Supporting Information

Direct enantioselective allylation of nitriles to NH_2-α-tertiary amines

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Contents

1. General experimental information

All reactions were carried out with anhydrous solvents (vide infra) under a nitrogen atmosphere using oven-dried glassware and standard Schlenk techniques. Reactions were monitored by ^{1}H NMR. Purification of the products was performed by column chromatography using Merck 60 Å 200-300 mesh silica gel. Components were visualized by UV and $KMnO_4$ staining (TLC). NMR data was collected on Bruker-Avance 400 MHz spectrometer (^{1}H at 400.0 MHz; ^{13}C at 100.58 MHz). Chemical shifts are reported in parts per million (ppm) relative to residual solvent peak ($CDCl_3$, ^{1}H: 7.26 ppm; ^{13}C: 77.16 ppm). Coupling constants are reported in Hertz. Multiplicity is reported with the usual abbreviations. Enantiomeric excess (*ee*) were determined by chiral HPLC analysis using a Agilent HPLC (1260). High resolution mass spectra (HRMS) were performed on a VG Autospec-3000 spectrometer with ESI ionization.

Unless otherwise indicated, reagents and substrates were purchased from commercial sources and used as received. Solvents not required to be dry were purchased as technical grade and used as received. Dry solvents were freshly collected from a dry solvent purification system prior to use. Inert atmosphere experiments were performed with standard Schlenk techniques. Organometallic reagents were purchased from commercial sources (*n*BuLi, MeLi (1.6 M in Et_2O), *n*HexLi (1.6 M in Hexane)). All new compounds were fully characterized by ^{1}H and ^{13}C NMR and HRMS techniques.

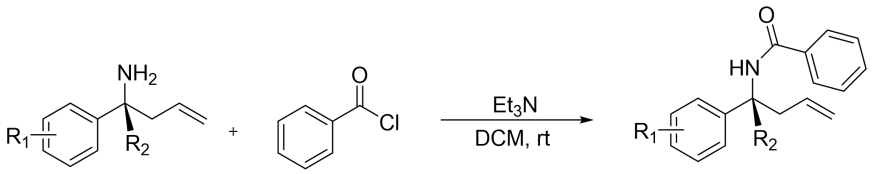
2. General procedures for asymmetric transformations

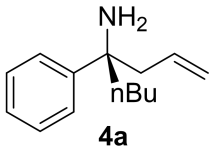
Cu-catalyzed asymmetric addition of Organolithium reagents and allylboronates to nitriles: In a dry Schlenk tube (A) equipped with magnetic stirring bar, Benzonitrile (0.2 mmol, 1.0 equiv.), CuTC (1.90 mg, 5 mol%), and ligand **L** (7.13 mg, 6 mol%) were dissolved in 2-Me-THF (2 mL) and stirred under nitrogen atmosphere for 30 min at -10 ^{o}C. In another one dry Schlenk tube (B) equipped with magnetic stirring bar, RLi (1.0 equiv.) was added dropwise in Benzonitrile were dissolved in 2-Me-THF (1 mL) and stirred under nitrogen atmosphere for 30 min at room temperature. Then, adding *t*BuOH (2.0 equiv.) to tube (B) and stirred for 10 min. Mix tube (A) and (B) and stir for ten minutes at -10^{o}C and allylboronate (1.0 equiv.) was added dropwise in it. After stirring overnight at -10^{o}C/-20^{o}C, the reaction was quenched by saturated aqueous NH_4Cl. Reaction mixture was extracted with EA (3×3 mL). Combined organic phases were dried over anhydrous Na_2SO_4, filtered and solvents were evaporated on rotary evaporator. The crude was purified by flash chromatography on silica gel.

General procedure for the preparation of racemic products: For the preparation of racemic products, we used the same method without ligands (Yields: 57-86%)

Characterization of chiral addition products

Unless otherwise indicated, The enantiomeric excesses (*ees*) of all products were determined with nitrogen-benzoyl protected derivatives [1]。

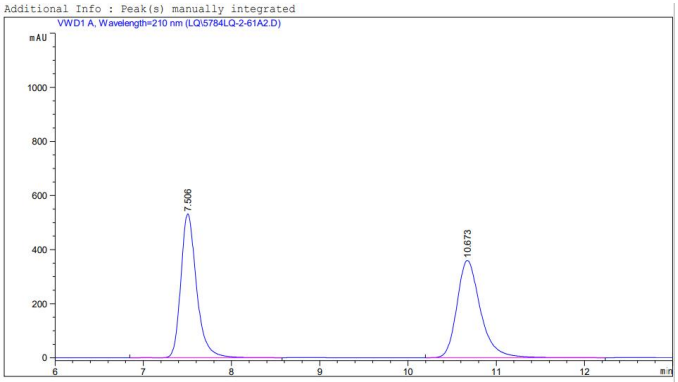




4a

4-phenyloct-1-en-4-amine (4a)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 70% yield, 91% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.31 (m, 2H), 7.29 – 7.23 (m, 2H), 7.17 – 7.11 (m, 1H), 5.52 – 5.36 (m, 1H), 5.06 – 4.91 (m, 2H), 2.62 – 2.50 (m, 1H), 2.38 – 2.27 (m, 1H), 1.84 – 1.71 (m, 1H), 1.67 – 1.54 (m, 1H), 1.50 (s, 2H), 1.18 – 1.10 (m, 3H), 0.94 – 0.85 (m, 1H), 0.75 (t, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 147.07, 134.19, 128.03, 125.96, 125.73, 118.47, 57.27, 48.78, 43.45, 25.88, 23.15, 14.00.
HRMS (ESI^{+}, m/z): calcd for $C_{14}H_{21}N$ $[M+H]^{+}$: 204.1747, found: 204.1745.
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 95:5, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 7.50 (minor) and 10.67 (major).



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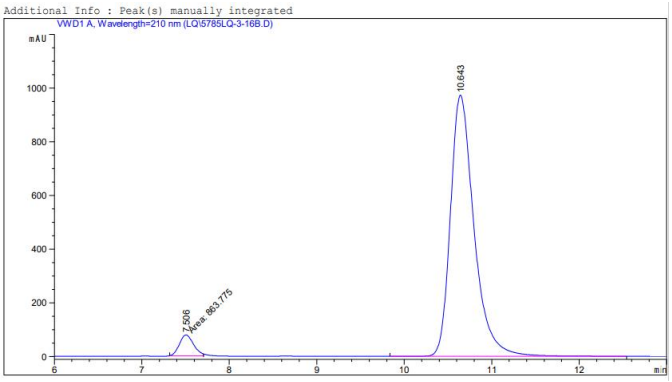

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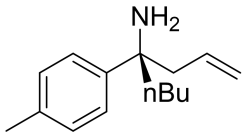
2	10.643	BB	0.2831	1.81765e4	972.12781	95.4634



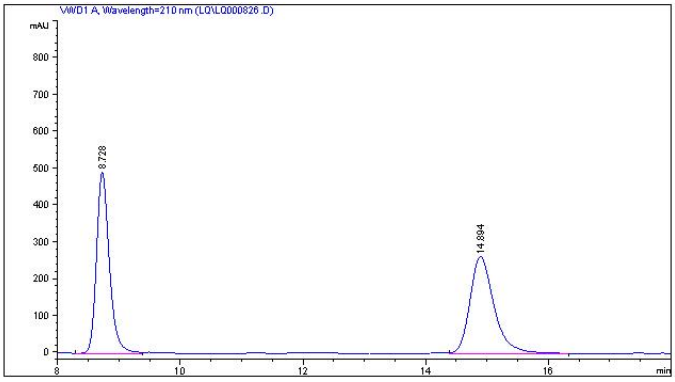
4b

4-(p-tolyl) oct-1-en-4-amine (4b)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 57% yield, 91% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.22 (m, 2H), 7.14 (d, J = 8.2 Hz, 2H), 5.60 – 5.41 (m, 1H), 5.14 – 4.94 (m, 2H), 2.60 (dd, J = 13.6, 6.1 Hz, 1H), 2.41 – 2.35 (m, 1H), 2.33 (s, 3H), 1.85 – 1.77 (m, 1H), 1.66 (dd, J = 12.6, 4.0 Hz, 1H), 1.59 (s, 2H), 1.25 – 1.20 (m, 3H), 1.02 – 0.93 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H). ^{13}C NMR (101 MHz, Chloroform-d) δ 144.06, 135.40, 134.32, 128.75, 125.63, 118.36, 57.04, 48.73, 43.44, 25.90, 23.17, 20.89, 14.01.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{23}N$ $[M+H]^{+}$: 218.1903, found: 218.1904.

HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 8.72 (minor) and 14.89 (major).



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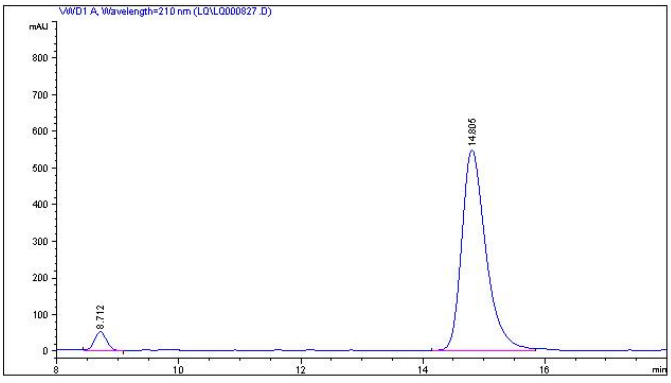

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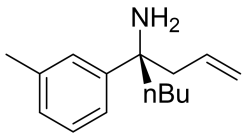
2	14.805	BV	0.4177	1.50537e4	547.60077	95.5989



4c

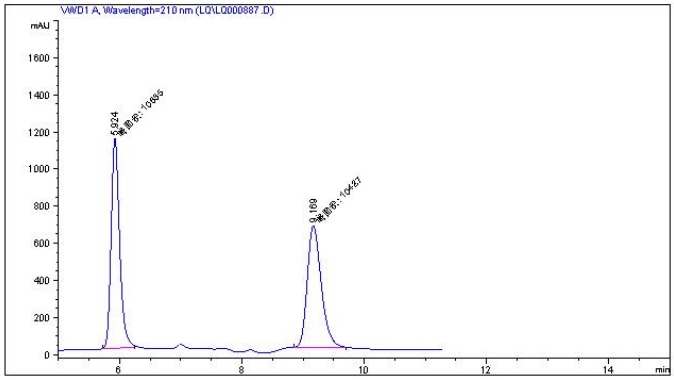
4-(m-tolyl)oct-1-en-4-amine (4c)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 81% yield, 95% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.24 – 7.16 (m, 3H), 7.08 – 6.98 (m, 1H), 5.58 – 5.44 (m, 1H), 5.13 – 4.99 (m, 2H), 2.61 (dd, J = 13.6, 6.1 Hz, 1H), 2.42 – 2.34 (m, 4H), 1.87 – 1.77 (m, 1H), 1.69 – 1.60 (m, 1H), 1.54 (s, 2H), 1.28 – 1.18 (m, 3H), 1.02 – 0.92 (m, 1H), 0.83 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-*d*) δ 147.05, 137.49, 134.31, 127.89, 126.69, 126.45, 122.79, 118.39, 57.18, 48.76, 43.45, 25.90, 23.16, 21.73, 14.01.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{23}N$ [M+H] $^{+}$: 218.1903, found: 218.1901.

HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 5.92 (minor) and 9.16 (major).



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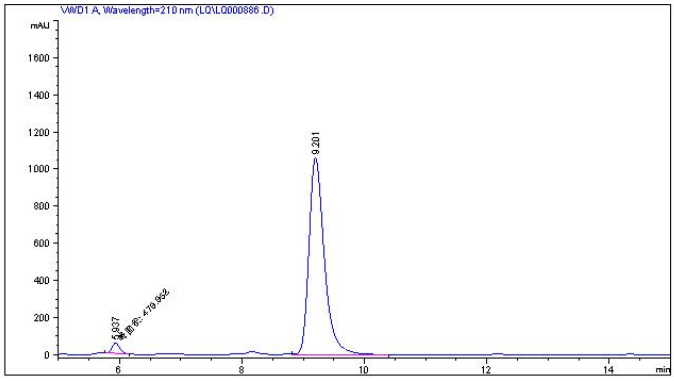

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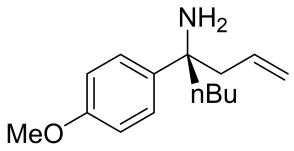


4d

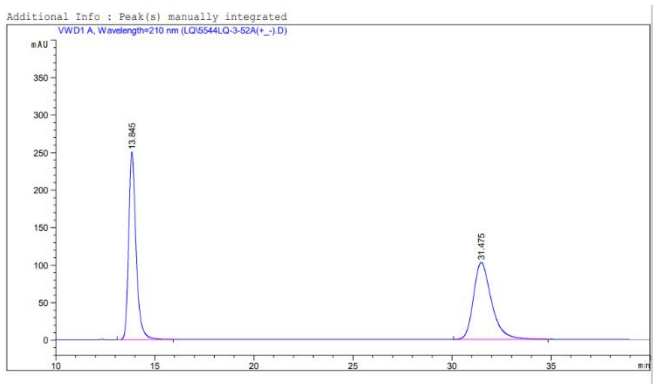
4-(4-methoxyphenyl)oct-1-en-4-amine (4d)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 78% yield, 90% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.28 (m, 2H), 6.89 – 6.82 (m, 2H), 5.63 – 5.45 (m, 1H), 5.14 – 4.97 (m, 2H), 3.80 (s, 3H), 2.65 – 2.51 (m, 1H), 2.46 – 2.31 (m, 1H), 1.84 – 1.74 (m, 1H), 1.68 – 1.57 (m, 1H), 1.55 (s, 2H), 1.28 – 1.18 (m, 3H), 1.05 – 0.91 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 157.72, 139.14, 134.32, 126.82, 118.37, 113.31, 56.82, 55.18, 48.79, 43.51, 25.91, 23.15, 14.02.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{23}NO$ $[M+H]^{+}$: 234.1586, found: 234.1582.

HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 13.84 (minor) and 31.47 (major).



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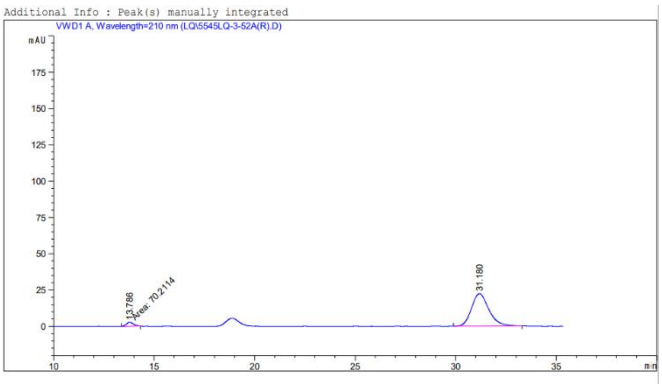
1	13.845	BB	0.3933	6478.36377	249.98828	50.1059
2	31.475	BB	0.9556	6450.96924	102.31236	49.8941



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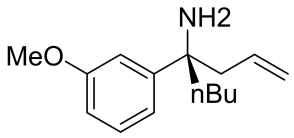


4e

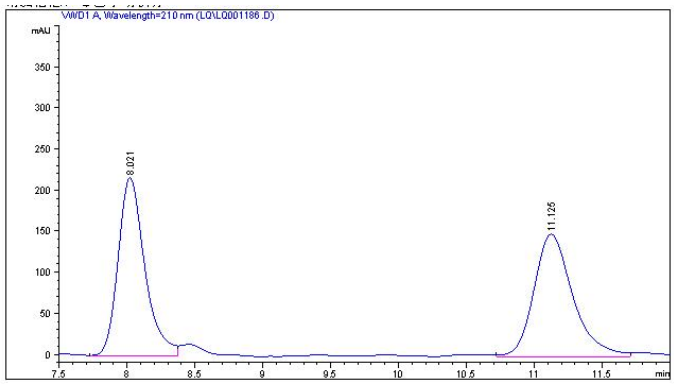
4-(3-methoxyphenyl)oct-1-en-4-amine (4e)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 67% yield, 90% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.31 – 7.27 (m, 1H), 7.03 – 6.99 (m, 2H), 6.81 – 6.76 (m, 1H), 5.63 – 5.48 (m, 1H), 5.17 – 4.99 (m, 2H), 3.85 (s, 3H), 2.73 – 2.57 (m, 1H), 2.40 (dd, J = 13.5, 8.6 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.74 – 1.64 (m, 1H), 1.60 (s, 2H), 1.30 – 1.23 (m, 3H), 1.06 – 0.95 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 159.51, 149.03, 134.16, 128.98, 118.50, 118.27, 112.30, 110.74, 57.35, 55.19, 48.76, 43.43, 25.87, 23.15, 14.01.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{23}NO$ $[M+H]^{+}$:234.1852, found: 234.1858.

HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 8.02 (minor) and 11.12 (major).



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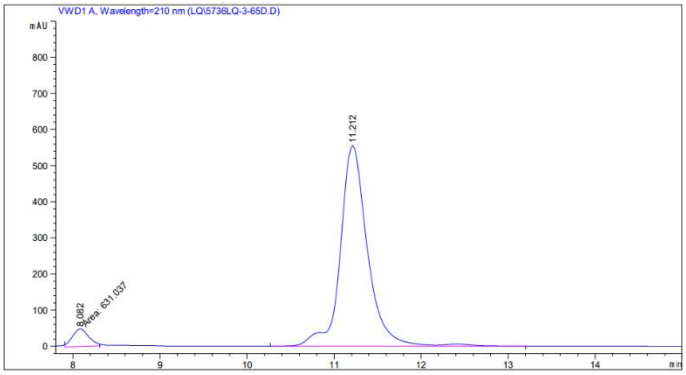

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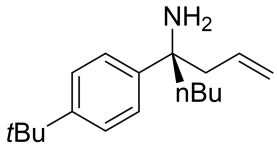


4f

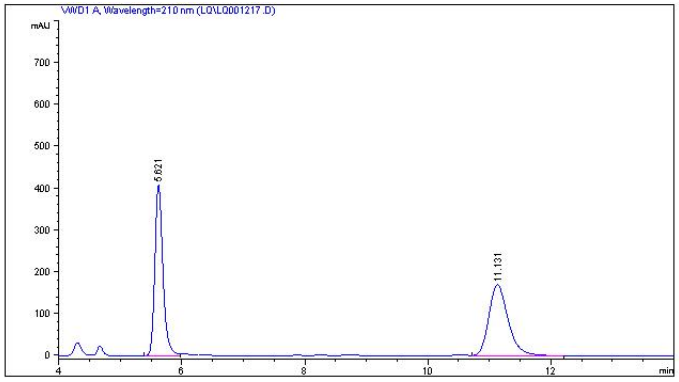
4-(4-(tert-butyl)phenyl)oct-1-en-4-amine (4f)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 44% yield, 90% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.37 – 7.28 (m, 4H), 5.63 – 5.47 (m, 1H), 5.15 – 4.97 (m, 2H), 2.59 (dd, J = 13.6, 6.1 Hz, 1H), 2.39 (dd, J = 13.6, 8.5 Hz, 1H), 1.81 (m, 1H), 1.71 – 1.60 (m, 1H), 1.55 (s, 2H), 1.32 (s, 9H), 1.27 – 1.19 (m, 3H), 1.05 – 0.97 (m, 1H), 0.83 (t, J = 7.2 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 148.62, 144.04, 134.46, 125.32, 124.86, 118.30, 56.90, 48.54, 43.27, 34.29, 31.39, 25.91, 23.18, 14.03.

HRMS (ESI^{+}, m/Z): calcd for $C_{18}H_{29}N$ [M+Na]$^{+}$: 282.2196, found: 282.2192.

HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 24.05 (major) and 26.50 (minor).



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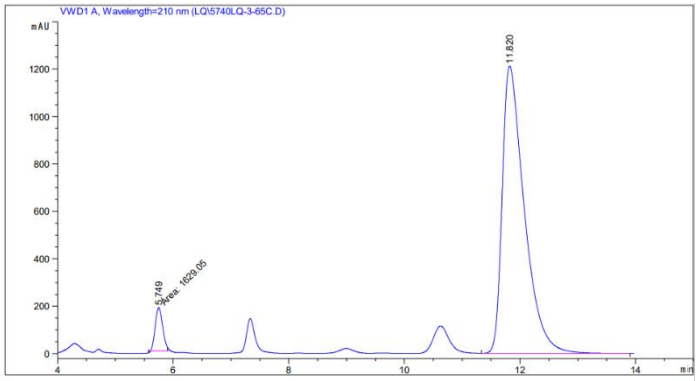
2	11.131	VB	0.3350	3744.65063	170.65646	50.1642



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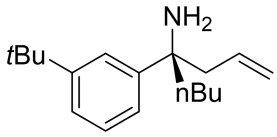
1	5.749	MM	0.1490	1629.04675	182.19687	4.8207
2	11.820	VB	0.3956	3.21635e4	1211.92554	95.1793



4g

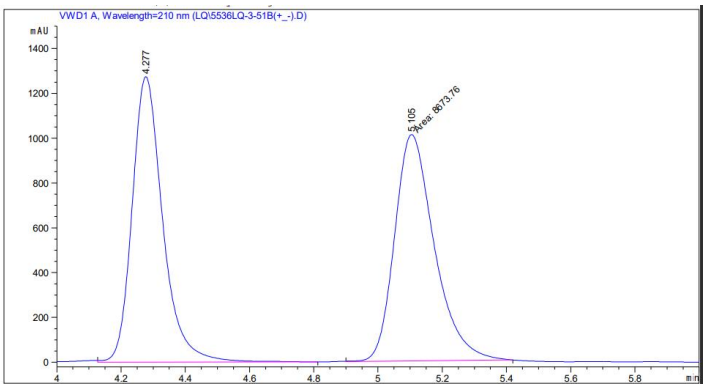
4-(3-(tert-butyl)phenyl)oct-1-en-4-amine (4g)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 52% yield, 93% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.45 – 7.41 (m, 1H), 7.27 – 7.18 (m, 3H), 5.63 – 5.46 (m, 1H), 5.14 – 4.98 (m, 2H), 2.70 – 2.54 (m, 1H), 2.49 – 2.34 (m, 1H), 1.90 – 1.78 (m, 1H), 1.72 – 1.60 (m, 1H), 1.56 (s, 2H), 1.33 (s, 9H), 1.27 – 1.20 (m, 3H), 1.05 – 0.95 (m, 1H), 0.83 (t, J = 7.1 Hz, 3H).

^{13}C NMR (101 MHz, Chloroform-d) δ 150.70, 146.65, 134.39, 127.57, 122.82, 122.79, 122.77, 118.32, 57.44, 48.72, 43.32, 34.76, 31.45, 25.89, 23.13, 13.98.

HRMS (ESI^{+}, m/Z): calcd for $C_{18}H_{29}N$ $[M+H]^{+}$: 260.2373, found: 260.2373.

HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 5.62 (minor) and 11.13(major).



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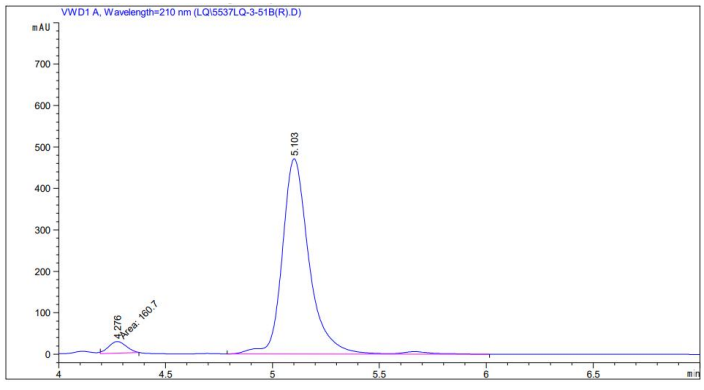
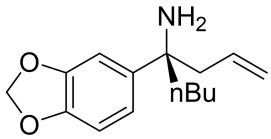


Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	4.276	MM	0.0951	160.70021	28.16960	3.7322
2	5.103	VV R	0.1303	4145.03125	471.17160	96.2678



4h

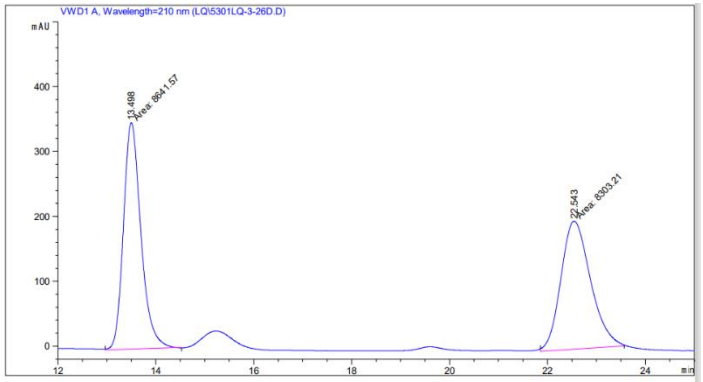
4-(benzo[d][1,3]dioxol-5-yl)oct-1-en-4-amine (4h)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 70% yield, 90% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 6.92 (d, J = 1.8 Hz, 1H), 6.86 (dd, J = 8.2, 1.9 Hz, 1H), 6.76 (d, J = 8.1 Hz, 1H), 5.95 (s, 2H), 5.60 – 5.45 (m, 1H), 5.11 – 4.99 (m, 2H), 2.56 (dd, J = 13.6, 6.1 Hz, 1H), 2.34 (dd, J = 13.6, 8.5 Hz, 1H), 1.84 – 1.71 (m, 1H), 1.66 – 1.57 (m, 1H), 1.50 (s, 2H), 1.28 – 1.17 (m, 3H), 1.05 – 0.95 (m, 1H), 0.83 (t, J = 7.2 Hz, 3H).

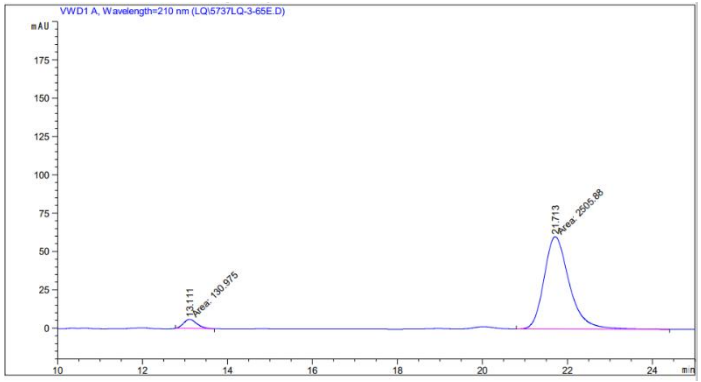
^{13}C NMR (101 MHz, Chloroform-d) δ 147.60, 145.59, 141.33, 134.15, 118.78, 118.49, 107.57, 106.67, 100.87, 57.22, 48.94, 43.63, 25.87, 23.14, 14.03.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{21}NO_2$ $[M+H]^{+}$: 248.1645, found: 248.1648.

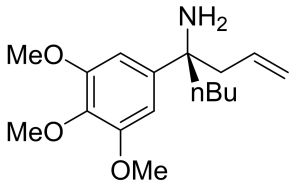
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210nm. Retention time (min): 13.49 (minor) and 22.54 (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.498	MM	0.4127	8641.57129	348.94565	50.9984
2	22.543	MM	0.7012	8303.20508	197.34331	49.0016



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.111	MM	0.3683	130.97549	5.92719	4.9671
2	21.713	MM	0.6921	2505.87622	60.34427	95.0329



4i

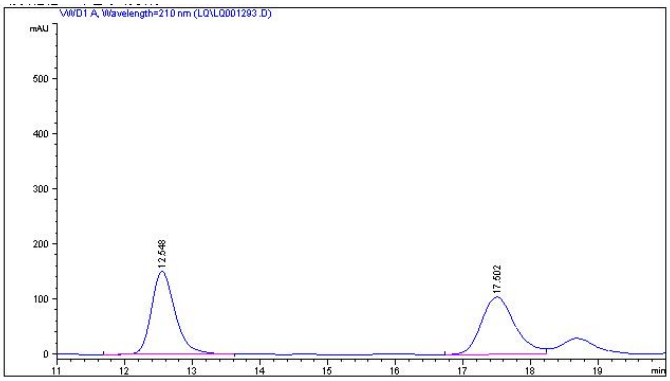
4-(3,4,5-trimethoxyphenyl) oct-1-en-4-amine (4i)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 52% yield, 94% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 6.64 (s, 2H), 5.65 – 5.50 (m, 1H), 5.16 – 5.01 (m, 2H), 3.87 (s, 6H), 3.85 (s, 3H), 2.60 (dd, J = 13.6, 6.1 Hz, 1H), 2.38 (dd, J = 13.7, 8.4 Hz, 1H), 1.85 – 1.75 (m, 1H), 1.70 –1.64 (m, 1H), 1.61 (s, 2H), 1.29 – 1.24 (m, 3H), 1.11 – 0.94 (m, 1H), 0.85 (t, J = 7.1 Hz, 3H).

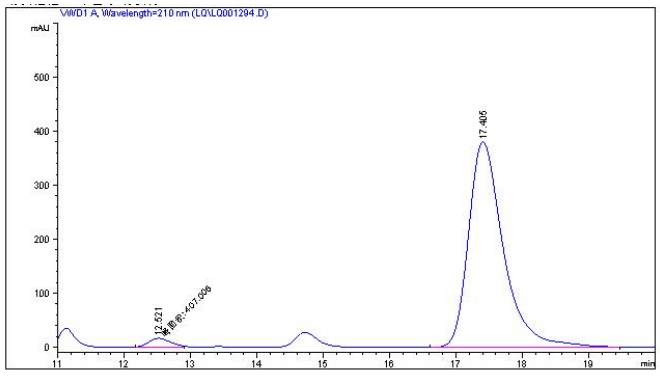
^{13}C NMR (101 MHz, Chloroform-d) δ 152.77, 136.29, 134.08, 118.66, 103.32, 60.83, 56.21, 25.86, 23.11, 14.01.

HRMS (ESI+, m/Z): calcd for $C_{17}H_{27}NO_3$ $[M+Na]^+$: 316.1883, found: 316.1885.

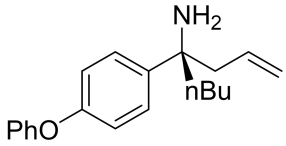
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 24.05 (major) and 26.50 (minor).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.548	BB	0.3698	3625.73364	150.61580	50.2541
2	17.502	BV	0.5351	3589.06201	103.86603	49.7459



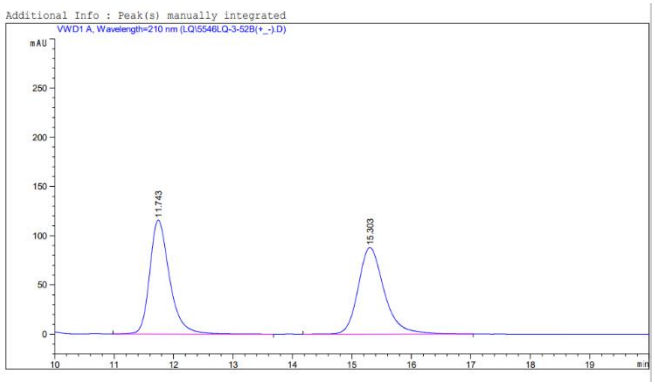
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	12.521	MM	0.3970	407.00754	17.08528	2.8415
2	17.405	VV	0.5539	1.39165e4	380.31180	97.1585



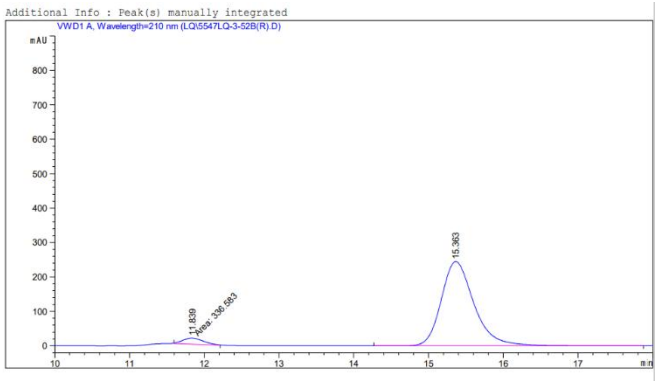
4j

4-(4-phenoxyphenyl)oct-1-en-4-amine (4j)

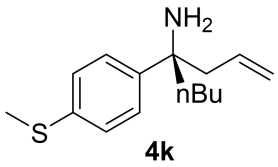
[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 59% yield, 91% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.29 (m, 4H), 7.12 – 7.03 (m, 1H), 7.04 – 6.90 (m, 4H), 5.62 – 5.47 (m, 1H), 5.13 – 5.00 (m, 2H), 2.65 – 2.53 (m, 1H), 2.38 (dd, J = 13.6, 8.4 Hz, 1H), 1.87 – 1.74 (m, 1H), 1.71 – 1.60 (m, 1H), 1.52 (s, 2H), 1.29 – 1.17 (m, 3H), 1.06 – 0.93 (m, 1H), 0.84 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 157.38, 155.29, 142.00, 134.16, 129.69, 127.16, 123.09, 118.77, 118.58, 118.33, 57.02, 48.81, 43.47, 25.94, 23.16, 14.06.
HRMS (ESI^{+}, m/Z): calcd for $C_{20}H_{25}NO$ $[M+H-NH_3]^{+}$: 279.1747, found: 279.1743.
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22°C, detection at 210 nm. Retention time (min): 11.74 (minor) and 15.30 (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.743	BB	0.3517	2685.03662	115.71075	50.1255
2	15.303	BB	0.4627	2671.59058	87.87061	49.8745



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	11.839	MM	0.3201	336.58273	17.52525	4.3056
2	15.363	BB	0.4648	7480.78955	244.61957	95.6944



4k

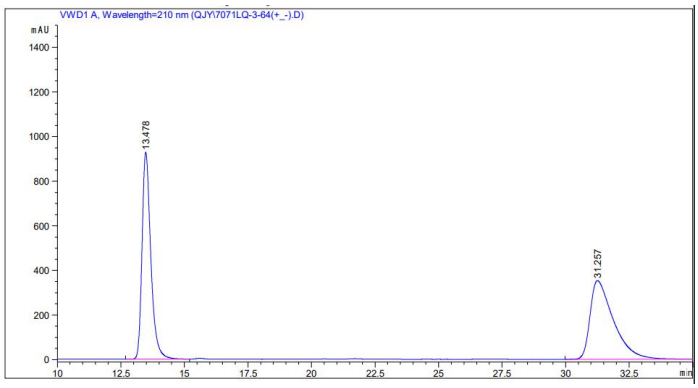
4-(4-(methylthio) phenyl) oct-1-en-4-amine (4k)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 1:1). Yellow oil, 75% yield, 90% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.36 – 7.30 (m, 2H), 7.24 – 7.18 (m, 2H), 5.62 – 5.41 (m, 1H), 5.13 – 4.95 (m, 2H), 2.63 – 2.54 (m, 1H), 2.48 (s, 3H), 2.41 – 2.32 (m, 1H), 1.85 – 1.74 (m, 1H), 1.68 – 1.59 (m, 1H), 1.51 (s, 2H), 1.29 – 1.14 (m, 3H), 1.01 – 0.91 (m, 1H), 0.82 (t, J = 7.2 Hz, 3H).

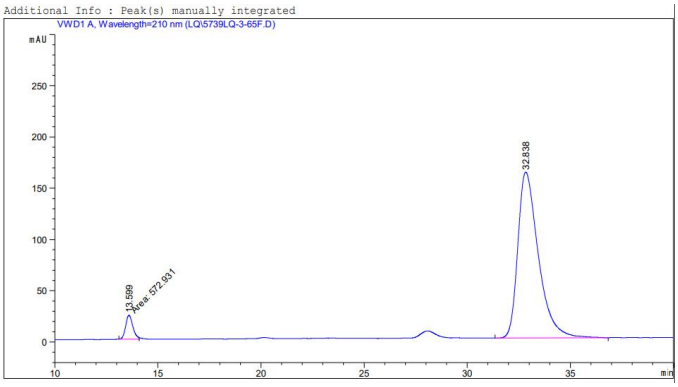
^{13}C NMR (101 MHz, Chloroform-d) δ 144.13, 135.61, 134.06, 126.39, 118.58, 57.06, 48.72, 43.41, 25.87, 23.14, 15.90, 14.01.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{23}NS$ $[M+Na]^{+}$: 272.1450, found: 272.1443.

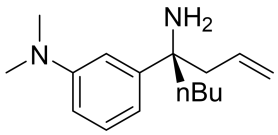
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 13.59 (minor) and 32.83 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.478	BB	0.3623	2.22255e4	928.44482	49.6516
2	31.257	BB	0.9524	2.25374e4	352.74500	50.3484



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	13.599	MM	0.4067	572.93121	23.47632	4.8622
2	32.838	BB	1.0434	1.12103e4	161.99010	95.1378



4l

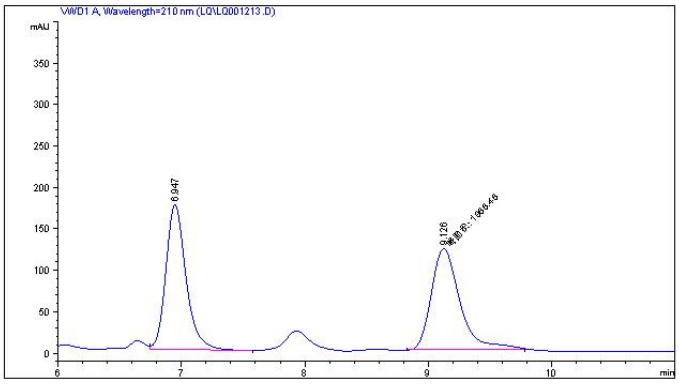
3-(4-aminooct-1-en-4-yl)-N, N-dimethylaniline (4l)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 38% yield, 94% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.22 – 7.16 (m, 1H), 6.83 – 6.81 (m, 1H), 6.78 – 6.72 (m, 1H), 6.67 – 6.56 (m, 1H), 5.64 – 5.46 (m, 1H), 5.15 – 4.97 (m, 2H), 2.96 (s, 6H), 2.70 – 2.54 (m, 1H), 2.37 (dd, J = 13.6, 8.6 Hz, 1H), 1.89 – 1.75 (m, 1H), 1.71 – 1.59 (m, 1H), 1.56 (s, 2H), 1.28 – 1.17 (m, 3H), 1.09 – 0.94 (m, 1H), 0.83 (t, J = 7.1 Hz, 3H).

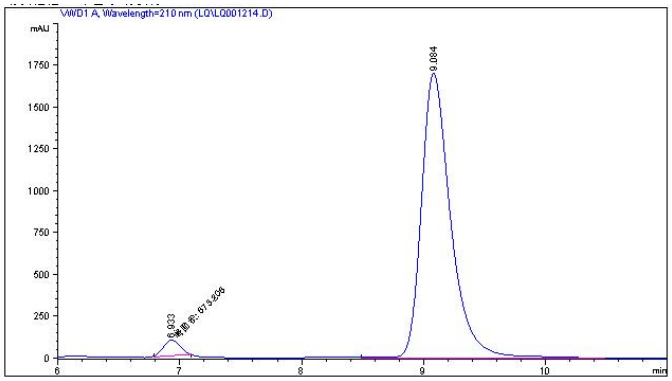
^{13}C NMR (101 MHz, Chloroform-d) δ 150.53, 148.01, 134.56, 128.61, 118.20, 114.47, 110.45, 110.37, 57.44, 48.82, 43.48, 40.81, 25.91, 23.20, 14.02.

HRMS (ESI^{+}, m/Z): calcd for $C_{16}H_{27}N_2$ $[M+H]^{+}$: 247.2169, found: 247.2169.

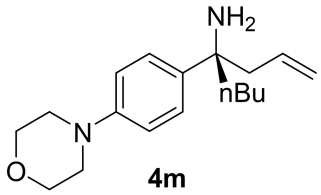
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 6.94 (minor) and 9.12 (major).



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.947	VB	0.1720	1976.59106	174.71445	49.8752
2	9.126	MM	0.2711	1986.48376	122.13435	50.1248



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.933	MM	0.1567	873.20819	92.88813	2.9895
2	9.084	VV	0.2513	2.83362e4	1701.43567	97.0105



4m

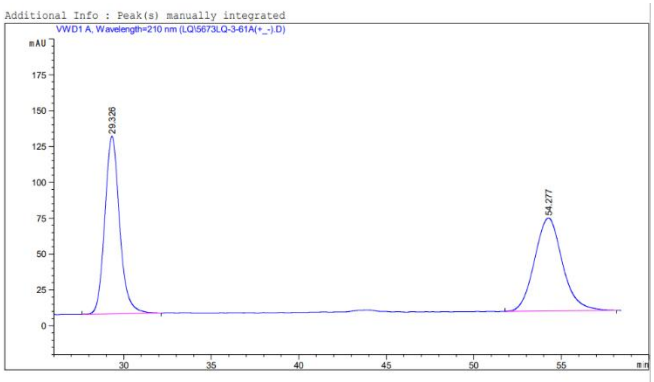
4-(4-morpholinophenyl) oct-1-en-4-amine (4m)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 1:1). Yellow oil, 61% yield, 91% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.33 – 7.27 (m, 2H), 6.92 – 6.81 (m, 2H), 5.62 – 5.47 (m, 1H), 5.13 – 4.96 (m, 2H), 3.94 – 3.78 (m, 4H), 3.23 – 3.10 (m, 4H), 2.64 – 2.52 (m, 1H), 2.36 (dd, J = 13.6, 8.4 Hz, 1H), 1.83 – 1.72 (m, 1H), 1.72 – 1.58 (m, 1H), 1.52 (s, 2H), 1.24 – 1.18 (m, 3H), 1.04 – 0.93 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H).

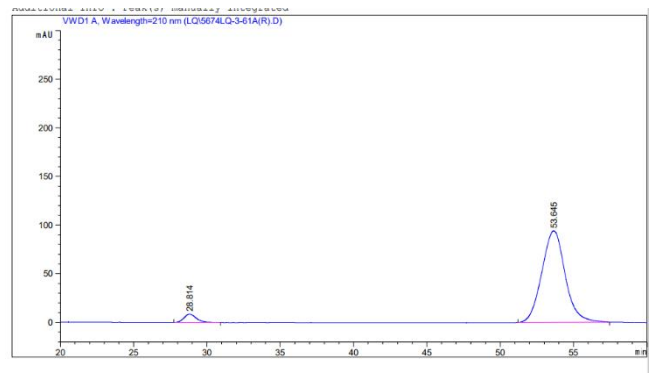
^{13}C NMR (101 MHz, Chloroform-d) δ 149.19, 138.54, 134.42, 126.57, 118.31, 115.09, 66.99, 56.76, 49.32, 48.67, 43.42, 25.93, 24.87, 23.17, 14.04.

HRMS (ESI^{+}, m/Z): calcd for $C_{18}H_{28}N_2O$ [M+H-NH$_3$]$^{+}$: 272.2010, found: 272.2009.

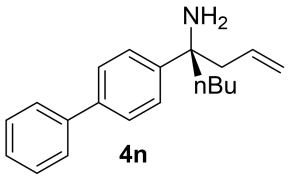
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22°C, detection at 210 nm. Retention time (min): 29.32 (minor) and 54.27 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	29.326	BB	0.8952	7289.74609	123.76376	50.4010
2	54.277	BB	1.6695	7173.75830	64.90317	49.5990



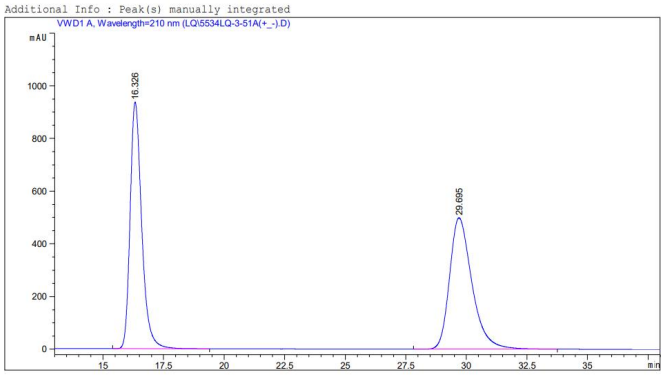
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	28.814	BB	0.8149	493.21359	8.55106	4.5263
2	53.645	BB	1.6633	1.04035e4	93.99607	95.4737



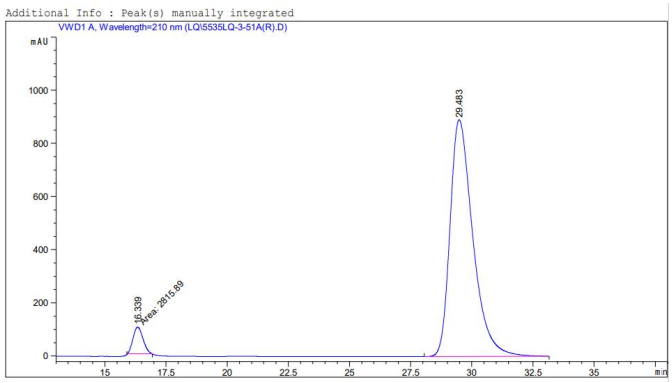
4n

4-([1,1'-biphenyl]-4-yl) oct-1-en-4-amine (4n)

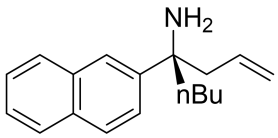
[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 90% yield, 90% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.66 – 7.55 (m, 4H), 7.51 – 7.39 (m, 4H), 7.37 – 7.30 (m, 1H), 5.67 – 5.47 (m, 1H), 5.16 – 4.99 (m, 2H), 2.74 – 2.61 (m, 1H), 2.43 (dd, J = 13.6, 8.5 Hz, 1H), 1.94 – 1.80 (m, 1H), 1.76 – 1.62 (m, 1H), 1.58 (s, 2H), 1.28 – 1.22 (m, 3H), 1.09 – 0.97 (m, 1H), 0.85 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 145.22, 139.77, 137.68, 133.14, 127.68, 126.06, 125.93, 125.67, 125.19, 117.55, 56.17, 47.71, 42.41, 24.90, 22.15, 12.99.
HRMS (ESI^{+}, m/Z): calcd for $C_{20}H_{25}N$ $[M+H]^{+}$: 280.2060, found: 280.2066.
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 24.05 (major) and 26.50 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.326	BB	0.5074	3.10788e4	935.92493	49.2267
2	29.695	BB	0.9871	3.20552e4	498.58823	50.7733



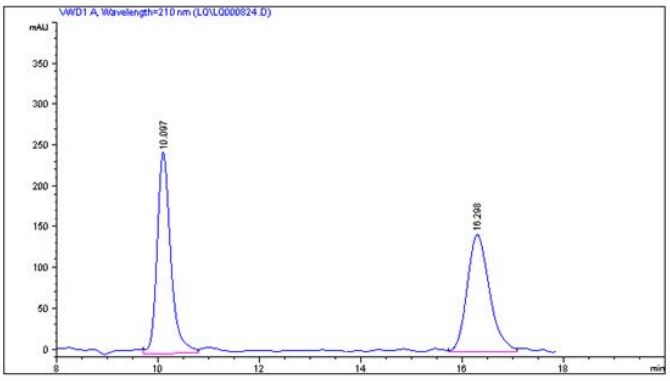
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	16.339	MM	0.4685	2815.89185	100.17746	4.6575
2	29.483	BBA	0.9803	5.76438e4	890.34869	95.3425



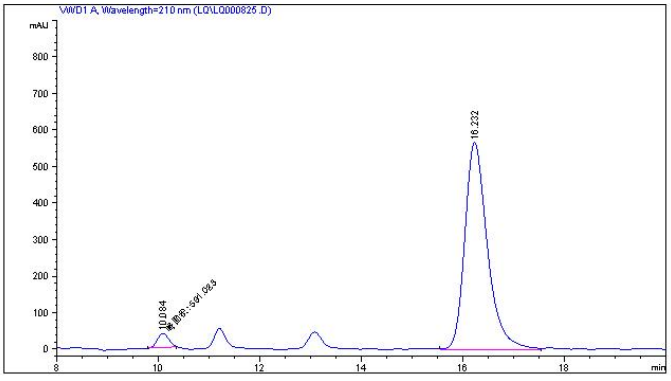
4o

4-(naphthalen-2-yl) oct-1-en-4-amine (4o)

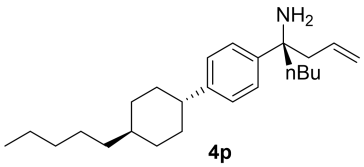
[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 55% yield, 93% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.81 – 7.71 (m, 4H), 7.49 – 7.43 (m, 1H), 7.43 – 7.33 (m, 2H), 5.53 – 5.34 (m, 1H), 5.07 – 4.89 (m, 2H), 2.70 – 2.59 (m, 1H), 2.39 (dd, J = 13.6, 8.6 Hz, 1H), 1.94 – 1.81 (m, 1H), 1.72 – 1.61 (m, 1H), 1.56 (s, 2H), 1.19 – 1.14 (m, 3H), 0.94 – 0.84 (m, 1H), 0.73 (t, J = 7.1 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 144.53, 134.10, 133.20, 131.94, 128.07, 127.74, 127.37, 125.91, 125.52, 124.45, 124.32, 118.58, 57.52, 48.72, 43.33, 25.94, 23.15, 13.99.
HRMS (ESI^{+}, m/Z): calcd for $C_{18}H_{23}N$ $[M+H]^{+}$: 254.1903, found: 254.1907.
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 10.09 (minor) and 16.29 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.097	VV	0.2824	4580.78955	245.77856	50.9778
2	16.298	VV	0.4783	4405.06152	143.84436	49.0222



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	10.084	MM	0.2573	591.02271	38.28829	3.2774
2	16.232	BV	0.4695	1.74421e4	565.97864	96.7226



4p

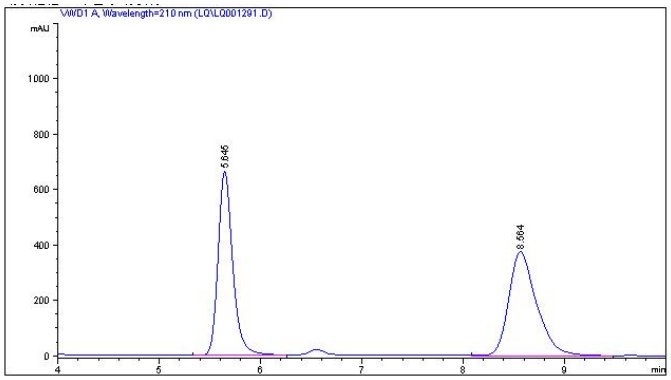
4-(4-((1s,4r)-4-pentylcyclohexyl)phenyl) oct-1-en-4-amine (4p)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 1:1). Yellow oil, 68% yield, 91% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.46 (m, 4H), 5.55 – 5.38 (m, 1H), 5.12 – 5.01 (m, 2H), 2.63 (dd, J = 13.3, 6.2 Hz, 1H), 2.40 (dd, J = 13.7, 8.8 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.74 – 1.62 (m, 1H), 1.58 (s, 2H), 1.25 – 1.15 (m, 3H), 0.97 – 0.87 (m, 1H), 0.82 (t, J = 7.2 Hz, 3H).

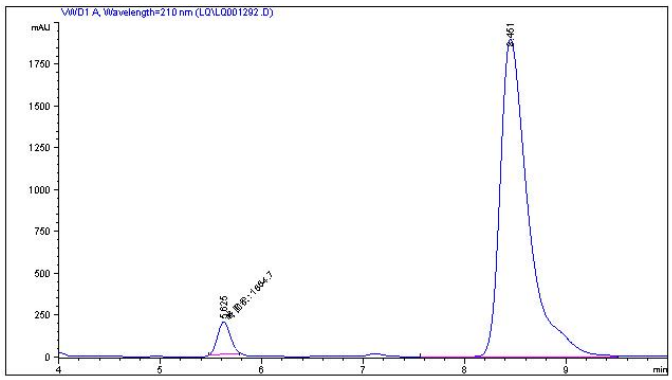
^{13}C NMR (101 MHz, Chloroform-d) δ 144.37, 143.41, 133.42, 125.38, 124.51, 117.26, 55.96, 47.55, 43.01, 42.28, 36.41, 36.35, 33.32, 32.65, 31.22, 25.65, 24.89, 22.15, 21.70, 13.10, 13.00.

HRMS (ESI^{+}, m/Z): calcd for $C_{25}H_{41}N$ $[M+Na]^{+}$: 356.3312, found: 356.3312.

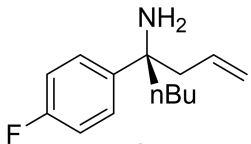
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 5.64 (minor) and 8.65 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.645	VV	0.1539	6721.89209	664.94727	48.4975
2	8.564	VV	0.2830	7138.40283	375.21704	51.5025



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.625	MM	0.1430	1664.70190	193.95982	4.3727
2	8.451	BV	0.2854	3.64058e4	1901.02698	95.6273



4q

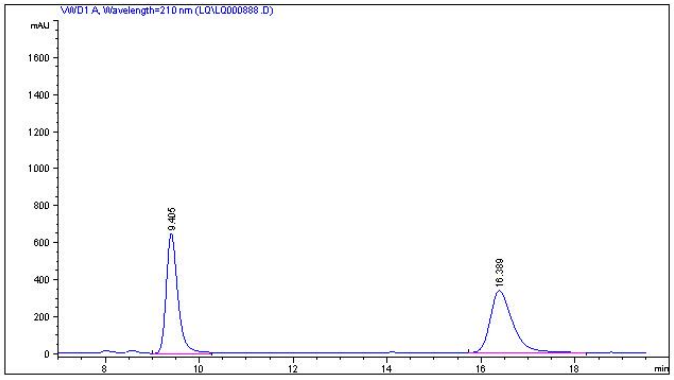
4-(4-fluorophenyl)oct-1-en-4-amine (4q)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 71% yield, 83% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.25 (m, 2H), 7.01 – 6.88 (m, 2H), 5.52 – 5.35 (m, 1H), 5.08 – 4.91 (m, 2H), 2.51 – 2.53 (m, 1H), 2.30 (dd, J = 13.7, 8.4 Hz, 1H), 1.71– 1.74 (m, 1H), 1.64 – 1.52 (m, 1H), 1.46 (s, 2H), 1.20 – 1.12 (m, 3H), 0.95 – 0.84 (m, 1H), 0.75 (t, J = 7.1 Hz, 3H).

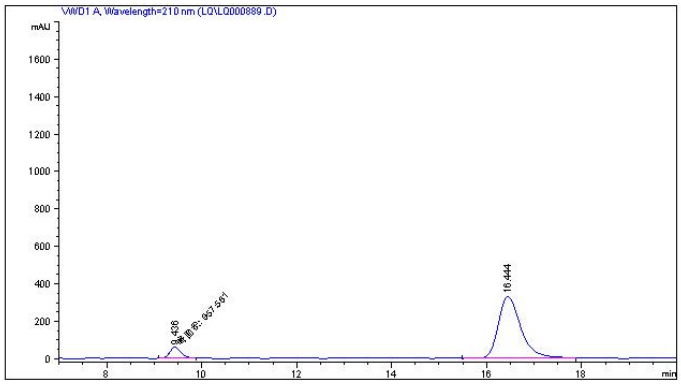
^{13}C NMR (101 MHz, Chloroform-d) δ 132.88, 126.41, 126.34, 117.69, 113.76, 113.55, 56.02, 47.85, 42.52, 24.83, 22.08, 12.98.

HRMS (ESI^{+}, m/Z): calcd for $C_{14}H_{20}FN$ $[M+H]^{+}$: 222.1653, found: 222.1656.

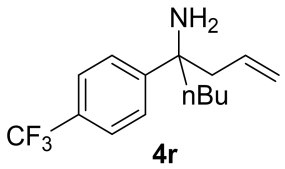
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 9.40 (minor) and 16.38 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.405	BV	0.2605	1.11187e4	646.86285	49.6532
2	16.389	VB	0.5005	1.12740e4	33.67319	50.3468



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.436	MM	0.2716	957.56128	58.76805	8.0252
2	16.444	BV	0.5080	1.09743e4	330.81934	91.9748



4r

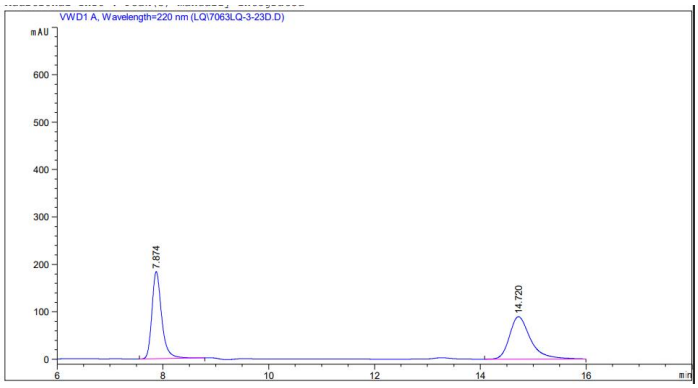
4-(4-(trifluoromethyl)phenyl)oct-1-en-4-amine (4r)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 27% yield, 37% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.63 – 7.46 (m, 4H), 5.55 – 5.38 (m, 1H), 5.12 – 5.01 (m, 2H), 2.63 (dd, J = 13.3, 6.2 Hz, 1H), 2.40 (dd, J = 13.7, 8.8 Hz, 1H), 1.89 – 1.79 (m, 1H), 1.74 – 1.62 (m, 1H), 1.58 (s, 2H), 1.25 – 1.15 (m, 3H), 0.97 – 0.87 (m, 1H), 0.82 (t, J = 7.2 Hz, 3H).

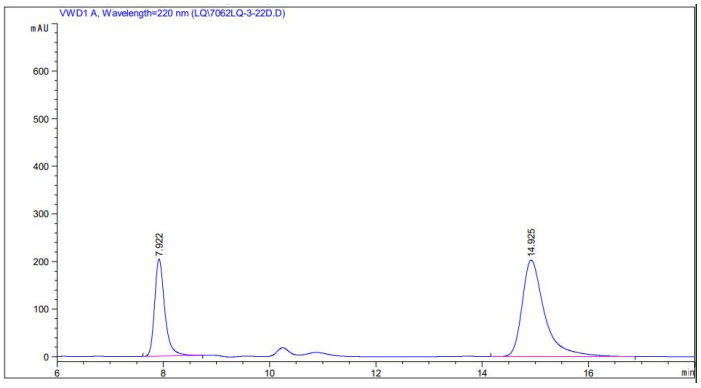
^{13}C NMR (101 MHz, Chloroform-d) δ 132.39, 132.12, 125.23, 124.00, 123.96, 118.11, 47.72, 42.34, 28.68, 24.76, 22.05, 12.93.

HRMS (ESI^{+}, m/Z): calcd for $C_{15}H_{20}F_3N$ [M+H]$^{+}$: 272.1621, found: 272.1627.

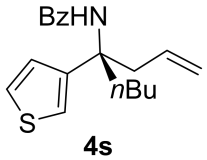
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 7.92 (minor) and 14.92 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.874	BB	0.1944	2351.91797	183.69128	48.9895
2	14.720	BBA	0.4138	2448.94067	89.32741	51.0105



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	7.922	BB	0.2002	2695.01807	203.95000	31.3077
2	14.925	BB	0.4346	5913.14551	202.54955	68.6923



4s

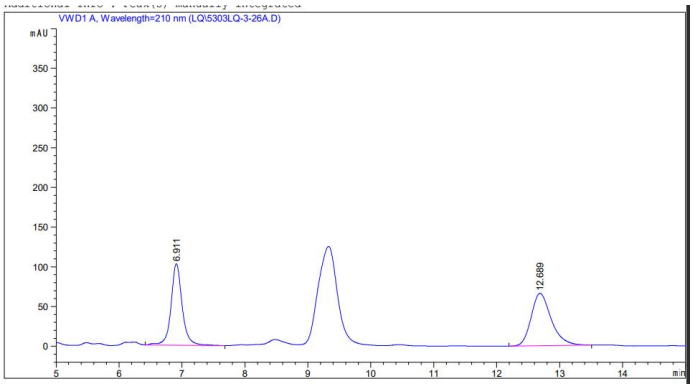
(R)-N-(4-(thiophen-3-yl)oct-1-en-4-yl)benzamide (4s)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). White solid, 26% yield, 89% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.80 – 7.68 (m, 2H), 7.53 – 7.48 (m, 1H), 7.47 – 7.40 (m, 2H), 7.30 (dd, J = 5.1, 3.0 Hz, 1H), 7.09 (dd, J = 3.0, 1.5 Hz, 1H), 7.05 (dd, J = 5.1, 1.5 Hz, 1H), 6.29 (s, 1H), 5.73 – 5.55 (m, 1H), 5.22 – 5.02 (m, 2H), 3.08 – 2.78 (m, 2H), 2.35 – 2.08 (m, 2H), 1.35 – 1.27 (m, 2H), 1.24 – 1.16 (m, 2H), 0.86 (t, J = 7.2 Hz, 3H).

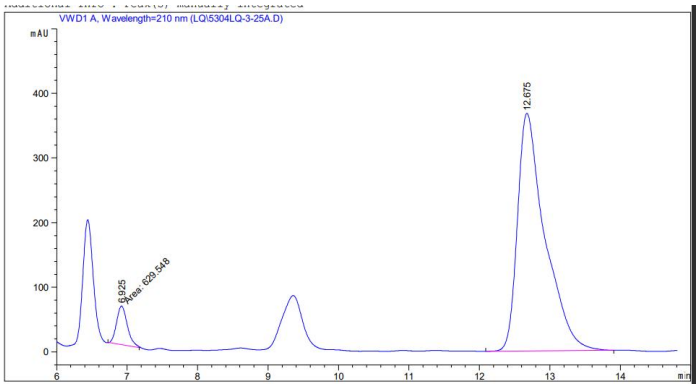
^{13}C NMR (101 MHz, Chloroform-d) δ 166.51, 133.57, 133.39, 131.41, 131.34, 128.64, 126.73, 120.37, 120.10, 119.35, 119.04, 43.11, 42.44, 38.42, 29.71, 25.92, 22.84.

HRMS (ESI^{+}, m/Z): calcd for $C_{19}H_{23}NOS$ $[M+H]^{+}$: 314.1573, found:314.1580.

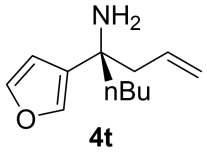
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 6.91 (minor) and 12.68 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.911	VB R	0.1848	1265.48877	102.65746	46.4557
2	12.689	BB	0.3363	1458.59021	65.88841	53.5443



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.925	MM	0.1760	629.54846	59.61303	5.9540
2	12.675	BB	0.3895	9943.98535	367.72729	94.0460



4t

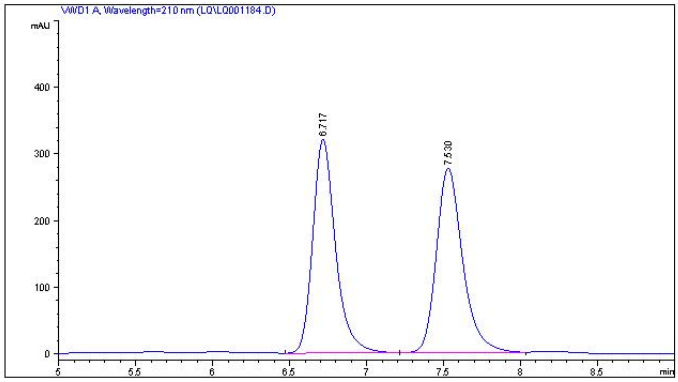
4-(furan-3-yl)oct-1-en-4-amine (4t)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 47% yield, 87% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.38 – 7.29 (m, 1H), 6.34 – 6.23 (m, 1H), 6.17 – 6.06 (m, 1H), 5.65 – 5.51 (m, 1H), 5.16 – 5.01 (m, 2H), 2.64 – 2.51 (m, 1H), 2.42 – 2.30 (m, 1H), 1.80 – 1.72 (m, 1H), 1.68 – 1.59 (m, 3H), 1.30 – 1.19 (m, 3H), 1.12 – 1.04 (m, 1H), 0.86 (t, J = 7.2 Hz, 3H).

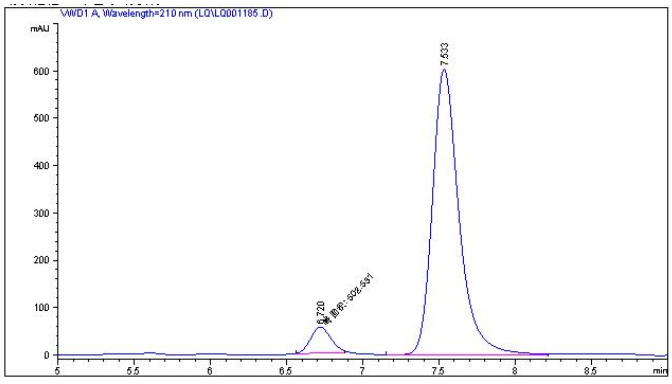
^{13}C NMR (101 MHz, Chloroform-d) δ 160.75, 141.10, 133.73, 118.55, 109.78, 104.82, 55.23, 45.44, 40.68, 25.95, 23.00, 14.03.

HRMS (ESI^{+}, m/Z): calcd for $C_{12}H_{19}NO$ $[M+H-NH_3]^{+}$: 177.1277, found: 177.1274.

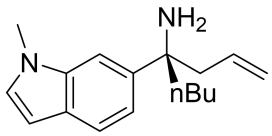
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 6.71 (minor) and 7.53 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.717	BB	0.1558	3290.71191	320.52753	49.9135
2	7.530	BV	0.1810	3302.11865	27.19037	50.0865



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	6.720	MM	0.1531	502.53149	54.72099	6.4135
2	7.533	BV	0.1837	7332.98682	603.77570	93.5865



4u

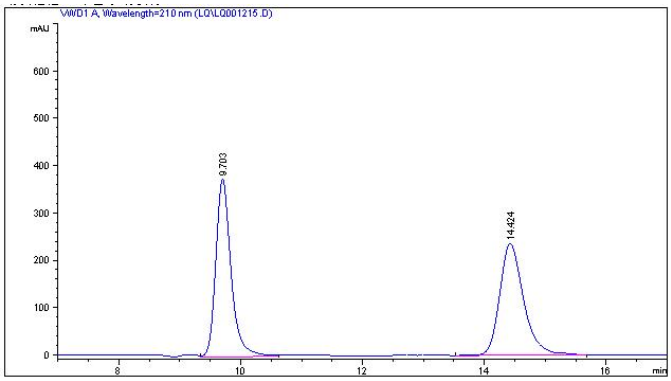
4-(1-methyl-1H-indol-6-yl) oct-1-en-4-amine (4u)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 43% yield, 93% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.58 (d, J = 8.4 Hz, 1H), 7.44 – 7.37 (m, 1H), 7.13 (dd, J = 8.3, 1.7 Hz, 1H), 7.03 (d, J = 3.1 Hz, 1H), 6.45 (dd, J = 3.1, 0.9 Hz, 1H), 5.62 – 5.45 (m, 1H), 5.15 – 4.97 (m, 2H), 3.80 (s, 3H), 2.8 – 2.68 (m, 1H), 2.45 (dd, J = 13.6, 8.6 Hz, 1H), 2.00 – 1.86 (m, 1H), 1.80 – 1.68 (m, 1H), 1.66 (s, 2H), 1.28 – 1.20 (m, 3H), 1.05 – 0.94 (m, 1H), 0.82 (t, J = 7.1 Hz, 3H).

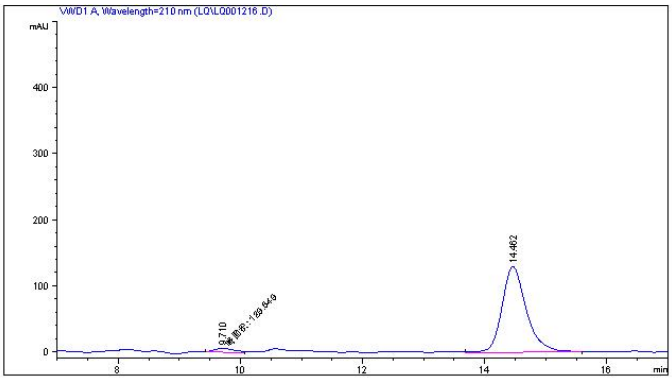
^{13}C NMR (101 MHz, Chloroform-d) δ 139.76, 135.73, 133.65, 127.70, 125.39, 119.33, 117.13, 116.64, 105.41, 99.38, 56.54, 48.32, 42.92, 31.82, 24.98, 22.17, 13.00.

HRMS (ESI^{+}, m/Z): calcd for $C_{17}H_{24}N_2$ [M+Na]+ : 279.1837, found: 279.1832.

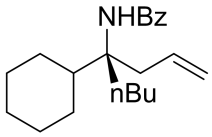
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 9.70 (minor) and 14.24 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.703	VV	0.2626	6520.96094	375.51501	50.2974
2	14.424	BB	0.4152	6443.83545	236.23663	49.7026



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.710	MM	0.3671	129.84944	5.89515	3.4835
2	14.462	VB	0.4179	3597.69287	129.57629	96.5165



4v

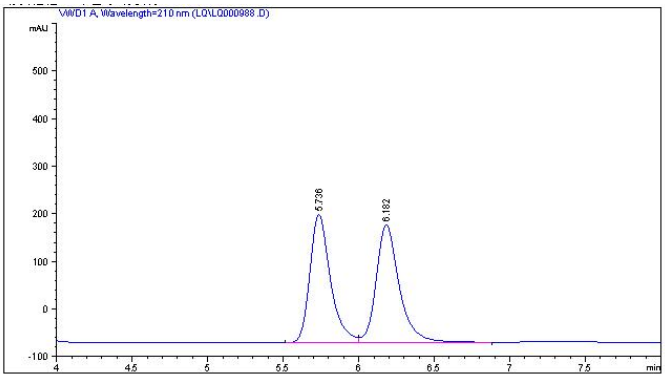
4-cyclohexyloct-1-en-4-amine (4v)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 27% yield, 23% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.73 – 7.68 (m, 2H), 7.50 – 7.45 (m, 1H), 7.45 – 7.38 (m, 2H), 5.98 – 5.87 (m, 1H), 5.86 (s, 1H), 5.25 – 5.08 (m, 2H), 2.80 – 2.60 (m, J = 14.2, 7.2, 1.3 Hz, 1H), 2.48 (dd, J = 14.1, 7.8 Hz, 1H), 2.11 – 1.99 (m, 2H), 1.85 – 1.74 (m, 4H), 1.70 – 1.62 (m, 2H), 1.36 – 1.12 (m, 9H), 0.93 – 0.87 (m, 3H).

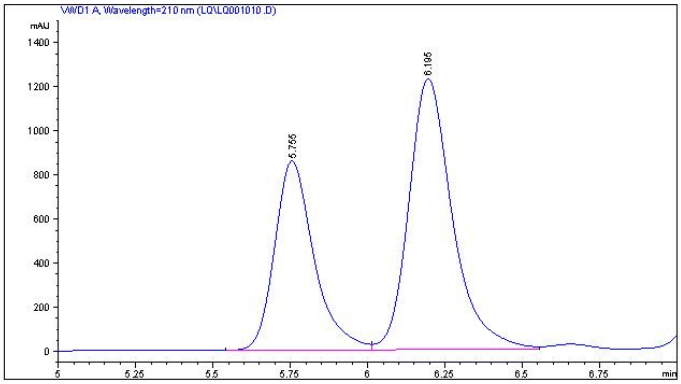
^{13}C NMR (101 MHz, Chloroform-d) δ 166.61, 136.37, 135.05, 131.00, 128.54, 126.62, 118.44, 61.23, 45.13, 39.35, 35.32, 28.11, 27.96, 27.05, 26.70, 26.47, 23.35, 14.16.

HRMS (ESI^{+}, m/Z): calcd for $C_{21}H_{31}NO$ $[M+H]^{+}$: 314.2478, found: 314.2478.

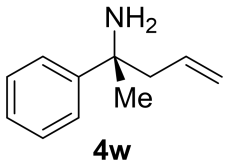
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22°C, detection at 210 nm. Retention time (min): 5.73 (minor) and 6.18 (major)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.736	BV	0.1424	2551.44556	269.62430	49.1882
2	6.182	VB	0.1591	2635.66211	247.71803	50.8118



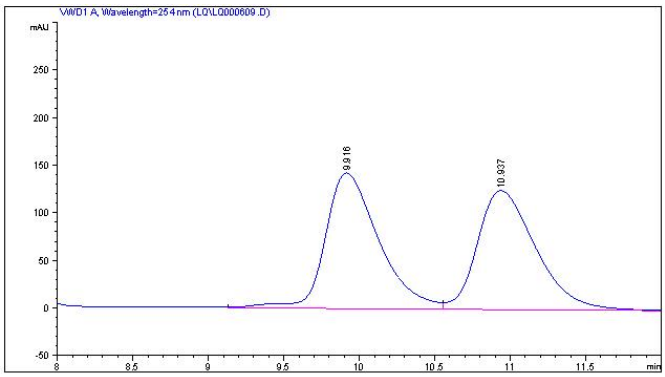
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	5.755	BV	0.1340	7564.46191	857.08514	38.5885
2	6.195	VV	0.1483	1.20384e4	1228.81231	61.4115



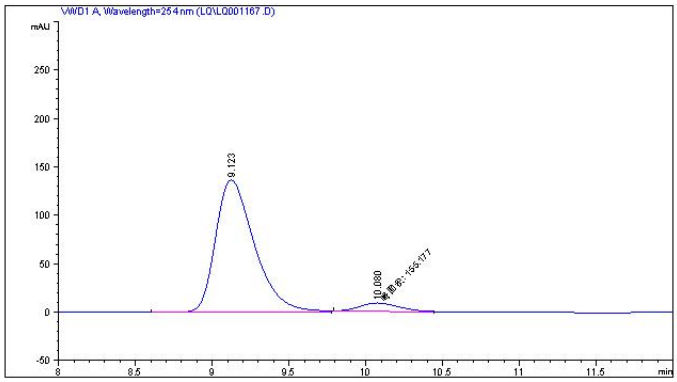
4w

2-phenylpent-4-en-2-amine (4w)

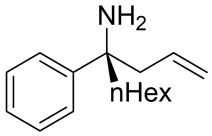
[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 83% yield, 87% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.49 – 7.43 (m, 2H), 7.37 – 7.30 (m, 2H), 7.27 – 7.19 (m, 1H), 5.62 – 5.49 (m, 1H), 5.11 – 5.02 (m, 2H), 2.62 – 2.53 (m, 1H), 2.47 – 2.38 (m, 1H), 1.81 (s, 2H), 1.48 (s, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 148.49, 134.26, 128.16, 126.23, 125.18, 118.55, 54.65, 49.66, 30.76.
HRMS (ESI^{+}, m/Z): calcd for $C_{11}H_{15}N[M+H]^{+}$: 162.1279, found: 162.1277.
HPLC analysis: Chiracel-ODH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 254 nm. Retention time (min): 9.91 (major) and 10.97 (minor)



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.916	VV	0.3713	3505.62769	142.35381	51.0766
2	10.937	VB	0.4133	3357.83960	125.03012	48.9234



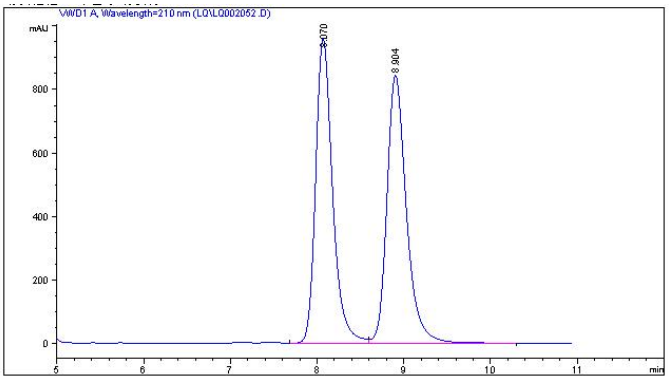
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	9.123	BV	0.2676	2391.02856	136.32307	93.9056
2	10.080	MM	0.2984	155.17705	8.66675	6.0944



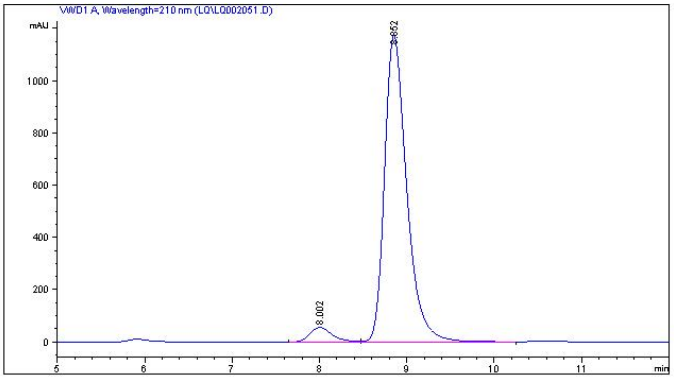
4x

4-phenyldec-1-en-4-amine (4x)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 78% yield, 91% *ee*] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.37 (m, 2H), 7.35 – 7.29 (m, 2H), 7.23 – 7.17 (m, 1H), 5.59 – 5.43 (m, 1H), 5.12 – 4.99 (m, 2H), 2.70 – 2.50 (m, 1H), 2.38 (dd, J = 13.6, 8.5 Hz, 1H), 1.89 – 1.77 (m, 1H), 1.69 – 1.51 (m, 3H), 1.36 – 1.30 (m, 1H), 1.22 – 1.15 (m, 6H), 1.03 – 0.91 (m, 1H), 0.86 – 0.79 (m, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 147.08, 134.20, 128.03, 125.96, 125.72, 118.46, 57.31, 48.78, 43.72, 31.71, 29.76, 23.63, 22.60, 14.04.
HRMS (ESI^{+}, m/Z): calcd for $C_{16}H_{25}N$ $[M+H]^{+}$: 232.2060, found: 232.2058.
HPLC analysis: Chiracel-ADH, *n*-heptane/*i*-PrOH 90:10, 1 mL/min, 22℃, detection at 210 nm. Retention time (min): 8.07 (minor) and 8.90 (major)



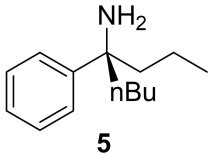
Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.070	BV	0.2061	1.29950e4	959.10602	49.7443
2	8.904	VB	0.2355	1.31286e4	843.81708	50.2557



Peak #	RetTime [min]	Type	Width [min]	Area [mAU*s]	Height [mAU]	Area %
1	8.002	BV	0.2703	987.84094	55.59589	4.5569
2	8.853	VV	0.2689	2.6903e4	1172.57776	95.4431

3. Conversions of homoallylic amines

Conversion of homoallylic amines to alkyl amine[2]: Charge an oven-dried 50 mL Teflon-lined screw cap-sealed tube (with a suction port) equipped with a stir bar with substrate (0.25 mmol), $Pd(OAc)_2$(0.02 mmol, 4.5 mg), solvent and proton source (if necessary) under a nitrogen atmosphere. Add HBPin (0.6 mmol) to the reaction mixture. Stir the reaction mixture at 25 °C for 12 hours. Dilute the reaction mixture with 10 ml of EA. Extract the reaction mixture with saturated $NaHCO_3$ and EA (x3). Dry the organic layer over Na_2SO_4 and concentrate under reduced pressure. Purify the reaction mixture by flash chromatography on silica gel to afford product (Yellow oil, 87% yield).



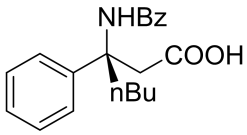
5

4-phenyloctan-4-amine (5)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). Yellow oil, 87% yield] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.42 – 7.37 (m, 2H), 7.32 (dd, J = 8.6, 6.9 Hz, 2H), 7.23 – 7.17 (m, 1H), 1.86 – 1.72 (m, 2H), 1.71 – 1.51 (m, 4H), 1.28 – 1.17 (m, 4H), 1.05 – 0.94 (m, 2H), 0.92 – 0.64.(m, 6H).
^{13}C NMR (101 MHz, Chloroform-d) δ 127.98, 125.67, 25.86, 23.20, 16.97, 14.58, 14.02.
HRMS (ESI^+, m/Z): calcd for $C_{14}H_{23}N$ $[M+H]^+$: 206.1903, found: 206.1903.

Conversion of homoallylic amines to β-amino acids[3]:

Di-tert-butyl dicarbonate (0.12g, 0.6mmol) was added to substrate (0.2 g,0.5 mmol) dissolved in Et_2O (12 mL) and the reaction was stirred for 6 h at RT, after which time the solvent was removed under reduced pressure. To the crude material dissolved in CH_3CN (5 mL) was added $RuCl_3 \cdot H_2O$ (10.3 mg, 0.05 mmol) and the mixture was cooled to 0 °C . After addition of $NaIO_4$ (0.2 g, 1 mmol) dissolved in water (5 mL), the mixture was stirred for 0.5 h, followed by extraction with EA. Dry the organic layer over Na_2SO_4 and concentrate under reduced pressure. Purify the reaction mixture by flash chromatography on silica gel to afford product (White solid, 68% yield).



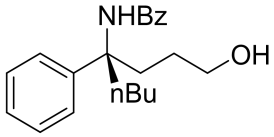
6

3-((tert-butoxycarbonyl)amino)-3-phenylheptanoic acid (6)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 2:1). White solid, 73% yield] ^{1}H NMR (400 MHz, DMSO-d6) δ 8.29 (s, 1H), 7.81 (dd, J = 7.1, 1.8 Hz, 2H), 7.56 – 7.49 (m, 1H), 7.46 (dd, J = 8.1, 6.5 Hz, 2H), 7.36 – 7.25 (m, 4H), 7.21 – 7.15 (m, 1H), 3.06 (d, J = 14.2 Hz, 1H), 2.41 – 2.27 (m, J = 12.6, 4.5 Hz, 1H), 2.07 – 1.94 (m, 1H), 1.25 – 1.15 (m, 3H), 1.25 – 1.07 (m, 2H), 0.78 (t, J = 7.2 Hz, 3H).
^{13}C NMR (101 MHz, DMSO-d6) δ 172.27, 165.82, 145.03, 135.45, 130.92, 128.10, 127.75, 127.31, 125.98, 125.28, 59.46, 38.45, 28.99, 25.29, 22.35, 13.88.
HRMS (ESI^+, m/Z): calcd for $C_{20}H_{23}NO_3$ $[M+Na]^+$: 348.1574, found: 348.1570.

Conversion of homoallylic amines to amino alcohol[4]:

BH_3 in THF (1M 0.4 mL, 0.4mmol) was added to substrate (92 mg,0.3 mmol) dissolved in THF (5 mL) and the reaction was stirred for 18 h at RT. When the reaction is complete, add NaOH (1M 0.9 mL) and 30% H_2O_2(0.5mL). The mixture was stirred for 7 h, followed by extraction with DCM. Dry the organic layer over Na_2SO_4 and concentrate under reduced pressure (White solid, 68% yield).



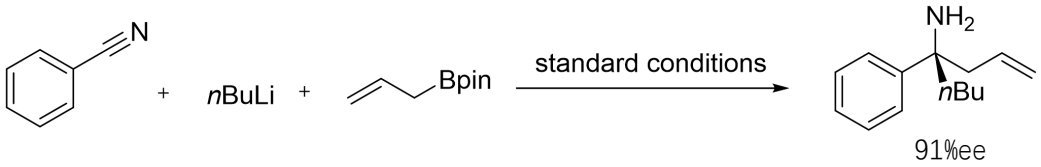
7

N-(1-hydroxy-4-phenyloctan-4-yl) benzamide (7)

[Purification by flash column chromatography on silica gel (eluent, PE: EA = 1:1). White solid, 68% yield] ^{1}H NMR (400 MHz, Chloroform-d) δ 7.82 – 7.76 (m, 2H), 7.52 – 7.46 (m, 1H), 7.45 – 7.39 (m, 2H), 7.38 – 7.30 (m, 4H), 7.26 – 7.20 (m, 1H), 6.59 (s, 1H), 3.61 – 3.52 (m, 2H), 2.32 – 2.23 (m, 3H), 2.17 – 2.09 (m, 1H), 1.47 – 1.38 (m, 2H), 1.34 – 1.23 (m, 3H), 1.20 – 1.10 (m, 2H), 0.84 (t, J = 7.3 Hz, 3H).
^{13}C NMR (101 MHz, Chloroform-d) δ 166.71, 144.41, 135.48, 131.39, 128.62, 128.36, 126.86, 126.63, 125.48, 62.66, 62.16, 38.04, 34.31, 26.89, 25.93, 22.93, 14.07.
HRMS (ESI$^+$, m/Z): calcd for $C_{21}H_{27}NO_2$ $[M+H]^+$: 326.2115, found: 326.2115.

4. Determination of absolute configuration

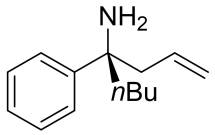
The absolute configuration was determined through the known compound as follows[5]. $[\alpha]_{D}^{20}$ = +62.5° (c = 0.576, $CHCl_3$). By comparison to the reported optical rotations $[\alpha]_{D}^{22}$ = +39.3° (c = 1.4, $CHCl_3$ for optically pure amine); the absolute configuration was determined to be (***R***).



91%ee

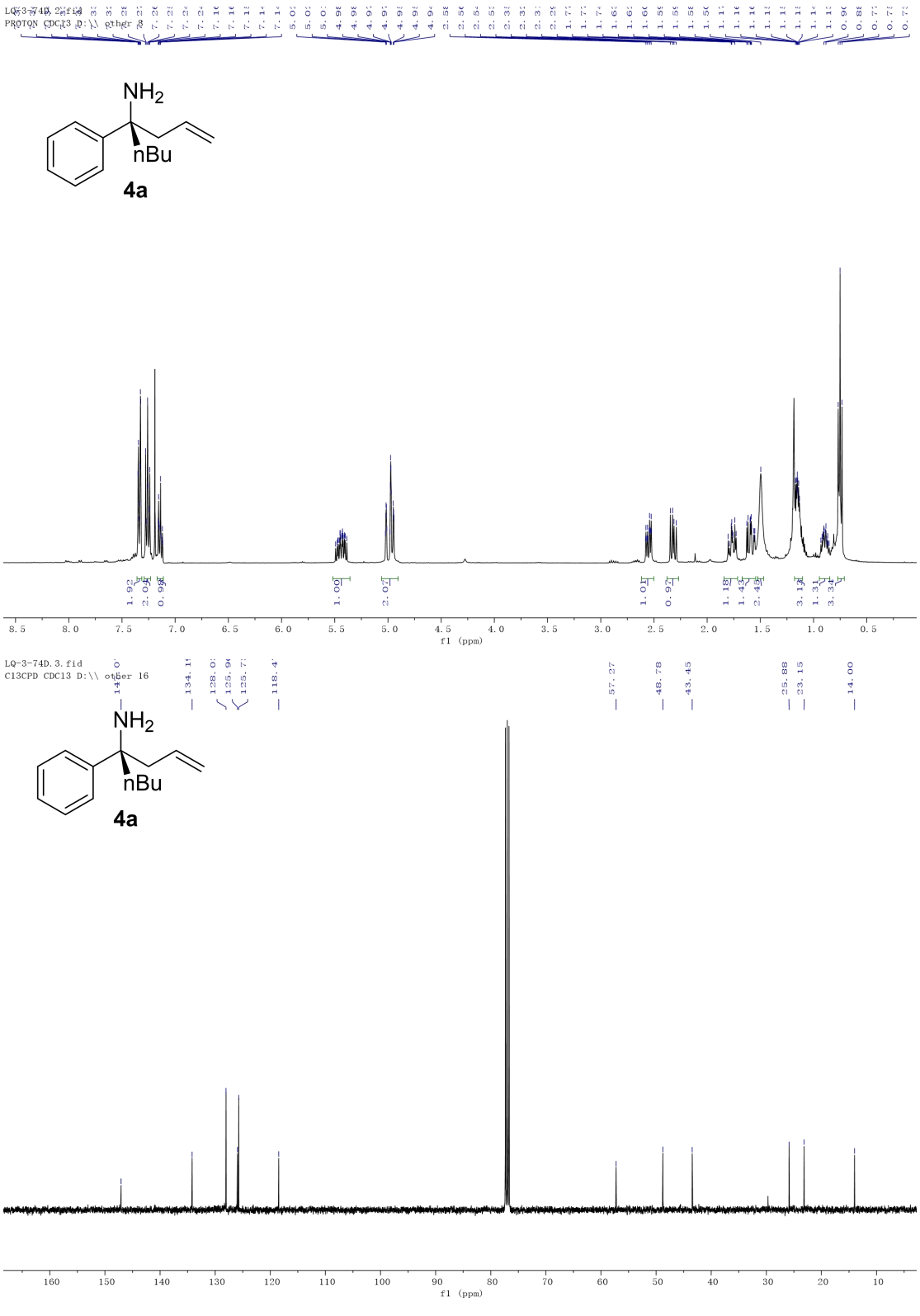
$[\alpha]_{D}^{20}$ = +62.5°
(c = 0.576, $CHCl_3$)

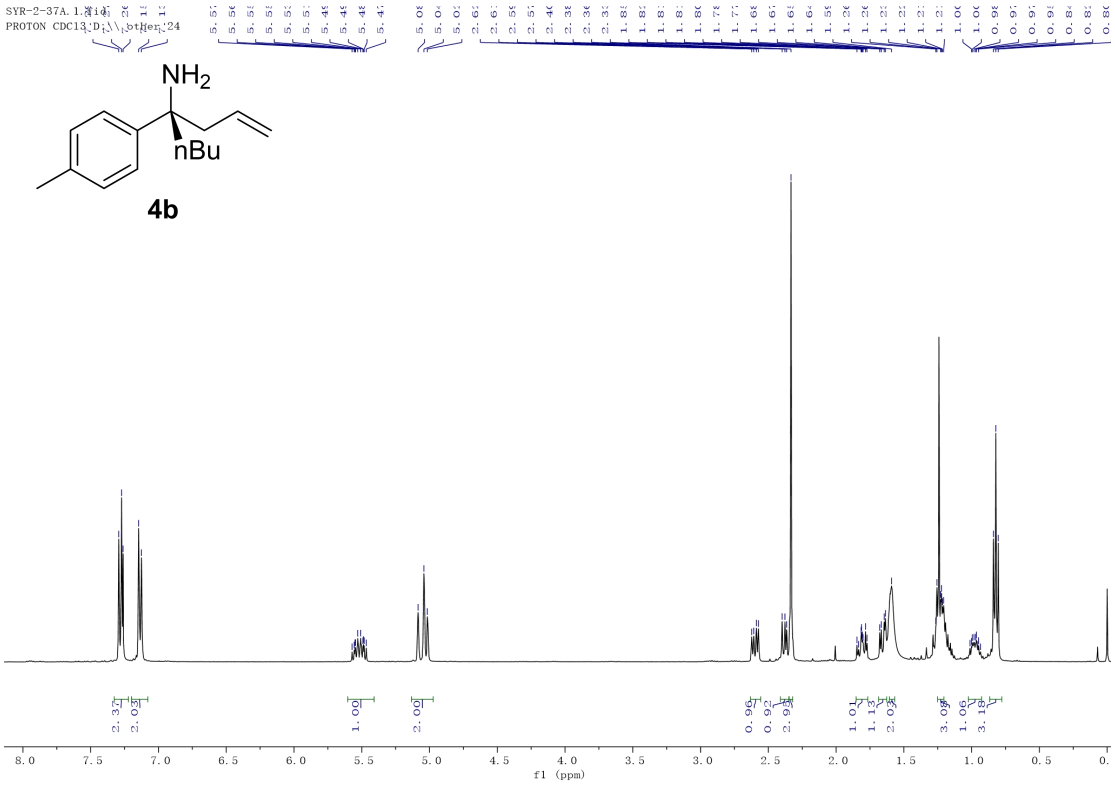
reported amine



$[\alpha]_{D}^{22}$ = +39.3°
c = 1.4, $CHCl_3$

5. NMR spectra

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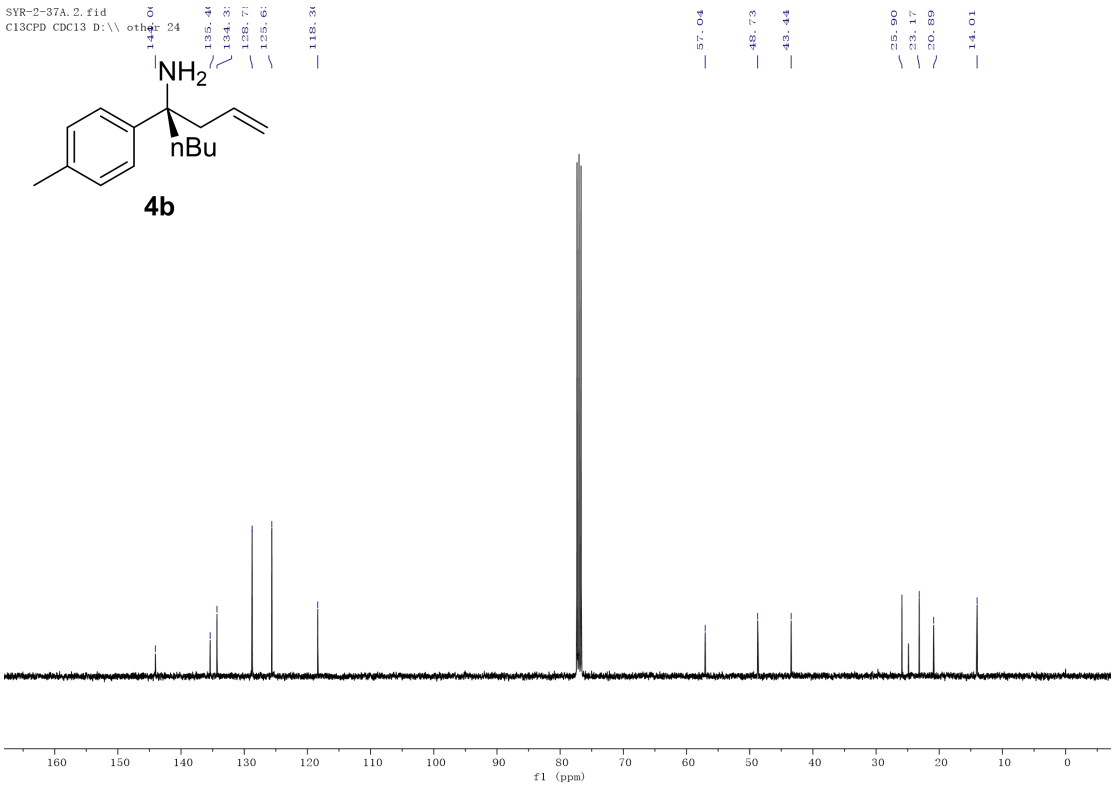
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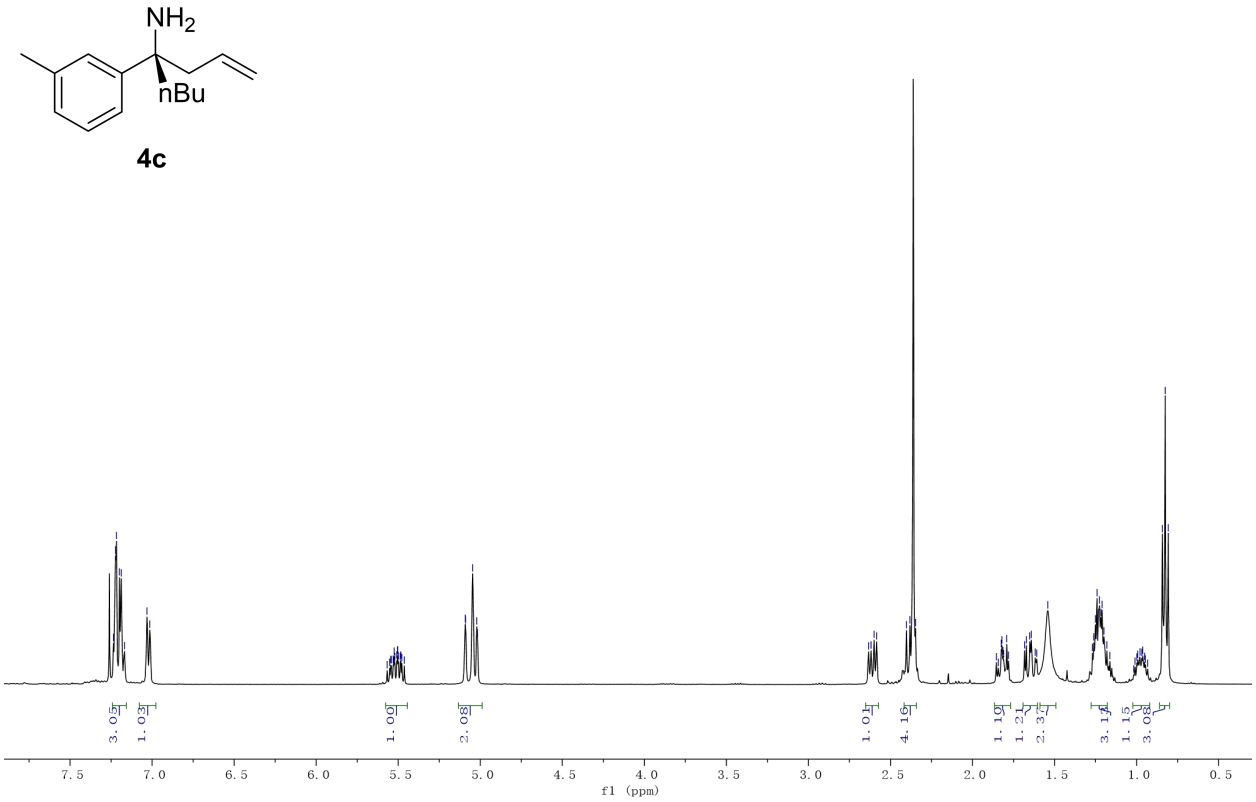
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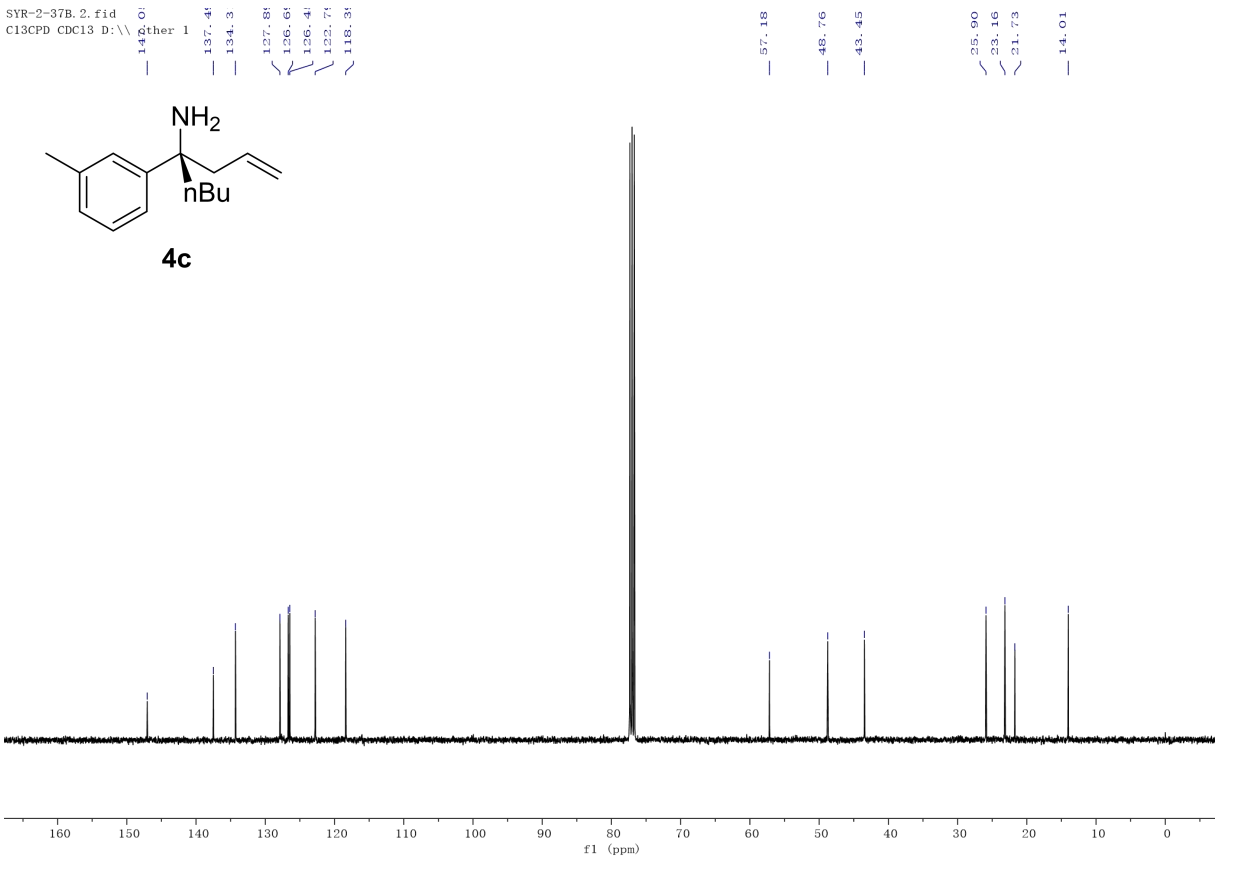
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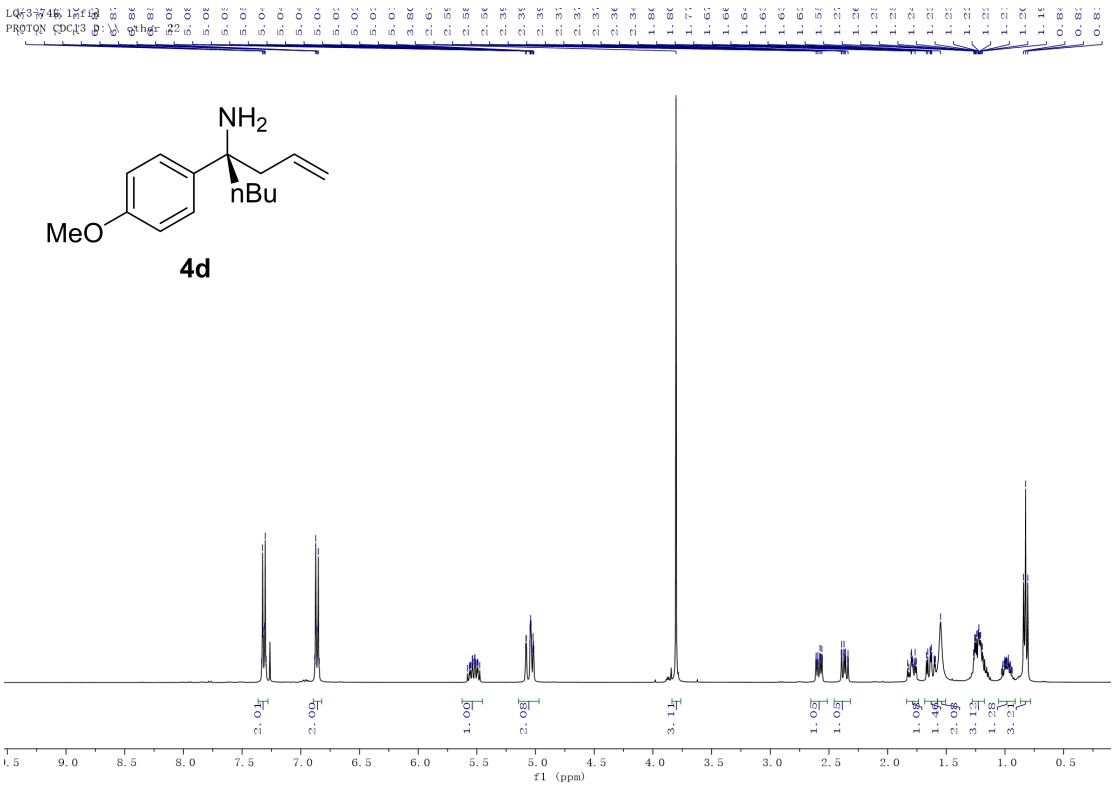
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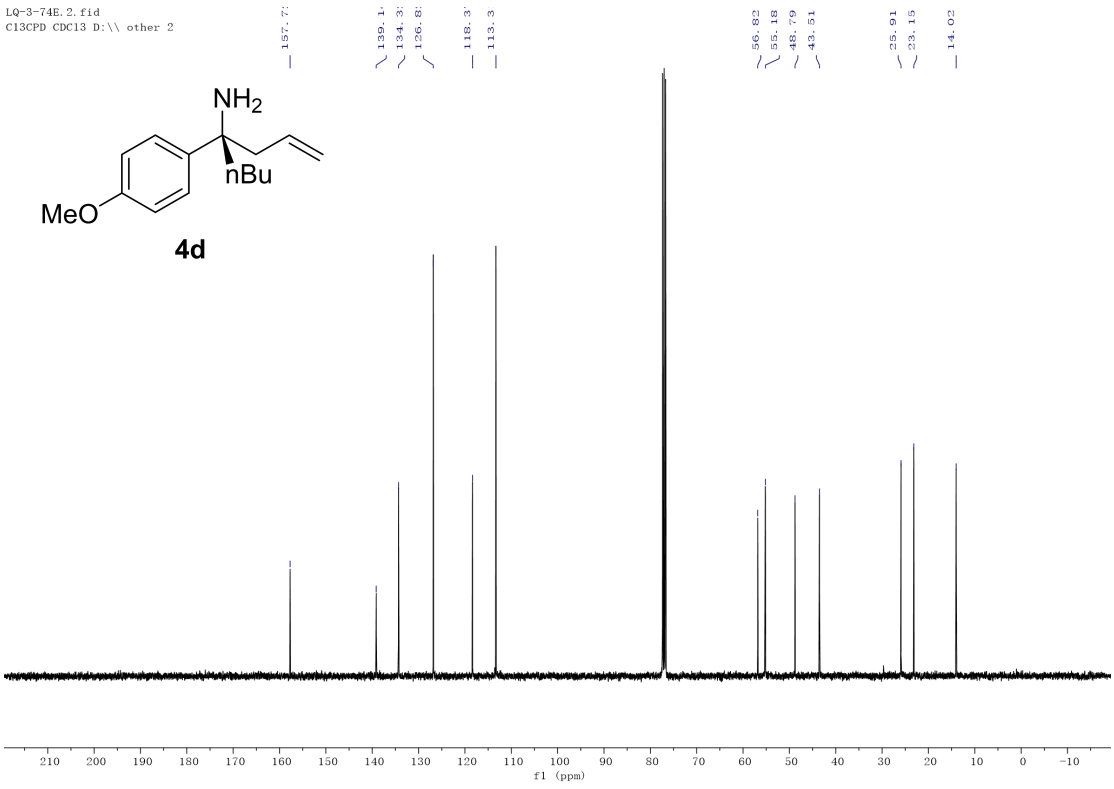
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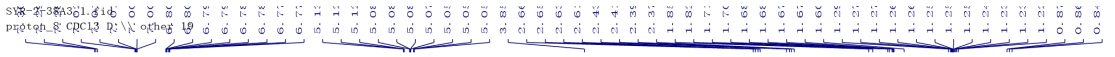

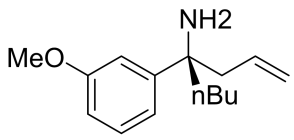
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MeO
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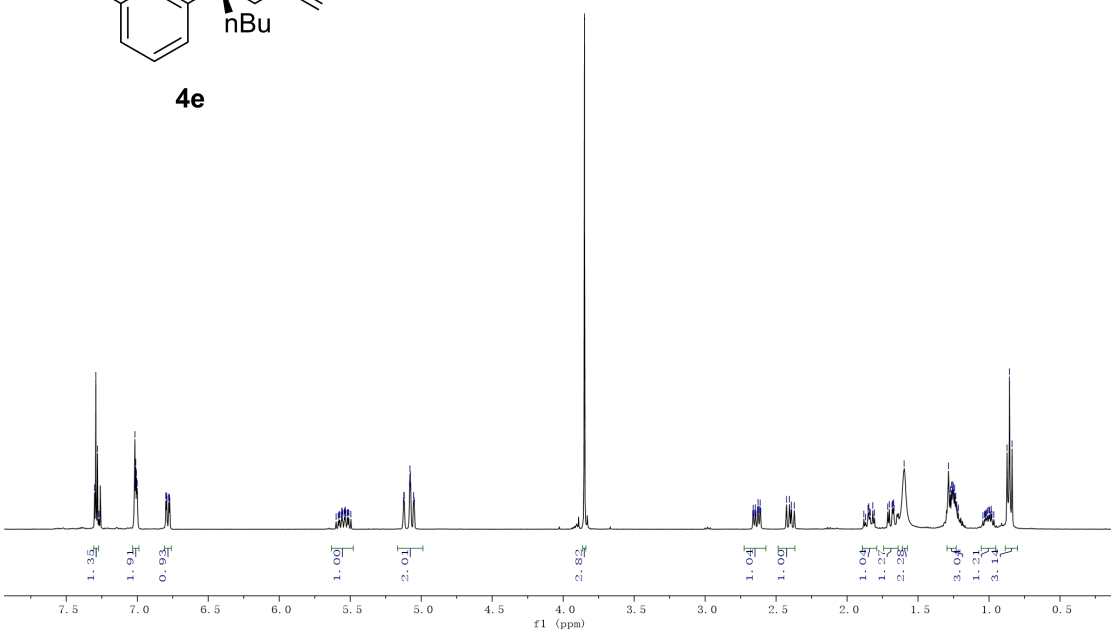
4e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6.5
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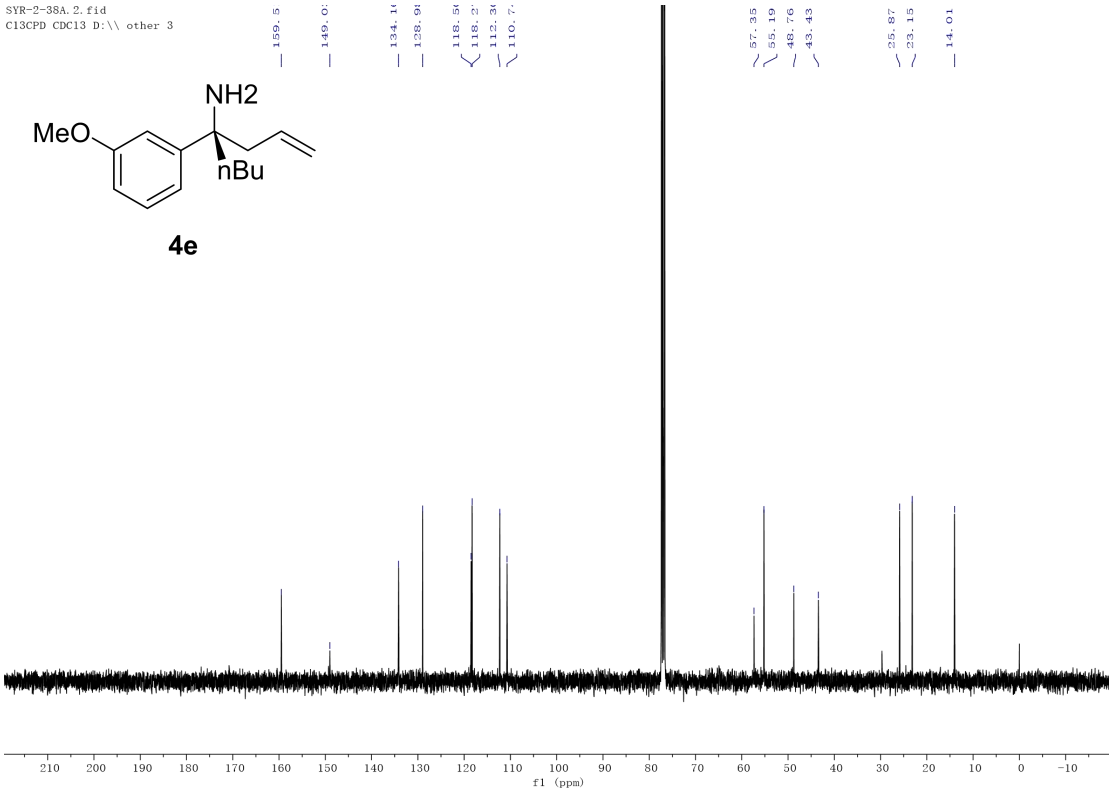
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128.9
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118.2
112.3
110.7
57.35
55.19
48.76
43.43
25.87
23.15
14.01
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200
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180
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160
150
140
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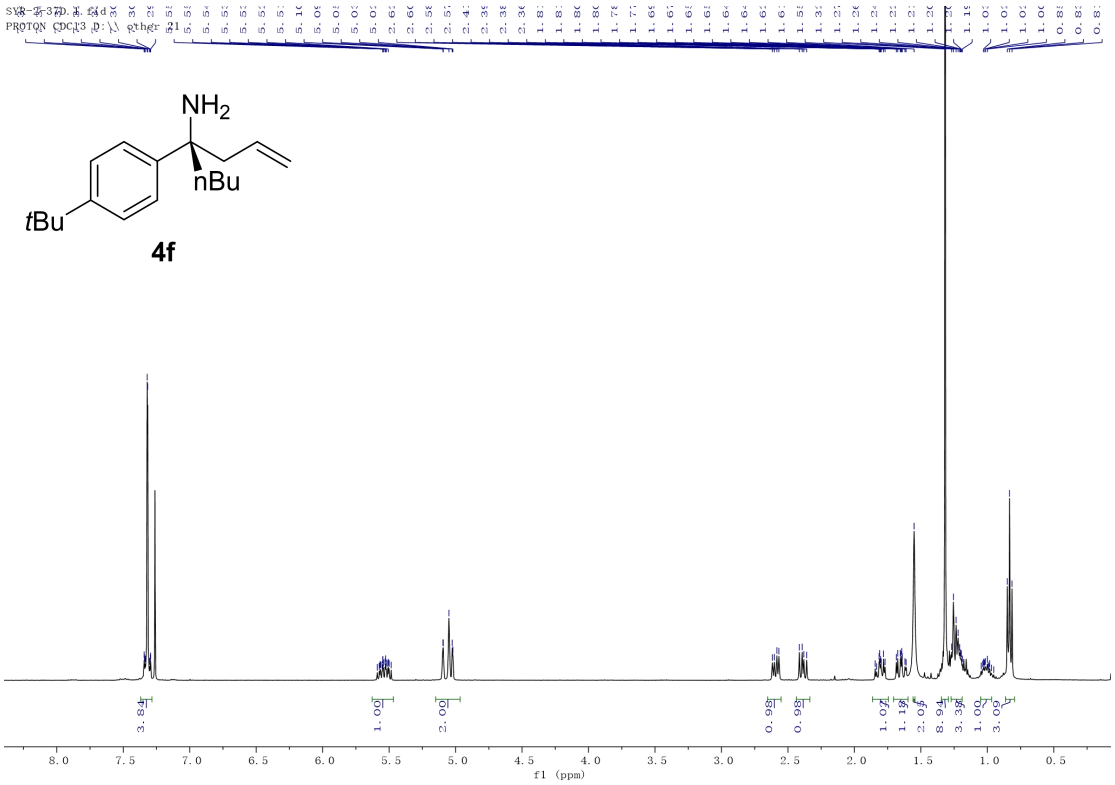
f1 (ppm)

NH2
MeO
nBu

4e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nBu
tBu
4f
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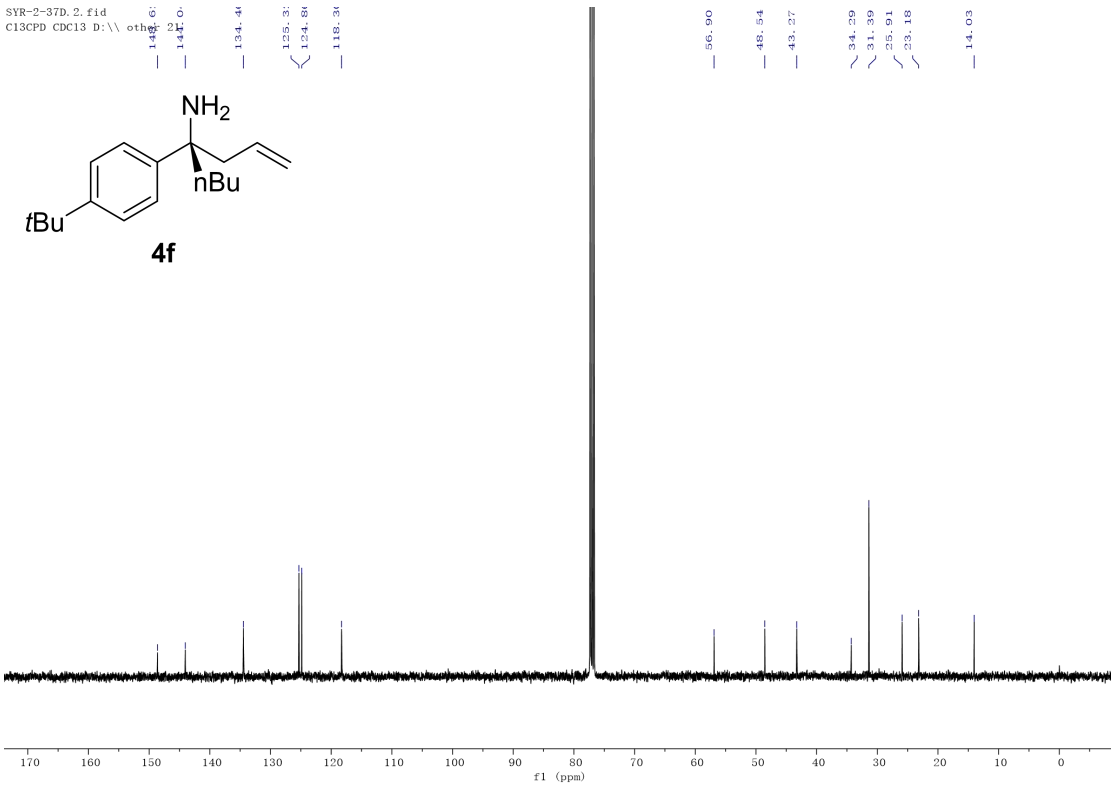
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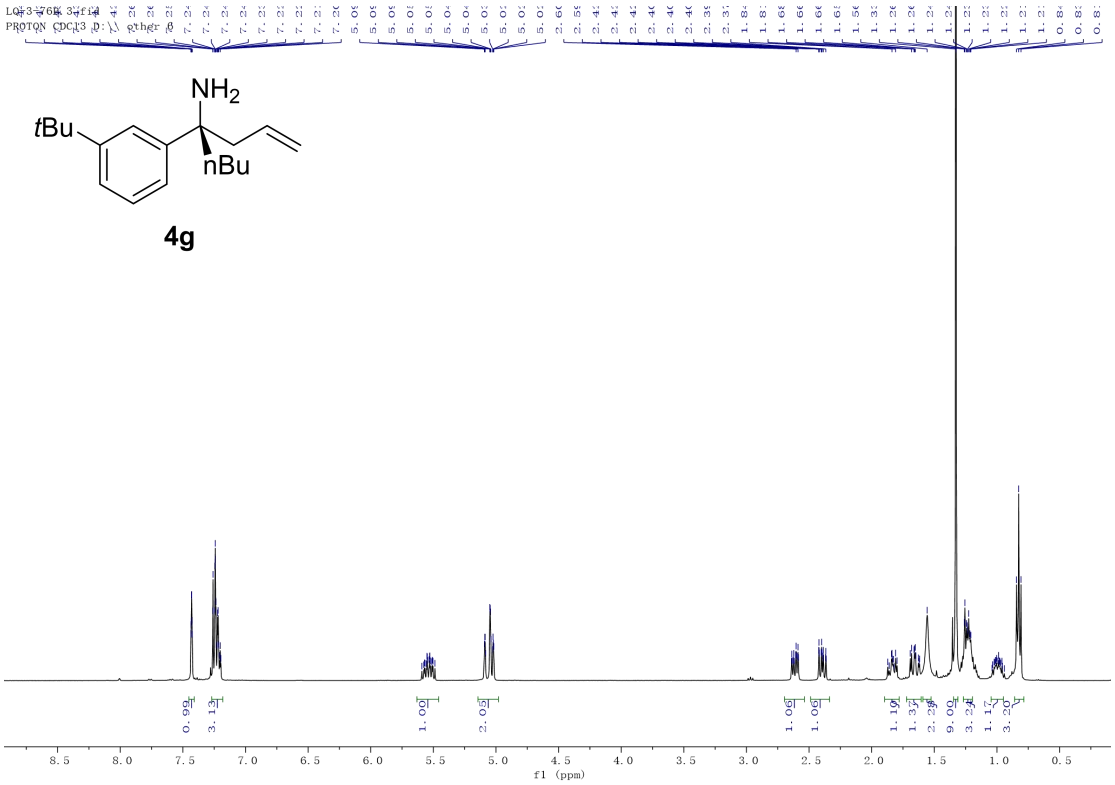
tBu
4f
f1 (ppm)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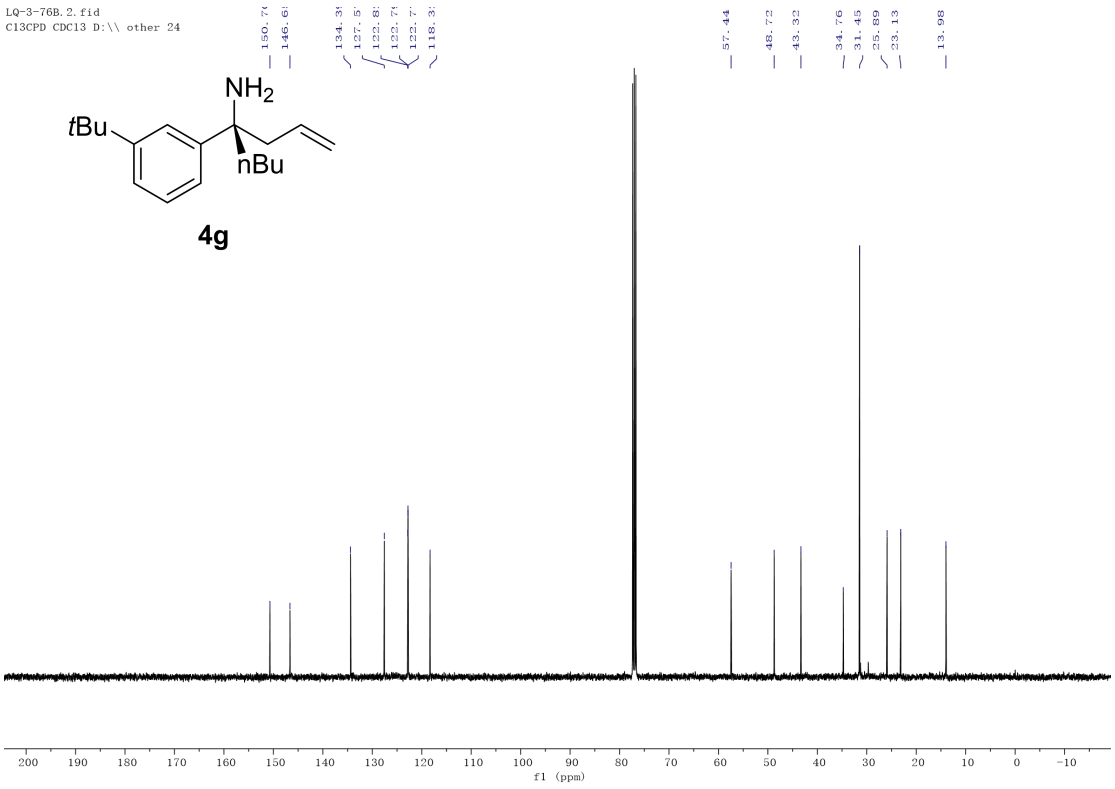
3.20
f1 (ppm)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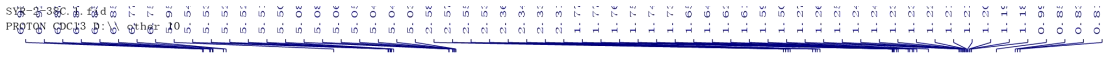
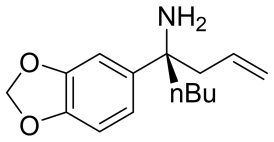
NH2
tBu
nBu
4g
f1 (ppm)





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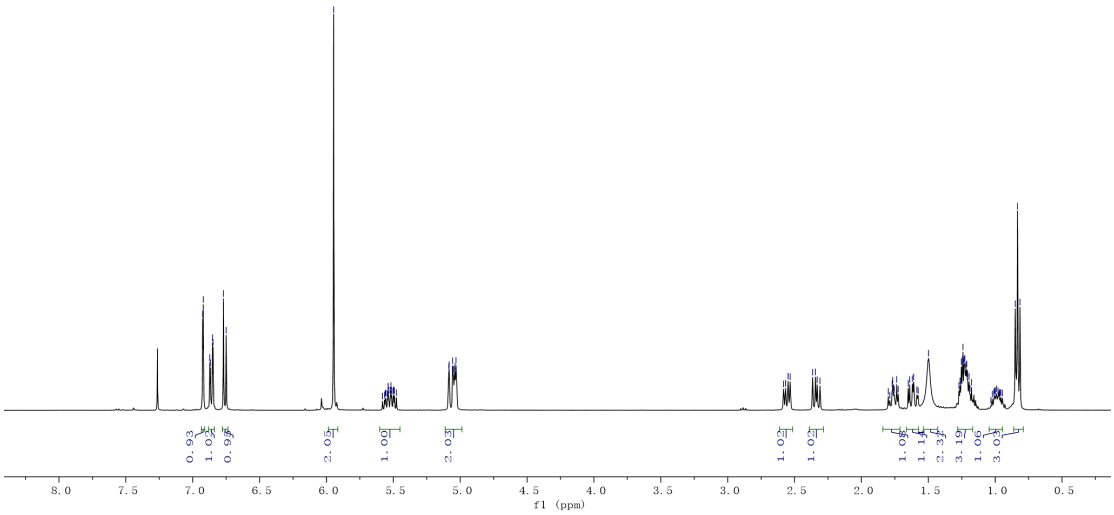

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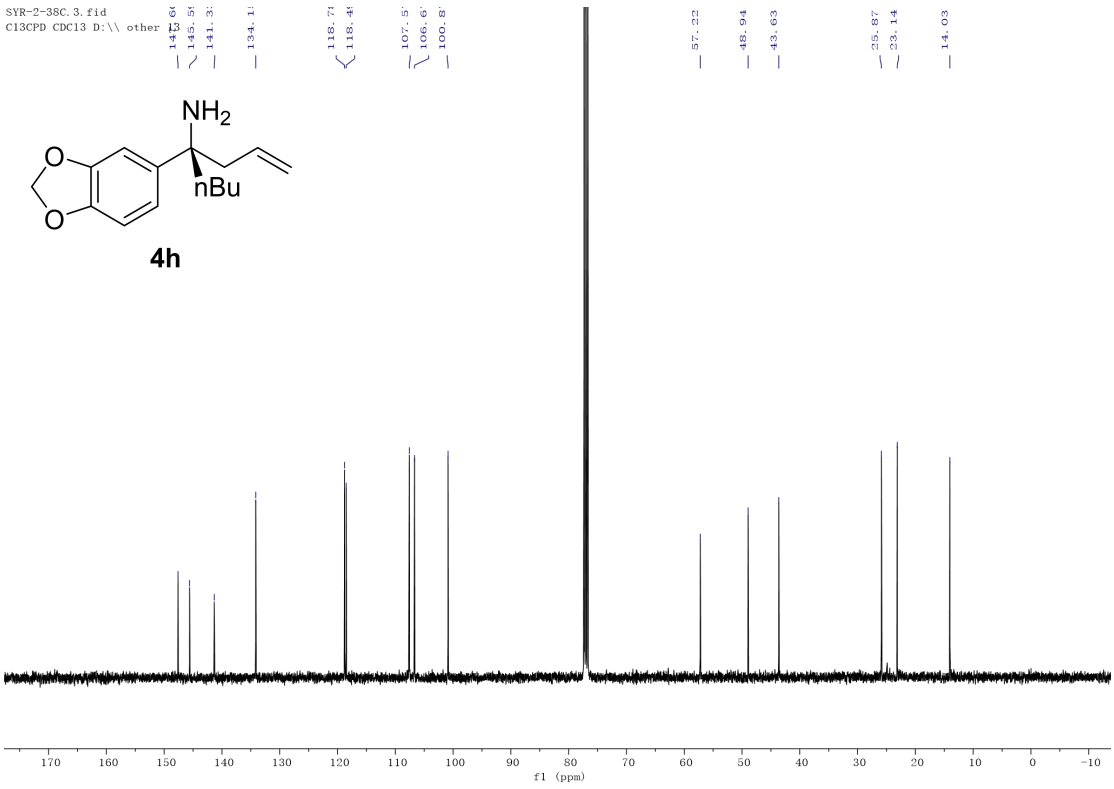

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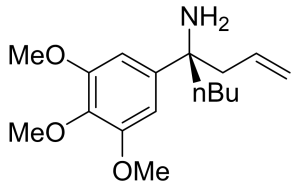

4i

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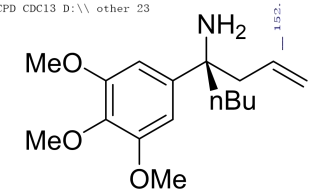

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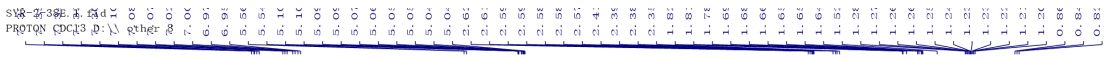

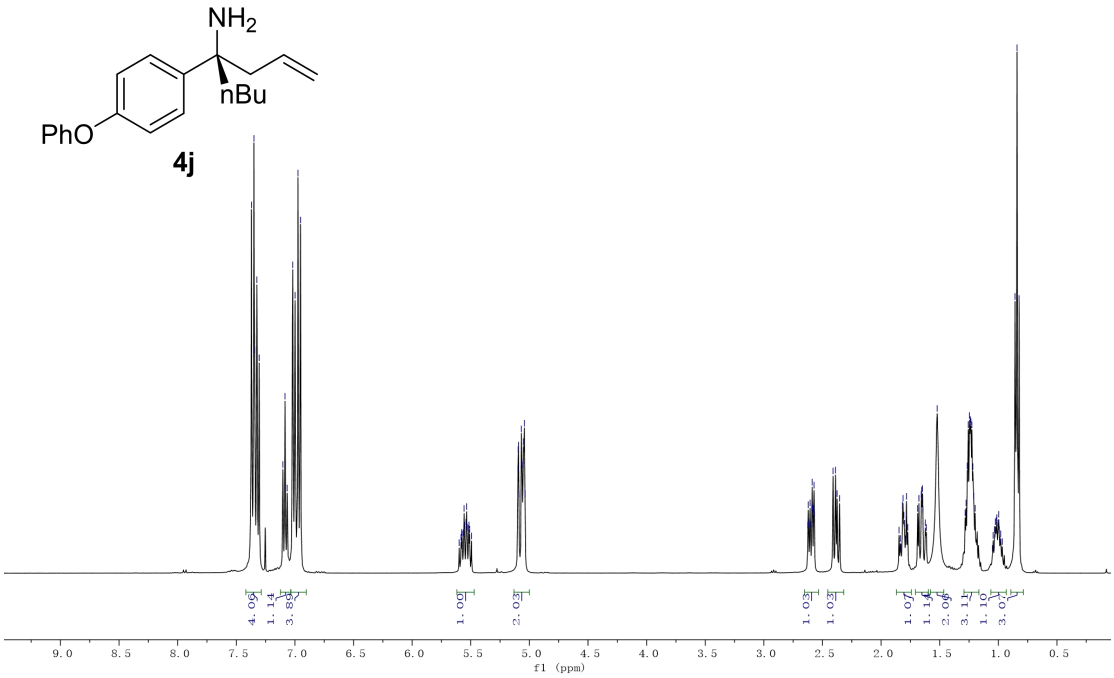

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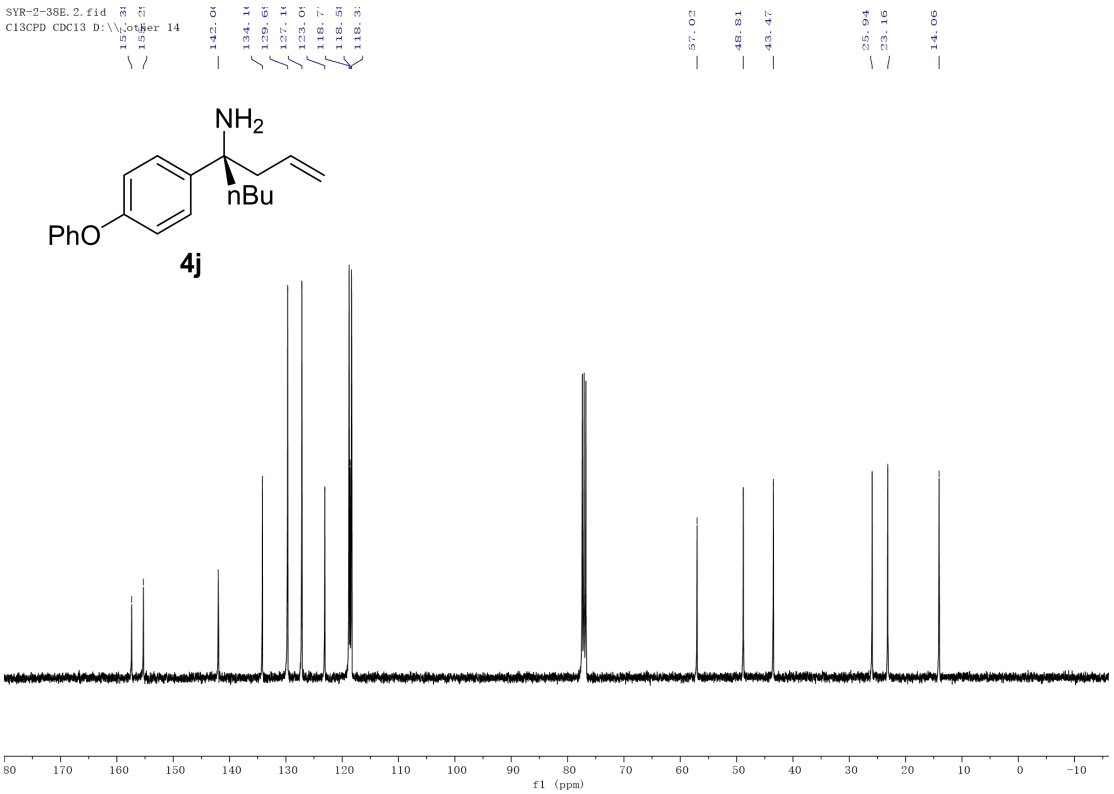

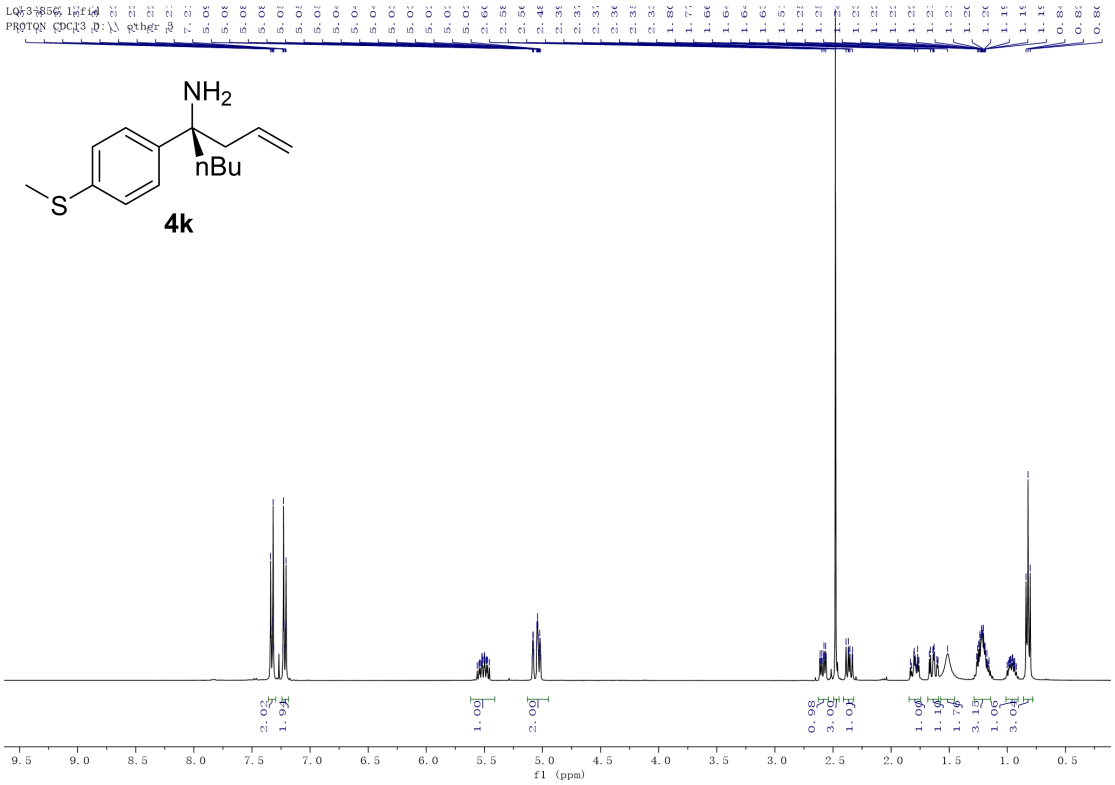
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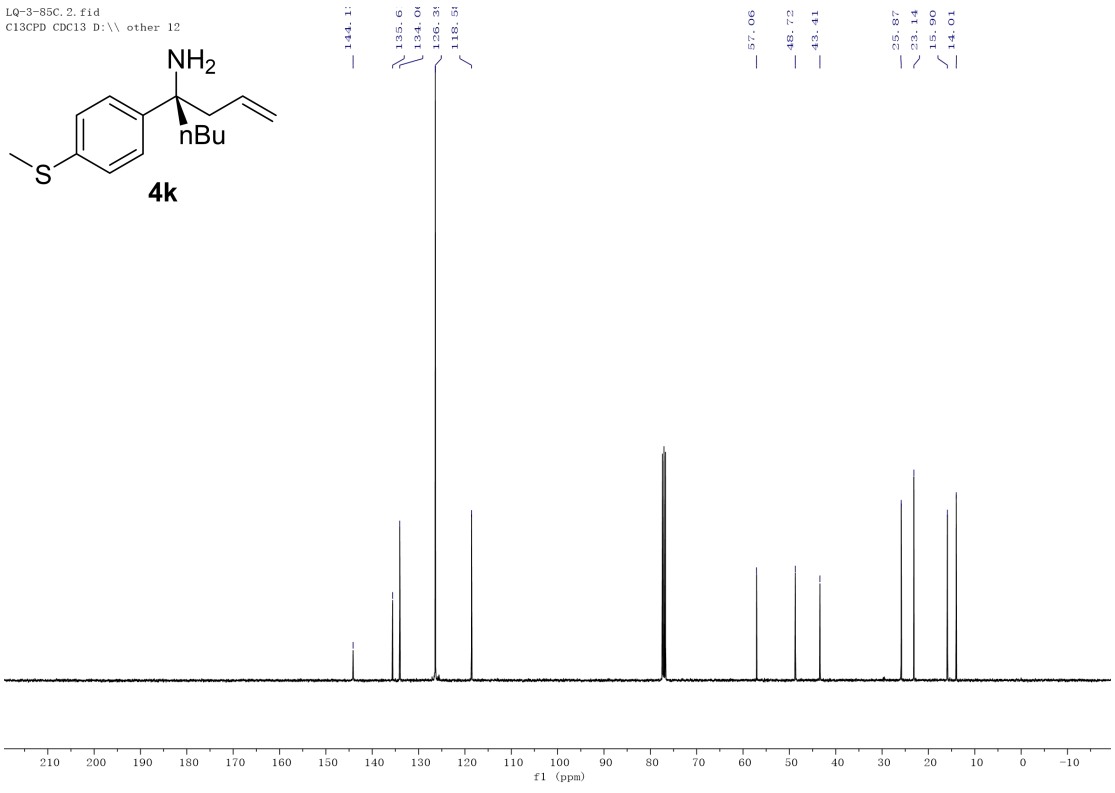
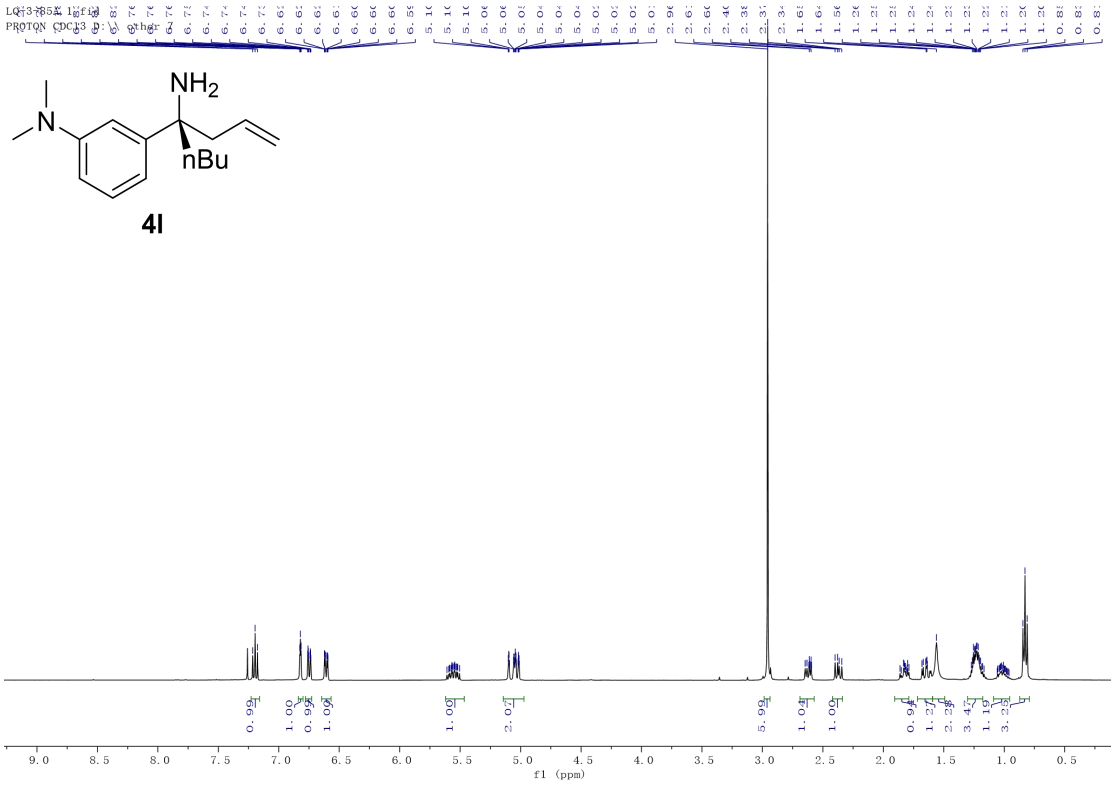
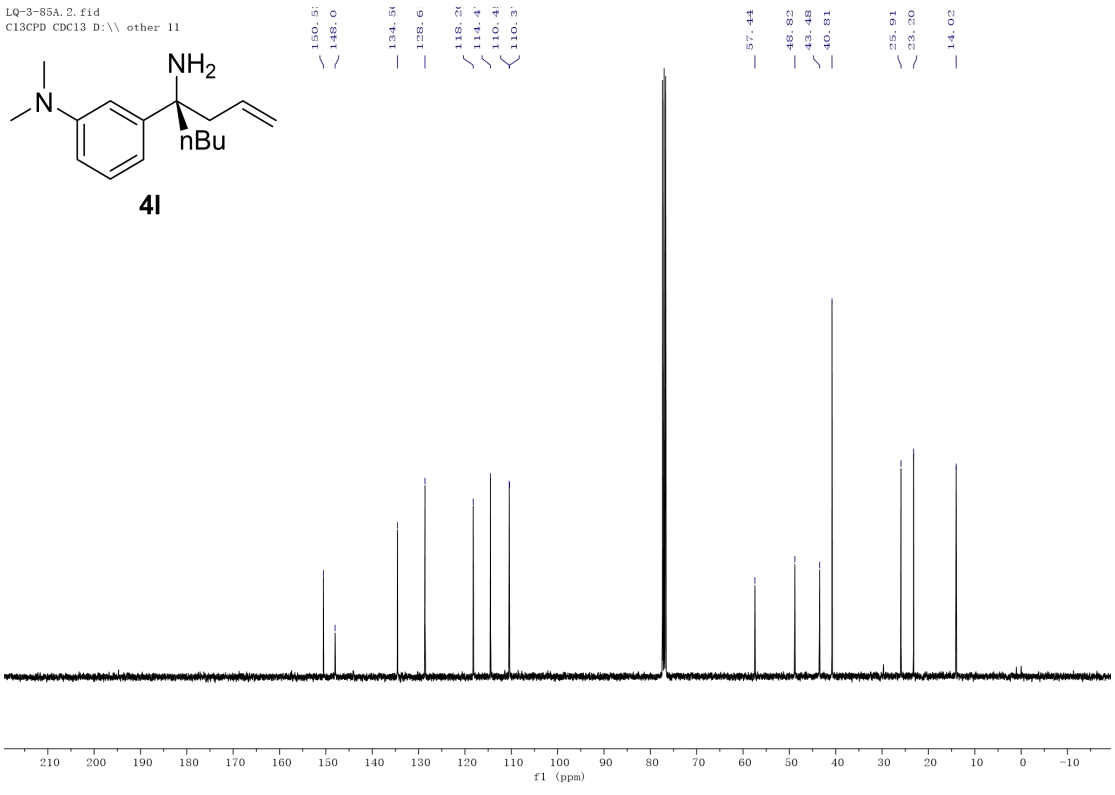
nBu
S
4k
f1 (ppm)

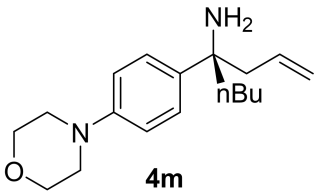

LQ-3-85C.2.fid
C13CPD CDC13 D:\\ other 12
NH2
nBu
S
4k
144.1
135.6
134.0
126.3
118.5
57.06
48.72
43.41
25.87
23.14
15.90
14.01
f1 (ppm)



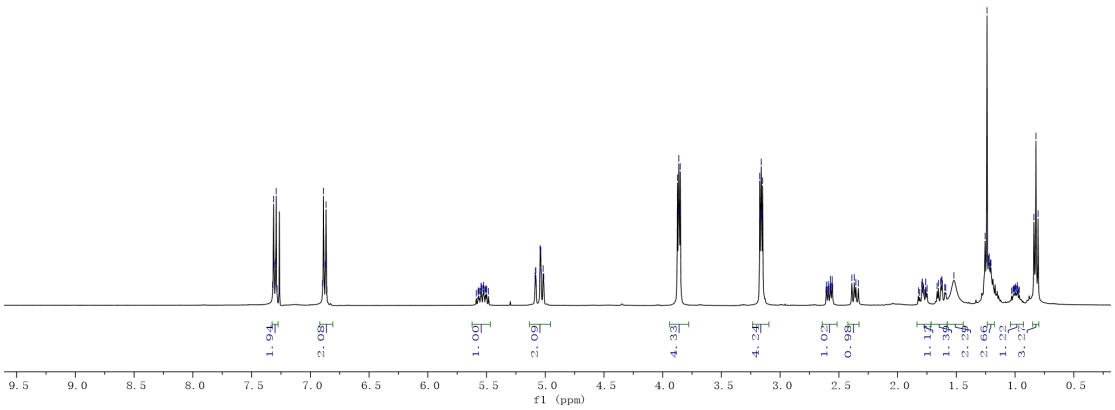
4l



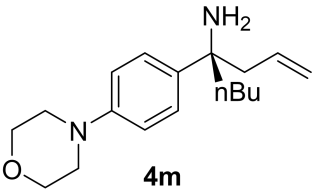
4l



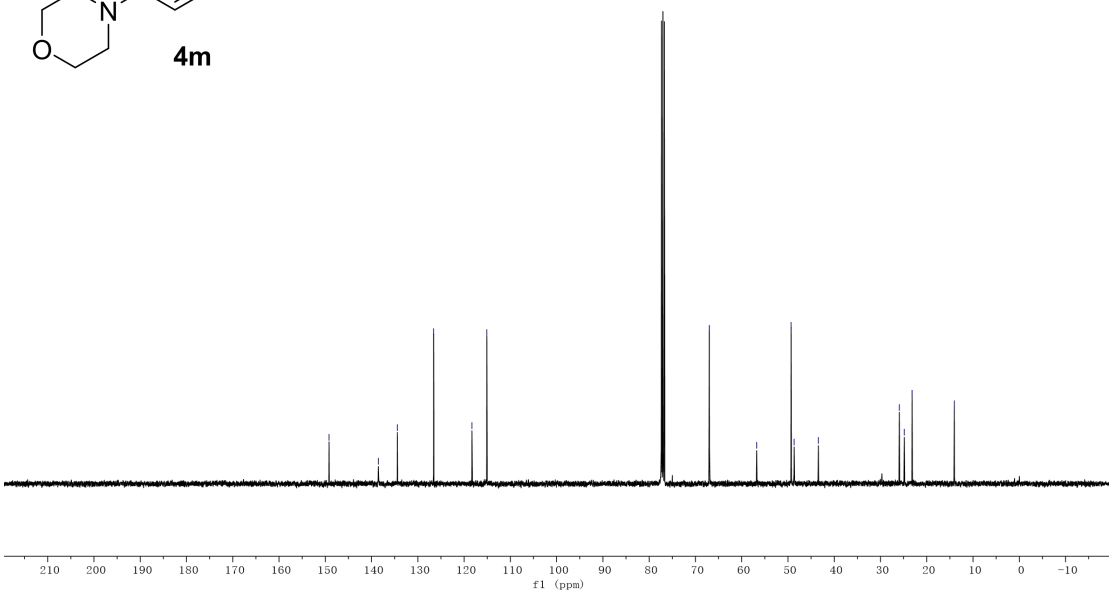
4m

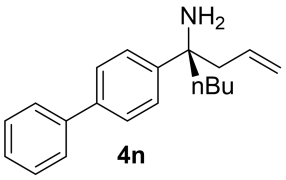


LQ-3-85B.3.fid
C13CPD CDC13 D:\\ other 7

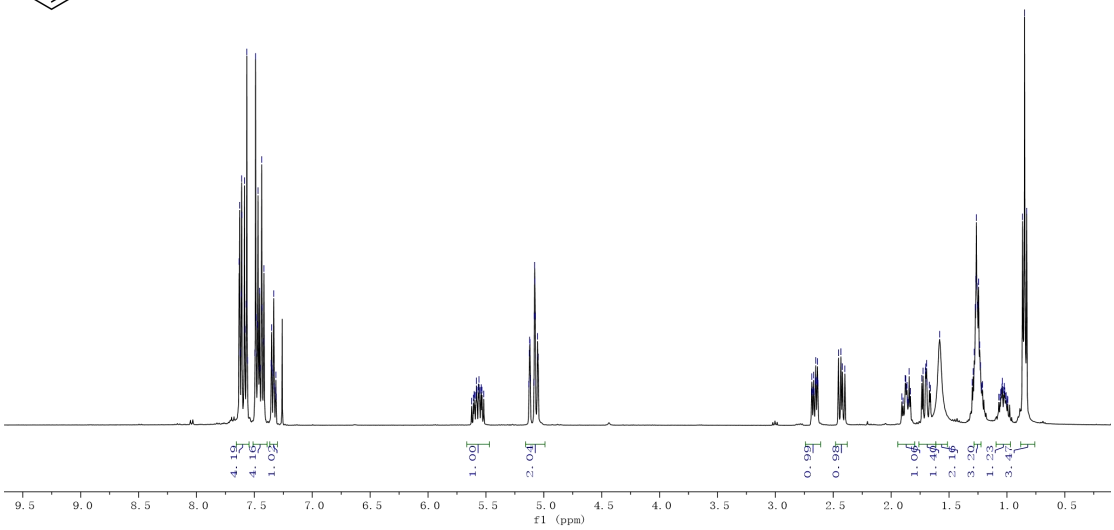


4m

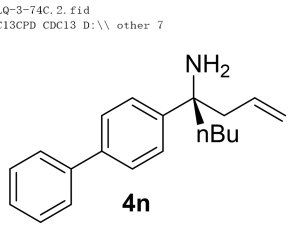




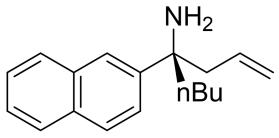
4n



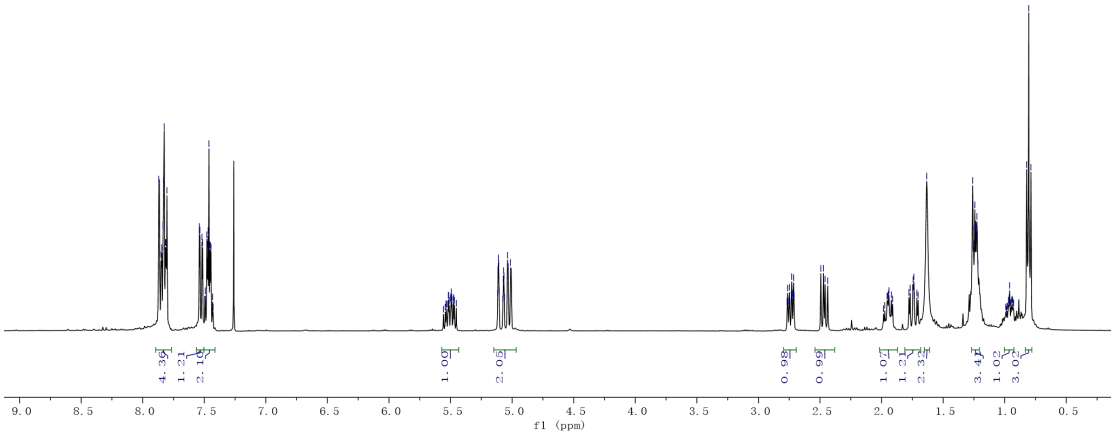
LQ-3-74C.2.fid
C13CPD CDC13 D:\\ other 7



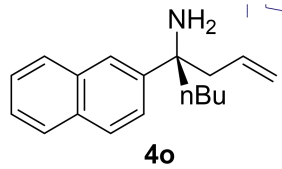
4n



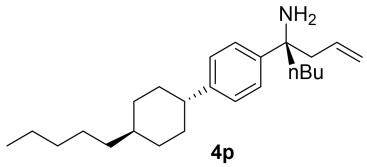
4o



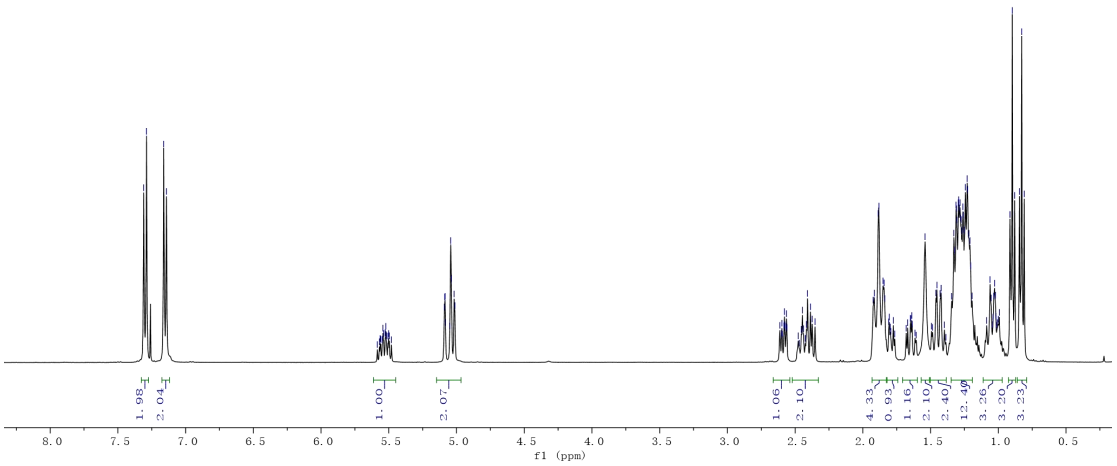
LQ-3-74B.3.fid
C13CPD CDC13 D:\\ other 8



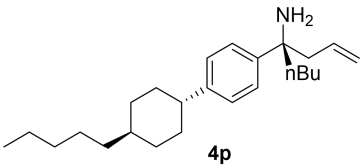
4o



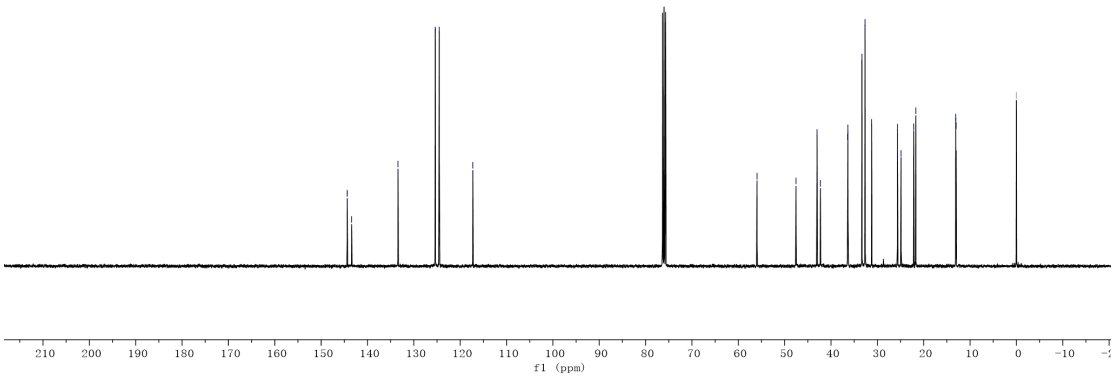
4p

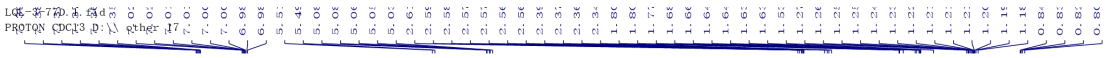


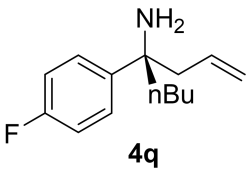
LQ-3-74A.2.fid
C13CPD CDC13 D:\\ other 2



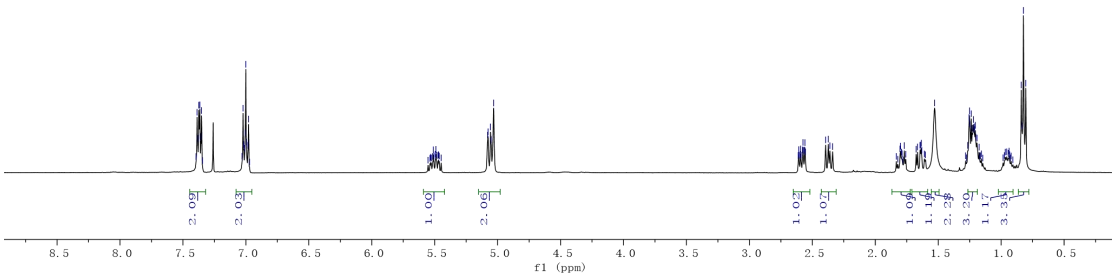
4p



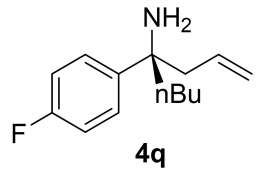




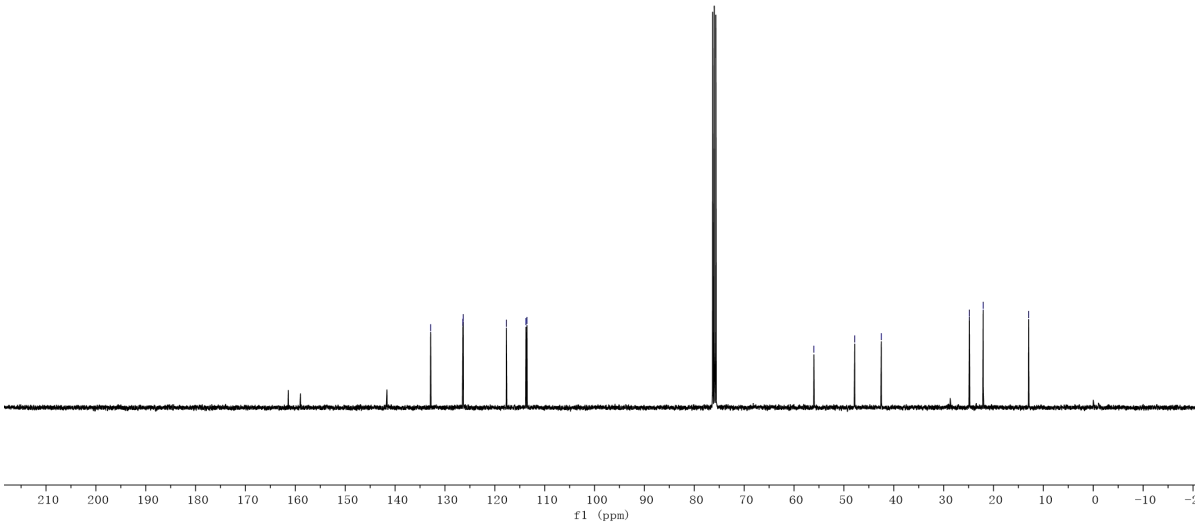
4q

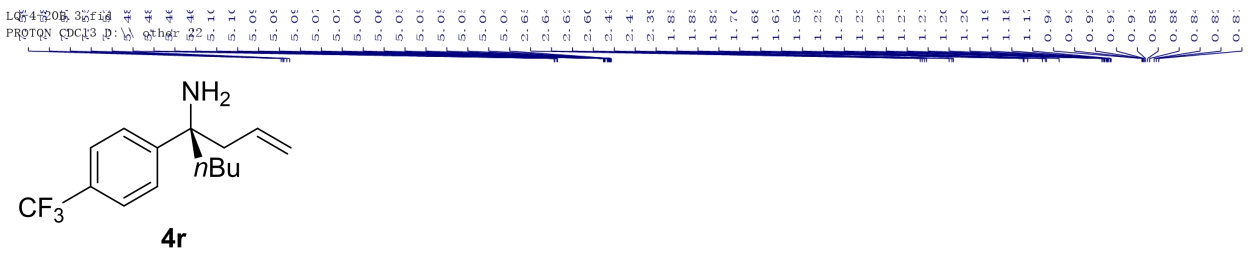


LQ-3-77D.1.fid
C13CPD CDC13 D:\\ other 1

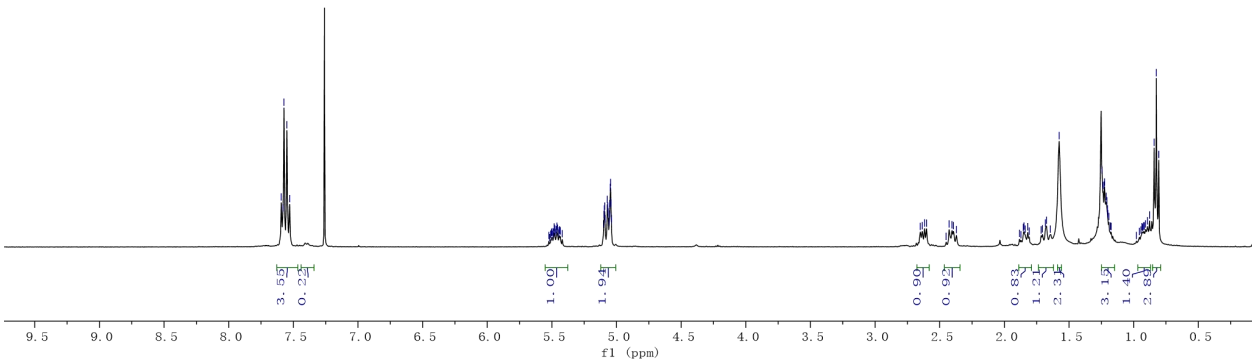


4q

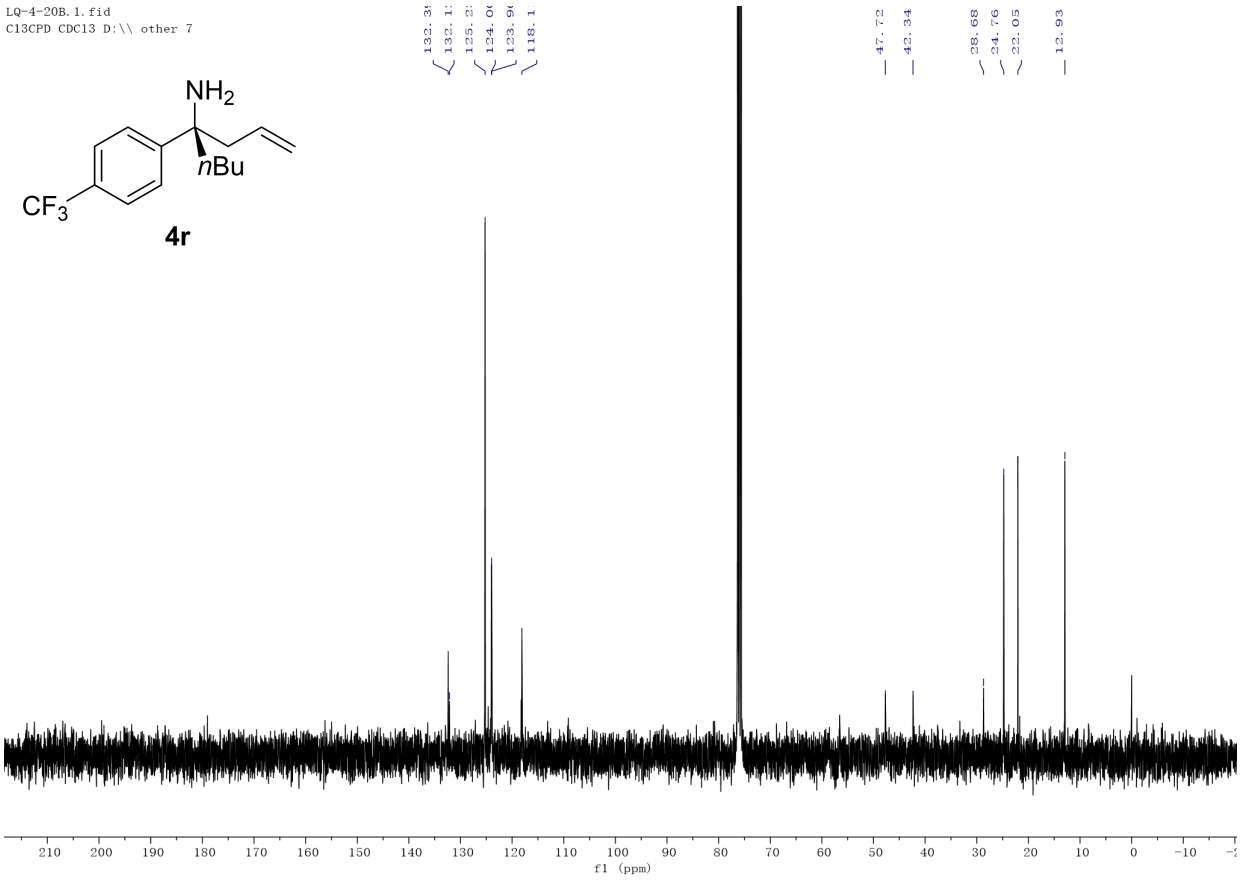




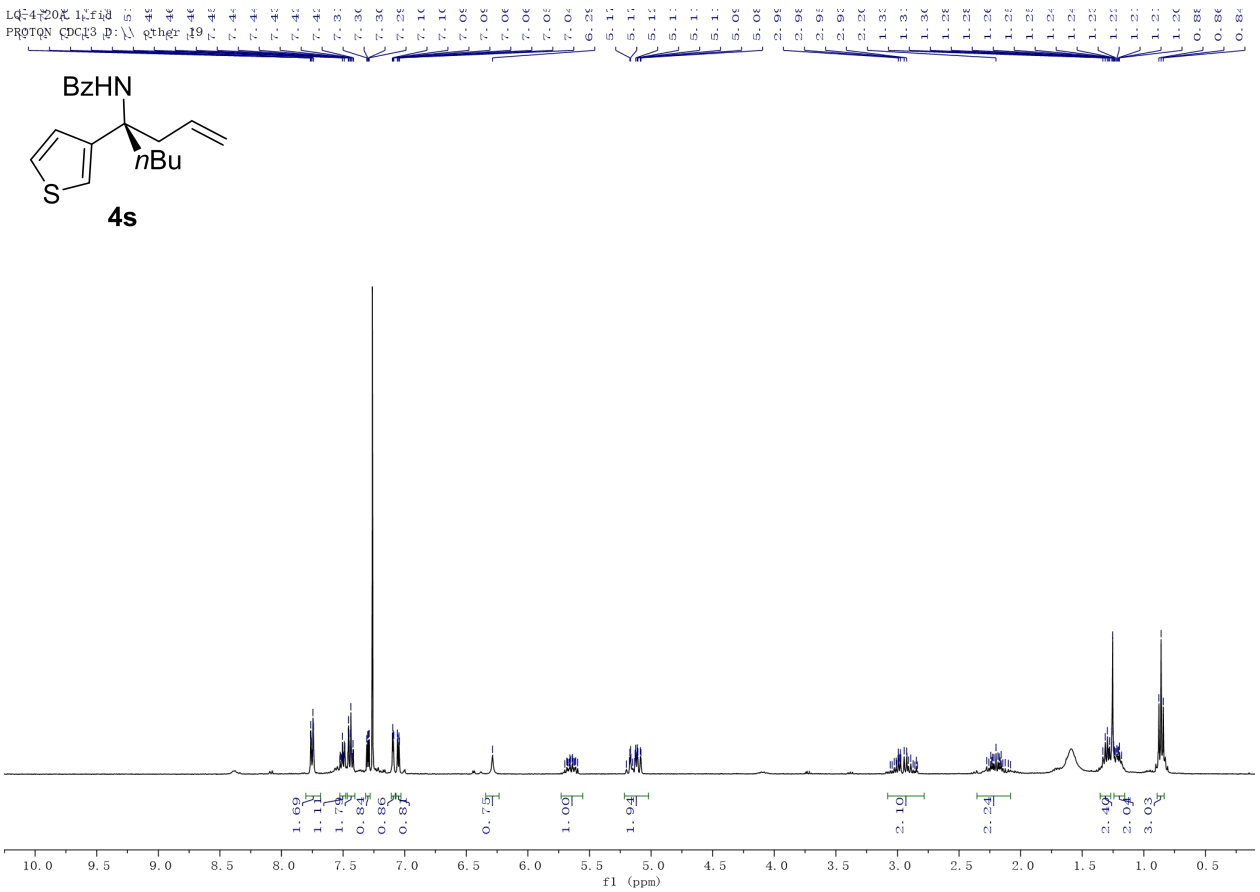
4r

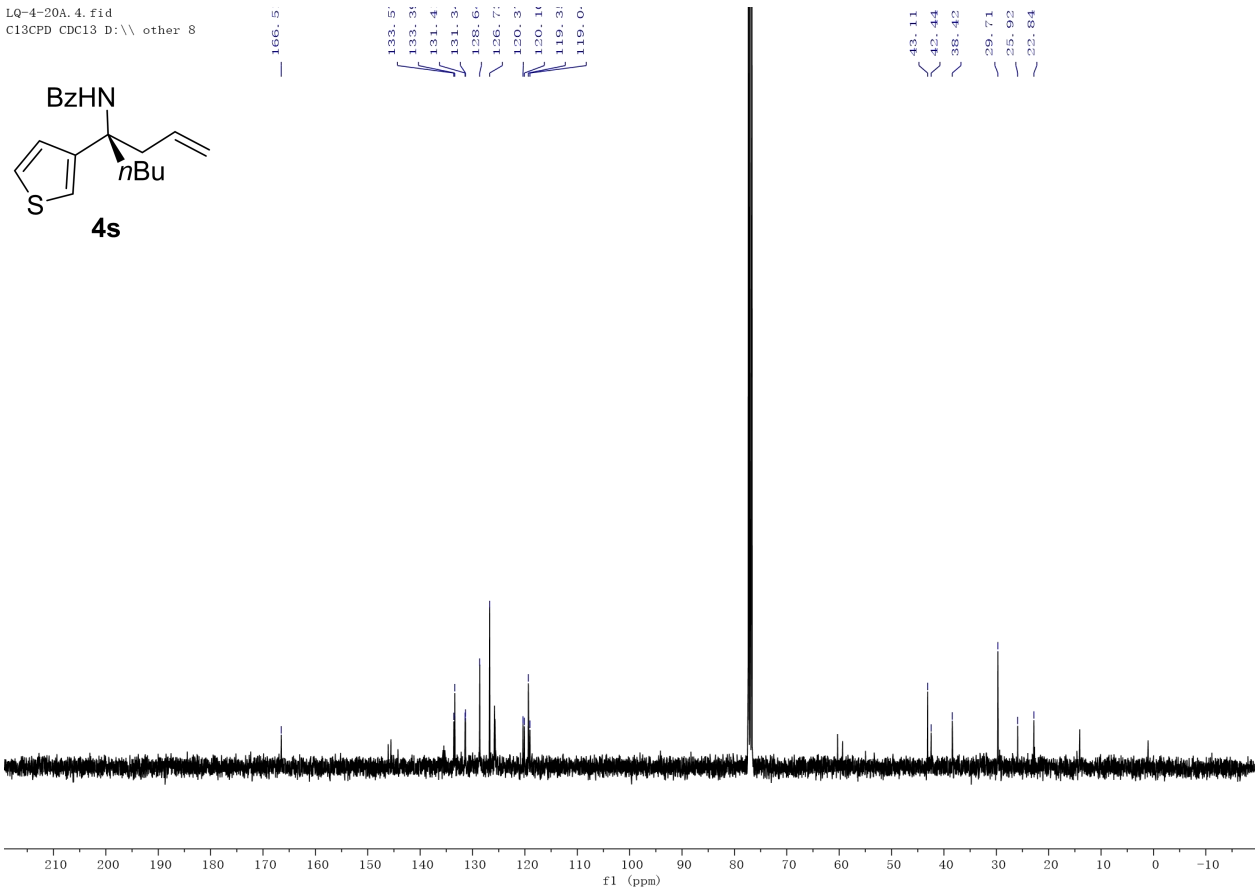


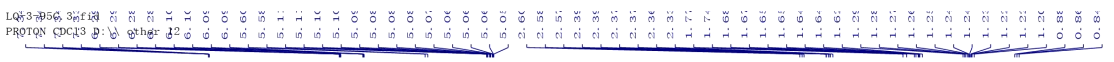
LQ-4-20B.1.fid
C13CPD CDC13 D:\\ other 7

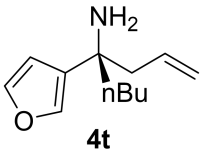


4r

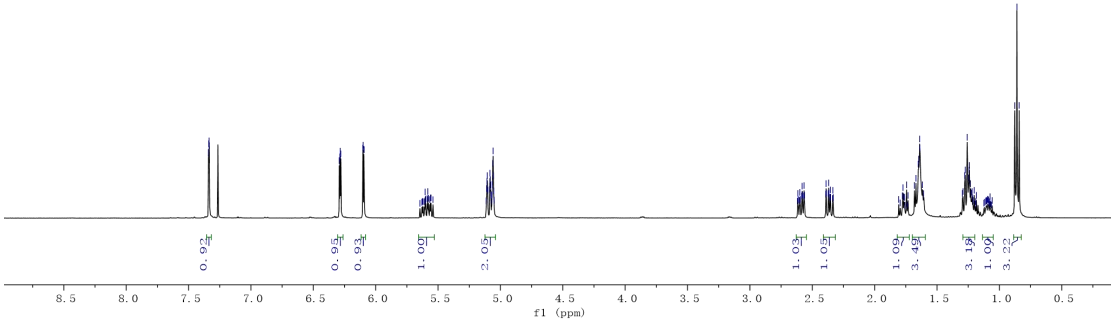

LQ-4-20A.1.fid
PROTON CDCl3 D:\\ other 19
BzHN
nBu
S
4s
1.69
1.11
1.78
0.84
0.86
0.87
0.75
1.00
1.94
2.10
2.24
2.40
2.04
3.03
f1 (ppm)


LQ-4-20A.4.fid
C13CPD CDCl3 D:\\ other 8
166.5
133.5
133.3
131.4
131.3
128.6
126.7
120.3
120.1
119.3
119.0
43.11
42.44
38.42
29.71
25.92
22.84
BzHN
nBu
S
4s
f1 (ppm)

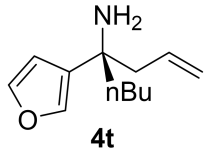




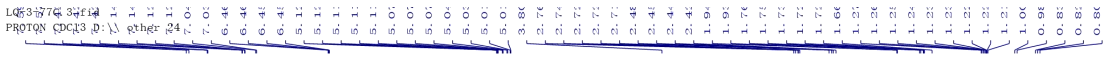
4t

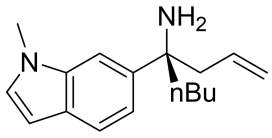


LQ-3-95C.1.fid
C13CPD CDCl3 D:\\ other 12

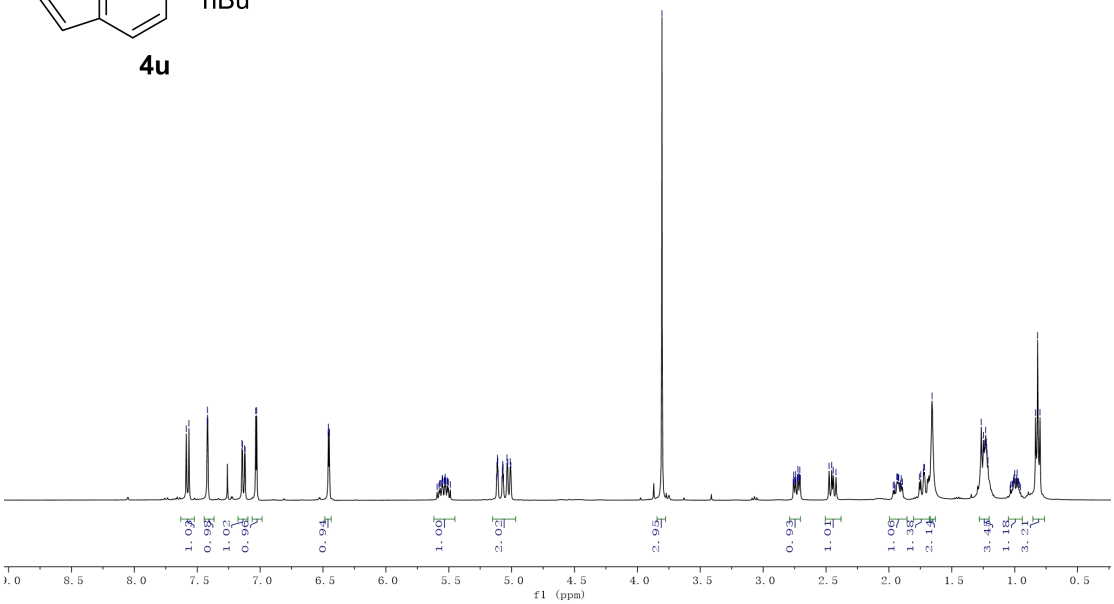


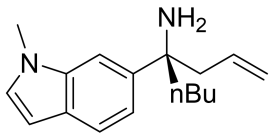
4t



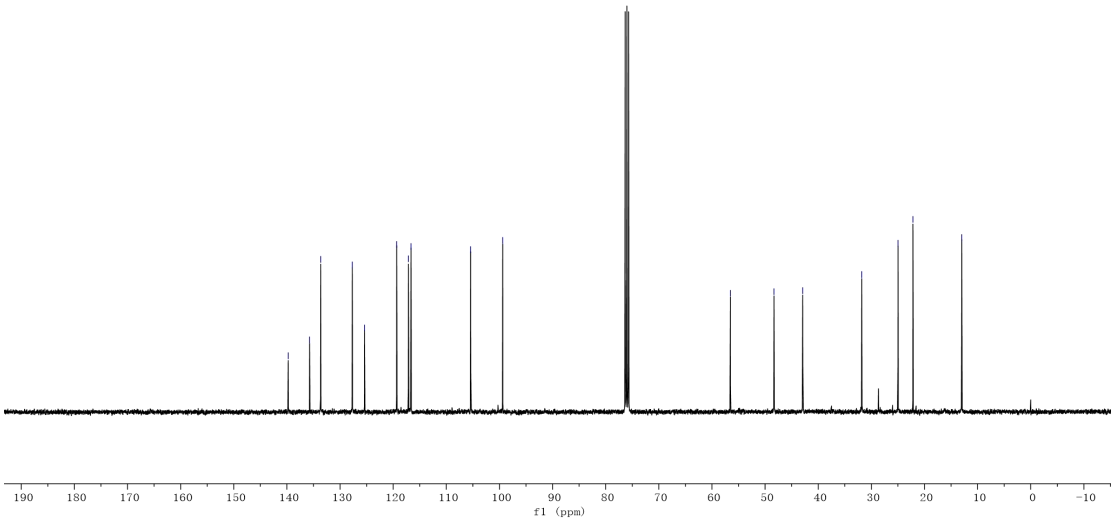

NH2
N
nBu

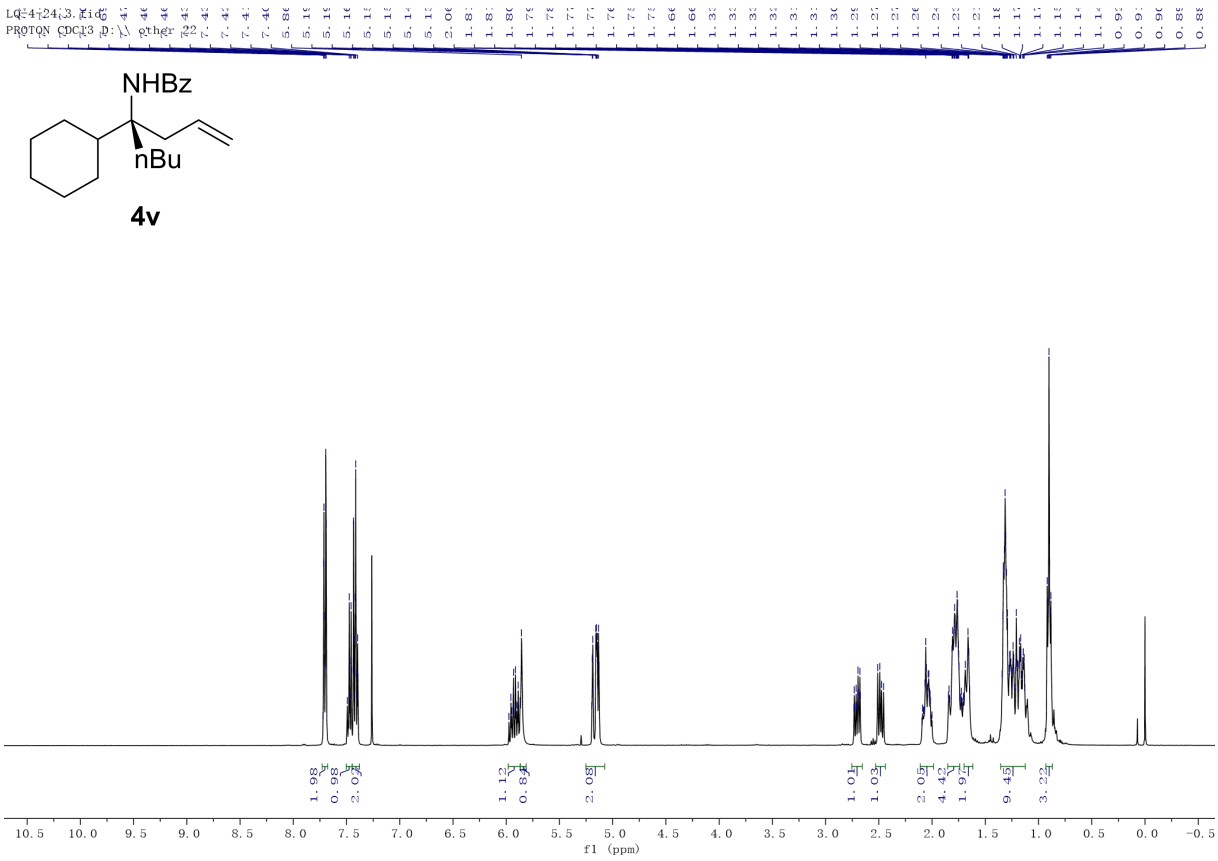
4u

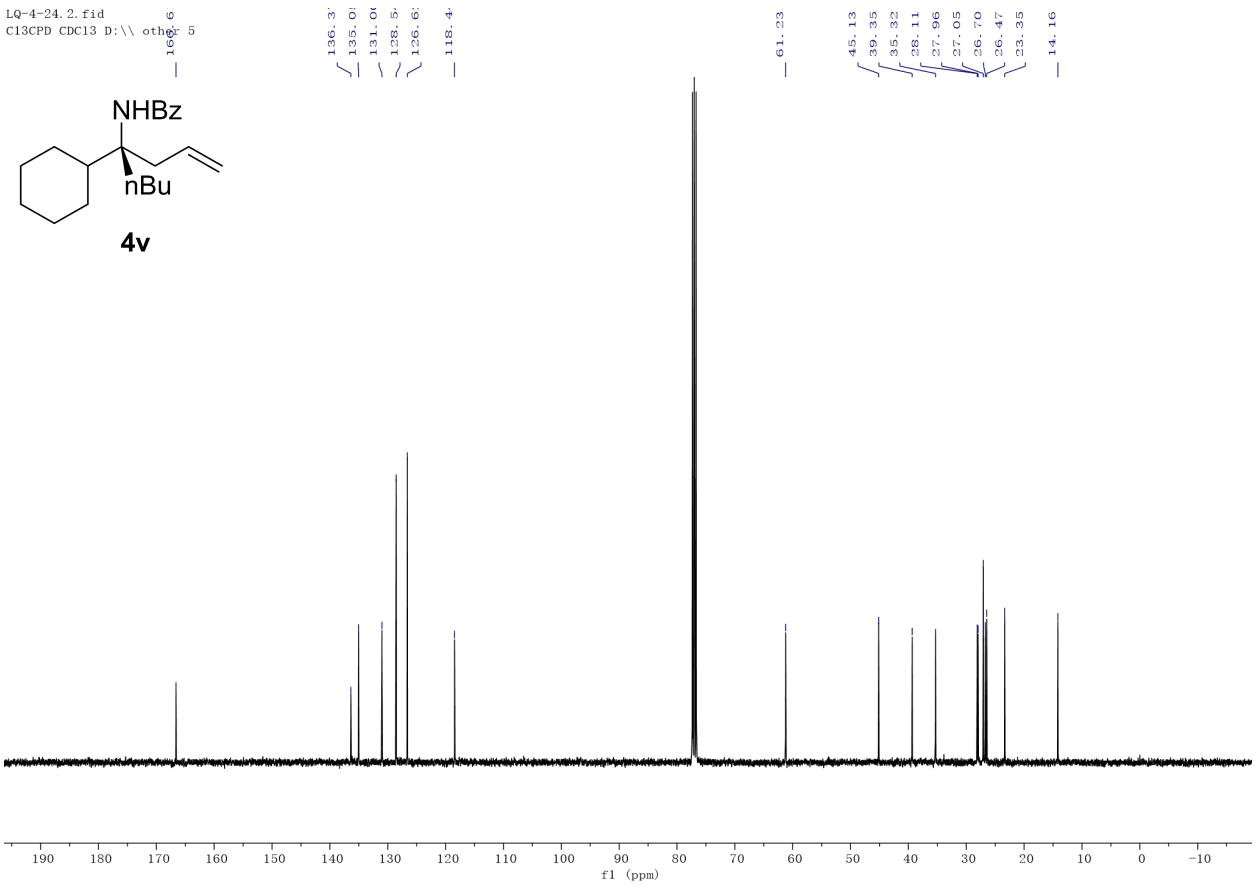

1.02
0.98
1.02
0.96
0.94
1.00
2.02
2.95
0.92
1.01
1.00
1.38
2.12
3.45
1.18
3.27
f1 (ppm)

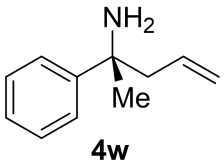

NH2
N
nBu

4u

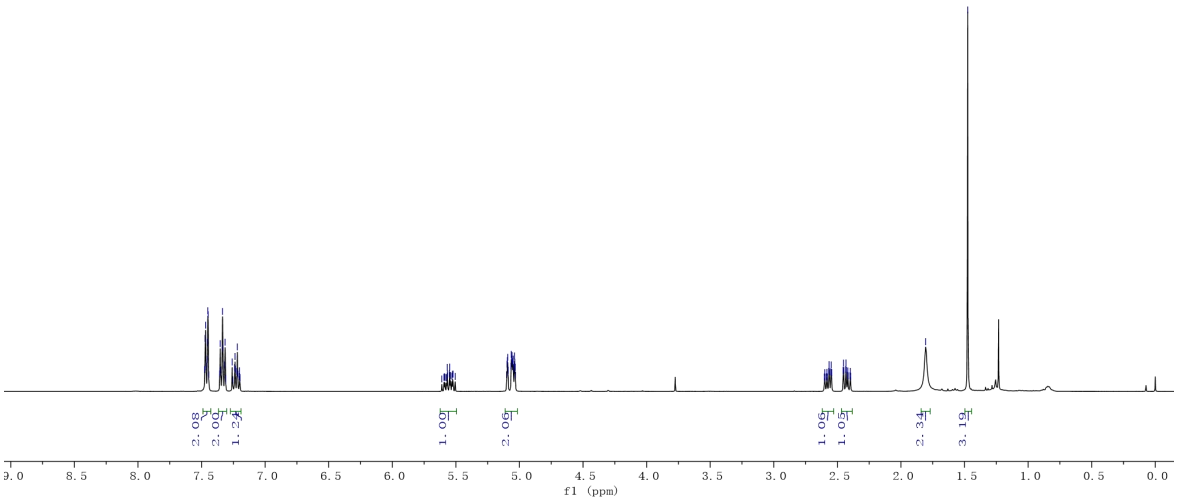

f1 (ppm)


LQ-4-24.3.fid
PROTON CDCl3 D:\\ other 22
NHBz
nBu
4v
1.98
0.98
2.07
1.12
0.83
2.05
1.01
1.03
2.05
4.42
1.97
9.45
3.22
f1 (ppm)

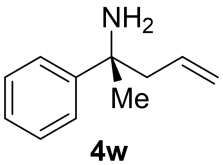

LQ-4-24.2.fid
C13CPD CDCl3 D:\\ other 5
NHBz
nBu
4v
168.6
136.3
135.0
131.0
128.5
126.6
118.4
61.23
45.13
39.35
35.32
28.11
27.96
27.05
26.70
26.47
23.35
14.16
f1 (ppm)


NH2
Me

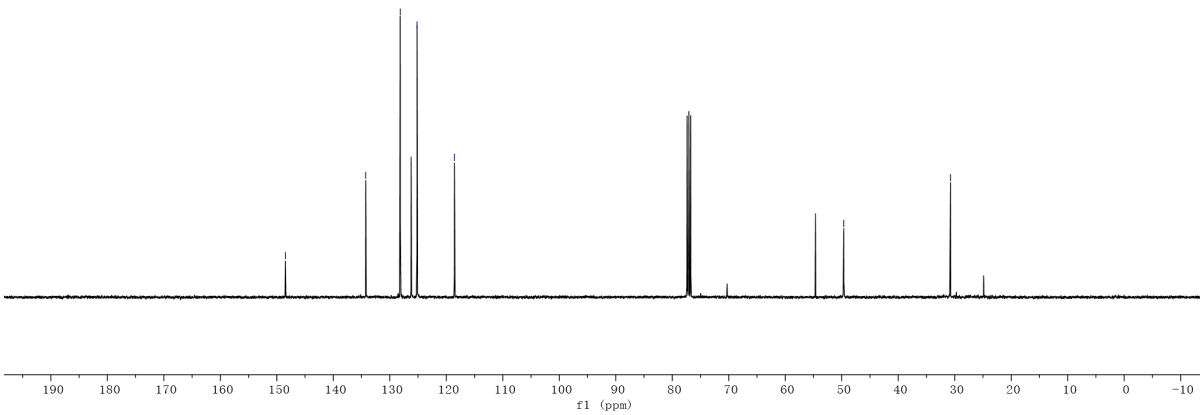
4w

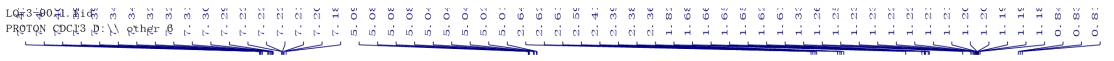

2.08
2.00
1.24
1.00
2.06
1.06
1.05
2.34
3.19
f1 (ppm)

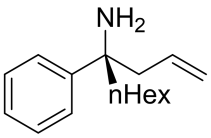

148.41
134.24
128.16
126.23
125.11
118.51
54.65
49.66
30.76


NH2
Me

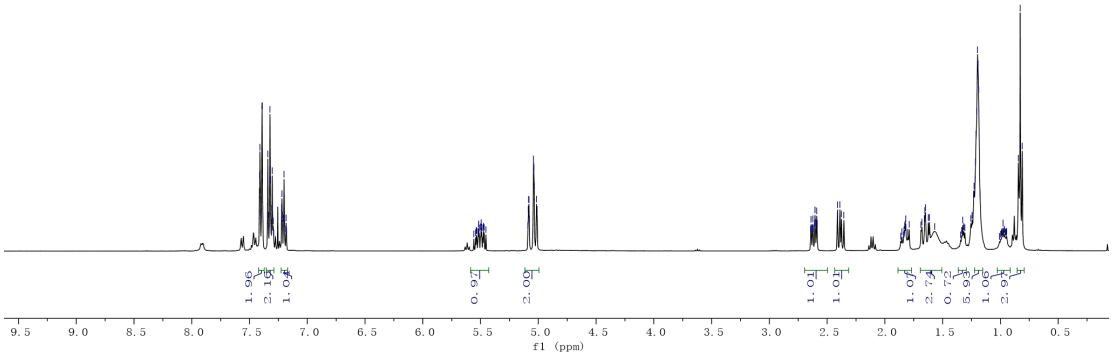
4w


f1 (ppm)

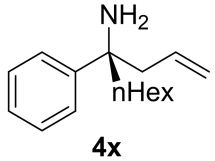




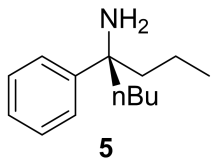
4x



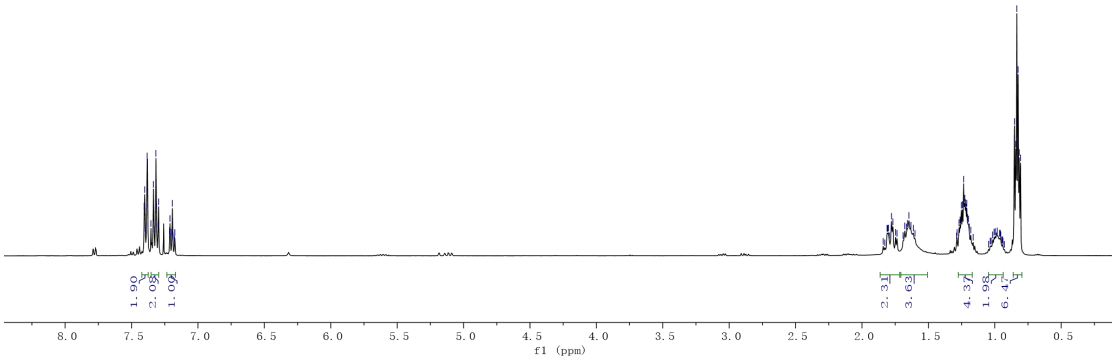
LQ-3-90.2.fid
C13CPD CDC13 D:\\ other 24



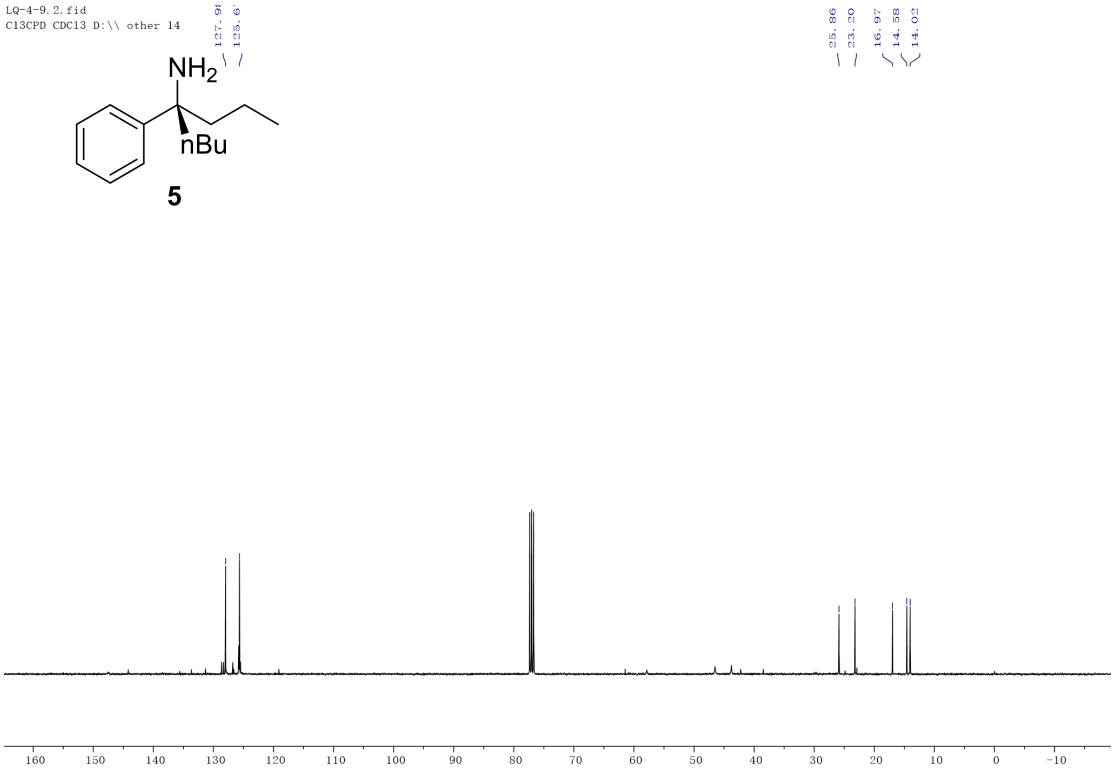
4x



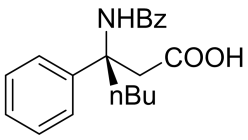
5



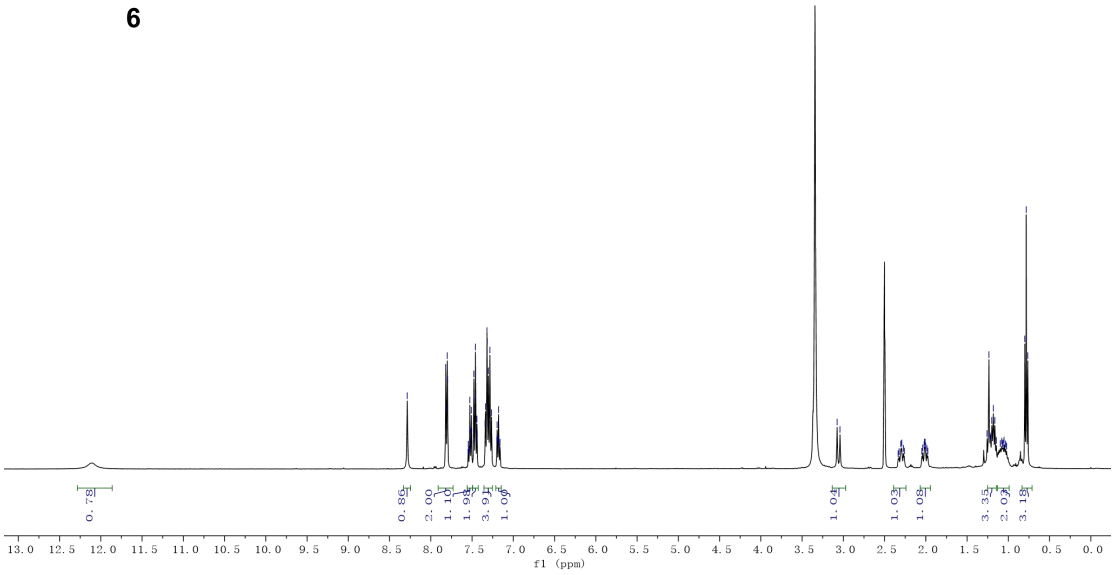
LQ-4-9.2.fid
C13CPD CDC13 D:\\ other 14

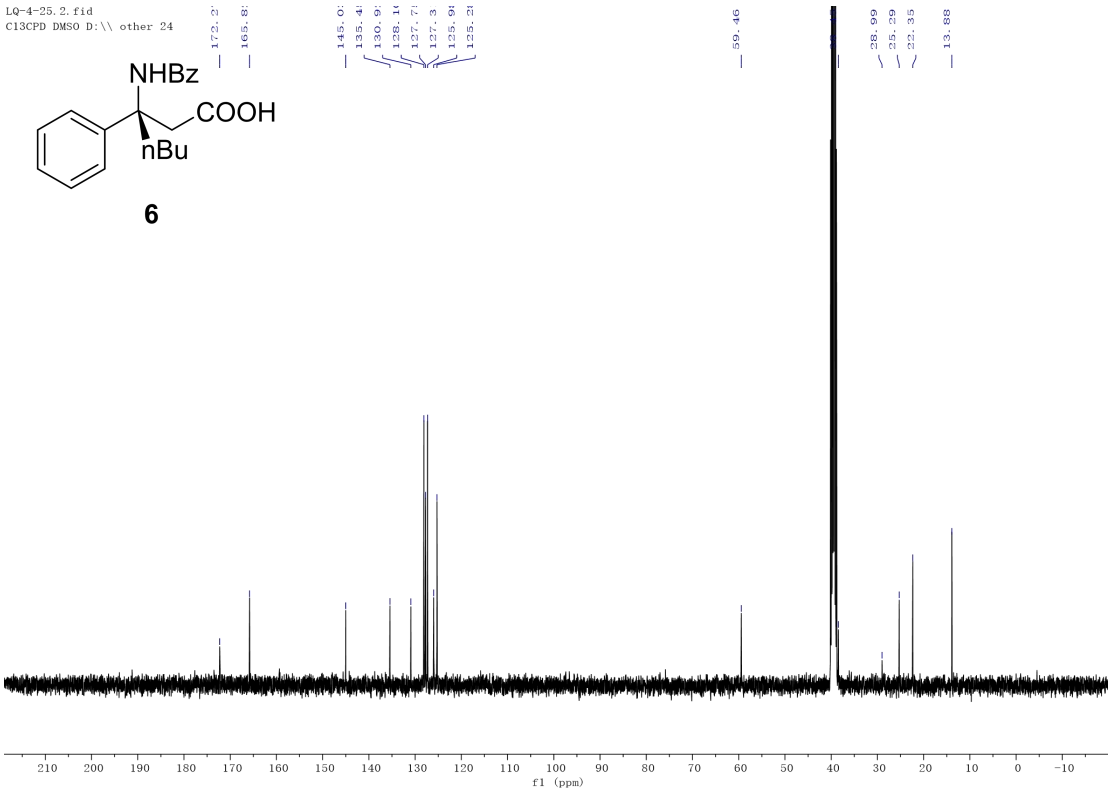


5


NHBz
COOH
nBu

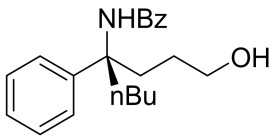
6


f1 (ppm)


LQ-4-25.2.fid
C13CPD DMSO D:\\ other 24
f1 (ppm)

NHBz
COOH
nBu

6



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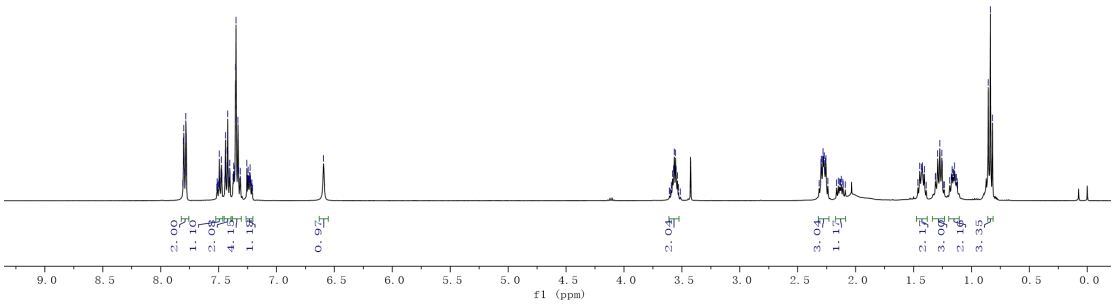

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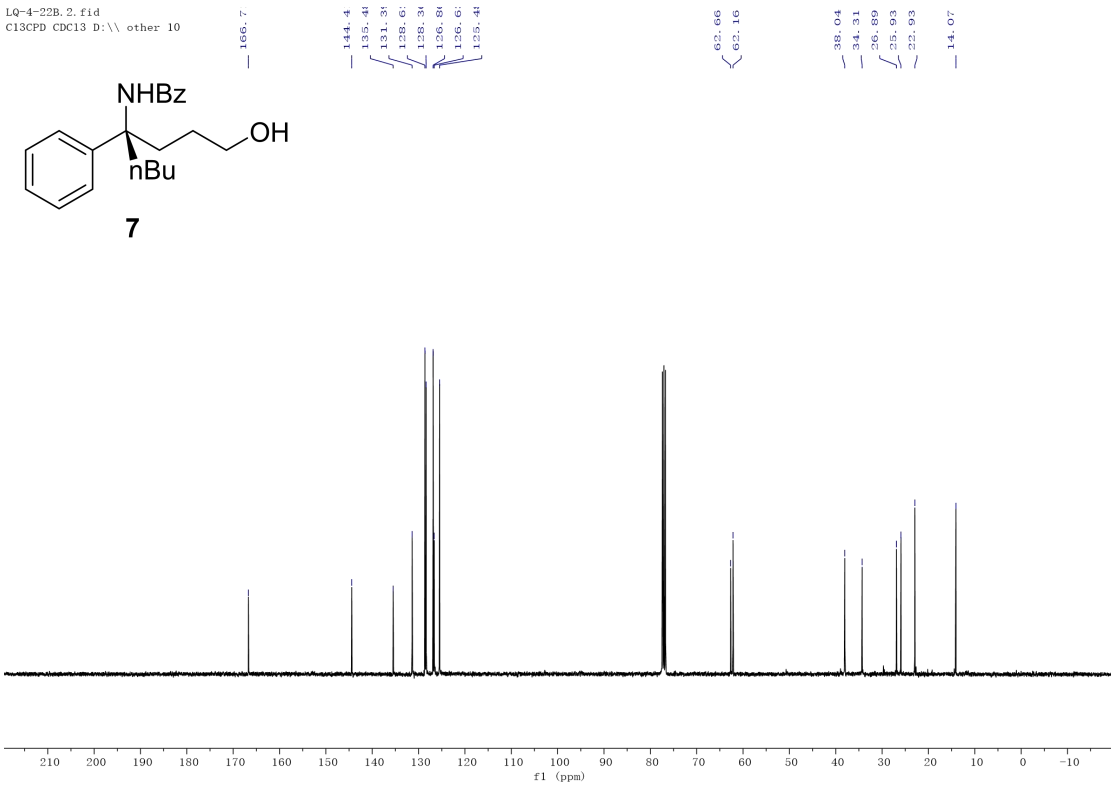
C13CPD CDC13 D:\\ other 10



7

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