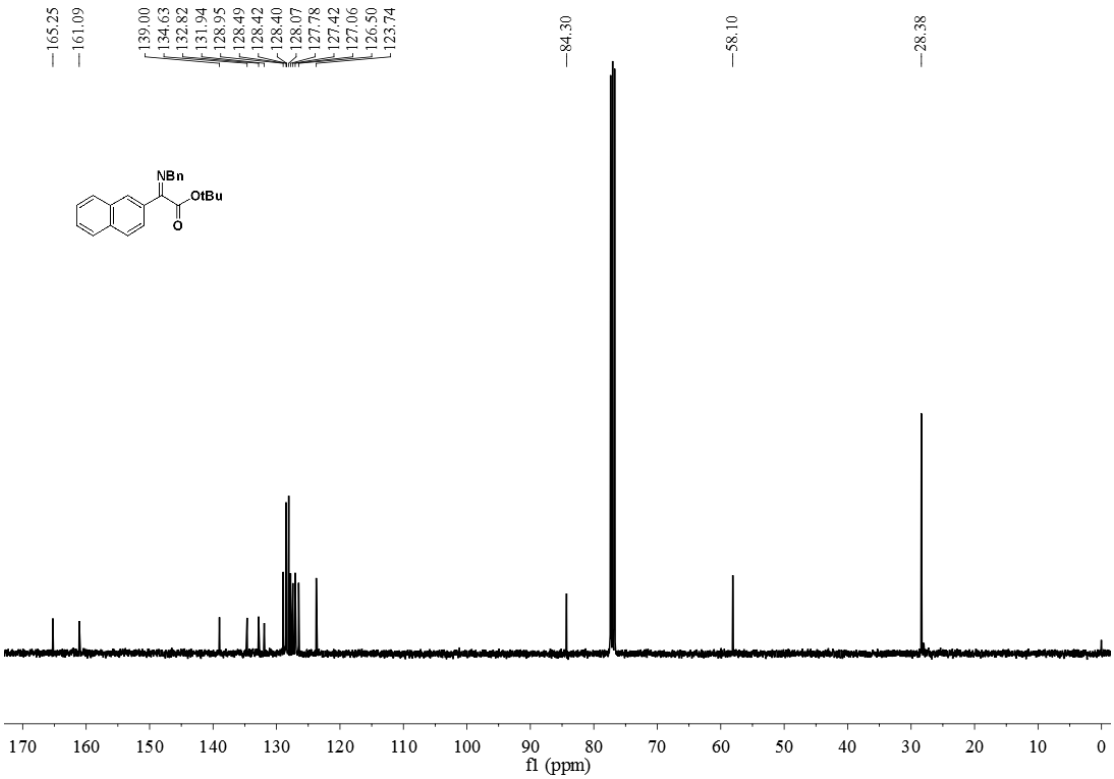
8.06
8.04
8.03
7.87
7.86
7.85
7.85
7.83
7.54
7.53
7.52
7.52
7.51
7.50
7.45
7.45
7.43
7.43
7.39
7.37
7.37
7.35
7.28
4.85
1.66
NBn
OtBu
O
1.02
1.11
3.04
2.05
2.05
2.14
0.98
2.00
9.03
fl (ppm)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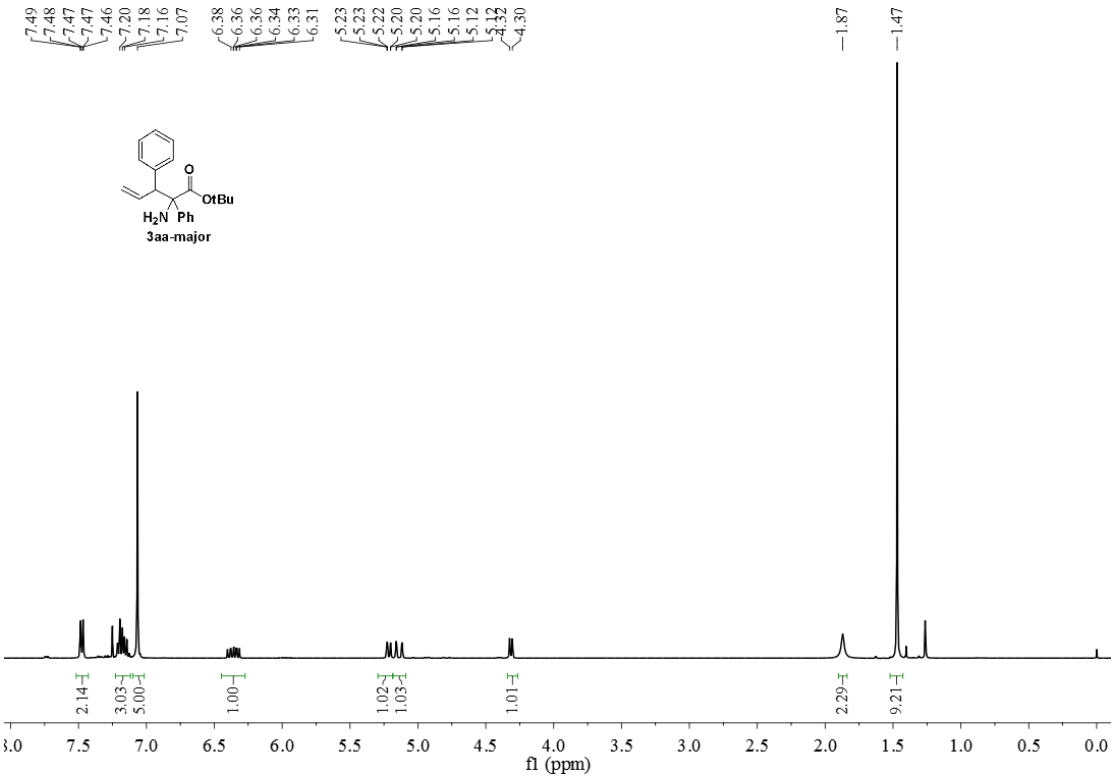
132.82
131.94
128.95
128.49
128.42
128.40
128.07
127.78
127.42
127.06
126.50
123.74
84.30
58.10
28.38
NBn
OtBu
O
fl (ppm)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7.48
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7.47
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7.16
7.07
6.38
6.36
6.36
6.34
6.33
6.31
5.23
5.23
5.22
5.20
5.16
5.16
5.12
4.32
4.30
1.87
1.47
O
OtBu
H2N Ph
3aa-major
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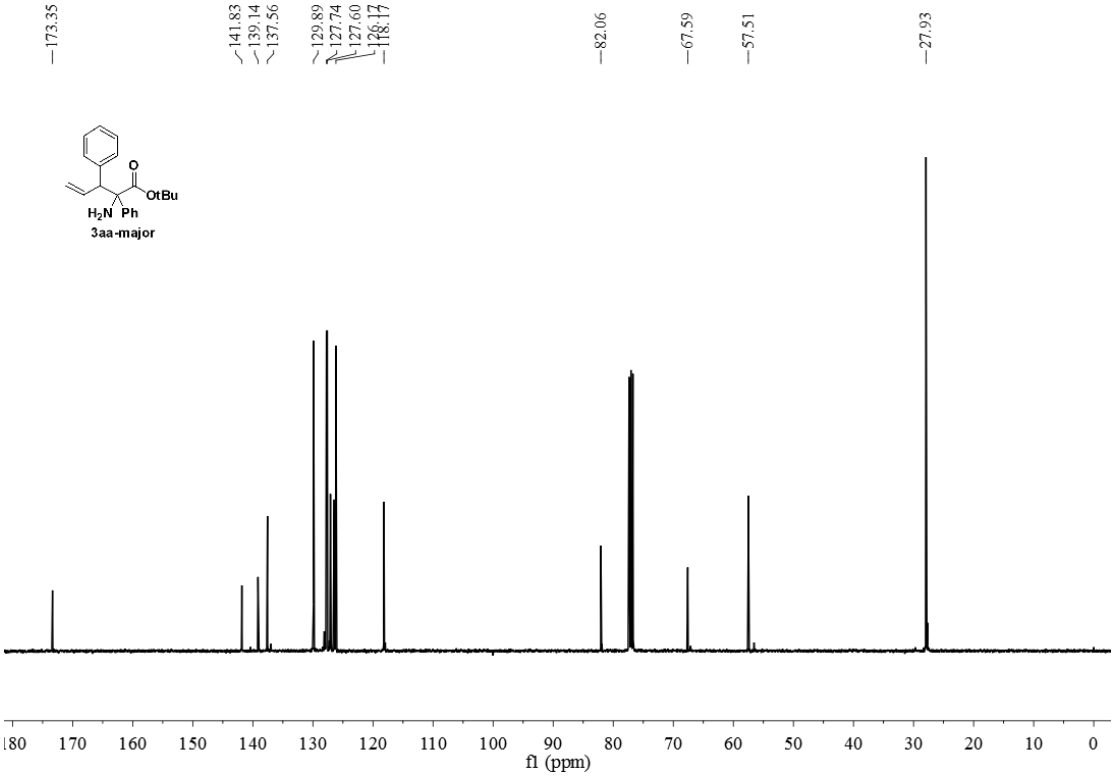
3.03
5.00
1.00
1.02
1.03
1.01
2.29
9.21
f1 (ppm)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126.17
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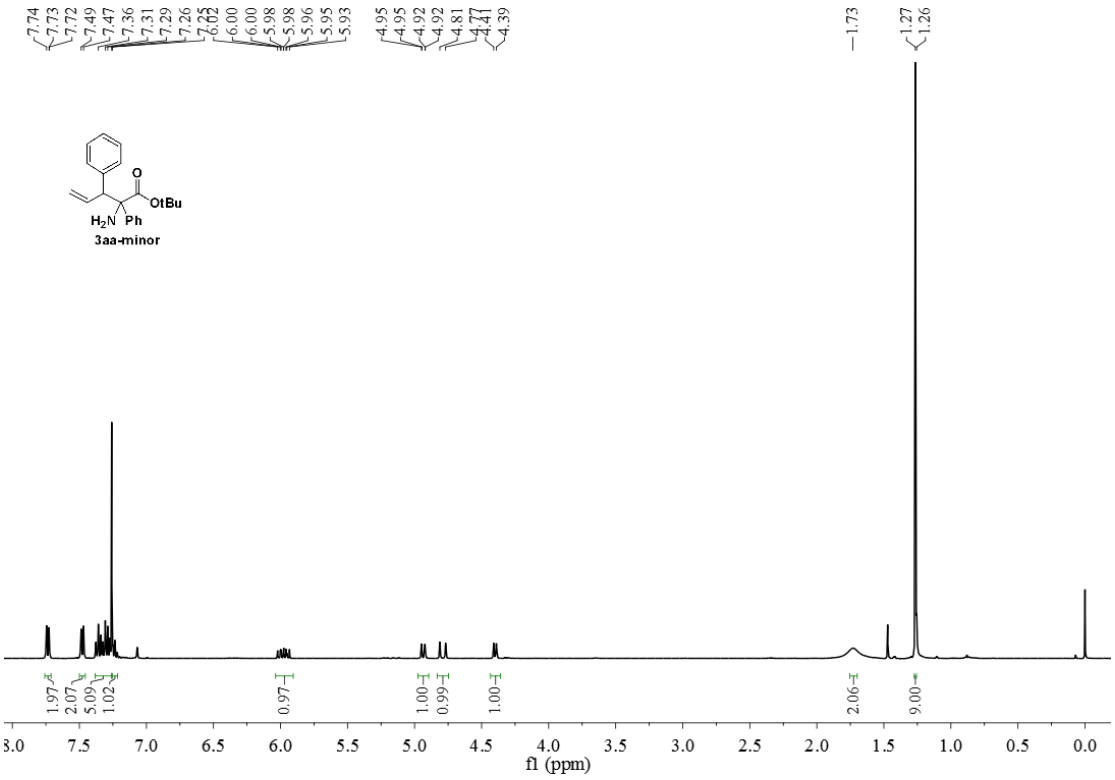
82.06
67.59
57.51
27.93
O
OtBu
H2N Ph
3aa-major
f1 (ppm)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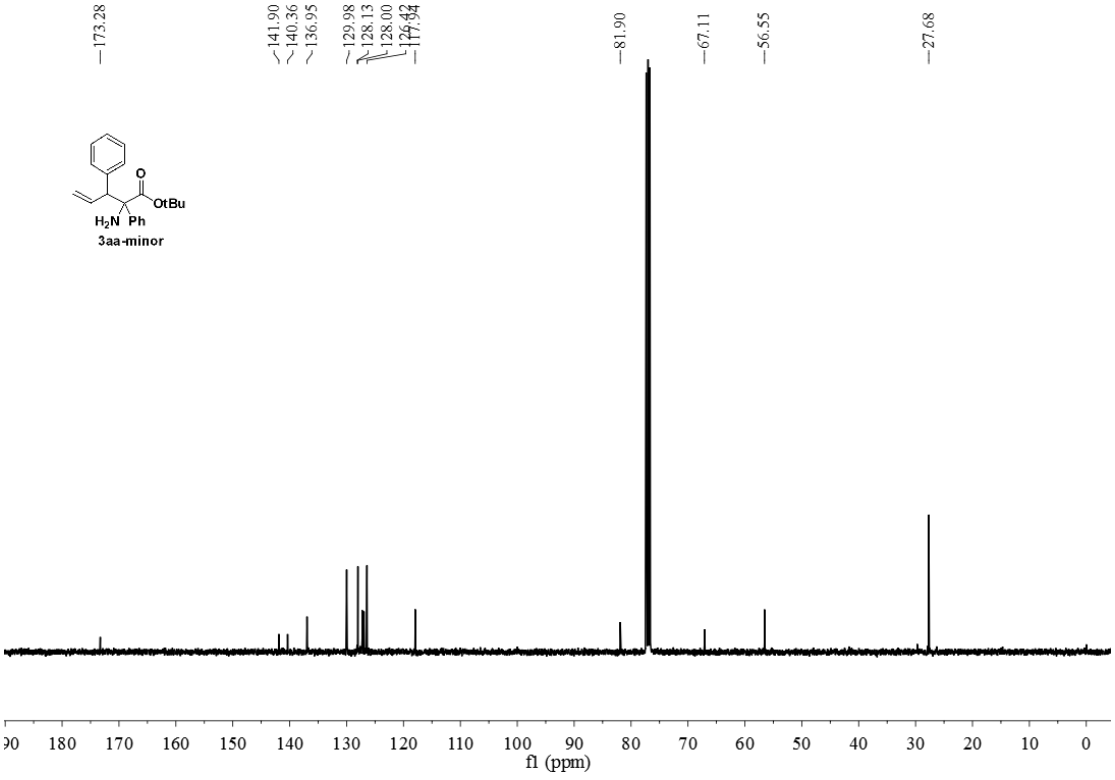
7.31
7.29
7.26
6.00
5.98
5.98
5.96
5.95
5.93
4.95
4.95
4.92
4.92
4.81
4.41
4.39
1.73
1.27
1.26
O
OtBu
H2N Ph
3aa-minor
1.97
2.07
5.09
1.02
0.97
1.00
0.99
1.00
2.06
9.00
fl (ppm)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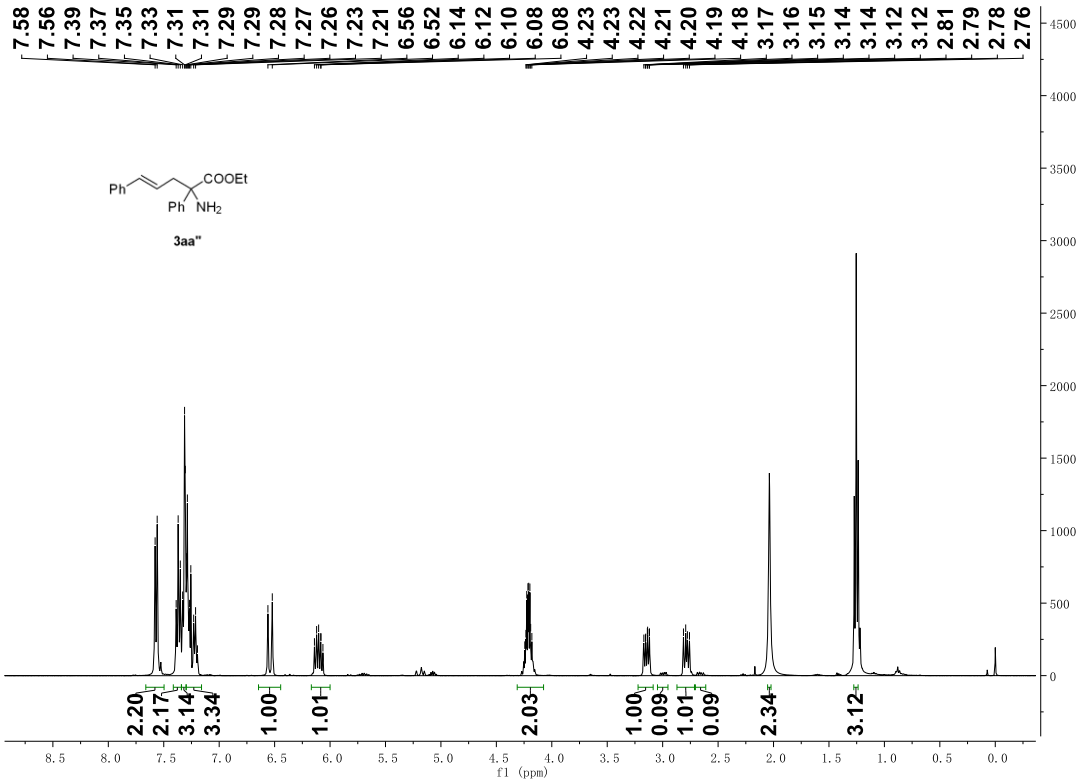
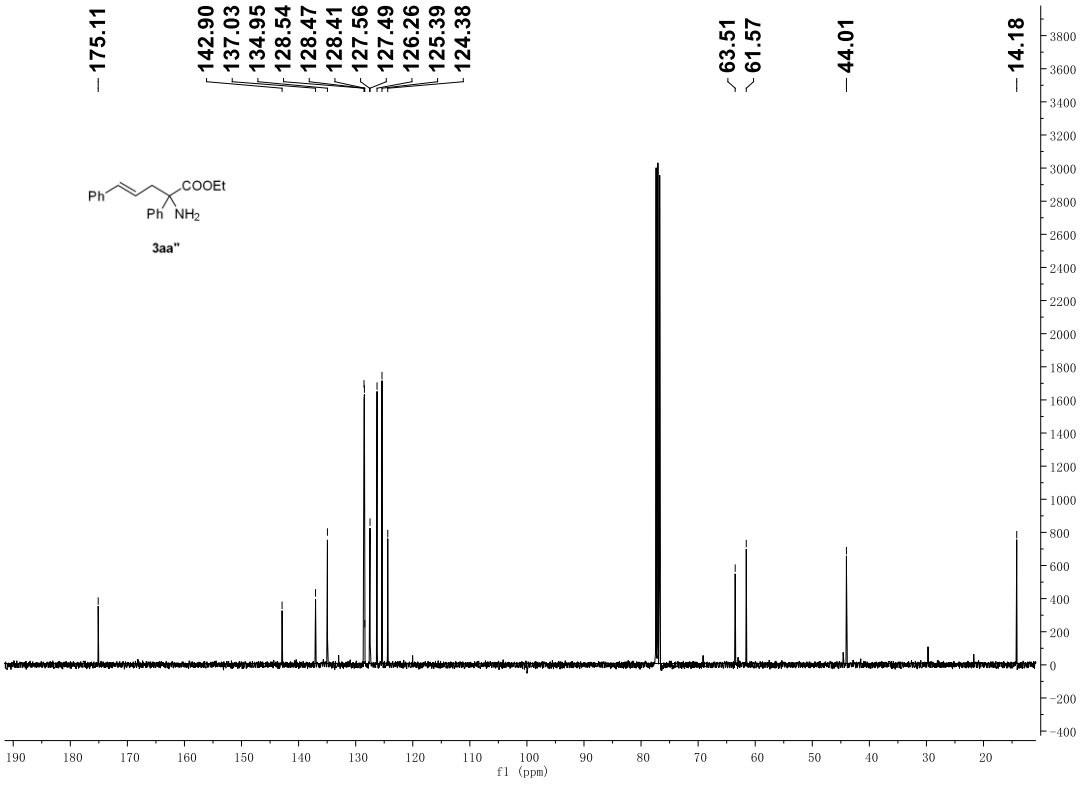
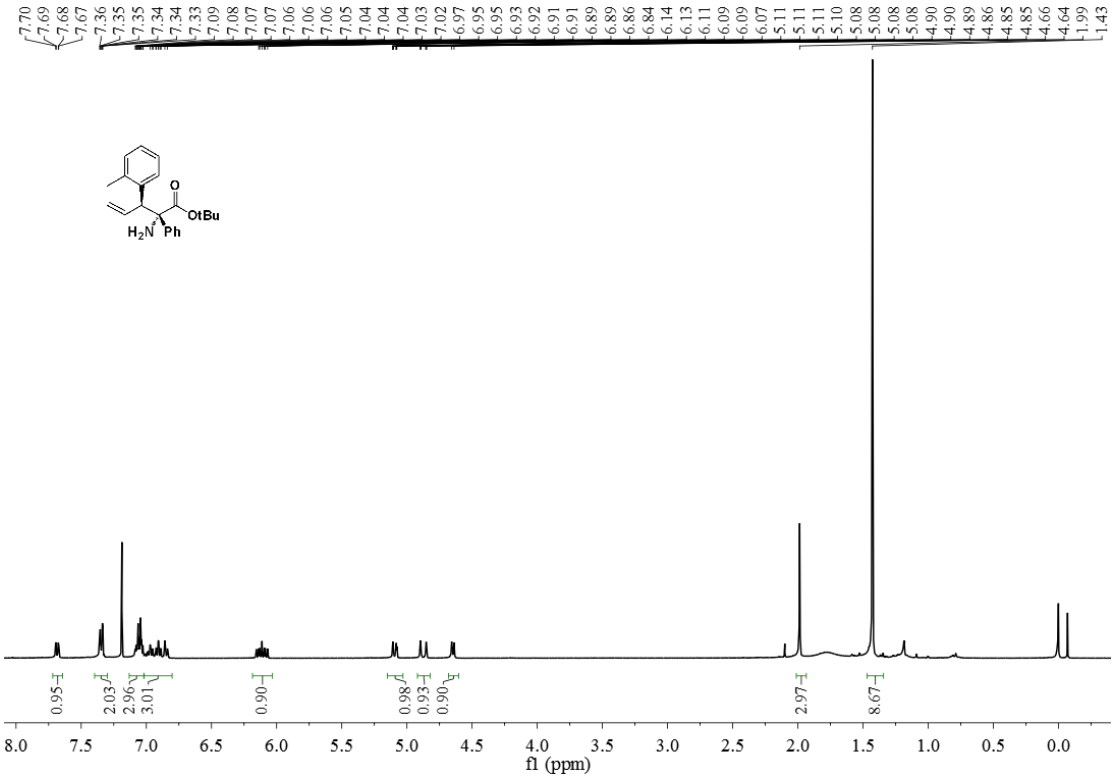
81.90
67.11
56.55
27.68
O
OtBu
H2N Ph
3aa-minor
fl (ppm)


7.58 7.56 7.39 7.37 7.35 7.33 7.31 7.31 7.29 7.29 7.28 7.27 7.26 7.23 7.21 6.56 6.52 6.14 6.12 6.10 6.08 6.08 4.23 4.23 4.22 4.21 4.20 4.19 4.18 3.17 3.16 3.15 3.14 3.14 3.12 2.81 2.79 2.78 2.76
Ph
COOEt
Ph NH2
3aa"
2.20 2.17 3.14 3.34 1.00 1.01 2.03 1.00 0.09 1.01 0.09 2.34 3.12
f1 (ppm)


175.11
142.90 137.03 134.95 128.54 128.47 128.41 127.56 127.49 126.26 125.39 124.38
63.51 61.57
44.01
14.18
Ph
COOEt
Ph NH2
3aa"
f1 (ppm)


7.70 7.69 7.68 7.67 7.36 7.35 7.35 7.34 7.34 7.33 7.09 7.08 7.07 7.07 7.06 7.06 7.06 7.05 7.04 7.04 7.04 7.03 7.02 6.97 6.95 6.95 6.93 6.92 6.91 6.91 6.89 6.89 6.86 6.84 6.14 6.13 6.11 6.09 6.09 6.07 5.11 5.11 5.11 5.10 5.08 5.08 5.08 5.08 4.90 4.90 4.89 4.86 4.85 4.85 4.66 4.64 1.99 1.43
O
OtBu
H2N
Ph
0.95 2.03 2.96 3.01 0.90 0.98 0.93 0.90 2.97 8.67
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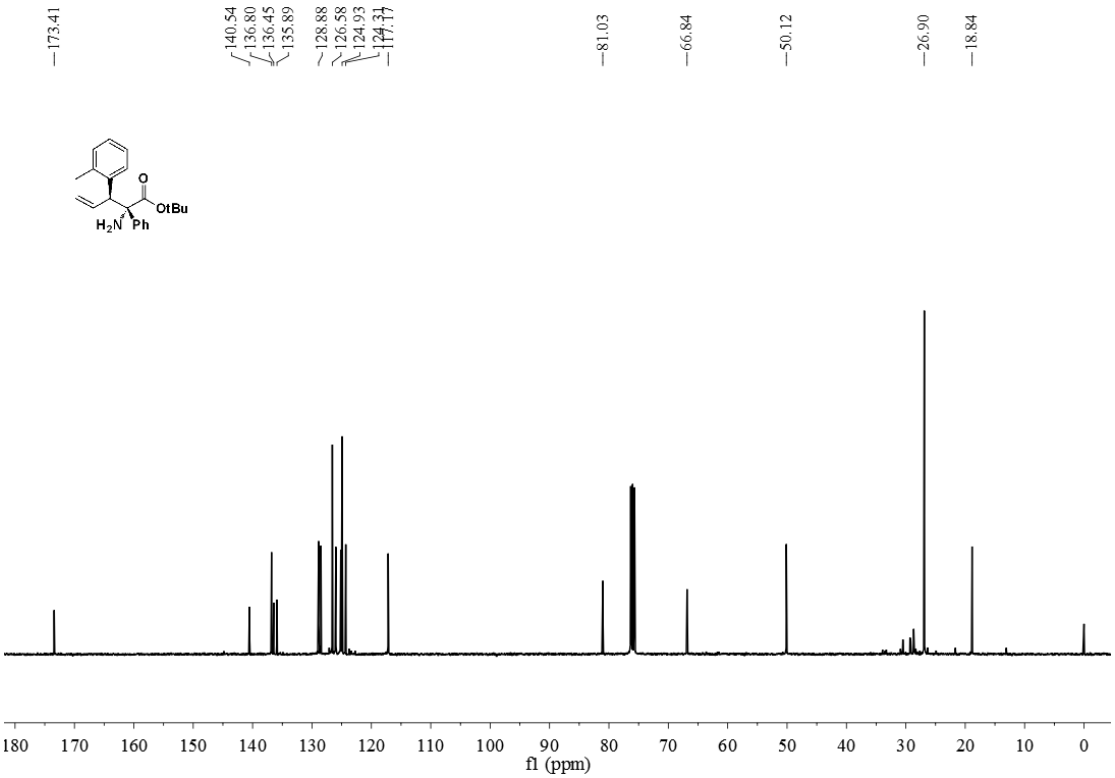
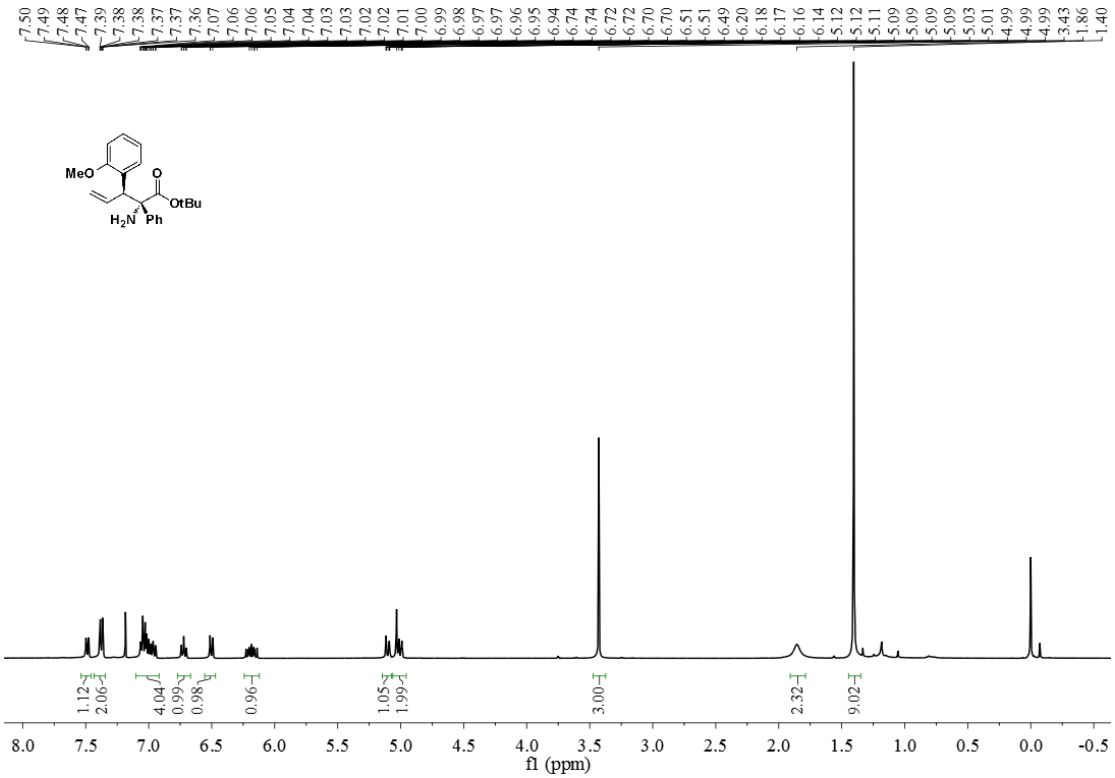
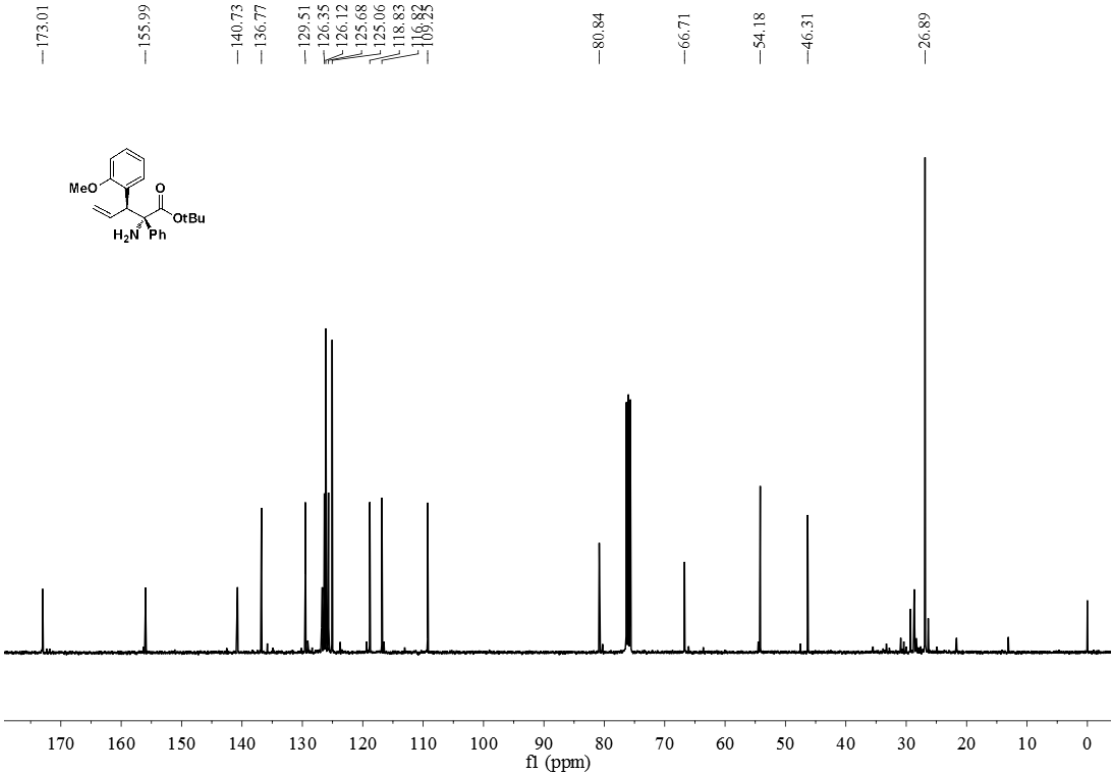
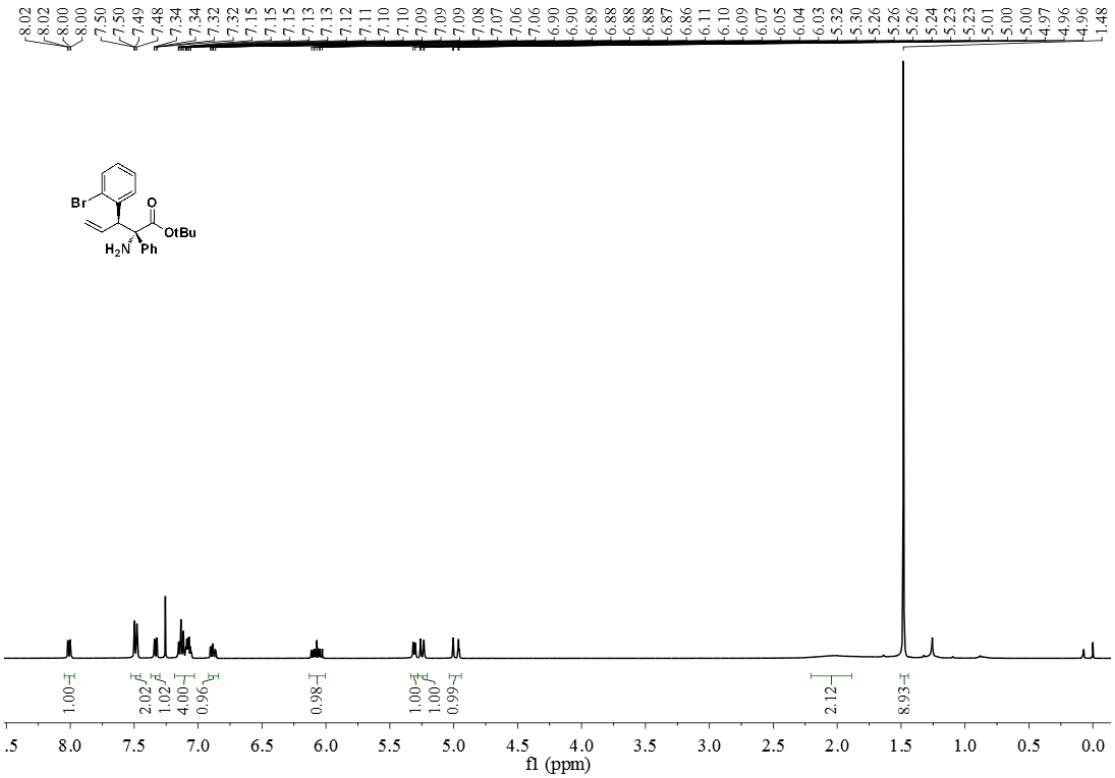
f1 (ppm)


173.41 140.54 136.80 136.45 135.89 128.88 126.58 124.93 124.31 117.17 81.03 66.84 50.12 26.90 18.84
O
OtBu
H2N
Ph
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)


MeO
O
OtBu
H2N
Ph
fl (ppm)


MeO
O
OtBu
H2N
Ph
fl (ppm)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8.00
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6.11
6.10
6.09
6.07
6.05
6.04
6.03
5.32
5.30
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5.26
5.24
5.23
5.23
5.01
5.00
5.00
4.97
4.96
4.96
1.48
Br
O
OtBu
H2N
Ph
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2.02
1.02
4.00
0.96
0.98
1.00
1.00
0.99
2.12
8.93
.5
8.0
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
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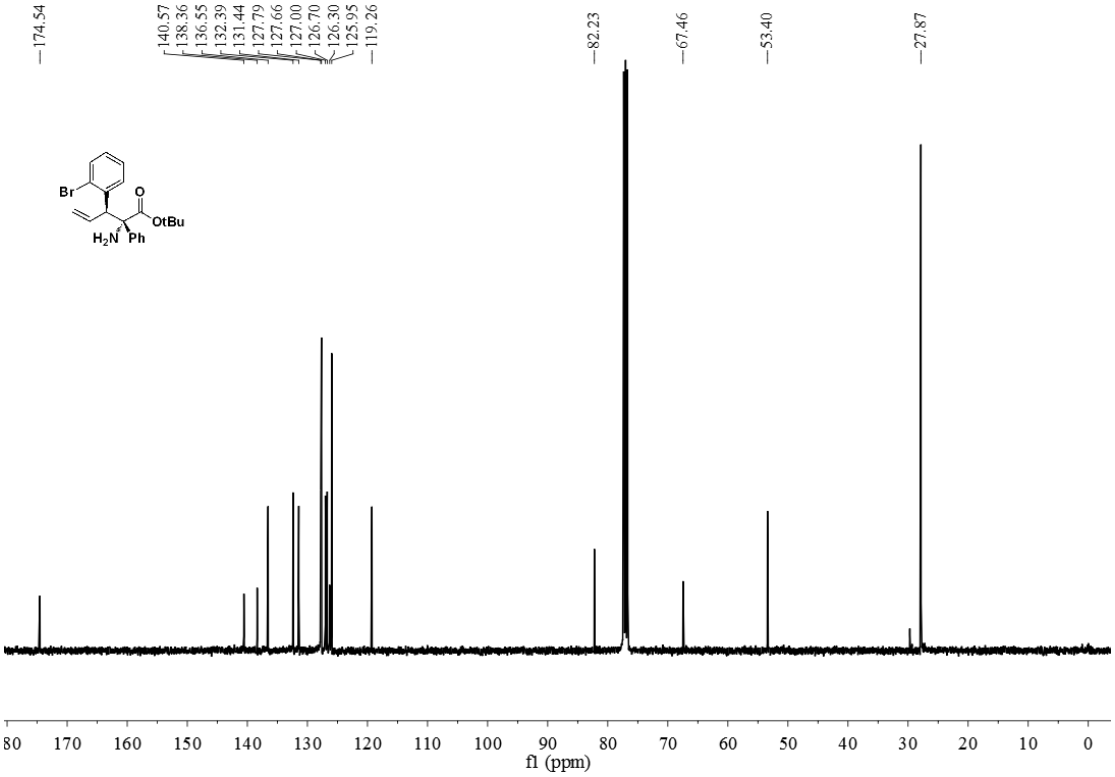
0.0
f1 (ppm)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67.46
53.40
27.87
Br
O
OtBu
H2N
Ph
80
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70
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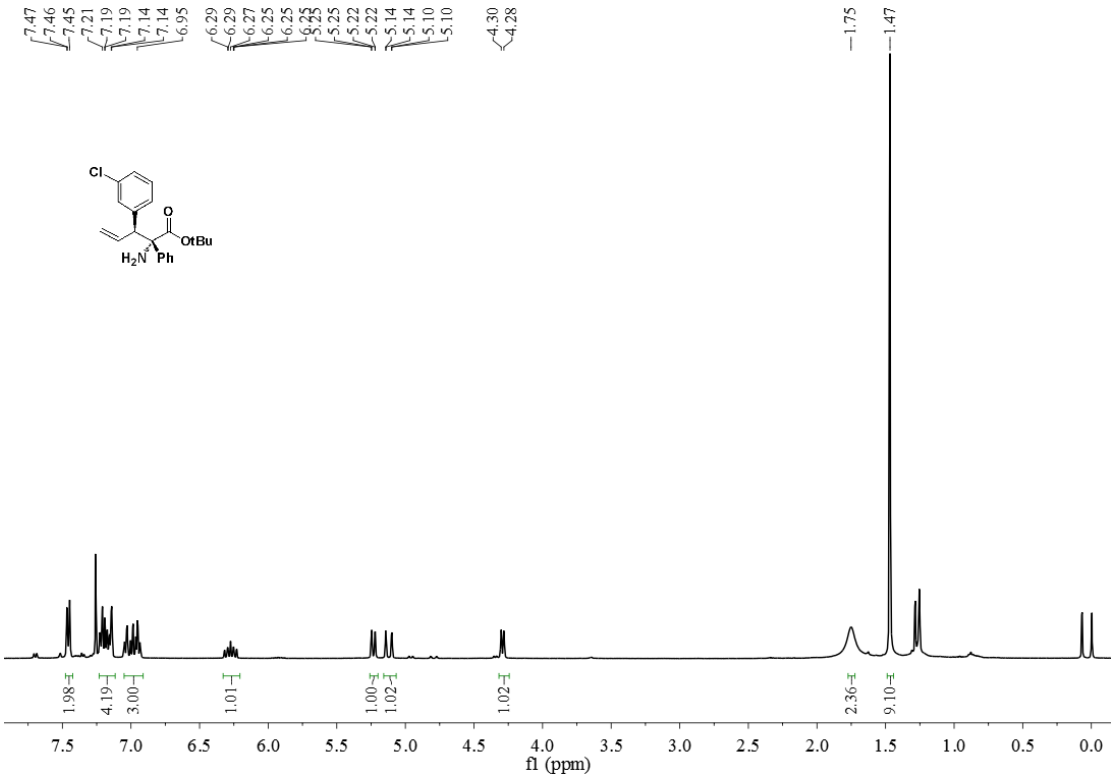
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5.25
5.22
5.22
5.14
5.14
5.10
5.10
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4.28
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1.47
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O
OtBu
H2N
Ph
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1.00
1.02
1.02
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6.0
5.5
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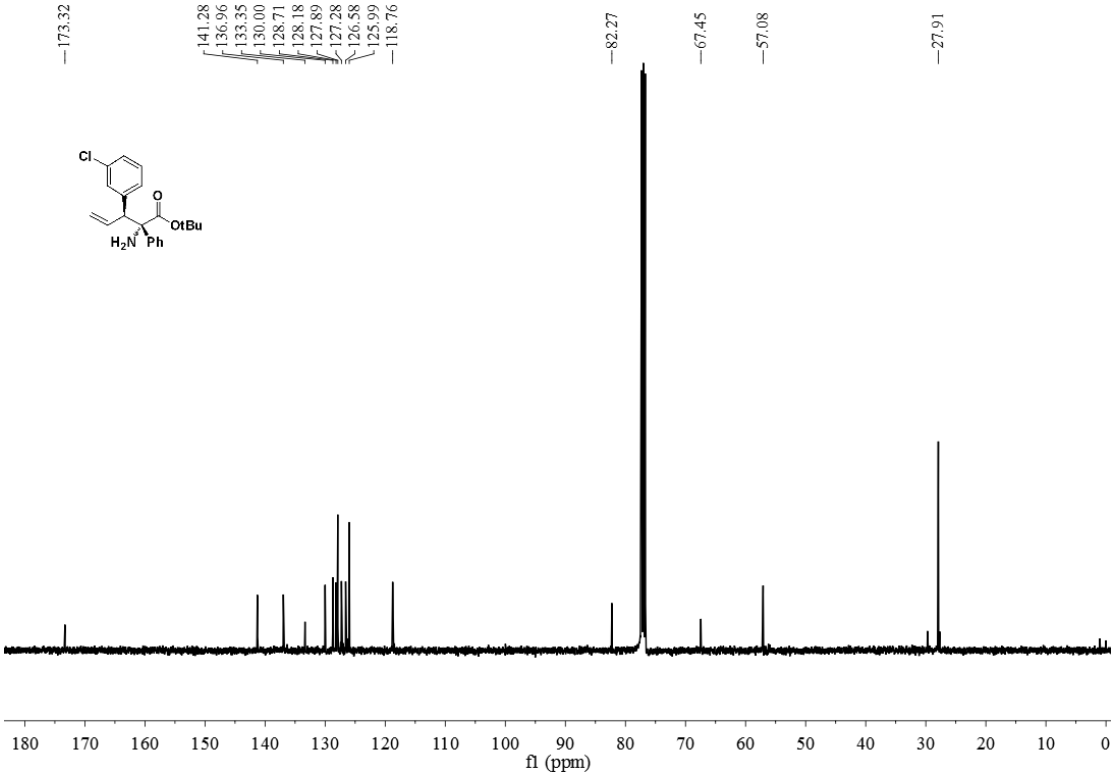
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27.91
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O
OtBu
H2N
Ph
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90
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50
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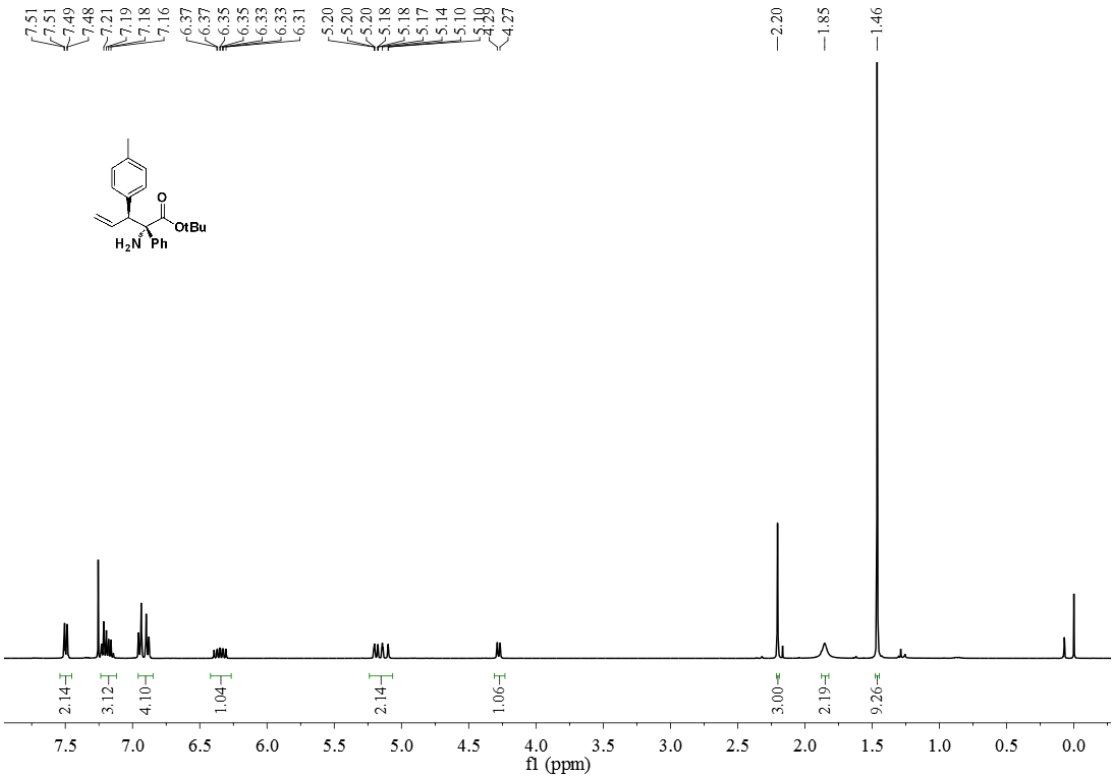
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6.31
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5.20
5.20
5.18
5.18
5.17
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5.10
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OtBu
H2N Ph
2.14
3.12
4.10
1.04
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1.06
3.00
2.19
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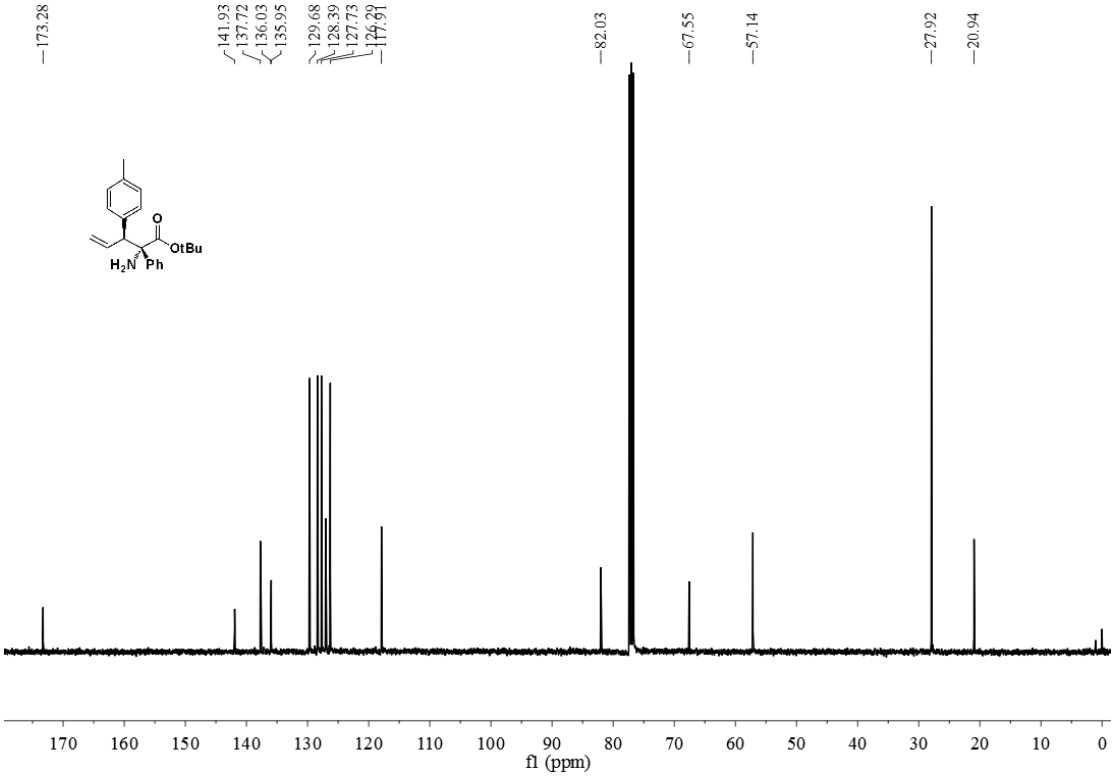
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OtBu
H2N Ph
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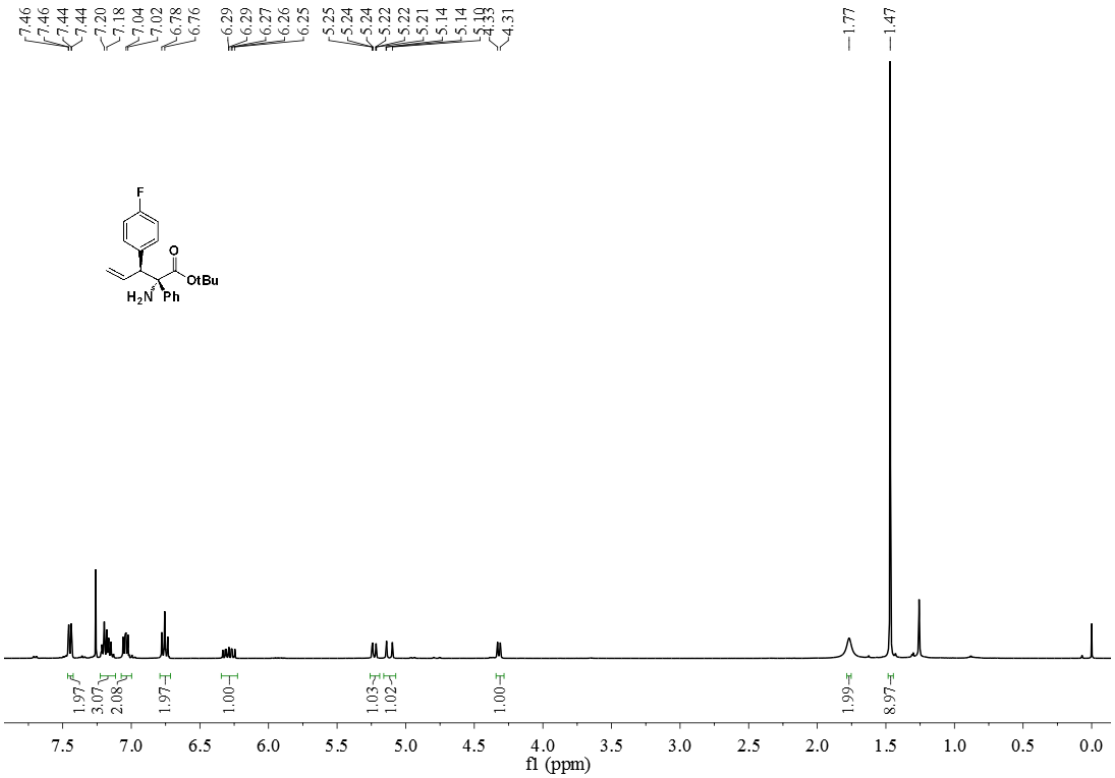
f1 (ppm)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6.25
5.25
5.24
5.24
5.22
5.22
5.21
5.14
5.14
4.33
4.31
1.77
1.47
F
O
OtBu
H2N
Ph
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3.07
2.08
1.97
1.00
1.03
1.02
1.00
1.99
8.97
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6.0
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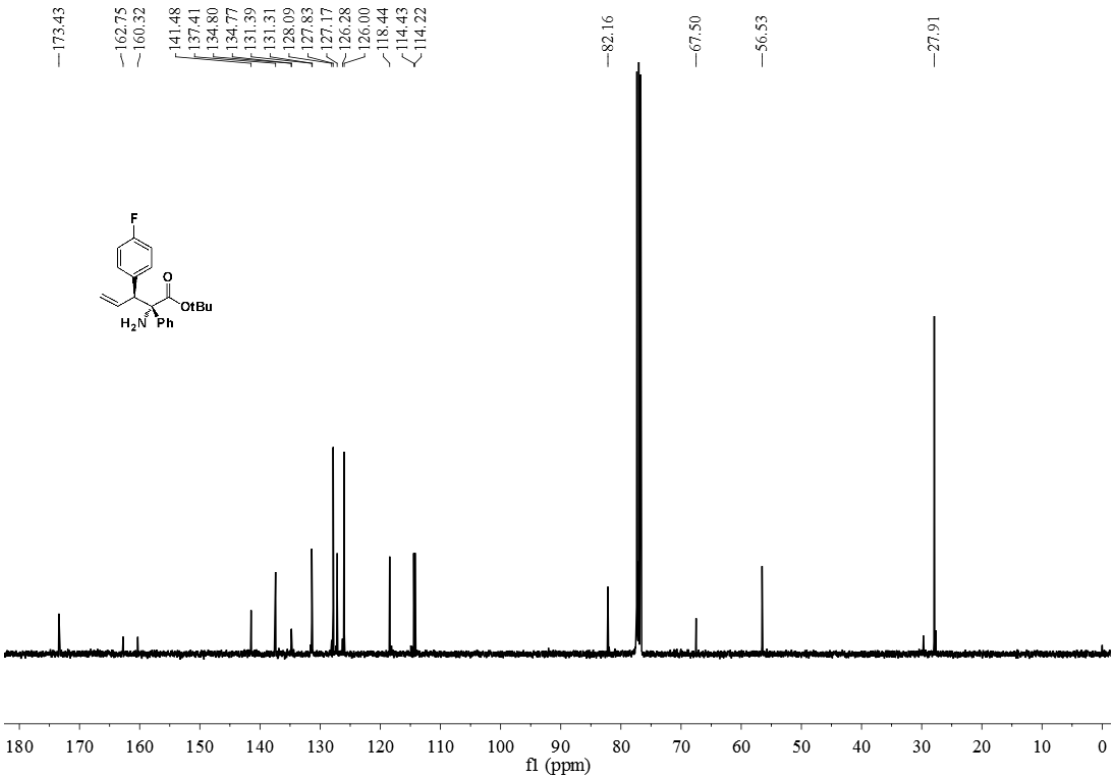
f1 (ppm)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131.39
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127.83
127.17
126.28
126.00
118.44
114.43
114.22
82.16
67.50
56.53
27.91
F
O
OtBu
H2N
Ph
180
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150
140
130
120
110
100
90
80
70
60
50
40
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10
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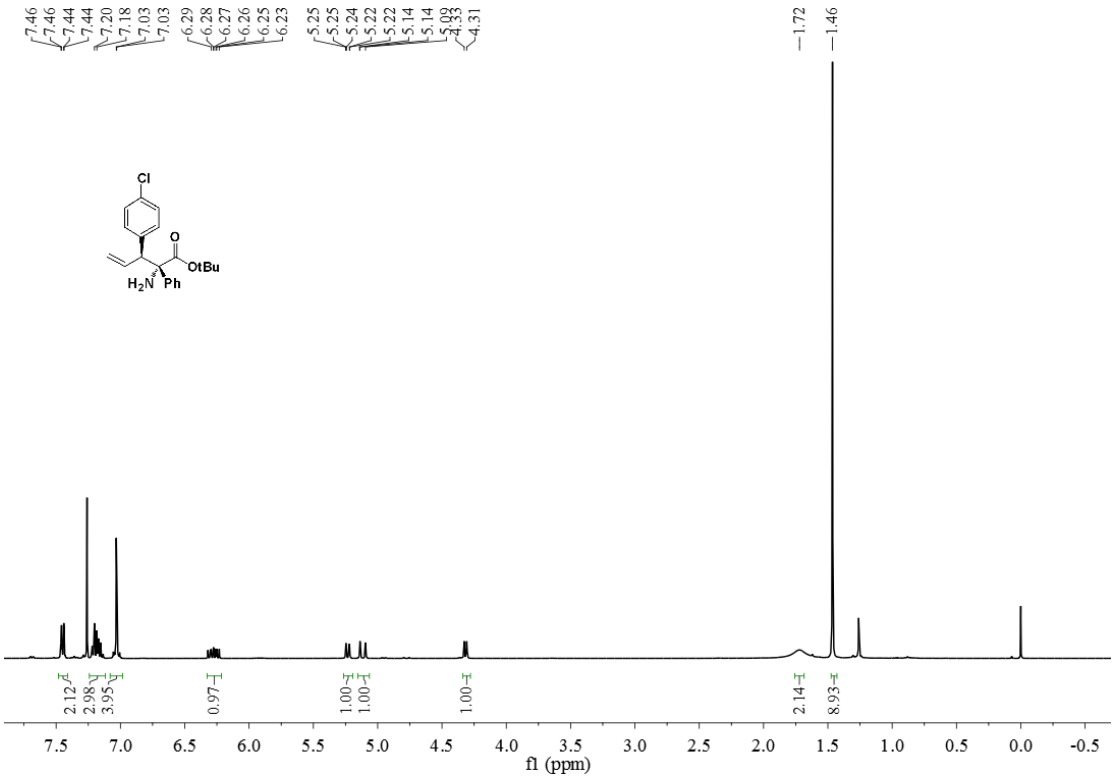
f1 (ppm)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7.03
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6.28
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6.26
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5.25
5.25
5.24
5.22
5.22
5.14
5.14
5.09
4.33
4.31
1.72
1.46
Cl
O
OtBu
H2N
Ph
2.12
2.98
3.95
0.97
1.00
1.00
1.00
2.14
8.93
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
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3.0
2.5
2.0
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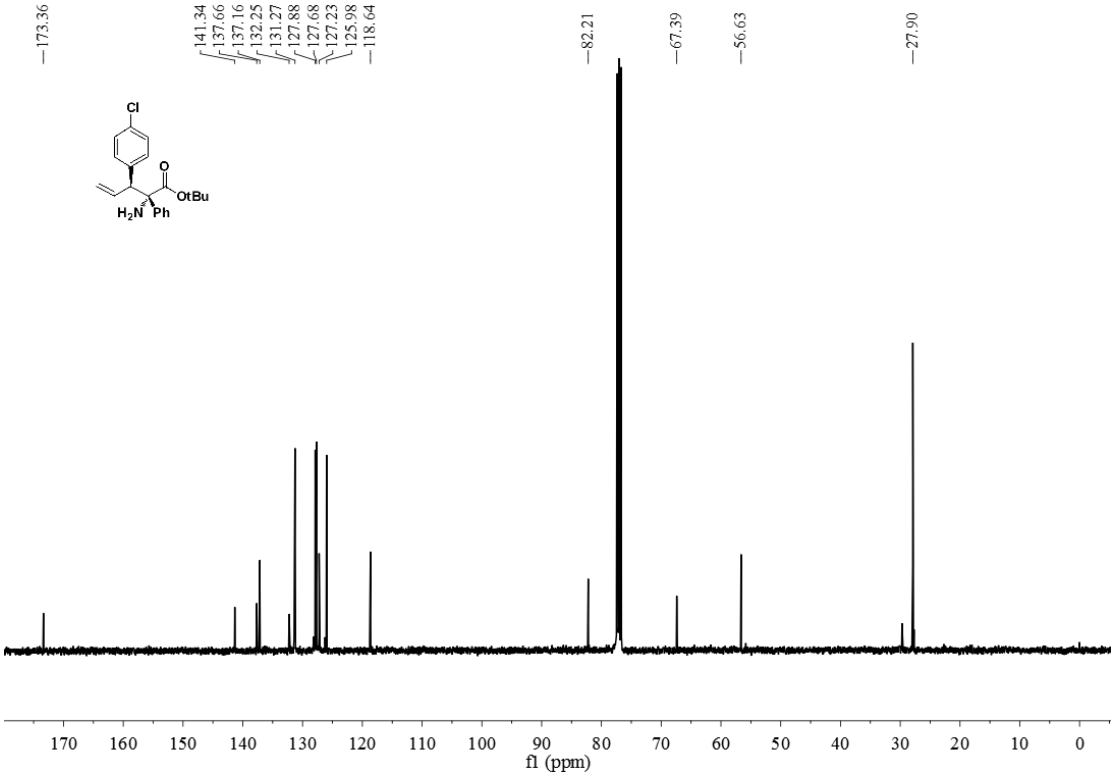
0.0
-0.5
f1 (ppm)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125.98
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67.39
56.63
27.90
Cl
O
OtBu
H2N
Ph
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130
120
110
100
90
80
70
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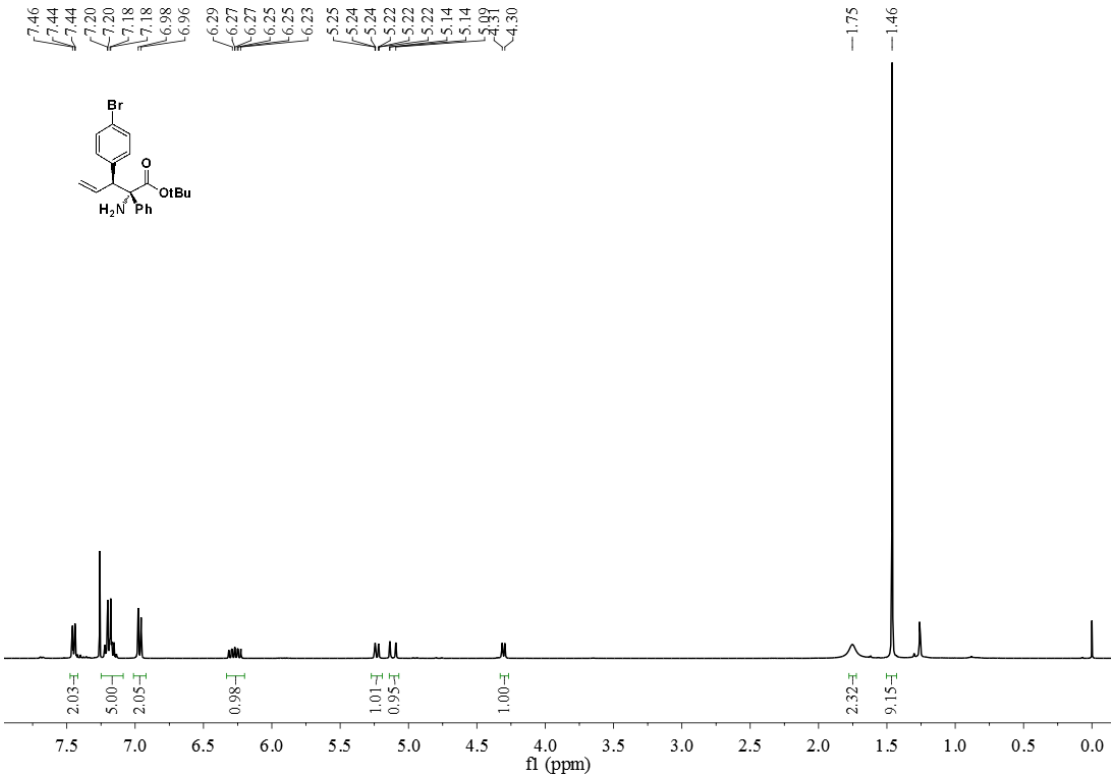
50
40
30
20
10
0
f1 (ppm)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5.09
4.31
4.30
1.75
1.46
Br
O
OtBu
H2N
Ph
2.03
5.00
2.05
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1.01
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1.00
2.32
9.15
7.5
7.0
6.5
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3.0
2.5
2.0
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1.0
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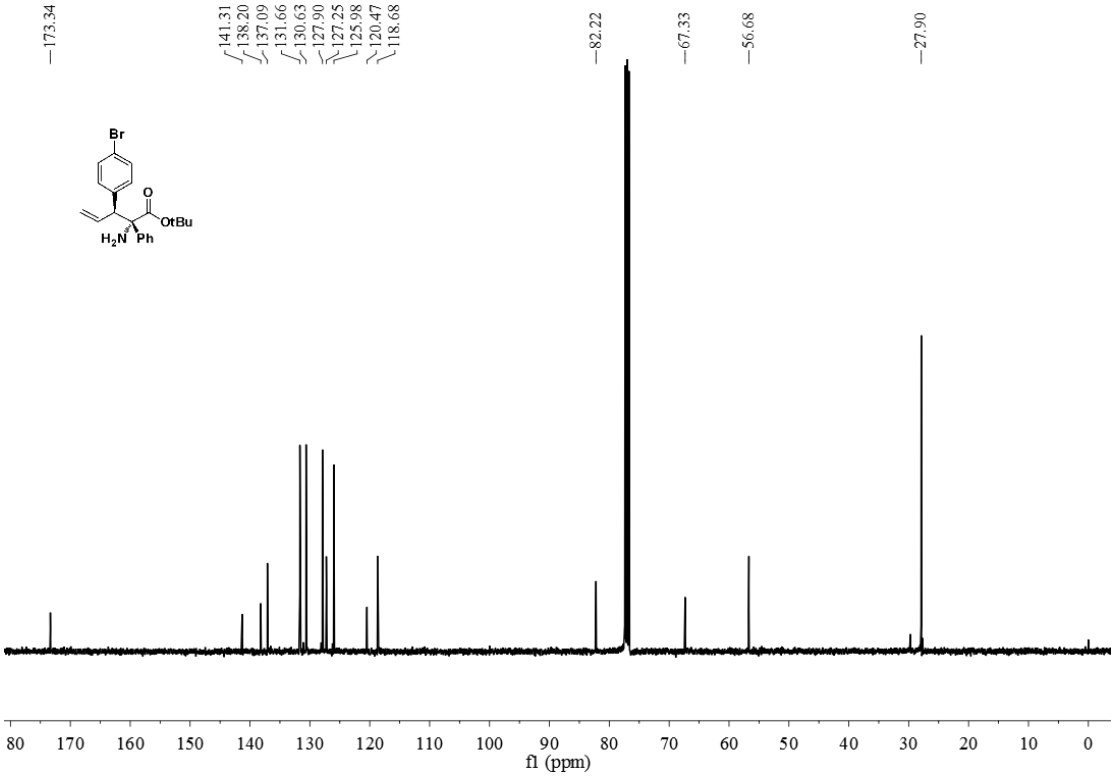
0.0
f1 (ppm)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127.25
125.98
120.47
118.68
82.22
67.33
56.68
27.90
Br
O
OtBu
H2N
Ph
80
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130
120
110
100
90
80
70
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50
40
30
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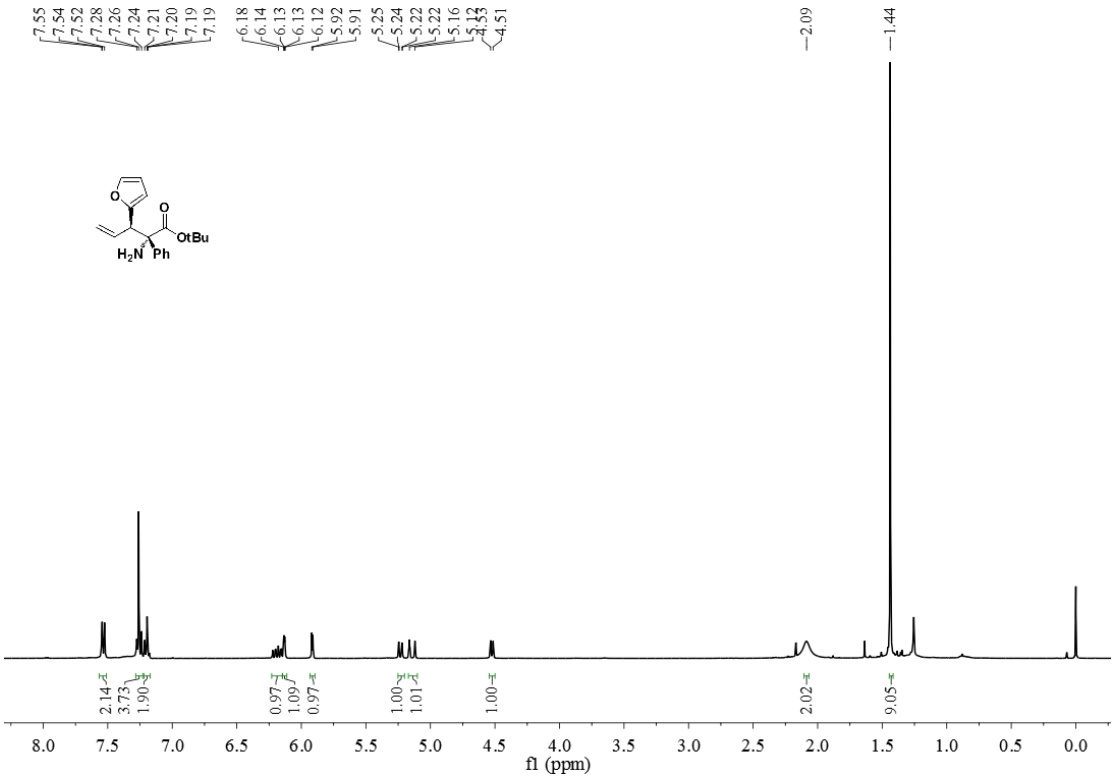
10
0
f1 (ppm)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6.13
6.12
5.92
5.91
5.25
5.24
5.22
5.22
5.16
5.12
4.53
4.51
2.09
1.44
O
O
OtBu
H2N
Ph
2.14
3.73
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0.97
1.09
0.97
1.00
1.01
1.00
2.02
9.05
8.0
7.5
7.0
6.5
6.0
5.5
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3.0
2.5
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1.0
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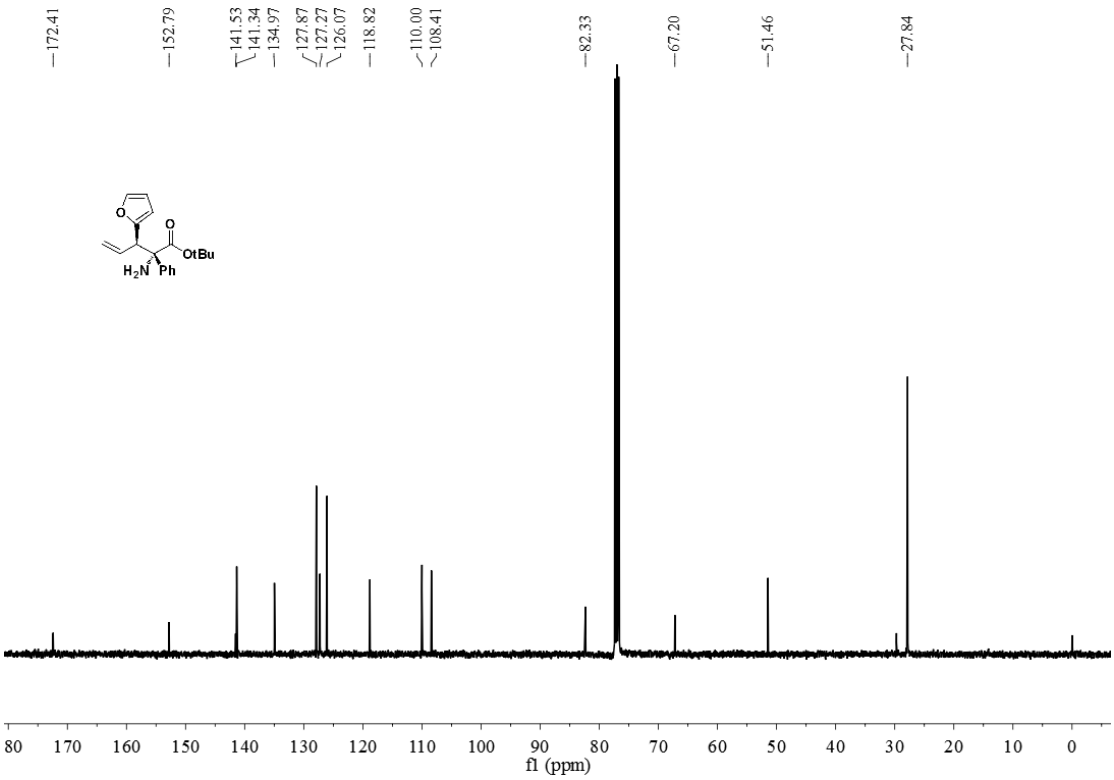
0.0
f1 (ppm)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O
O
OtBu
H2N
Ph
80
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130
120
110
100
90
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50
40
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10
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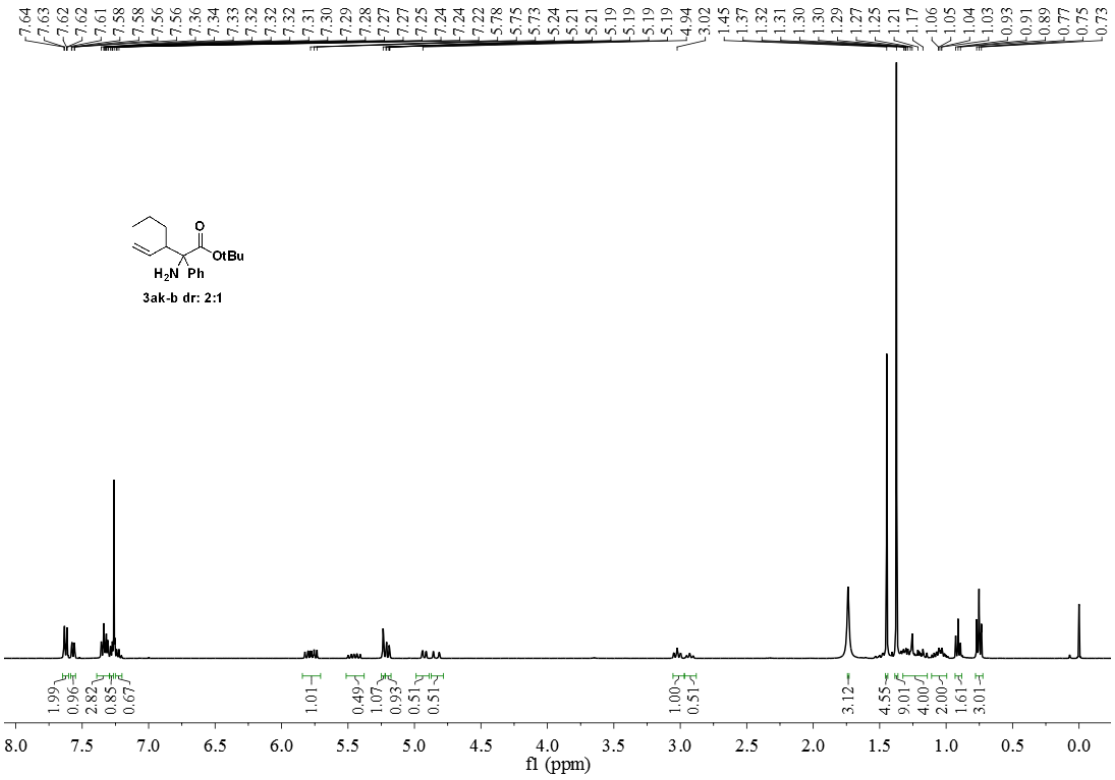
f1 (ppm)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OtBu
H2N Ph
3ak-b dr: 2:1
1.99 0.96 2.82 0.85 0.67 1.01 0.49 1.07 0.93 0.51 0.51 1.00 0.51 3.12 4.55 9.01 4.00 2.00 1.61 3.01
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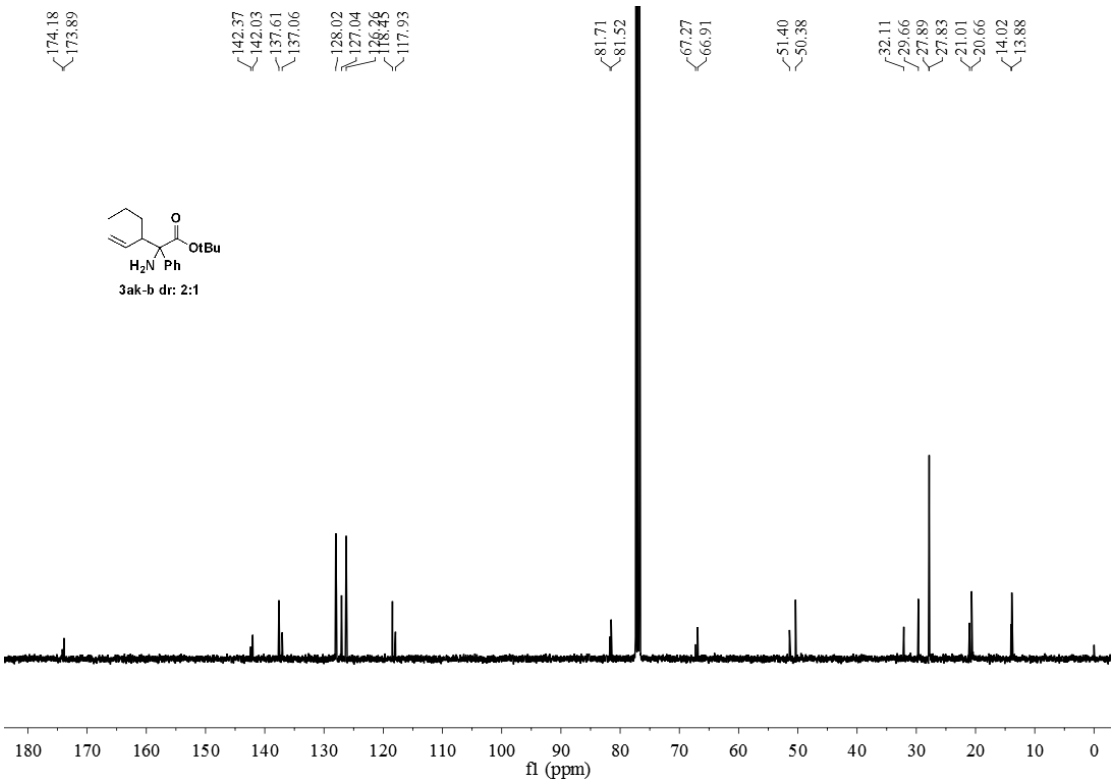
f1 (ppm)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OtBu
H2N Ph
3ak-b dr: 2:1
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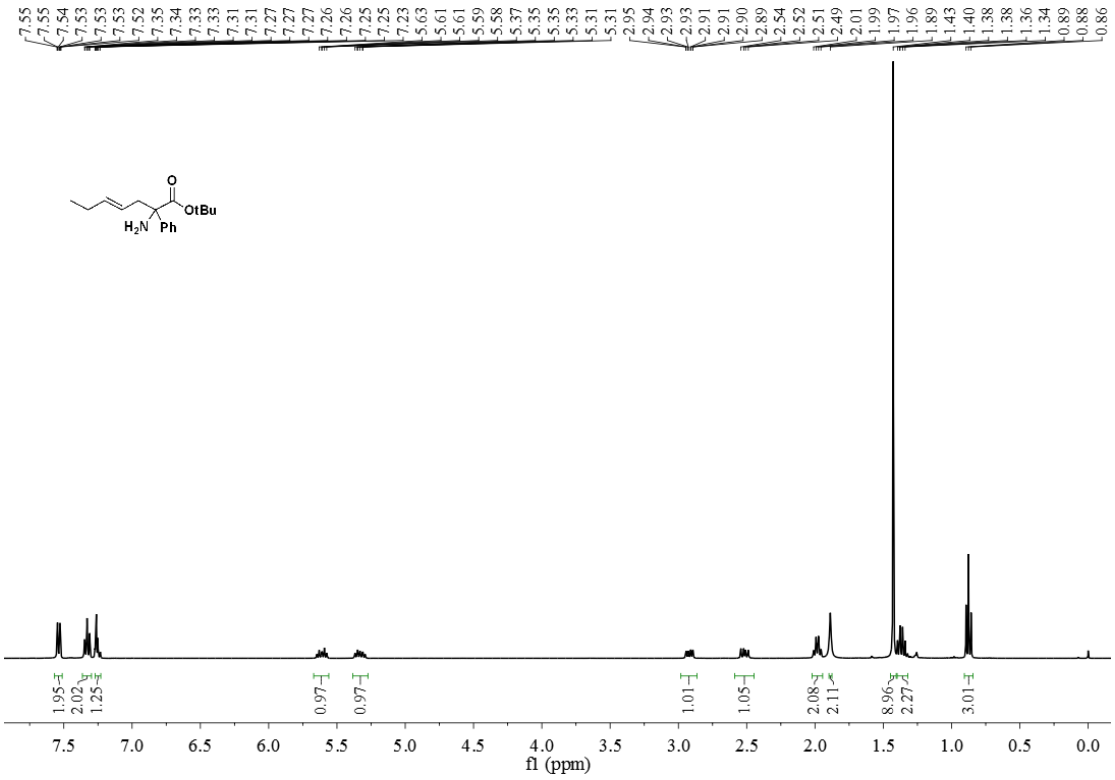
f1 (ppm)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2.95 2.94 2.93 2.93 2.91 2.91 2.90 2.89 2.54 2.52 2.51 2.49 2.01 1.99 1.97 1.96 1.89 1.43 1.40 1.38 1.38 1.36 1.34 0.89 0.88 0.86
O
OtBu
H2N Ph
1.95 2.02 1.25 0.97 0.97 1.01 1.05 2.08 2.11 8.96 2.27 3.01
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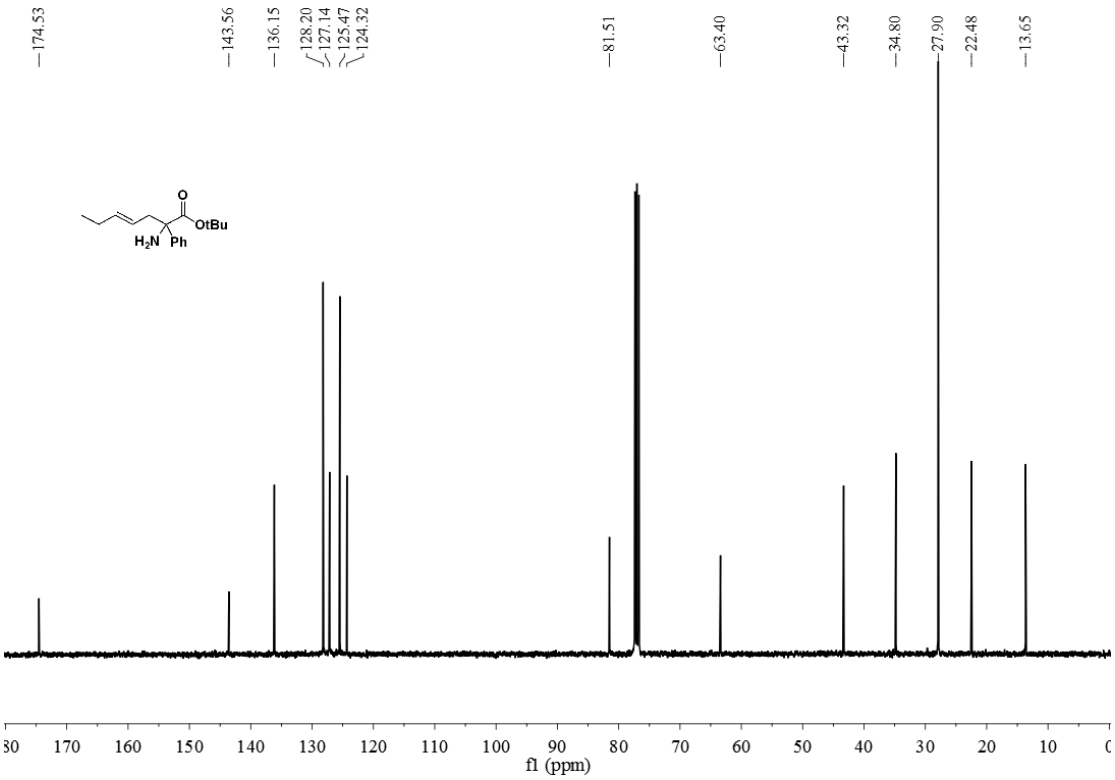
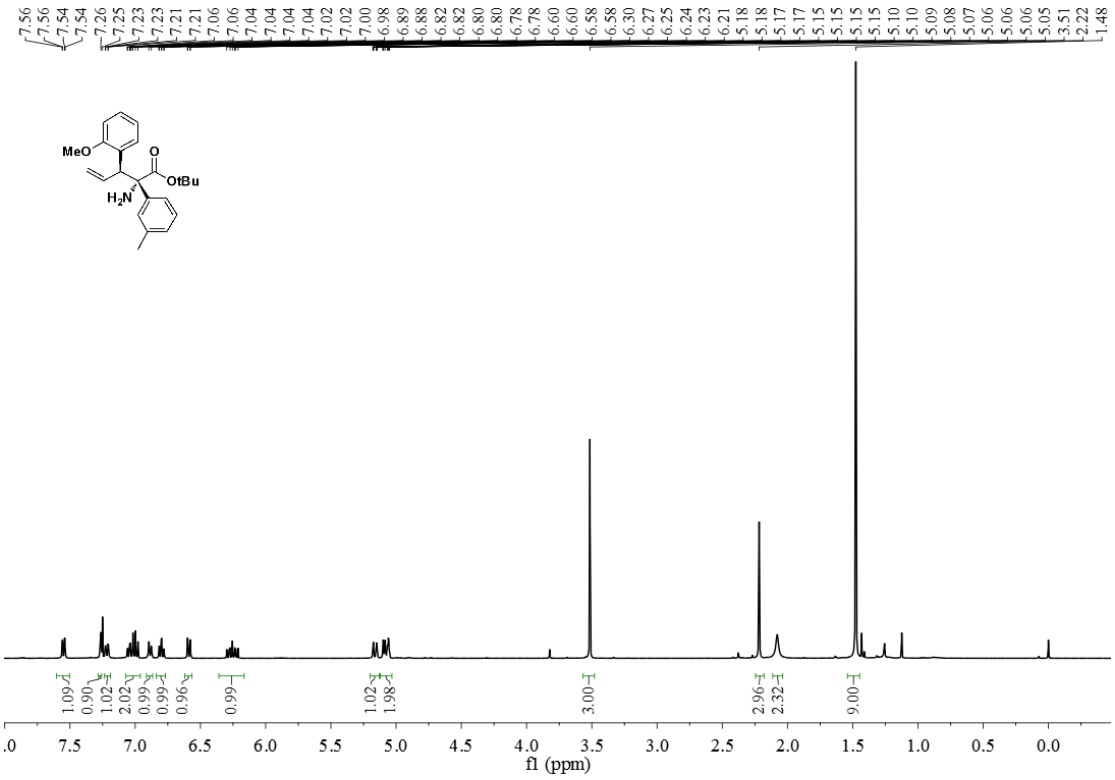
f1 (ppm)


174.53 143.56 136.15 128.20 127.14 125.47 124.32 81.51 63.40 43.32 34.80 27.90 22.48 13.65
O
OtBu
H2N Ph
170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10
f1 (ppm)


MeO
O
OtBu
H2N
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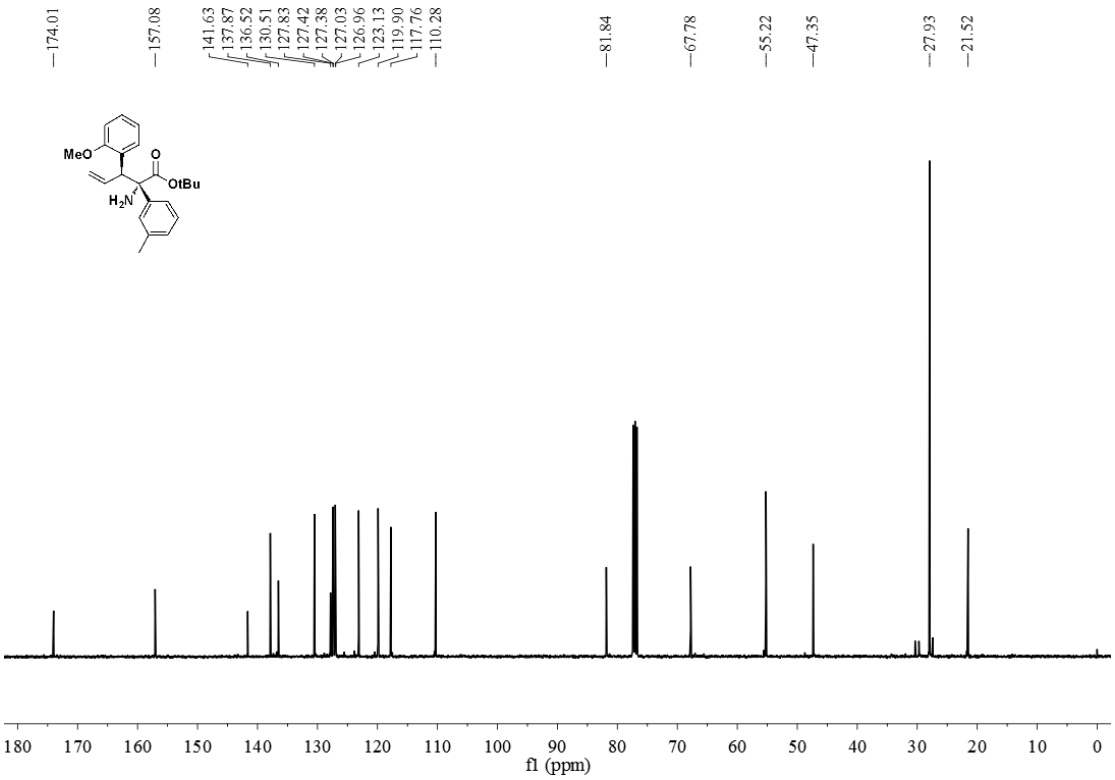
f1 (ppm)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O
OtBu
H2N
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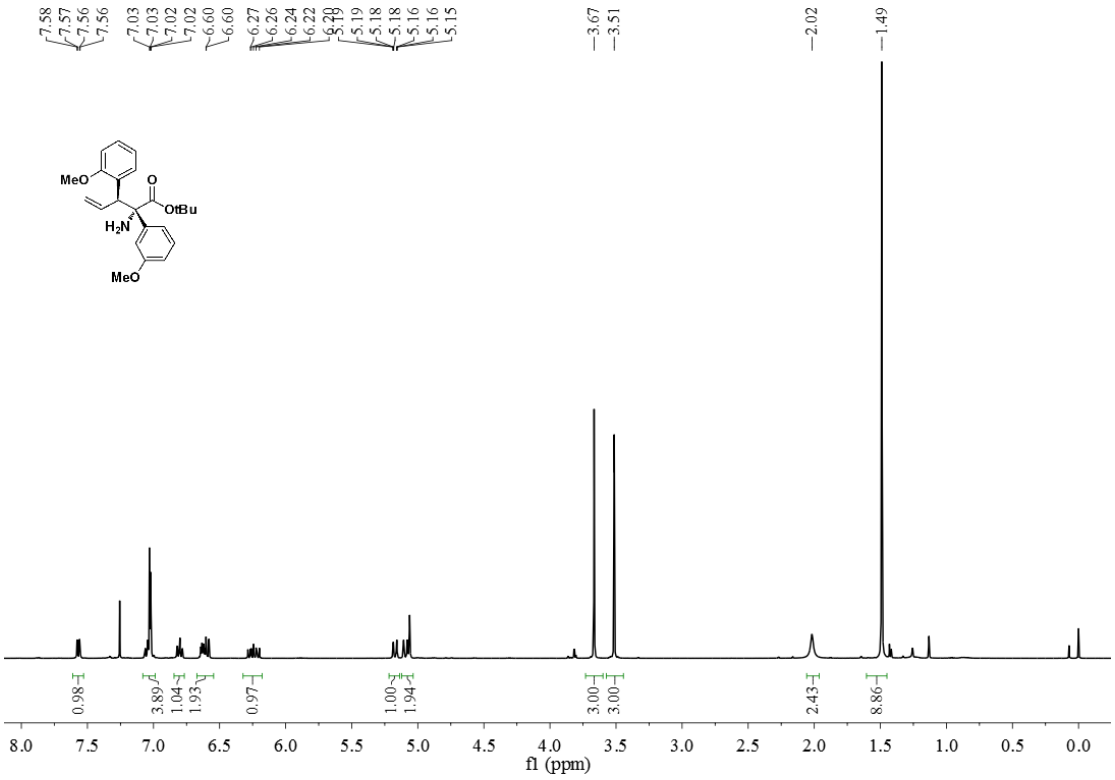
f1 (ppm)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5.18
5.16
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5.15
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2.02
1.49
MeO
O
OtBu
H2N
MeO
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3.89
1.04
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1.94
3.00
3.00
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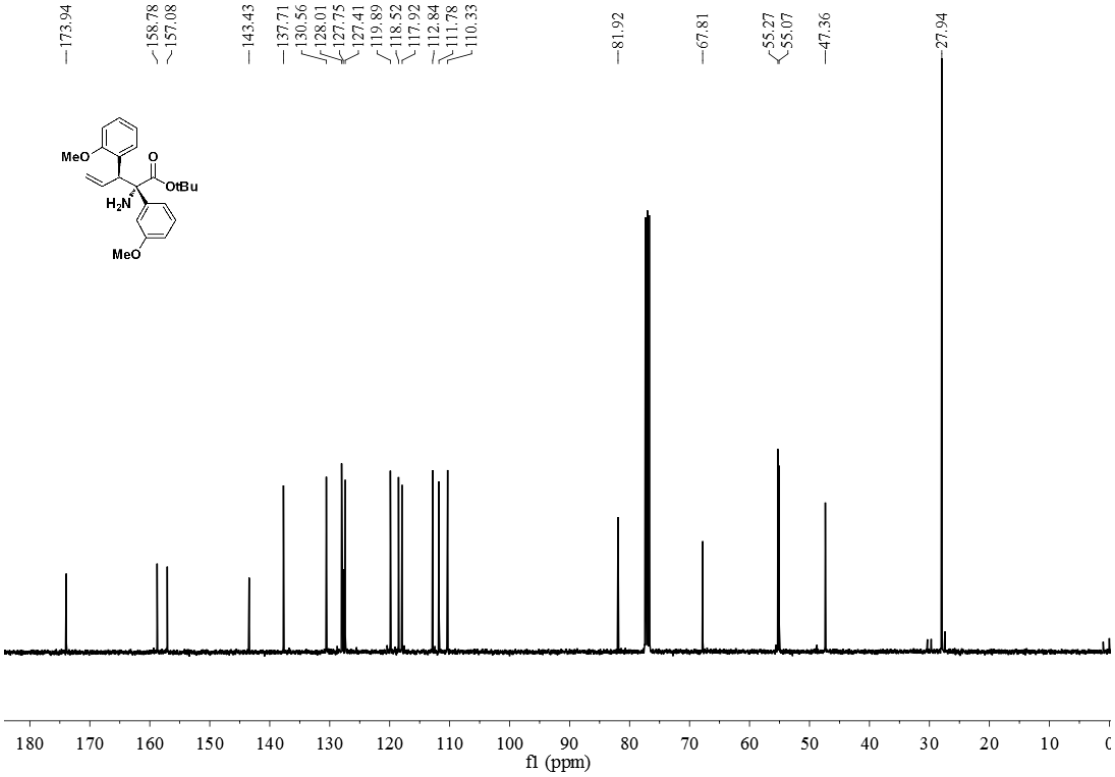
f1 (ppm)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127.41
119.89
118.52
117.92
112.84
111.78
110.33
81.92
67.81
55.27
55.07
47.36
27.94
MeO
O
OtBu
H2N
MeO
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100
90
80
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60
50
40
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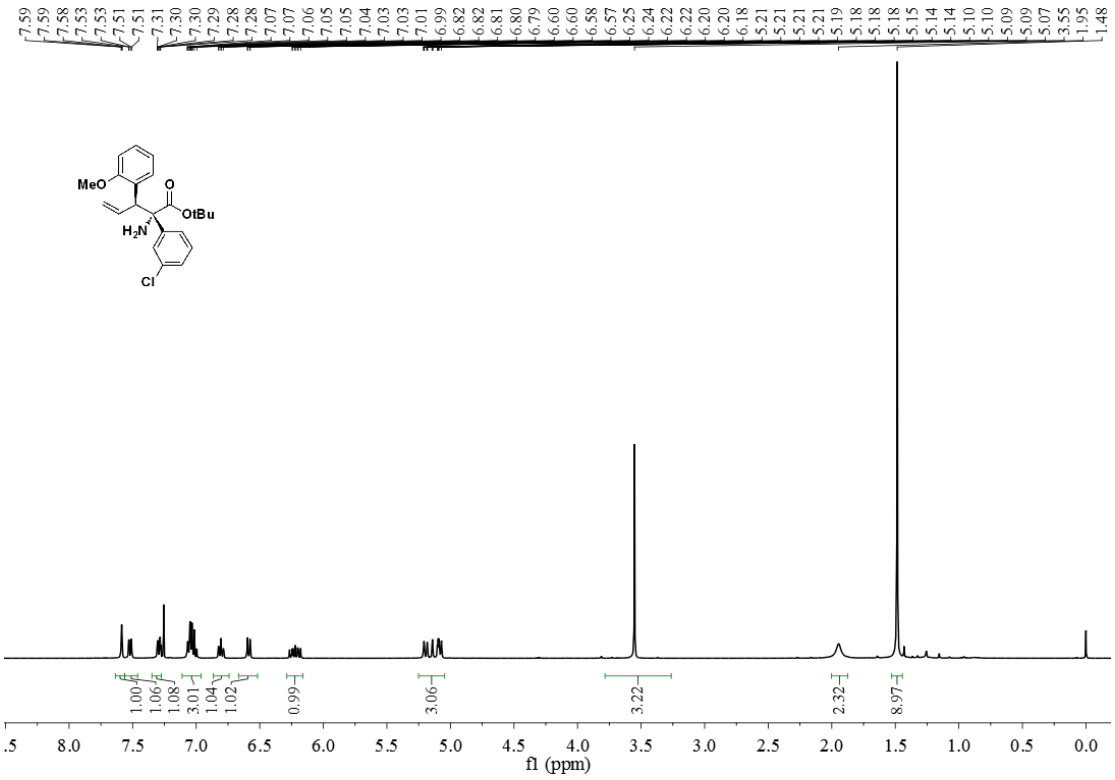
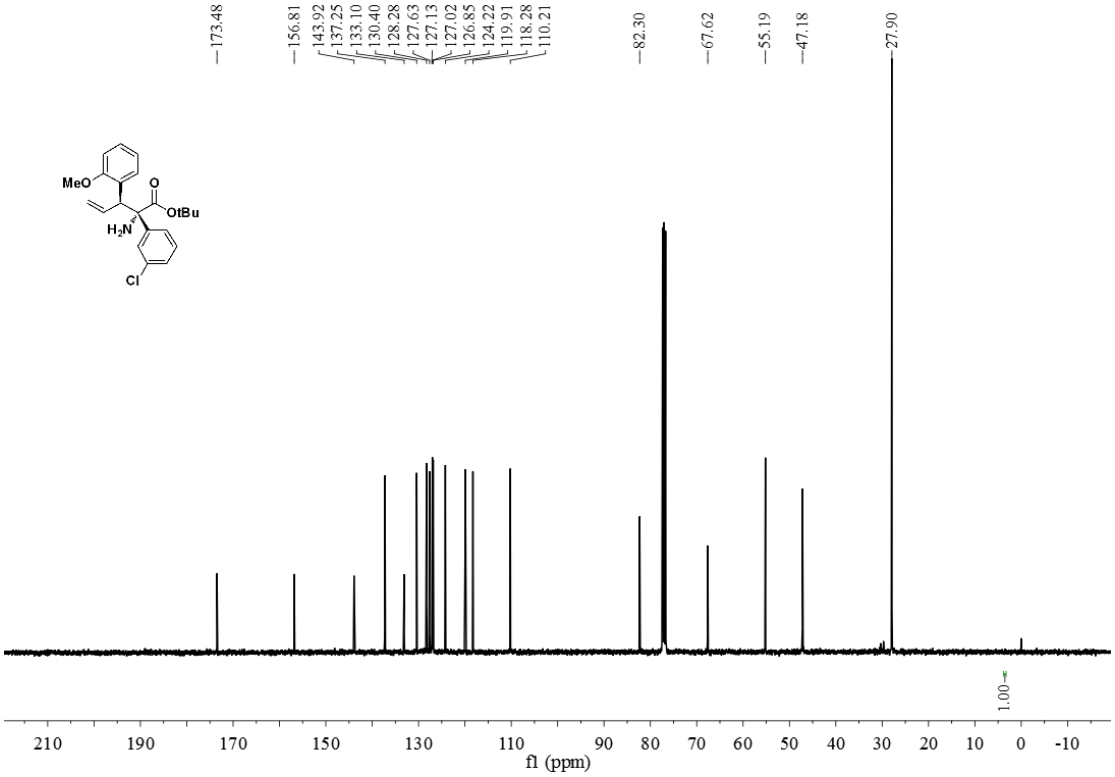
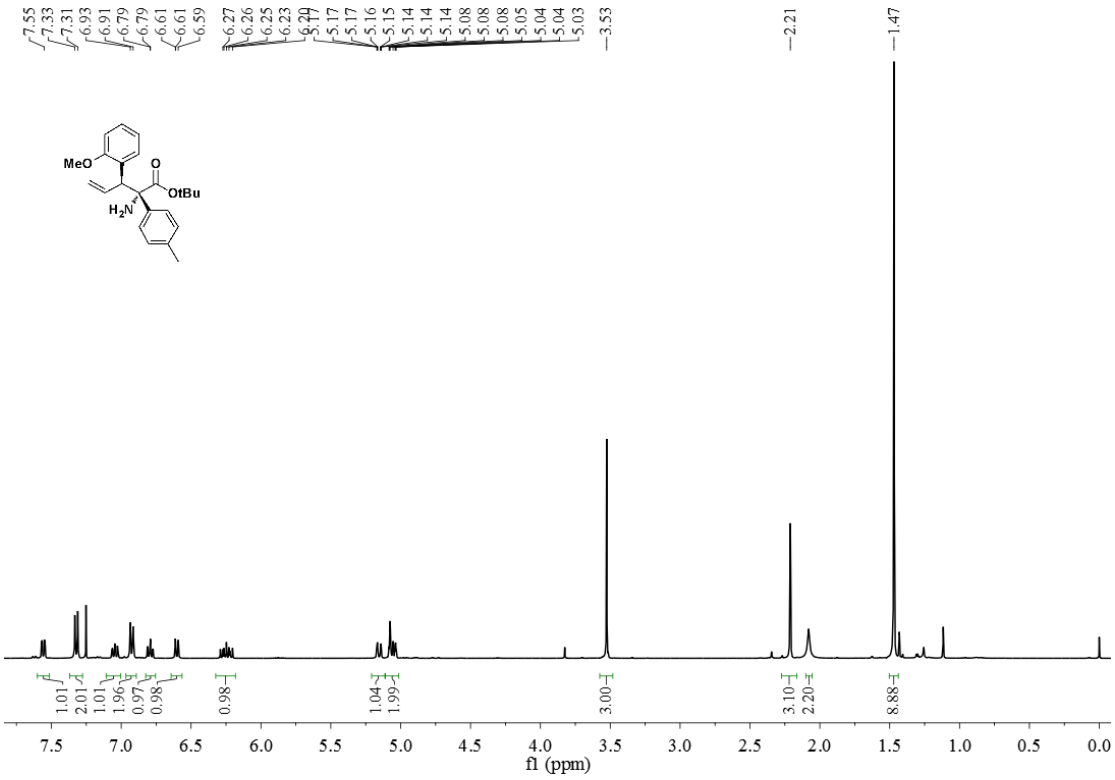
20
10
f1 (ppm)


MeO
O
OtBu
H2N
Cl
fl (ppm)


MeO
O
OtBu
H2N
Cl
fl (ppm)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5.14
5.14
5.08
5.08
5.05
5.04
5.04
5.03
3.53
2.21
1.47
MeO
O
OtBu
H2N
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2.01
1.01
1.96
0.97
0.98
0.98
1.04
1.99
3.00
3.10
2.20
8.88
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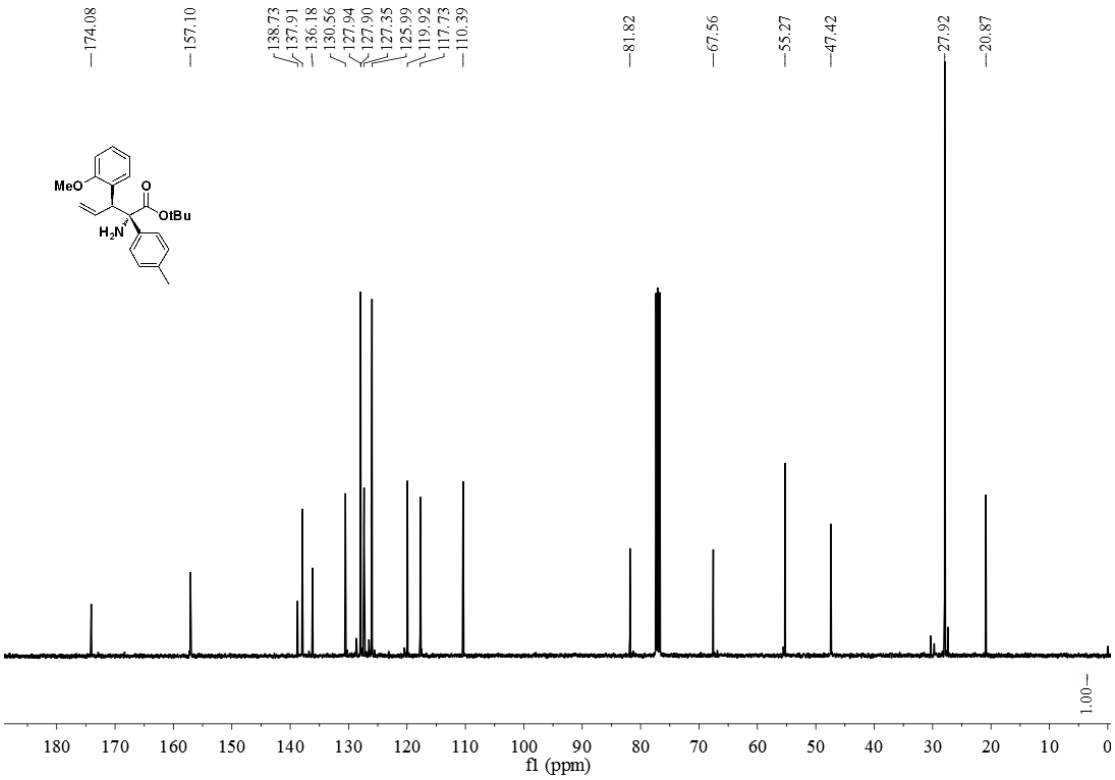
f1 (ppm)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125.99
119.92
117.73
110.39
81.82
67.56
55.27
47.42
27.92
20.87
MeO
O
OtBu
H2N
1.00
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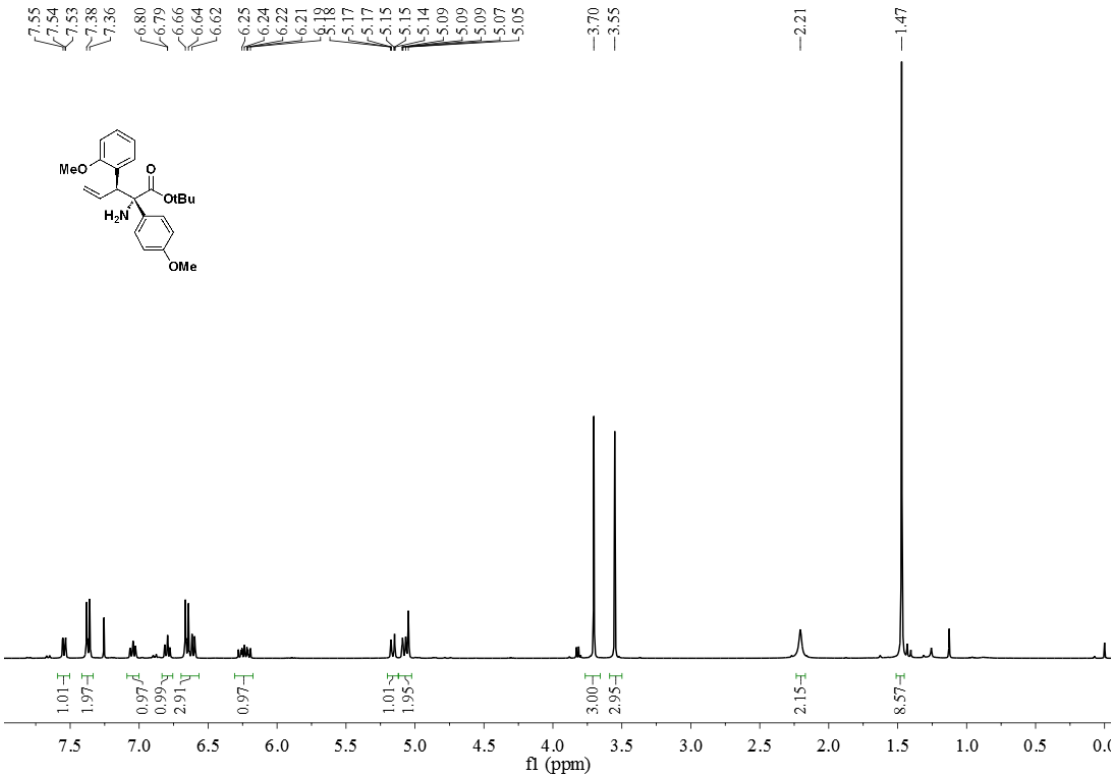
f1 (ppm)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6.22
6.21
6.19
5.18
5.17
5.17
5.15
5.15
5.14
5.09
5.09
5.09
5.07
5.05
3.70
3.55
2.21
1.47
MeO
O
OtBu
H2N
OMe
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3.00
2.95
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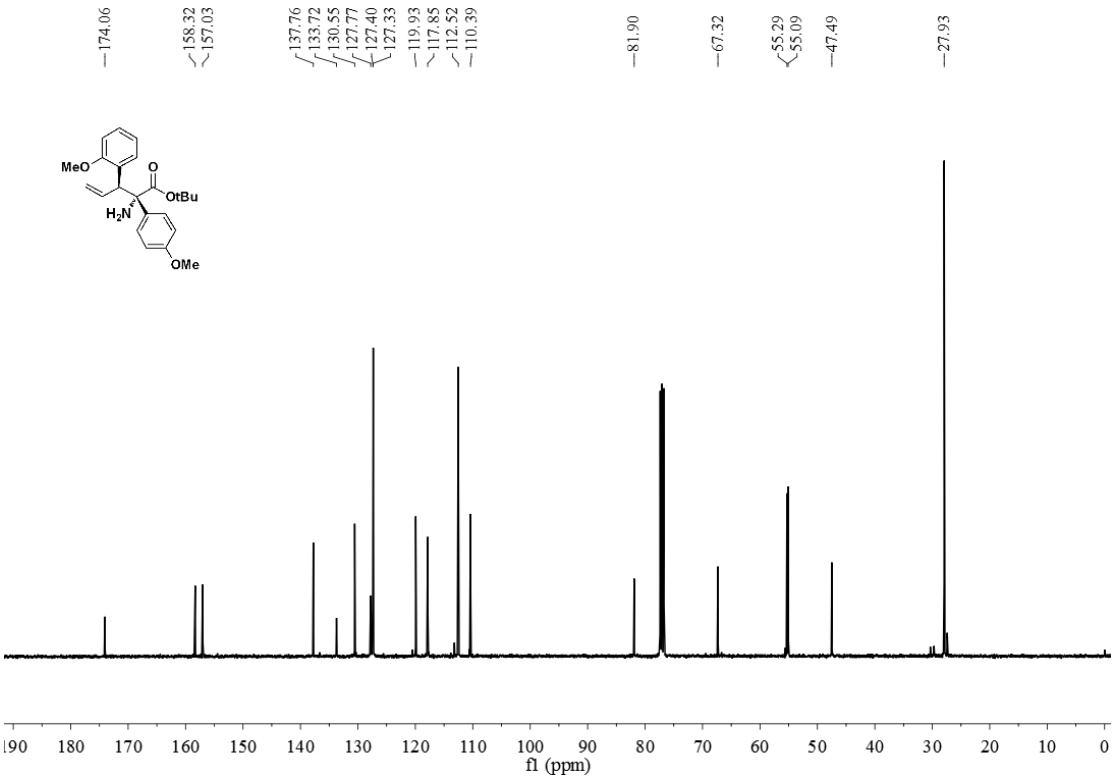
fl (ppm)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112.52
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81.90
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55.29
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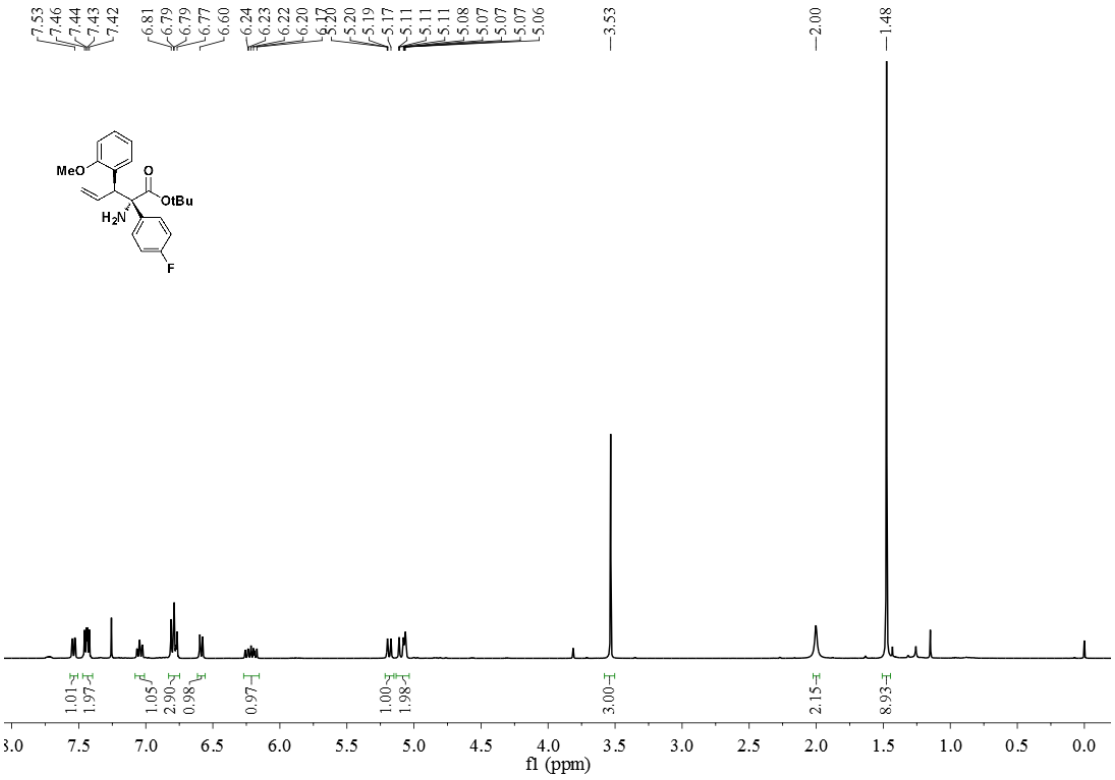
47.49
27.93
MeO
O
OtBu
H2N
OMe
fl (ppm)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6.23
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6.20
5.20
5.20
5.19
5.17
5.11
5.11
5.11
5.08
5.07
5.07
5.07
5.06
3.53
2.00
1.48
MeO
O
OtBu
H2N
F
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1.97
1.05
2.90
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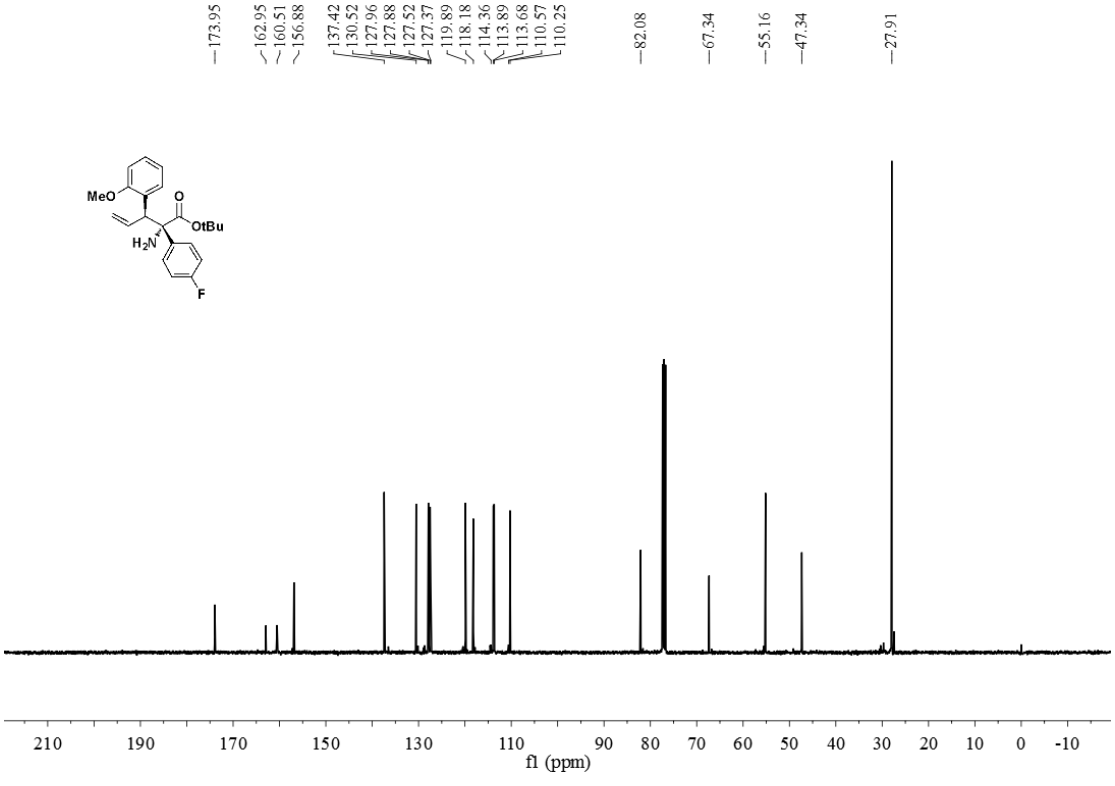
0.97
1.00
1.98
3.00
2.15
8.93
fl (ppm)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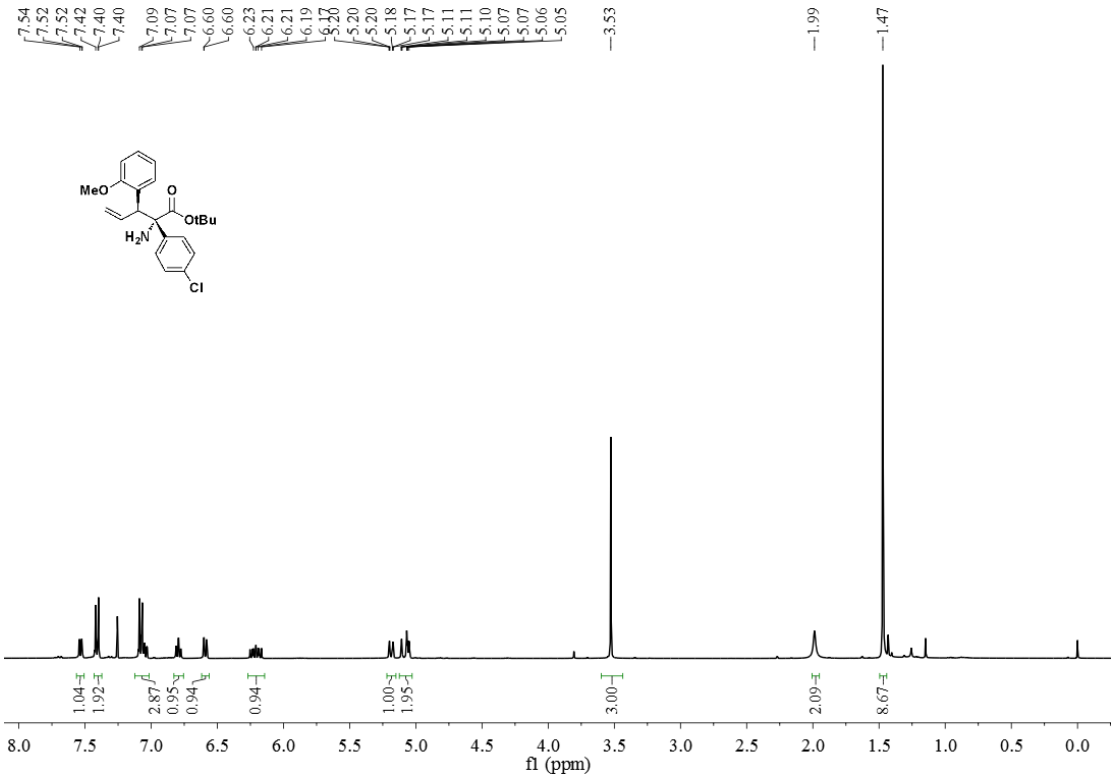
127.37
119.89
118.18
114.36
113.89
113.68
110.57
110.25
82.08
67.34
55.16
47.34
27.91
MeO
O
OtBu
H2N
F
fl (ppm)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7.07
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6.60
6.23
6.21
6.21
6.19
5.20
5.20
5.18
5.17
5.17
5.11
5.10
5.07
5.07
5.06
5.05
3.53
1.99
1.47
MeO
O
OtBu
H2N
Cl
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1.92
2.87
0.95
0.94
0.94
1.00
1.95
3.00
2.09
8.67
8.0
7.5
7.0
6.5
6.0
5.5
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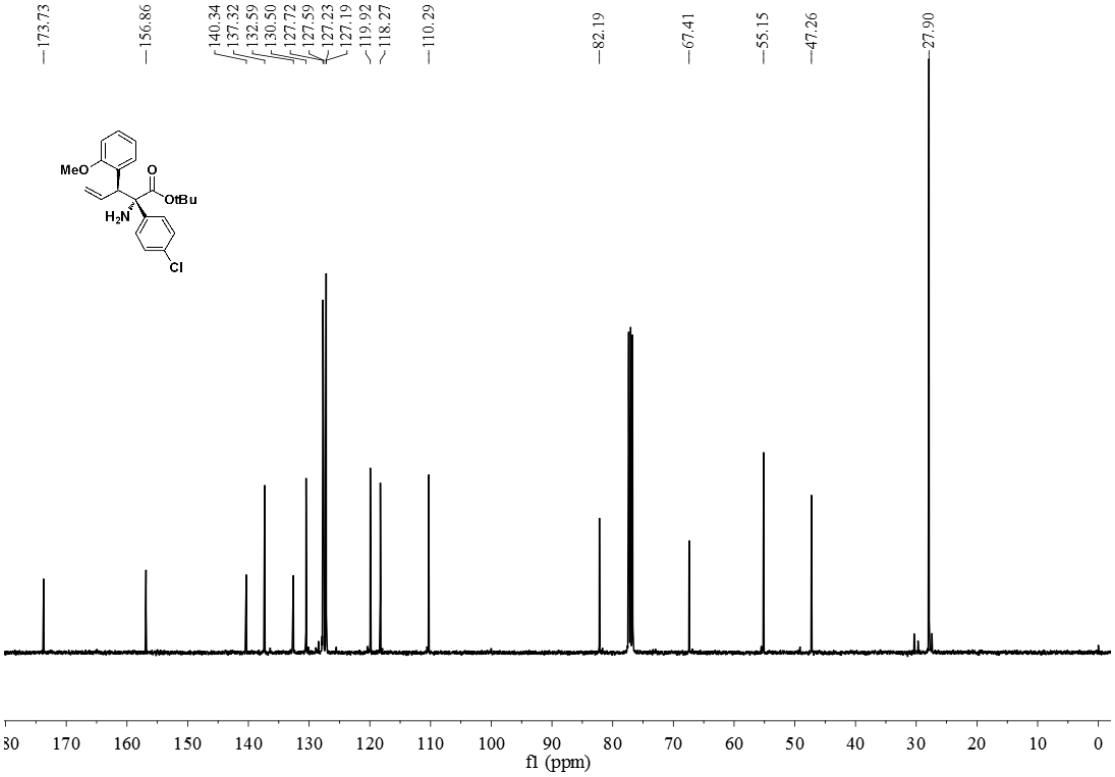
0.0
f1 (ppm)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118.27
110.29
82.19
67.41
55.15
47.26
27.90
MeO
O
OtBu
H2N
Cl
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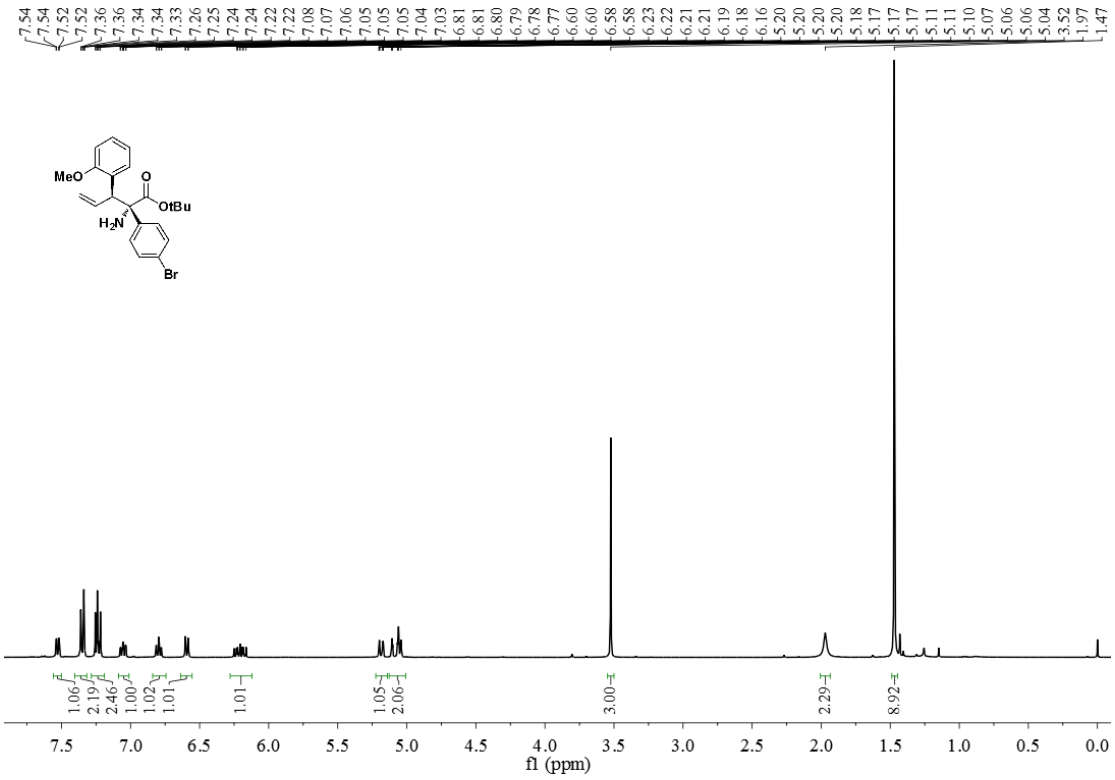
160
150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0
f1 (ppm)


MeO
O
OtBu
H2N
Br
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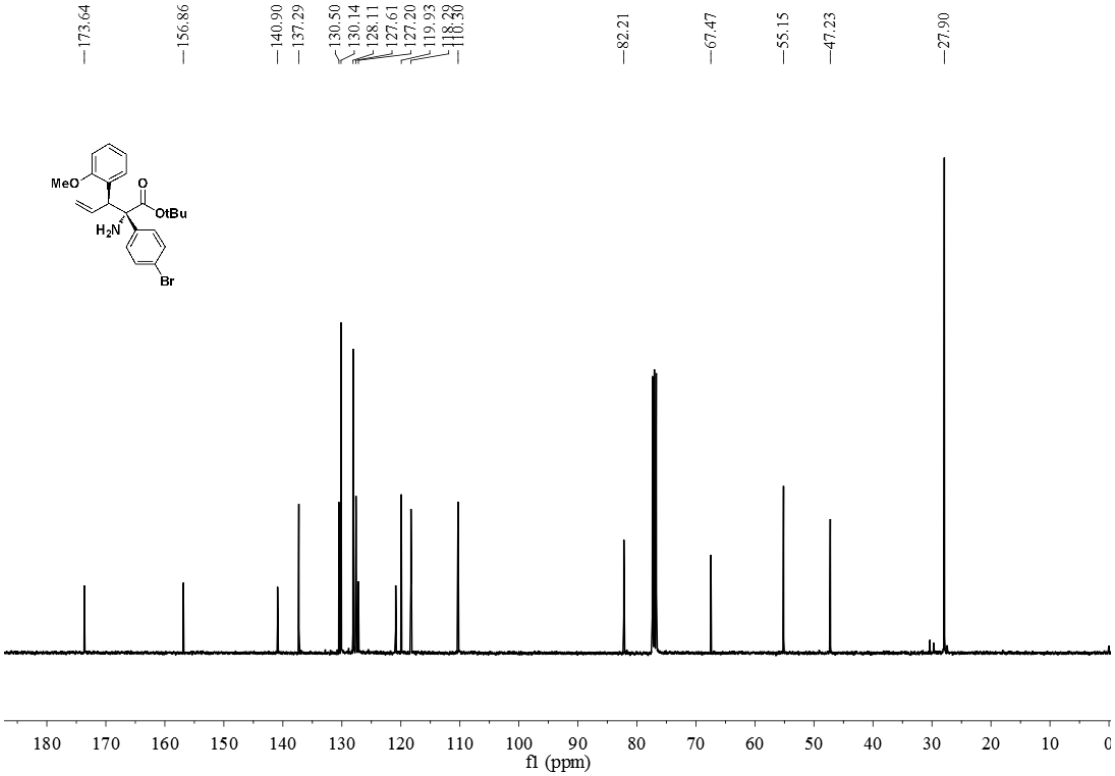
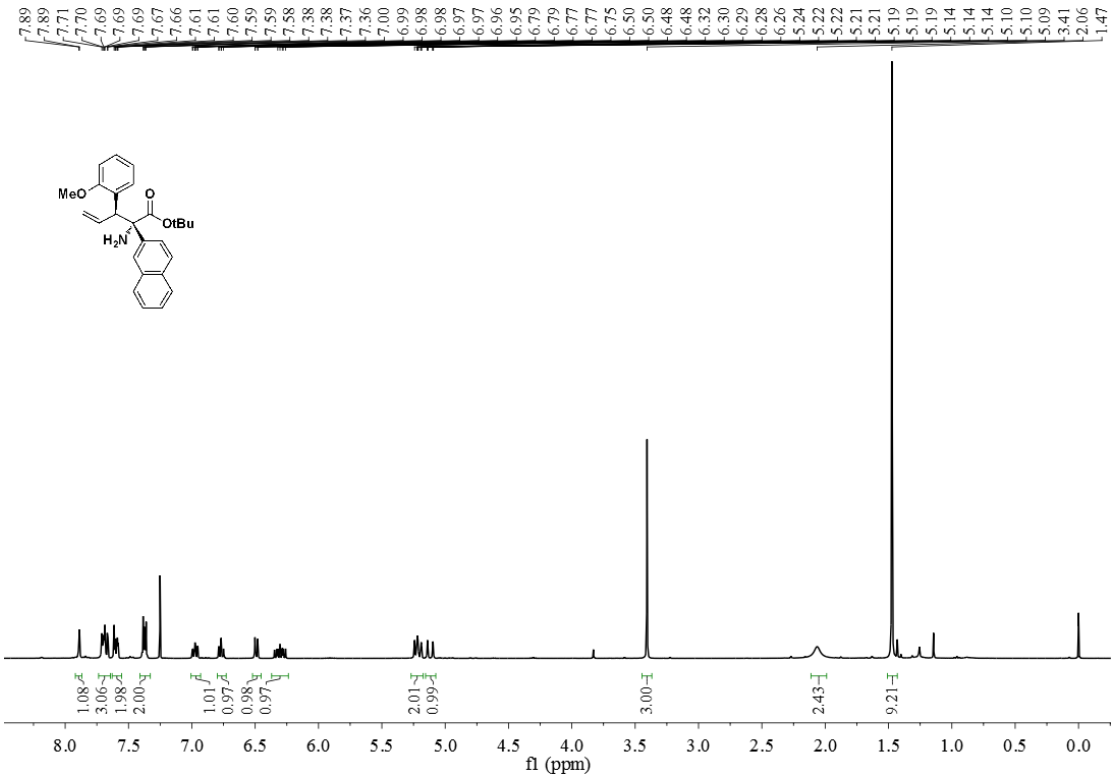
1.06 2.19 2.46 1.00 1.02 1.01 1.01 1.05 2.06 3.00 2.29 8.92
7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)


173.64 156.86 140.90 137.29 130.50 130.14 128.11 127.61 127.20 119.93 118.29 118.30 82.21 67.47 55.15 47.23 27.90
MeO
O
OtBu
H2N
Br
180 170 160 150 140 130 120 110 100 90 80 70 60 50 40 30 20 10 0
f1 (ppm)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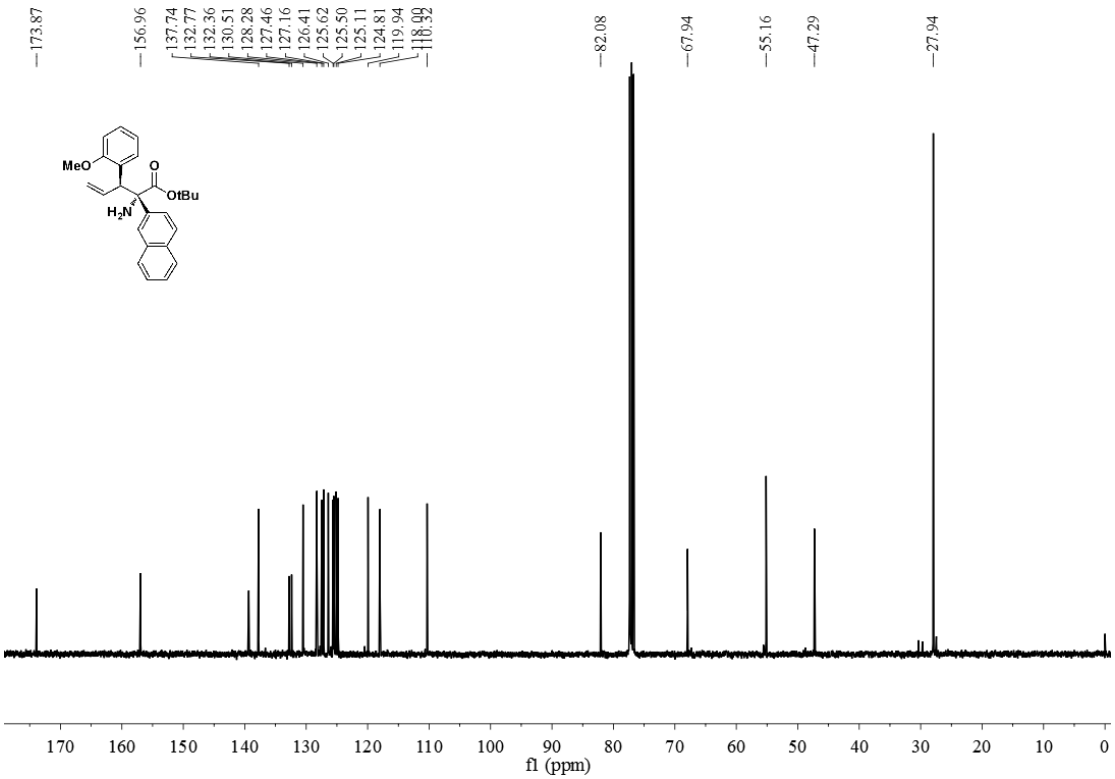
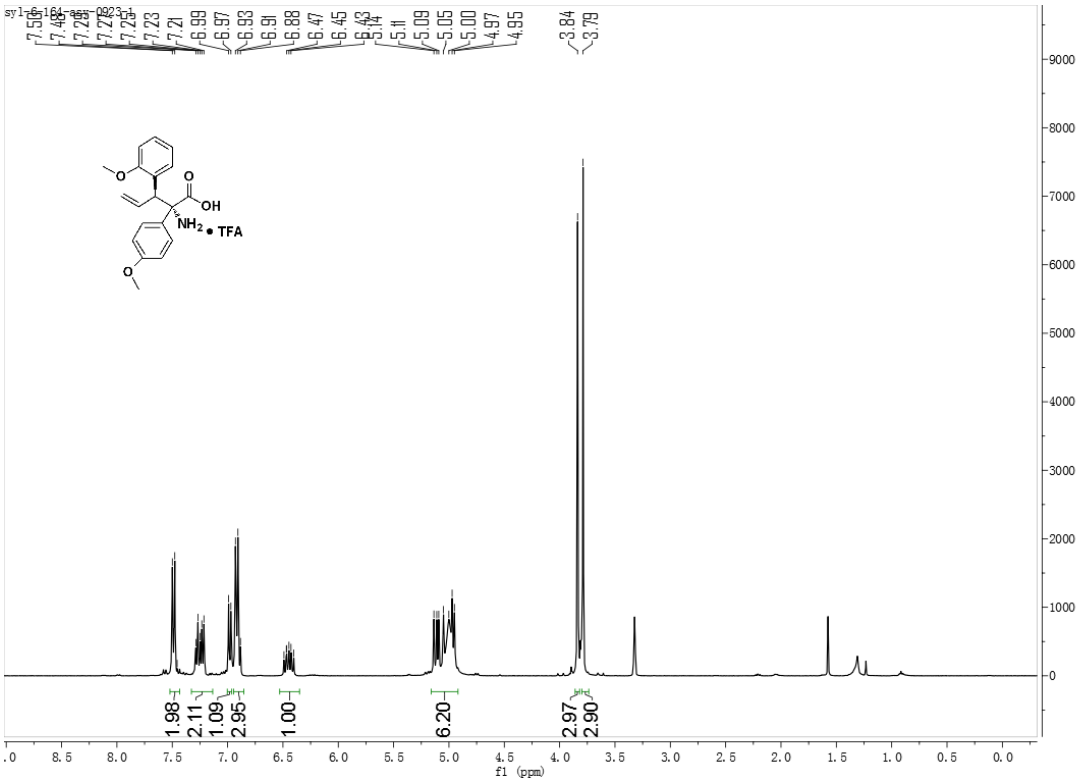
O
OtBu
H2N
fl (ppm)


MeO
O
OtBu
H2N
fl (ppm)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6.97
6.93
6.91
6.88
6.47
6.45
6.43
5.14
5.11
5.09
5.05
5.00
4.97
4.95
3.84
3.79
OH
NH2 • TFA
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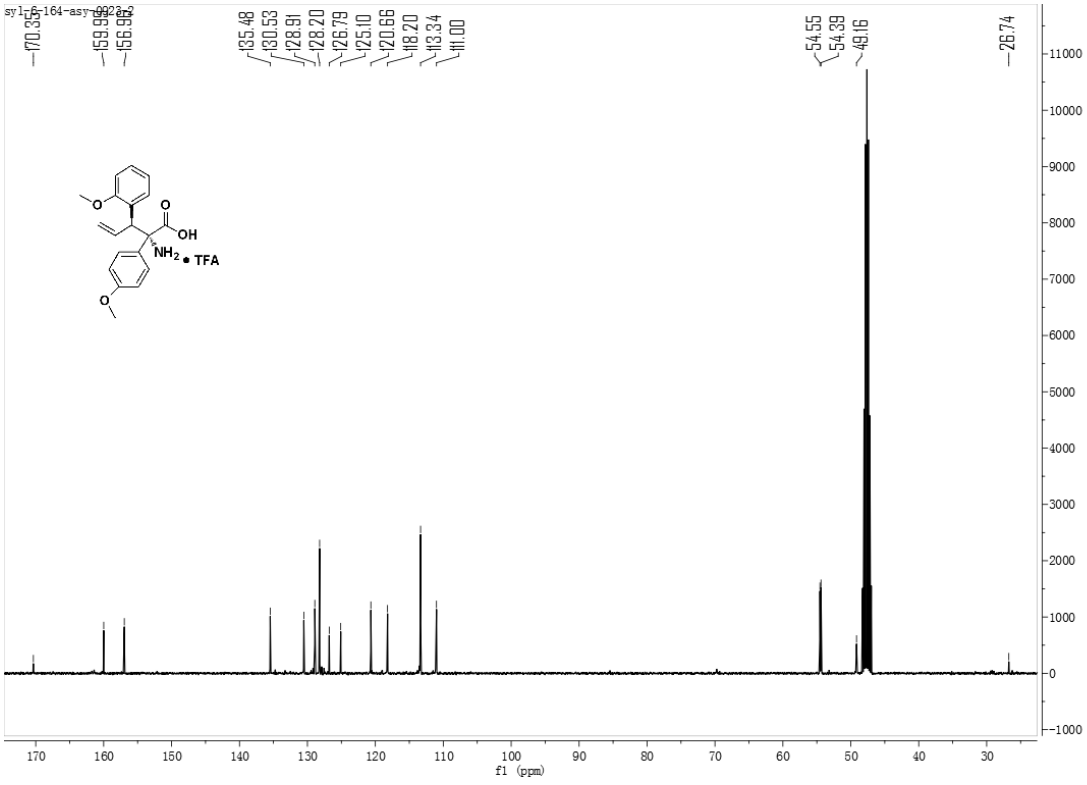
2.11
1.09
2.95
1.00
6.20
2.97
2.90
f1 (ppm)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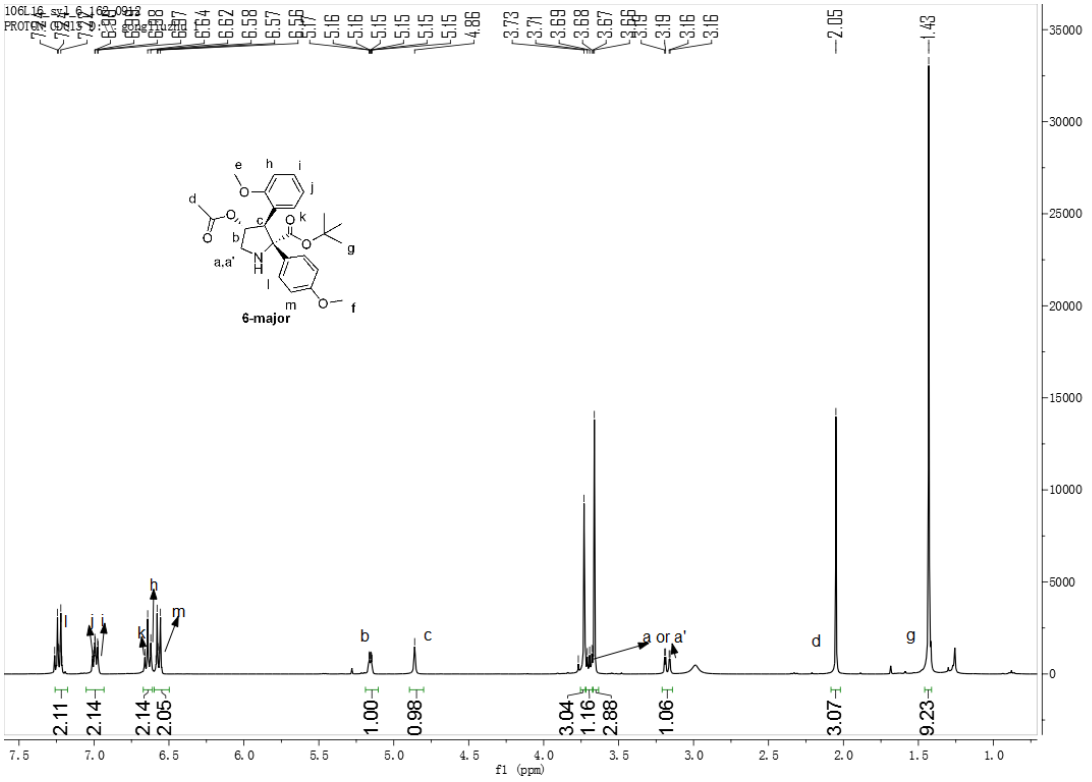
48.16
26.74
OH
NH2 • TFA
f1 (ppm)


6-major
2.11
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2.14
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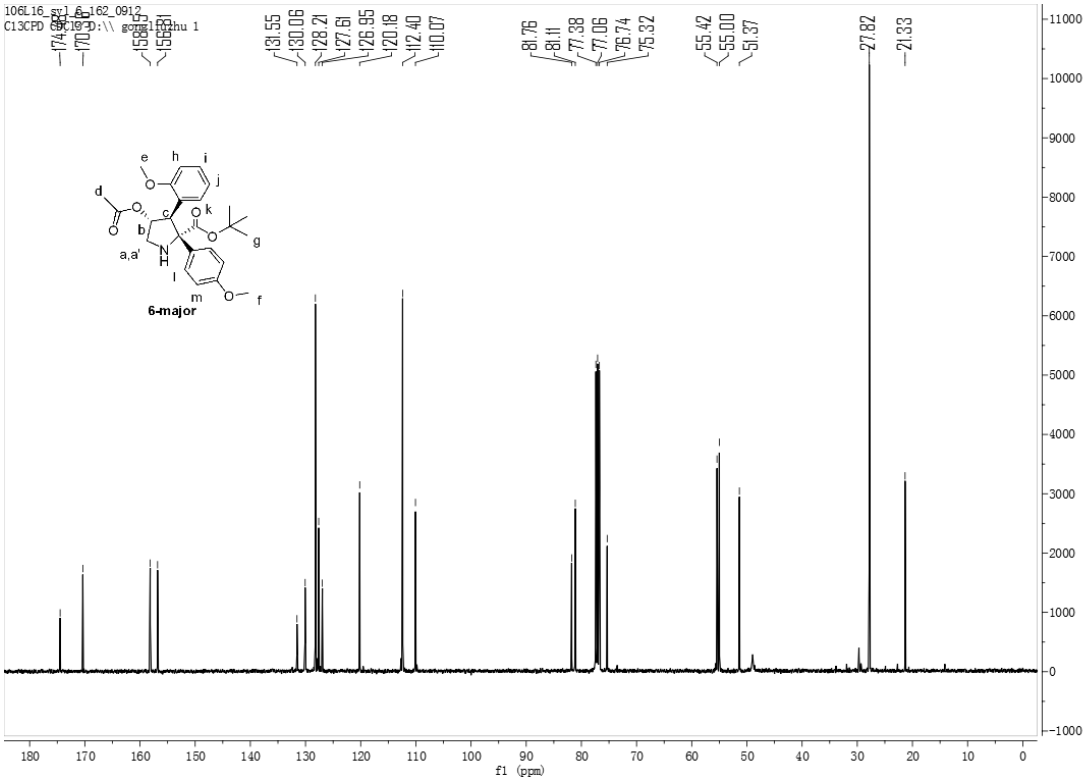
3.04
1.16
2.88
1.06
3.07
9.23
f1 (ppm)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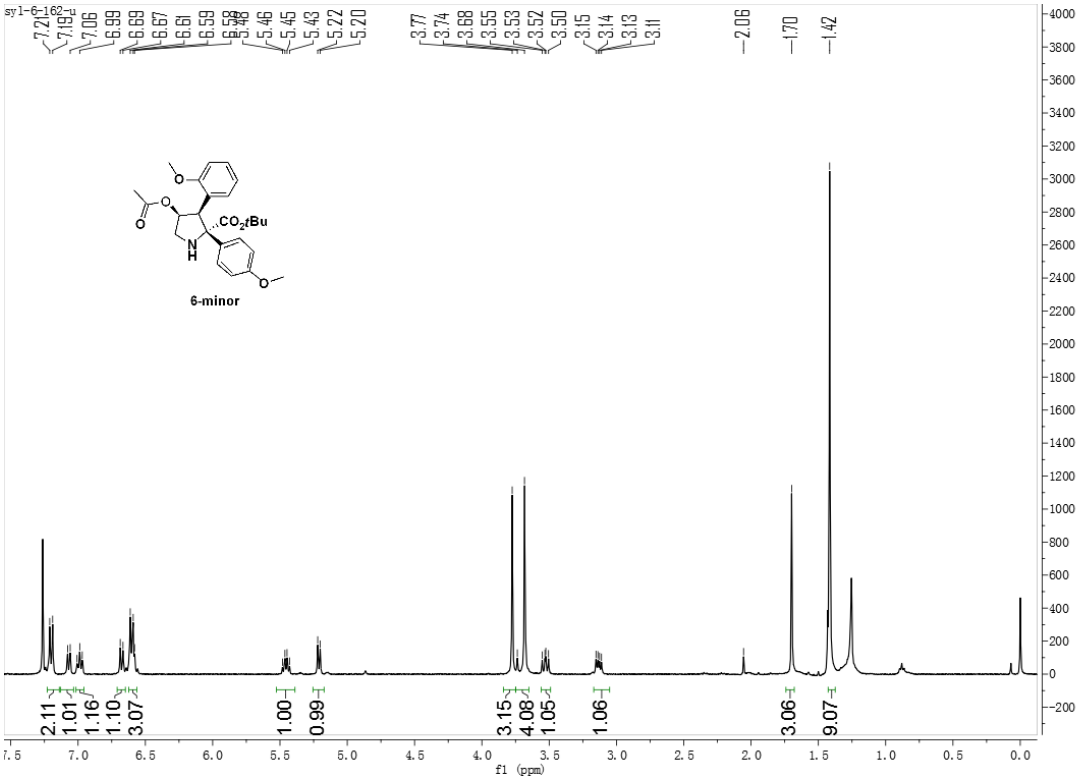
f1 (ppm)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5.45
5.43
5.22
5.20
3.77
3.74
3.68
3.55
3.53
3.52
3.50
3.15
3.14
3.13
3.11
2.06
1.70
1.42
CO2tBu
6-minor
2.11
1.01
1.16
1.10
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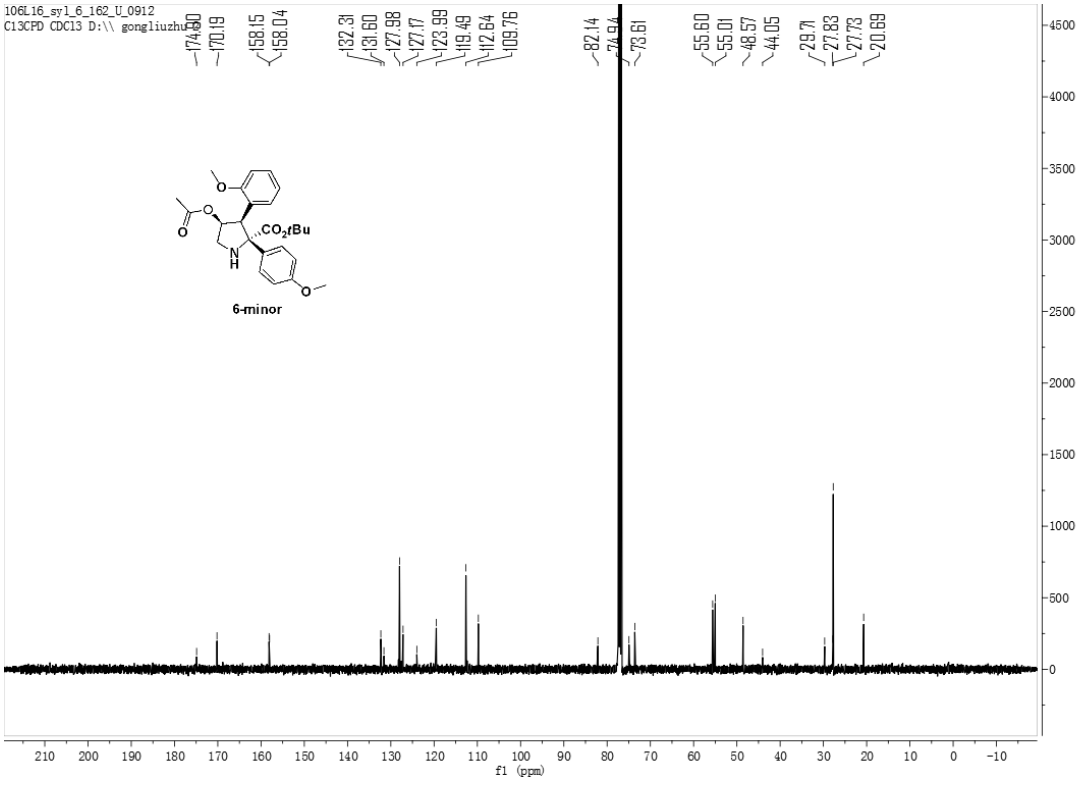
1.00
0.99
3.15
4.08
1.05
1.06
3.06
9.07
f1 (ppm)


106L16_syl_6_162_U_0912
C13CPD CDCl3 D:\\ gongliuzhu
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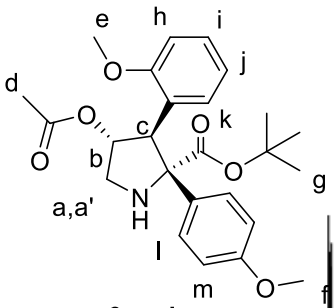
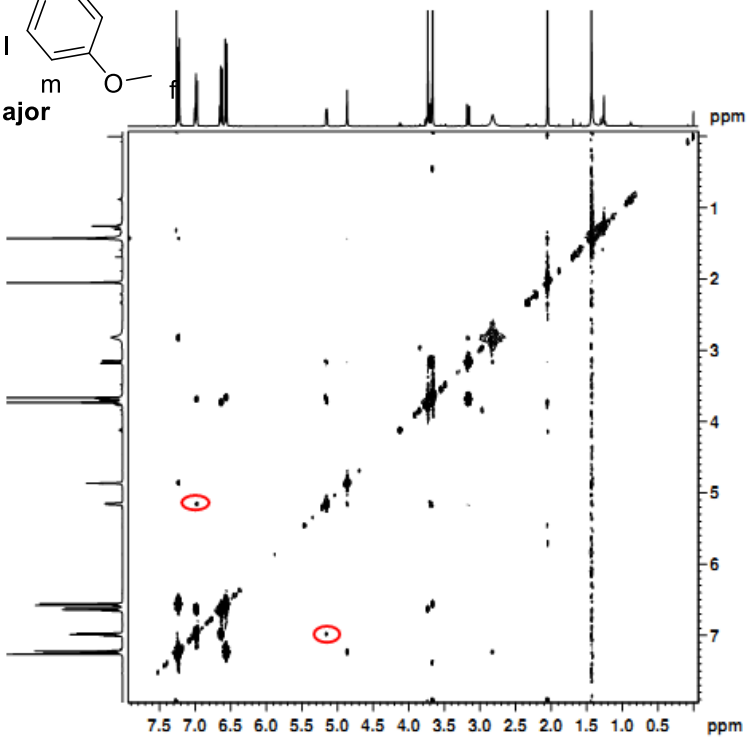
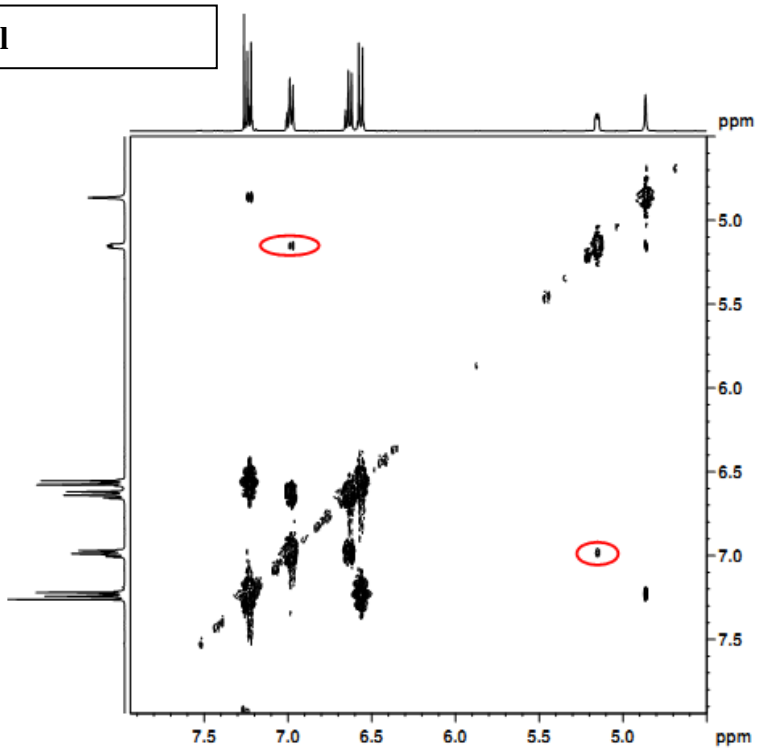
170.19
158.15
158.04
132.31
131.60
127.98
127.17
123.99
119.49
112.64
109.76
82.14
74.94
73.61
55.60
55.01
48.57
44.05
29.71
27.83
27.73
20.69
CO2tBu
6-minor
f1 (ppm)

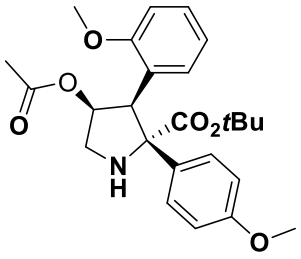


6-major

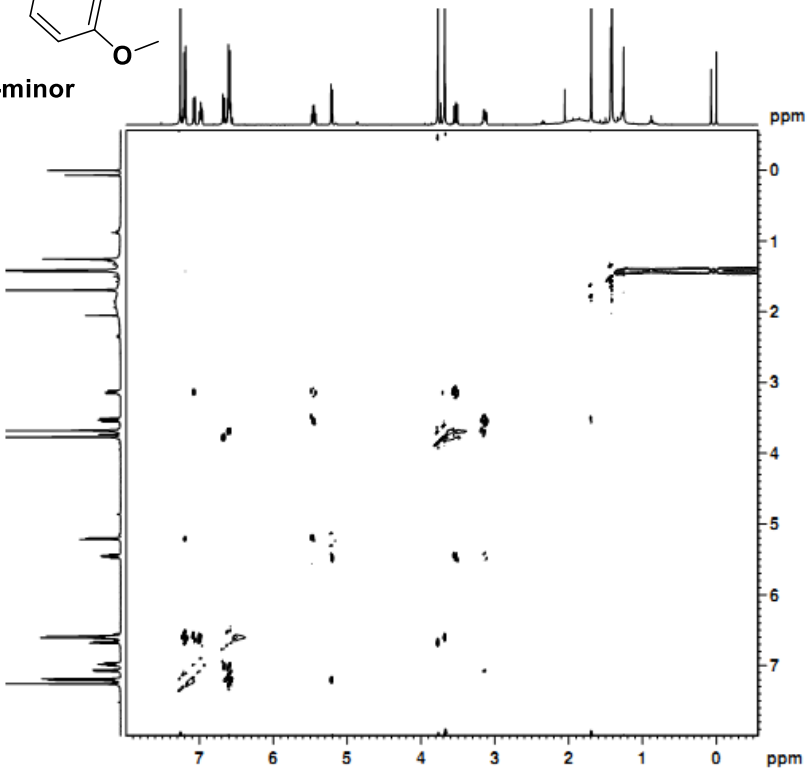


6-major partial

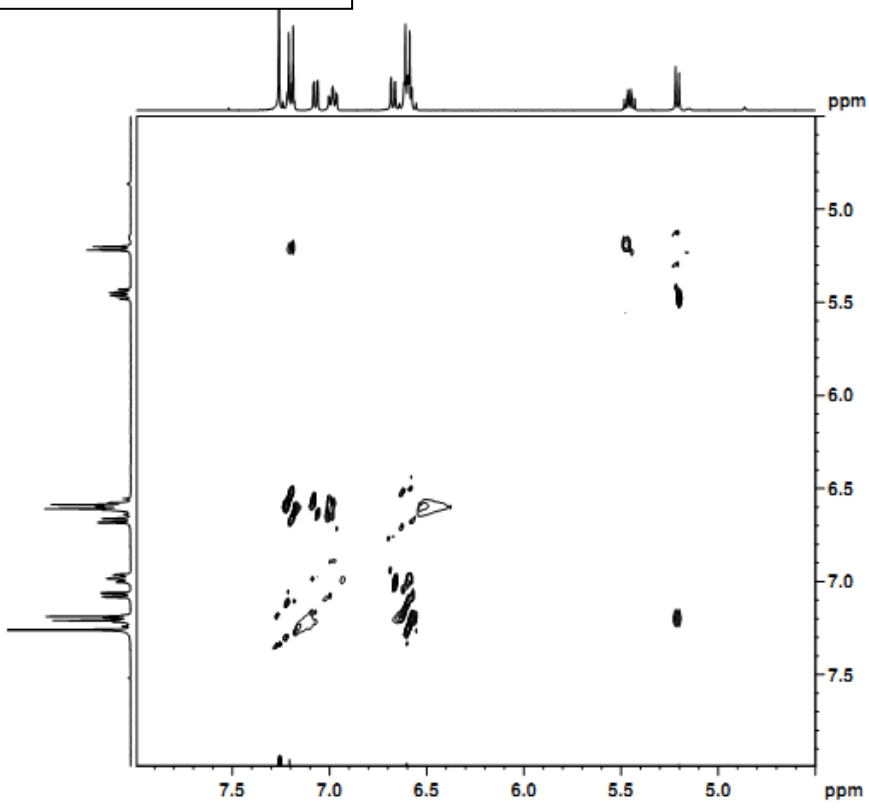




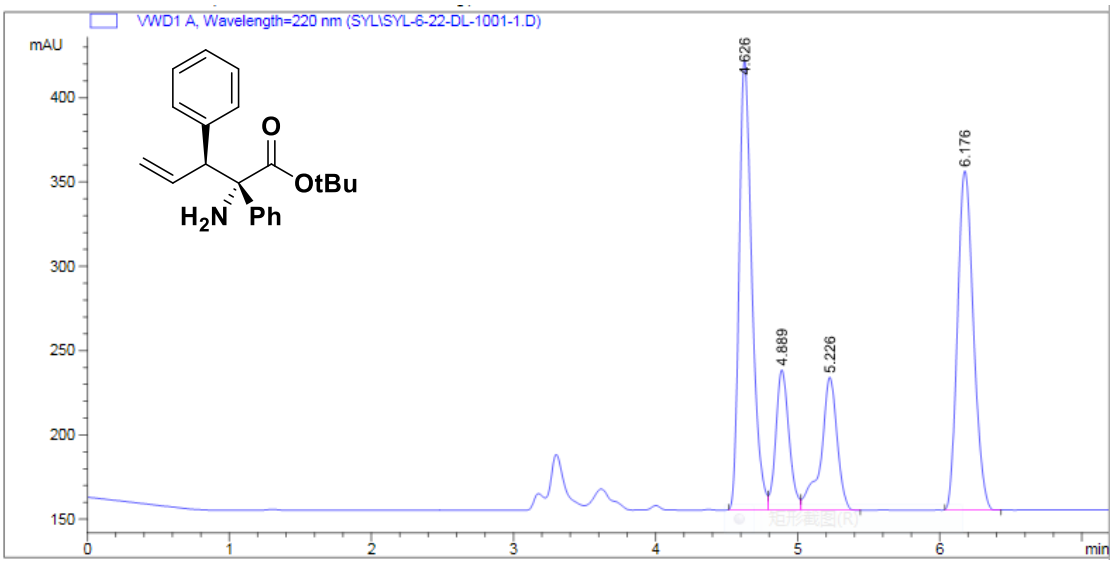
6-minor



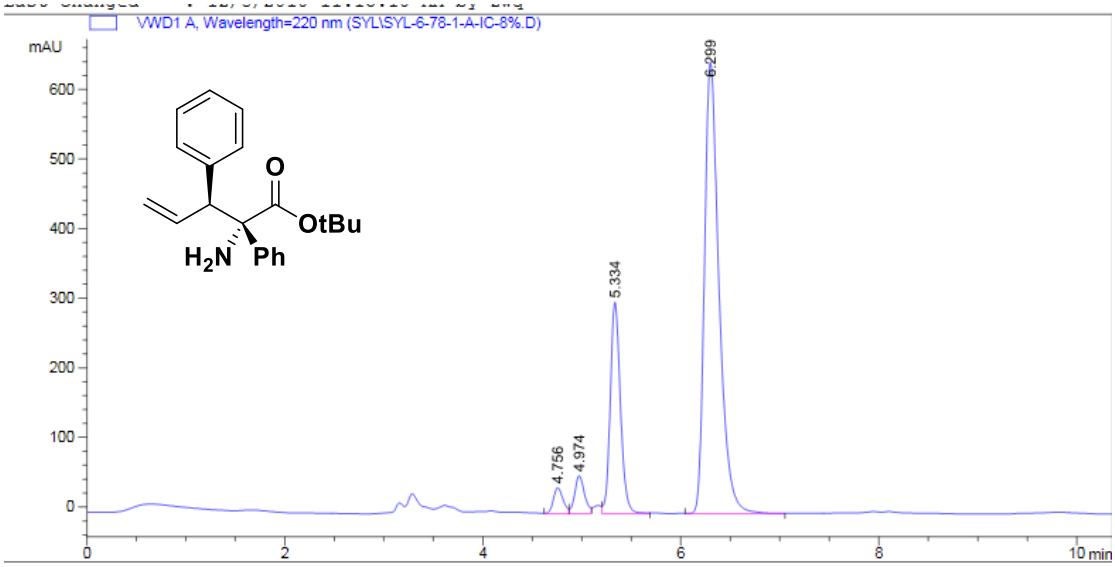
6-minor partial



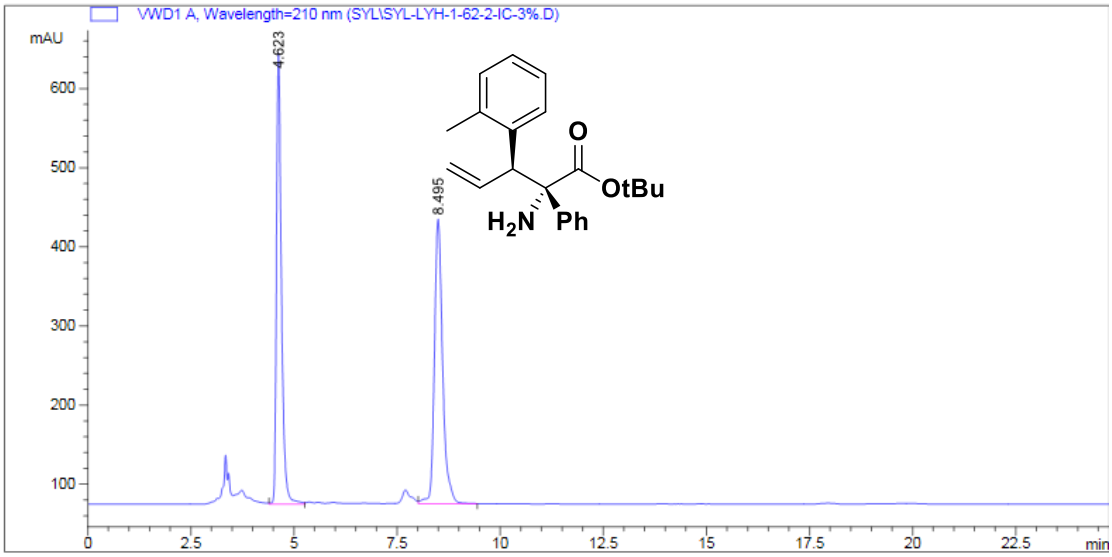
11. HPLC Data



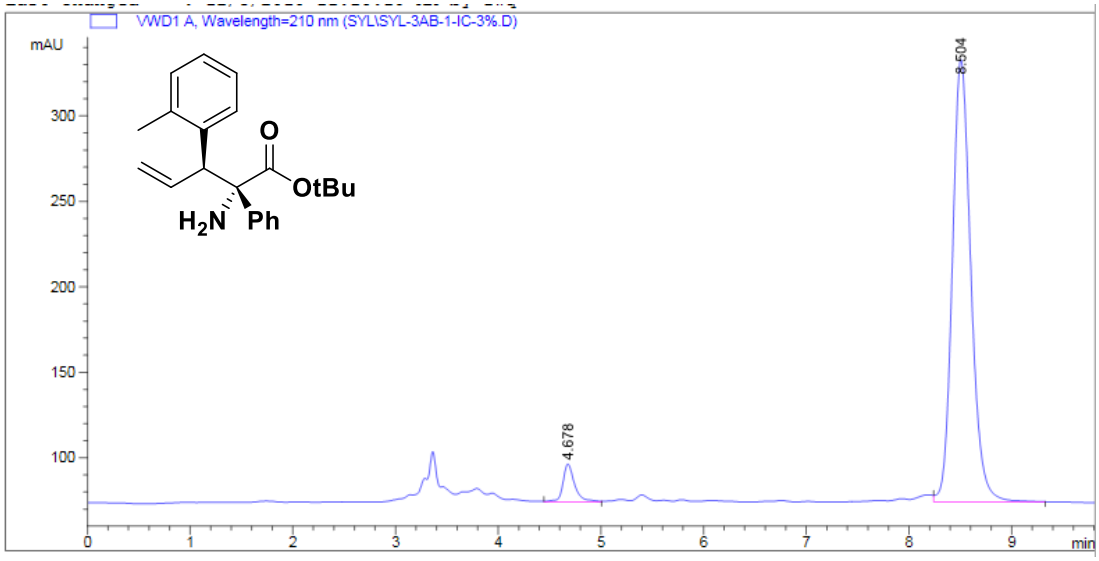
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.626	BV	0.0946	1664.73706	267.08313	37.8568
2	4.889	VV	0.0989	538.57343	83.15480	12.2474
3	5.226	VB	0.1176	626.52289	78.76604	14.2474
4	6.176	BB	0.1216	1567.62378	201.02400	35.6484



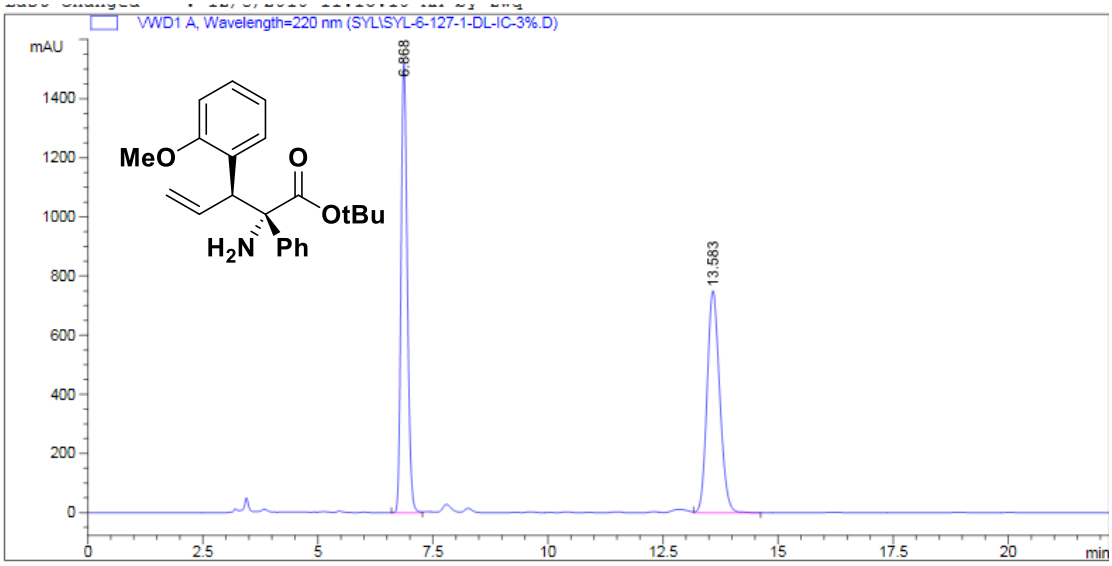
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.756	VV	0.1043	256.15799	37.58692	2.7168
2	4.974	VV	0.1036	375.48337	54.56294	3.9823
3	5.334	VV	0.1096	2174.23047	304.11163	23.0596
4	6.299	VB	0.1540	6622.88281	649.09631	70.2413



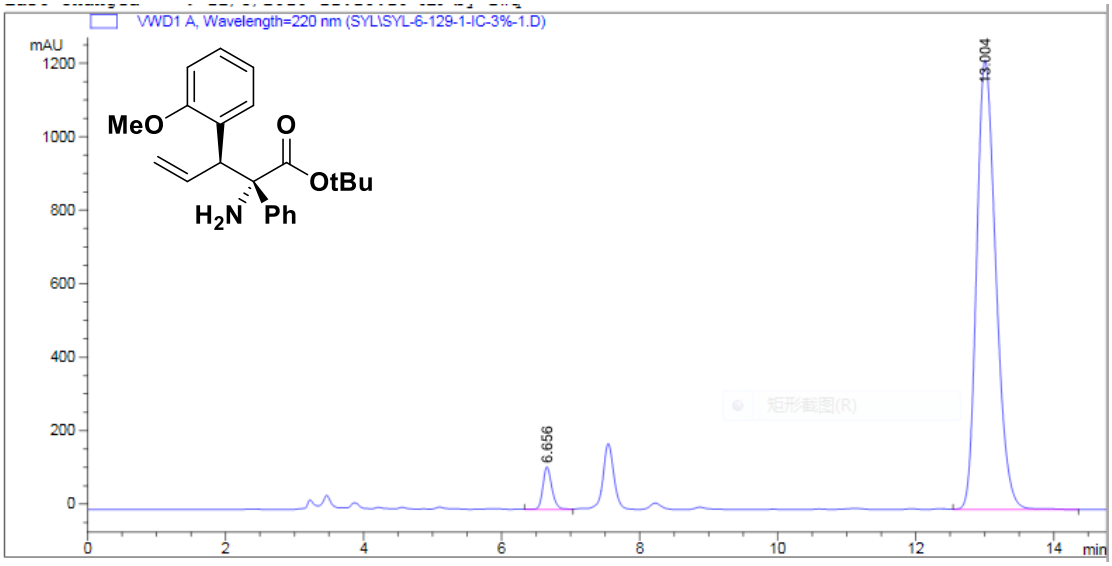
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.623	VV	0.1255	4783.83203	570.36462	48.8971
2	8.495	VB	0.2117	4999.64502	359.70532	51.1029



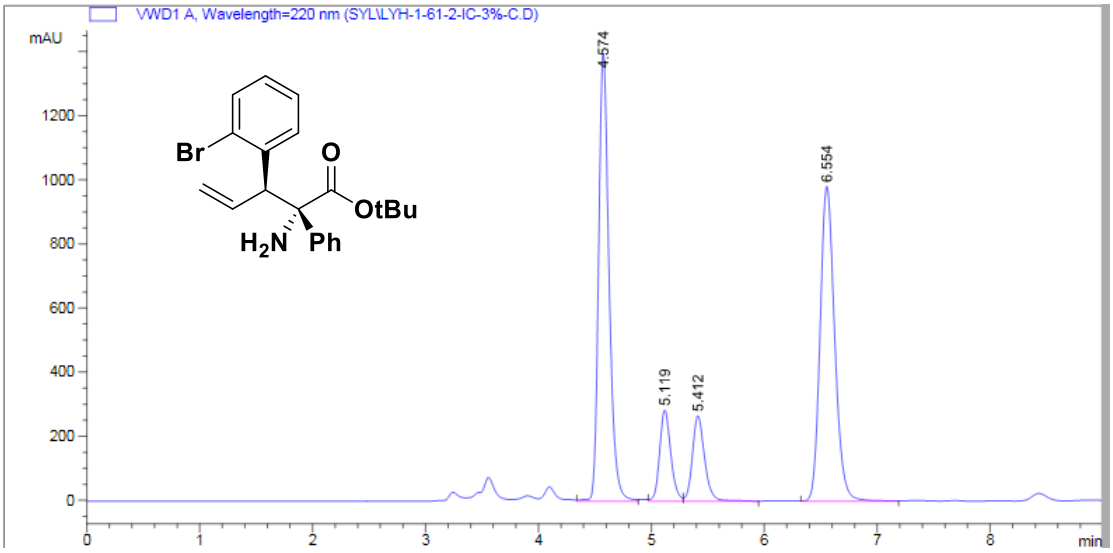
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.678	BV	0.1187	178.48561	22.15644	5.2060
2	8.504	VB	0.1931	3249.99463	258.80453	94.7940



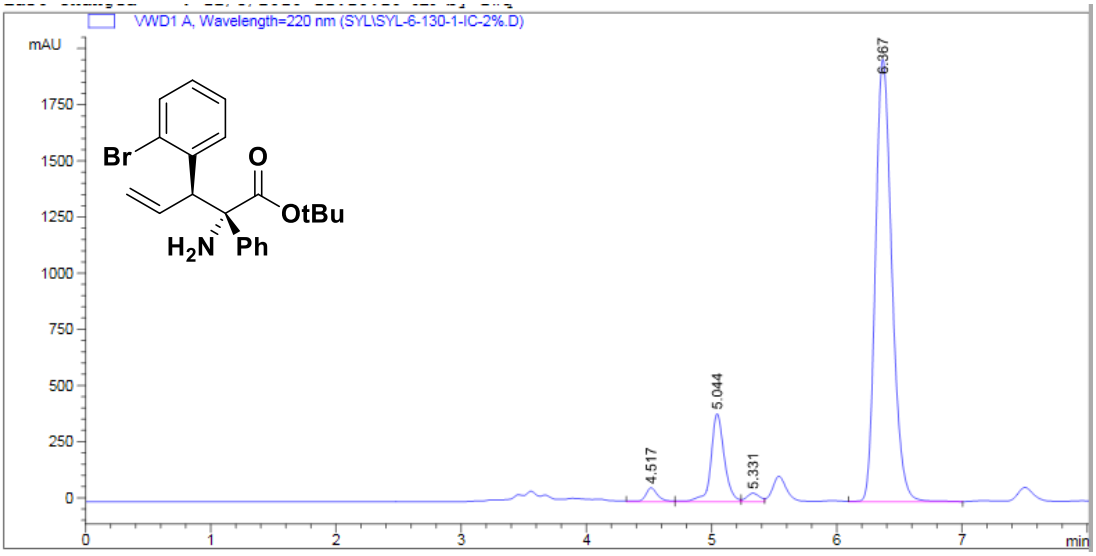
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.868	VV	0.1455	1.42599e4	1525.47522	49.8117
2	13.583	VB	0.2990	1.43678e4	750.63843	50.1883



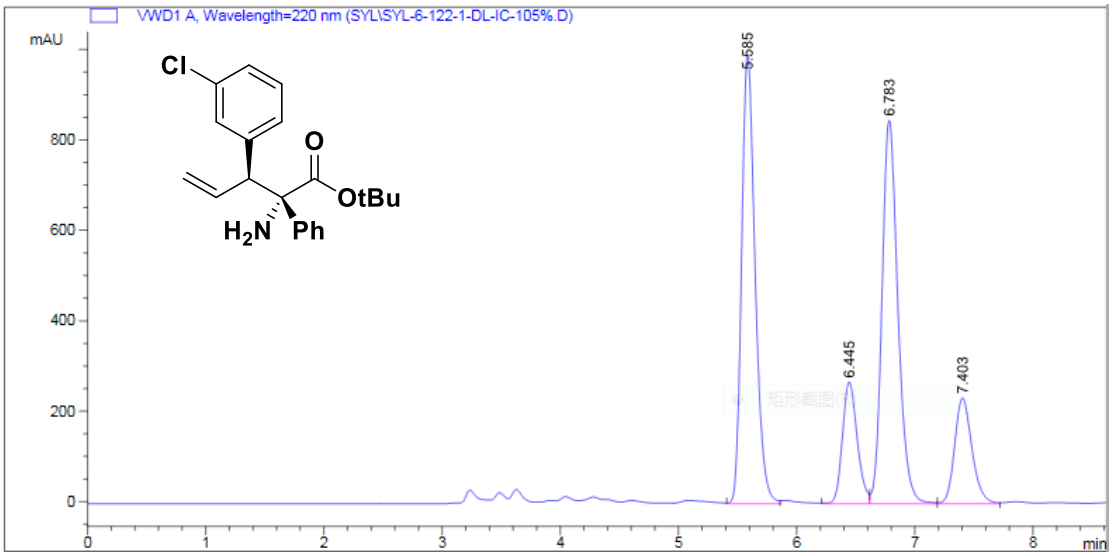
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.656	VV	0.1398	1071.02466	115.97517	4.3320
2	13.004	VB	0.3012	2.36526e4	1223.84521	95.6680



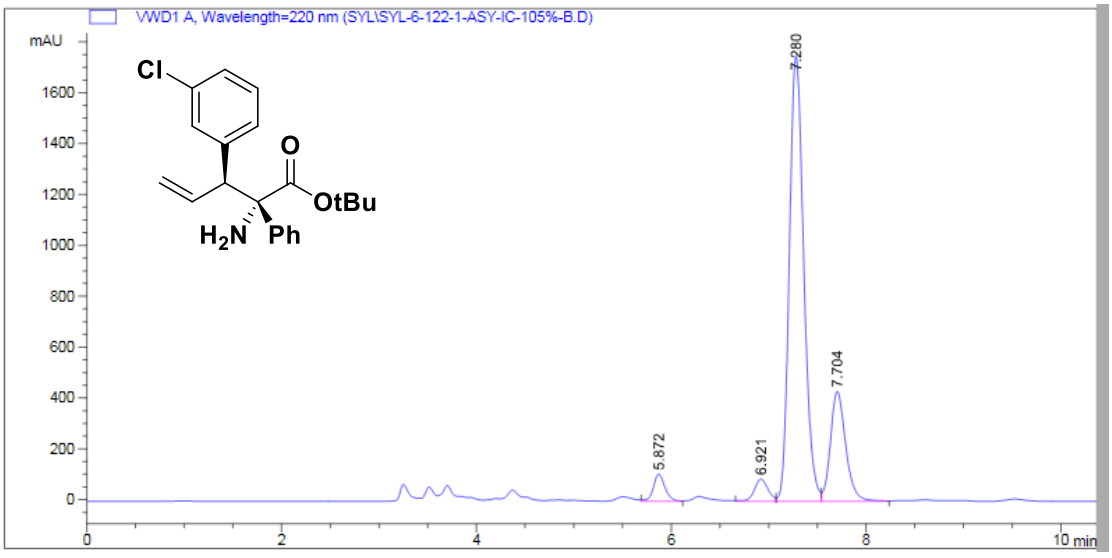
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.574	VV	0.0981	8978.67773	1400.25623	41.2361
2	5.119	VV	0.1065	1960.29468	284.95309	9.0030
3	5.412	VV	0.1157	2015.32471	266.92566	9.2557
4	6.554	VV	0.1382	8819.52930	983.06055	40.5052



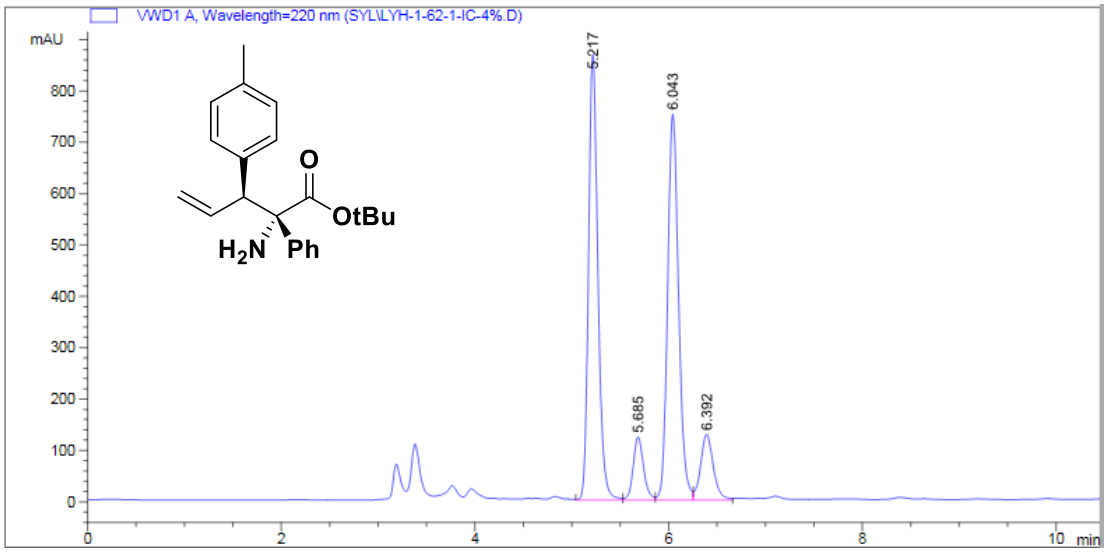
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.517	VV	0.1003	425.78748	62.16889	1.9697
2	5.044	VV	0.1111	2905.27417	392.72418	13.4397
3	5.331	VV	0.1102	275.07199	38.19458	1.2725
4	6.367	VV	0.1416	1.80110e4	1970.43469	83.3182



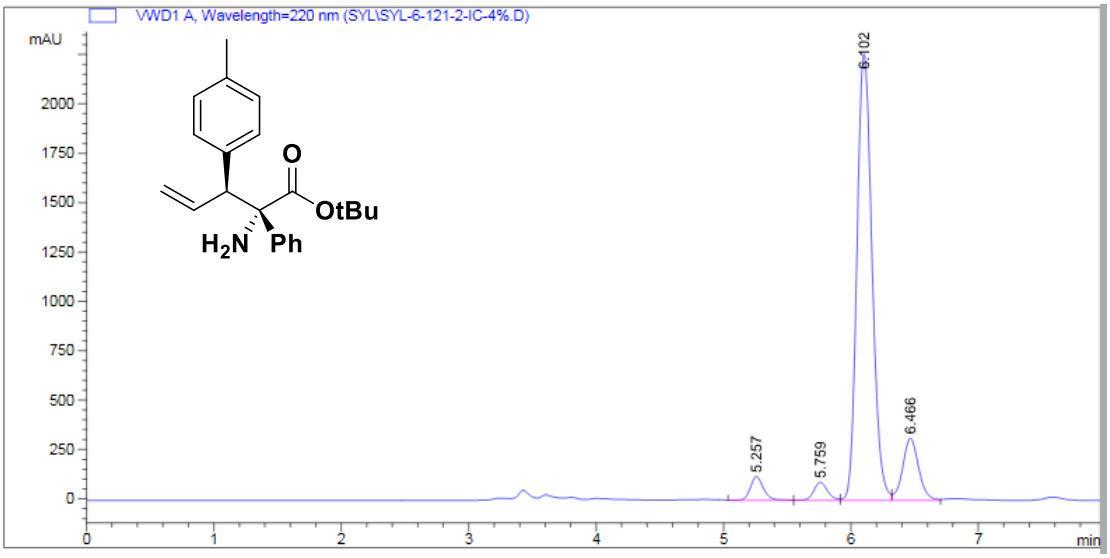
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.585	VV	0.1215	7874.87402	994.27972	38.3641
2	6.445	VV	0.1335	2345.31470	269.68839	11.4257
3	6.783	VV	0.1437	7909.11719	848.66016	38.5309
4	7.403	VV	0.1572	2397.38989	234.36644	11.6794



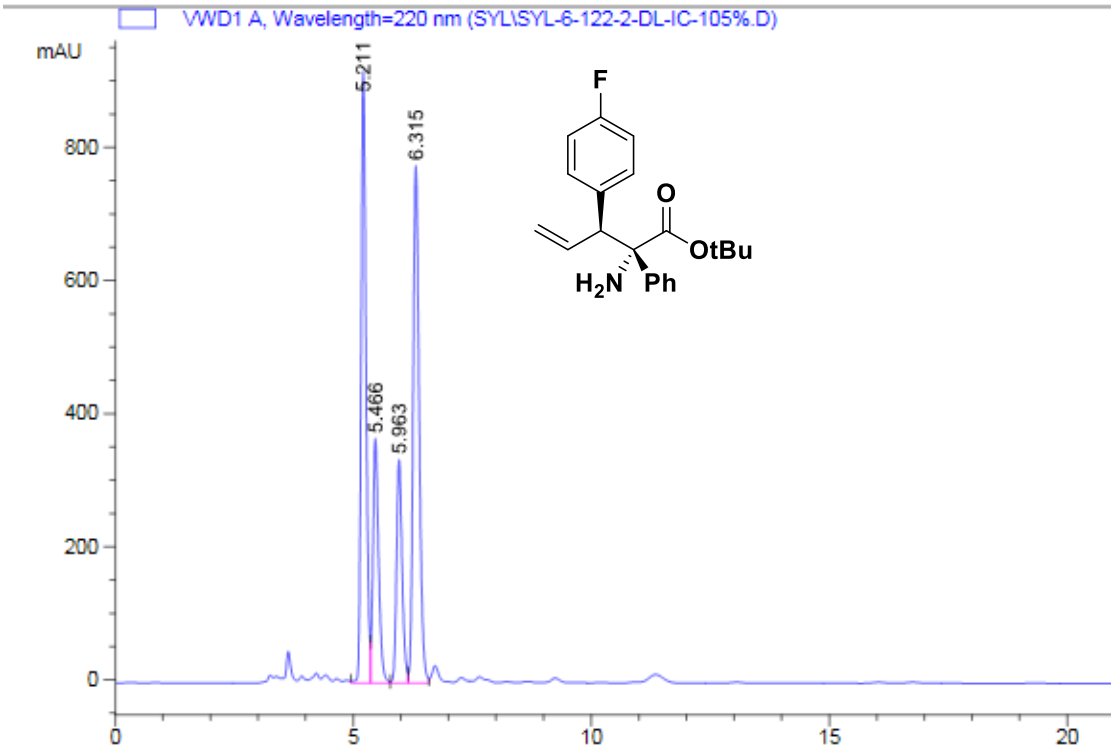
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.872	VV	0.1279	906.29004	107.02917	3.6983
2	6.921	VV	0.1486	858.31659	88.07263	3.5025
3	7.280	VV	0.1591	1.79942e4	1753.07129	73.4283
4	7.704	VV	0.1673	4746.97559	432.74091	19.3709



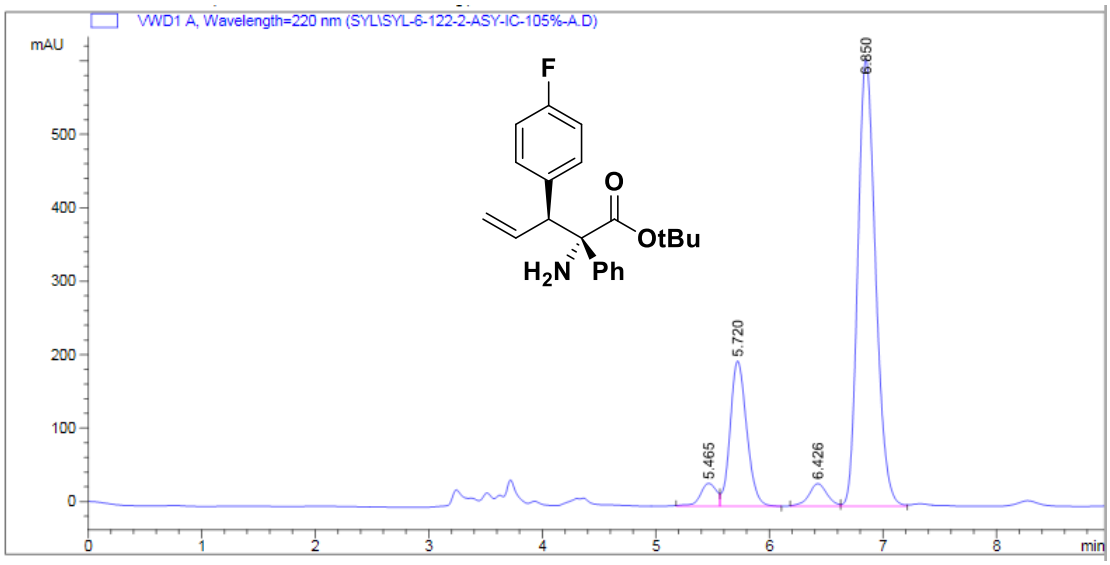
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.217	VV	0.1028	5810.57959	868.16418	42.1094
2	5.685	VV	0.1145	914.31915	122.82539	6.6261
3	6.043	VV	0.1222	5904.13916	751.96149	42.7874
4	6.392	VV	0.1404	1169.74194	127.68608	8.4771



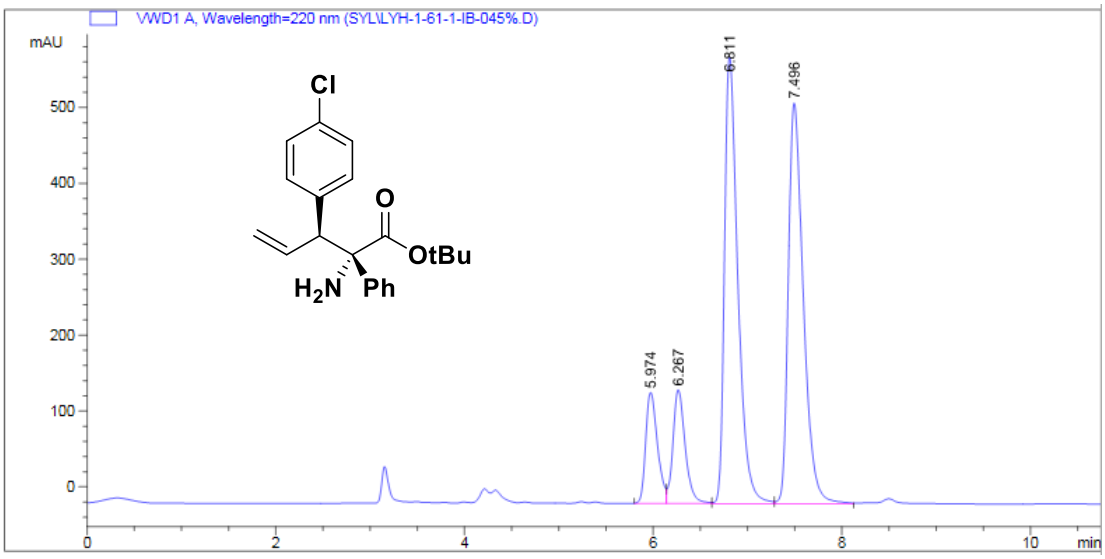
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.257	VV	0.1107	892.76685	121.15079	3.8952
2	5.759	VV	0.1171	704.91785	91.97272	3.0756
3	6.102	VV	0.1279	1.85729e4	2260.57446	81.0350
4	6.466	VV	0.1337	2749.03418	315.52789	11.9942



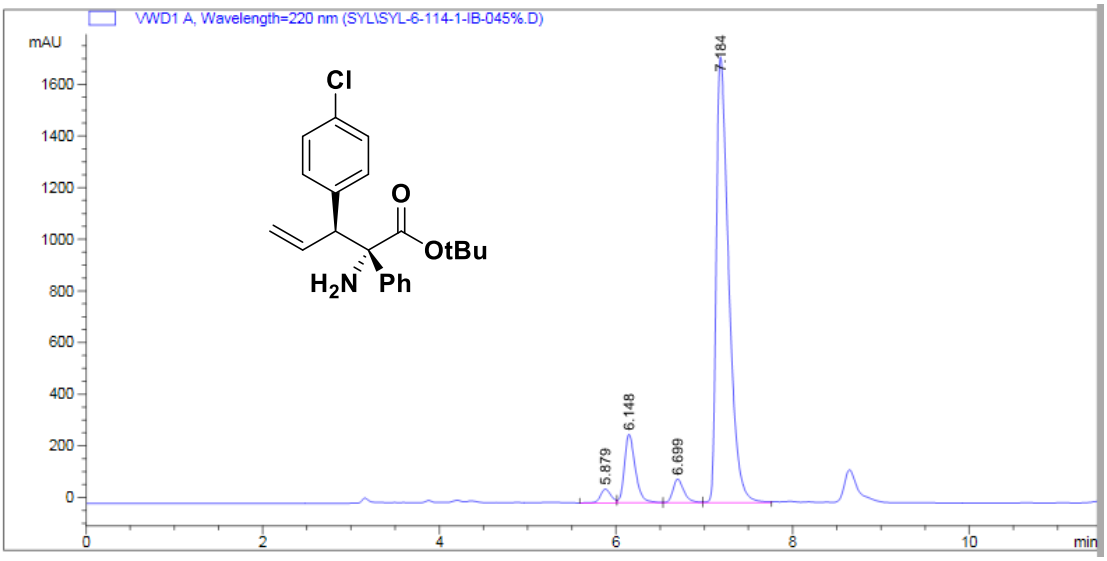
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.211	VV	0.1095	6567.09473	919.30725	34.2370
2	5.466	VV	0.1239	3029.56201	367.38980	15.7944
3	5.963	VV	0.1241	2735.37915	335.86105	14.2607
4	6.315	VV	0.1363	6849.23291	777.34583	35.7079



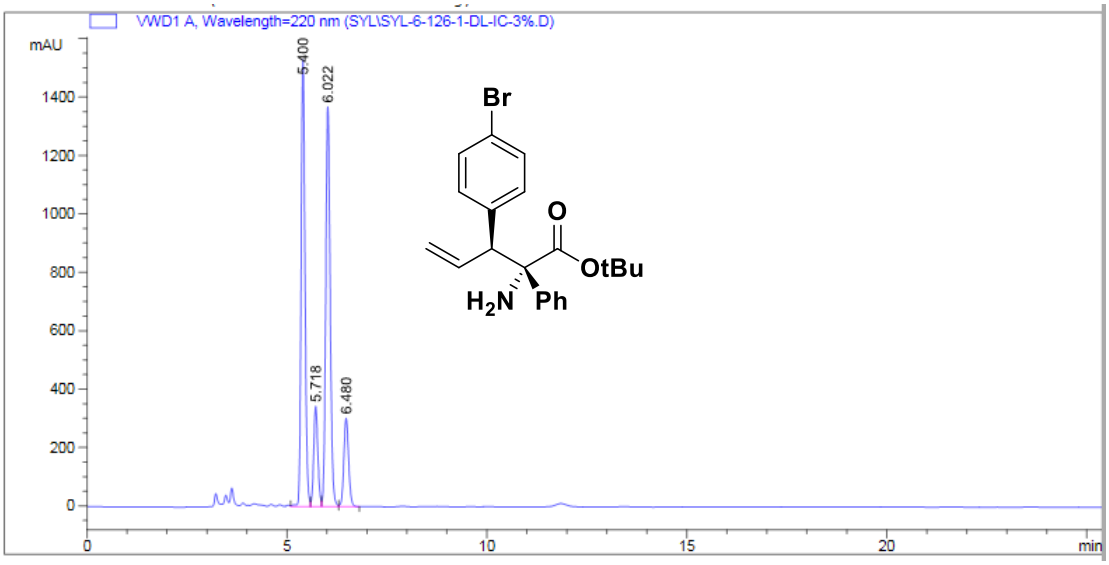
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.465	BV	0.1529	304.77878	30.90909	3.2925
2	5.720	VB	0.1574	2000.72241	197.58469	21.6134
3	6.426	BV	0.1670	341.25531	30.82786	3.6865
4	6.850	VV	0.1689	6610.11475	608.76031	71.4077



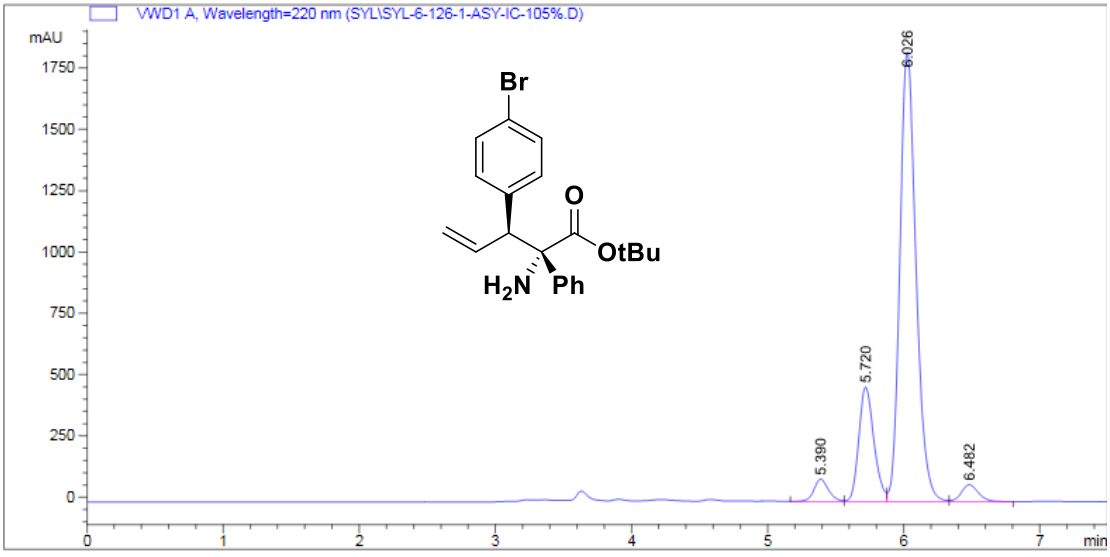
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.974	BV	0.1319	1275.63196	146.81128	8.9444
2	6.267	VV	0.1380	1362.85522	150.07509	9.5560
3	6.811	VV	0.1496	5787.04297	589.10675	40.5772
4	7.496	VB	0.1682	5836.26953	528.37860	40.9224



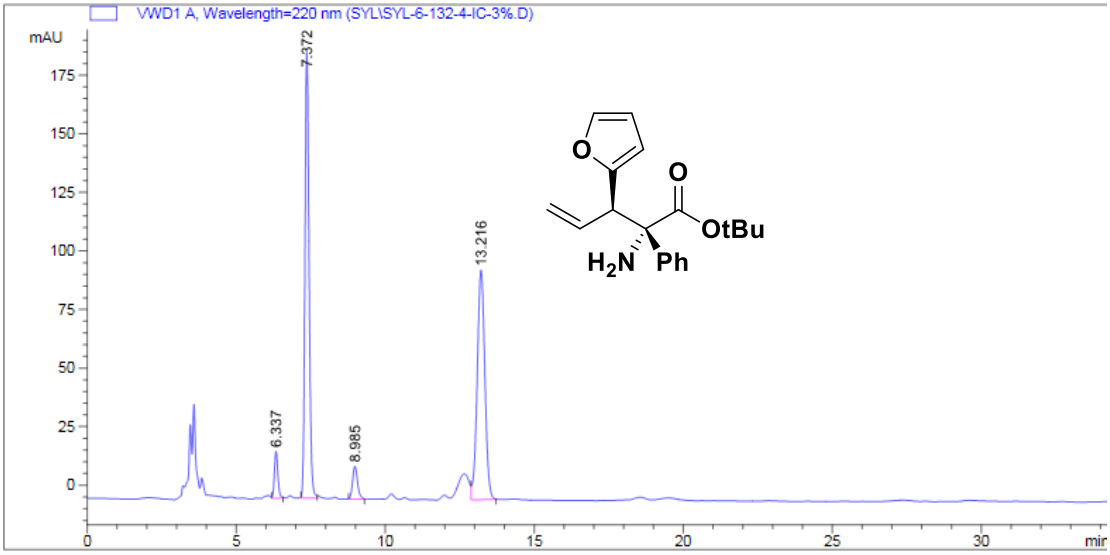
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.879	VV	0.1263	449.76904	54.01993	2.1906
2	6.148	VV	0.1313	2297.90479	266.12900	11.1918
3	6.699	VV	0.1345	823.63245	92.46188	4.0114
4	7.184	VB	0.1494	1.69608e4	1729.08691	82.6062



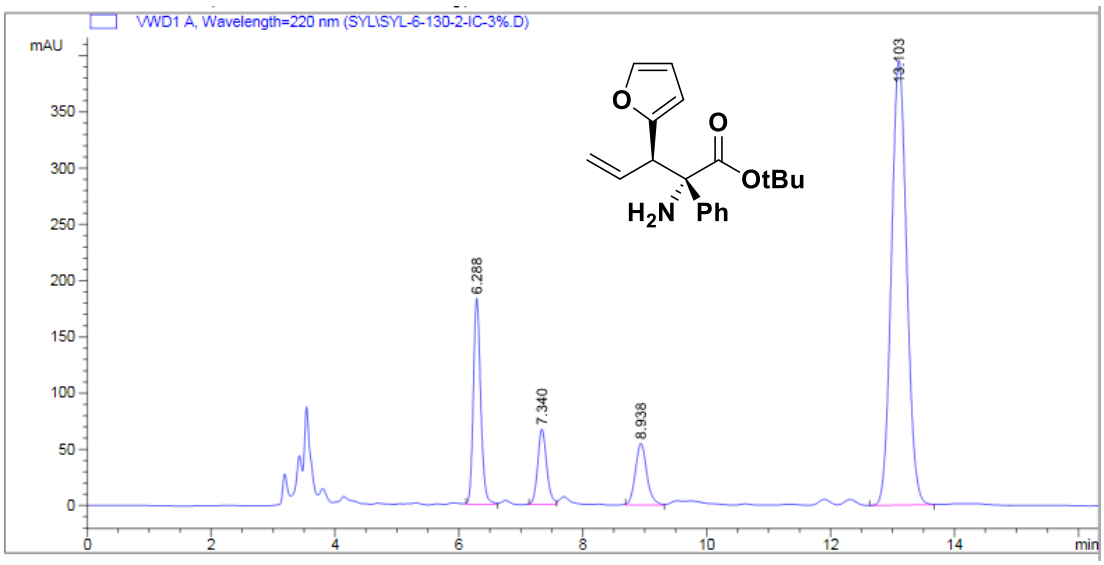
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.400	VV	0.1049	1.03339e4	1532.03418	39.8029
2	5.718	VV	0.1128	2512.32739	344.28156	9.6767
3	6.022	VV	0.1194	1.05906e4	1369.24255	40.7917
4	6.480	VB	0.1277	2525.80981	303.38721	9.7286



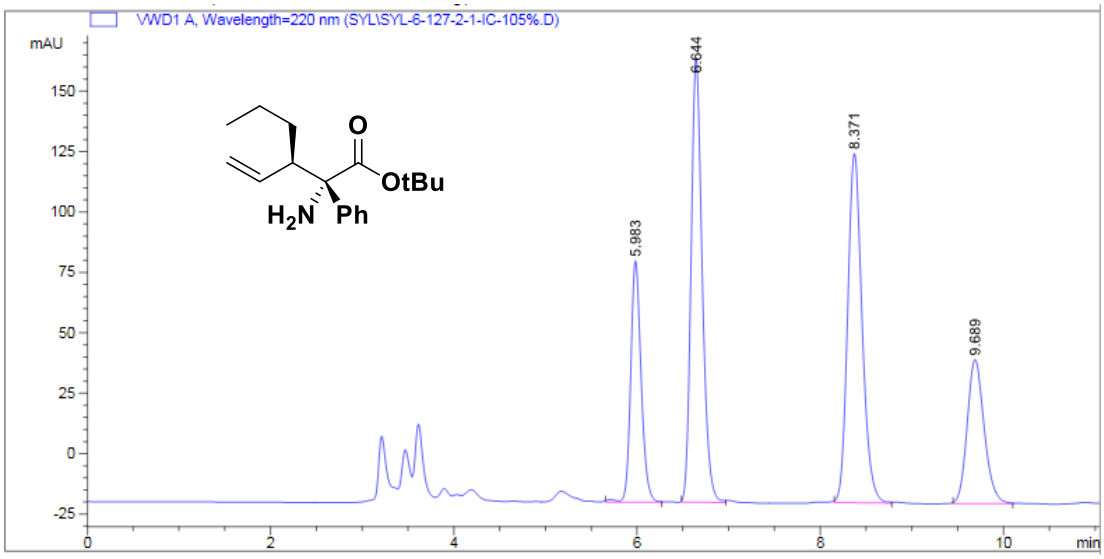
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.390	VV	0.1168	715.28308	92.13207	3.5564
2	5.720	VV	0.1196	3629.34229	467.91174	18.0453
3	6.026	VV	0.1284	1.51419e4	1834.03418	75.2867
4	6.482	VB	0.1363	625.81006	70.03636	3.1116



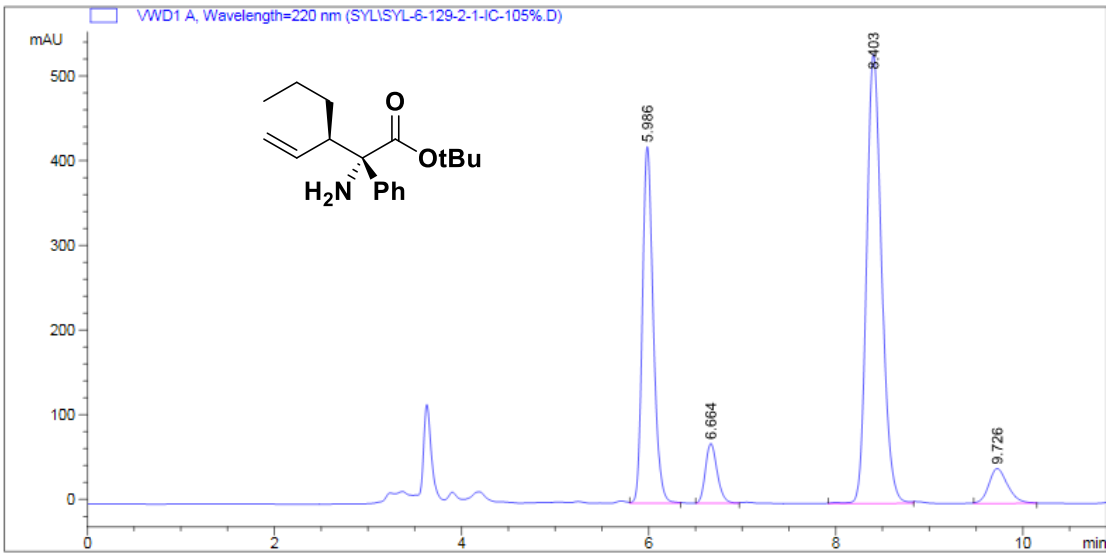
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.337	BB	0.1230	161.13722	20.02720	4.1432
2	7.372	BB	0.1477	1815.75256	190.30737	46.6868
3	8.985	BB	0.1777	162.51727	13.99810	4.1787
4	13.216	VB	0.2753	1749.81470	97.98747	44.9914



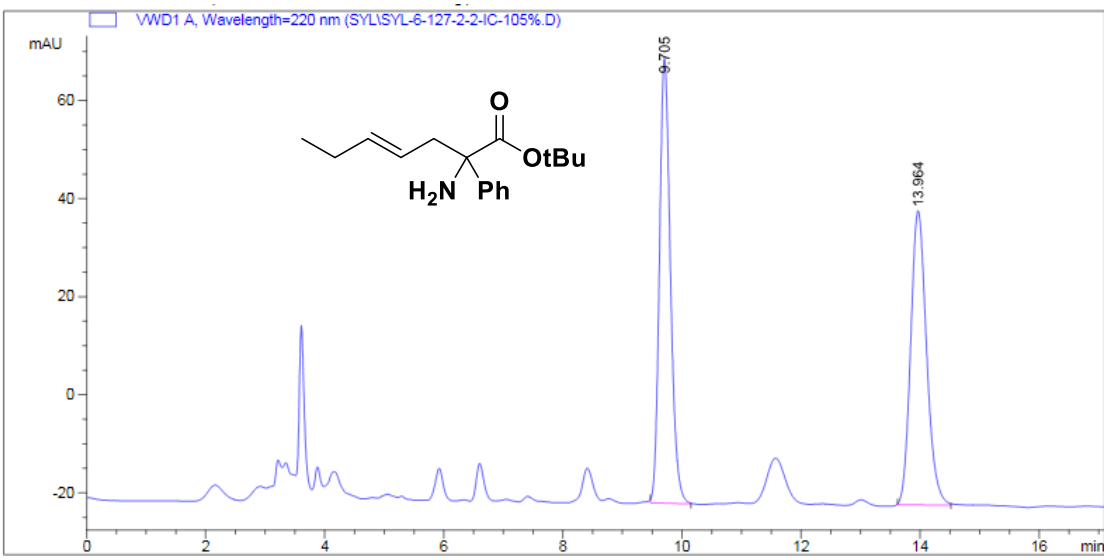
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.288	BV	0.1269	1513.81641	183.39919	15.6213
2	7.340	BV	0.1542	677.14215	67.06628	6.9875
3	8.938	BV	0.1982	704.49597	54.73976	7.2698
4	13.103	VB	0.2674	6795.28271	395.57550	70.1214



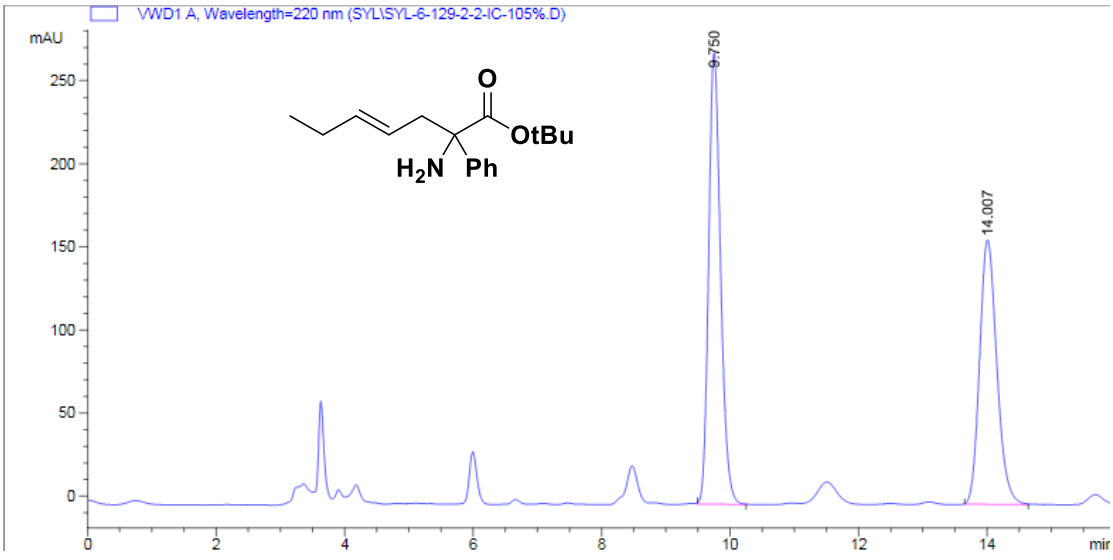
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.983	BB	0.1206	782.88062	99.89395	16.6220
2	6.644	BB	0.1299	1564.46655	183.84996	33.2165
3	8.371	BB	0.1690	1588.11646	144.53581	33.7186
4	9.689	BB	0.1994	774.44617	59.68591	16.4429



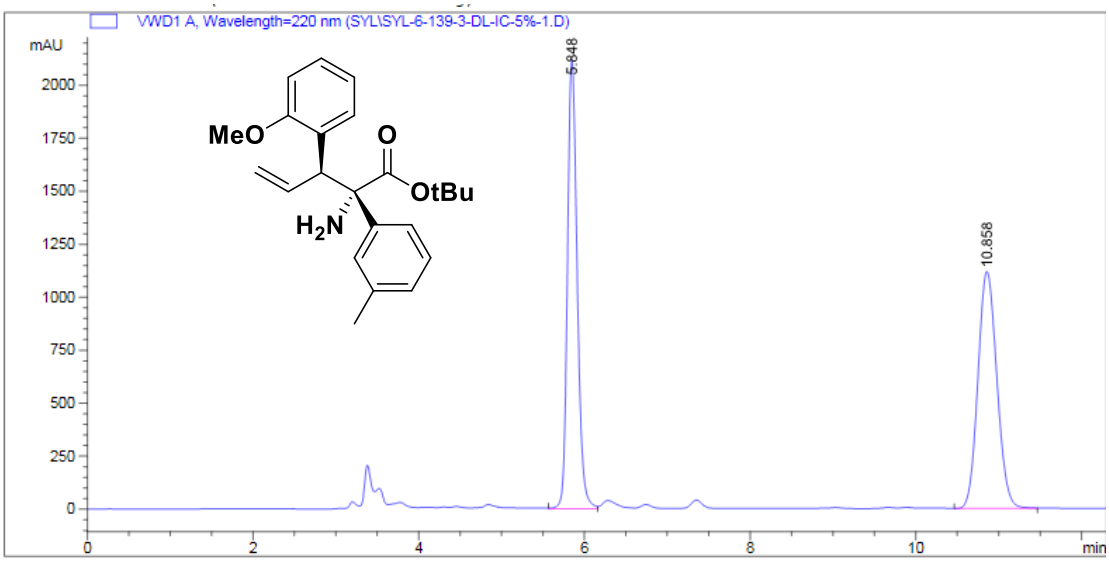
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.986	VB	0.1250	3407.38428	421.21509	32.2533
2	6.664	BB	0.1346	610.31421	70.42142	5.7770
3	8.403	BB	0.1733	5960.13281	530.31769	56.4168
4	9.726	BB	0.2168	586.63013	41.26667	5.5529



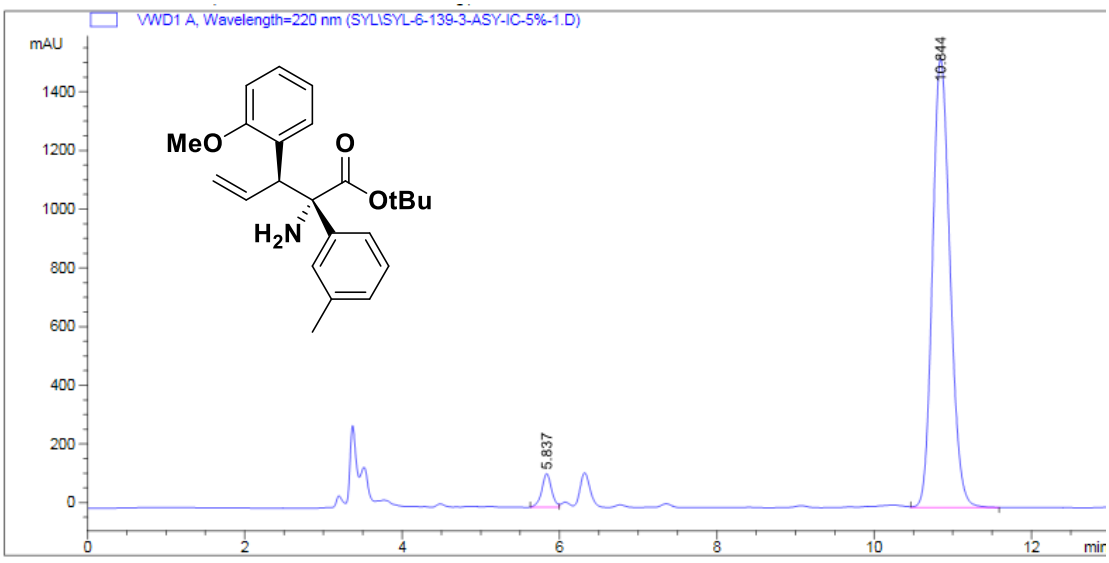
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.705	BB	0.1956	1158.90149	90.71311	51.0564
2	13.964	BB	0.2860	1110.94299	59.96161	48.9436



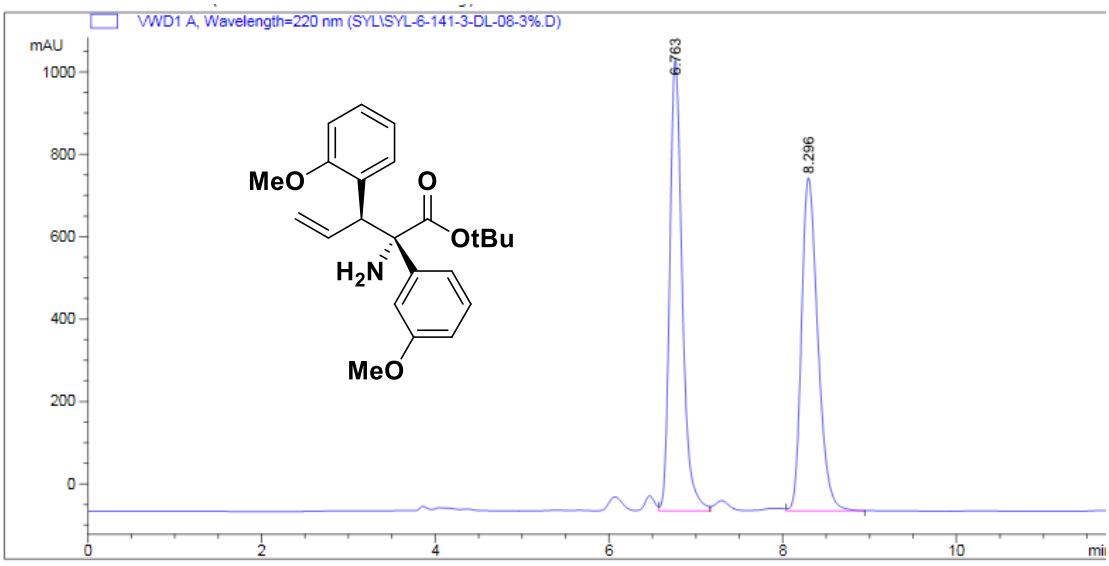
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	9.750	BB	0.1983	3497.63647	271.62146	54.1641
2	14.007	BB	0.2869	2959.84521	159.14784	45.8359



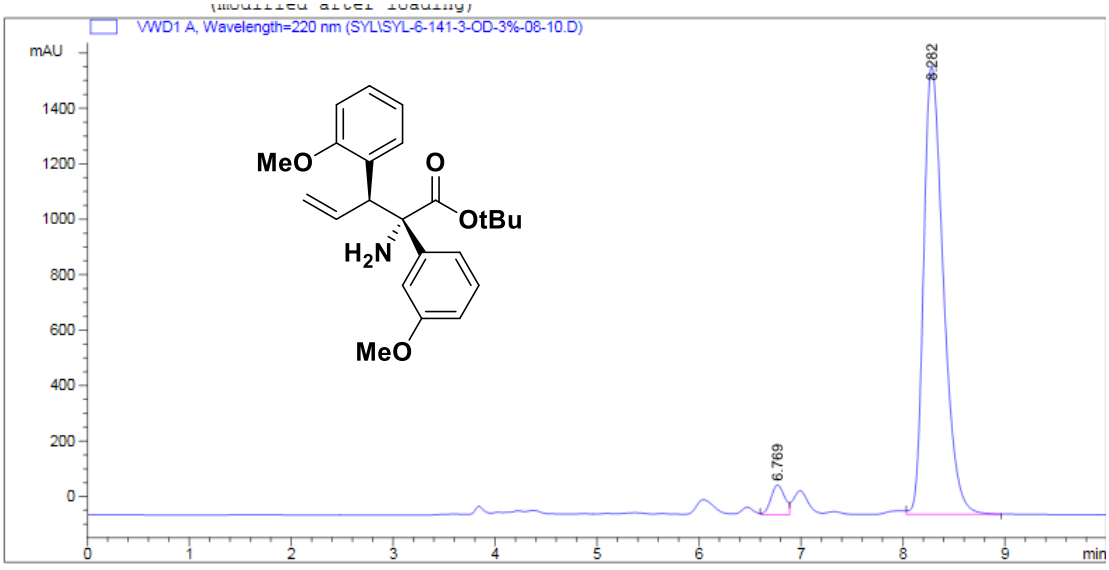
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.848	VV	0.1258	1.72773e4	2117.50293	49.3361
2	10.858	VB	0.2491	1.77424e4	1118.49231	50.6639



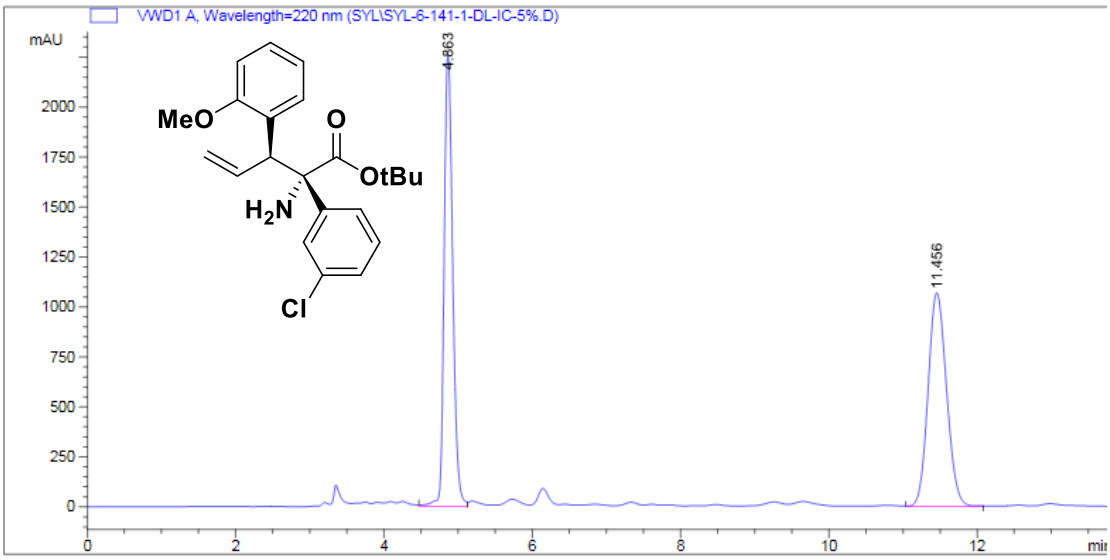
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.837	BV	0.1323	1002.32806	114.93716	4.0449
2	10.844	VB	0.2423	2.37776e4	1531.71509	95.9551



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.763	VV	0.1527	1.09179e4	1095.01111	50.8132
2	8.296	VB	0.2020	1.05684e4	808.65082	49.1868

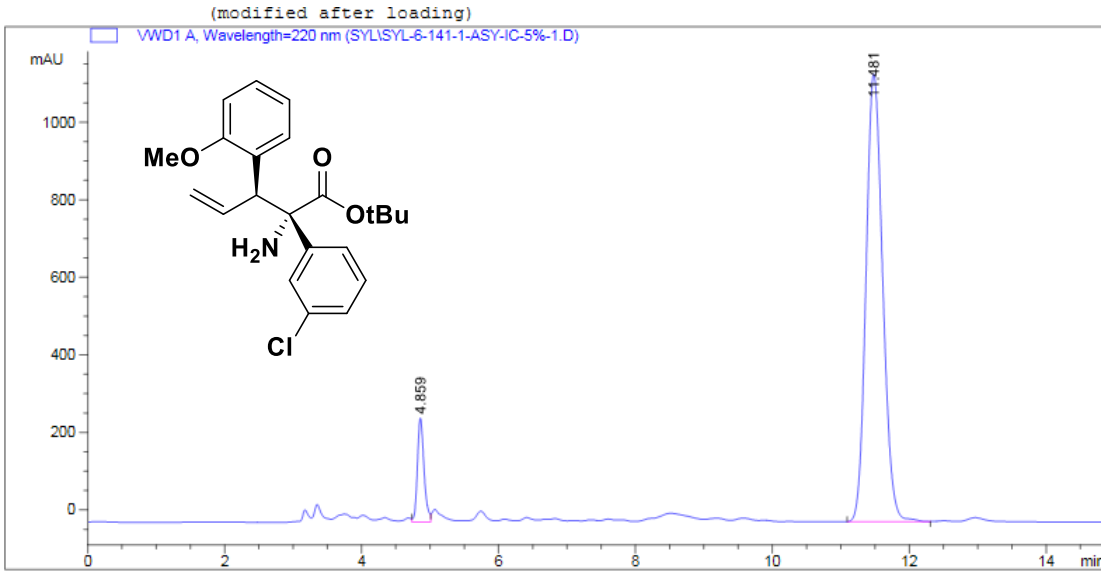


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.769	VV	0.1425	1002.95630	107.34361	4.3980
2	8.282	VB	0.2079	2.18020e4	1620.30066	95.6020

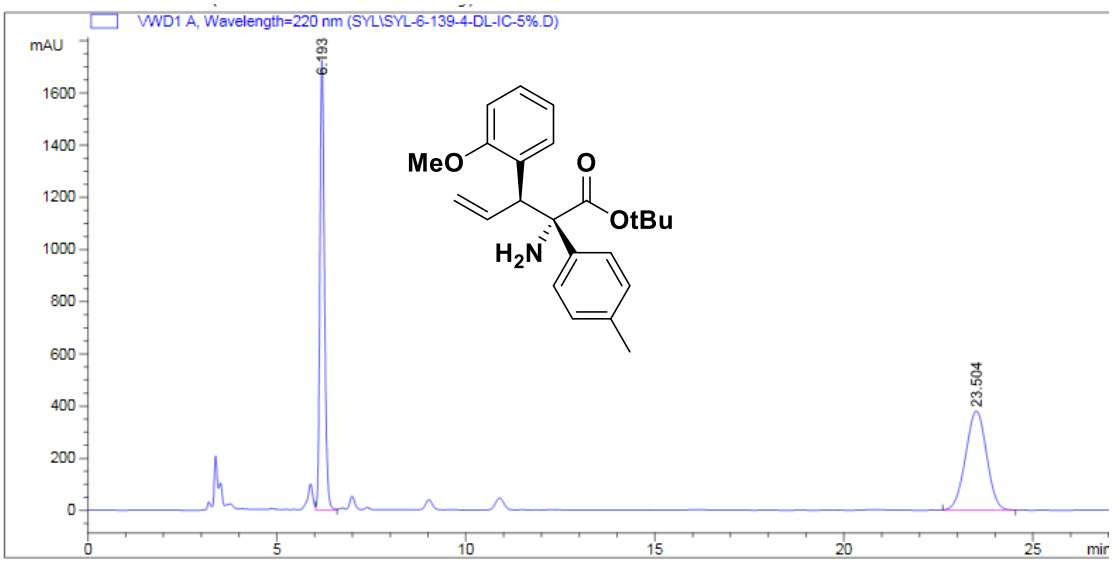


Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.863	VV	0.1249	1.82808e4	2261.46069	49.7436
2	11.456	VB	0.2714	1.84693e4	1069.17224	50.2564

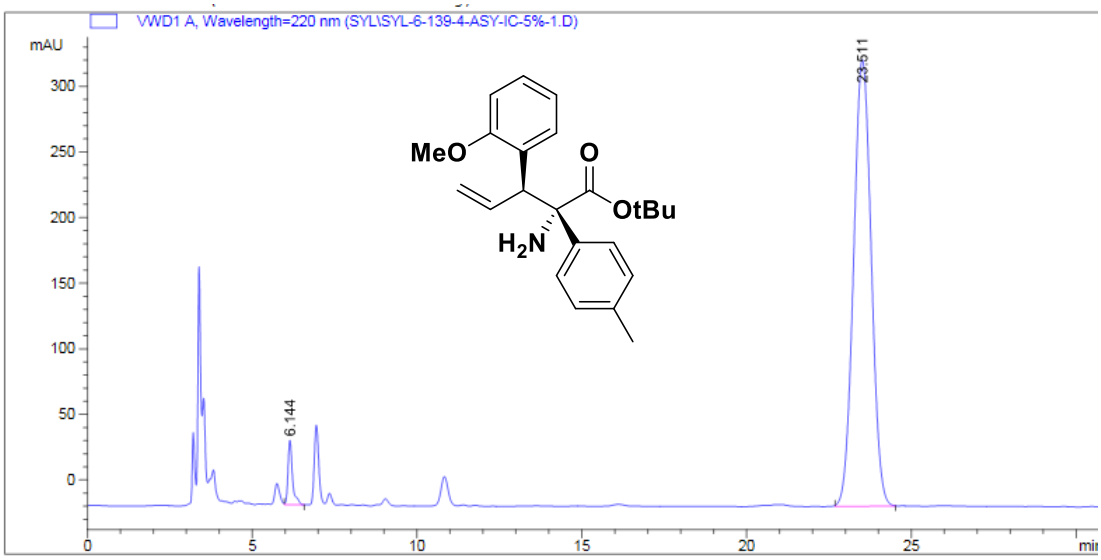
(modified after loading)



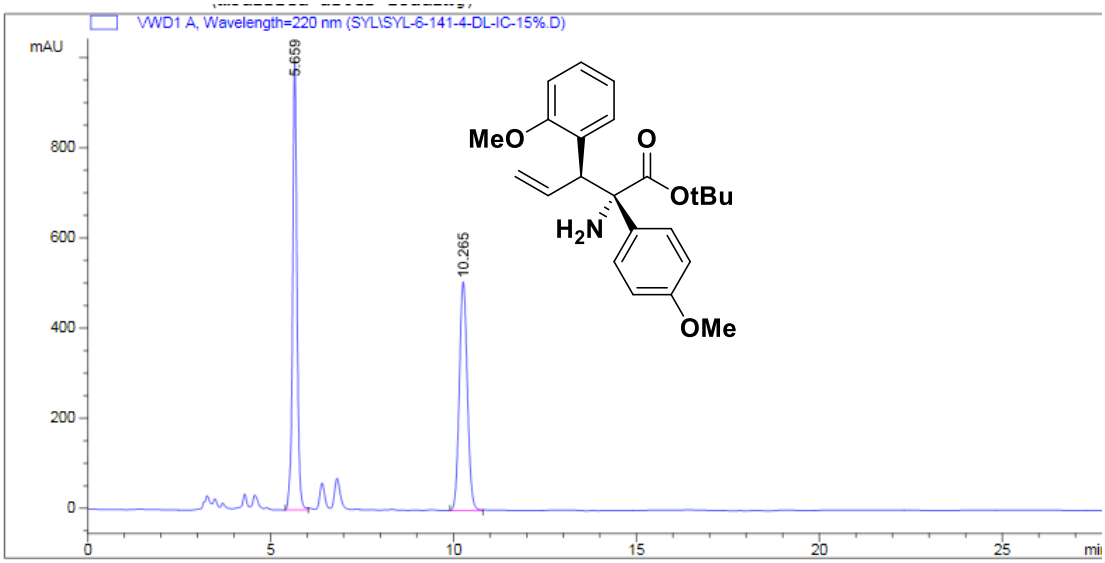
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.859	VV	0.1030	1801.72961	268.48557	8.4470
2	11.481	BB	0.2641	1.95282e4	1155.54675	91.5530



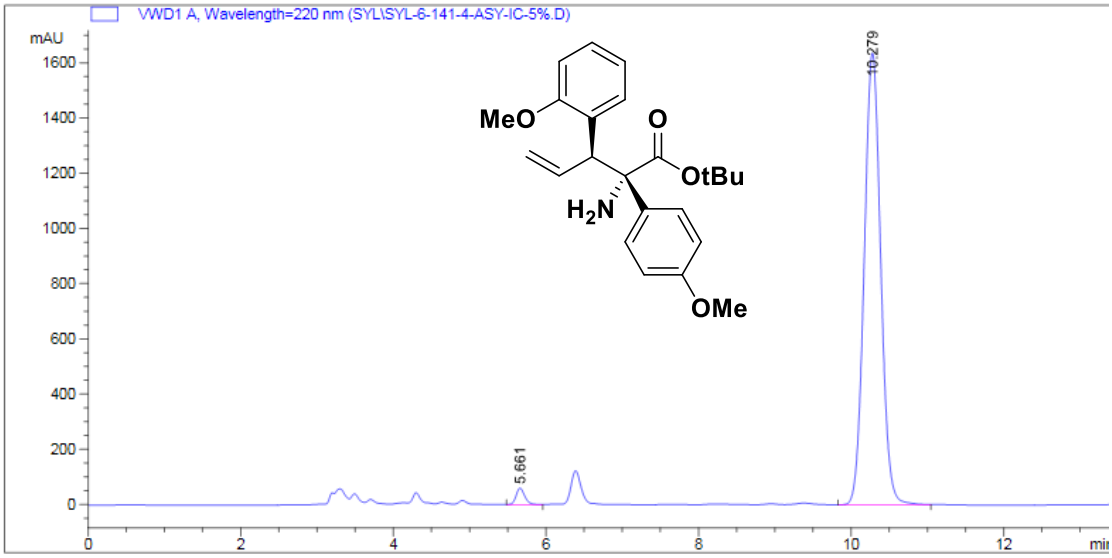
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.193	VV	0.1284	1.44611e4	1724.43689	49.6413
2	23.504	BB	0.6052	1.46701e4	379.61639	50.3587



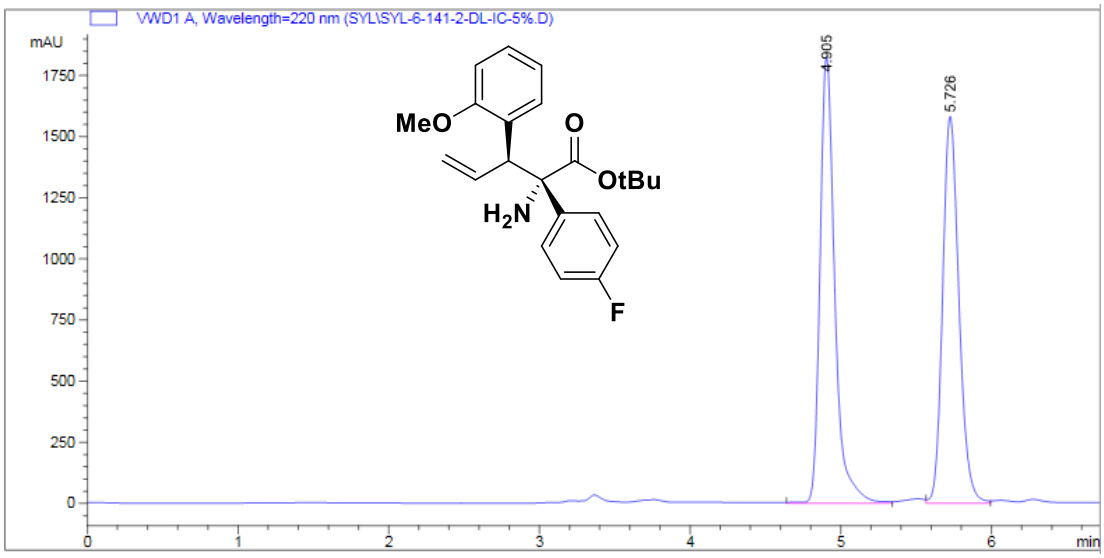
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	6.144	VB	0.1429	466.34137	49.06750	3.5551
2	23.511	BB	0.5852	1.26513e4	340.28830	96.4449



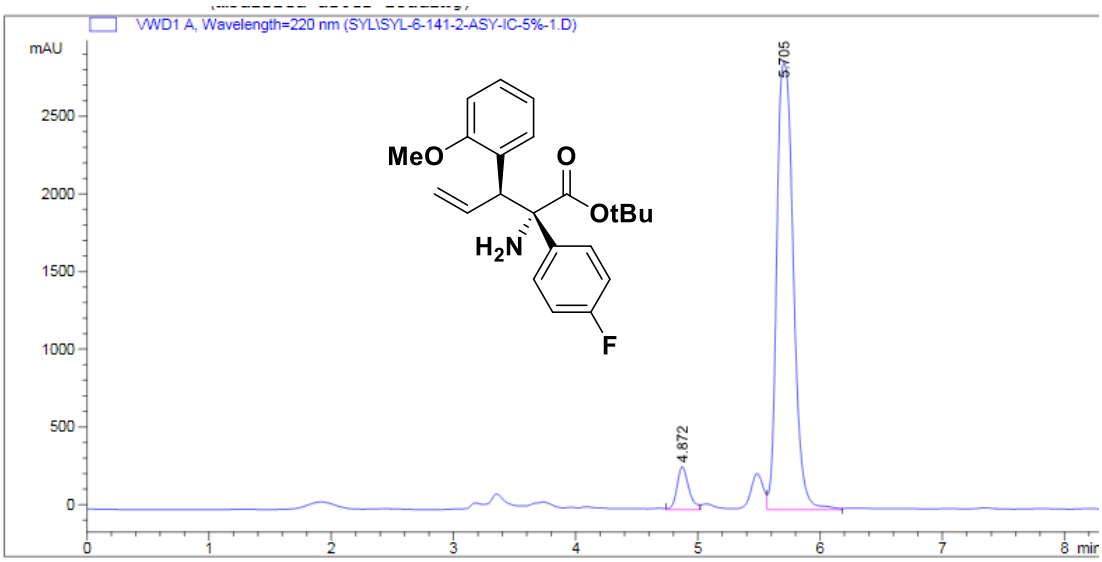
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.659	BB	0.1253	8324.59180	994.94403	51.8162
2	10.265	BB	0.2377	7741.01904	507.30960	48.1838



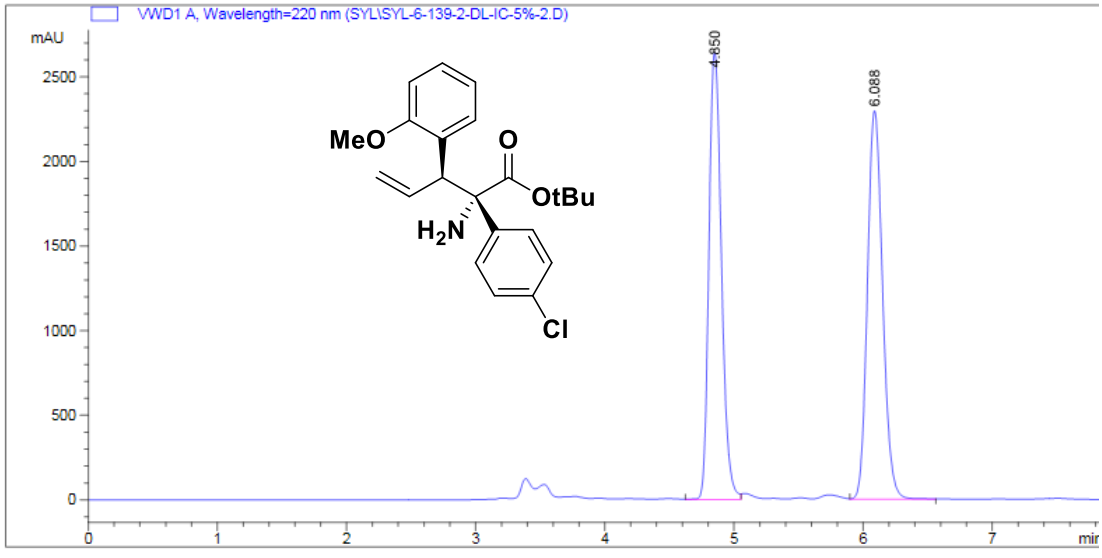
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.661	BB	0.1244	492.59399	60.31541	1.9673
2	10.279	VB	0.2332	2.45469e4	1637.21631	98.0327



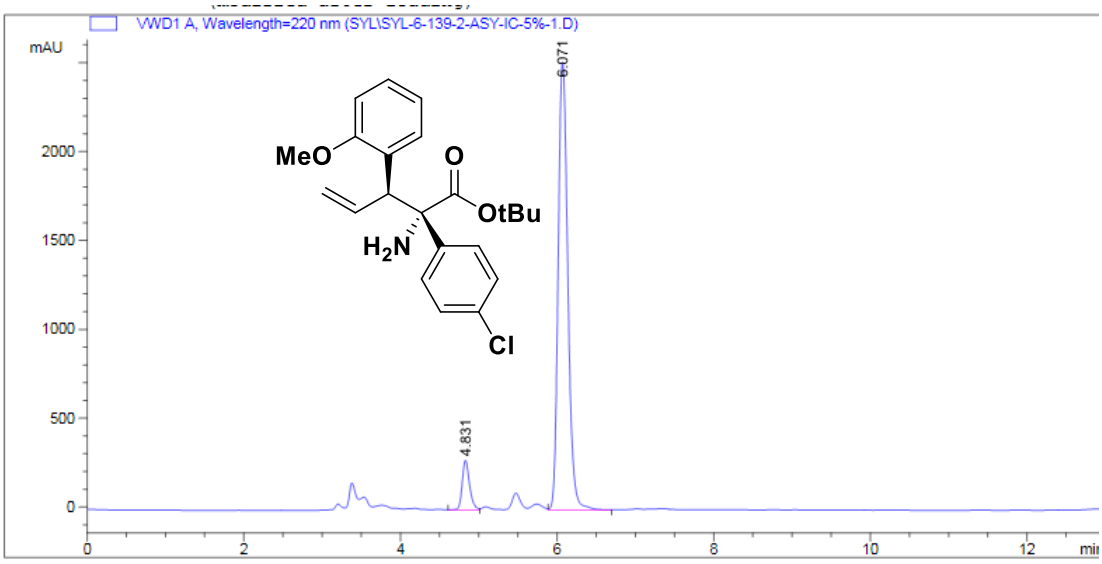
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.905	BV	0.1042	1.24305e4	1826.51672	51.1292
2	5.726	VV	0.1167	1.18814e4	1582.23828	48.8708



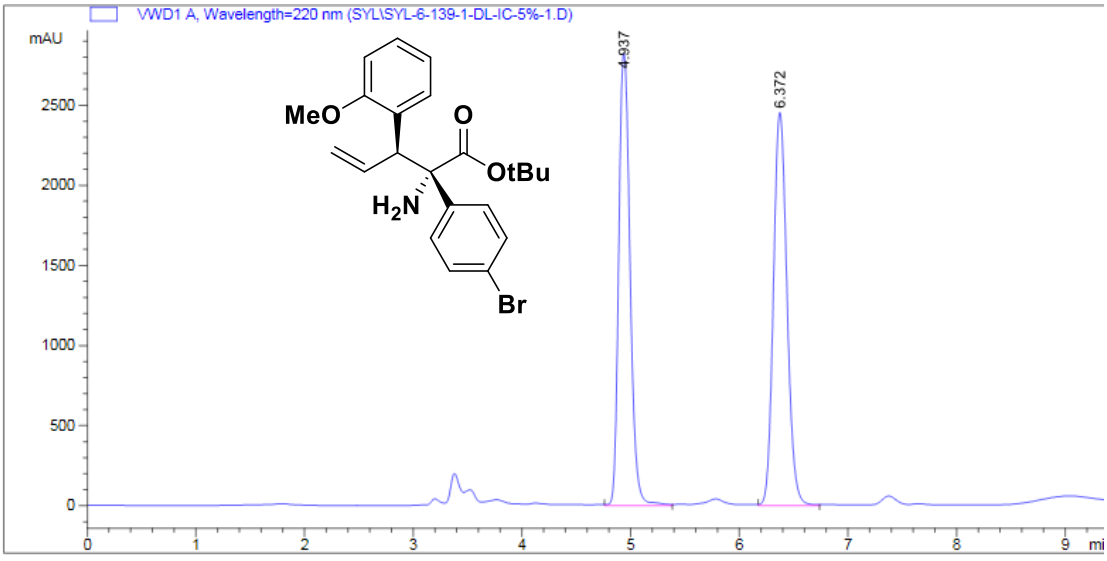
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.872	VV	0.1013	1842.19214	275.53305	6.3717
2	5.705	VV	0.1492	2.70700e4	2874.46729	93.6283



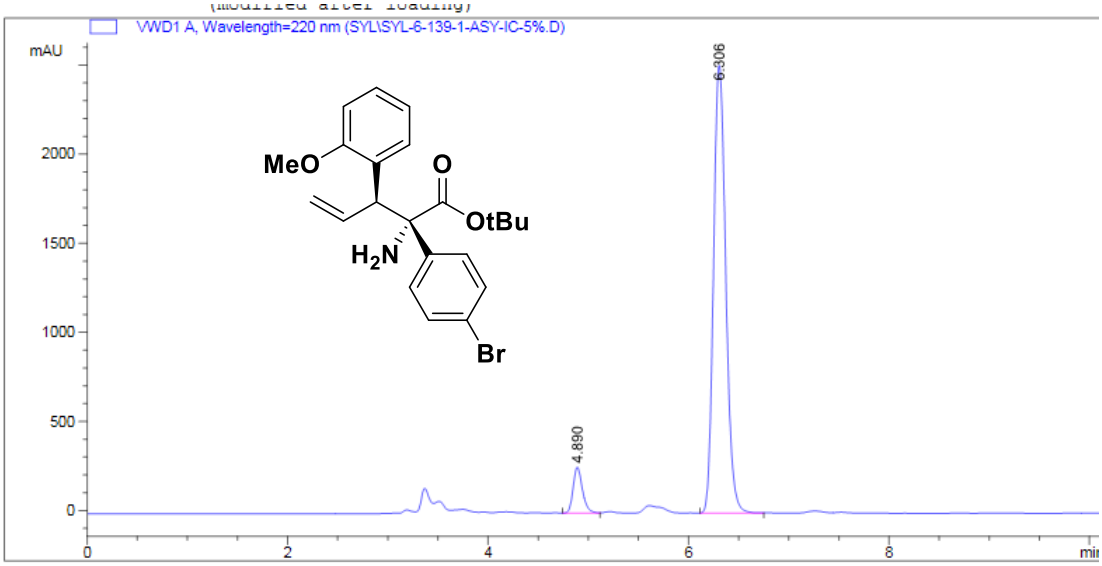
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.850	VV	0.1047	1.77757e4	2642.80127	48.6234
2	6.088	VB	0.1274	1.87822e4	2297.50830	51.3766



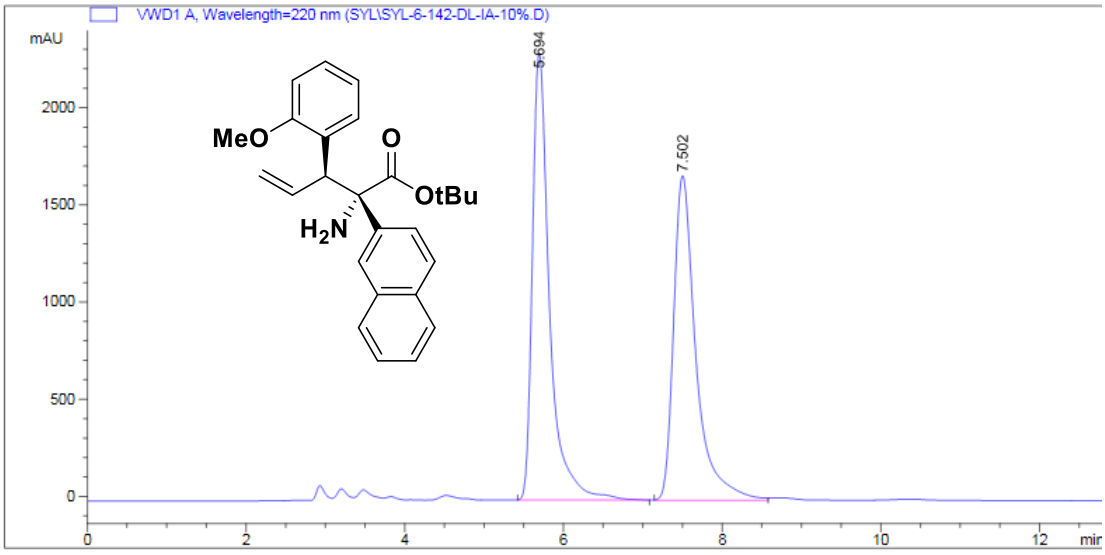
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.831	VV	0.1006	1858.49329	280.59793	7.9534
2	6.071	VB	0.1331	2.15089e4	2519.54443	92.0466



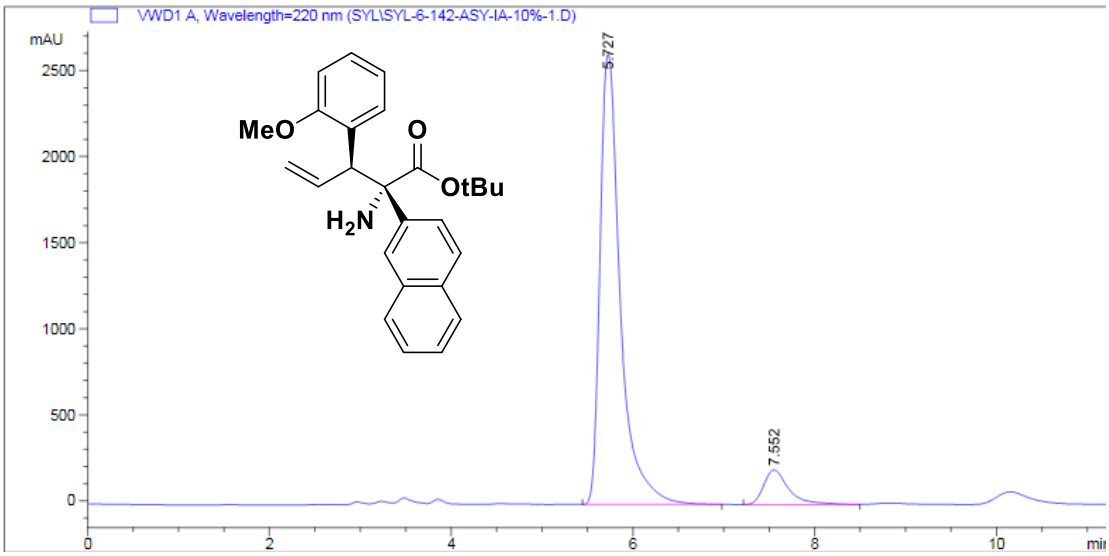
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.937	VV	0.1131	2.03284e4	2824.21924	48.8287
2	6.372	BV	0.1348	2.13037e4	2454.16870	51.1713



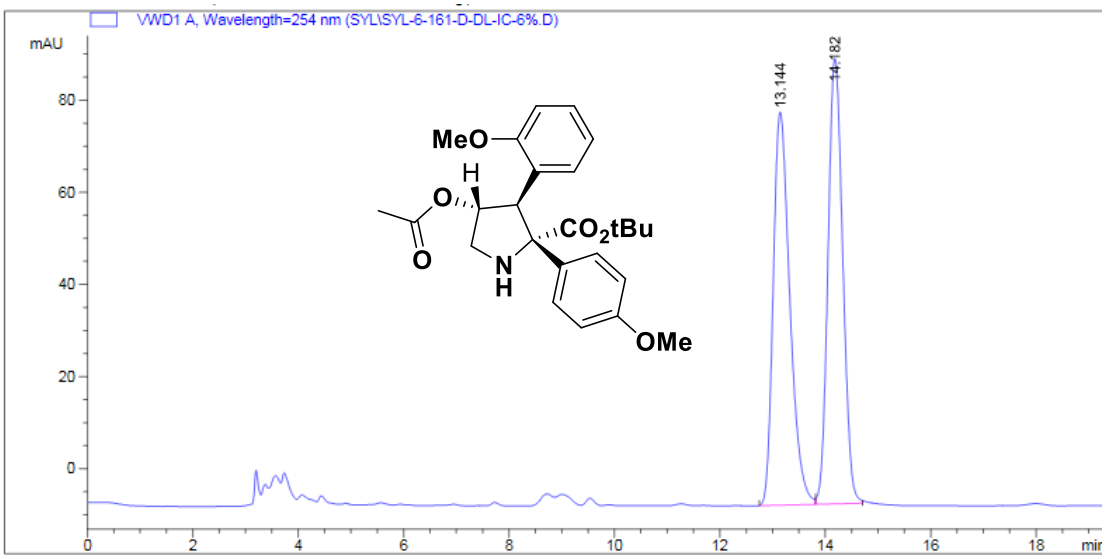
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	4.890	VV	0.1003	1708.87817	258.97928	7.4308
2	6.306	BB	0.1323	2.12884e4	2513.95313	92.5692



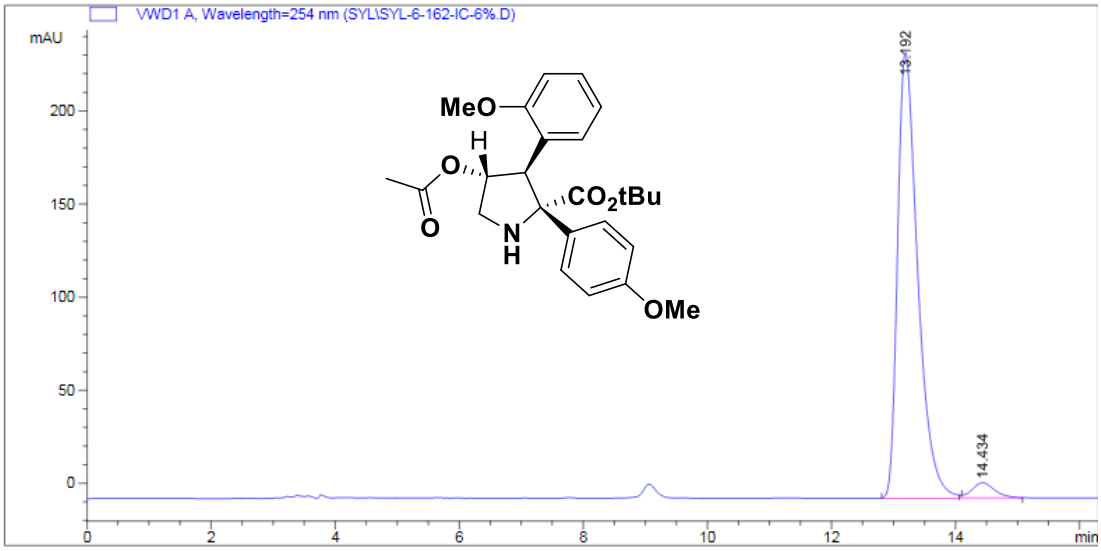
Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.694	BB	0.2267	3.46333e4	2299.62231	51.5718
2	7.502	BV	0.2912	3.25223e4	1670.28479	48.4282



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	5.727	BB	0.2345	4.04985e4	2615.38062	91.2244
2	7.552	BB	0.2895	3895.86304	201.59706	8.7756



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.144	BB	0.3374	1871.89612	85.34509	49.9235
2	14.182	BB	0.3037	1877.63269	96.72069	50.0765



Peak #	RetTime [min]	Type	Width [min]	Area mAU *s	Height [mAU]	Area %
1	13.192	BB	0.3434	5405.62305	239.49092	96.2107
2	14.434	BB	0.3883	212.90292	8.29300	3.7893