Supporting Information

$Rh_2(esp)_2$-catalyzed three-component reaction of diazo compound, alkyl azide and allylboronate for synthesis of homoallylic amine derivatives

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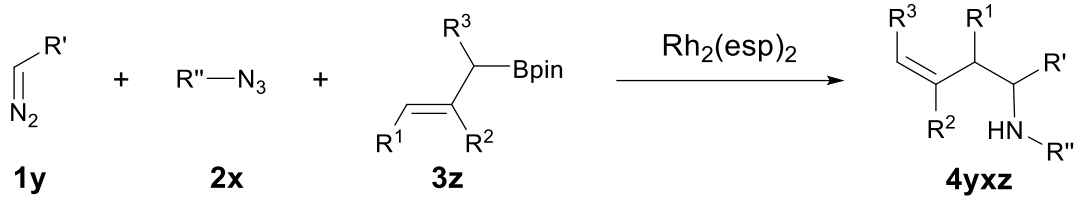
General Information :

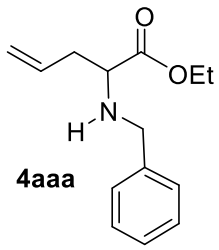
Unless specified, all reactions were carried out under a nitrogen atmosphere with dry solvents under anhydrous conditions. Anhydrous dichloromethane (DCM) and acetonitrile(MeCN) all come from solvent re evaporation systems. Anhydrous acetone is obtained through molecular sieve treatment. Other anhydrous solvents: ethyl acetate (EA), ethanol (C_2H_5OH), etc., all come from Energy Chemical. All compounds were subjected to rapid column chromatography using Laishan Jiangye silica gel (200-300 or 300-400 mesh). TLC analyses were performed on EMD 250 m Silica Gel HSGF 254 plates and visualized by quenching of UV fluorescence (λmax=254 nm), or by staining ceric ammonium molybdate, ammonium molybdate, or potassium permanganate. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker-500, 400 spectrometer. Chemical shifts for ^{1}H and ^{13}C NMR spectra are reported in ppm (δ) relative to residue protium in the solvent ($CDCl_3$: δ 7.26, 77.16 ppm, the multiplicities are presented as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet). Infrared Spectroscopy (IR) were provided by the Fourier Transform Infrared Spectrometer IR Spirit-L. High-resolution mass spectra (HRMS) were acquired on Thermo fisher Q Exactive HR MS.

S.1. Experimental Section



1y **2x** **3z** **4yxz**

In a 10ml Shlenk reaction tubes, to 2ml DCM dissolved $Rh_2(esp)_2$（0.01%eq 0.01mmol ）catalyst solution, azide compound **2x** (2eq 0.2mmol) was added, then 4ml DCM solution of nitrogen compound **1y** (1eq 0.1mmol) was slowly dropped, reacted for 30 min, and then allyl ester **3z** (1.5 eq 0.15mmol) was added for 2 h. Upon completion of the reaction, the DCM was diluted and vacuum-concentrated. By chromatography (ethyl acetate-petroleum ether, 1:10) and purified, the corresponding compound (**4yxz**) .

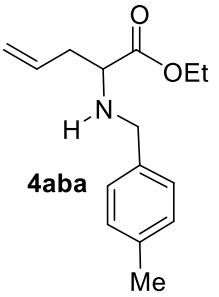


4aaa

Ethyl 2-(benzylamino)-pent-4-enoate.

yellow oil.; R_f = 0.25 (EtOAc/PE = 1/10, stain in $KMnO_4$);

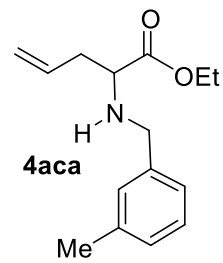
^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 – 7.22 (m, 5H), 5.76 (td, *J* = 17.2, 7.1 Hz, 1H), 5.26 – 4.87 (m, 2H), 4.19 (q, *J* = 7.1, 6.0 Hz, 2H), 3.84 (d, *J* = 13.0 Hz, 1H), 3.68 (d, *J* = 13.0 Hz, 1H), 3.36 (t, *J* = 6.4 Hz, 1H), 2.44 (t, *J* = 6.9 Hz, 2H), 2.05 (s, 1H), 1.33 – 1.21 (m, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.19, 139.32, 118.34, 60.91, 51.98, 37.66. δ (down) 133.55, 128.56, 127.36, 60.19, 14.50.



4aba

Ethyl 2-((4-methylbenzyl)amino)pent-4-enoate.

yellow oil; R_f = 0.49 (EtOAc/PE = 1/5, stain in $KMnO_4$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (d, *J* = 7.8 Hz, 2H), 7.12 (d, *J* = 7.8 Hz, 2H), 5.76 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.19 – 4.98 (m, 2H), 4.18 (qd, *J* = 7.1, 2.7 Hz, 2H), 3.80 (d, *J* = 12.8 Hz, 1H), 3.64 (d, *J* = 12.8 Hz, 1H), 3.36 (t, *J* = 6.5 Hz, 1H), 2.43 (t, *J* = 6.8 Hz, 2H), 2.33 (s, 3H), 1.73 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.34, 136.52, 136.41, 117.74, 60.41. δ (down) 133.62, 128.91, 128.14, 59.98, 20.96, 14.23.

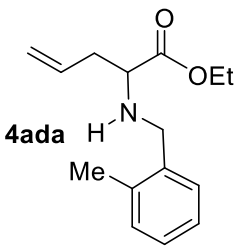


4aca

Ethyl 2-((3-methylbenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.54 (EtOAc/PE = 1/5, stain in $KMnO_4$); **^{1}H NMR** (400 MHz, $CDCl_3$) δ 7.21 (t, *J* = 7.5 Hz, 1H), 7.16 – 7.09 (m, 2H), 7.06 (d, *J* = 7.5 Hz, 1H), 5.77 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.16 – 4.99 (m, 2H), 4.18 (qd, *J* = 7.1, 2.4 Hz, 2H), 3.80 (d, *J* = 12.8 Hz, 1H), 3.65 (d, *J* = 12.8 Hz, 1H), 3.37 (t, *J* = 6.5 Hz, 1H), 2.45 (t, *J* = 6.8 Hz, 2H), 2.34 (s, 3H), 1.79 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100

MHz, plus, APT) δ (up) 174.37, 139.47, 137.82, 117.83, 60.50, 51.88, 37.55. δ (down) 133.61, 128.99, 128.19, 127.72, 125.28, 60.16, 14.27. **IR** (film) 3333.53, 1733.3, 1641.97, 1608.91, 1184.6 cm^{-1} . **HRMS** (ESI-TOF) m/z [$(M+H)^+$], calcd for $[C_{15}H_{22}NO_2]^+$: 248.1645, found 248.1642.

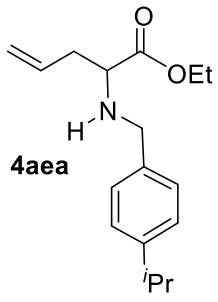


4ada

Ethyl 2-((2-methylbenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.50 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.31 – 7.27 (m, 1H), 7.21 – 7.11 (m, 3H), 5.78 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.17 – 5.00 (m, 2H), 4.19 (qd, *J* = 7.1, 2.5 Hz, 2H), 3.81 (d, *J* = 12.8 Hz, 1H), 3.65 (d, *J* = 12.9 Hz, 1H), 3.37 (t, *J* = 6.5 Hz, 1H), 2.47 – 2.41 (m, 2H), 2.35 (s, 3H), 1.73 (s, 1H), 1.28 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.51, 137.55, 136.58, 117.79, 60.55, 49.83, 37.69. δ (down) 133.75, 130.19, 128.77, 127.10, 125.80, 60.52, 18.88, 14.30. **IR** (film) 3333.76, 1733.48, 1640.64, 1605.28, 1184.27 cm^{-1} . **HRMS** (ESI-TOF) m/z [$(M+H)^+$], calcd for $[C_{15}H_{22}NO_2]^+$: 248.1645, found 248.1644.

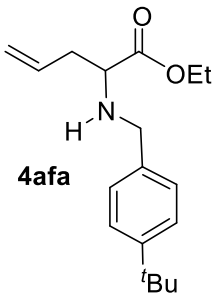


4aea

Ethyl 2-((4-isopropylbenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.55 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.25 (d, *J* =9.0 Hz, 2H), 7.18 (d, *J* = 8.1 Hz, 2H), 5.77 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.17 (qd, *J* = 7.1, 2.9 Hz, 2H), 3.80 (d, *J* = 12.8 Hz, 1H), 3.66 (d, *J* = 12.8 Hz, 1H), 3.37 (t, *J* = 6.5 Hz, 1H), 2.89 (hept, *J* = 6.9 Hz, 1H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.77 (s, 1H), 1.30 – 1.22 (m, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.48, 147.63, 137.07, 117.85, 60.54, 51.72, 37.66. δ (down) 133.74, 128.29, 126.39, 60.27, 33.79, 24.03, 14.35. **IR** (film) 3334.77, 1733.94, 1642.28, 1512.3, 1183.74 cm^{-1} . **HRMS** (ESI-TOF) m/z [$(M+H)^+$], calcdfor $[C_{17}H_{26}NO_2]^+$: 276.1958, found 276.1952

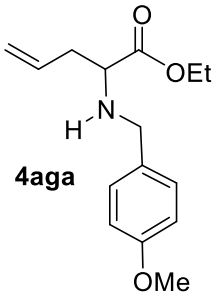


4afa

Ethyl 2-((4-(tert-butyl)benzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.56 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.34 (d, *J* = 8.3 Hz, 2H), 7.26 (d, *J* = 8.3 Hz, 2H), 5.77 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.16 – 5.04 (m, 2H), 4.17 (qd, *J* = 7.1, 3.0 Hz, 2H), 3.80 (d, *J* = 12.9 Hz, 1H), 3.66 (d, *J* = 12.9 Hz, 1H), 3.38 (t, *J* = 6.5 Hz, 1H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.86 (s, 1H), 1.31 (s, 9H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.40, 149.77, 136.62, 117.81, 60.46, 51.56, 37.62, 34.36. δ (down) 133.67, 127.96, 125.18, 60.22, 31.32, 14.30. **IR** (film) 3334.96, 1734.28, 1641.31, 1512.79, 1184.05 cm^{-1}. **HRMS** (ESI-TOF) m/z [$(M+H)^+$], calcd for $[C_{18}H_{28}NO_2]^+$: 290.2115, found 290.2108.

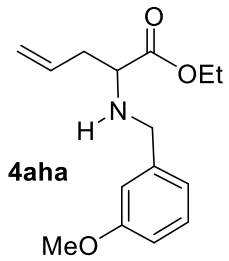


4aga

Ethyl 2-((4-methoxybenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.48 (EtOAc/PE= 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.28 – 7.20 (m, 2H), 6.89 – 6.83 (m, 2H), 5.76 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.18 (qd, *J* = 7.1, 2.3 Hz, 2H), 3.80 (s, 3H), 3.79 (s, 1H), 3.62 (d, *J* = 12.7 Hz, 1H), 3.35 (t, *J* = 6.5 Hz, 1H), 2.43 (t, *J* = 6.8 Hz, 2H), 1.87 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}CNMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.55, 158.75, 131.82, 117.91, 60.62, 51.37, 37.68. δ (down) 133.75, 129.51, 113.77, 60.11, 55.21, 14.39. **IR** (film) 3333.04, 1732.64, 1612.31, 1512.31, 1182.17 cm^{-1} . **HRMS** (ESI-TOF) m/z [$(M+H)^+$], calcd for $[C_{15}H_{22}NO_3]^+$:264.1594, found 264.1588.

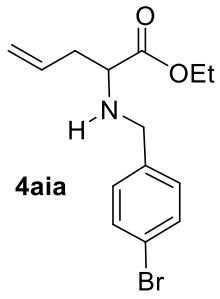


4aha

Ethyl 2-((3-methoxybenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.48 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.23 (t, *J* =8.0 Hz, 1H), 6.90 (d, *J* = 6.6 Hz, 2H), 6.79 (d, *J* = 8.3 Hz, 1H), 5.77 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.14 – 5.05 (m, 2H), 4.18 (qd, *J* = 7.1, 2.8 Hz, 2H), 3.85 (s, 3H), 3.80 (s, 1H), 3.66 (d, *J* = 13.2 Hz, 1H), 3.36 (t, *J* = 6.5 Hz,1H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.78 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.22, 159.53, 141.19, 117.67, 60.39, 51.66, 37.48. δ (down) 133.60, 129.13, 120.32, 113.39, 112.43, 59.93, 54.87, 14.16. **IR** (film) 3336.59, 1732.71, 1598.56, 1463.76, 1184.92 cm^{-1} . **HRMS** (ESI-TOF) m/z[$(M+H)^+$], calcd for $[C_{15}H_{22}NO_3]^+$: 264.1594, found 264.1586.

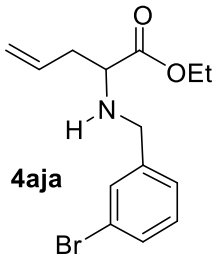


4aia

Ethyl 2-((4-bromobenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.49 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.43 (d, *J* = 8.3 Hz, 2H), 7.21 (d, *J* = 8.4 Hz, 2H), 5.75 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.16 – 5.04 (m, 2H), 4.18 (qd, *J* = 7.1, 3.1 Hz, 2H), 3.80 (d, *J* = 13.3 Hz, 1H), 3.62 (d, *J* = 13.3 Hz, 1H), 3.32 (t, *J* = 6.4 Hz, 1H), 2.42 (t, *J* = 6.8 Hz, 2H), 1.78 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.28, 138.68, 120.73, 117.97, 60.61, 51.14, 37.59. δ (down) 133.51, 131.32, 129.90, 60.00, 14.31. **IR** (film) 3334.77, 1732.41, 1641.83, 1586.68, 1186.21 cm^{-1}. **HRMS**(ESI-TOF)m/z[$(M+H)^+$],calcd for $[C_{14}H_{19}BrNO_2]^+$: 312.0594, found 312.0590

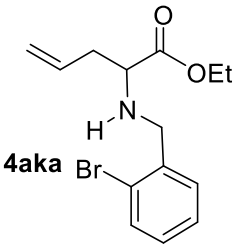


4aja

Ethyl 2-((3-bromobenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.50 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.50 (s, 1H), 7.38 (d, *J* = 7.9 Hz, 1H), 7.24 (s, 1H), 7.18 (t, *J* = 7.7 Hz, 1H), 5.77 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.20 – 5.05 (m, 2H), 4.19 (qd, *J* = 7.1, 1.9 Hz, 2H), 3.81 (d, *J* = 13.4 Hz, 1H), 3.63 (d, *J* = 13.4 Hz, 1H), 3.32 (t, *J* = 6.4 Hz, 1H), 2.43 (t, *J* = 6.8 Hz, 2H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.38, 142.24, 122.49, 118.10, 60.74, 51.32, 37.72. δ (down) 133.56, 131.23, 130.14, 129.93, 126.80, 60.19, 14.39. **IR** (film) 3335.51, 1732.2, 1641.5, 1594.2, 1188.15 cm^{-1} . **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{14}H_{19}BrNO_2]^+$: 312.0594, found 312.0594.

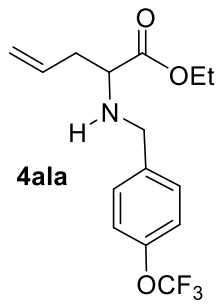


4aka

Ethyl 2-((2-bromobenzyl)amino)-pent-4-enoate.

yellow oil; R_f = 0.61 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.57 – 7.46 (m, 1H), 7.41 (dd, *J* = 7.6, 1.8 Hz, 1H), 7.29 (dd, *J* = 7.4, 1.3 Hz, 1H), 7.11 (td, *J* = 7.6, 1.8 Hz, 1H), 5.77 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.21 – 5.03 (m, 2H), 4.16 (q, *J* = 7.1 Hz, 2H), 3.92 (d, *J* = 14.0 Hz, 1H), 3.78 (d, *J* = 14.0 Hz, 1H), 3.35 (t, *J* = 6.5 Hz, 1H), 2.45 (td, *J* = 7.1, 3.4 Hz, 2H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 173.90, 138.61, 123.84, 117.79, 60.44, 51.59, 37.45. δ (down) 133.52, 132.47, 130.00, 128.42, 127.19, 60.12. **IR** (film) 3337.53, 1733.07, 1641.47, 1567.9, 1187.32 cm^{-1} . **HRMS**(ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{14}H_{19}BrNO_2]^+$: 312.0594, found 312.0591



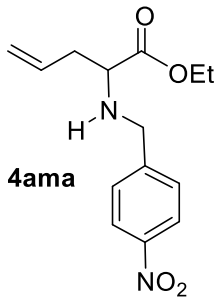
4ala

Ethyl 2-((4-(trifluoromethoxy)benzyl)amino)-pent-4-enoate.

yellow oil; R_f =0.53(EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 8.6 Hz, 2H), 7.16 (d, *J* = 8.1 Hz, 2H), 5.76 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.14 – 5.03 (m, 2H), 4.17 (qt, *J* = 7.2, 3.6 Hz, 2H), 3.85 (d, *J* = 13.3 Hz, 1H), 3.68 (d, *J* = 13.3 Hz, 1H), 3.34 (t, *J* = 6.5 Hz, 1H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.63 (s, 1H), 1.27 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.39, 148.23, 138.63, 121.80, 117.96, 60.67, 51.15, 37.67. δ (down) 133.60, 129.56, 120.88, 60.26, 14.24. **IR** (film) 3335.95, 1733.38, 1643.37, 1507.44, 1174.42 cm^{-1}. **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{15}H_{19}F_3NO_3]^+$: 318.1312, found 318.1304.

Ethyl 2-((4-nitrobenzyl)amino)-pent-4-enoate.

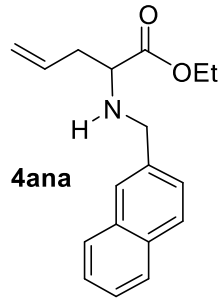


4ama

yellow oil; R_f = 0.58 (EtOAc/PE = 1/2, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 8.18 (d, *J* = 8.7 Hz, 2H), 7.52 (d, *J* = 8.4 Hz, 2H), 5.77 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.19 – 5.04 (m, 2H), 4.20 (qd, *J* = 7.2, 4.2 Hz, 2H), 3.98 (d, *J* = 14.3 Hz, 1H), 3.76 (d, *J* = 14.3 Hz, 1H), 3.32 (t, *J* = 6.4 Hz, 1H), 2.46 (t, *J* = 6.9 Hz, 2H), 1.77 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.13, 147.59, 146.92, 118.11, 60.76, 51.01, 37.56. δ (down) 133.36, 128.65, 123.44, 60.18, 14.25. **IR** (film) 3341.5, 1732.12, 1602.04, 1521.59, 1188.94 cm^{-1}. **HRMS** (ESI-TOF)m/z[(M+H)$^+$], calcd for $[C_{14}H_{19}N_2O_4]^+$: 279.1339, found 279.1332.

Ethyl 2-((naphthalen-2-ylmethyl)amino)-pent-4-enoate.

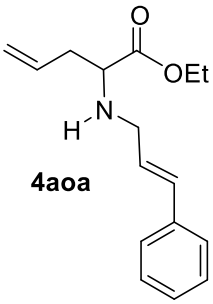


4ana

yellow oil; R_f = 0.43 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.86 – 7.78 (m,3H), 7.76 (s, 1H), 7.52 – 7.41 (m, 3H), 5.79 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.16 – 5.06 (m, 2H), 4.18 (qd, *J* = 7.1, 3.2 Hz, 2H), 4.02 (d, *J* = 13.2 Hz, 1H), 3.86 (d, *J* = 13.2 Hz, 1H), 3.41 (t, *J* = 6.5 Hz, 1H), 2.47 (t, *J* = 6.8 Hz, 2H), 1.96 (s, 1H), 1.27 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.51, 137.20, 133.41, 132.75, 117.97, 60.65, 52.11, 37.70. δ (down) 133.75, 128.08, 127.73, 127.65, 126.74, 126.71, 125.99, 125.60, 60.21, 14.36. **IR** (film) 3334.33, 1731.8, 1639.75, 1507.99, 1185.3 cm^{-1}. **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{18}H_{22}NO_2]^+$: 284.1645, found 284.1637.

Ethyl 2-(cinnamylamino)-pent-4-enoate.

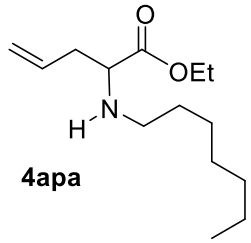


4aoa

yellow oil; R_f = 0.40 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.36 (d, *J* = 7.2 Hz, 2H), 7.30 (t, *J* = 7.5 Hz, 2H), 7.22 (d, *J* = 14.5 Hz, 1H), 6.51 (d, *J* = 15.9 Hz, 1H), 6.24 (dt, *J* = 15.9, 6.4 Hz, 1H), 5.77 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.17 – 5.06 (m, 2H), 4.18 (qq, *J* = 7.1, 3.6 Hz, 2H), 3.48 – 3.40 (m, 1H), 3.38 (d, *J* = 6.4 Hz, 1H), 3.32 (dd, *J* = 13.7, 6.4 Hz, 1H), 2.44 (t, *J* = 6.8 Hz, 2H), 1.77 (s, 1H), 1.26 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.43, 136.84, 118.08, 60.59, 50.10, 37.63. δ (down) 133.40, 131.83, 128.42, 127.59, 127.34, 126.22, 60.03, 14.25. **IR** (film) 3330.83, 1732.5, 1642.44, 1586.24, 1185.39 cm^{-1} . **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{16}H_{22}NO_2]^+$: 260.1645, found 260.1640.

Ethyl 2-(heptylamino)-pent-4-enoate.

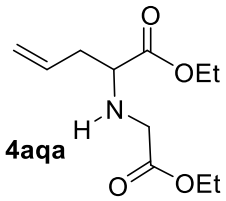


4apa

yellow oil; R_f = 0.55 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.75 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.14 – 5.04 (m, 2H), 4.18 (qd, *J* = 7.1, 2.6 Hz, 2H), 3.32 (t, *J* = 6.5 Hz, 1H), 2.62 – 2.45 (m, 2H), 2.41 (t, *J* = 6.9 Hz, 2H), 1.61 (s, 1H), 1.27 (t, *J* = 7.1 Hz, 8H), 0.87 (q, *J* = 7.0, 6.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.38, 117.56, 60.24, 47.96, 37.52, 31.60, 29.89, 28.96, 27.00, 22.39. δ (down) 133.52, 60.95, 14.11, 13.83. **IR** (film) 3332.17, 2928.13, 1735.64, 1181.08 cm^{-1} . **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{14}H_{28}NO_2]^+$: 242.2115, found 242.2107.

Ethyl 2-((2-ethoxy-2-oxoethyl)amino)-pent-4-enoate.

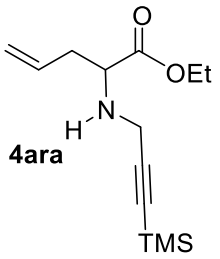


4aqa

yellow oil; R_f = 0.32 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.78 (ddt, *J* = 17.2, 10.1, 7.1 Hz, 1H), 5.19 – 5.08 (m, 2H), 4.17 (q, *J* = 7.1 Hz, 4H), 3.42 – 3.37 (m, 1H), 2.53 – 2.41 (m, 2H), 1.98 (s, 1H), 1.27 (d, *J* = 3.8 Hz, 6H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 173.31, 171.40, 118.13, 60.57, 48.69, 37.11. δ (down) 133.09, 59.85, 24.31, 14.03, 13.91

Ethyl 2-((3-(trimethylsilyl)prop-2-yn-1-yl)amino)-pent-4-enoate.

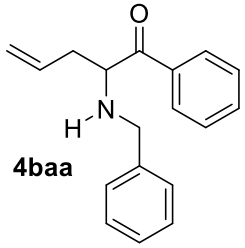


4ara

yellow oil; R_f = 0.37 (EtOAc/PE = 1/10, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 5.74 (ddt, *J* = 17.2, 10.2, 7.1 Hz, 1H), 5.17 – 5.08 (m, 2H), 4.19 (dd, J = 7.1, 5.7 Hz, 2H), 3.51 (t, J = 6.3 Hz, 1H), 3.46 (s, 1H), 3.39 (d, *J* = 17.1 Hz, 1H), 2.52 – 2.37 (m, 2H), 1.77 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 0.15 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 173.61, 118.14, 103.73, 60.69, 37.66, 37.17. δ (down) 133.41, 59.19, 14.21, 0.17. **IR** (film) 3336.9, 2173.81, 1735.7, 1188.07, 847.48 cm^{-1} . **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{13}H_{24}NO_2Si]^+$: 254.1571, found 254.1567.

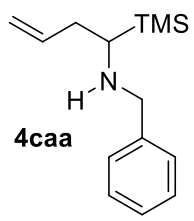
N-benzyl-1-(trimethylsilyl)but-3-en-1-amine.



4baa

yellow oil; R_f = 0.20 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 5H), 5.76 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.81 (d, *J* = 12.9 Hz, 1H), 3.68 (d, *J* = 12.9 Hz, 1H), 2.43 – 2.33 (m, 1H), 2.18 (dt, *J* = 14.2, 7.3 Hz, 1H), 2.09 (dd, *J* = 7.2, 4.9 Hz, 1H), 1.48 (s, 1H), -0.00 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 116.57, 53.14, 34.78. δ (down) 137.57, 128.43, 128.38, 126.94, 46.93, 2.37. **IR** (film) 1452.69, 1602, **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{14}H_{24}NSi]^+$: 234.1673, found 234.1666.

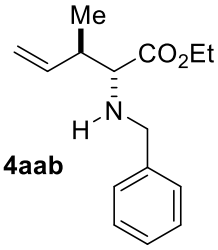


4caa

N-benzyl-1-(trimethylsilyl)but-3-en-1-amine.

yellow oil; R_f = 0.20 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.29 – 7.25 (m, 5H), 5.76 (ddt, *J* = 17.1, 10.1, 7.1 Hz, 1H), 5.08 – 4.96 (m, 2H), 3.81 (d, *J* = 12.9 Hz, 1H), 3.68 (d, *J* = 12.9 Hz, 1H), 2.43 – 2.33 (m, 1H), 2.18 (dt, *J* = 14.2, 7.3 Hz, 1H), 2.09 (dd, *J* =7.2, 4.9 Hz, 1H), 1.48 (s, 1H), -0.00 (s, 9H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 116.57, 53.14, 34.78. δ (down) 137.57, 128.43, 128.38, 126.94, 46.93, 2.37. **IR** (film) 1452.69, 1602, **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{14}H_{24}NSi]^+$: 234.1673, found 234.1666.

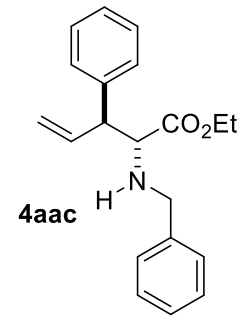


4aab

Ethyl 2-(benzylamino)-3-methylpent-4-enoate.

yellow oil; *Rf* = 0.52 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m,3H), 7.25 – 7.21 (m, 1H), 5.80 – 5.68 (m, 1H), 5.09 – 5.02 (m, 2H), 4.19 (qd, *J* = 7.2, 4.4 Hz, 2H), 3.85 (d, *J* = 13.2 Hz, 1H), 3.61 (d, *J* = 13.2 Hz, 1H), 3.12 (d, *J* = 6.2 Hz, 1H), 2.55 (q, *J* = 6.4, 5.8 Hz, 1H), 1.82 (s, 1H), 1.28 (t, *J* = 7.1 Hz, 3H), 1.07 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.26, 139.87, 115.52, 60.42, 52.37. δ (down) 139.58,128.21, 126.92, 65.26, 40.95, 16.67, 14.34. **IR** (film) 3339.22, 1732.19, 1604.23, 1459.59, 1186.8 cm^{-1} . **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{15}H_{22}NO_2]^+$: 248.1645, found 248.1640.

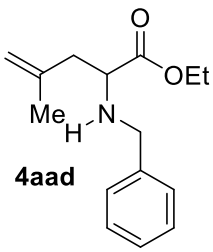


4aac

Ethyl 2-(benzylamino)-3-phenylpent-4-enoate.

yellow oil; R_f = 0.56 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 – 7.18 (m,10H), 6.14 (ddd, *J* = 17.1, 10.2, 8.2 Hz, 1H), 5.19 – 5.05 (m, 2H), 3.95 (q, *J* = 7.1 Hz, 2H), 3.83 (d, *J* = 13.3 Hz, 1H), 3.62 (d, *J* = 9.3 Hz, 1H), 3.61 – 3.56 (m, 1H), 3.53 (d, *J* = 7.9 Hz, 1H), 1.96 (s, 1H), 1.01 (t, *J* = 7.1 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 173.78, 140.49, 139.67, 117.41, 60.49, 52.36. δ (down) 137.77, 128.42, 128.36, 128.33, 128.27, 127.05, 126.89, 65.50, 53.44, 14.05. **IR** (film) 3333.73, 1731.41, 1601.25, 1490.26, 1182.13 cm^{-1} . **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{20}H_{24}NO_2]^+$: 310.1802, found 310.1798.

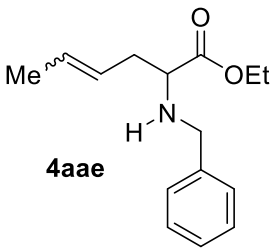


4aad

Ethyl 2-(benzylamino)-4-methylpent-4-enoate.

yellow oil; R_f = 0.50 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.22 (d, *J* = 18.6Hz, 5H), 4.74 (s, 1H), 4.68 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.77 (d, *J* = 13.0 Hz, 1H), 3.59 (d, *J* = 13.0 Hz, 1H), 3.36 (t, *J* = 7.3 Hz, 1H), 2.30 (d, *J* = 7.3 Hz, 2H), 1.71 (s, 1H), 1.62 (s, 3H), 1.21 (t, *J* = 7.2 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 175.06, 141.59, 139.74, 113.77, 60.76, 52.23, 42.06. δ(down) 128.51, 128.43, 127.22, 59.11, 22.09, 14.47.



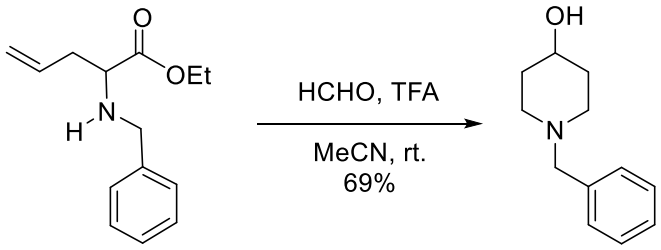
4aae

Ethyl 2-(benzylamino)hex-4-enoate.

yellow oil; R_f = 0.52 (EtOAc/PE = 1/5, stain in KMnO4);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.21 (m,5H), 5.64 – 5.47 (m, 1H), 5.37 (ddddd, *J* = 17.1, 10.1, 7.2, 3.4, 1.7 Hz, 1H), 4.18 (ddp, *J* = 10.2, 7.1, 3.4 Hz, 2H), 3.83 (dd, *J* = 13.0, 1.5 Hz, 1H), 3.66(dd, *J* = 13.0, 3.5 Hz, 1H), 3.32 (dt, *J* = 10.4, 6.5 Hz, 1H), 2.44 (q, *J* = 7.1 Hz, 1H), 2.40 – 2.31 (m, 1H), 1.85 (s, 1H), 1.70 – 1.57 (m, 3H), 1.28 (td, *J* = 7.1, 2.7 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 100 MHz, plus, APT) δ (up) 174.75, 174.66, 139.84, 60.56, 60.49, 52.03, 52.00, 36.54, 30.83. δ (down) 128.63, 128.36, 128.30, 128.24, 127.03, 126.95, 125.99, 125.19, 60.63, 60.60, 17.97, 14.38, 14.34, 12.94. **IR** (film) 3332.64, 1732.47, 1587.13, 1455.86, 1182.98 cm^{-1}. **HRMS** (ESI-TOF) m/z [(M+H)$^+$], calcd for $[C_{15}H_{22}NO_2]^+$: 248.1645, found 248.1641.

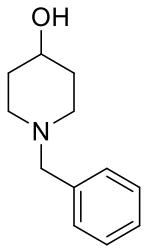
S.2. Conversions of the α-amino ester 4aaa and 4aab



4aaa **6aaa**

In a 10ml Shlenk reaction tubes, to a solution of 4aaa (1.0 mmol) in MeCN (1.0 mL) were sequentially added formaldehyde (37% solution in H_2O, 0.8 mL, 10 mmol) and TFA (1.2 mmol). The reaction mixture was stirred at room temperature 1h. It was then treated with saturated aqueous $NaHCO_3$ (2.0 mL), and

the resulting mixture was extracted with DCM (3*10 mL). The combined organic layers were washed with brine, dried with Na_2SO_4, and concentrated. The residue was purified by column chromatography.

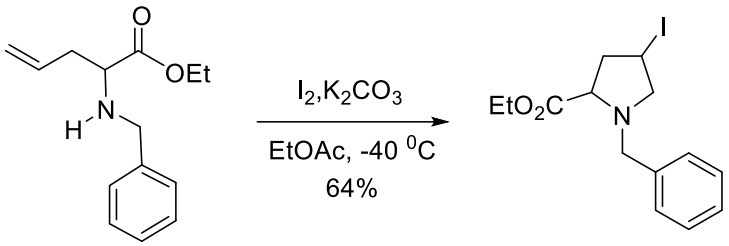


6aaa

1-Benzylpiperidin-4-ol.

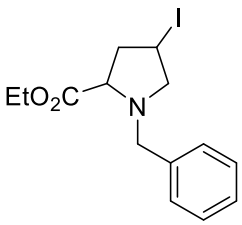
Colorless oil; R_f = 0.05 (EtOAc, stain in PMA);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.33 (d, *J* = 4.4 Hz, 4H), 7.28 – 7.24 (m, 1H), 3.71 (tt, *J* = 8.9, 4.2 Hz, 1H), 3.51 (s, 2H), 2.77 (dt, *J* = 10.3, 4.4 Hz, 2H), 2.23 – 2.09 (m, 2H), 1.89 (dq, *J* = 11.8, 3.3, 2.6 Hz, 2H), 1.60 (dtd, *J* = 13.1, 9.4, 3.7 Hz, 2H), 1.48 (s, 1H). **^{13}C NMR** (126 MHz, $CDCl_3$, CPD) δ 138.70, 129.23, 128.34, 127.12, 68.34, 63.10, 51.17, 34.73.



4aaa **7aaa**

In a 10ml Shlenk reaction tubes, to a stirred solution of **4aaa** (1 mmol) in EtOAc(4 mL) was successively added K_2CO_3 (5 mmol) and iodine (3 mmol) at -40°C. The mixture was stirred at the same temperature for 1.5 h, diluted with AcOEt (20 mL), and extracted with 20% aqueous $Na_2S_2O_3$ solution (20 mL × 3). The organic solution was washed with H_2O (20 mL × 3) and brine (20 mL × 3), dried, and evaporated. The residue was purified by column chromatography.

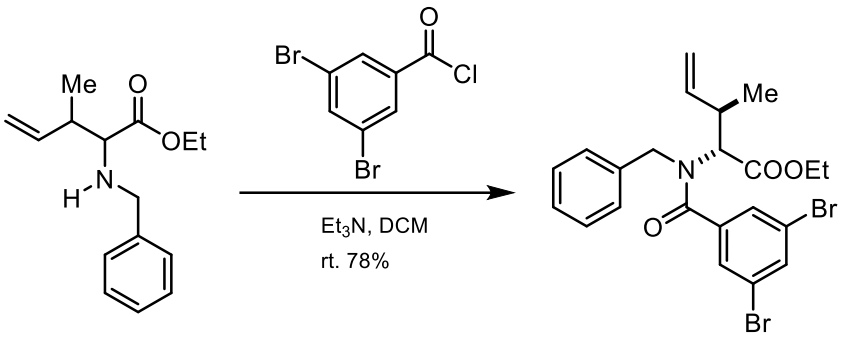


7aaa

Eethyl 1-benzyl-4-iodopyrrolidine-2-carboxylate

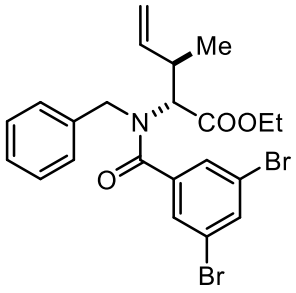
yellow oil; R_f = 0.49 (EtOAc/PE = 1/10, stain in $KMnO_4$);

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.35 – 7.29 (m, 4H), 7.26 (s, 1H), 4.17 – 4.05 (m, 2H), 3.94 (d, J = 12.7 Hz, 1H), 3.70 (d, J = 12.7 Hz, 1H), 3.48 (t, J = 8.3 Hz, 1H), 3.31 – 3.23 (m, 1H), 2.91 (t, J = 9.4 Hz, 1H), 2.85 (dd, J = 9.5, 4.6 Hz, 1H), 2.43 (ddd, J = 10.8, 8.2, 7.2 Hz, 1H), 1.91 (dt, J = 10.8, 8.3 Hz, 1H), 1.20 (t, J = 7.1 Hz, 3H). **^{13}C NMR** (126 MHz, $CDCl_3$, CPD) δ 172.35, 137.21, 129.62, 128.50, 127.71, 62.92, 61.18, 60.84, 58.82, 29.34, 14.28, 10.64.



4aab **5aab**

In a 10 ml Shlenk reaction tube, a solution of Et_3N (1.2 eq) and 3,5 dibromobenzoyl chloride (1.2 eq) in DCM (2 ml) was added sequentially to a stirred solution in DCM (3 ml) at 0°C. The mixture was stirred at the same temperature for 0.5 h. 2 ml of 4aab (1 mmol, 1eq) dissolved in DCM was added to the reaction and the reaction was continued for 1h. Diluted with water (10 mL), and extracted with DCM (10 mL × 3). The organic solution was washed with H_2O (20 mL × 3) and brine (20 mL × 3), dried and evaporated. The residue was purified by column chromatography.



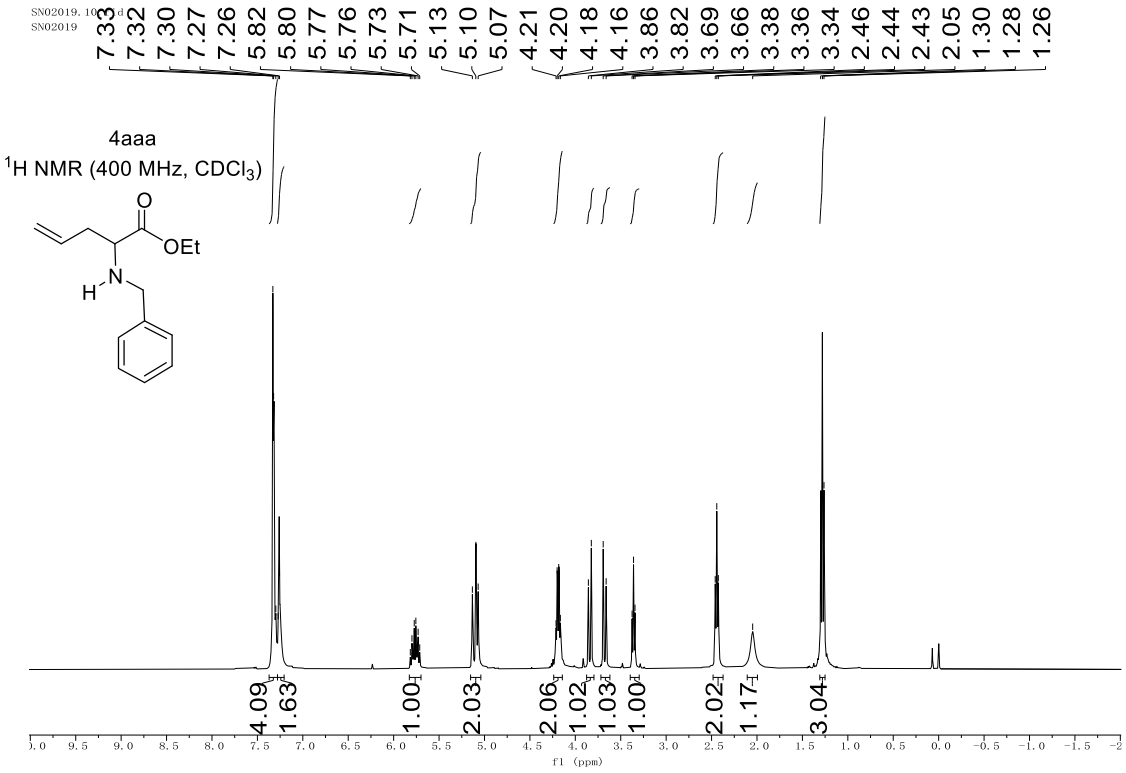
5aab

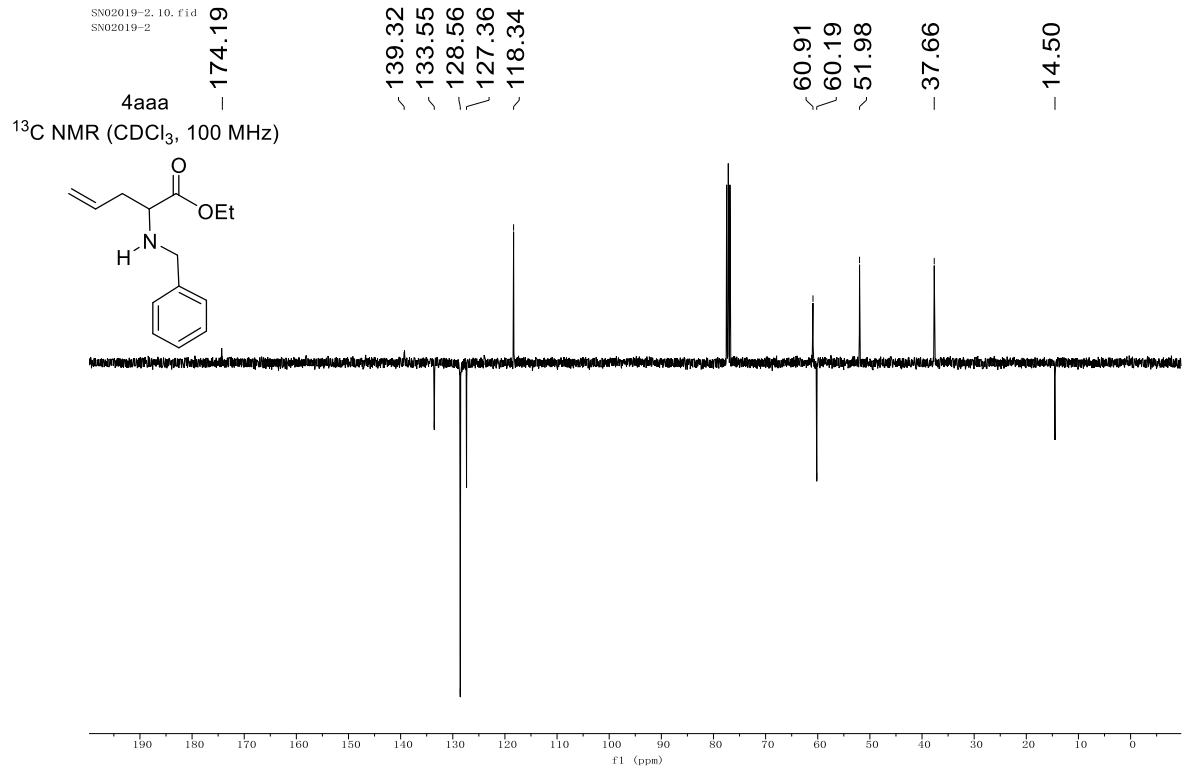
Ethyl-2-(N-benzyl-3,5-dibromobenzamido)-3-methylpent-4-enoate

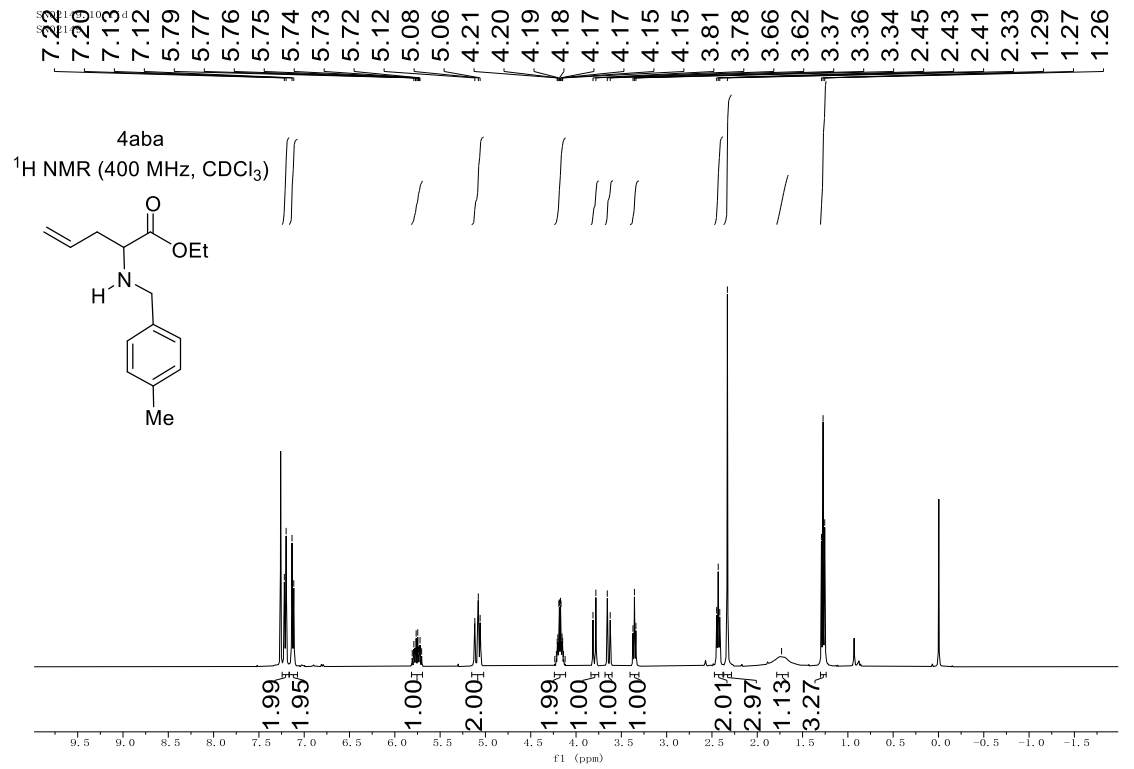
Colorless oil; *Rf* = 0.55 (EtOAc/PE = 1/5, stain in $KMnO_4$);

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.39 –7.20 (m, 8H), 5.83 – 5.67 (m, 1H), 5.11 – 5.05 (m, 2H), 4.23 (qd, *J* = 7.0, 4.9 Hz, 2H), 3.91 (d, *J* = 13.5 Hz, 1H), 3.66 (d, *J* = 13.5 Hz, 1H), 3.17 (d, *J* = 6.2 Hz, 1H), 2.55 (q, *J* = 6.4, 5.8 Hz, 1H), 1.82 (s, 1H), 1.28 (t, *J* = 7.0 Hz, 3H), 1.15 (d, *J* = 6.9 Hz, 3H). **^{13}C NMR** ($CDCl_3$, 126 MHz, CPD) δ 175.17, 174.26, 140.15, 138.89, 137.89, 135.32, 129.86, 128.28, 127.87, 127.37, 126.09, 124.97, 117.62, 116.34, 65.71, 61.42, 51.90, 41.00, 17.35, 14.40.

S.3. Spectral and Analytical data of Compounds



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7.20
7.13
7.12
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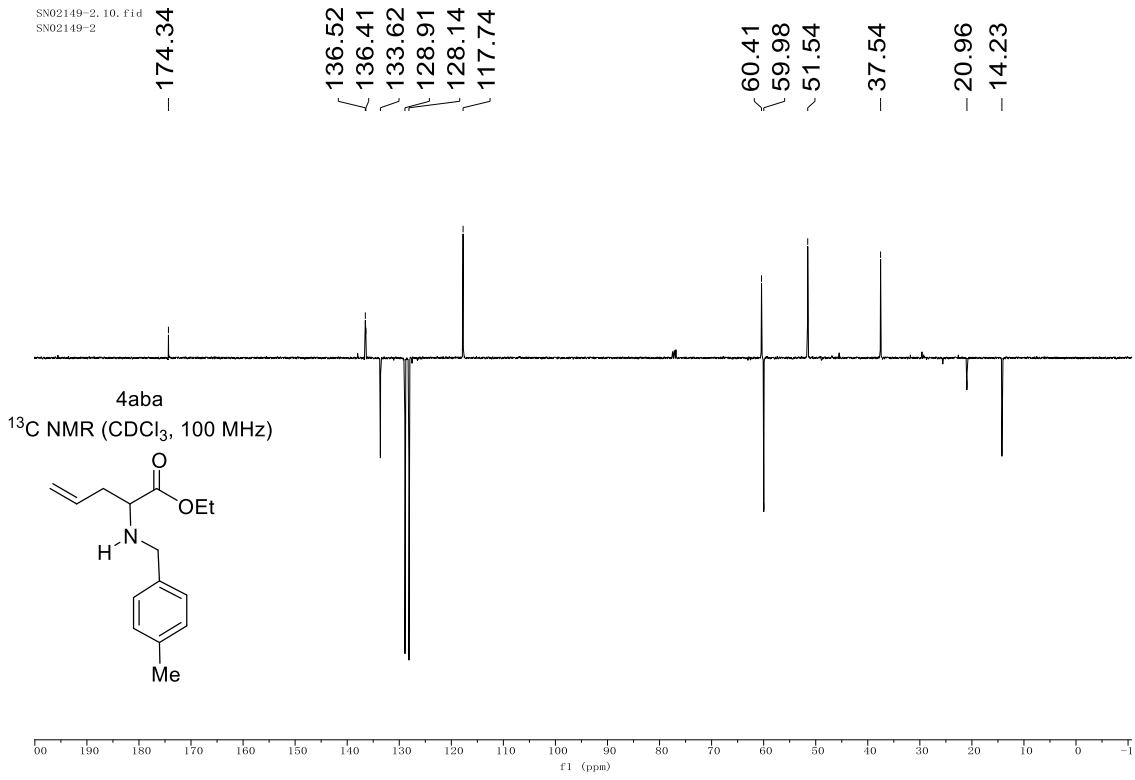
5.77
5.76
5.75
5.74
5.73
5.72
5.12
5.08
5.06
4.21
4.20
4.19
4.18
4.17
4.17
4.15
4.15
3.81
3.78
3.66
3.62
3.37
3.36
3.34
2.45
2.43
2.41
2.33
1.29
1.27
1.26
4aba
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
Me
1.99
1.95
1.00
2.00
1.99
1.00
1.00
1.00
2.01
2.97
1.13
3.27
f1 (ppm)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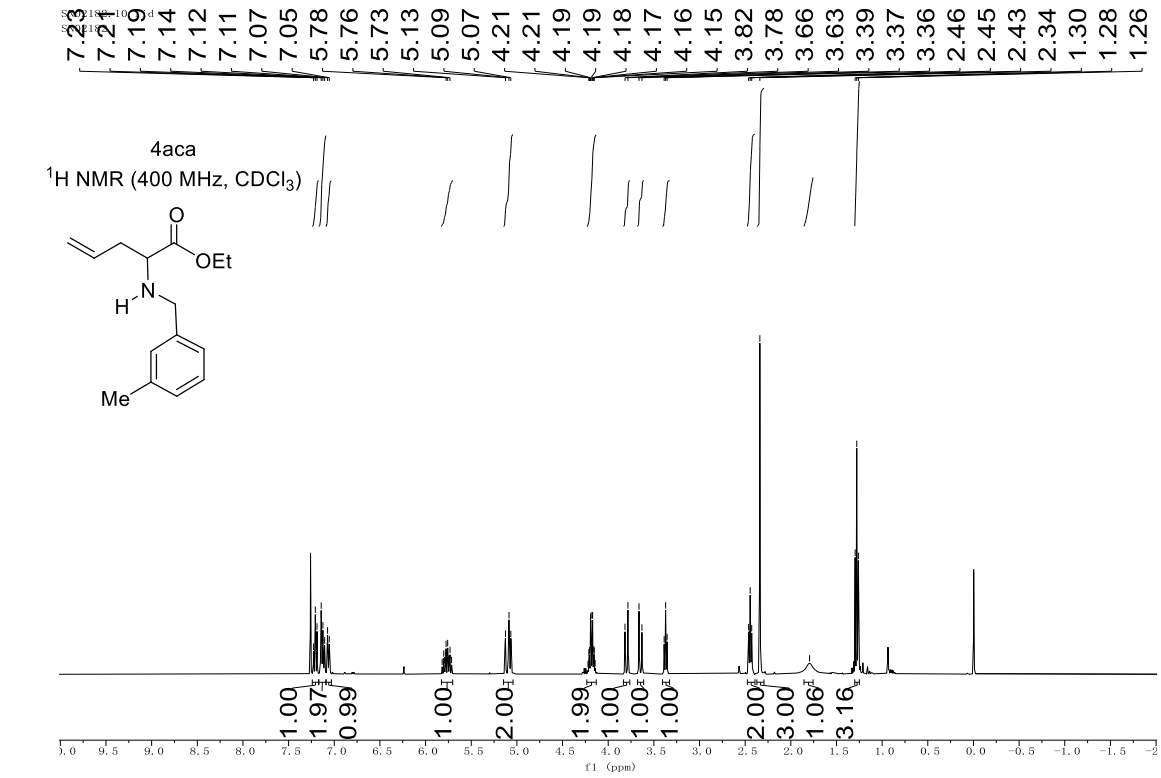
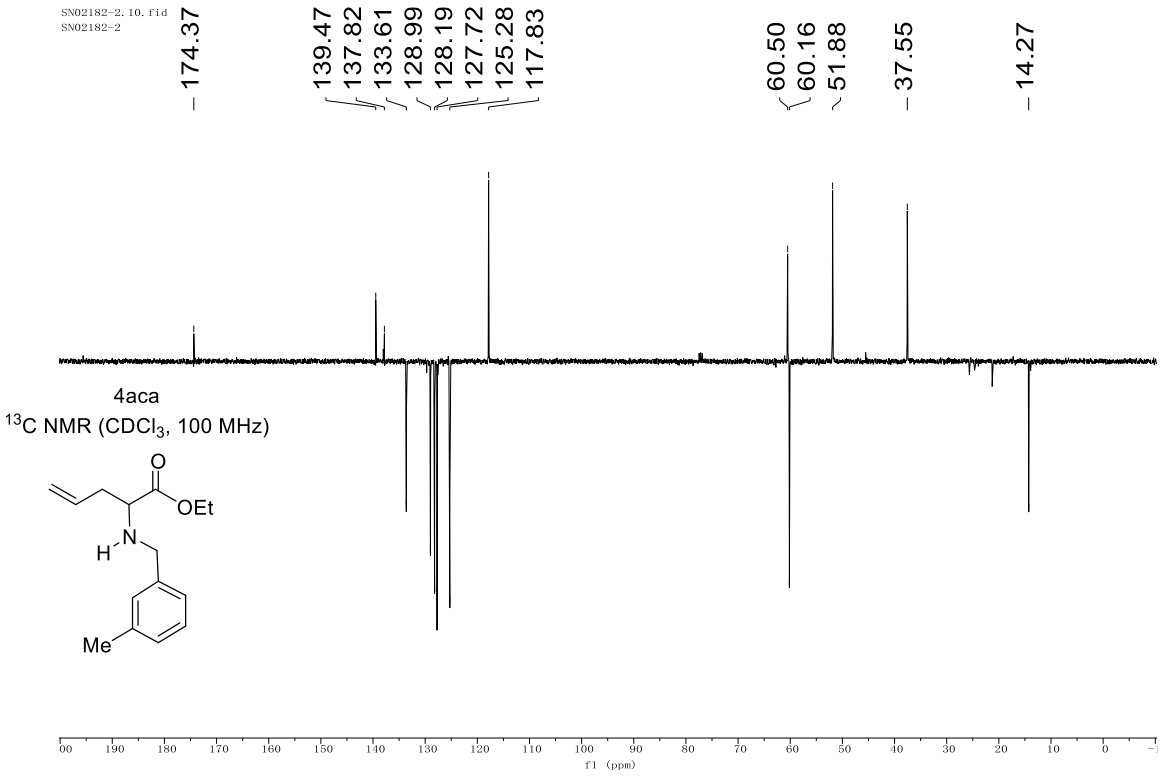
136.52
136.41
133.62
128.91
128.14
117.74
60.41
59.98
51.54
37.54
20.96
14.23
4aba
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
Me
f1 (ppm)


7.23
7.21
7.19
7.14
7.12
7.11
7.07
7.05
5.78
5.76
5.73
5.13
5.09
5.07
4.21
4.21
4.19
4.19
4.18
4.17
4.16
4.15
3.82
3.78
3.66
3.63
3.39
3.37
3.36
2.46
2.45
2.43
2.34
1.30
1.28
1.26
4aca
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
Me
1.00
1.97
0.99
1.00
2.00
1.99
1.00
1.00
1.00
2.00
3.00
1.06
3.16
f1 (ppm)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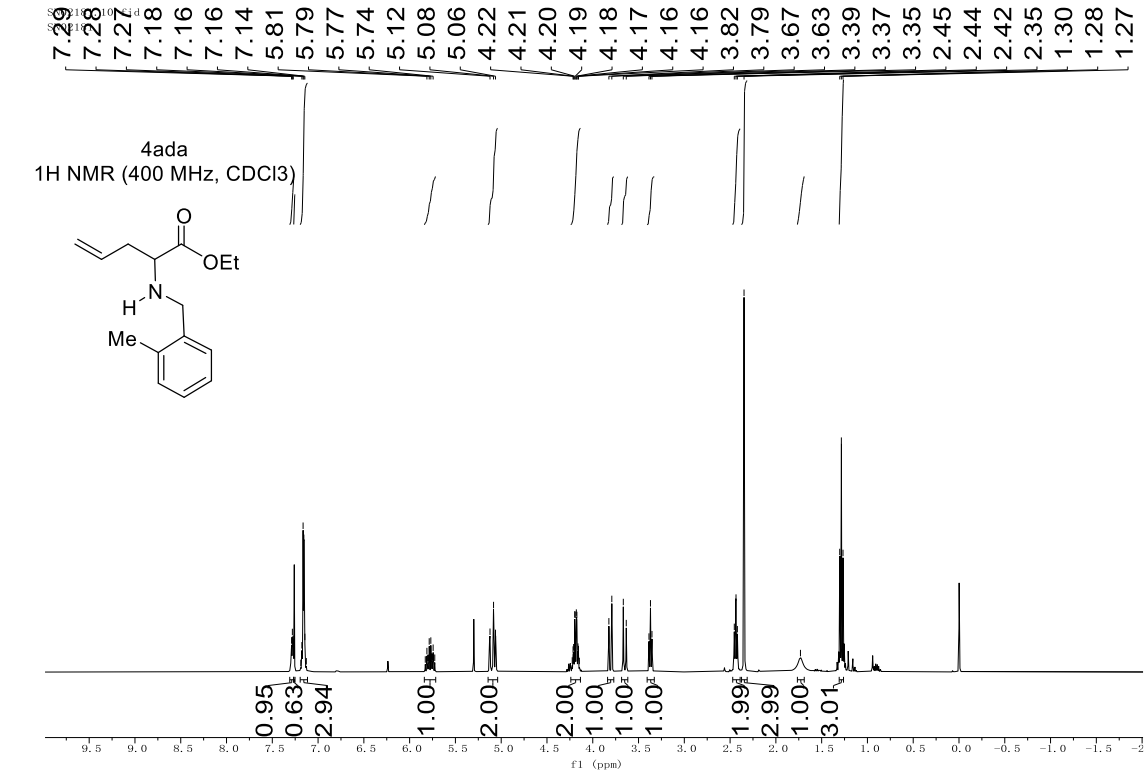
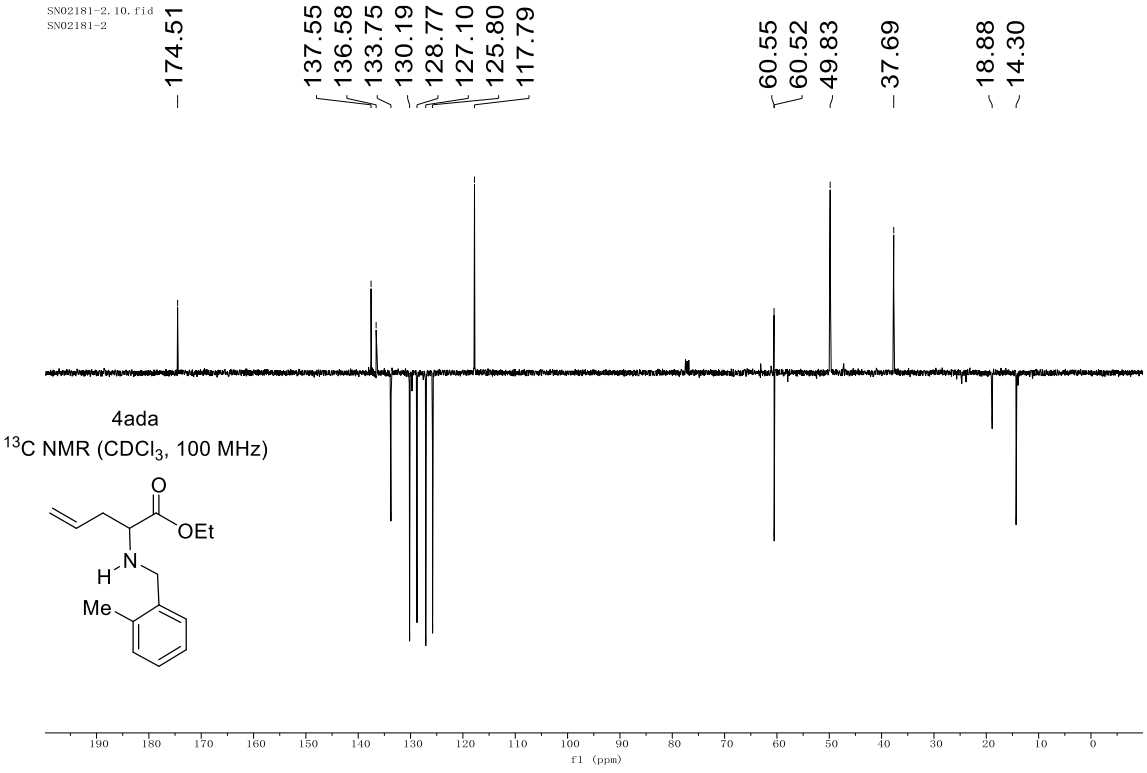
SN02182-2
174.37
139.47
137.82
133.61
128.99
128.19
127.72
125.28
117.83
60.50
60.16
51.88
37.55
14.27
4aca
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
Me
f1 (ppm)


7.29
7.28
7.27
7.18
7.16
7.16
7.14
5.81
5.79
5.77
5.74
5.12
5.08
5.06
4.22
4.21
4.20
4.19
4.18
4.17
4.16
4.16
3.82
3.79
3.67
3.63
3.39
3.37
3.35
2.45
2.44
2.42
2.35
1.30
1.28
1.27
4ada
1H NMR (400 MHz, CDCl3)
O
OEt
N
H
Me
0.95
0.63
2.94
1.00
2.00
2.00
1.00
1.00
1.00
1.99
2.99
1.00
3.01
f1 (ppm)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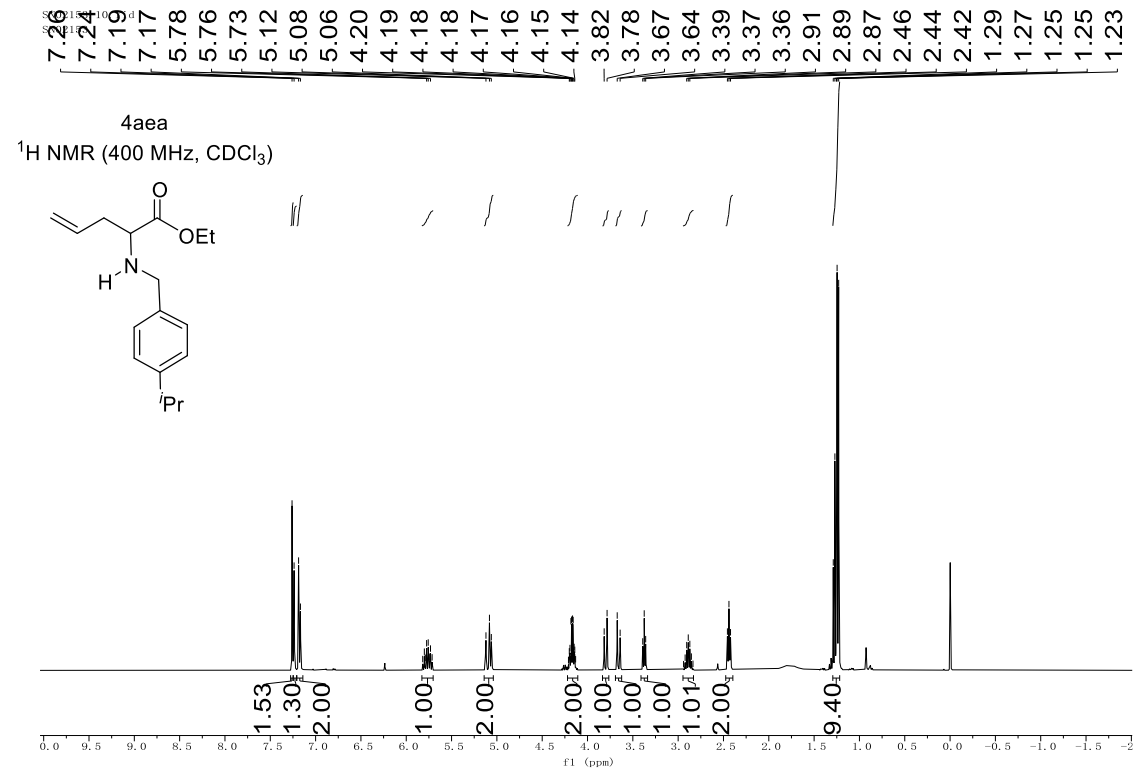
SN02181-2
174.51
137.55
136.58
133.75
130.19
128.77
127.10
125.80
117.79
60.55
60.52
49.83
37.69
18.88
14.30
4ada
13C NMR (CDCl3, 100 MHz)
O
OEt
N
H
Me
f1 (ppm)


7.26
7.24
7.19
7.17
5.78
5.76
5.73
5.12
5.08
5.06
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
3.82
3.78
3.67
3.64
3.39
3.37
3.36
2.91
2.89
2.87
2.46
2.44
2.42
1.29
1.27
1.25
1.25
1.23
4aea
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
iPr
1.53
1.30
2.00
1.00
2.00
2.00
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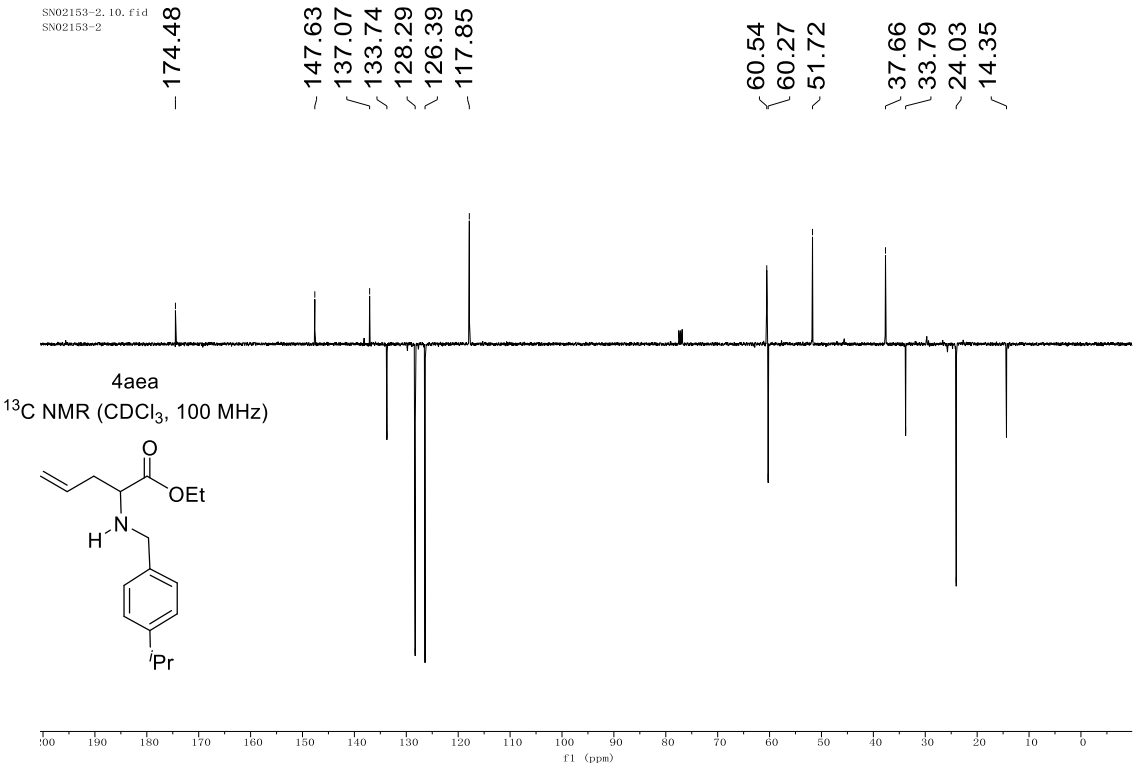
1.00
1.01
2.00
9.40
f1 (ppm)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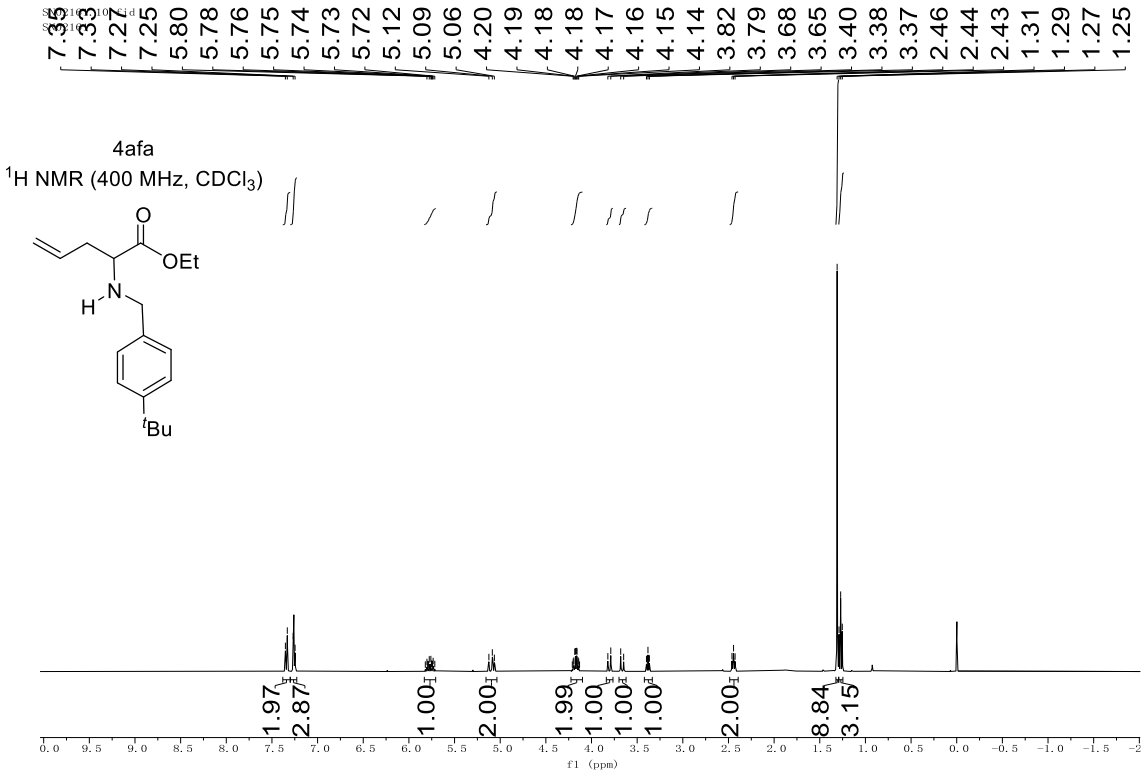
SN02153-2
174.48
147.63
137.07
133.74
128.29
126.39
117.85
60.54
60.27
51.72
37.66
33.79
24.03
14.35
4aea
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
iPr
f1 (ppm)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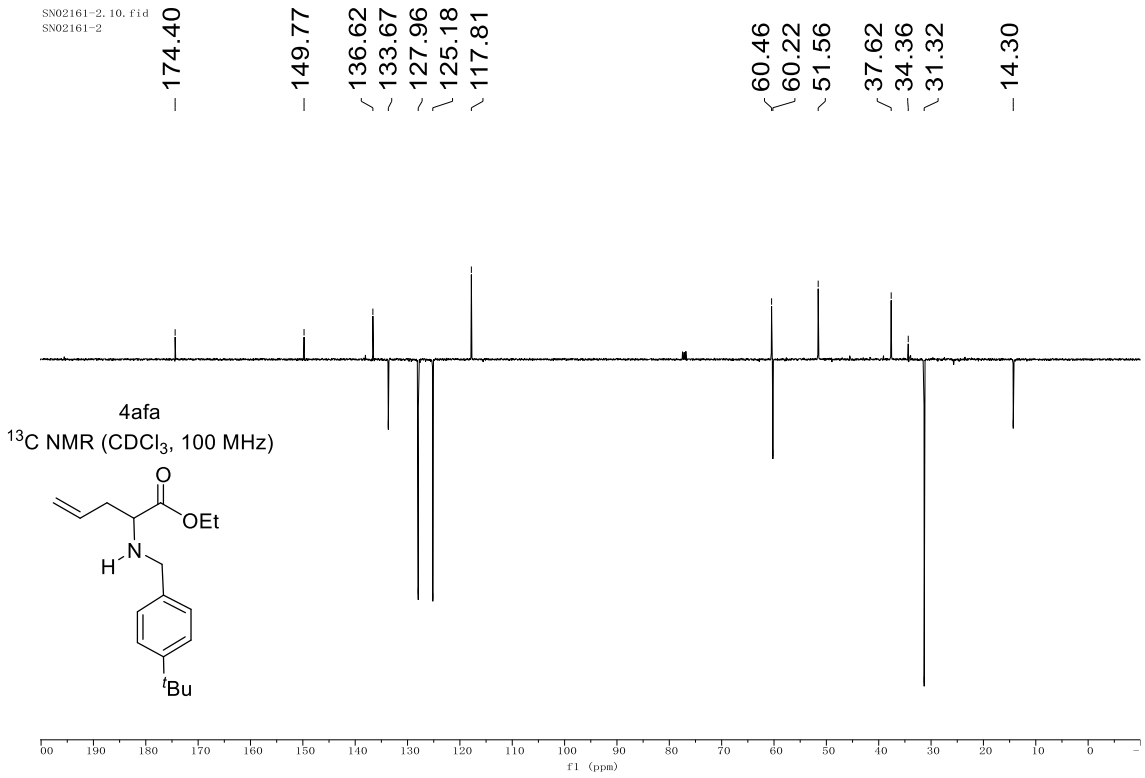
7.33
7.27
7.25
5.80
5.78
5.76
5.75
5.74
5.73
5.72
5.12
5.09
5.06
4.20
4.19
4.18
4.18
4.17
4.16
4.15
4.14
3.82
3.79
3.68
3.65
3.40
3.38
3.37
2.46
2.44
2.43
1.31
1.29
1.27
1.25
4afa
^{1}H NMR (400 MHz, $CDCl_3$)
O
OEt
H
N
^{t}Bu
1.97
2.87
1.00
2.00
1.99
1.00
1.00
1.00
2.00
8.84
3.15
f1 (ppm)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SN02161-2
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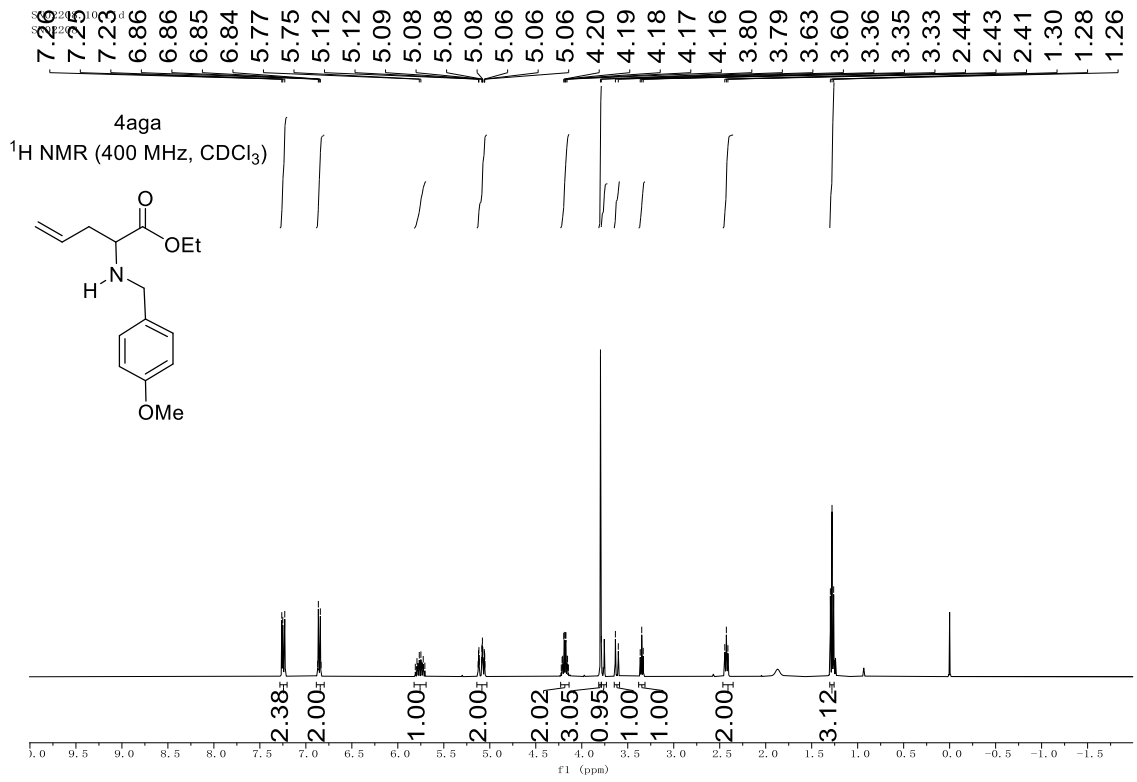
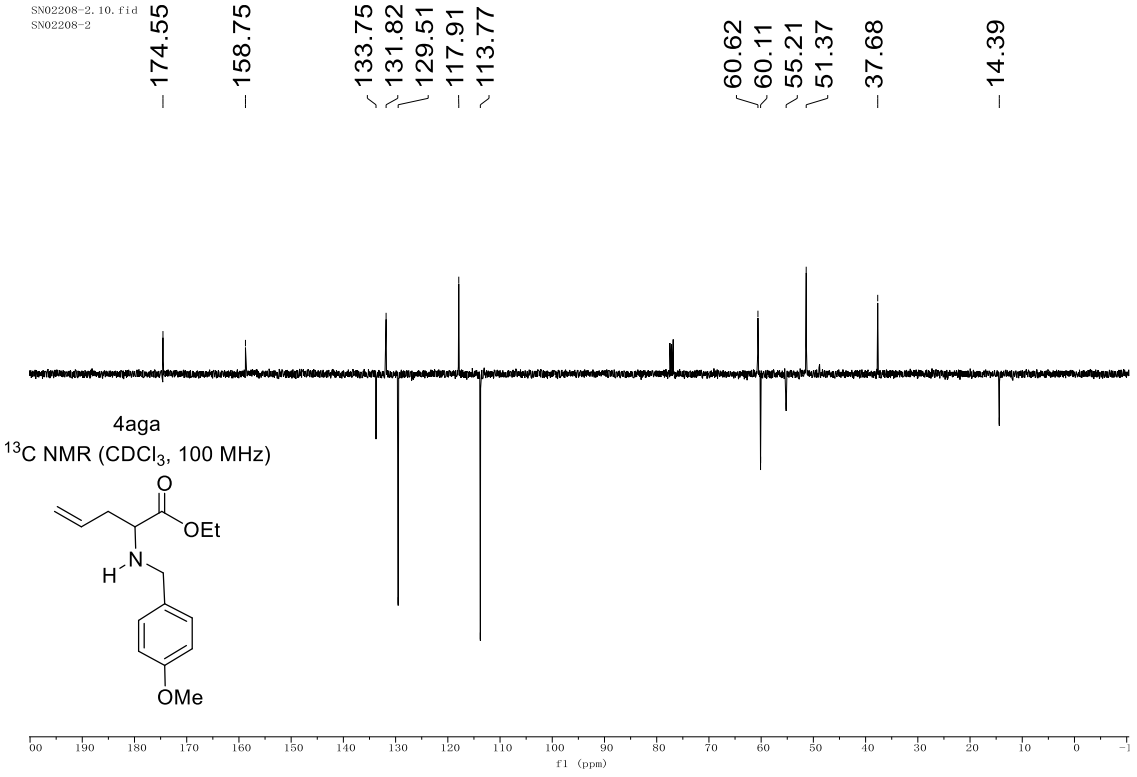
149.77
136.62
133.67
127.96
125.18
117.81
60.46
60.22
51.56
37.62
34.36
31.32
14.30
4afa
^{13}C NMR ($CDCl_3$, 100 MHz)
O
OEt
H
N
^{t}Bu
f1 (ppm)


7.26
7.25
7.23
6.86
6.86
6.85
6.84
5.77
5.75
5.12
5.12
5.09
5.08
5.08
5.08
5.06
5.06
5.06
4.20
4.19
4.18
4.17
4.16
3.80
3.79
3.63
3.60
3.36
3.35
3.33
2.44
2.43
2.41
1.30
1.28
1.26
4aga
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
OMe
2.38
2.00
1.00
2.00
2.02
3.05
0.95
1.00
1.00
2.00
3.12
f1 (ppm)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SN02208-2
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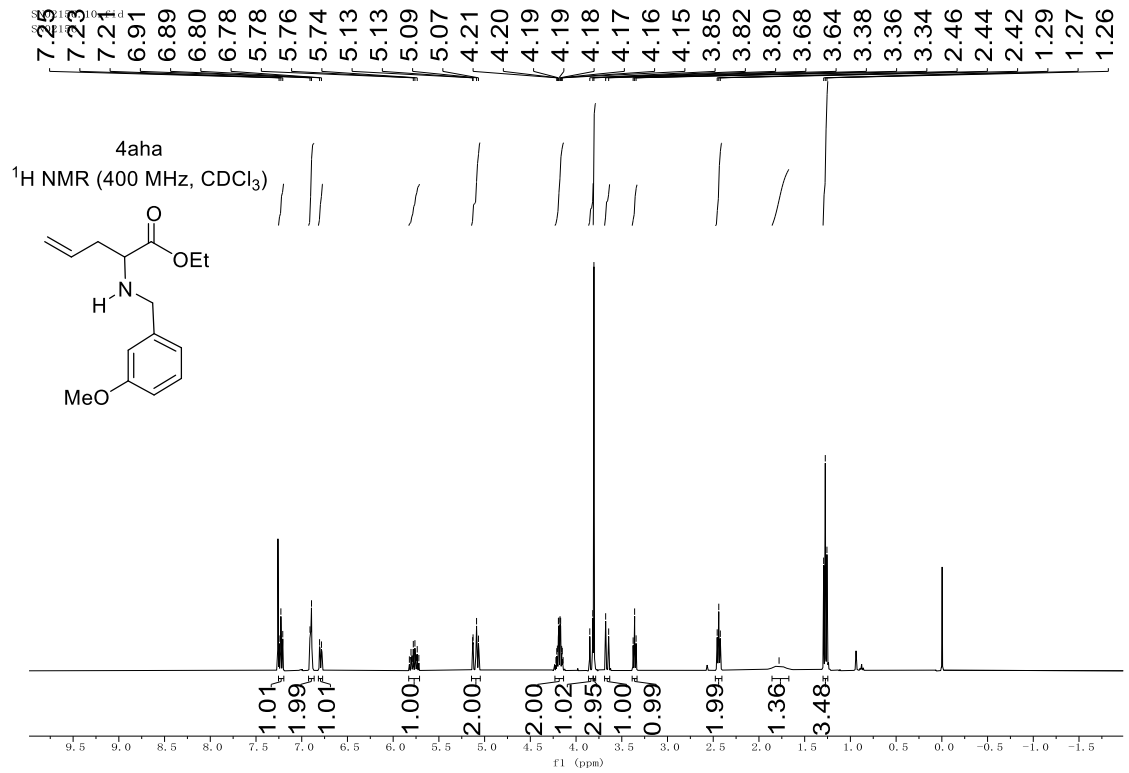
158.75
133.75
131.82
129.51
117.91
113.77
60.62
60.11
55.21
51.37
37.68
14.39
4aga
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
OMe
f1 (ppm)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7.23
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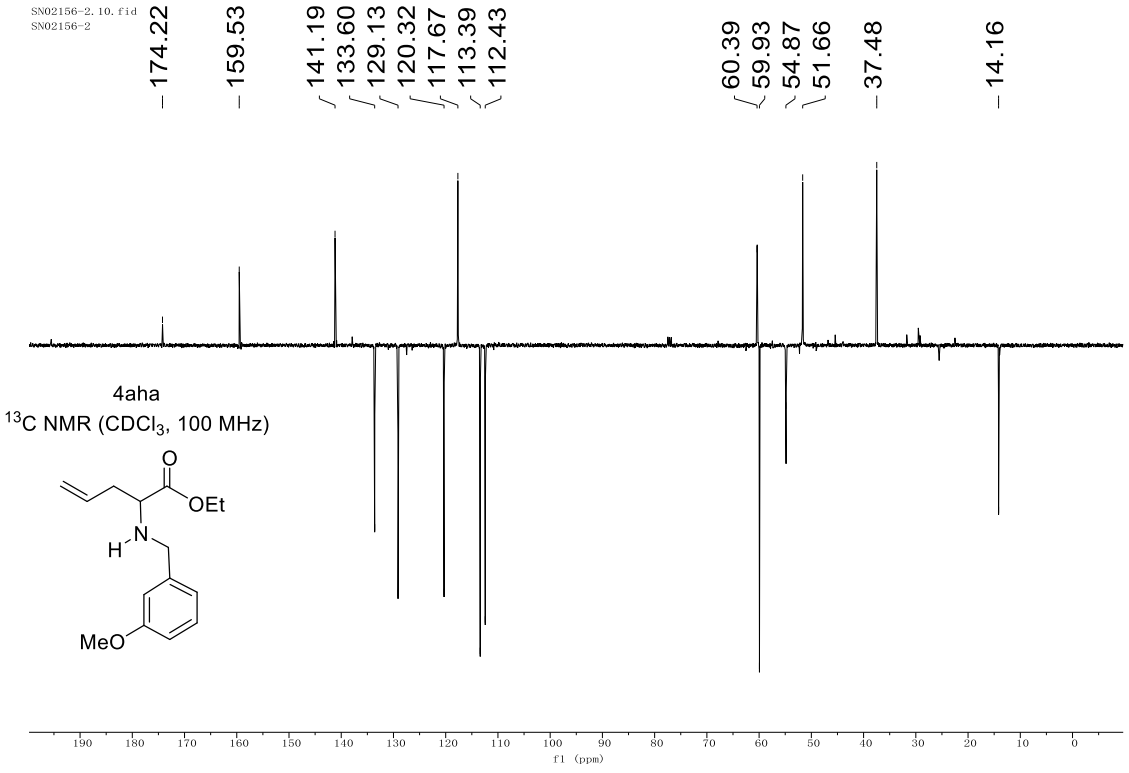
6.89
6.80
6.78
5.78
5.76
5.74
5.13
5.13
5.09
5.07
4.21
4.20
4.19
4.19
4.18
4.17
4.16
4.15
3.85
3.82
3.80
3.68
3.64
3.38
3.36
3.34
2.46
2.44
2.42
1.29
1.27
1.26
4aha
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
MeO
1.01
1.99
1.01
1.00
2.00
2.00
1.02
2.95
1.00
0.99
1.99
1.36
3.48
f1 (ppm)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SN02156-2
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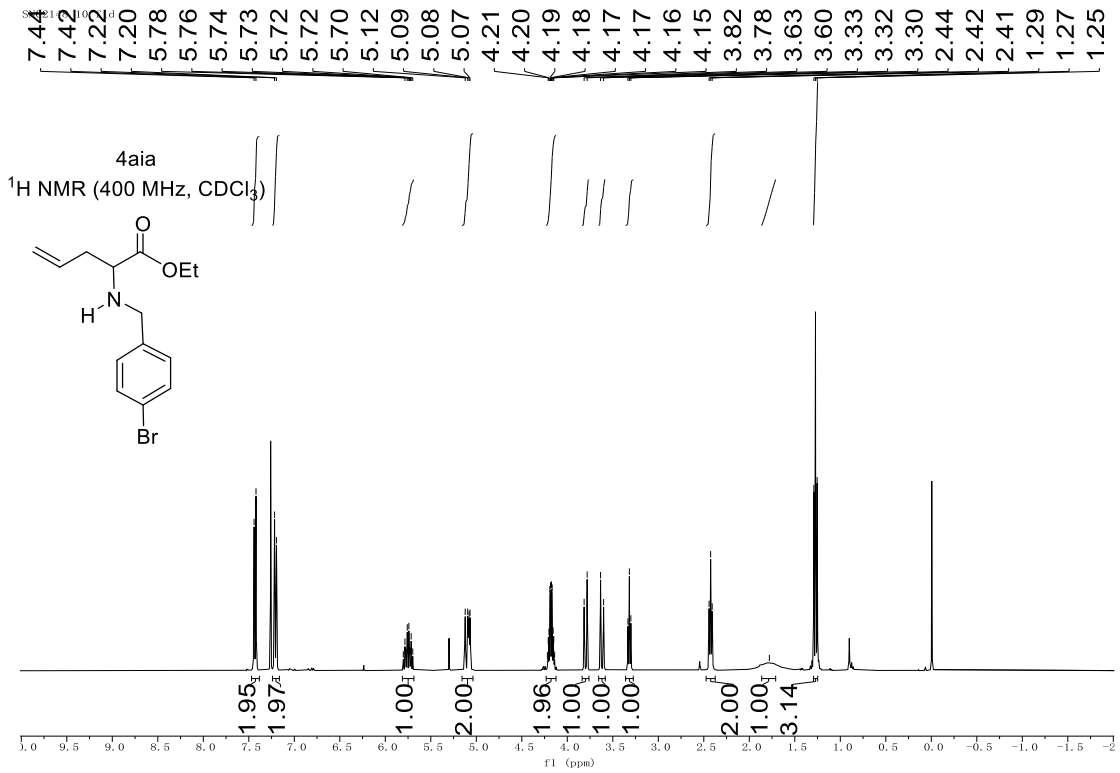
159.53
141.19
133.60
129.13
120.32
117.67
113.39
112.43
60.39
59.93
54.87
51.66
37.48
14.16
4aha
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
MeO
f1 (ppm)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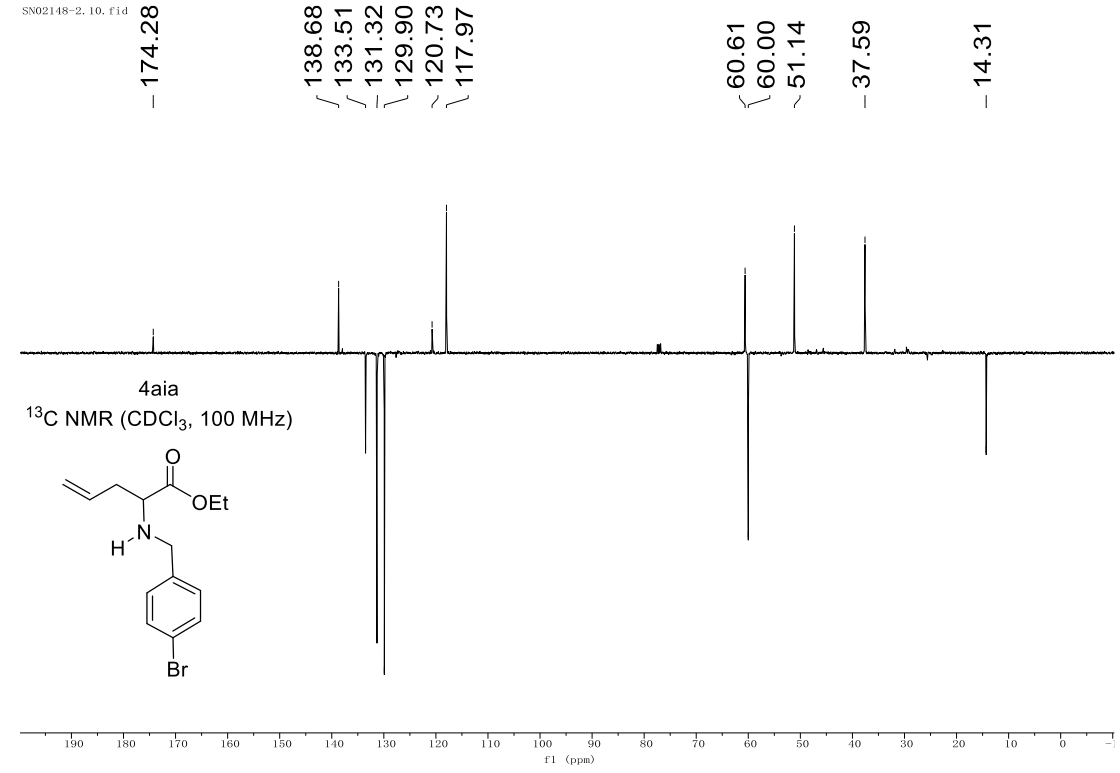
5.76
5.74
5.73
5.72
5.72
5.70
5.12
5.09
5.08
5.07
4.21
4.20
4.19
4.18
4.17
4.17
4.16
4.15
3.82
3.78
3.63
3.60
3.33
3.32
3.30
2.44
2.42
2.41
1.29
1.27
1.25
4aia
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
Br
1.95
1.97
1.00
2.00
1.96
1.00
1.00
1.00
2.00
1.00
3.14
f1 (ppm)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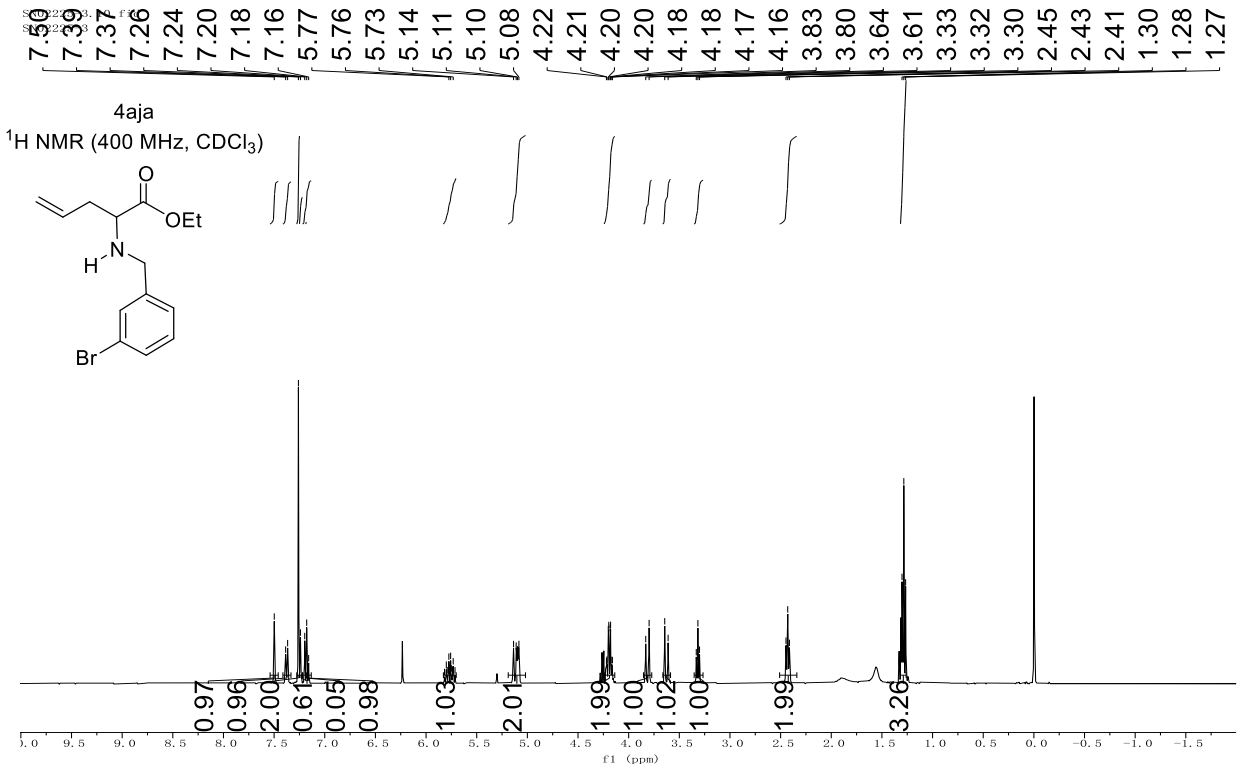
138.68
133.51
131.32
129.90
120.73
117.97
60.61
60.00
51.14
37.59
14.31
4aia
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
Br
f1 (ppm)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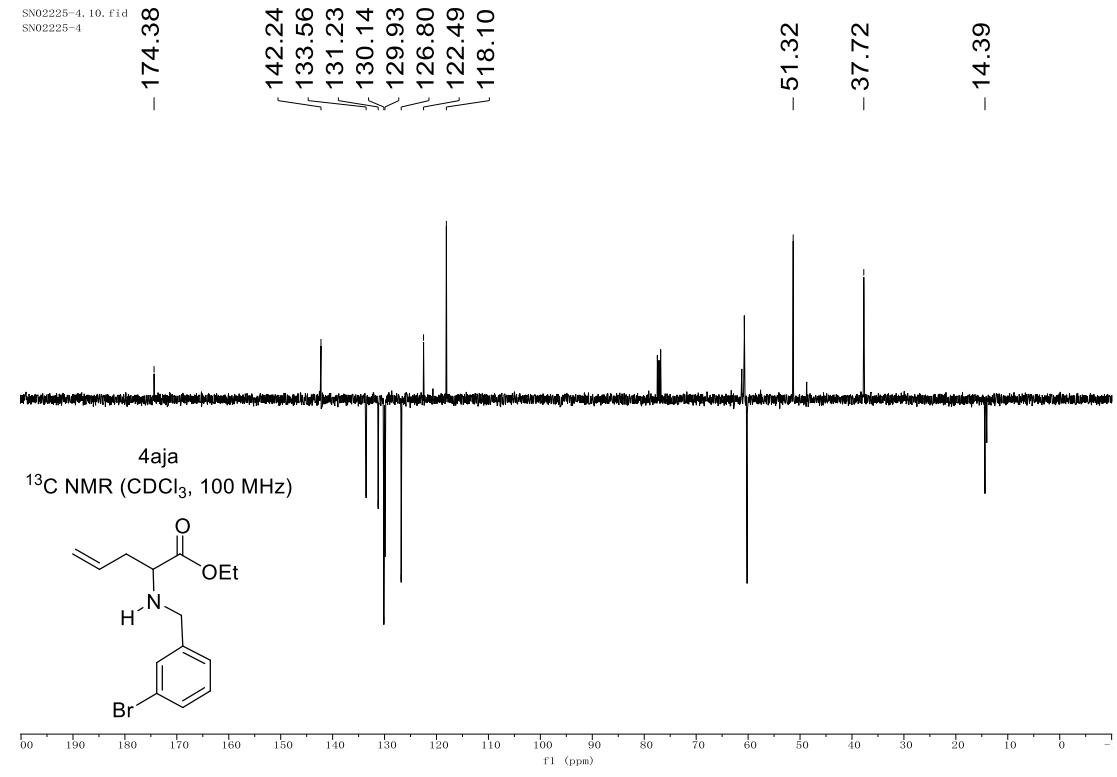
7.24
7.20
7.18
7.16
5.77
5.76
5.73
5.14
5.11
5.10
5.08
4.22
4.21
4.20
4.20
4.18
4.18
4.17
4.16
3.83
3.80
3.64
3.61
3.33
3.32
3.30
2.45
2.43
2.41
1.30
1.28
1.27
4aja
1H NMR (400 MHz, CDCl3)
O
OEt
N
H
Br
0.97
0.96
2.00
0.61
0.05
0.98
1.03
2.01
1.99
1.00
1.02
1.00
1.99
3.26
f1 (ppm)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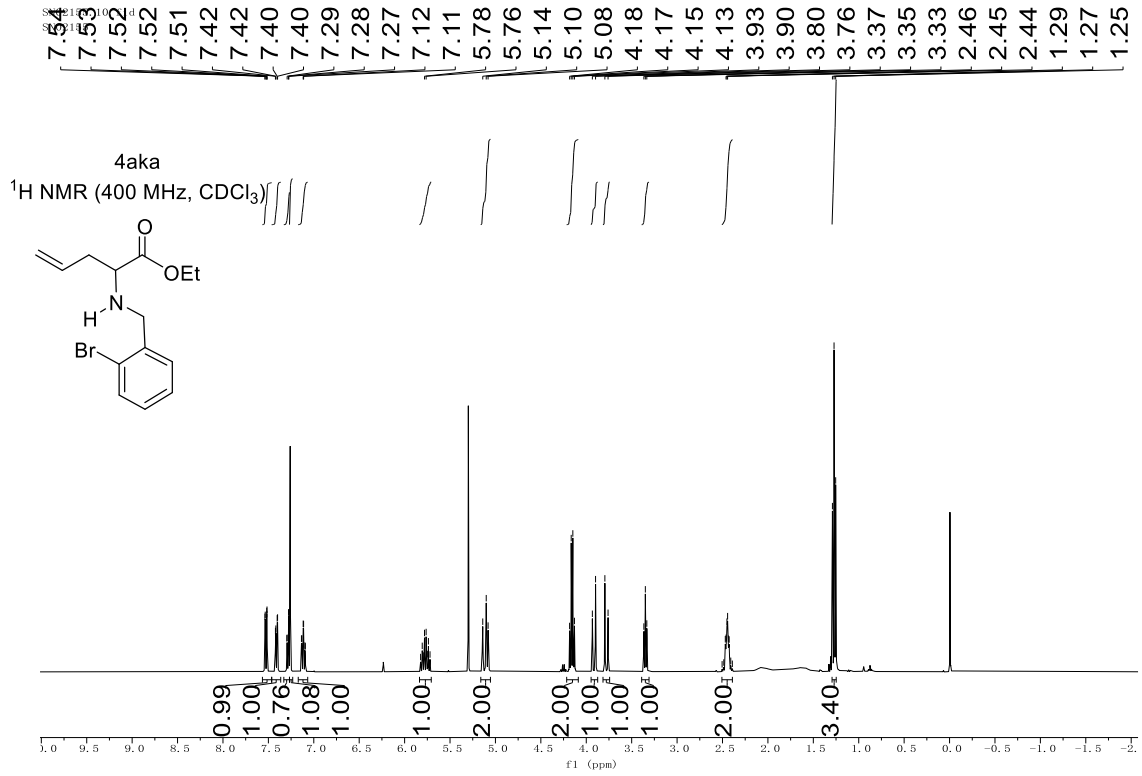
SN02225-4
174.38
142.24
133.56
131.23
130.14
129.93
126.80
122.49
118.10
51.32
37.72
14.39
4aja
13C NMR (CDCl3, 100 MHz)
O
OEt
N
H
Br
f1 (ppm)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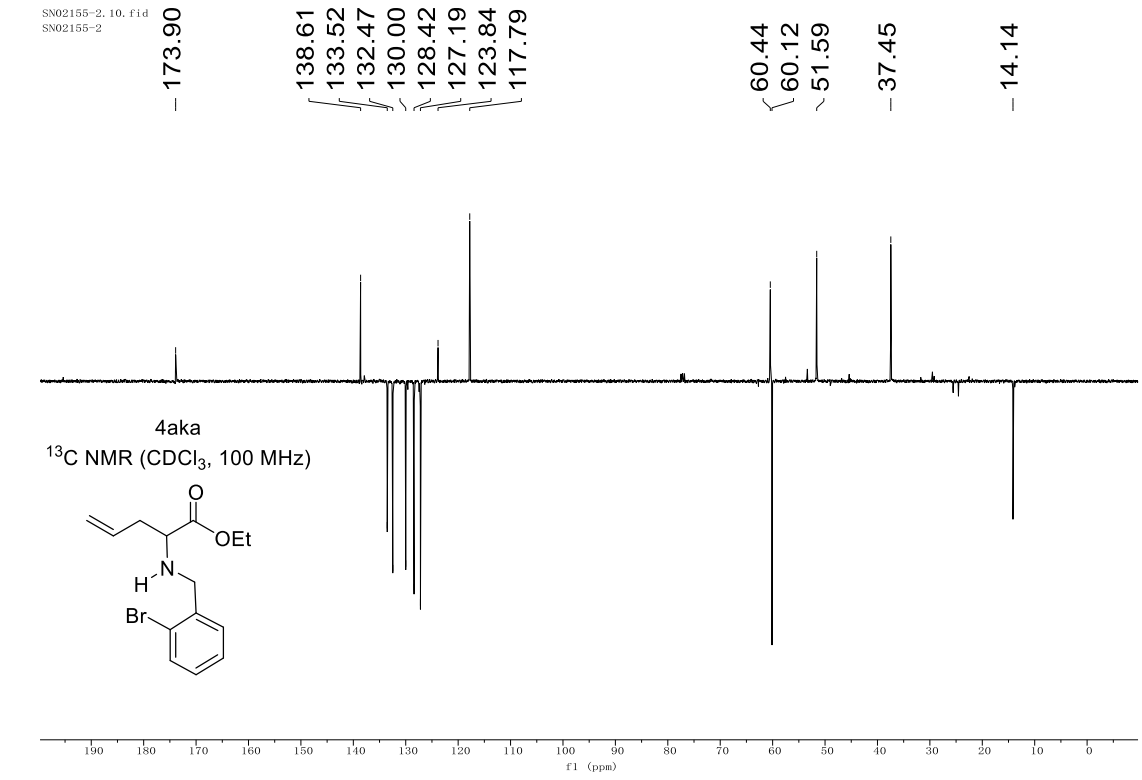
7.51
7.42
7.42
7.40
7.40
7.29
7.28
7.27
7.12
7.11
5.78
5.76
5.14
5.10
5.08
4.18
4.17
4.15
4.13
3.93
3.90
3.80
3.76
3.37
3.35
3.33
2.46
2.45
2.44
1.29
1.27
1.25
4aka
1H NMR (400 MHz, CDCl3)
O
OEt
N
H
Br
0.99
1.00
0.76
1.08
1.00
1.00
2.00
2.00
1.00
1.00
1.00
2.00
3.40
f1 (ppm)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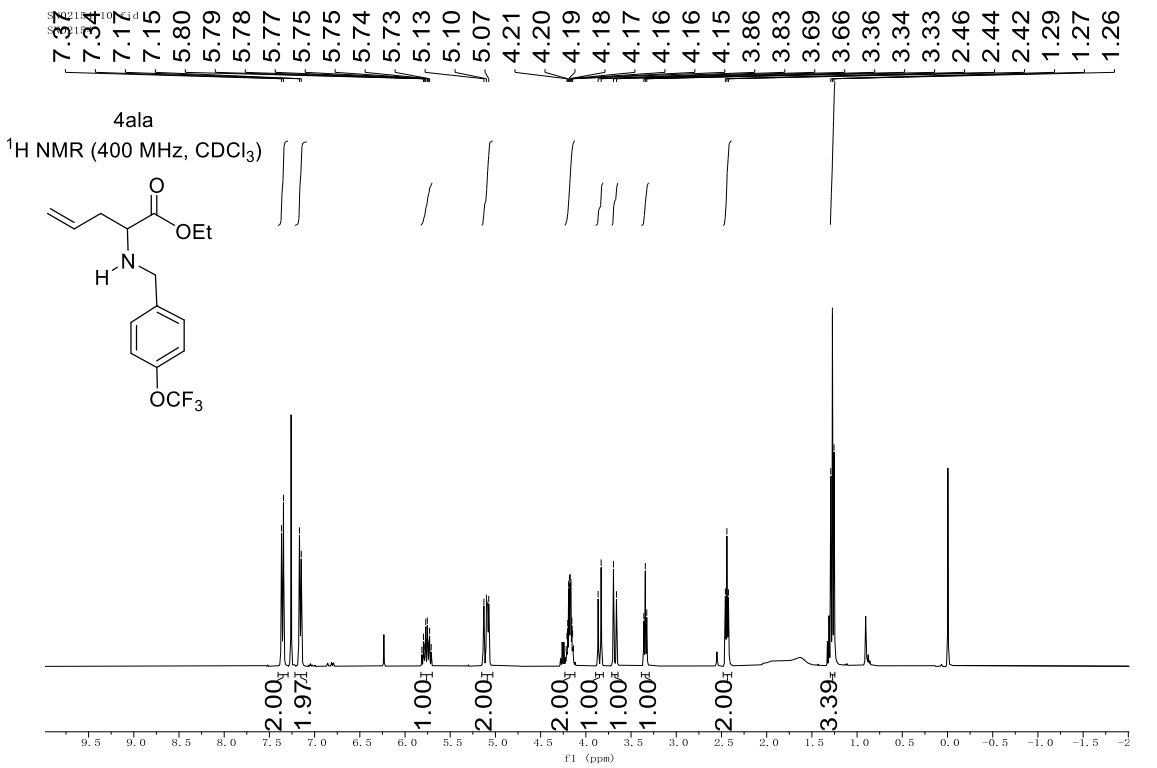
SN02155-2
173.90
138.61
133.52
132.47
130.00
128.42
127.19
123.84
117.79
60.44
60.12
51.59
37.45
14.14
4aka
13C NMR (CDCl3, 100 MHz)
O
OEt
N
H
Br
f1 (ppm)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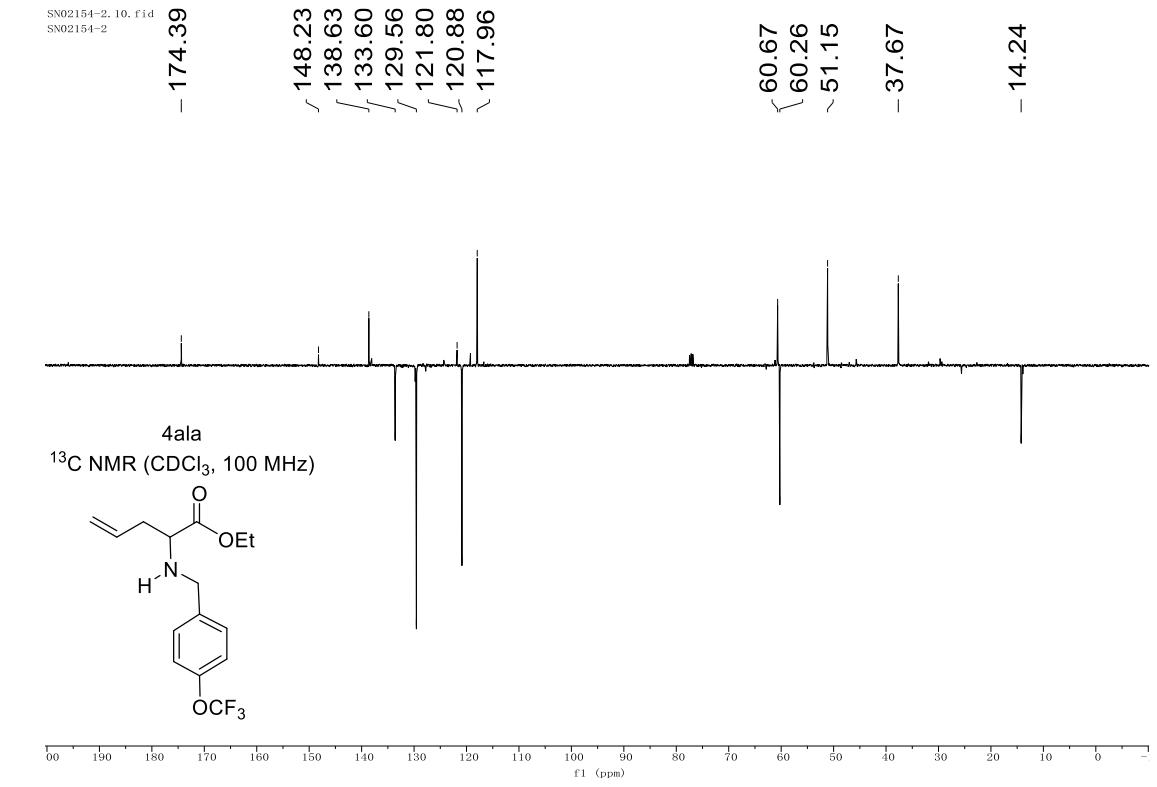
7.34
7.17
7.15
5.80
5.79
5.78
5.77
5.75
5.75
5.74
5.73
5.13
5.10
5.07
4.21
4.20
4.19
4.18
4.17
4.16
4.16
4.15
3.86
3.83
3.69
3.66
3.36
3.34
3.33
2.46
2.44
2.42
1.29
1.27
1.26
4ala
1H NMR (400 MHz, CDCl3)
O
OEt
N
H
OCF3
2.00
1.97
1.00
2.00
2.00
1.00
1.00
1.00
2.00
3.39
f1 (ppm)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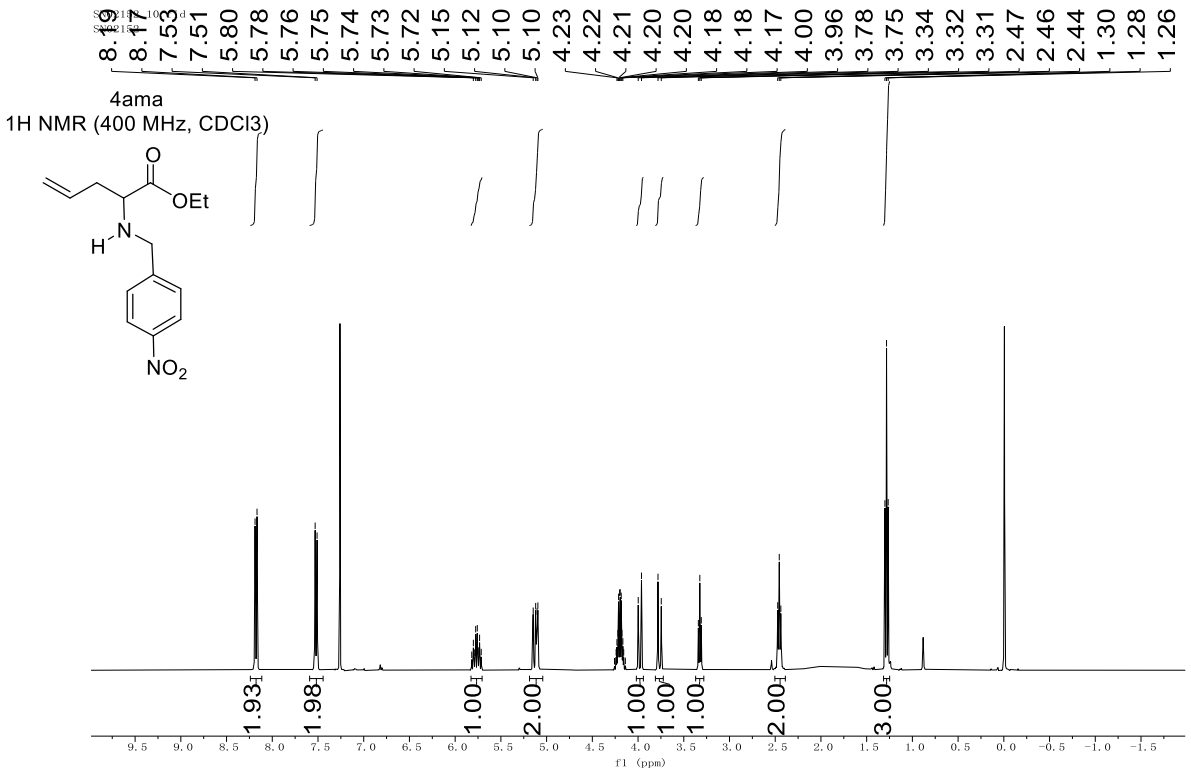
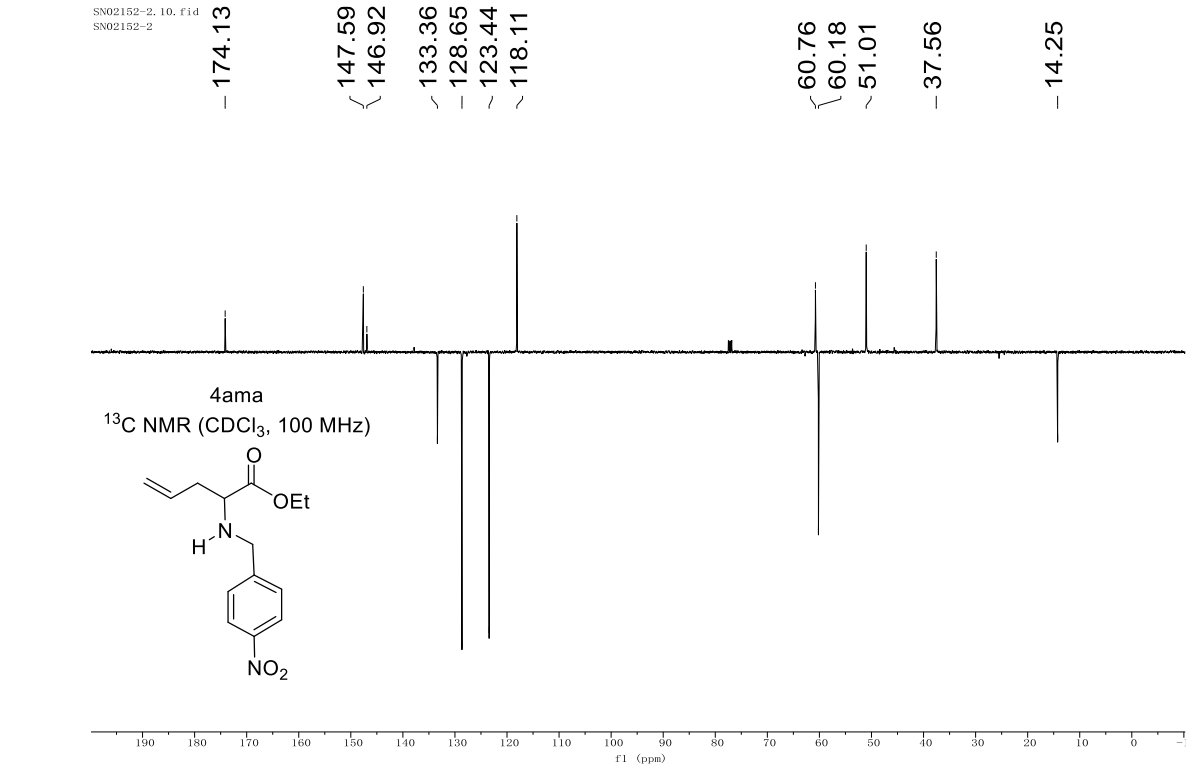
SN02154-2
174.39
148.23
138.63
133.60
129.56
121.80
120.88
117.96
60.67
60.26
51.15
37.67
14.24
4ala
13C NMR (CDCl3, 100 MHz)
O
OEt
N
H
OCF3
f1 (ppm)


8.19
8.17
7.53
7.51
5.80
5.78
5.76
5.75
5.74
5.73
5.72
5.15
5.12
5.10
5.10
4.23
4.22
4.21
4.20
4.20
4.18
4.18
4.17
4.00
3.96
3.78
3.75
3.34
3.32
3.31
2.47
2.46
2.44
1.30
1.28
1.26
4ama
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
NO2
1.93
1.98
1.00
2.00
1.00
1.00
1.00
2.00
3.00
f1 (ppm)


SN02152-2.10.fid
SN02152-2
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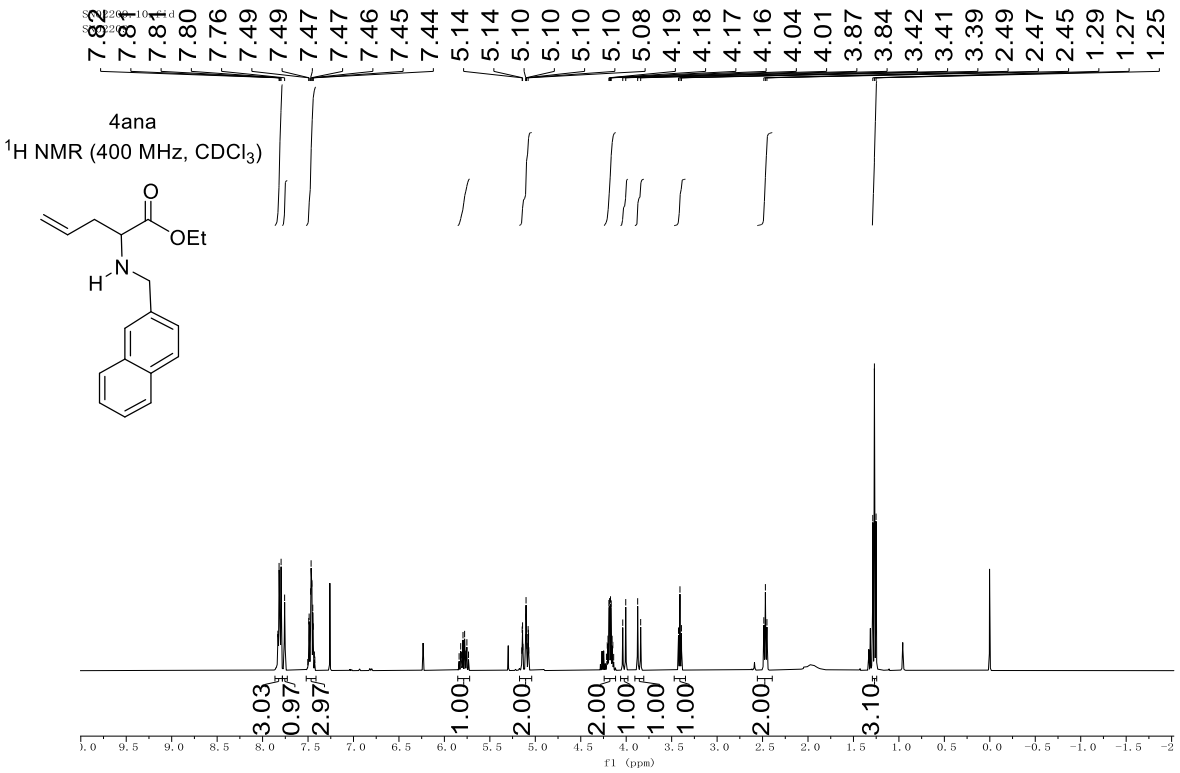
147.59
146.92
133.36
128.65
123.44
118.11
60.76
60.18
51.01
37.56
14.25
4ama
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
NO2
f1 (ppm)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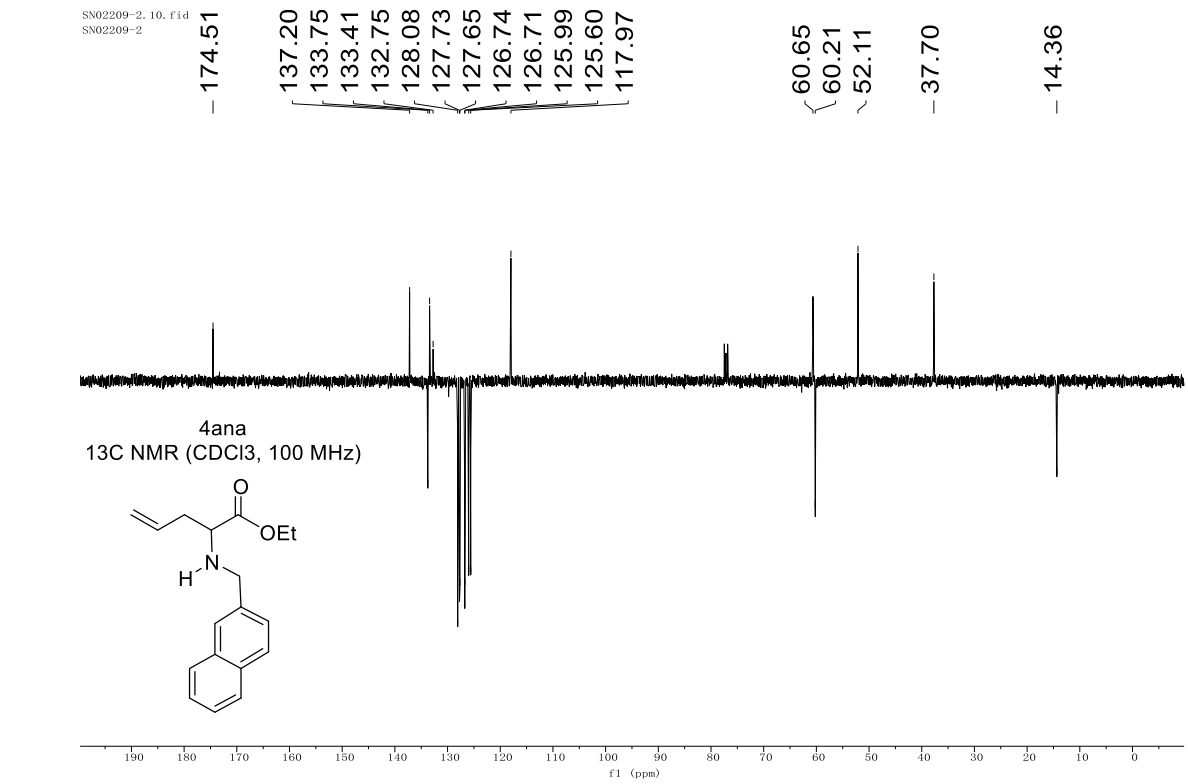
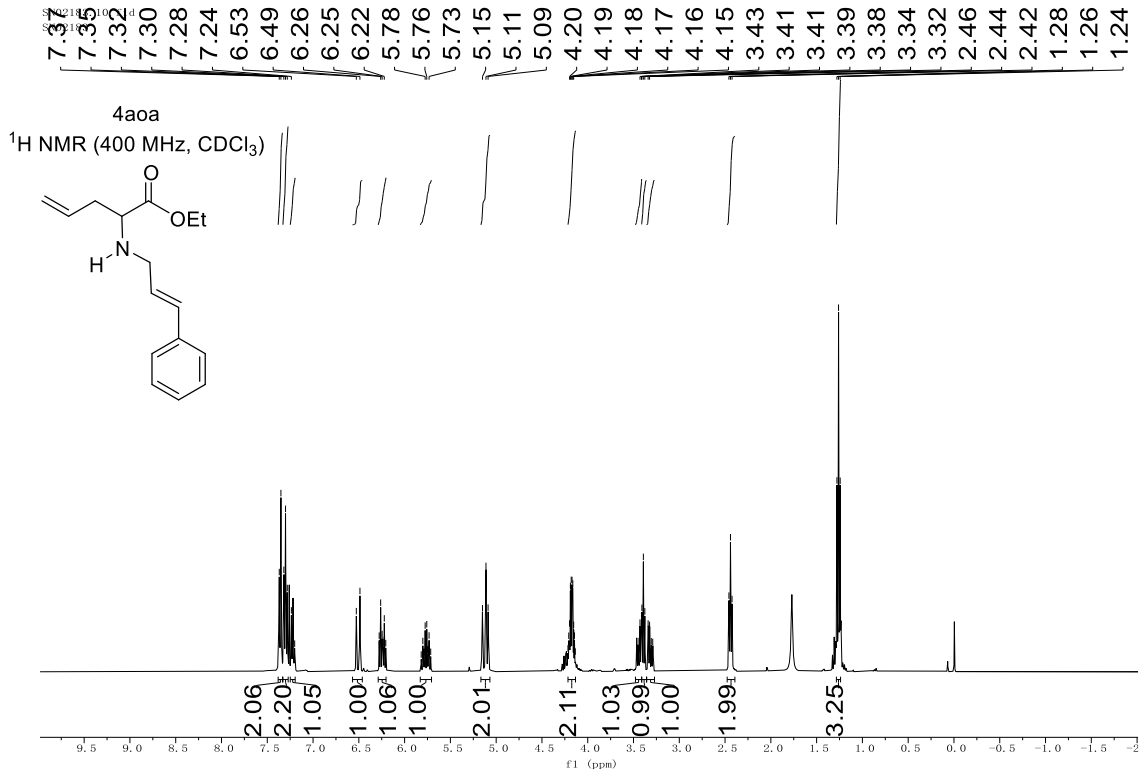
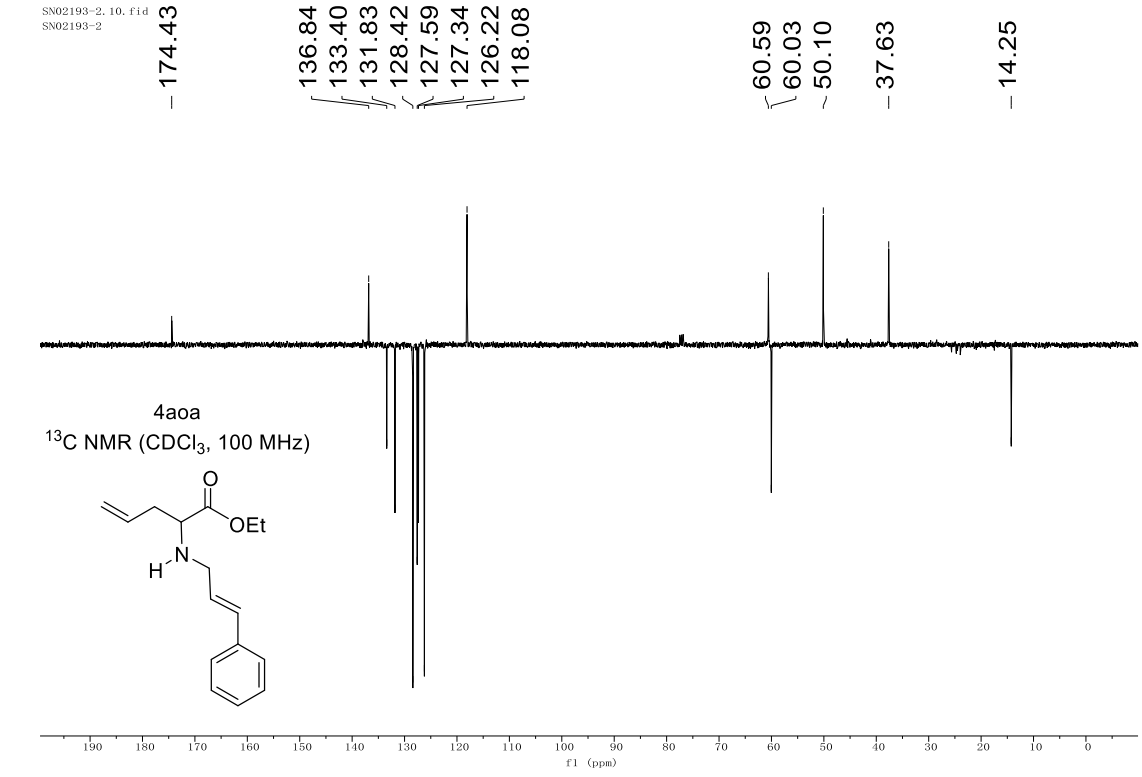
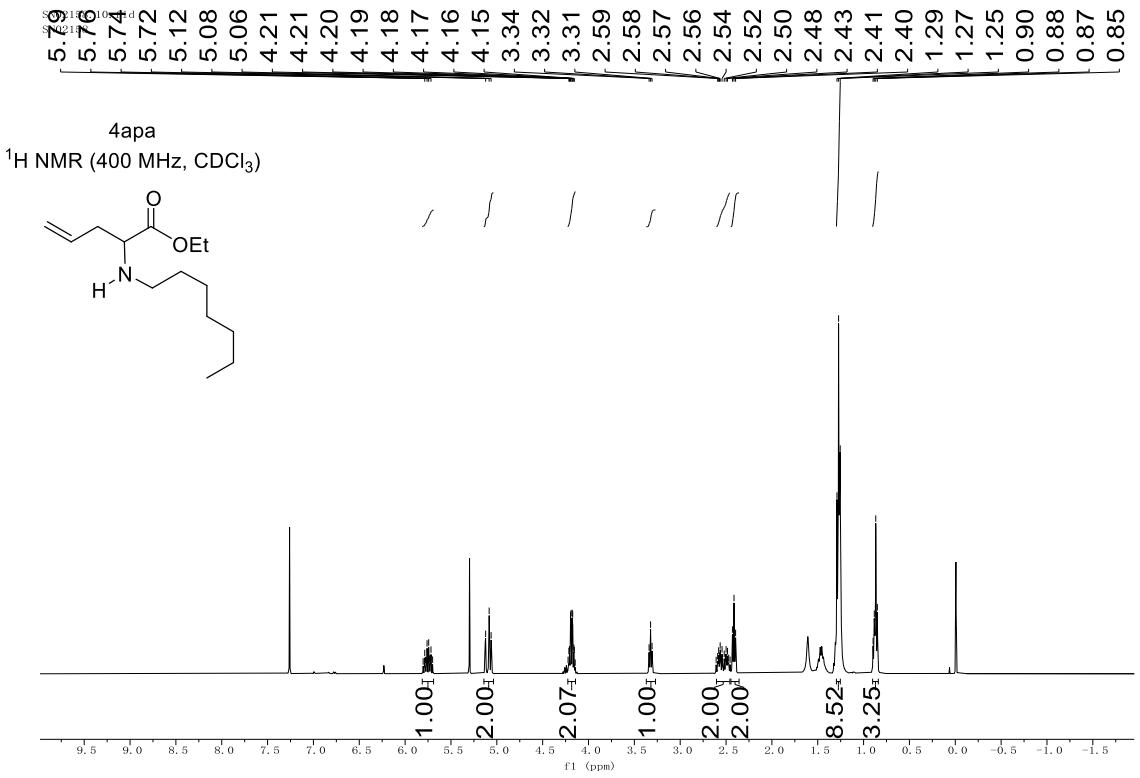
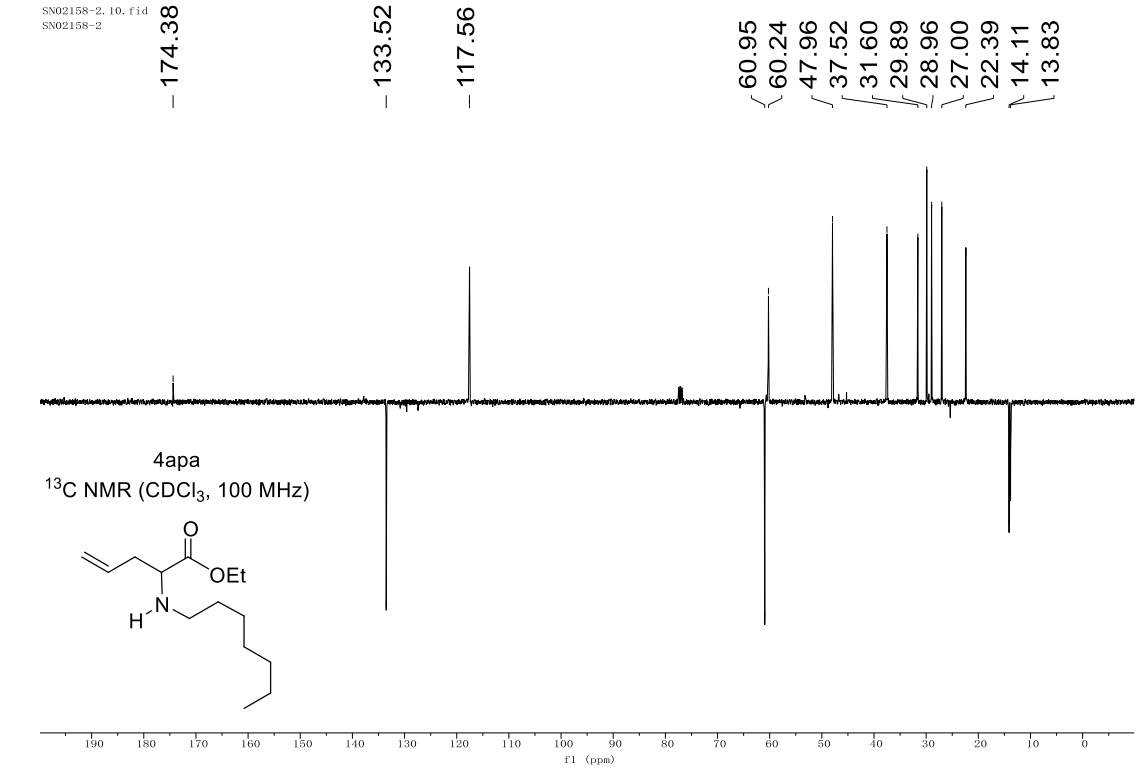
7.81
7.81
7.80
7.76
7.49
7.49
7.47
7.47
7.46
7.45
7.44
5.14
5.14
5.10
5.10
5.10
5.10
5.08
4.19
4.18
4.17
4.16
4.04
4.01
3.87
3.84
3.42
3.41
3.39
2.49
2.47
2.45
1.29
1.27
1.25
4ana
1H NMR (400 MHz, CDCl3)
O
OEt
N
H
3.03
0.97
2.97
1.00
2.00
2.00
1.00
1.00
1.00
2.00
3.10
f1 (ppm)

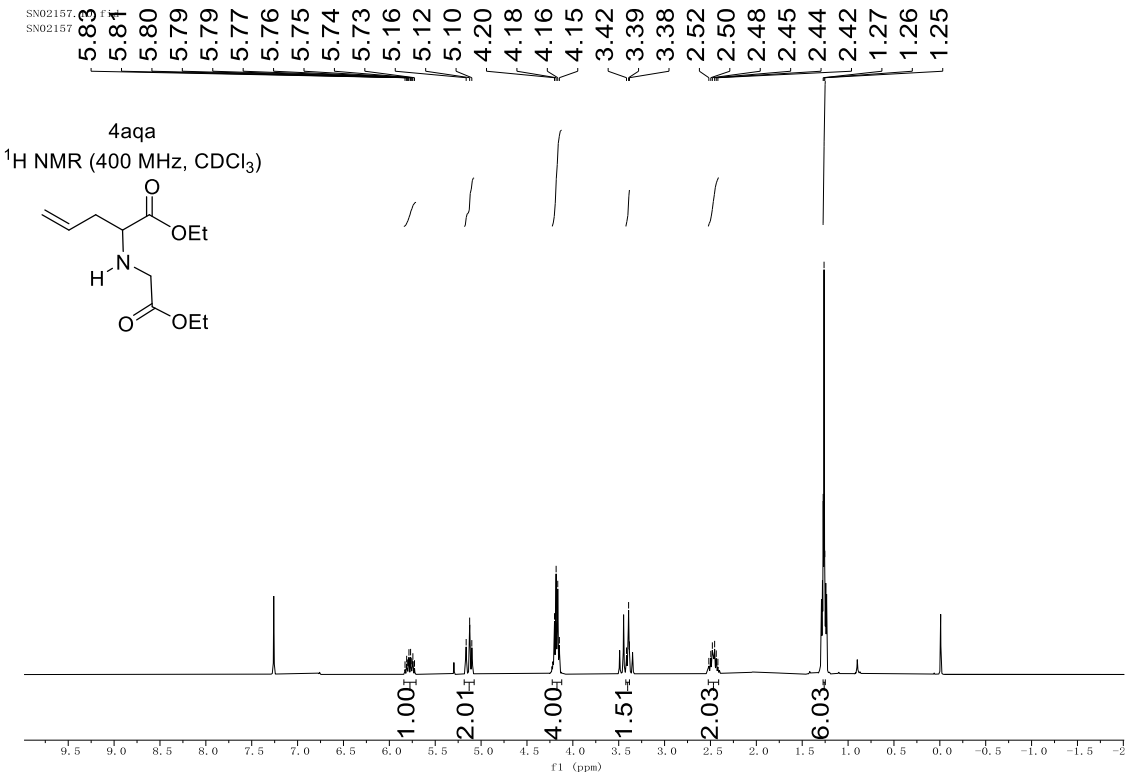

SN02209-2.10.fid
SN02209-2
174.51
137.20
133.75
133.41
132.75
128.08
127.73
127.65
126.74
126.71
125.99
125.60
117.97
60.65
60.21
52.11
37.70
14.36
4ana
13C NMR (CDCl3, 100 MHz)
O
OEt
N
H
f1 (ppm)

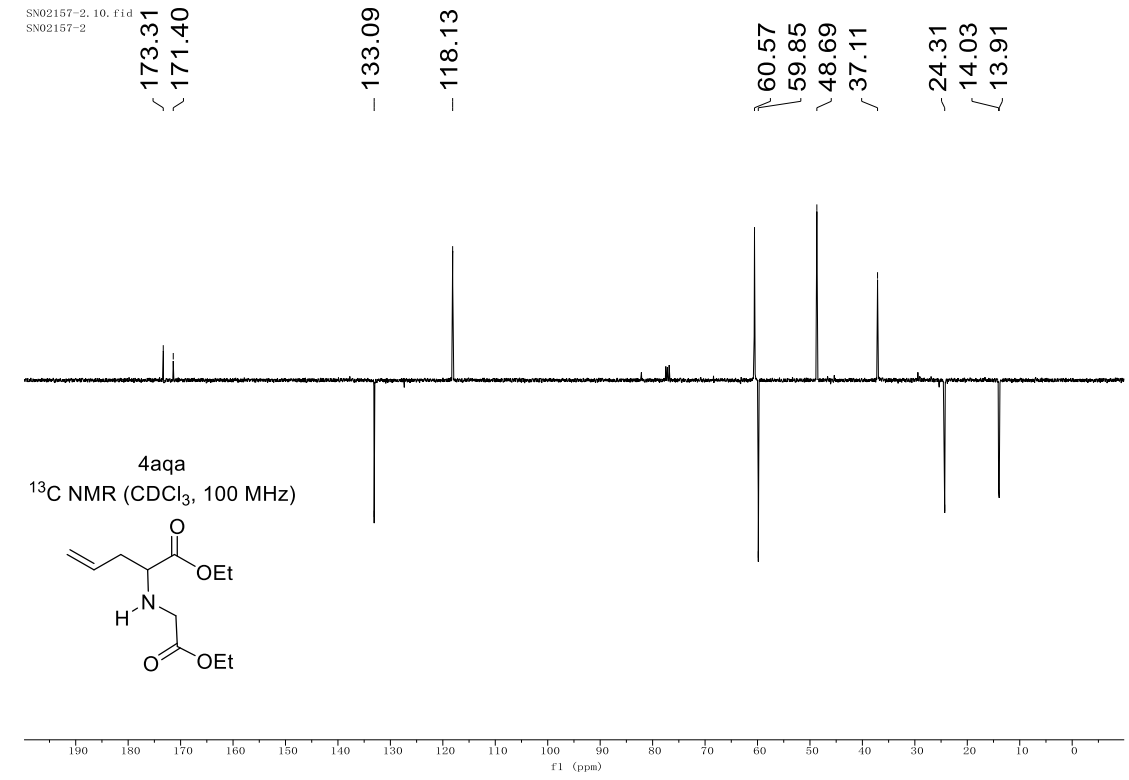

7.37
7.35
7.32
7.30
7.28
7.24
6.53
6.49
6.26
6.25
6.22
5.78
5.76
5.73
5.15
5.11
5.09
4.20
4.19
4.18
4.17
4.16
4.15
3.43
3.41
3.41
3.39
3.38
3.34
3.32
2.46
2.44
2.42
1.28
1.26
1.24
4aoa
1H NMR (400 MHz, CDCl3)
O
OEt
N
H
2.06
2.20
1.05
1.00
1.06
1.00
2.01
2.11
1.03
0.99
1.00
1.99
3.25
f1 (ppm)

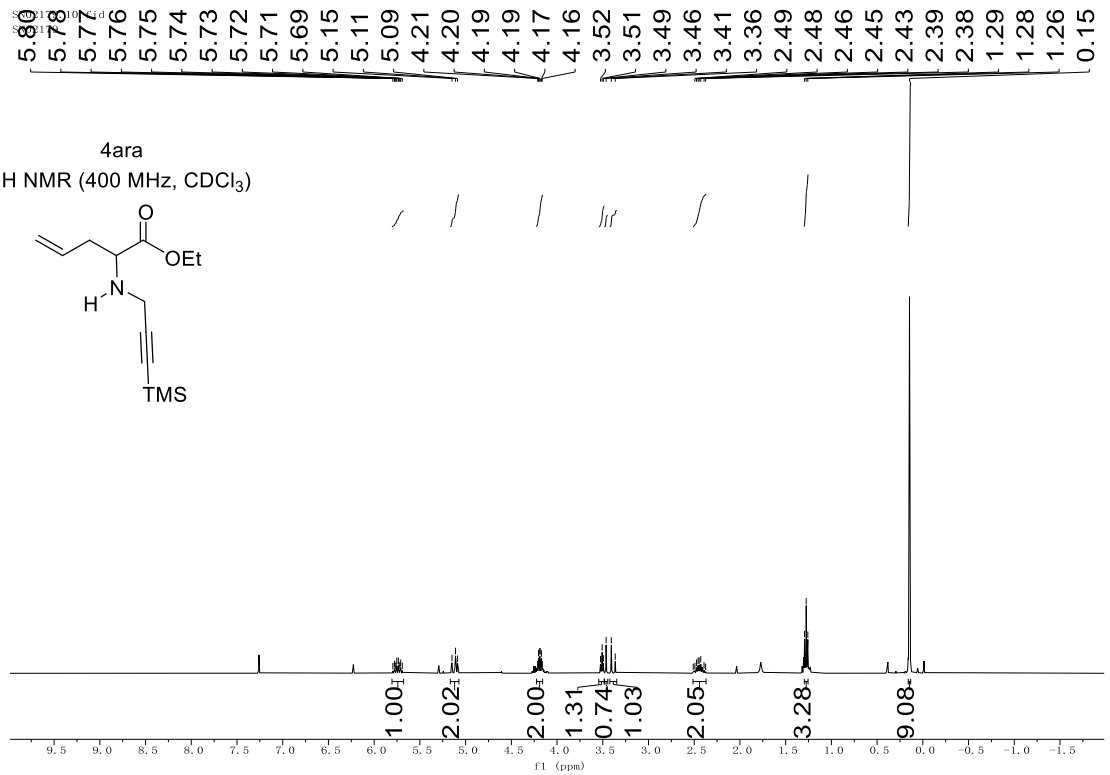

SN02193-2.10.fid
SN02193-2
174.43
136.84
133.40
131.83
128.42
127.59
127.34
126.22
118.08
60.59
60.03
50.10
37.63
14.25
4aoa
13C NMR (CDCl3, 100 MHz)
O
OEt
N
H
f1 (ppm)

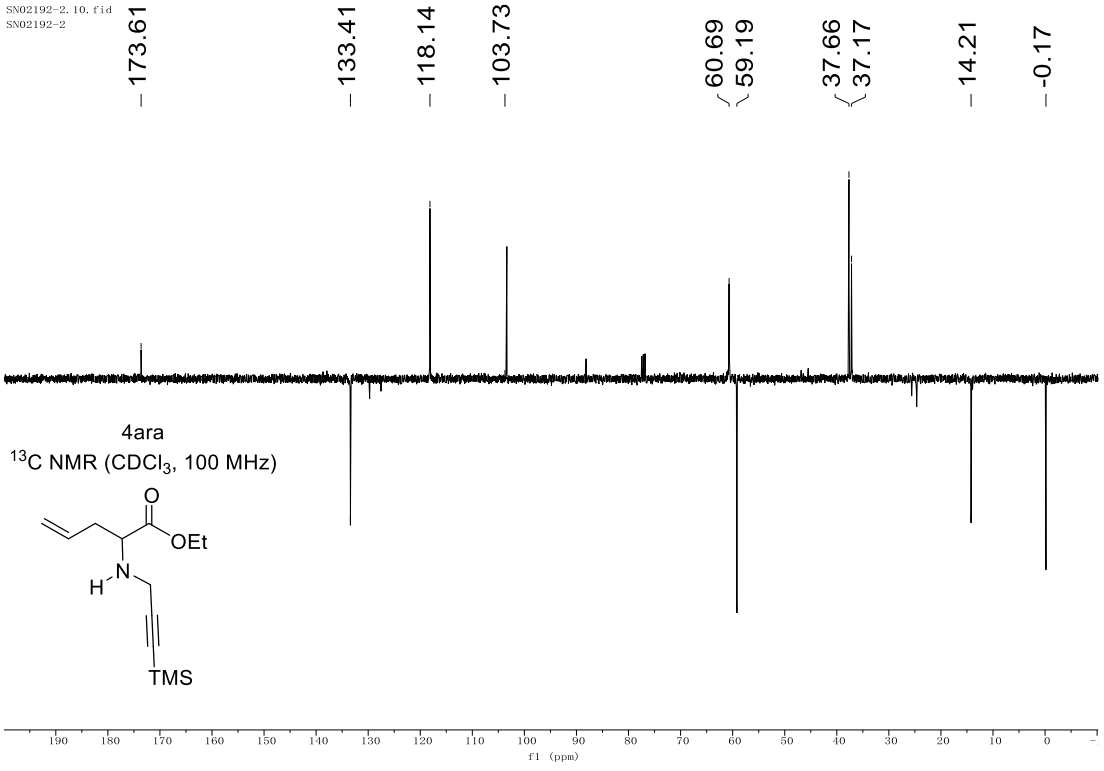

5.79
5.76
5.74
5.72
5.12
5.08
5.06
4.21
4.21
4.20
4.19
4.18
4.17
4.16
4.15
3.34
3.32
3.31
2.59
2.58
2.57
2.56
2.54
2.52
2.50
2.48
2.43
2.41
2.40
1.29
1.27
1.25
0.90
0.88
0.87
0.85
4apa
1H NMR (400 MHz, CDCl3)
O
OEt
H
N
1.00
2.00
2.07
1.00
2.00
2.00
8.52
3.25
f1 (ppm)

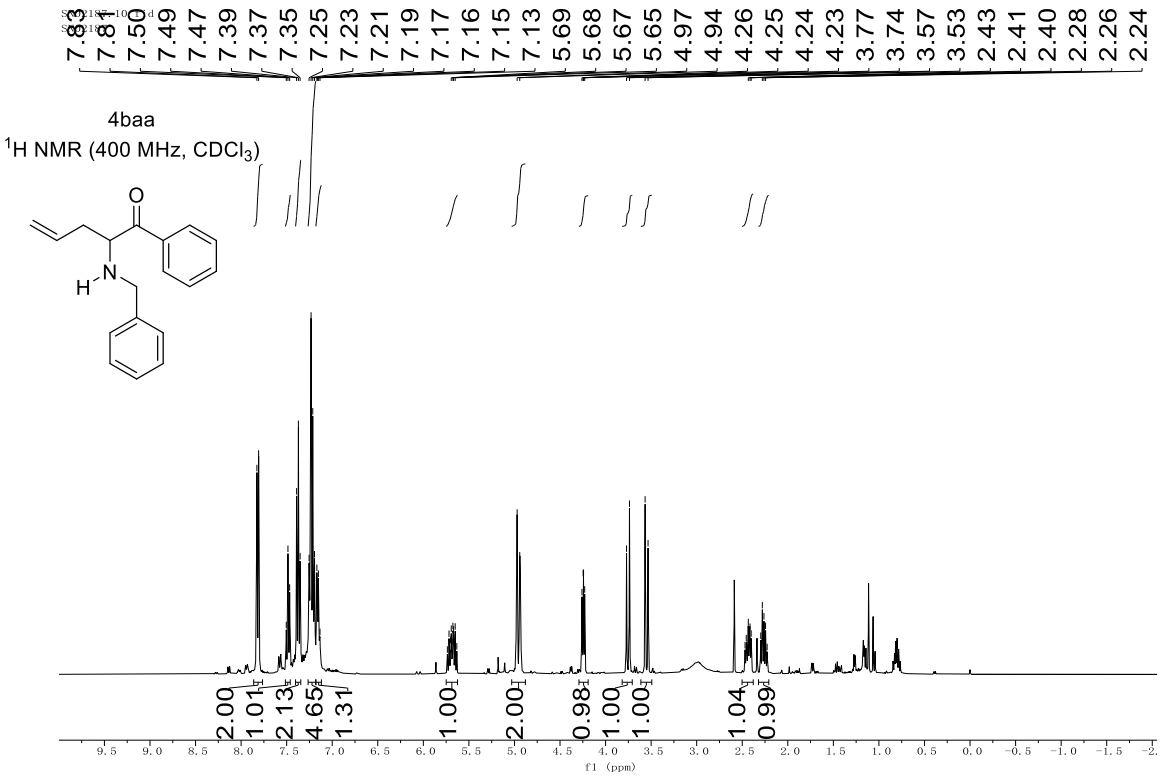

SN02158-2.10.fid
SN02158-2
174.38
133.52
117.56
60.95
60.24
47.96
37.52
31.60
29.89
28.96
27.00
22.39
14.11
13.83
4apa
13C NMR (CDCl3, 100 MHz)
O
OEt
H
N
f1 (ppm)

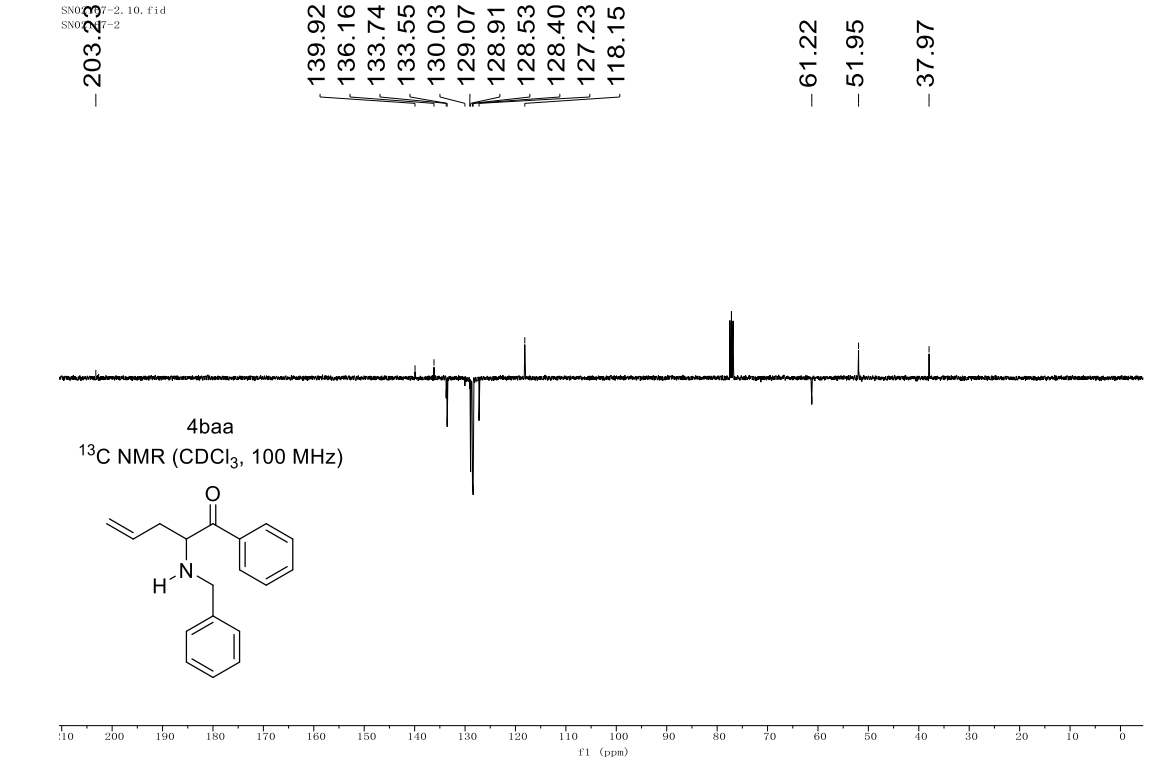

SN02157-1.fid
SN02157-1
5.83
5.81
5.80
5.79
5.79
5.77
5.76
5.75
5.74
5.73
5.16
5.12
5.10
4.20
4.18
4.16
4.15
3.42
3.39
3.38
2.52
2.50
2.48
2.45
2.44
2.42
1.27
1.26
1.25
4aqa
^{1}H NMR (400 MHz, $CDCl_3$)
1.00
2.01
4.00
1.51
2.03
6.03
f1 (ppm)

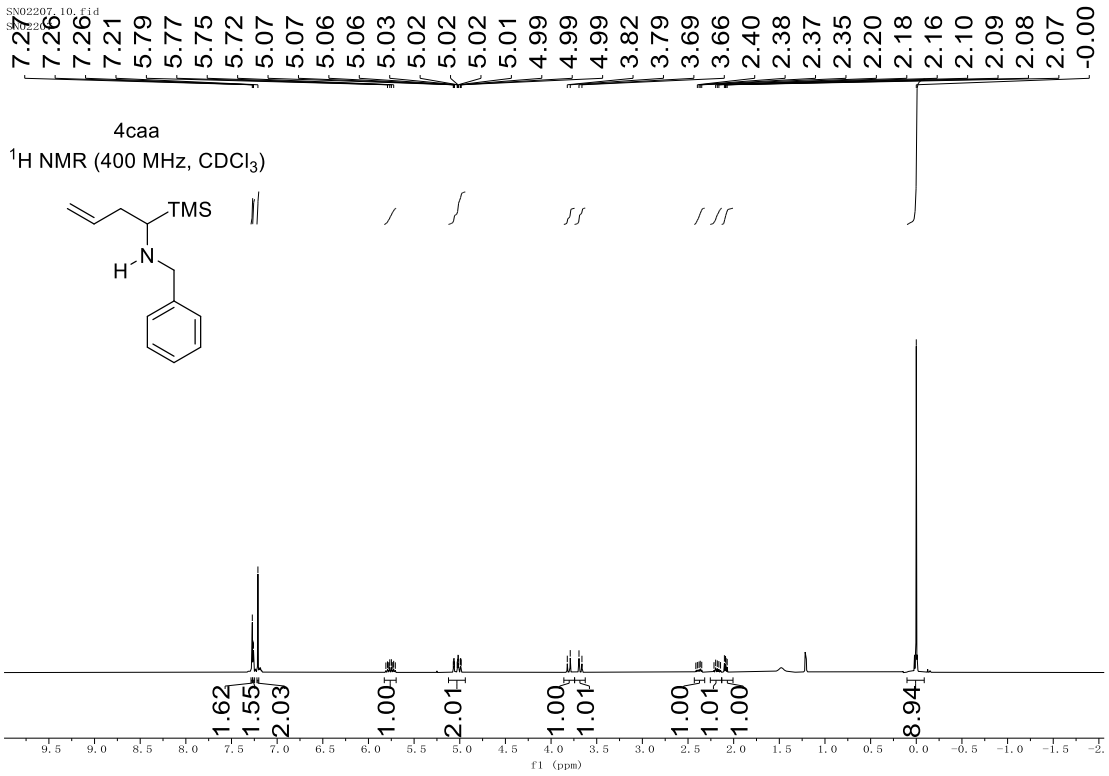

SN02157-2.10.fid
SN02157-2
173.31
171.40
133.09
118.13
60.57
59.85
48.69
37.11
24.31
14.03
13.91
4aqa
^{13}C NMR ($CDCl_3$, 100 MHz)
f1 (ppm)

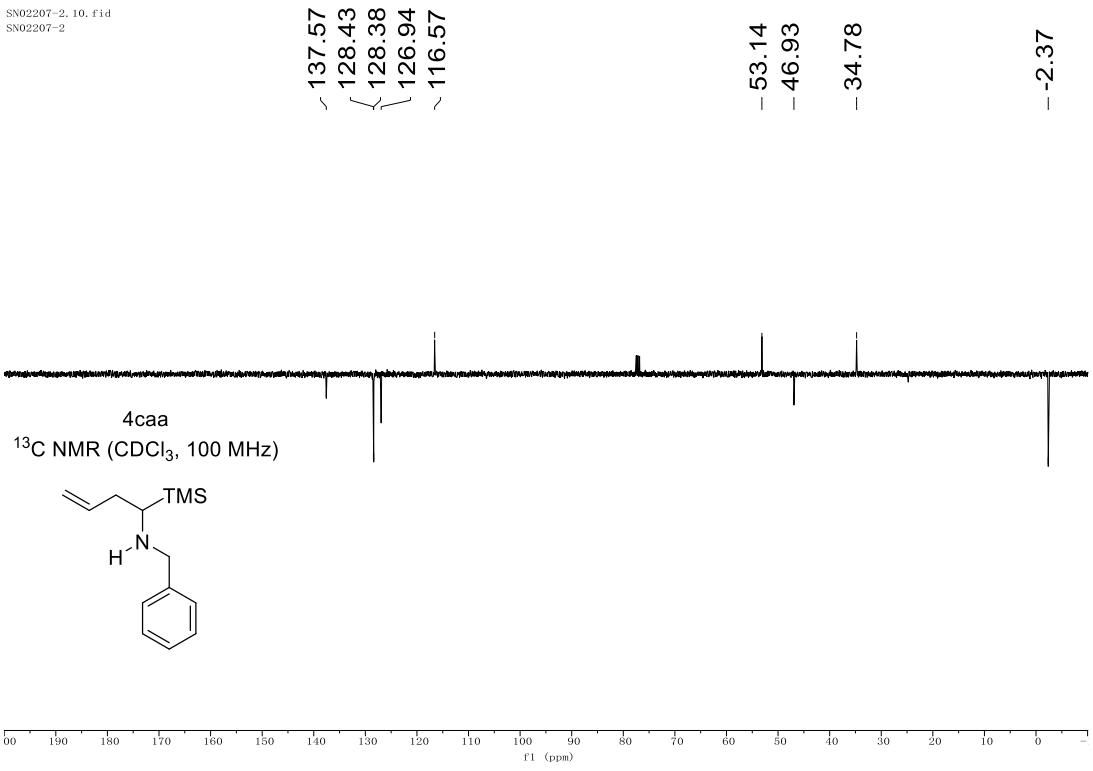

5.80
5.78
5.77
5.76
5.75
5.74
5.73
5.72
5.71
5.69
5.15
5.11
5.09
4.21
4.20
4.19
4.19
4.17
4.16
3.52
3.51
3.49
3.46
3.41
3.36
2.49
2.48
2.46
2.45
2.43
2.39
2.38
1.29
1.28
1.26
0.15
4ara
^{1}H NMR (400 MHz, $CDCl_3$)
O
OEt
H
N
TMS
1.00
2.02
2.00
1.31
0.74
1.03
2.05
3.28
9.08
f1 (ppm)

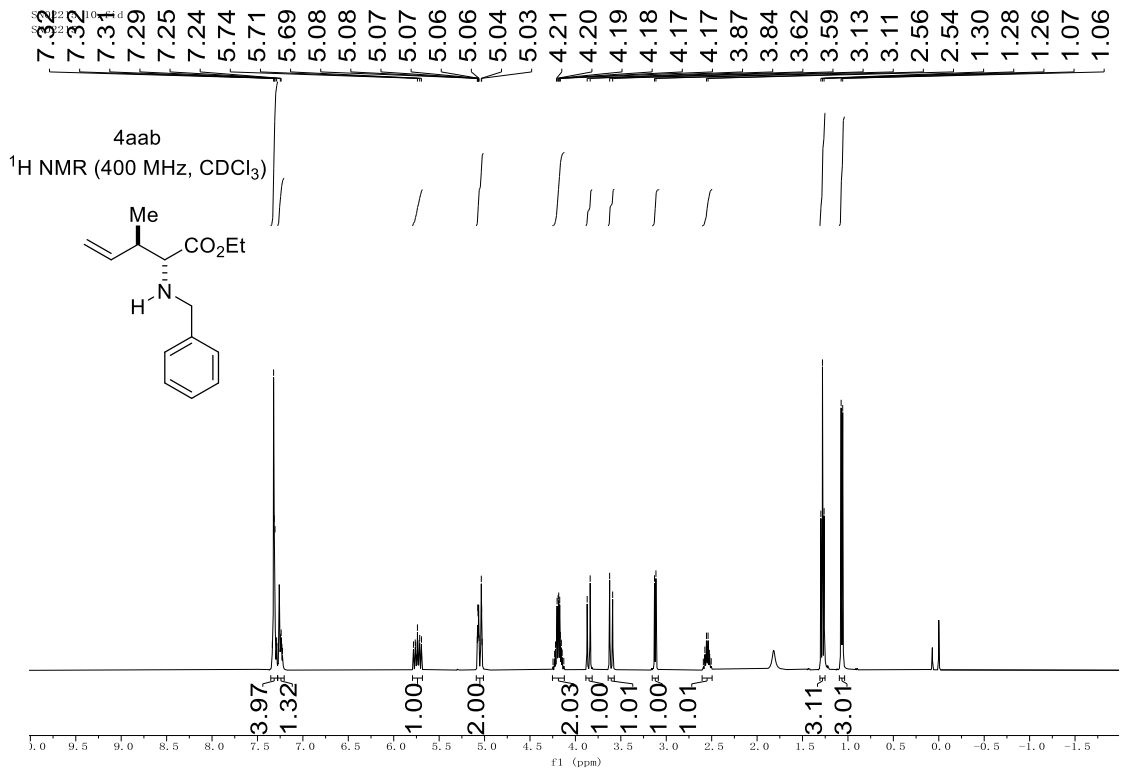

SN02192-2.10.fid
SN02192-2
173.61
133.41
118.14
103.73
60.69
59.19
37.66
37.17
14.21
-0.17
4ara
^{13}C NMR ($CDCl_3$, 100 MHz)
O
OEt
H
N
TMS
f1 (ppm)


7.83
7.81
7.50
7.49
7.47
7.39
7.37
7.35
7.25
7.23
7.21
7.19
7.17
7.16
7.15
7.13
5.69
5.68
5.67
5.65
4.97
4.94
4.26
4.25
4.24
4.23
3.77
3.74
3.57
3.53
2.43
2.41
2.40
2.28
2.26
2.24
4baa
1H NMR (400 MHz, CDCl3)
O
H
N
2.00
1.01
2.13
4.65
1.31
1.00
2.00
0.98
1.00
1.00
1.04
0.99
f1 (ppm)


203.23
139.92
136.16
133.74
133.55
130.03
129.07
128.91
128.53
128.40
127.23
118.15
61.22
51.95
37.97
4baa
13C NMR (CDCl3, 100 MHz)
O
H
N
f1 (ppm)


SN02207_10.fid
7.27
7.26
7.26
7.21
5.79
5.77
5.75
5.72
5.07
5.07
5.06
5.06
5.03
5.02
5.02
5.02
5.01
4.99
4.99
4.99
3.82
3.79
3.69
3.66
2.40
2.38
2.37
2.35
2.20
2.18
2.16
2.10
2.09
2.08
2.07
-0.00
4caa
1H NMR (400 MHz, CDCl3)
TMS
H
N
1.62
1.55
2.03
1.00
2.01
1.00
1.01
1.00
1.01
1.00
8.94
f1 (ppm)


SN02207-2_10.fid
SN02207-2
137.57
128.43
128.38
126.94
116.57
53.14
46.93
34.78
-2.37
4caa
13C NMR (CDCl3, 100 MHz)
TMS
H
N
f1 (ppm)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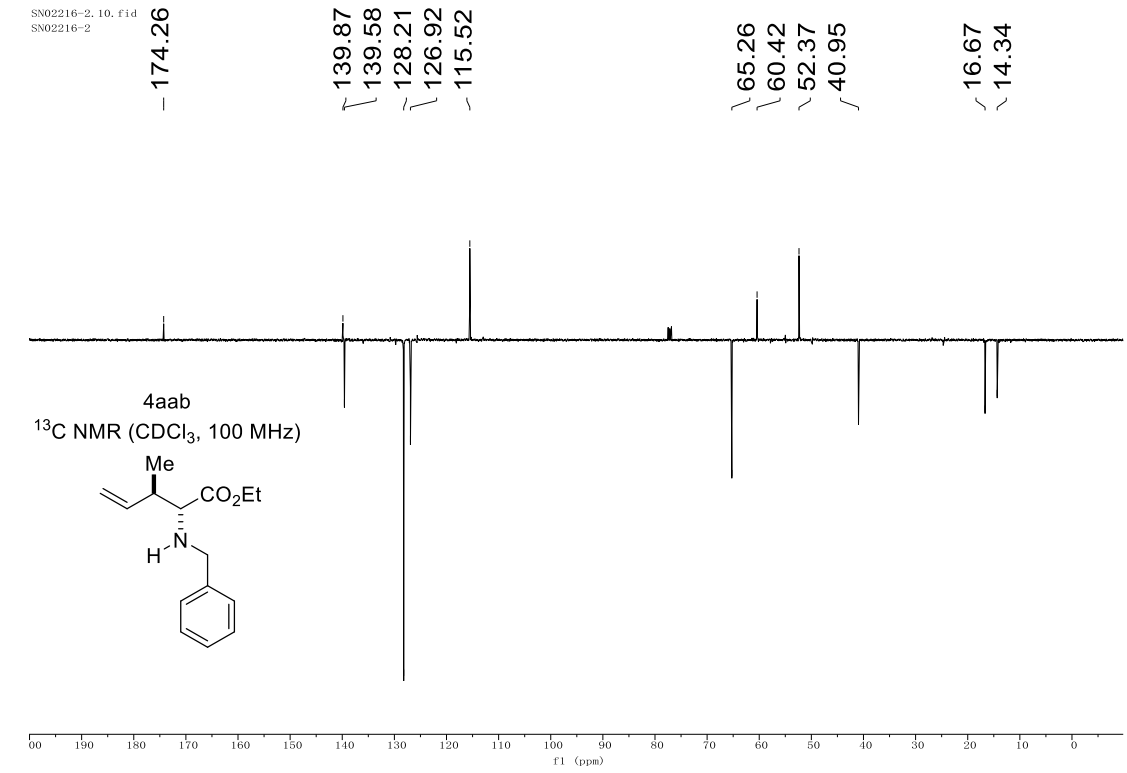
7.32
7.31
7.29
7.25
7.24
5.74
5.71
5.69
5.08
5.08
5.07
5.07
5.06
5.06
5.04
5.03
4.21
4.20
4.19
4.18
4.17
4.17
3.87
3.84
3.62
3.59
3.13
3.11
2.56
2.54
1.30
1.28
1.26
1.07
1.06
4aab
1H NMR (400 MHz, CDCl3)
Me
CO2Et
H
N
3.97
1.32
1.00
2.00
2.03
1.00
1.01
1.00
1.01
3.11
3.01
f1 (ppm)


SN02216-2.10.fid
SN02216-2
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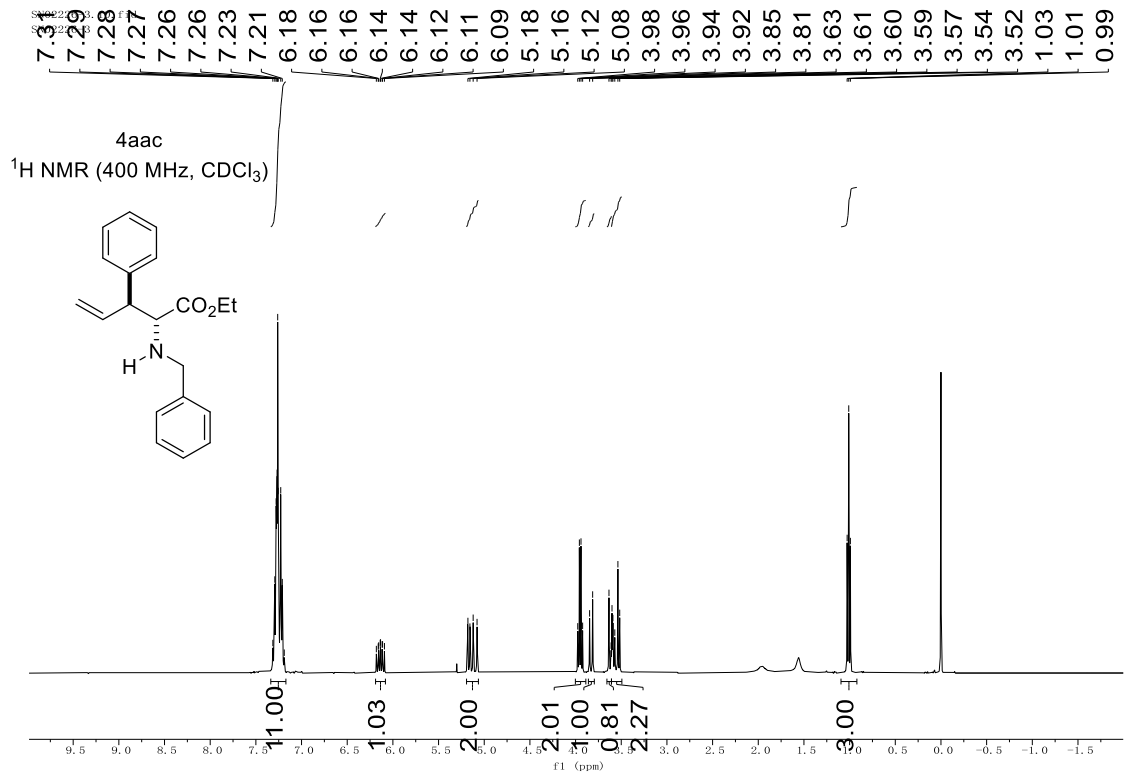
139.87
139.58
128.21
126.92
115.52
65.26
60.42
52.37
40.95
16.67
14.34
4aab
13C NMR (CDCl3, 100 MHz)
Me
CO2Et
H
N
f1 (ppm)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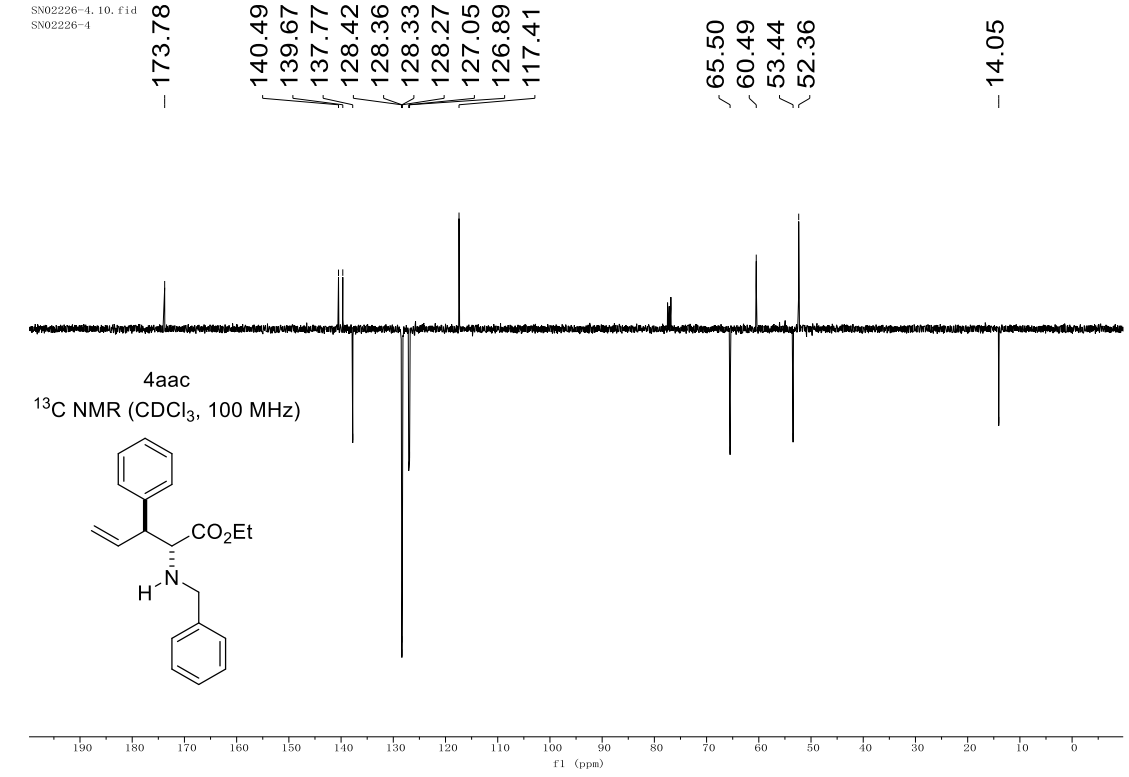
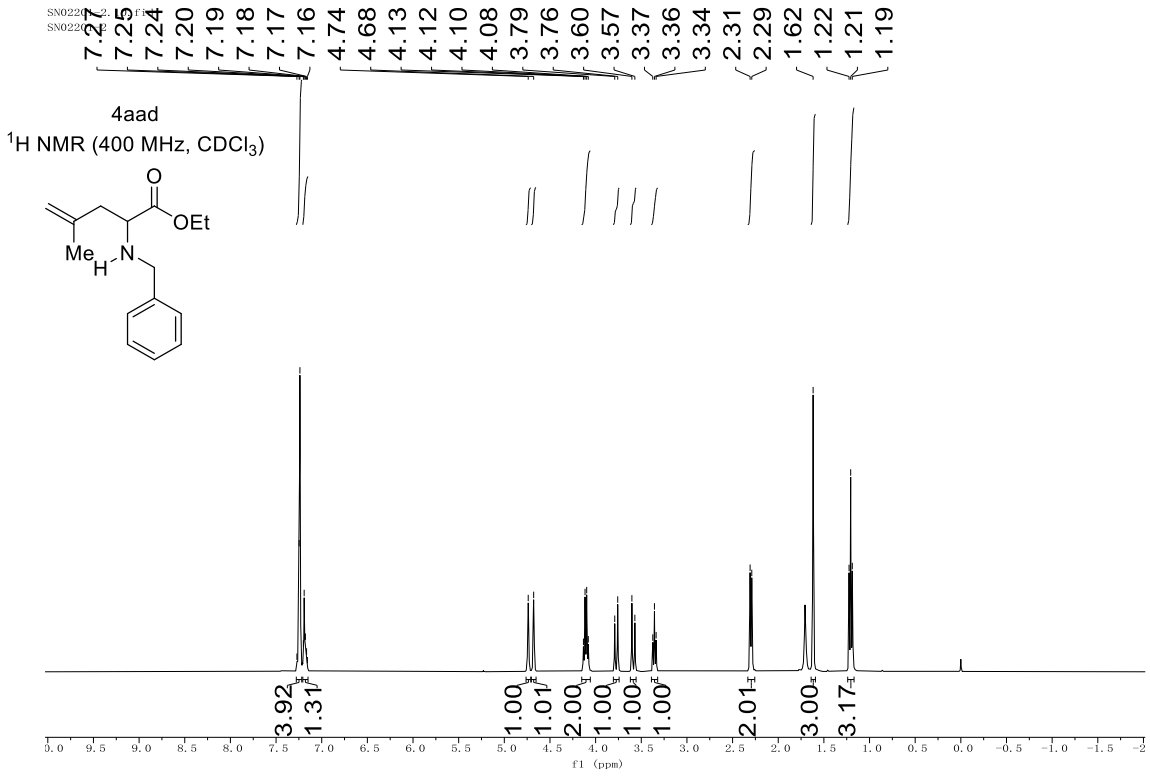
7.29
7.28
7.27
7.26
7.26
7.23
7.21
6.18
6.16
6.16
6.14
6.14
6.12
6.11
6.09
5.18
5.16
5.12
5.08
3.98
3.96
3.94
3.92
3.85
3.81
3.63
3.61
3.60
3.59
3.57
3.54
3.52
1.03
1.01
0.99
4aac
1H NMR (400 MHz, CDCl3)
CO2Et
H
N
11.00
1.03
2.00
2.01
1.00
0.81
2.27
3.00
f1 (ppm)


SN02226-4.10.fid
SN02226-4
173.78
140.49
139.67
137.77
128.42
128.36
128.33
128.27
127.05
126.89
117.41
65.50
60.49
53.44
52.36
14.05
4aac
13C NMR (CDCl3, 100 MHz)
CO2Et
H
N
f1 (ppm)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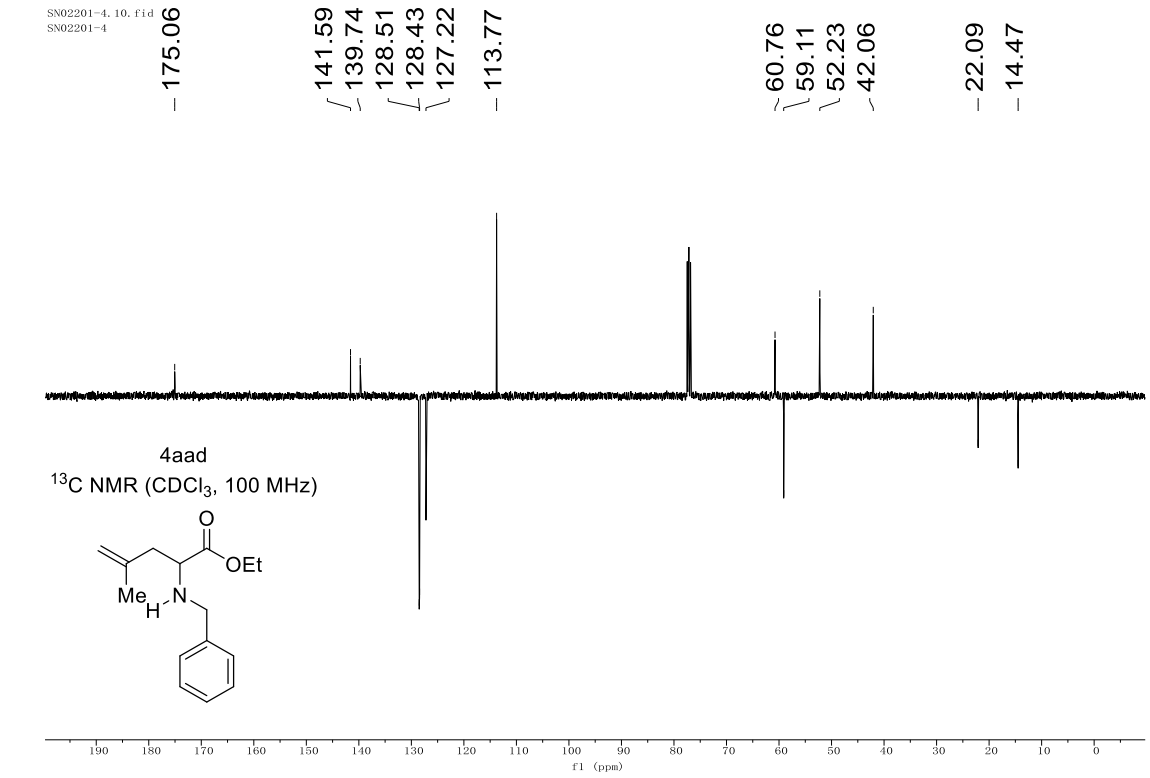
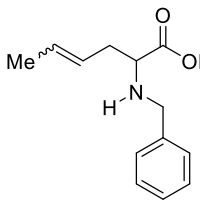
7.25
7.24
7.20
7.19
7.18
7.17
7.16
4.74
4.68
4.13
4.12
4.10
4.08
3.79
3.76
3.60
3.57
3.37
3.36
3.34
2.31
2.29
1.62
1.22
1.21
1.19
4aad
1H NMR (400 MHz, CDCl3)
O
OEt
Me
H
N
3.92
1.31
1.00
1.01
2.00
1.00
1.00
1.00
2.01
3.00
3.17
f1 (ppm)


175.06
141.59
139.74
128.51
128.43
127.22
113.77
60.76
59.11
52.23
42.06
22.09
14.47
4aad
13C NMR (CDCl3, 100 MHz)
O
OEt
Me
H
N
f1 (ppm)

SN02213.10.fid
SN02213

4aae

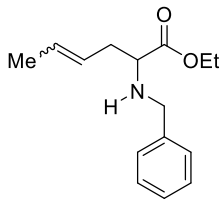
^{1}H NMR (400 MHz, $CDCl_3$)

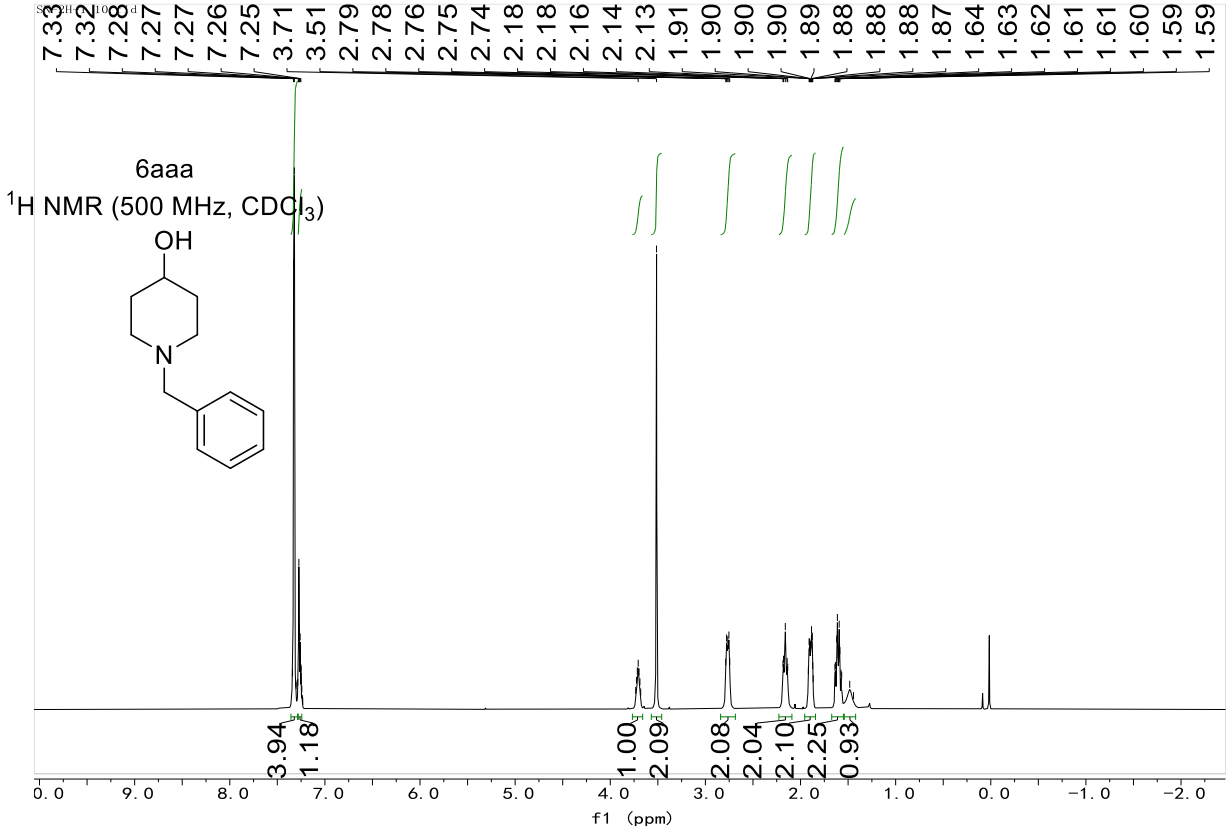


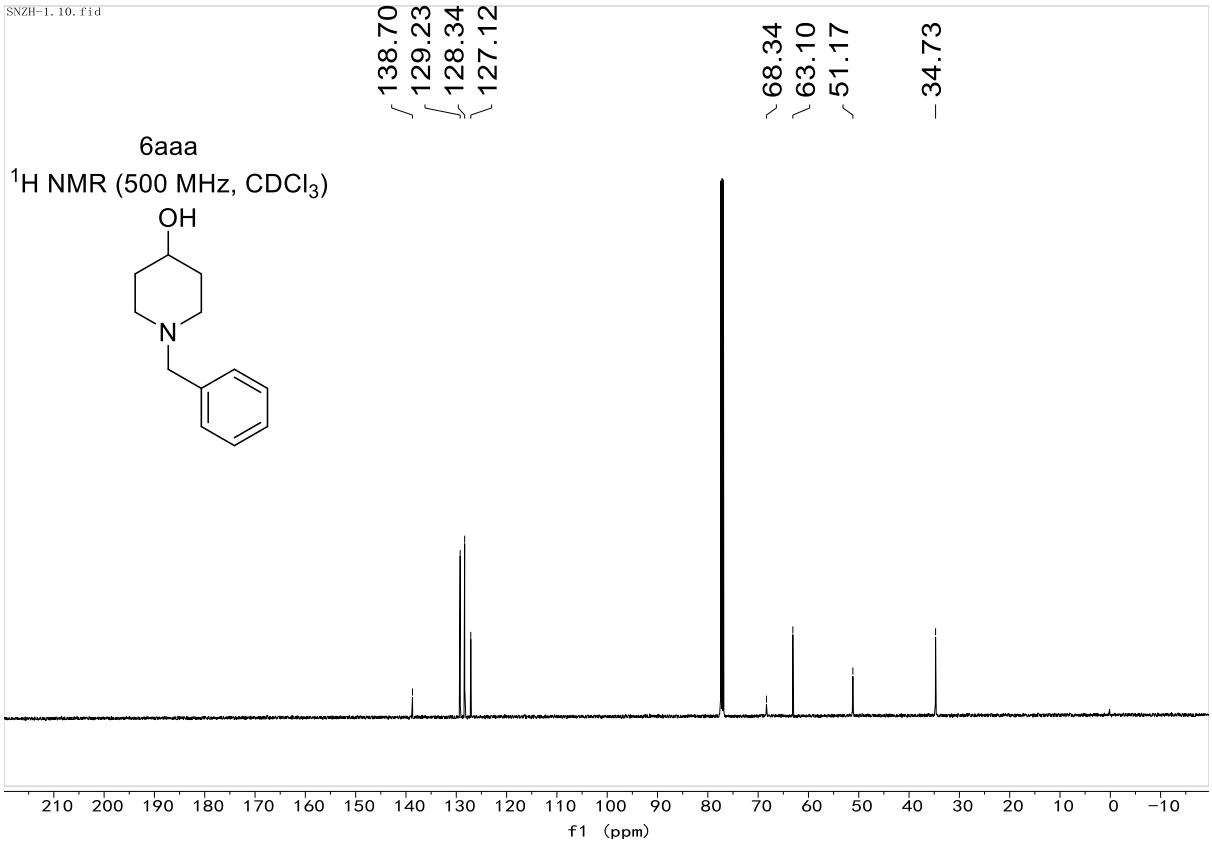
SN02213-2.10.fid
SN02213-2

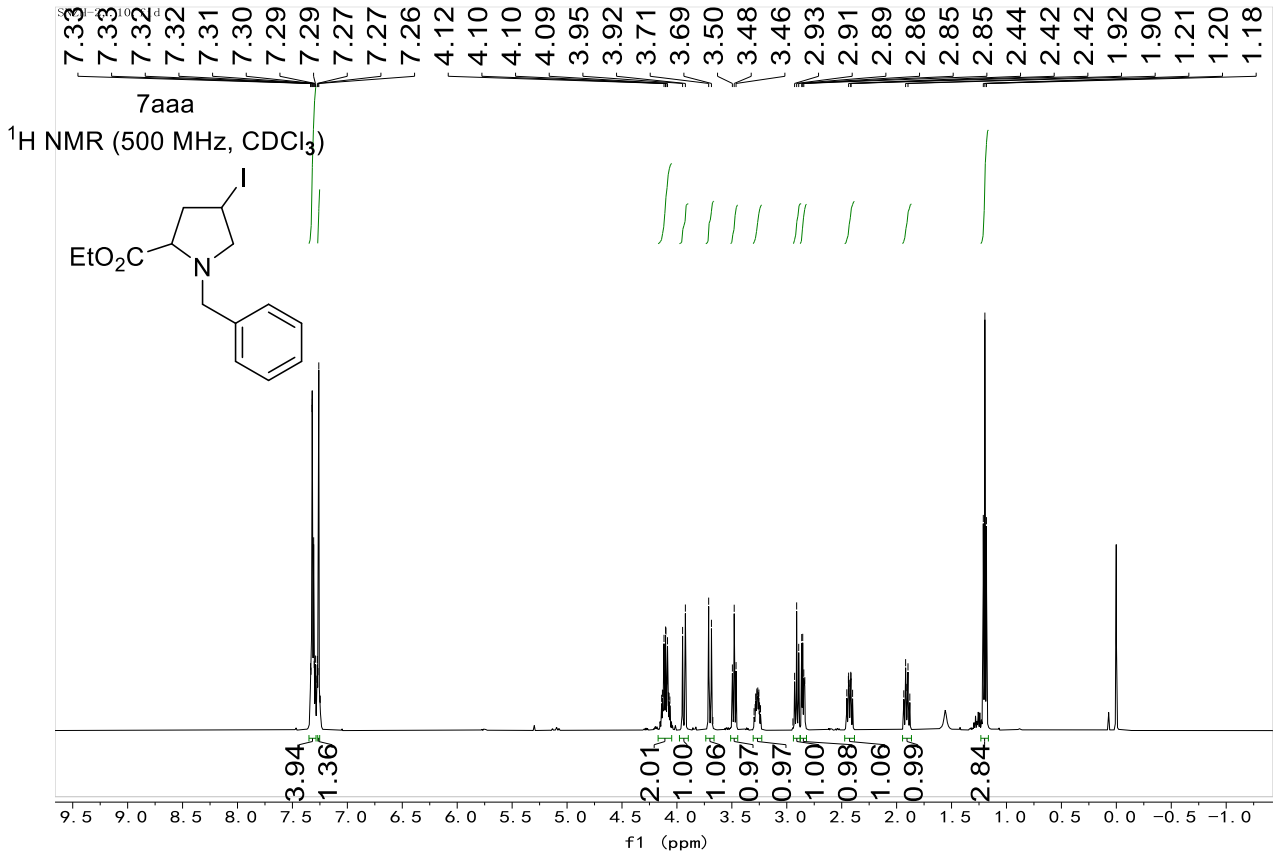
4aae

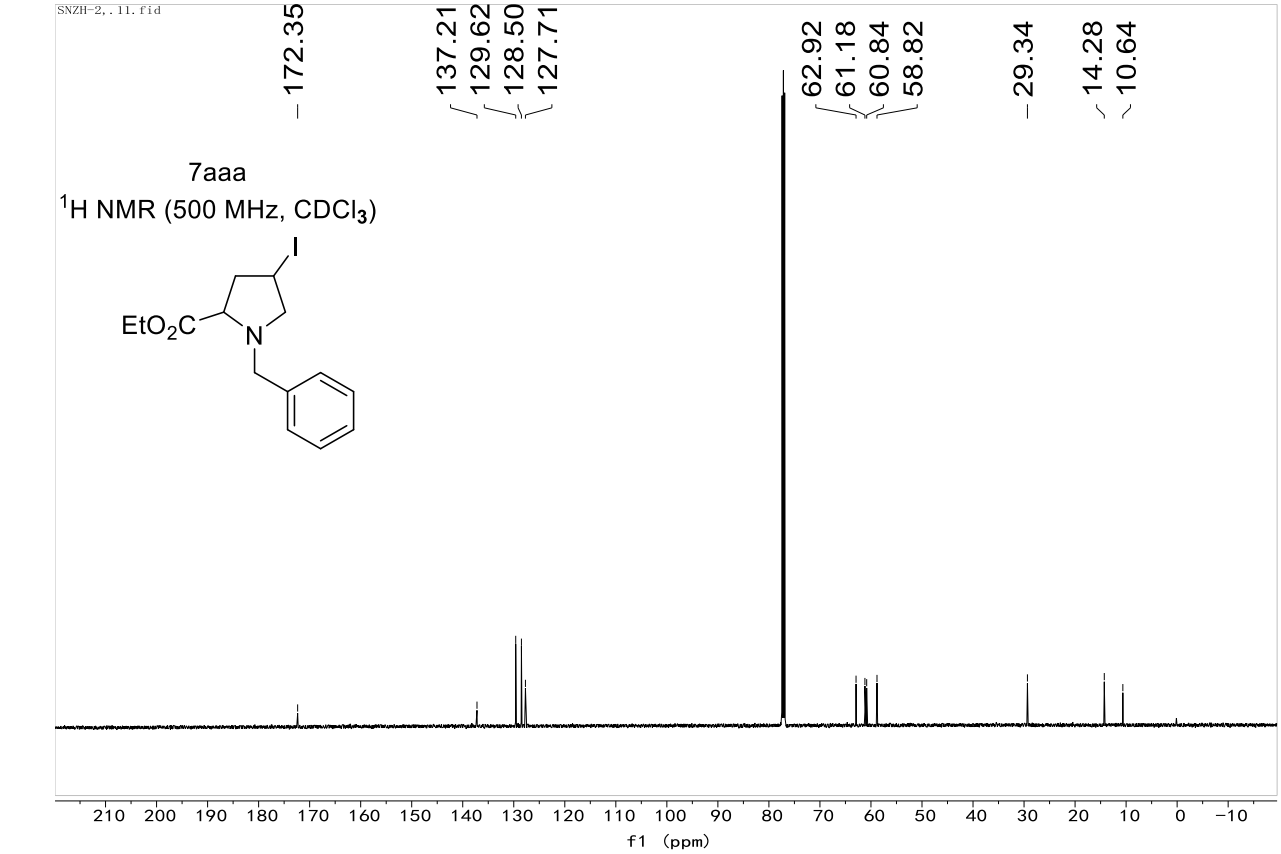
^{13}C NMR ($CDCl_3$, 100 MHz)




7.33
7.32
7.28
7.27
7.27
7.26
7.25
3.71
3.51
2.79
2.78
2.76
2.75
2.74
2.18
2.18
2.16
2.14
2.13
1.91
1.90
1.90
1.90
1.89
1.88
1.88
1.88
1.87
1.64
1.63
1.62
1.61
1.61
1.60
1.59
1.59
6aaa
1H NMR (500 MHz, CDCl3)
OH
N
3.94
1.18
1.00
2.09
2.08
2.04
2.10
2.25
0.93
f1 (ppm)


SNZH-1.10.fid
138.70
129.23
128.34
127.12
68.34
63.10
51.17
34.73
6aaa
1H NMR (500 MHz, CDCl3)
OH
N
f1 (ppm)

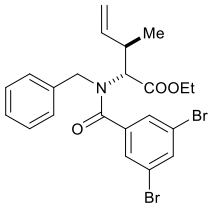

7aaa
1H NMR (500 MHz, CDCl3)
I
EtO2C
N
7.33 7.33 7.32 7.32 7.31 7.30 7.29 7.29 7.27 7.27 7.26 4.12 4.10 4.10 4.09 3.95 3.92 3.71 3.69 3.50 3.48 3.46 2.93 2.91 2.89 2.86 2.85 2.85 2.44 2.42 2.42 1.92 1.90 1.21 1.20 1.18
3.94 1.36 2.01 1.00 1.06 0.97 0.97 1.00 0.98 1.06 0.99 2.84
f1 (ppm)


SNZH-2,.11.fid
172.35
137.21 129.62 128.50 127.71
62.92 61.18 60.84 58.82
29.34
14.28 10.64
7aaa
1H NMR (500 MHz, CDCl3)
I
EtO2C
N
f1 (ppm)

S.4. X-Ray Data of Compounds 5aab

Crystallographic experimental data and structure refinement parameters are given in **Table 1**.

Table 1 Crystal Data and Structural Refinement Details for**5aab**

complex	
Empirical formula	$C_{22}H_{23}Br_2NO_3$
Formula weight	509.23
Crystal system	triclinic
Space group	$P\bar{1}$
Temperature(K)	300.0
a (Å)	8.149(3)
b (Å)	9.669(3)
c (Å)	14.769(4)
α (°)	101.961(9)
β (°)	96.161(10)
γ (°)	95.866(10)
V (Å^3)	1122.7(6)
Z	2
μ (mm^{-1})	3.631
Unique reflections	4612
Observed reflections	21353
R_{int}	0.0343
R_1, wR_2 [$I > 2\sigma(I)$]	0.0463, 0.1361

R_1, wR_2 (all data)	0.0713, 0.1575

X-ray structure of compound