Supporting Information

Rhodium-Catalyzed Asymmetric Hydrogenation of *β*-Branched Enamides for the Synthesis of *β*-Stereogenic Amines

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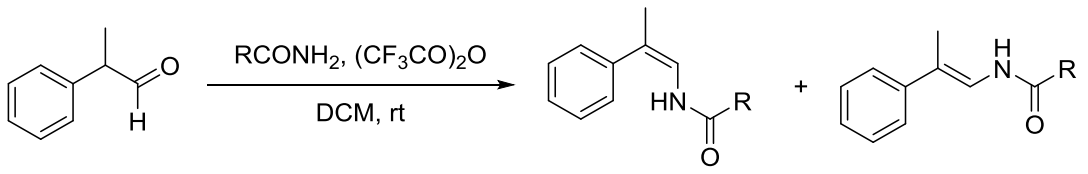
1. General Details

All hydrogenation reactions were performed in an autoclave under an atmosphere of hydrogen. All air- and moisture-sensitive reactions were performed in dried glassware under an atmosphere of nitrogen. The workup was carried out in air, unless otherwise noted. Column chromatography was performed using silica gel (100-200 mesh). Solvents were dried and distilled before use by standard procedures. Commercially available reagents were used without further purification.

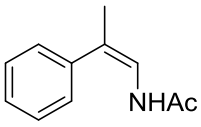
Melting points were measured with SGW X-4 micro melting point apparatus. ^{1}H NMR (400 and 500 MHz) and ^{13}C NMR (100 and 125 MHz) spectra were recorded on an AGILENT Technologies 400-MR (400/54 Premium Shielded) spectrometer and a Bruker Avance III HD 500 MHz NMR Spectrometer. HRMS was performed on a Waters Micromass Q-TOF Premier mass spectrometer at the Instrumental Analysis Center of Shanghai Jiao Tong University. Optical rotations were measured on a Rudolph Research Analytical Autopol VI automatic polarimeter using a 50 mm path-length cell at 589 nm. Enantioselectivity was measured by high performance liquid chromatography (HPLC) using Daicel Chiralcel columns with hexane/isopropanol as eluent.

2. Preparation of Substrates



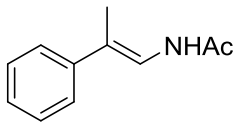
General Procedure for Substrates 1a-f: To a solution of 2-phenylpropanal (2.0 g, 0.015 mol) and amide (0.030 mol) in DCM (20 mL) was added trifluoroacetic anhydride (6.3 g, 0.030 mol). The mixture was stirred at room temperature. After the reaction was completed (monitored by TLC), H_2O (20 mL) was added and the system was neutralized with saturated K_2CO_3 aqueous solution. The mixture was extracted with DCM (20 mL × 3) and the organic phases were combined, dried over Na_2SO_4, filtered and concentrated. The residue was purified on a silica gel column with petroleum ether / ethyl acetate (abbreviate to PE/EtOAc) as eluent to afford the (*Z*)- and (*E*)-*β*-phenyl acrylic amide (>98% purity according to ^{1}H NMR).

(*Z*)-*N*-(2-phenylprop-1-en-1-yl)acetamide (1a)



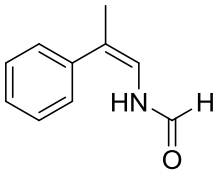
PE/EtOAc = 10/1 as the eluent. White solid (0.26 g, 10% yield). Melting point: 66-68 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.08 (d, J = 8.8 Hz, 1H), 7.44-7.22 (m, 5H), 6.70 (d, J = 9.6 Hz, 1H), 1.97 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.82, 139.30, 128.52, 127.71, 126.68, 119.14, 116.65, 22.50, 22.12. HRMS (ESI): *m/z* for $C_{11}H_{14}NO$ $[M+H]^+$ calcd 176.1070, found 176.1075.

(*E*)-*N*-(2-phenylprop-1-en-1-yl)acetamide (1a')



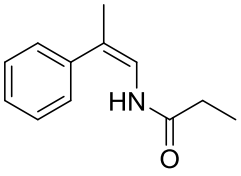
PE/EtOAc = 8/1 as the eluent. White solid (0.78 g, 30% yield). Melting point: 123-124 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.51 (d, J = 10.0 Hz, 1H), 7.41-7.23 (m, 4H), 7.23-7.14 (m, 1H), 7.08 (d, J = 10.4 Hz, 1H), 2.04 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.85, 141.35, 128.40, 126.12, 124.80, 120.41, 115.95, 22.66, 14.30. HRMS (ESI): *m/z* for $C_{11}H_{14}NO$ $[M+H]^+$ calcd 176.1070, found 176.1075.

(*Z*)-*N*-(2-phenylprop-1-en-1-yl)formamide (1b)



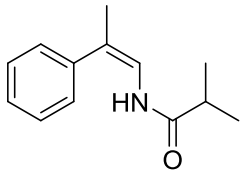
PE/EtOAc = 10/1 as the eluent. White solid (0.24 g, 10% yield). Melting point: 105-106 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.37 (d, J = 9.2 Hz, 1H), 7.93 (s, 1H), 7.45-7.37 (m, 2H), 7.34-7.25 (m, 3H), 6.76 (d, J = 10.8 Hz, 1H), 1.99 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 159.28, 138.99, 128.69, 127.69, 127.01, 118.44, 116.85, 21.96. HRMS (ESI): *m/z* for $C_{10}H_{12}NO$ $[M+H]^+$ calcd 162.0913, found 162.0920.

(*Z*)-*N*-(2-phenylprop-1-en-1-yl)propionamide (1c)



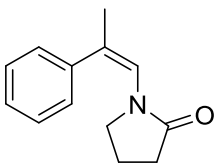
PE/EtOAc = 10/1 as the eluent. White solid (0.40 g, 14% yield). Melting point: 43-45 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.45-7.36 (m, 2H), 7.32-7.23 (m, 3H), 7.12 (d, J = 8.4 Hz, 1H), 6.86 (d, J = 10.8 Hz, 1H), 2.14 (q, J = 7.6 Hz, 2H), 2.02 (s, 3H), 1.09 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.63, 139.54, 129.11, 127.56, 127.31, 118.36, 118.24, 29.62, 21.88, 9.51. HRMS (ESI): *m/z* for $C_{12}H_{16}NO$ $[M+H]^+$ calcd 190.1226, found 190.1234.

(*Z*)-*N*-(2-phenylprop-1-en-1-yl)isobutyramide (1d)



PE/EtOAc = 10/1 as the eluent. White solid (0.40 g, 13% yield). Melting point: 68-69 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.47-7.37 (m, 2H), 7.34-7.22 (m, 3H), 7.11 (s, 1H), 6.87 (d, J = 10.8 Hz, 1H), 2.34-2.20 (m, 1H), 2.03 (s, 3H), 1.10 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.67, 139.47, 129.08, 127.47, 127.28, 118.44, 118.21, 35.51, 21.77, 19.30. HRMS (ESI): *m/z* for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1391.

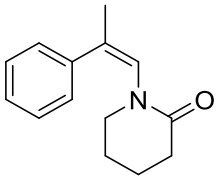
(*Z*)-1-(2-phenylprop-1-en-1-yl)pyrrolidin-2-one (1e)



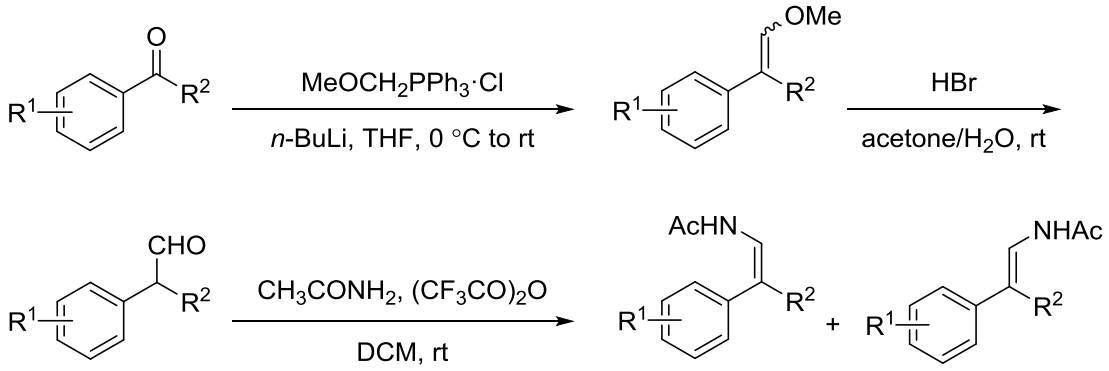
PE/EtOAc = 10/1 as the eluent. Colorless oil (0.60 g, 20% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.17 (m, 5H), 6.68 (s, 1H), 2.93 (t, J = 7.2 Hz, 2H), 2.35 (t, J = 8.0 Hz, 2H), 2.06 (s, 3H), 1.89-1.77 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.22, 140.72, 128.36, 128.10, 127.25, 124.11, 120.61, 48.26, 30.57, 24.05, 18.89. HRMS (ESI): *m/z*

for $C_{13}H_{16}NO$ $[M+H]^+$ calcd 202.1226, found 202.1233.

(*Z*)-1-(2-phenylprop-1-en-1-yl)piperidin-2-one (1f)



PE/EtOAc = 10/1 as the eluent. Colorless oil (0.52 g, 16% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.38-7.20 (m, 5H), 6.59 (s, 1H), 2.93 (t, J = 4.8 Hz, 2H), 2.43 (t, J = 6.4 Hz, 2H), 2.08 (s, 3H), 1.73-1.62 (m, 2H), 1.55-1.45 (m, 2H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.97, 140.02, 130.48, 128.42, 127.55, 126.08, 49.34, 32.32, 23.21, 22.58, 21.04. HRMS (ESI): *m/z* for $C_{14}H_{18}NO$ $[M+H]^+$ calcd 216.1383, found 216.1387.



General Procedure for Substrates 1g-y: A suspension of (methoxymethyl)triphenylphosphonium chloride (68.6 g, 0.2 mol) in THF (120 mL) was cooled to 0 ℃ and *n*-butyllithium (2.5 mol/L in hexane, 80 mL, 0.2 mol) was added dropwise to give a brownish red solution.

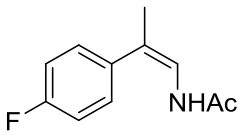
After stirring for 1.0 h, the substituted ketone (0.1 mol) was added in one portion and the mixture was warmed up to room temperature and stirred for 24 h. After the reaction was completed (monitored by TLC), H_2O (120 mL) was added and the

system was neutralized with 12 N HCl. The mixture was extracted with EtOAc (100 mL × 3). The organic phases were combined, washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was purified on a silica gel column with PE/AcOEt as eluent to afford the enol methyl ether.

The enol methyl ether was dissolved in acetone/H_2O (90 mL/10 mL) and to this solution was slowly added a 48% aqueous solution of HBr (1.2 eq). After the reaction was completed (monitored by TLC), the mixture was added slowly to a saturated K_2CO_3 aqueous solution (100 mL). The mixture was extracted with EtOAc (100 mL × 3). The organic phases were combined, washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was purified on a silica gel column with PE/AcOEt as eluent to afford the corresponding α-arylaldehyde.[1]

A solution of α-arylaldehyde and acetamide (2.0 eq) in DCM (100 mL) was cooled to 0 ℃ and trifluoroacetic anhydride (2.0 eq) was added dropwise. After stirring for 0.5 h, the mixture was warmed up to room temperature and stirred for 24 h. After the reaction was completed (monitored by TLC), H_2O was added and the system was neutralized with saturated K_2CO_3 aqueous solution. The mixture was extracted with EtOAc (100 mL × 3). The organic phases were combined, washed with water and brine, dried over Na_2SO_4 and concentrated. The residue was purified on a silica gel column with PE/AcOEt as eluent to afford (*Z*)- and (*E*)-*β*,*β*-disubstituted vinyl acetamide.[2]

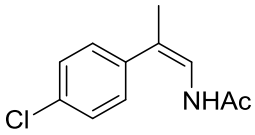
(*Z*)-*N*-(2-(4-fluorophenyl)prop-1-en-1-yl)acetamide (1g)



PE/EtOAc = 10/1 as the eluent. White solid (0.6 g, 4% yield). Melting point: 123-124 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.09 (d, J = 8.8 Hz, 1H), 7.39-7.29 (m,

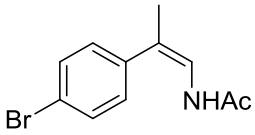
2H), 7.20 (t, J = 8.4 Hz, 2H), 6.69 (d, J = 10.0 Hz, 1H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.83, 162.15 (159.73, J = 242 Hz), 135.67 (135.64, J = 3 Hz), 129.84 (129.76, J = 8 Hz), 119.35, 115.86, 115.41 (115.20, J = 21 Hz), 22.48, 22.18. HRMS (ESI): m/z for $C_{11}H_{13}FNO$ $[M+H]^+$ calcd 194.0976, found 194.0982.

(*Z*)-*N*-(2-(4-chlorophenyl)prop-1-en-1-yl)acetamide (1h)



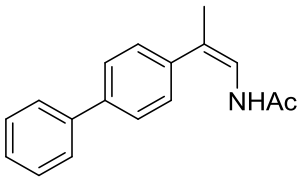
PE/EtOAc = 9/1 as the eluent. Yellow solid (0.7 g, 5% yield). Melting point: 110-113 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (d, J = 9.6 Hz, 1H), 7.42 (d, J = 8.0 Hz, 2H), 7.32 (d, J = 8.0 Hz, 2H), 6.71 (d, J = 10.0 Hz, 1H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.83, 138.21, 131.14, 129.68, 128.47, 119.76, 115.49, 22.45, 21.87. HRMS (ESI): m/z for $C_{11}H_{13}ClNO$ $[M+H]^+$ calcd 210.0680, found 210.0687.

(*Z*)-*N*-(2-(4-bromophenyl)prop-1-en-1-yl)acetamide (1i)



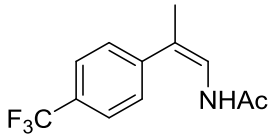
PE/EtOAc = 9/1 as the eluent. White solid (0.7 g, 6% yield). Melting point: 126-129 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.14 (d, J = 9.2 Hz, 1H), 7.55 (d, J = 7.6 Hz, 2H), 7.26 (d, J = 7.6 Hz, 2H), 6.71 (d, J = 10.0 Hz, 1H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.84, 138.59, 131.38, 130.04, 119.76, 119.70, 115.50, 22.46, 21.82. HRMS (ESI): m/z for $C_{11}H_{13}BrNO$ $[M+H]^+$ calcd 254.0175, found 254.0188.

(*Z*)-*N*-(2-([1,1'-biphenyl]-4-yl)prop-1-en-1-yl)acetamide (1j)



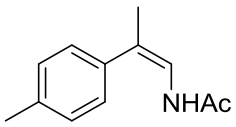
PE/EtOAc = 10/1 as the eluent. White solid (1.2 g, 9% yield). Melting point: 118-119 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.26 (d, J = 9.6 Hz, 1H), 7.69 (d, J = 7.2 Hz, 4H), 7.54-7.33 (m, 5H), 6.76 (d, J = 9.6 Hz, 1H), 2.01 (s, 3H), 1.93 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.91, 139.89, 138.50, 138.41, 129.01, 128.37, 127.39, 126.75, 126.48, 119.52, 116.16, 22.54, 22.00. HRMS (ESI): *m/z* for $C_{17}H_{18}NO$ $[M+H]^+$ calcd 252.1383, found 252.1387.

(*Z*)-*N*-(2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)acetamide (1k)



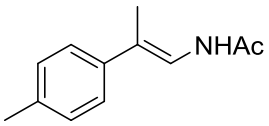
PE/EtOAc = 10/1 as the eluent. White solid (0.5 g, 4% yield). Melting point: 81-83 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.27 (d, J = 8.8 Hz, 1H), 7.72 (d, J = 6.8 Hz, 2H), 7.52 (d, J = 6.4 Hz, 2H), 6.78 (d, J = 9.6 Hz, 1H), 1.99 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.03, 143.79, 128.66, 128.47 (125.75, 123.04, 120.14, J = 270 Hz), 126.86, 125.75 (125.43, 125.39, 125.36, J = 4 Hz), 120.63, 115.27 (115.24, J = 3 Hz), 22.49, 21.73. HRMS (ESI): *m/z* for $C_{12}H_{13}F_3NO$ $[M+H]^+$ calcd 244.0944, found 244.0947.

(*Z*)-*N*-(2-(*p*-tolyl)prop-1-en-1-yl)acetamide (1l)



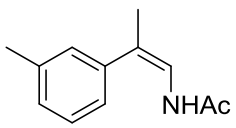
PE/EtOAc = 10/1 as the eluent. White solid (1.3 g, 9% yield). Melting point: 104-105 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.02 (d, J = 9.6 Hz, 1H), 7.27-7.16 (m, 4H), 6.67 (d, J = 10.0 Hz, 1H), 2.31 (s, 3H), 1.95 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.75, 135.33, 134.81, 128.10, 126.59, 117.82, 115.64, 21.49, 21.12, 19.77. HRMS (ESI): *m/z* for $C_{12}H_{16}NO$ $[M+H]^+$ calcd 190.1226, found 190.1232.

(*E*)-*N*-(2-(*p*-tolyl)prop-1-en-1-yl)acetamide (1l')



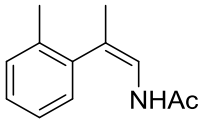
PE/EtOAc = 10/1 as the eluent. White solid (3.9 g, 27% yield). Melting point: 124-126 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.39 (d, J = 10.5 Hz, 1H), 7.18 (d, J = 8.0 Hz, 2H), 7.04 (d, J = 8.5 Hz, 2H), 6.98 (d, J = 10.5 Hz, 1H), 2.20 (s, 3H), 1.97 (s, 3H), 1.95 (d, J = 1.0 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 167.74, 138.43, 135.21, 128.97, 124.66, 119.72, 115.89, 22.64, 20.58, 14.30. HRMS (ESI): *m/z* for $C_{12}H_{16}NO$ $[M+H]^+$ calcd 190.1226, found 190.1230.

(*Z*)-*N*-(2-(*m*-tolyl)prop-1-en-1-yl)acetamide (1m)



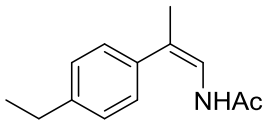
PE/EtOAc = 10/1 as the eluent. White solid (1.0 g, 7% yield). Melting point: 75-76 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.03 (d, J = 7.6 Hz, 1H), 7.33-6.98 (m, 4H), 6.69 (d, J = 8.8 Hz, 1H), 2.32 (s, 3H), 1.95 (s, 3H), 1.90 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.76, 139.24, 137.54, 128.42, 128.34, 127.37, 124.80, 118.97, 116.74, 22.51, 22.20, 21.14. HRMS (ESI): *m/z* for $C_{12}H_{16}NO$ $[M+H]^+$ calcd 190.1226, found 190.1234.

(*Z*)-*N*-(2-(*o*-tolyl)prop-1-en-1-yl)acetamide (1n)



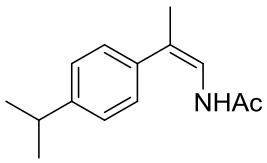
PE/EtOAc = 10/1 as the eluent. White solid (2.5 g, 18% yield). Melting point: 78-79 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.56 (d, J = 9.2 Hz, 1H), 7.28-7.11 (m, 3H), 7.06 (s, 1H), 6.74 (d, J = 10.4 Hz, 1H), 2.16 (s, 3H), 1.87 (s, 3H), 1.83 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.47, 138.87, 135.17, 130.13, 128.48, 127.00, 125.94, 119.18, 116.87, 22.77, 22.38, 19.00. HRMS (ESI): *m/z* for $C_{12}H_{16}NO$ $[M+H]^+$ calcd 190.1226, found 190.1234.

(*Z*)-*N*-(2-(4-ethylphenyl)prop-1-en-1-yl)acetamide (1o)



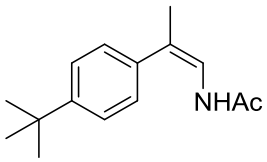
PE/EtOAc = 10/1 as the eluent. White solid (1.5 g, 11% yield). Melting point: 76-77 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.06 (d, J = 9.6 Hz, 1H), 7.28-7.18 (m, 4H), 6.66 (d, J = 9.6 Hz, 1H), 2.61 (q, J = 6.8 Hz, 2H), 1.95 (s, 3H), 1.90 (s, 3H), 1.20 (t, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.79, 142.09, 136.58, 127.91, 127.62, 118.83, 116.60, 27.90, 22.50, 22.13, 15.48. HRMS (ESI): *m/z* for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1392.

(*Z*)-*N*-(2-(4-isopropylphenyl)prop-1-en-1-yl)acetamide (1p)



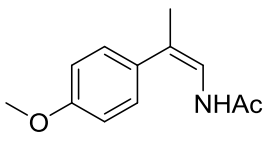
PE/EtOAc = 10/1 as the eluent. White solid (1.5 g, 11% yield). Melting point: 91-92 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.11 (d, J = 8.4 Hz, 1H), 7.25 (s, 4H), 6.67 (d, J = 8.8 Hz, 1H), 2.98-2.81 (m, 1H), 1.95 (s, 3H), 1.91 (s, 3H), 1.22 (d, J = 6.8 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.28, 146.15, 136.17, 127.08, 125.90, 118.33, 115.95, 32.67, 23.32, 21.99, 21.61. HRMS (ESI): *m/z* for $C_{14}H_{20}NO$ $[M+H]^+$ calcd 218.1539, found 218.1547.

(*Z*)-*N*-(2-(4-(tert-butyl)phenyl)prop-1-en-1-yl)acetamide (1q)



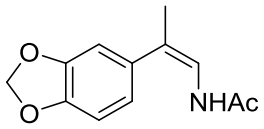
PE/EtOAc = 10/1 as the eluent. White solid (0.8 g, 6% yield). Melting point: 136-137 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.13 (d, J = 8.4 Hz, 1H), 7.40 (d, J = 7.6 Hz, 2H), 7.27 (d, J = 7.6 Hz, 2H), 6.67 (d, J = 9.2 Hz, 1H), 1.95 (s, 3H), 1.91 (s, 3H), 1.30 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.83, 148.88, 136.28, 127.33, 125.24, 118.92, 116.31, 34.22, 31.12, 22.51, 22.09. HRMS (ESI): *m/z* for $C_{15}H_{22}NO$ $[M+H]^+$ calcd 232.1696, found 232.1701.

(*Z*)-*N*-(2-(4-methoxyphenyl)prop-1-en-1-yl)acetamide (1r)



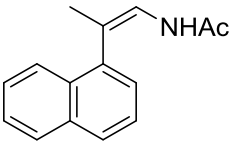
PE/EtOAc = 10/1 as the eluent. White solid (1.2 g, 9% yield). Melting point: 111-113 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (d, J = 8.4 Hz, 1H), 7.25 (d, J = 7.2 Hz, 2 H), 6.95 (d, J = 7.6 Hz, 2H), 6.64 (d, J = 10.0 Hz, 1H), 3.77 (s, 3H), 1.94 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.72, 158.00, 131.48, 128.88, 118.48, 116.52, 113.95, 55.08, 22.50, 22.21. HRMS (ESI): *m/z* for $C_{12}H_{16}NO_2$ $[M+H]^+$ calcd 206.1176, found 206.1182.

(*Z*)-*N*-(2-(benzo[d][1,3]dioxol-5-yl)prop-1-en-1-yl)acetamide (1s)



PE/EtOAc = 7/1 as the eluent. White solid (1.5 g, 11% yield). Melting point: 133-134 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.01 (d, J = 9.2 Hz, 1H), 6.91 (d, J = 8.0 Hz, 1H), 6.85 (s, 1H), 6.76 (d, J = 6.4 Hz, 1H), 6.63 (d, J = 9.2 Hz, 1H), 6.01 (s, 2H), 1.91 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.70, 147.33, 145.93, 133.17, 121.17, 118.79, 116.57, 108.43, 108.33, 100.85, 22.51, 22.38. HRMS (ESI): *m/z* for $C_{12}H_{14}NO_3$ $[M+H]^+$ calcd 220.0968, found 220.0976.

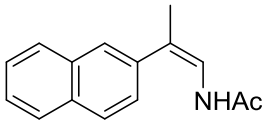
(*Z*)-*N*-(2-(naphthalen-1-yl)prop-1-en-1-yl)acetamide (1t)



PE/EtOAc = 9/1 as the eluent. White solid (2.0 g, 15% yield). Melting point: 125-126 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63 (d, J = 9.2 Hz, 1H), 8.05-7.26 (m, 7H), 6.99 (d, J = 10.0 Hz, 1H), 2.02 (s, 3H), 1.73 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 166.46, 136.38, 132.65, 129.29, 127.41, 126.30, 125.13, 125.06, 125.00, 124.77, 123.95, 119.47, 114.58, 22.46, 21.31. HRMS (ESI): *m/z* for $C_{15}H_{16}NO$

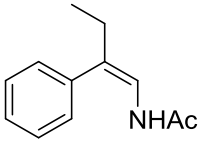
$[M+H]^+$ calcd 226.1226, found 226.1234.

(*Z*)-*N*-(2-(naphthalen-2-yl)prop-1-en-1-yl)acetamide (1u)



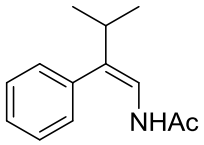
PE/EtOAc = 10/1 as the eluent. White solid (1.5 g, 11% yield). Melting point: 91-92 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.22 (d, J = 9.6 Hz, 1H), 8.00-7.74 (m, 4H), 7.60-7.36 (m, 3H), 6.79 (d, J = 10.0 Hz, 1H), 2.06 (s, 3H), 1.89 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.88, 136.94, 133.22, 132.01, 127.99, 127.87, 127.39, 126.51, 126.23, 126.05, 125.83, 119.61, 116.73, 22.53, 22.20. HRMS (ESI): *m/z* for $C_{15}H_{16}NO$ $[M+H]^+$ calcd 226.1226, found 226.1233.

(*Z*)-*N*-(2-phenylbut-1-en-1-yl)acetamide (1v)



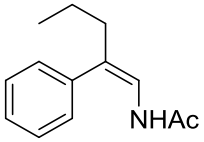
PE/EtOAc = 10/1 as the eluent. White solid (1.5 g, 12% yield). Melting point: 73-75 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.93 (d, J = 9.2 Hz, 1H), 7.47-7.10 (m, 5H), 6.70 (d, J = 10.0 Hz, 1H), 2.34 (q, J = 7.2 Hz, 2H), 1.88 (s, 3H), 0.89 (t, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.85, 138.33, 128.59, 128.24, 126.73, 123.18, 118.18, 28.78, 22.53, 13.40. HRMS (ESI): *m/z* for $C_{12}H_{16}NO$ $[M+H]^+$ calcd 190.1226, found 190.1232.

(*Z*)-*N*-(3-methyl-2-phenylbut-1-en-1-yl)acetamide (1w)



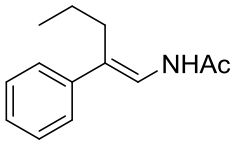
PE/EtOAc = 10/1 as the eluent. White solid (2.0 g, 16% yield). Melting point: 107-108 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.63 (d, J = 10.0 Hz, 1H), 7.45-7.26 (m, 3H), 7.15 (d, J = 7.6 Hz, 2H), 6.69 (d, J = 10.4 Hz, 1H), 2.67-2.52 (m, 1H), 1.85 (s, 3H), 0.96 (d, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.77, 138.25, 128.83, 128.50, 128.08, 126.81, 117.38, 33.31, 22.54, 21.92. HRMS (ESI): *m/z* for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1391.

(*Z*)-*N*-(2-phenylpent-1-en-1-yl)acetamide (1x)



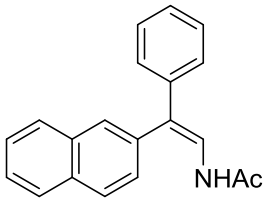
PE/EtOAc = 10/1 as the eluent. White solid (2.0 g, 16% yield). Melting point: 82-83 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 8.94 (d, J = 10.0 Hz, 1H), 7.45-7.21 (m, 5H), 6.70 (d, J = 10.0 Hz, 1H), 2.31 (t, J = 7.2 Hz, 2H), 1.88 (s, 3H), 1.27-1.14 (m, 2H), 0.80 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 167.81, 138.19, 128.58, 128.26, 126.69, 121.27, 119.01, 37.67, 22.52, 20.92, 13.25. HRMS (ESI): *m/z* for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1391.

(*E*)-*N*-(2-phenylpent-1-en-1-yl)acetamide (1x')



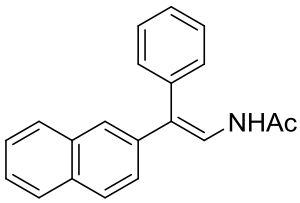
PE/EtOAc = 10/1 as the eluent. White solid (4.0 g, 32% yield). Melting point: 101-103 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.44 (d, J = 10.5 Hz, 1H), 7.33-7.21 (m, 4H), 7.14 (d, J = 7.0 Hz, 1H), 6.93 (d, J = 10.5 Hz, 1H), 2.50 (t, J = 7.5 Hz, 2H), 1.99 (s, 3H), 1.35-1.20 (m, 2H), 0.82 (t, J = 7.5 Hz, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 167.68, 140.60, 128.41, 126.10, 125.46, 121.11, 120.53, 29.08, 22.67, 20.90, 13.54. HRMS (ESI): *m/z* for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1388.

(*Z*)-*N*-(2-(naphthalen-2-yl)-2-phenylvinyl)acetamide (1y)



PE/EtOAc = 10/1 as the eluent. White solid (1.2 g, 10% yield). Melting point: 137-138 ℃. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.49 (d, J = 9.6 Hz, 1H), 8.10-7.07 (m, 13H), 1.95 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 168.53, 141.19, 135.06, 133.43, 132.37, 129.04, 128.45, 128.28, 128.12, 127.52, 126.63, 126.53, 126.11, 122.47, 121.48, 22.62. HRMS (ESI): *m/z* for $C_{20}H_{18}NO$ $[M+H]^+$ calcd 288.1383, found 288.1386.

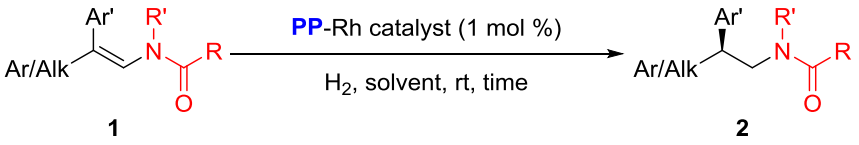
(*E*)-*N*-(2-(naphthalen-2-yl)-2-phenylvinyl)acetamide (1y')



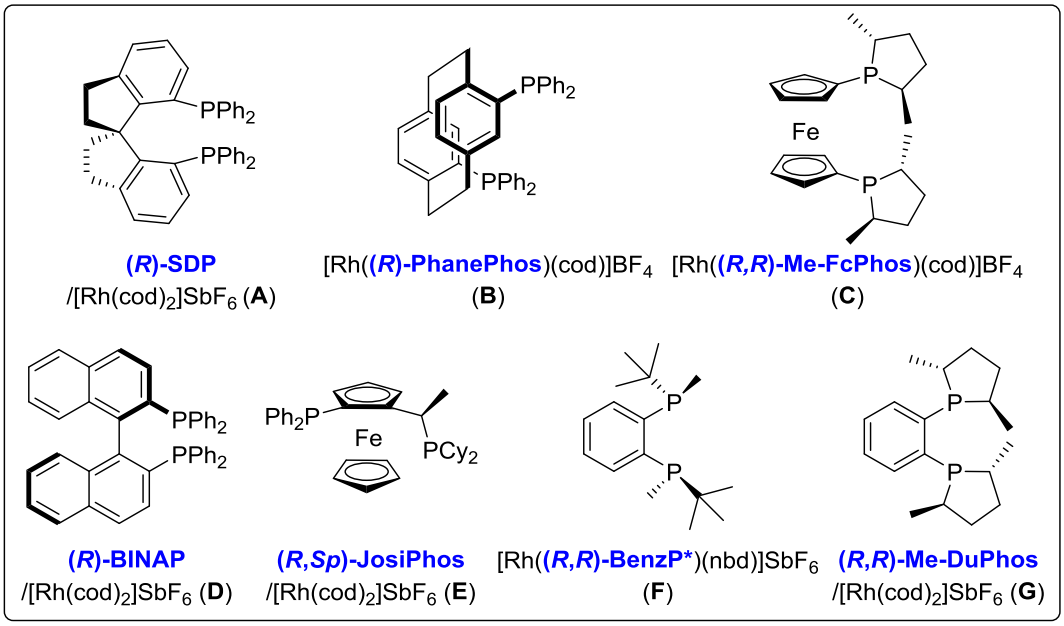
PE/EtOAc = 10/1 as the eluent. Yellow solid (2.4 g, 20% yield). Melting point: 166-168 ℃. ^{1}H NMR (500 MHz, DMSO-d_6): δ 9.32 (d, J = 10.5 Hz, 1H), 7.79-7.73

(m, 1H), 7.73-7.66 (m, 2H), 7.48 (s, 1H), 7.43-7.27 (m, 6H), 7.21 (d, J = 8.5 Hz, 1H), 7.17 (d, J = 8.0 Hz, 2H), 1.90 (s, 3H). ^{13}C NMR (125 MHz, DMSO-d_6): δ 188.53, 138.84, 137.47, 133.08, 131.82, 130.04, 128.92, 127.76, 127.73, 127.45, 127.36, 126.27, 125.61, 125.22, 124.93, 122.56, 121.74, 22.66. HRMS (ESI): *m/z* for $C_{20}H_{18}NO$ $[M+H]^+$ calcd 288.1383, found 288.1386.

3. Asymmetric Hydrogenation



1 2



(*R*)-SDP /[Rh(cod)$_2$]SbF$_6$ (**A**)

[Rh(**(*R*)-PhanePhos**)(cod)]BF$_4$ (**B**)

[Rh(**(*R,R*)-Me-FcPhos**)(cod)]BF$_4$ (**C**)

(*R*)-BINAP /[Rh(cod)$_2$]SbF$_6$ (**D**)

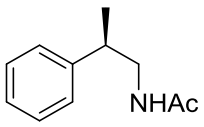
(*R,Sp*)-JosiPhos /[Rh(cod)$_2$]SbF$_6$ (**E**)

[Rh(**(*R,R*)-BenzP***)(nbd)]SbF$_6$ (**F**)

(*R,R*)-Me-DuPhos /[Rh(cod)$_2$]SbF$_6$ (**G**)

General Procedure: (*R*)-SDP ligand (1.18 mg, 0.002 mmol) and [Rh(cod)$_2$]SbF$_6$ (1.11 mg, 0.002 mmol) were dissolved in anhydrous and degassed THF (2 mL) under nitrogen. The mixture was allowed to stir for 30 min at room temperature. The substrate (0.2 mmol) was placed in a 5.0 mL tube equipped with a magnetic stirrer bar. This tube was put into an autoclave. After purging with hydrogen three times, the pre-prepared solvent of catalyst was added under hydrogen atmosphere. The hydrogen pressure was finally pressurized to 20 bar. The reaction mixture was vigorously stirred at room temperature for 8 h. The conversion of the product was determined by ^{1}H NMR spectroscopic analysis of the crude reaction mixture and the yield was calculated after isolation by flash chromatography. The *ee* value was determined by chiral HPLC. By comparison of the HPLC chromatogram to (*S*)-**4a** which is synthesized from commercially available (*S*)-**3a**, the absolute configuration of **4a** in this article was confirmed to be (*R*). Therefore, the absolute configurations of **2a-y** were assigned to be (*R*).

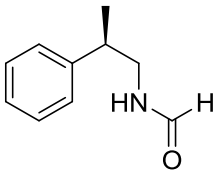
(*R*)-*N*-(2-phenylpropyl)acetamide (2a)



PE/AcOEt = 1/1 as the eluent. Colorless oil (34.0 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 2H), 7.29-7.17 (m, 3H), 5.42 (s, 1H), 3.69-3.57 (m, 1H), 3.27-3.16 (m, 1H), 3.00-2.87 (m, 1H), 1.89 (s, 3H), 1.27 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.13, 114.19, 128.83, 127.29, 126.83, 46.24, 39.62, 23.39, 19.57. HRMS (ESI): *m/z* for $C_{11}H_{16}NO$ $[M+H]^+$ calcd 178.1226, found 178.1233.

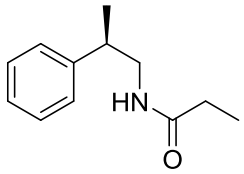
$[\alpha]_D^{20}$ +10.2 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using a Daicel Chiralcel OD-H column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 78.6 min, t_R (major) = 58.2 min.

(*R*)-*N*-(2-phenylpropyl)formamide (2b)



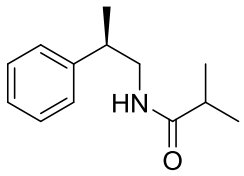
PE/AcOEt = 3/1 as the eluent. Colorless oil (31.0 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): mixture of rotamers is observed, major rotamer is given;[3] δ 8.02 (s, 1H), 7.37-7.14 (m, 5H), 5.73 (s, 1H), 3.74-3.55 (m, 1H), 3.40-3.19 (m, 1H), 3.03-2.89 (m, 1H), 1.28 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): mixture of rotamers is observed, major rotamer is given; δ 161.24, 143.80, 128.81, 127.25, 126.87, 44.65, 39.72, 19.48. HRMS (ESI): *m/z* for $C_{10}H_{14}NO$ $[M+H]^+$ calcd 164.1070, found 164.1075.

(*R*)-*N*-(2-phenylpropyl)propionamide (2c)



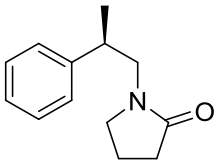
PE/AcOEt = 3/1 as the eluent. Colorless oil (36.3 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.28 (m, 2H), 7.27-7.16 (m, 3H), 5.49 (s, 1H), 3.66-3.55 (m, 1H), 3.29-3.17 (m, 1H), 3.01-2.88 (m, 1H), 2.10 (q, J = 7.6 Hz, 2H), 1.27 (d, J = 7.2 Hz, 3H), 1.09 (t, J = 7.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 173.82, 144.21, 128.73, 127.25, 126.74, 46.07, 39.80, 29.78, 19.39, 9.98. HRMS (ESI): *m/z* for $C_{12}H_{18}NO$ $[M+H]^+$ calcd 192.1383, found 192.1391.

(*R*)-*N*-(2-phenylpropyl)isobutyramide (2d)



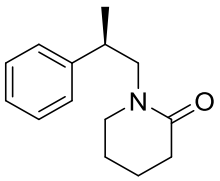
PE/AcOEt = 3/1 as the eluent. Colorless oil (39.0 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.29 (m, 2H), 7.28-7.17 (m, 3H), 5.32 (s, 1H), 3.68-3.55 (m, 1H), 3.27-3.15 (m, 1H), 3.00-2.89 (m, 1H), 2.29-2.15 (m, 1H), 1.27 (d, J = 8.0 Hz, 3H), 1.06 (t, J = 6.4 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 176.94, 144.27, 128.79, 127.35, 126.82, 46.01, 39.91, 35.79, 19.76, 19.65, 19.36. HRMS (ESI): *m/z* for $C_{13}H_{20}NO$ $[M+H]^+$ calcd 206.1539, found 206.1544.

(*R*)-1-(2-phenylpropyl)pyrrolidin-2-one (2e)



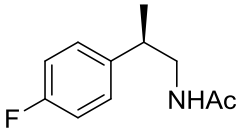
PE/AcOEt = 1/1 as the eluent. Colorless oil (39.0 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.26-7.18 (m, 2H), 7.18-7.10 (m, 3H), 3.68-3.47 (m, 1H), 3.23-3.13 (m, 1H), 3.13-2.88 (m, 3H), 2.32-2.11 (m, 2H), 1.84-1.70 (m, 2H), 1.18 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 175.13, 144.27, 128.55, 127.20, 126.64, 49.76, 47.90, 38.35, 31.01, 19.42, 18.17. HRMS (ESI): *m/z* for $C_{13}H_{18}NO$ $[M+H]^+$ calcd 204.1383, found 204.1384.

(*R*)-1-(2-phenylpropyl)piperidin-2-one (2f)



PE/AcOEt = 1/1 as the eluent. Colorless oil (41.3 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33-7.26 (m, 2H), 7.26-7.17 (m, 3H), 3.93-3.81 (m, 1H), 3.29-3.13 (m, 1H), 3.13-3.00 (m, 2H), 2.83-2.69 (m, 1H), 2.45-2.25 (m, 2H), 1.70-1.48 (m, 4H), 1.26 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.01, 144.66, 128.48, 127.49, 126.60, 55.02, 49.14, 37.86, 32.47, 23.28, 21.31, 18.95. HRMS (ESI): *m/z* for $C_{14}H_{20}NO$ $[M+H]^+$ calcd 218.1539, found 218.1544.

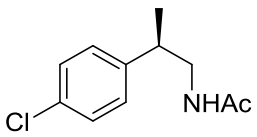
(*R*)-*N*-(2-(4-fluorophenyl)propyl)acetamide (2j)



PE/AcOEt = 1/1 as the eluent. Colorless oil (37.5 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.19-7.10 (m, 2H), 6.99 (t, J = 8.4 Hz, 2H), 5.52 (s, 1H), 3.61-3.48 (m, 1H), 3.26-3.12 (m, 1H), 3.00-2.85 (m, 1H), 1.88 (s, 3H), 1.23 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.19, 162.92 (160.48, J = 243 Hz), 139.87 (139.84, J = 3 Hz), 128.68 (128.61, J = 8 Hz), 115.64 (115.43, J = 21 Hz), 46.34, 39.12, 23.31, 19.61. HRMS (ESI): *m/z* for $C_{11}H_{15}FNO$ $[M+H]^+$ calcd 196.1132, found 196.1143.

$[\alpha]_D^{20}$ +9.4 (*c* 0.70, CH_2Cl_2). 90% ee. Determined by HPLC analysis using two Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 97.0/3.0, 0.7 mL/min, 210 nm, t_R (minor) = 77.9 min, t_R (major) = 85.3 min.

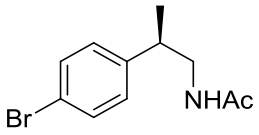
(*R*)-*N*-(2-(4-chlorophenyl)propyl)acetamide (2h)



PE/AcOEt = 1/1 as the eluent. Colorless oil (40.6 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.29 (d, J = 7.6 Hz, 2H), 7.13 (d, J = 7.6 Hz, 2H), 5.36 (s, 1H), 3.64-3.53 (m, 1H), 3.24-3.13 (m, 1H), 3.00-2.85 (m, 1H), 1.89 (s, 3H), 1.24 (d, J = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.14, 142.68, 132.49, 128.94, 128.67, 46.16, 39.32, 23.43, 19.51. HRMS (ESI): *m/z* for $C_{11}H_{15}ClNO$ $[M+H]^+$ calcd 212.0837, found 212.0843.

$[\alpha]_D^{20}$ +20.5 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using two Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 115.4 min, t_R (major) = 121.9 min.

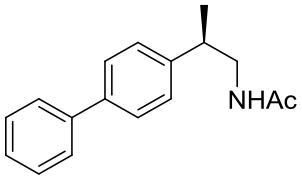
(*R*)-*N*-(2-(4-bromophenyl)propyl)acetamide (2i)



PE/AcOEt = 1/1 as the eluent. Colorless oil (48.7 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.43 (d, J = 7.6 Hz, 2H), 7.07 (d, J = 7.6 Hz, 2H), 5.44 (s, 1H), 3.63-3.50 (m, 1H), 3.24-3.12 (m, 1H), 2.98-2.83 (m, 1H), 1.89 (s, 3H), 1.23 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.21, 143.23, 131.84, 129.04, 120.50, 46.11, 39.35, 23.32, 19.40. HRMS (ESI): *m/z* for $C_{11}H_{15}BrNO$ $[M+H]^+$ calcd 256.0332, found 256.0341.

$[\alpha]_D^{20}$ +25.6 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using two Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 122.6 min, t_R (major) = 127.4 min.

(*R*)-*N*-(2-([1,1'-biphenyl]-4-yl)propyl)acetamide (2j)

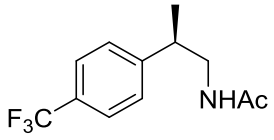


PE/AcOEt = 1/1 as the eluent. White solid (48.6 mg, 96% yield). Melting point: 113-114 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (t, J = 8.8 Hz, 4H), 7.42 (t, J = 7.6 Hz, 2H), 7.37-7.29 (m, 1H), 7.26 (d, J = 7.6 Hz, 2H), 5.61 (s, 1H), 3.68-3.57 (m, 1H), 3.30-3.19 (m, 1H), 3.04-2.92 (m, 1H), 1.89 (s, 3H), 1.29 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.21, 143.27, 140.79, 139.65, 128.84, 127.67, 127.44, 127.29, 127.01, 46.22, 39.43, 23.30, 19.53. HRMS (ESI): *m/z* for $C_{17}H_{20}NO$ $[M+H]^+$ calcd 254.1539, found 254.1543.

$[\alpha]_D^{20}$ +8.8 (*c* 0.70, CH_2Cl_2). 91% ee. Determined by HPLC analysis using two Daicel

Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 95.0/5.0, 0.8 mL/min, 210 nm, t_R (minor) = 143.6 min, t_R (major) = 159.8 min.

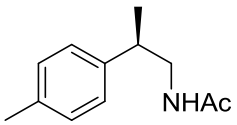
(*R*)-*N*-(2-(4-(trifluoromethyl)phenyl)propyl)acetamide (2k)



PE/AcOEt = 1/1 as the eluent. Colorless oil (47.1 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.57 (d, J = 7.6 Hz, 2H), 7.31 (d, J = 7.6 Hz, 2H), 5.50 (s, 1H), 3.64-3.52 (m, 1H), 3.31-3.19 (m, 1H), 3.09-2.97 (m, 1H), 1.88 (s, 3H), 1.27 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.22, 148.43, 129.29 (128.97, J = 32 Hz), 128.34 (125.63, 122.93, 120.22, J = 271 Hz), 127.69, 125.78 (125.74, 125.71, 125.67, J = 4 Hz), 46.07, 39.81, 23.34, 19.33. HRMS (ESI): *m/z* for $C_{12}H_{15}F_3NO$ $[M+H]^+$ calcd 246.1100, found 246.1104.

$[\alpha]_D^{20}$ +17.2 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 96.5/3.5, 0.7 mL/min, 210 nm, t_R (minor) = 120.9 min, t_R (major) = 97.7 min.

(*R*)-*N*-(2-(*p*-tolyl)propyl)acetamide (2l)

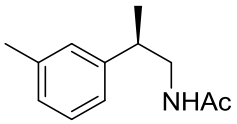


PE/AcOEt = 1/1 as the eluent. Colorless oil (36.7 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.18-7.03 (m, 4H), 5.69 (s, 1H), 3.63-3.50 (m, 1H), 3.25-3.12 (m, 1H), 2.95-2.80 (m, 1H), 2.32 (s, 3H), 1.87 (s, 3H), 1.24 (d, J = 5.6 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.18, 114.06, 136.20, 129.38, 127.04, 46.21, 39.25, 23.23,

21.03, 19.59. HRMS (ESI): *m/z* for $C_{12}H_{18}NO$ $[M+H]^+$ calcd 192.1383, found 192.1392.

$[\alpha]_D^{20}$ +20.4 (*c* 0.70, CH_2Cl_2). 93% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 205.6 min, t_R (major) = 181.5 min.

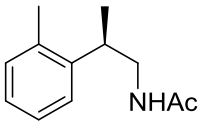
(*R*)-*N*-(2-(*m*-tolyl)propyl)acetamide (2m)



PE/AcOEt = 1/1 as the eluent. Colorless oil (36.3 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.20 (t, *J* = 7.2 Hz, 1H), 7.08-6.95 (m, 3H), 5.66 (s, 1H), 3.64-3.52 (m, 1H), 3.26-3.15 (m, 1H), 2.95-2.82 (m, 1H), 2.33 (s, 3H), 1.88 (s, 3H), 1.24 (d, *J* = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.14, 144.12, 138.29, 128.59, 127.96, 127.46, 124.18, 46.18, 39.63, 23.26, 21.51, 19.55. HRMS (ESI): *m/z* for $C_{12}H_{18}NO$ $[M+H]^+$ calcd 192.1383, found 192.1388.

$[\alpha]_D^{20}$ +17.9 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 224.7 min, t_R (major) = 194.8 min.

(*R*)-*N*-(2-(*o*-tolyl)propyl)acetamide (2n)

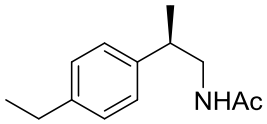


PE/AcOEt = 1/1 as the eluent. Colorless oil (36.7 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.25-7.08 (m, 4H), 5.63 (s, 1H), 3.62-3.50 (m, 1H), 3.33-3.18 (m,

2H), 2.33 (s, 3H), 1.89 (s, 3H), 1.22 (d, J = 4.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.20, 142.26, 136.22, 130.65, 126.51, 126.34, 125.20, 45.51, 34.58, 23.33, 19.59, 19.16. HRMS (ESI): *m/z* for $C_{12}H_{18}NO$ $[M+H]^+$ calcd 192.1383, found 192.1387.

$[\alpha]_D^{20}$ +9.4 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 97.0/3.0, 0.8 mL/min, 210 nm, t_R (minor) = 122.4 min, t_R (major) = 99.7 min.

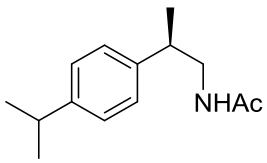
(*R*)-*N*-(2-(4-ethylphenyl)propyl)acetamide (2o)



PE/AcOEt = 1/1 as the eluent. Colorless oil (39.4 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.13 (dd, J = 7.6, 6.4 Hz, 4H), 5.60 (s, 1H), 3.65-3.53 (m, 1H), 3.25-3.12 (m, 1H), 2.96-2.82 (m, 1H), 2.62 (q, J = 6.8 Hz, 2H), 1.88 (s, 3H), 1.32-1.20 (m, 6H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.13, 142.60, 141.28, 128.20, 127.12, 46.23, 39.30, 28.46, 23.32, 19.61, 15.60. HRMS (ESI): *m/z* for $C_{13}H_{20}NO$ $[M+H]^+$ calcd 206.1539, found 206.1544.

$[\alpha]_D^{20}$ +6.3 (*c* 0.70, CH_2Cl_2). 95% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 170.3 min, t_R (major) = 153.3 min.

(*R*)-*N*-(2-(4-isopropylphenyl)propyl)acetamide (2p)

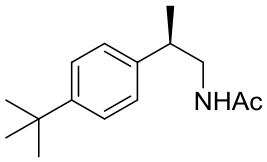


PE/AcOEt = 1/1 as the eluent. Colorless oil (41.7 mg, 95% yield). ^{1}H NMR (400

MHz, $CDCl_3$): δ 7.14 (dd, J = 7.6, 7.2 Hz, 4H), 5.70 (s, 1H), 3.63-3.50 (m, 1H), 3.26-3.13 (m, 1H), 1.28-1.17 (m, 2H), 1.88 (s, 3H), 1.28-1.17 (m, 9H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.18, 147.17, 141.38, 127.07, 126.72, 46.23, 39.25, 33.70, 24.04, 23.29, 19.54. HRMS (ESI): *m/z* for $C_{14}H_{22}NO$ $[M+H]^+$ calcd 220.1696, found 220.1702.

$[\alpha]_D^{20}$ +8.0 (*c* 0.70, CH_2Cl_2). 94% ee. Determined by HPLC analysis using two Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.7 mL/min, 210 nm, t_R (minor) = 56.0 min, t_R (major) = 62.3 min.

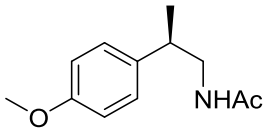
(*R*)-*N*-(2-(4-(tert-butyl)phenyl)propyl)acetamide (2q)



PE/AcOEt = 1/1 as the eluent. Colorless oil (41.7 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.33 (d, J = 7.2 Hz, 2H), 7.12 (d, J = 7.2 Hz, 2H), 5.54 (s, 1H), 3.65-3.53 (m, 1H), 3.26-3.14 (m, 1H), 2.96-2.83 (m, 1H), 1.89 (s, 3H), 1.31 (s, 9H), 1.25 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.15, 149.53, 141.00, 126.86, 125.64, 46.24, 39.20, 34.49, 31.45, 23.37, 19.54. HRMS (ESI): *m/z* for $C_{15}H_{24}NO$ $[M+H]^+$ calcd 234.1852, found 234.1859.

$[\alpha]_D^{20}$ +8.3 (*c* 0.70, CH_2Cl_2). 94% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 227.6 min, t_R (major) = 203.5 min.

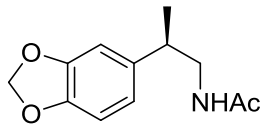
(*R*)-*N*-(2-(4-methoxyphenyl)propyl)acetamide (2r)



PE/AcOEt = 1/1 as the eluent. Colorless oil (40.6 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.09 (d, J = 7.6 Hz, 2H), 6.83 (d, J = 8.0 Hz, 2H), 5.65 (s, 1H), 3.76 (s, 3H), 3.60-3.47 (m, 1H), 3.21-3.10 (m, 1H), 2.93-2.79 (m, 1H), 1.86 (s, 3H), 1.21 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.17, 158.30, 136.12, 128.09, 114.07, 55.26, 46.34, 38.84, 23.24, 19.66. HRMS (ESI): *m/z* for $C_{12}H_{18}NO_2$ $[M+H]^+$ calcd 208.1332, found 208.1338.

$[\alpha]_D^{20}$ +7.3 (*c* 0.70, CH_2Cl_2). 94% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.5/1.5, 0.8 mL/min, 210 nm, t_R (minor) = 260.4 min, t_R (major) = 232.5 min.

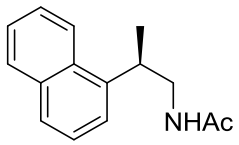
(*R*)-*N*-(2-(benzo[d][1,3]dioxol-5-yl)propyl)acetamide (2s)



PE/AcOEt = 1/1 as the eluent. Colorless oil (43.4 mg, 98% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 6.69 (d, J = 8.0 Hz, 1H), 6.68 (s, 1H), 6.59 (d, J = 8.0 Hz, 1H), 5.93-5.77 (m, 3H), 3.52-3.41 (m, 1H), 3.17-3.05 (m, 1H), 2.88-2.74 (m, 1H), 1.84 (s, 3H), 1.17 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.17, 147.85, 146.14, 138.07, 120.15, 108.27, 107.26, 100.88, 46.28, 39.40, 23.12, 19.62. HRMS (ESI): *m/z* for $C_{12}H_{16}NO_3$ $[M+H]^+$ calcd 222.1125, found 222.1129.

$[\alpha]_D^{20}$ +20.0 (*c* 0.70, CH_2Cl_2). 92% ee. Determined by HPLC analysis using two Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 95.0/5.0, 0.8 mL/min, 210 nm, t_R (minor) = 90.5 min, t_R (major) = 96.4 min.

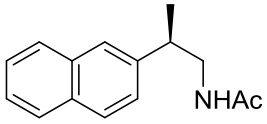
(*R*)-*N*-(2-(naphthalen-1-yl)propyl)acetamide (2t)



PE/AcOEt = 1/1 as the eluent. Colorless oil (43.3 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.08 (d, J = 7.6 Hz, 1H), 7.76 (d, J = 7.6 Hz, 1H), 7.64 (d, J = 8.0 Hz, 1H), 7.48-7.33 (m, 3H), 7.29 (d, J = 7.2 Hz, 1H), 5.61 (s, 1H), 3.86-3.74 (m, 1H), 3.57-3.47 (m, 1H), 3.47-3.37 (m, 1H), 1.73 (s, 3H), 1.30 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.39, 140.18, 133.99, 131.99, 128.97, 127.14, 126.19, 125.67, 125.63, 123.15, 122.65, 45.98, 33.62, 23.26, 19.30. HRMS (ESI): *m/z* for $C_{15}H_{18}NO$ $[M+H]^+$ calcd 228.1383, found 228.1386.

$[\alpha]_D^{20}$ +9.4 (*c* 0.70, CH_2Cl_2). 90% ee. Determined by HPLC analysis using two Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 95.0/5.0, 0.8 mL/min, 210 nm, t_R (minor) = 69.5 min, t_R (major) = 61.2 min.

(*R*)-*N*-(2-(naphthalen-2-yl)propyl)acetamide (2u)

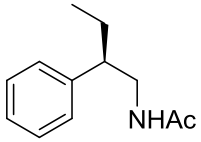


PE/AcOEt = 1/1 as the eluent. Colorless oil (43.3 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.87-7.77 (m, 3H), 7.64 (s, 1H), 7.54-7.43 (m, 2H), 7.36 (d, J = 7.6 Hz, 1H), 5.38 (s, 1H), 3.78-3.67 (m, 1H), 3.37-3.25 (m, 1H), 3.17-3.03 (m, 1H), 1.86 (s, 3H), 1.36 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.16, 141.60, 133.64, 132.58, 128.62, 127.76, 127.70, 126.32, 125.85, 125.74, 125.55, 46.09, 39.94, 23.41, 19.67. HRMS (ESI): *m/z* for $C_{15}H_{18}NO$ $[M+H]^+$ calcd 228.1383, found 228.1388.

$[\alpha]_D^{20}$ +20.4 (*c* 0.70, CH_2Cl_2). 92% ee. Determined by HPLC analysis using two

Daicel Chiralcel OJ-H columns (25 cm × 0.46 cm), hexane/isopropanol = 97.0/3.0, 0.8 mL/min, 210 nm, t_R (minor) = 195.3 min, t_R (major) = 167.9 min.

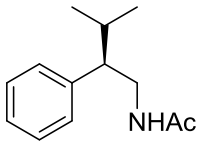
(*R*)-*N*-(2-phenylbutyl)acetamide (2v)



PE/AcOEt = 1/1 as the eluent. Colorless oil (36.3 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35-7.26 (m, 2H), 7.26-7.18 (m, 1H), 7.15 (d, J = 7.2 Hz, 2H), 5.51 (s, 1H), 3.77-3.64 (m, 1H), 3.21-3.11 (m, 1H), 2.71-2.58 (m, 1H), 1.83 (s, 3H), 1.79-1.63 (m, 1H), 1.63-1.47 (m, 1H), 0.79 (t, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.09, 142.58, 128.69, 127.87, 126.76, 47.49, 44.87, 26.89, 23.27, 11.89. HRMS (ESI): *m/z* for $C_{12}H_{18}NO$ $[M+H]^+$ calcd 192.1383, found 192.1389.

$[\alpha]_D^{20}$ +10.5 (*c* 0.70, CH_2Cl_2). 95% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 187.3 min, t_R (major) = 149.1 min.

(*R*)-*N*-(3-methyl-2-phenylbutyl)acetamide (2w)

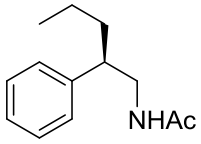


PE/AcOEt = 1/1 as the eluent. Colorless oil (39.0 mg, 96% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.27-7.19 (m, 2H), 7.19-7.10 (m, 1H), 7.06 (d, J = 7.2 Hz, 2H), 5.41 (s, 1H), 3.88-3.74 (m, 1H), 3.22-3.09 (m, 1H), 2.49-2.36 (m, 1H), 1.87-1.75 (m, 1H), 1.70 (s, 3H), 0.92 (d, J = 6.4 Hz, 3H), 0.65 (d, J = 6.4 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 169.96, 141.58, 128.45, 128.41, 126.63, 52.35, 42.30, 31.61, 23.12, 20.80,

20.47. HRMS (ESI): *m/z* for $C_{13}H_{20}NO$ $[M+H]^+$ calcd 206.1539, found 206.1547.

$[\alpha]_D^{20}$ +13.4 (*c* 0.70, CH_2Cl_2). 92% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 152.5 min, t_R (major) = 119.9 min.

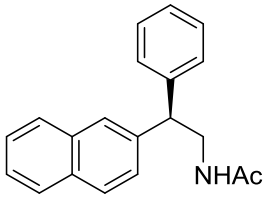
(*R*)-*N*-(2-phenylpentyl)acetamide (2x)



PE/AcOEt = 1/1 as the eluent. Colorless oil (38.6 mg, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.28-7.19 (m, 2H), 7.19-7.11 (m, 1H), 7.08 (d, *J* = 7.2 Hz, 2H), 5.55 (s, 1H), 3.67-3.56 (m, 1H), 3.15-3.03 (m, 1H), 2.75-2.62 (m, 1H), 1.76 (s, 3H), 1.62-1.39 (m, 2H), 1.18-1.03 (m, 2H), 0.77 (t, *J* = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.09, 142.83, 128.64, 127.77, 126.67, 45.45, 45.13, 36.08, 23.20, 20.38, 14.06. HRMS (ESI): *m/z* for $C_{13}H_{20}NO$ $[M+H]^+$ calcd 206.1539, found 206.1545.

$[\alpha]_D^{20}$ +8.2 (*c* 0.70, CH_2Cl_2). 88% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 168.5 min, t_R (major) = 126.4 min.

(*R*)-*N*-(2-(naphthalen-2-yl)-2-phenylethyl)acetamide (2y)



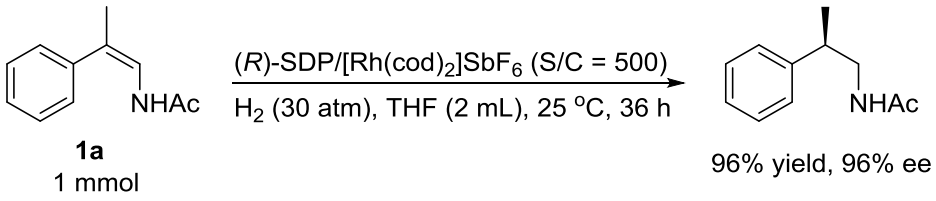
PE/AcOEt = 1/1 as the eluent. White solid (55.2 mg, 96% yield). Melting point: 106-108 ℃. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.84-7.72 (m, 3H), 7.70 (s, 1H),

7.50-7.39 (m, 2H), 7.35-7.17 (m, 6H), 5.61 (s, 1H), 4.37-4.28 (m, 1H), 4.00-3.91 (m, 2H), 1.82 (s, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 170.22, 141.85, 139.35, 133.50, 132.43, 128.82, 128.56, 128.18, 127.84, 127.68, 126.96, 126.66, 126.32, 126.31, 125.89, 50.60, 43.81, 23.33. HRMS (ESI): *m/z* for $C_{20}H_{20}NO$ $[M+H]^+$ calcd 290.1539, found 290.1547.

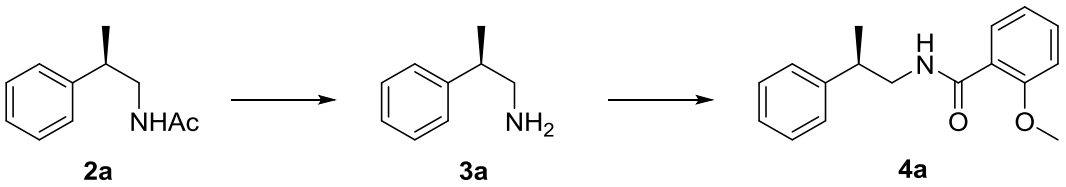
$[\alpha]_D^{20}$ +17.5 (*c* 0.70, CH_2Cl_2). 96% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 97.0/3.0, 0.7 mL/min, 210 nm, t_R (minor) = 143.1 min, t_R (major) = 115.5 min; or AD column (25 cm × 0.46 cm), hexane/isopropanol = 98.0/2.0, 0.8 mL/min, 210 nm, t_R (minor) = 32.1 min, t_R (major) = 38.2 min.

4. Applications

The substrate **1a** (176 mg, 1 mmol) was placed in a 5.0 mL tube equipped with a magnetic stirrer bar. This tube was put into an autoclave. After purging with hydrogen three times, the pre-prepared solvent of catalyst (S/C = 500) in THF (2 mL) was added under hydrogen atmosphere. The hydrogen pressure was finally pressurized to 30 atm. The reaction mixture was vigorously stirred at room temperature for 36 h. The reaction mixture was concentrated and purified through silica gel column with PE/AcOEt = 1/1 as eluent. The enantioselectivity of the product was determined by HPLC using chiral columns. The product (*R*)-*N*-(2-phenylpropyl)acetamide was obtained with 96% yield and 96% ee.



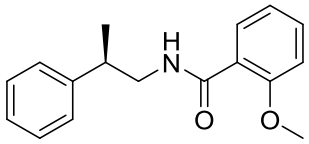
Synthesis of (*R*)-2-methoxy-*N*-(2-phenylpropyl)benzamide (4a)



A solution of (*R*)-*N*-(2-phenylpropyl)acetamide **2a** (200 mg, 1.13 mmol) in 6 mol/L H_2SO_4 (2 mL) was stirred at 100 °C in the dark for 2 days. Then, H_2O (1 mL) and EtOAc (5 mL) were added. The water layer was separated and extracted with EtOAc (5 mL). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated to obtain a colorless oil **3a**. To this oil, DCM (5 mL) and triethylamine (0.36 mL) were added. The mixture was cooled to 0 °C and 2-methoxybenzoyl chloride (0.2 mL) was added dropwise in the dark. After the starting material was completely consumed, H_2O (2 mL) was added and the water layer was extracted with DCM (5 mL). The combined organic layer was washed with

brine (2 mL), dried over Na_2SO_4, filtered and concentrated to give the target product **4a** (280 mg). The overall yield is 92% over two steps.

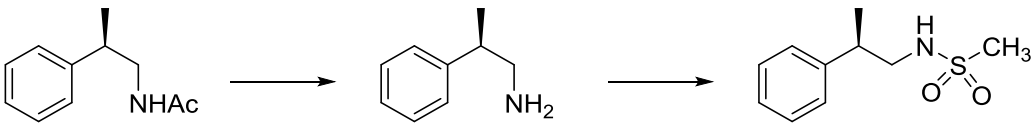
(*R*)-2-methoxy-*N*-(2-phenylpropyl)benzamide (4a)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.10 (d, J = 8.0 Hz, 1H), 7.70 (s, 1H), 7.33-7.21 (m, 3H), 7.21-7.10 (m, 3H), 6.92 (t, J = 7.6 Hz, 1H), 6.74 (d, J = 8.0 Hz, 1H), 3.87-3.78 (m, 1H), 3.50 (s, 3H), 3.42-3.30 (m, 1H), 3.02-2.88 (m, 1H), 1.23 (d, J = 6.8 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 165.03, 157.39, 144.48, 132.55, 132.12, 128.60, 127.35, 126.58, 121.44, 121.11, 111.21, 55.46, 46.35, 39.74, 19.55. HRMS (ESI): *m/z* for $C_{17}H_{20}NO_2$ $[M+H]^+$ calcd 270.1489, found 270.1493.

$[\alpha]_D^{20}$ +74.4 (*c* 0.70, CH_2Cl_2). 95% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 97.5/2.5, 0.8 mL/min, 210 nm, t_R (minor) = 158.1 min, t_R (major) = 127.3 min.

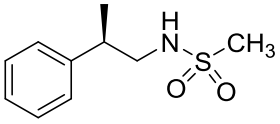
Synthesis of (*R*)-*N*-(2-phenylpropyl)methanesulfonamide (5a)



A solution of (*R*)-*N*-(2-phenylpropyl)acetamide **2a** (200 mg, 1.13 mmol) in 6 mol/L H_2SO_4 (2 mL) was stirred at 100 °C in the dark for 2 days. Then, H_2O (1 mL) and EtOAc (5 mL) were added. The water layer was separated and extracted with EtOAc (5 mL). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated to obtain a colorless oil **3a**. To this oil, DCM (5 mL) and triethylamine (0.36 mL) were added. The mixture was cooled to 0 °C and

methanesulfonyl chloride (0.2 mL) was added dropwise in the dark. After the starting material was completely consumed, H_2O (2 mL) was added and the water layer was extracted with DCM (5 mL). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated to give the target product **5a** (229 mg). The overall yield is 95% over two steps.

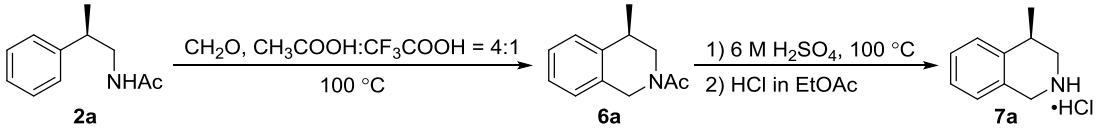
(*R*)-*N*-(2-phenylpropyl)methanesulfonamide (5a)



Colorless oil. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.37-7.15 (m, 5H), 4.63 (s, 1H), 3.35-3.17 (m, 2H), 3.01-2.87 (m, 1H), 2.72 (s, 3H), 1.30 (d, J = 7.2 Hz, 3H). ^{13}C NMR (100 MHz, $CDCl_3$): δ 143.26, 128.81, 127.30, 126.99, 49.95, 40.28, 40.03, 18.99. HRMS (ESI): *m/z* for $C_{10}H_{16}NO_2S$ $[M+H]^+$ calcd 214.0896, found 214.0901.

$[\alpha]_D^{20}$ +9.3 (*c* 0.70, CH_2Cl_2). 95% ee. Determined by HPLC analysis using a Daicel Chiralcel IC-3 column (25 cm × 0.46 cm), hexane/isopropanol = 97.0/3.0, 0.75 mL/min, 210 nm, t_R (minor) = 122.1 min, t_R (major) = 99.9 min.

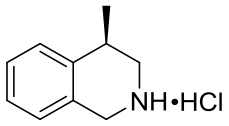
Synthesis of (*R*)-4-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (7a)



(*R*)-*N*-(2-phenylpropyl)acetamide **2a** (200 mg, 1.13 mmol) and paraformaldehyde (68 mg, 2.26 mmol) were dissolved in a mixture of CH_3COOH/CF_3COOH = 4:1 (5 mL). This mixture was stirred at 100 ^{o}C for 1 h. The solution was poured on the crushed ice and extracted with DCM (20 mL × 3). The extract was washed with 20% aq. Na_2CO_3 (20 mL × 3), dried over Na_2SO_4, filtered and concentrated to give compound **6a** without further purification.

A solution of (*R*)-1-(4-methyl-3,4-dihydroisoquinolin-2(1*H*)-yl)ethan-1-one **6a** (209 mg, 1.11 mmol) in 6 mol/L H_2SO_4 (2 mL) was stirred at 100 ^oC for 2 days. Then, H_2O (1 mL) and EtOAc (5 mL) were added. The water layer was separated and extracted with EtOAc (5 mL). The combined organic layer was washed with brine (2 mL), dried over Na_2SO_4, filtered and concentrated. A solution of hydrochloric acid in ethyl acetate (10 mL) was added to the solution of obtained compound in EtOAc (5 mL), The precipitate was filtered and dried to obtain the target compound (*R*)-4-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride **7a** (172 mg). The overall yield is 83% over two steps.

(*R*)-4-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (7a)



Yellow solid. Melting point: 129-130 ℃. ^1H NMR (400 MHz, D_2O): δ 7.50-7.26 (m, 3H), 7.26-7.16 (m, 1H), 4.47-4.23 (m, 2H), 3.70-3.52 (m, 1H), 3.40-3.22 (m, 1H), 3.22-3.06 (m, 1H), 1.47-1.26 (m, 3H). ^{13}C NMR (100 MHz, D_2O): δ 136.79, 128.39, 127.53, 127.16, 127.05, 126.70, 47.55, 44.82, 29.95, 18.54. HRMS (ESI): *m/z* for $C_{10}H_{14}N$ [M-Cl]$^+$ calcd 148.1121, found 148.1128.

$[\alpha]_D^{20}$ +32.8 (*c* 0.70, CH_2Cl_2). 94% ee. After neutralization, determined by HPLC analysis using a Daicel Chiralcel OJ column (25 cm × 0.46 cm), hexane/isopropanol = 95.0/5.0, 0.8 mL/min, 210 nm, t_R (minor) = 20.5 min, t_R (major) = 43.6 min.

Reference

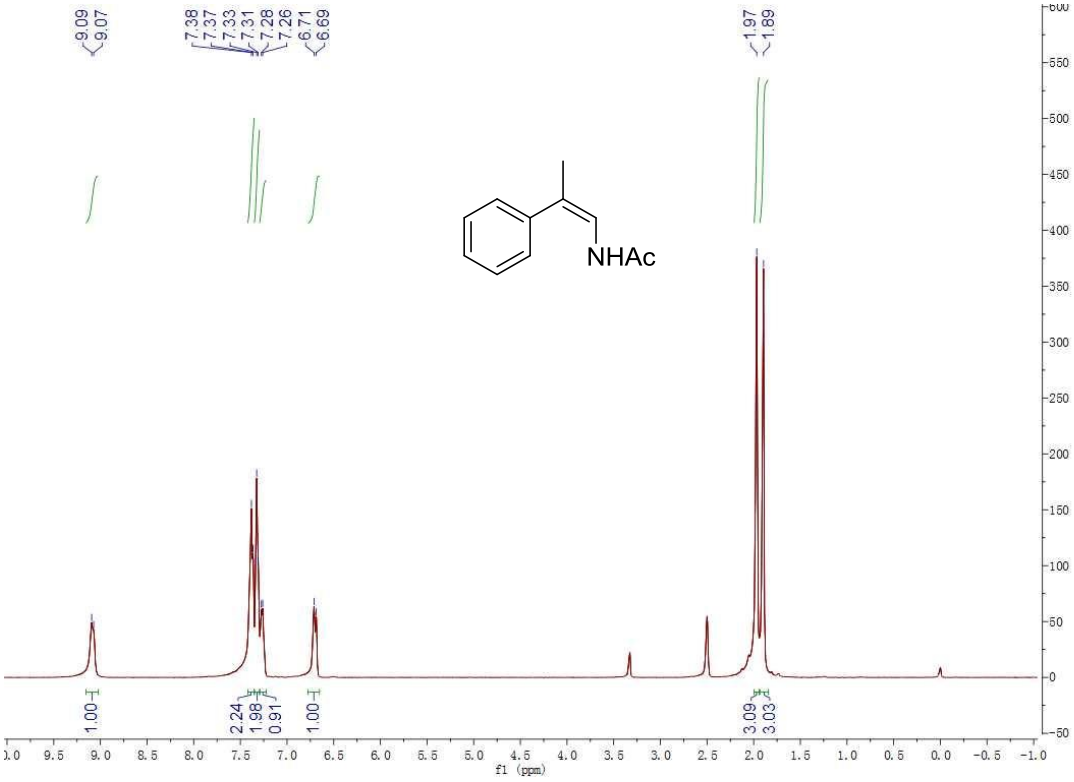
[1] J.-H. Xie, Z.-T. Zhou, W.-L. Kong and Q.-L. Zhou, *J. Am. Chem. Soc.*, 2007, **129**, 1868–1869.

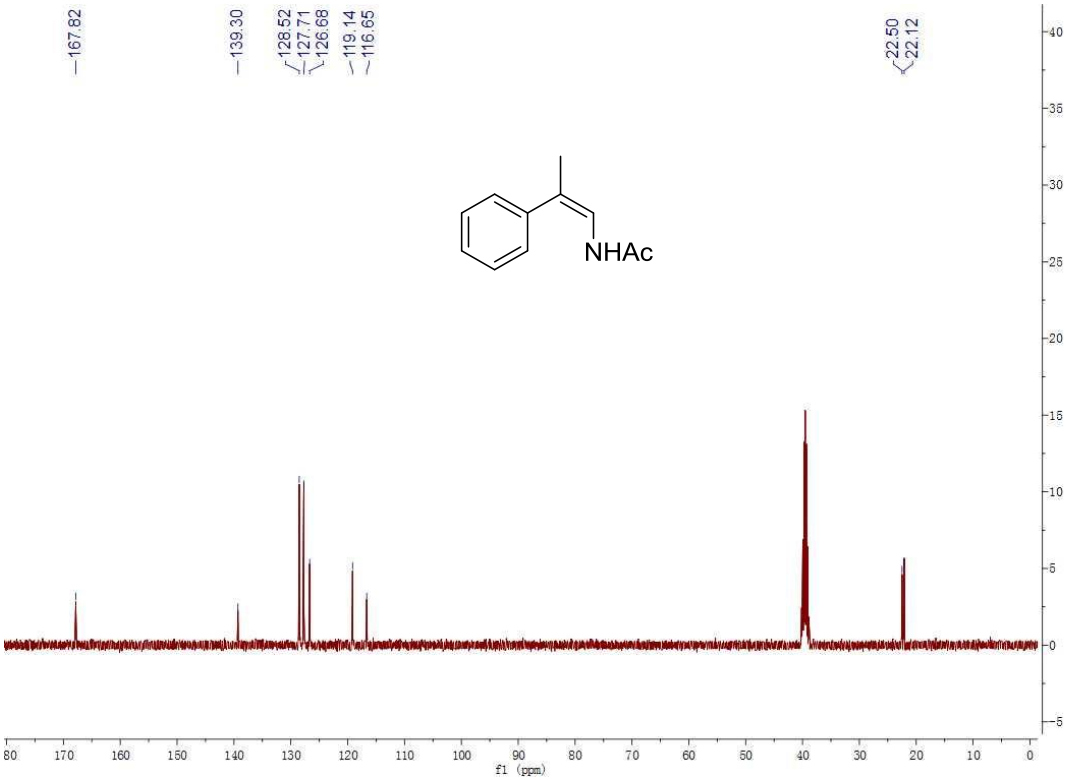
[2] T. Honjo, B. J. Phipps, V. Rauniyar and F. D. Toste, *Angew. Chem. Int. Ed.*, 2012, **51**, 9684–9688.

[3] R. E. Patre, S. Mal, P. R. Nilkanth, S. K. Ghorai, S. H. Deshpande, M. E. Qacemi, T. Smejkal, S. Pal and B. N. Manjunath, *Chem. Commun.*, 2017, **53**, 2382–2385.

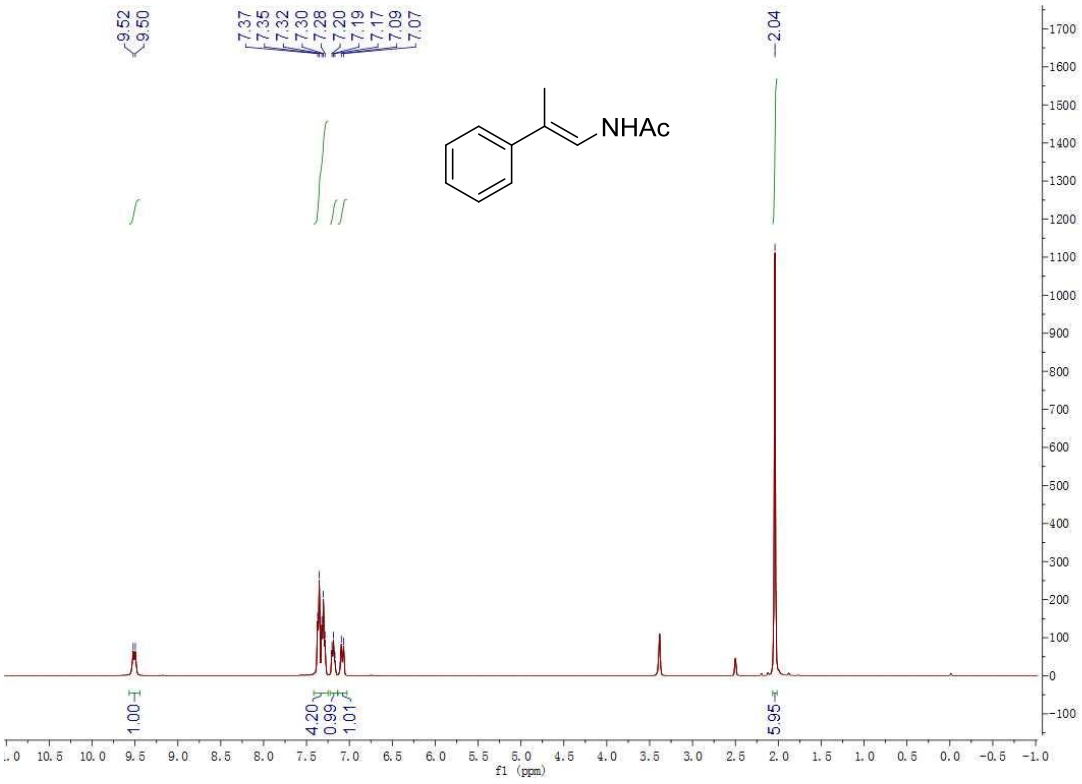
5. NMR Spectra

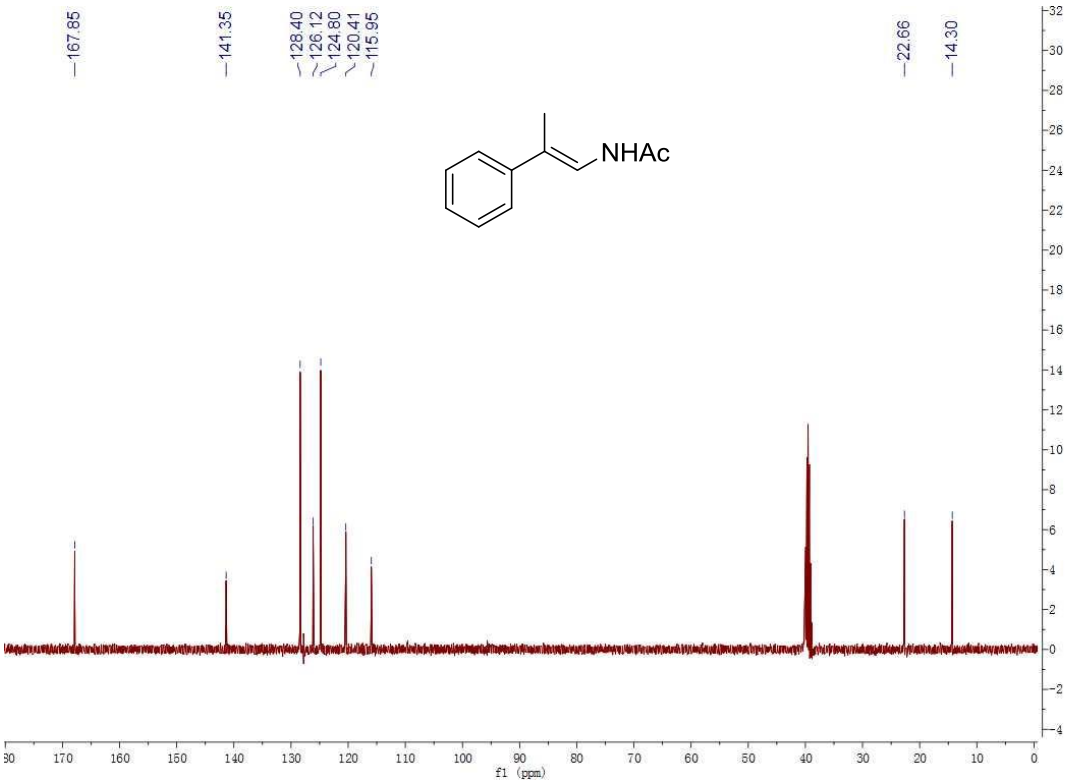
(*Z*)-*N*-(2-phenylprop-1-en-1-yl)acetamide (1a)



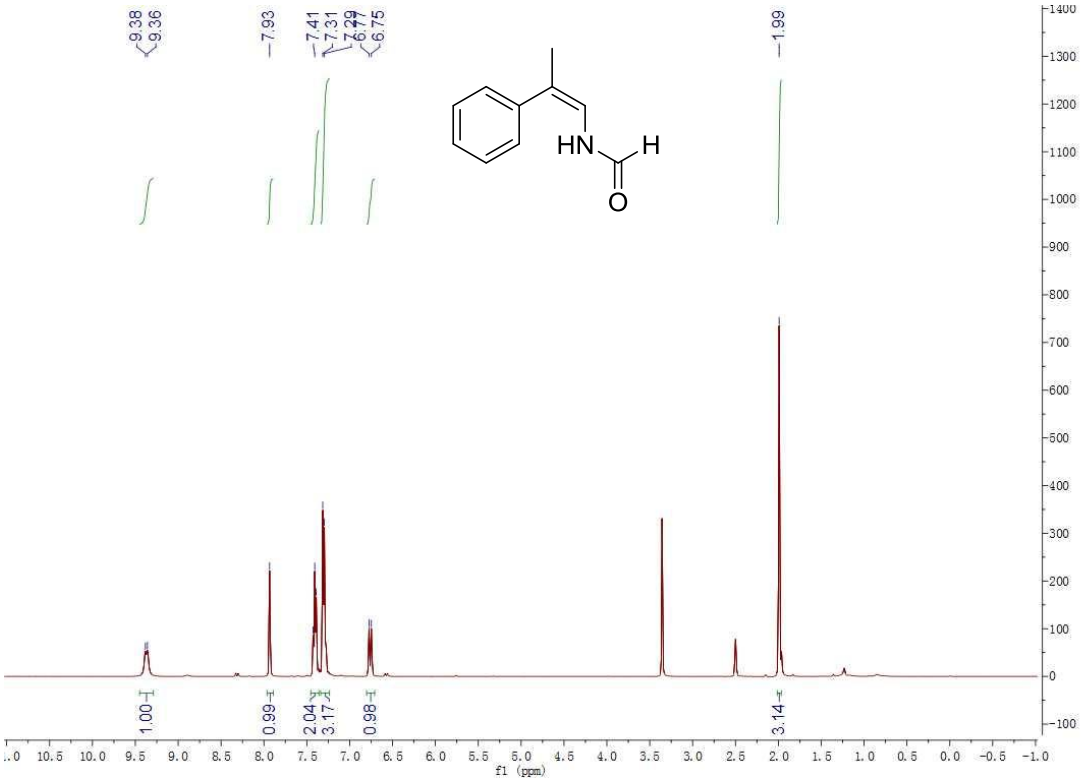


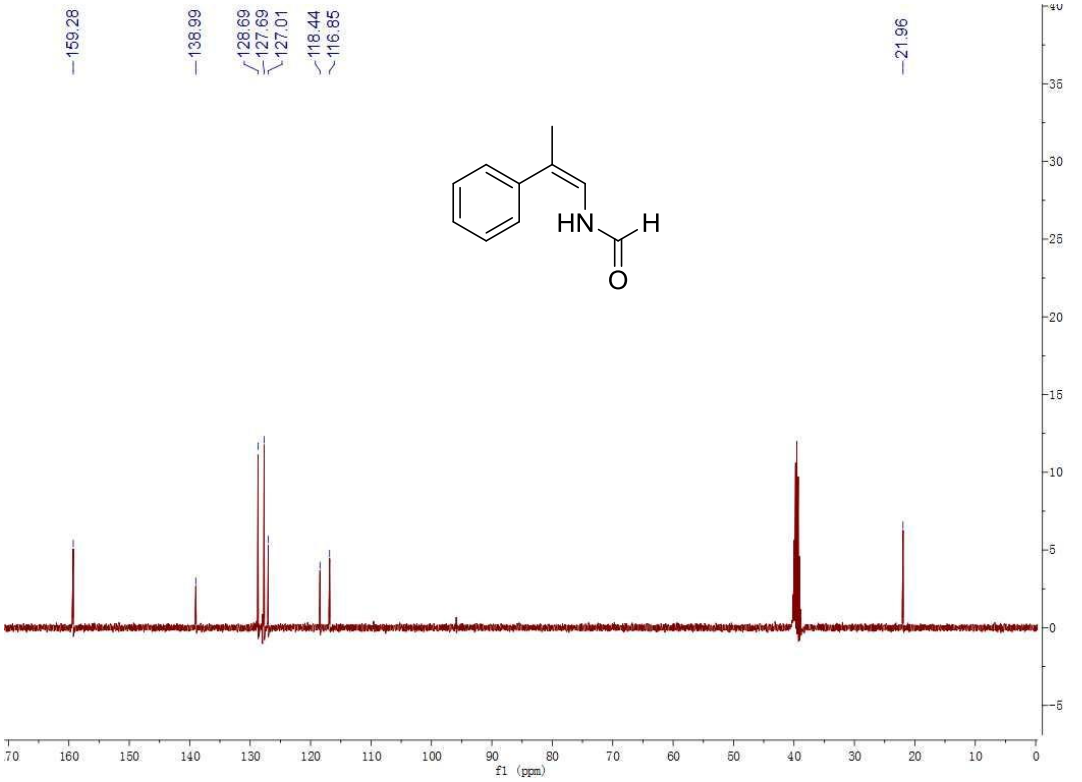
(*E*)-*N*-(2-phenylprop-1-en-1-yl)acetamide (1a')



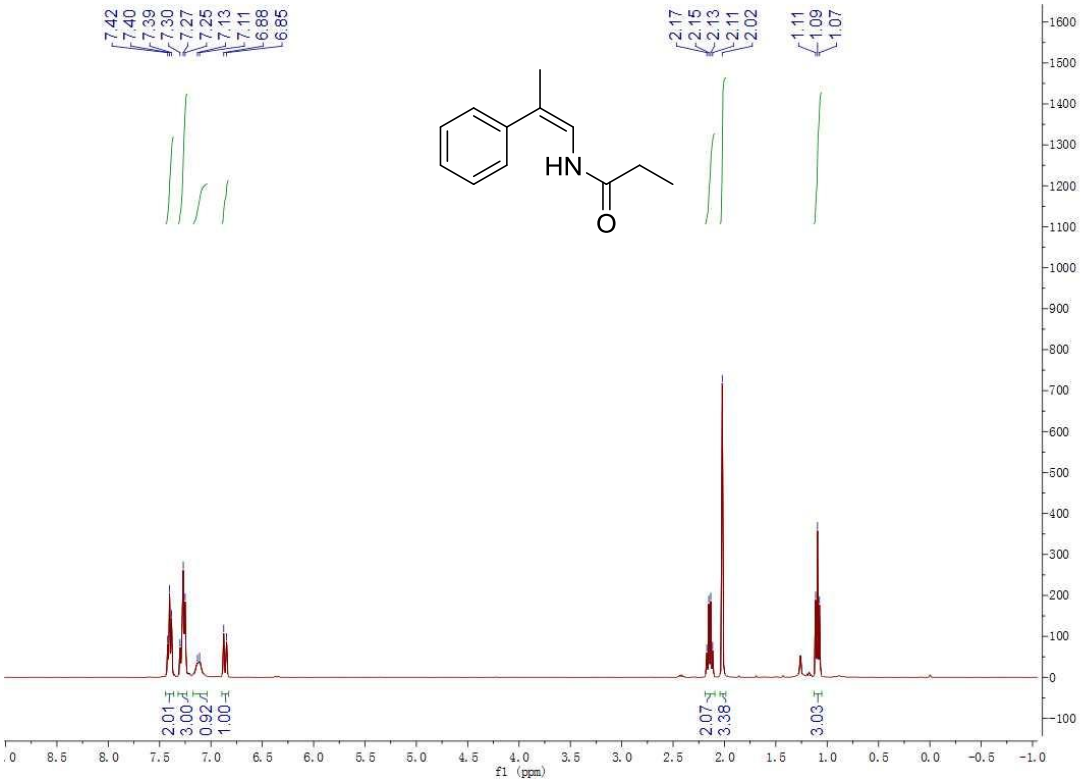


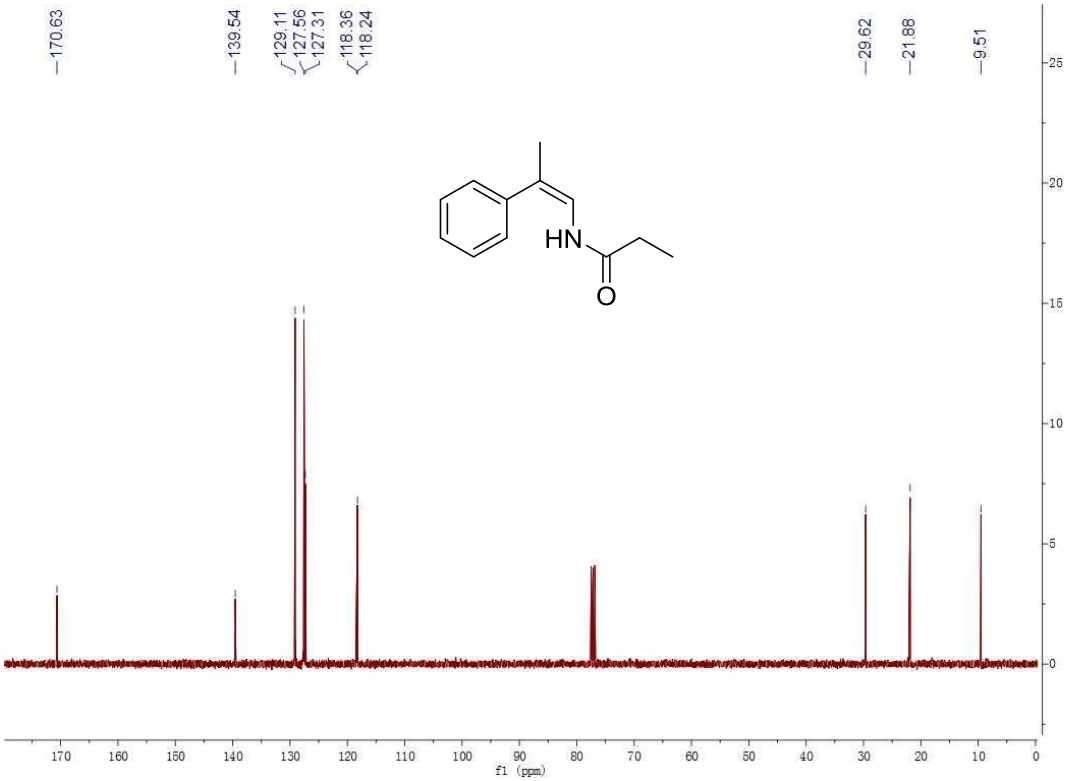
(*Z*)-*N*-(2-phenylprop-1-en-1-yl)formamide (1b)



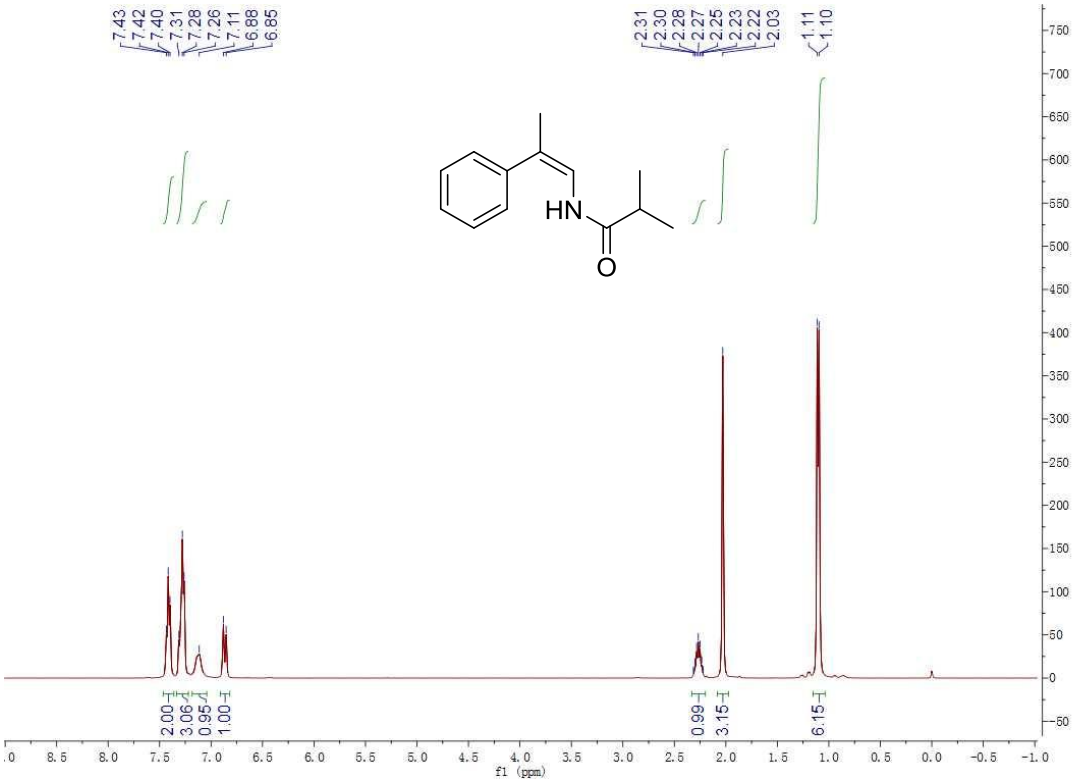


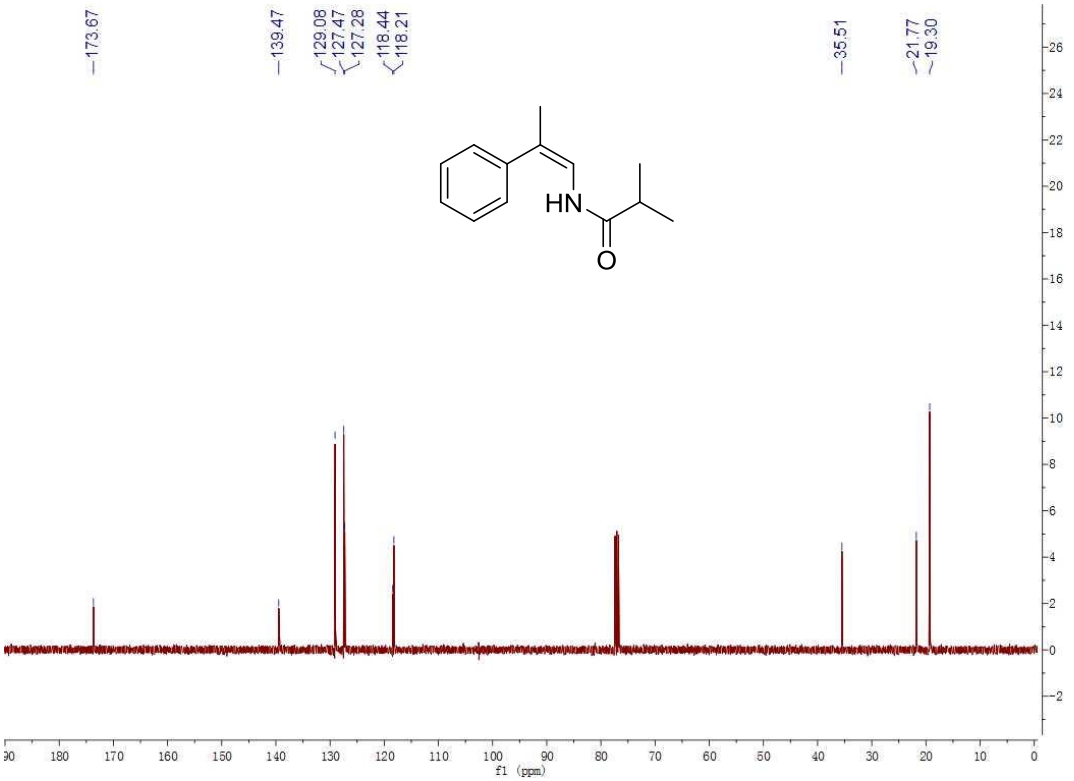
(*Z*)-*N*-(2-phenylprop-1-en-1-yl)propionamide (1c)



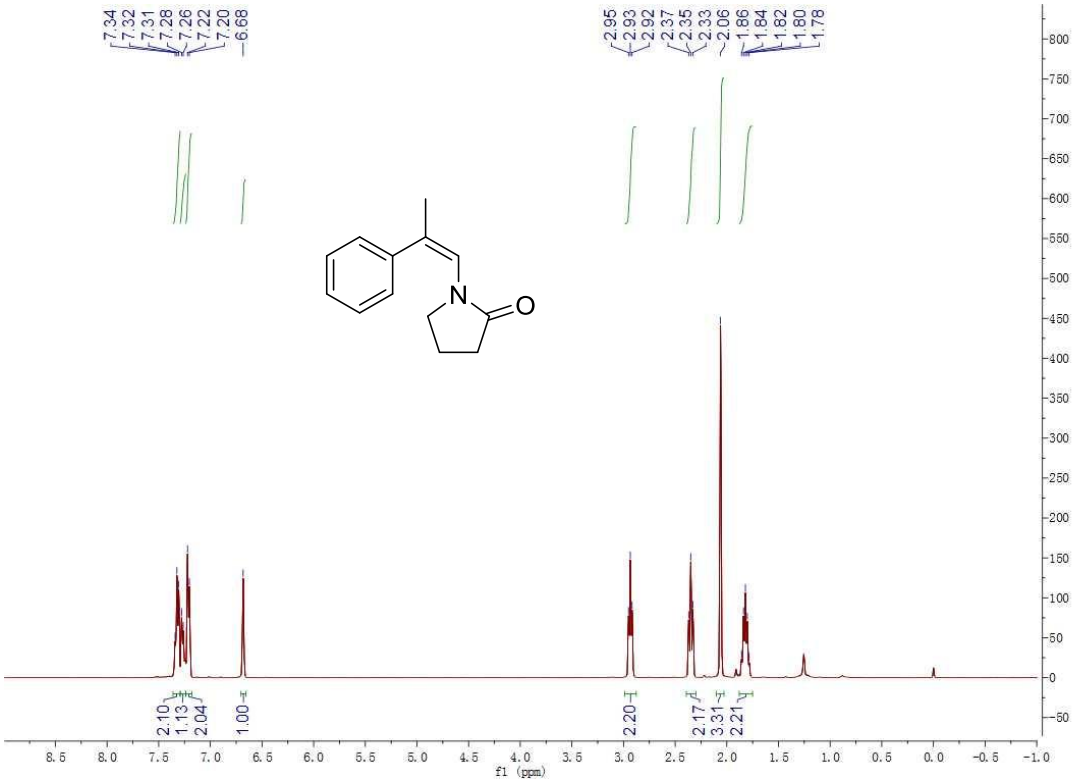


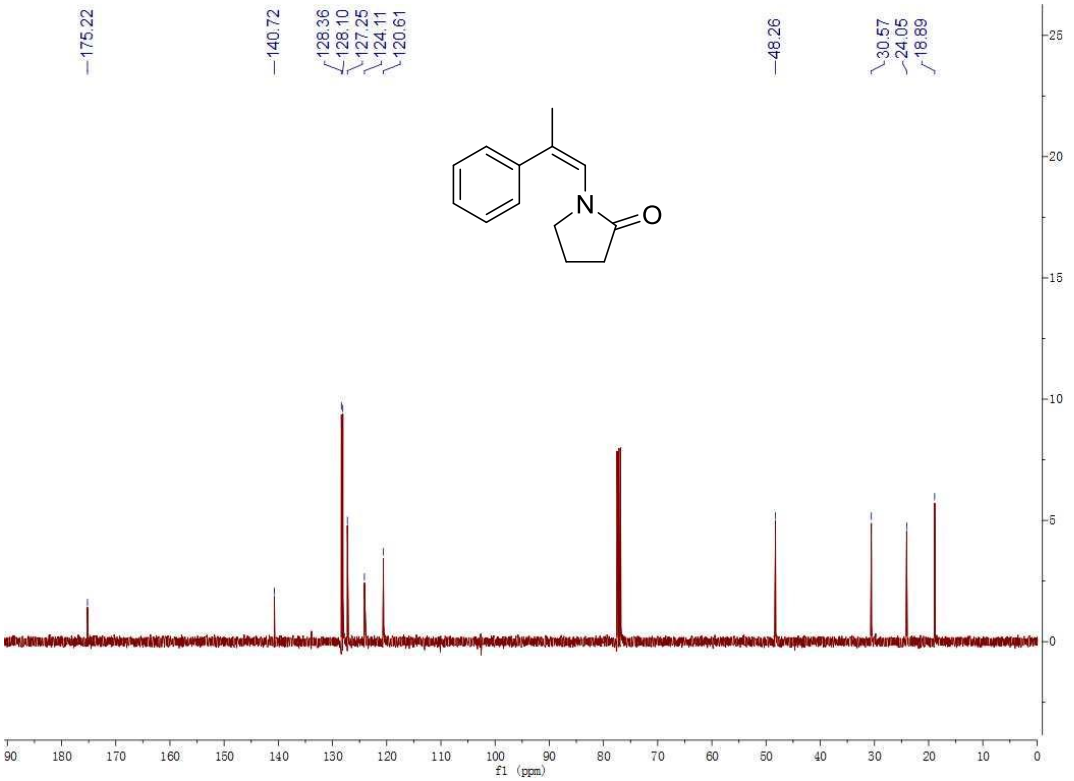
(*Z*)-*N*-(2-phenylprop-1-en-1-yl)isobutyramide (1d)



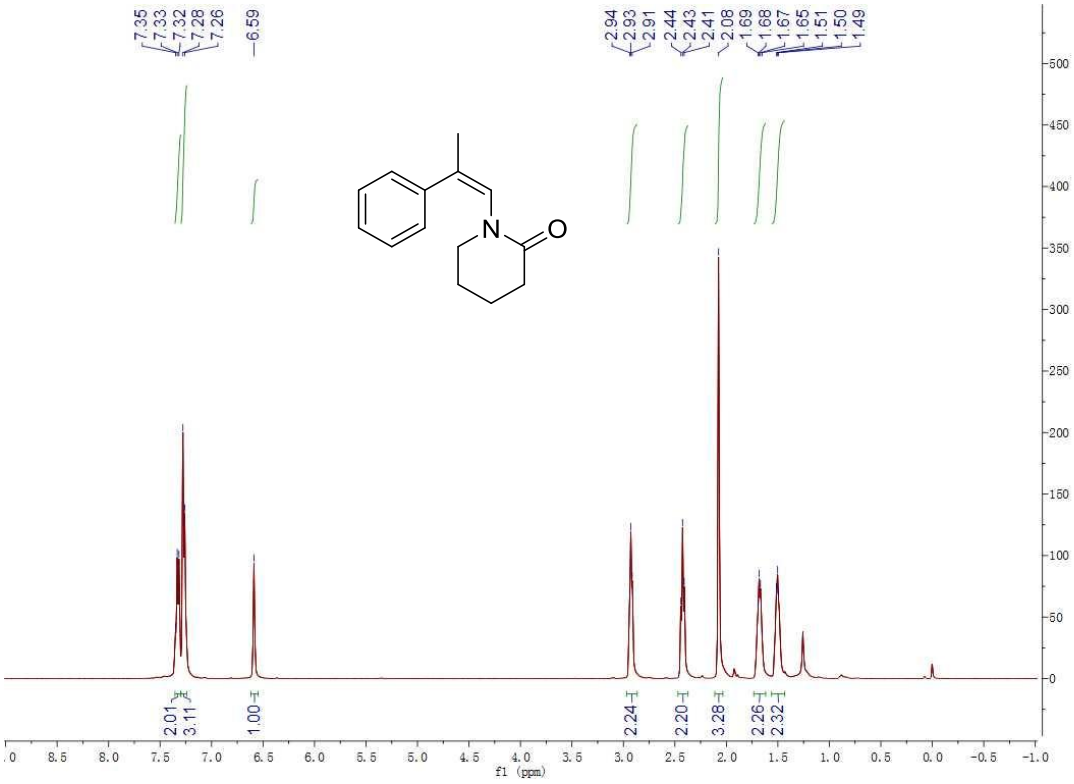


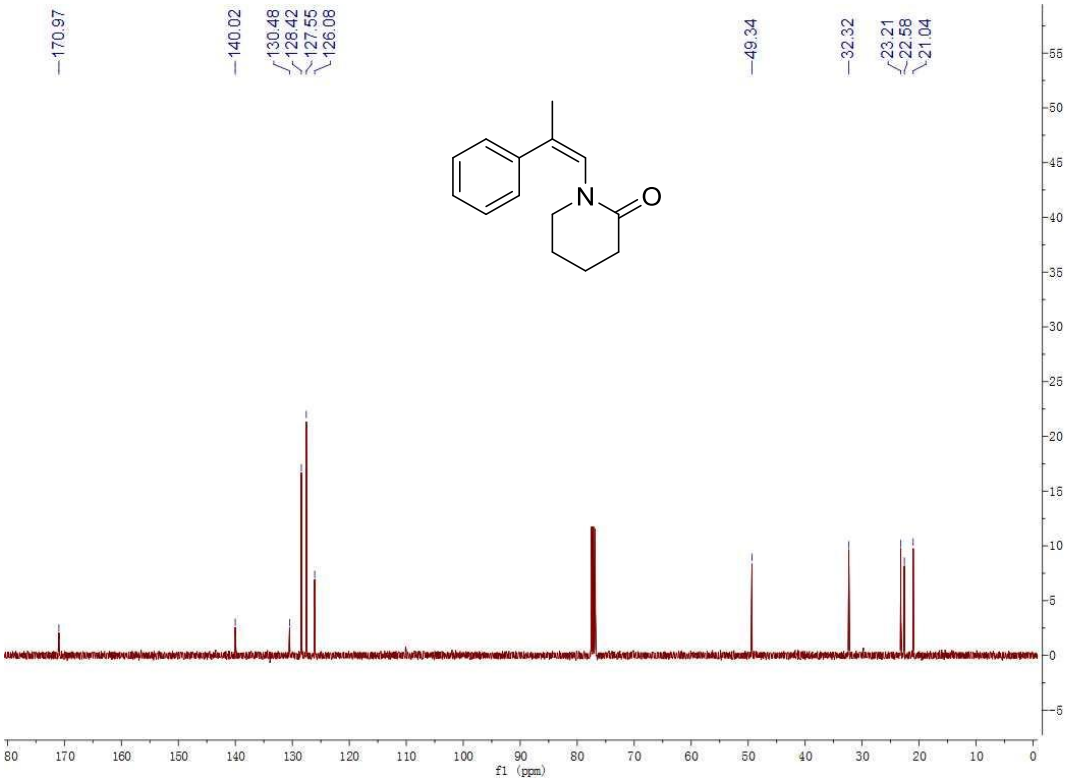
(*Z*)-1-(2-phenylprop-1-en-1-yl)pyrrolidin-2-one (1e)



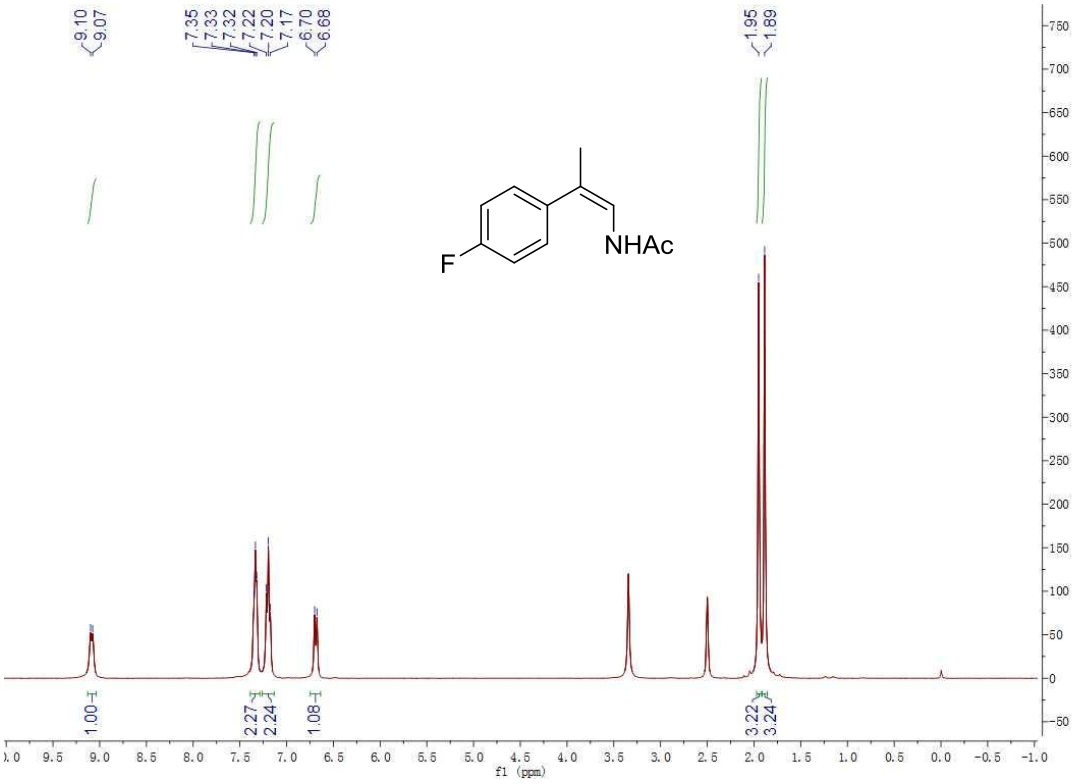


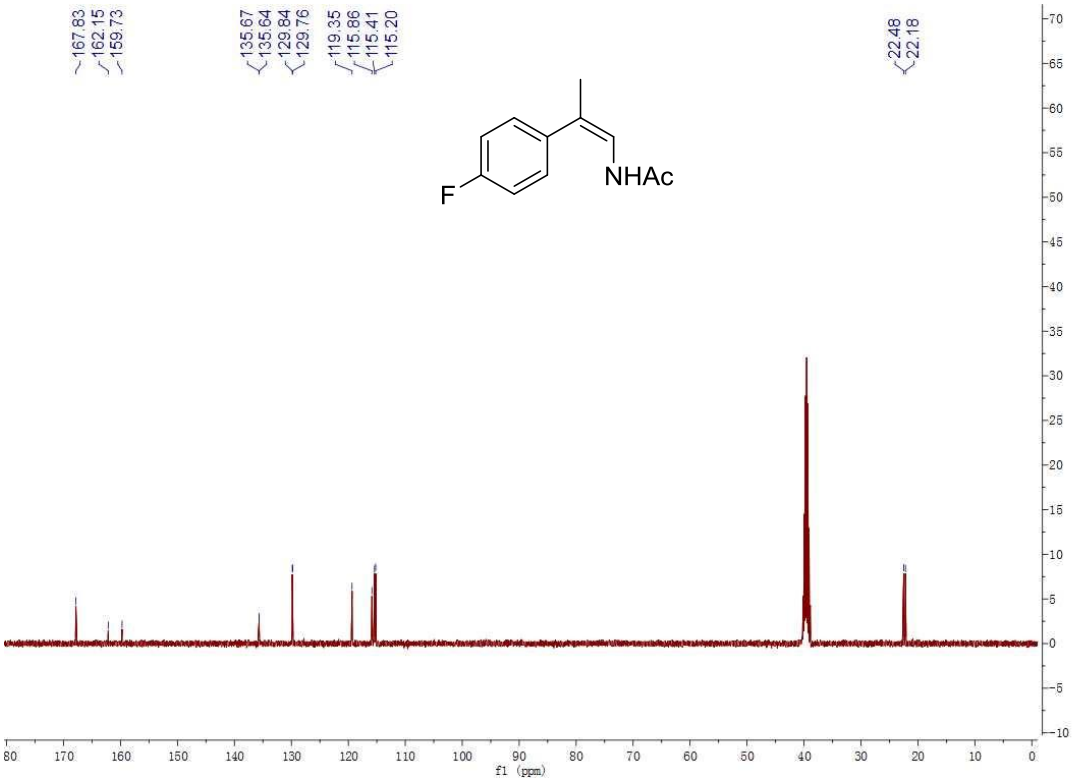
(*Z*)-1-(2-phenylprop-1-en-1-yl)piperidin-2-one (1f)



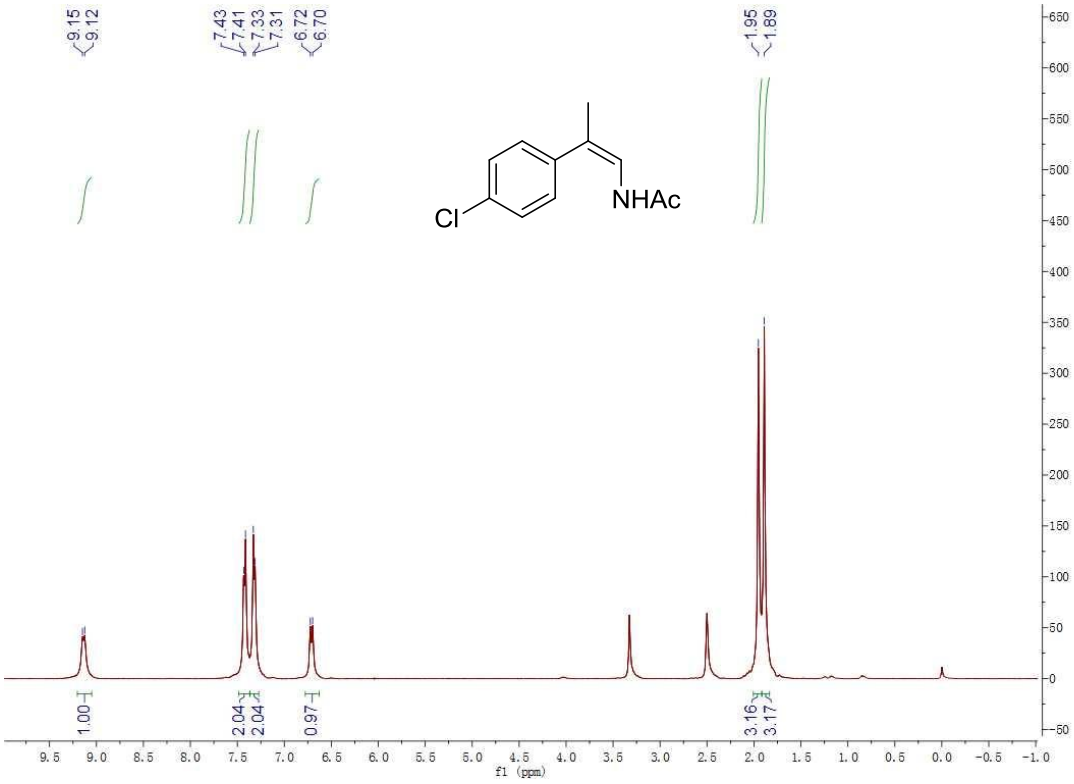


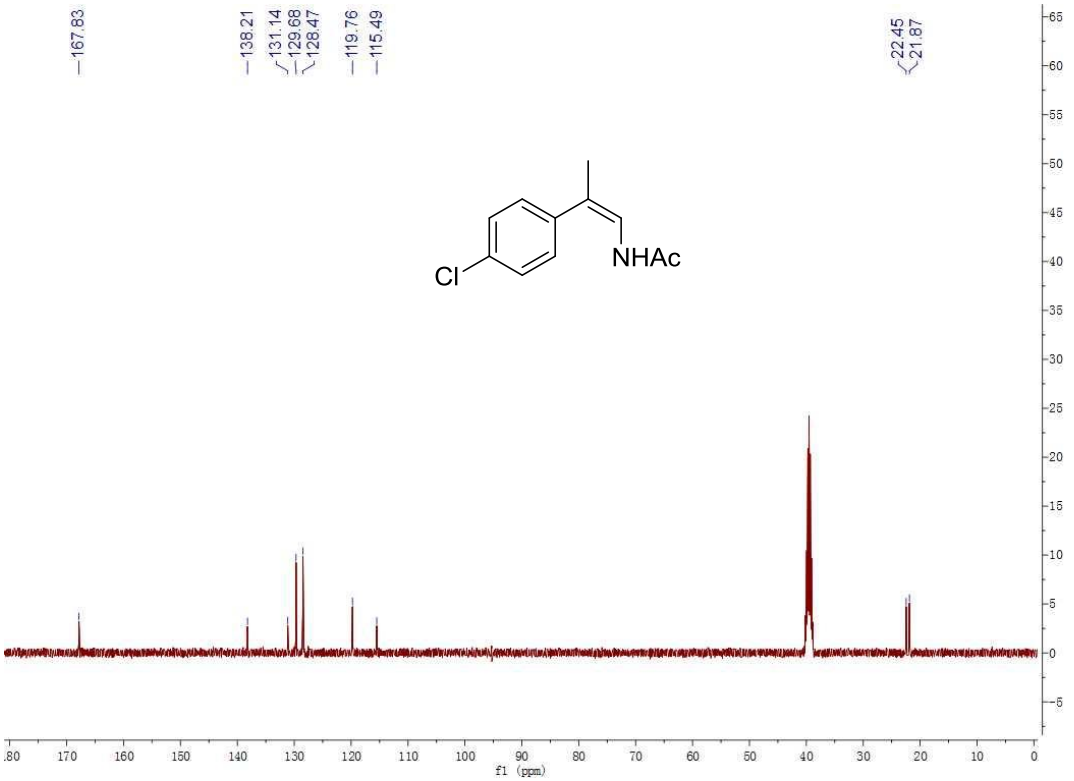
(*Z*)-*N*-(2-(4-fluorophenyl)prop-1-en-1-yl)acetamide (1g)



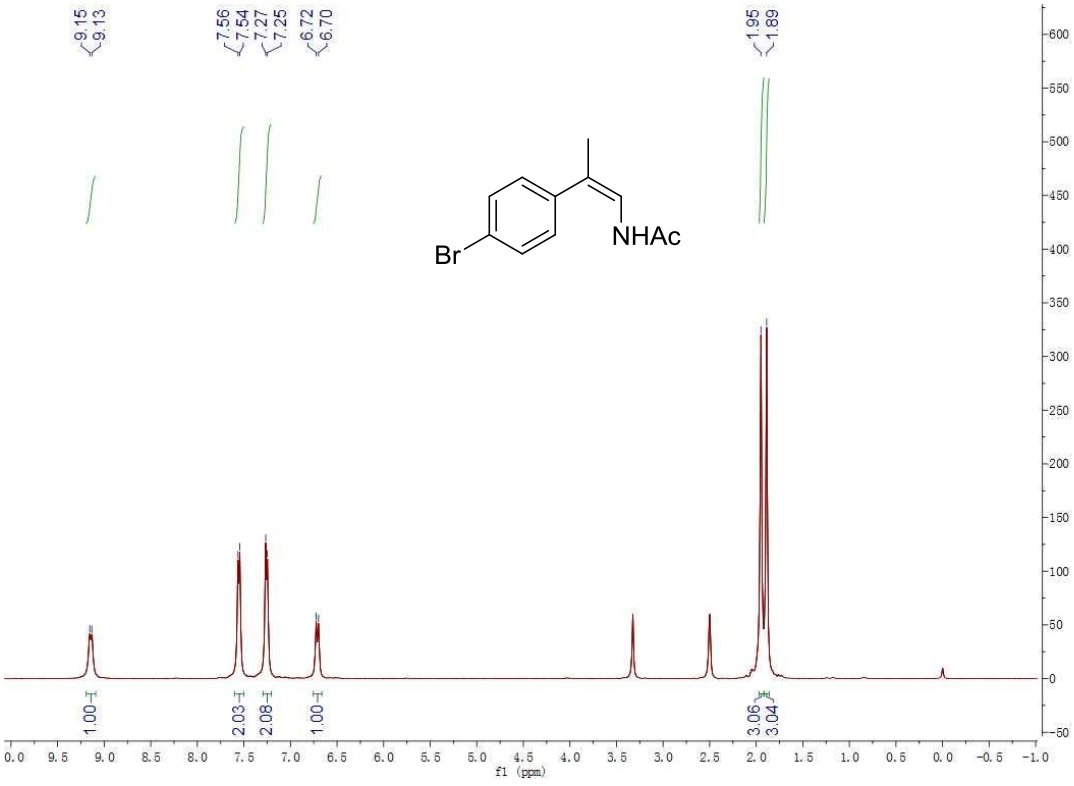


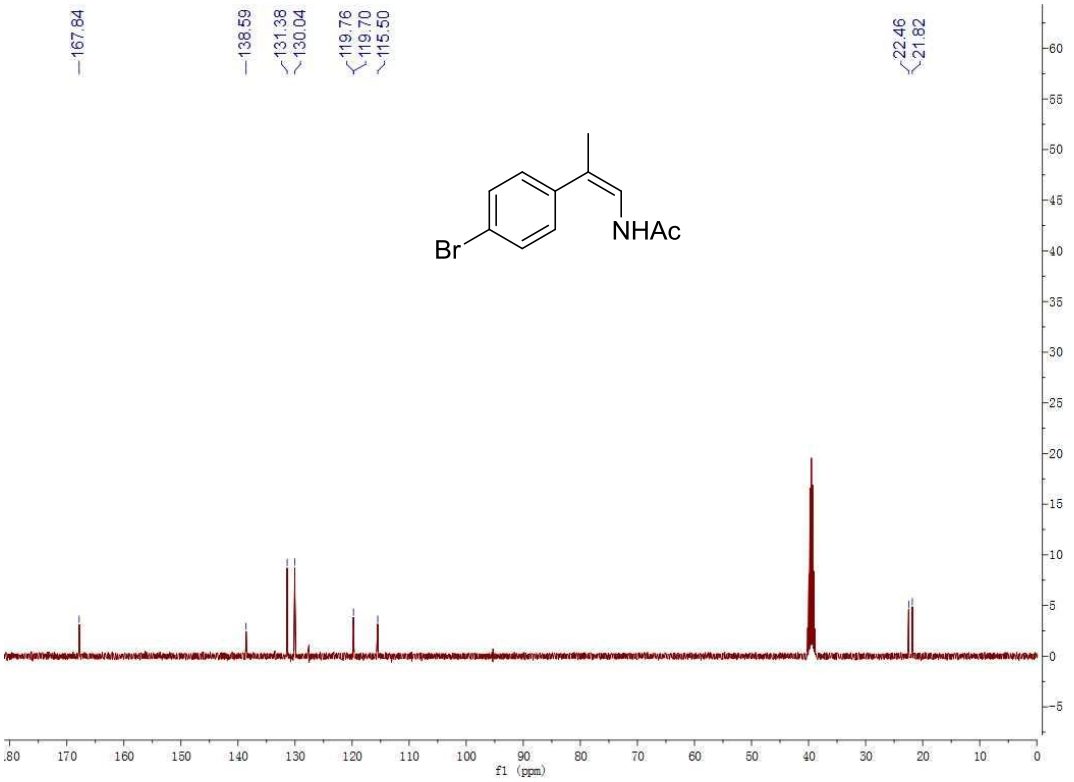
(*Z*)-*N*-(2-(4-chlorophenyl)prop-1-en-1-yl)acetamide (1h)



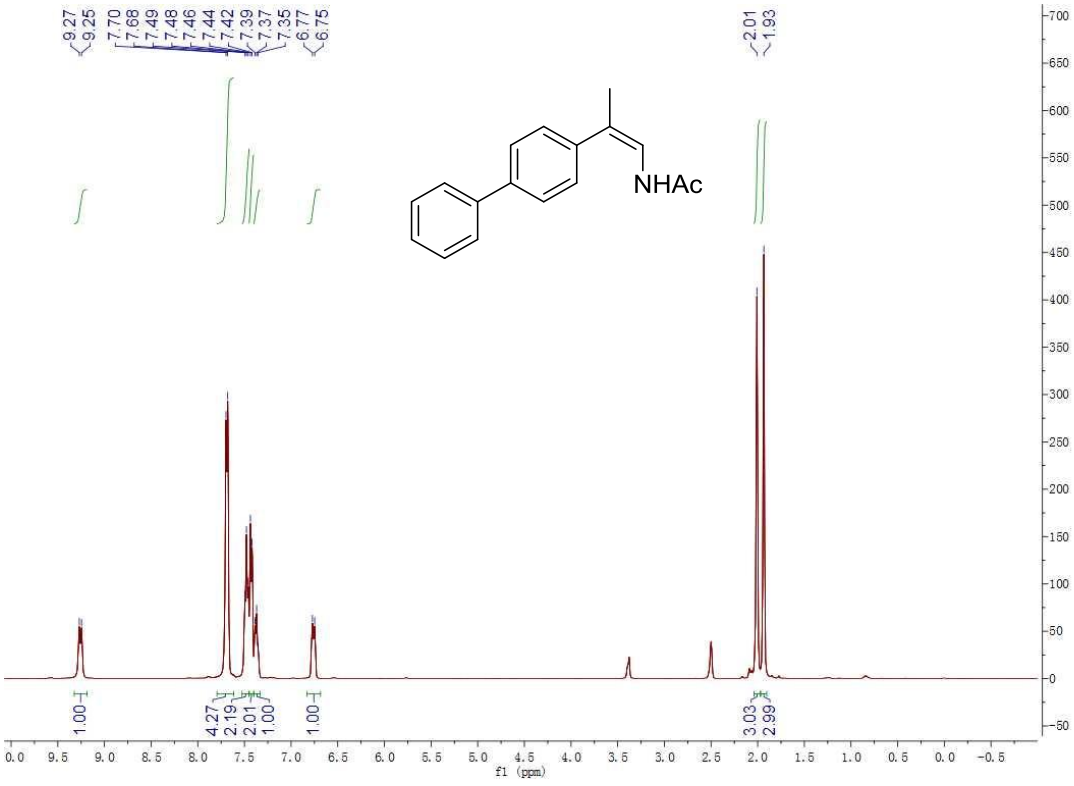


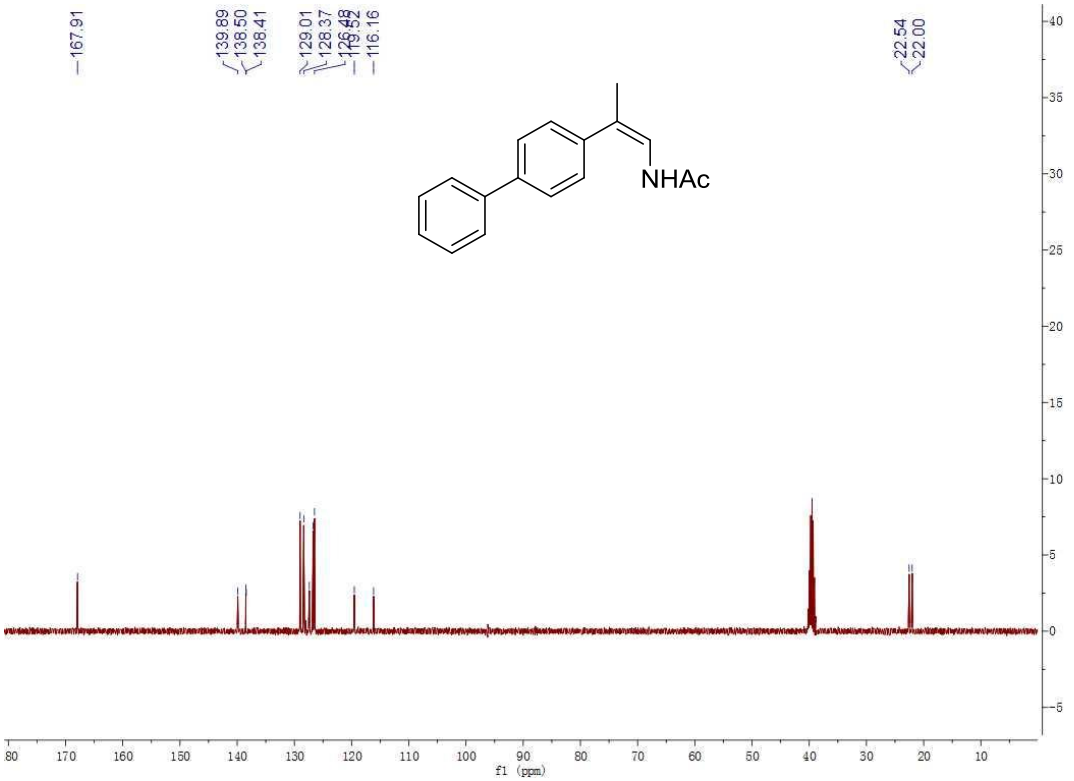
(*Z*)-*N*-(2-(4-bromophenyl)prop-1-en-1-yl)acetamide (1i)



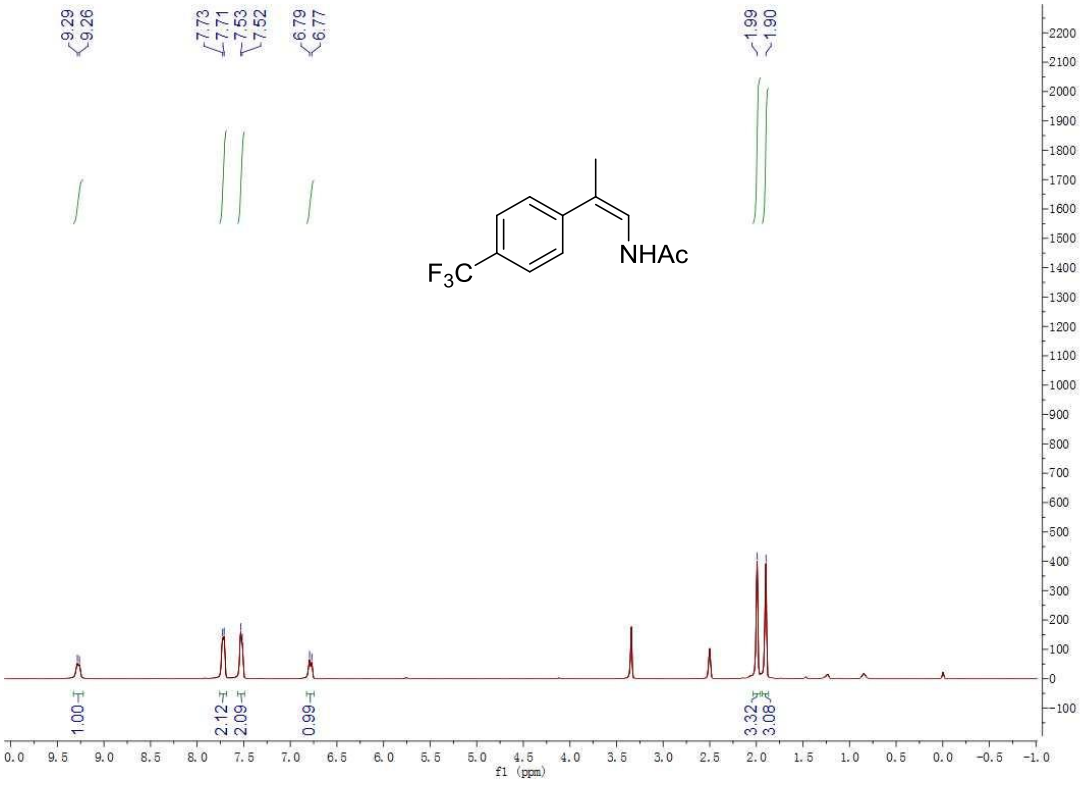


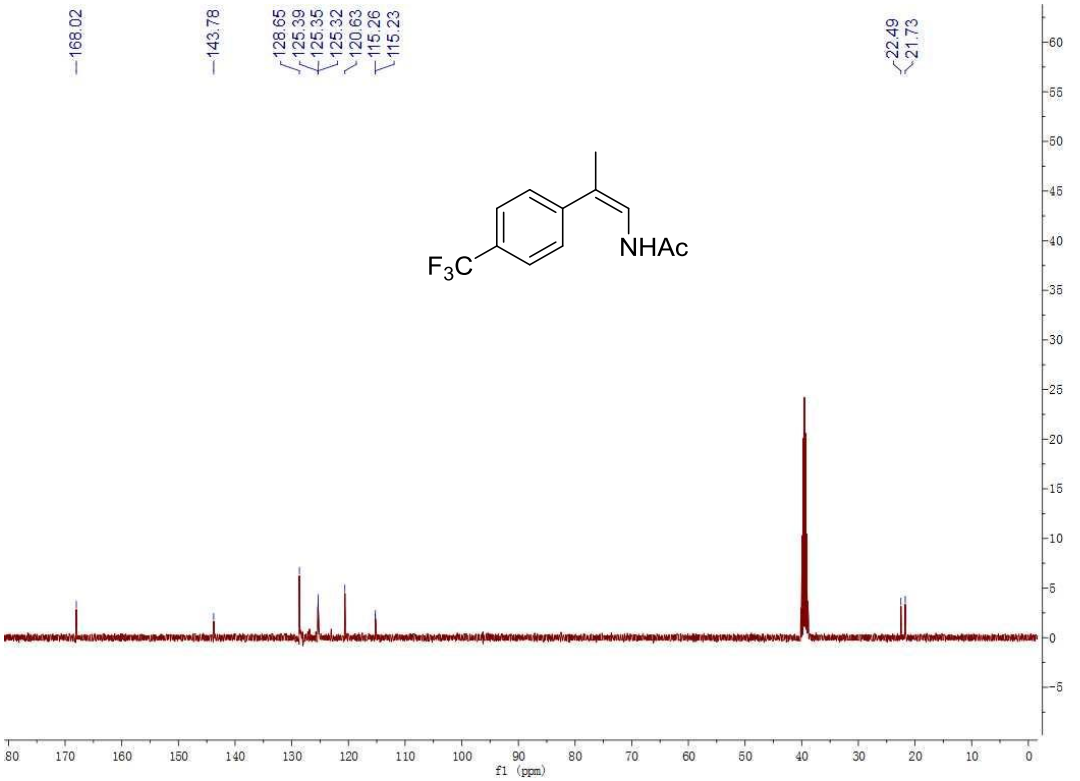
(*Z*)-*N*-(2-([1,1'-biphenyl]-4-yl)prop-1-en-1-yl)acetamide (1j)



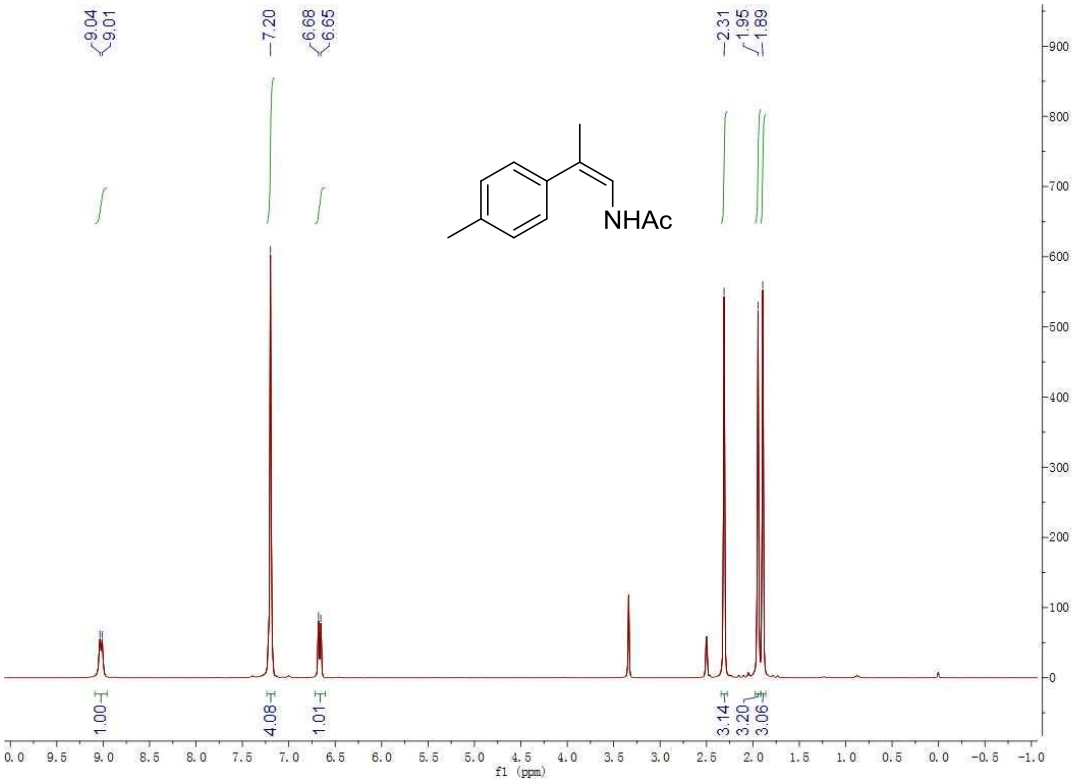


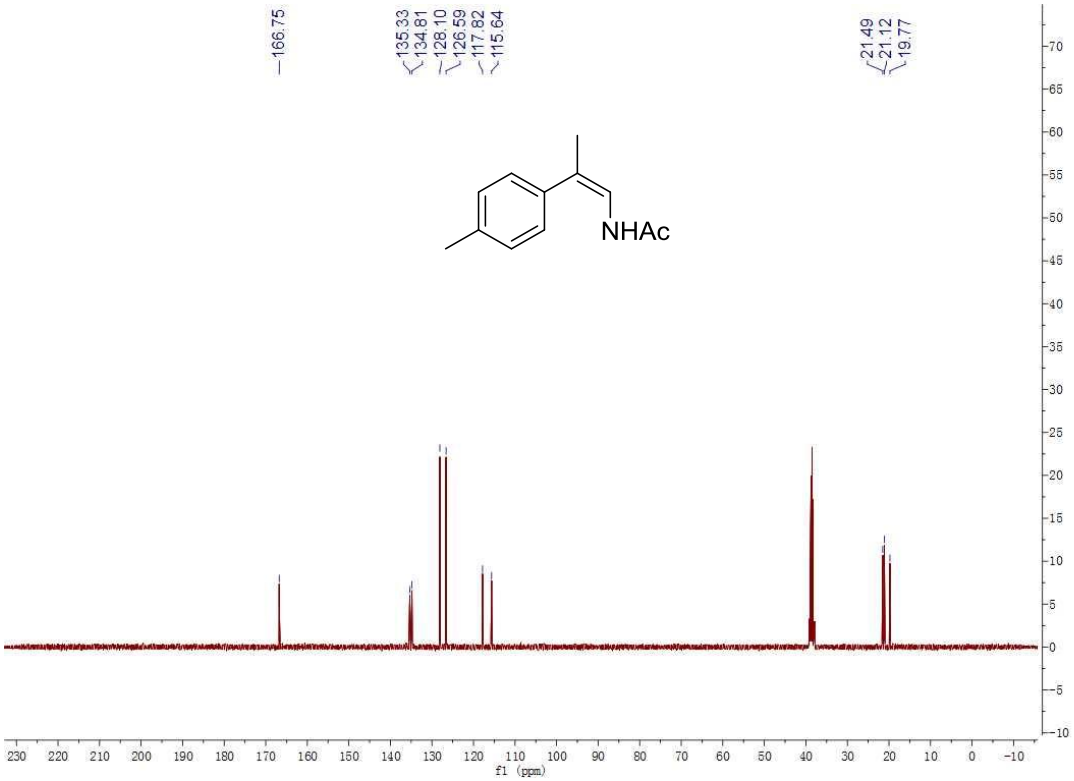
(*Z*)-*N*-(2-(4-(trifluoromethyl)phenyl)prop-1-en-1-yl)acetamide (1k)



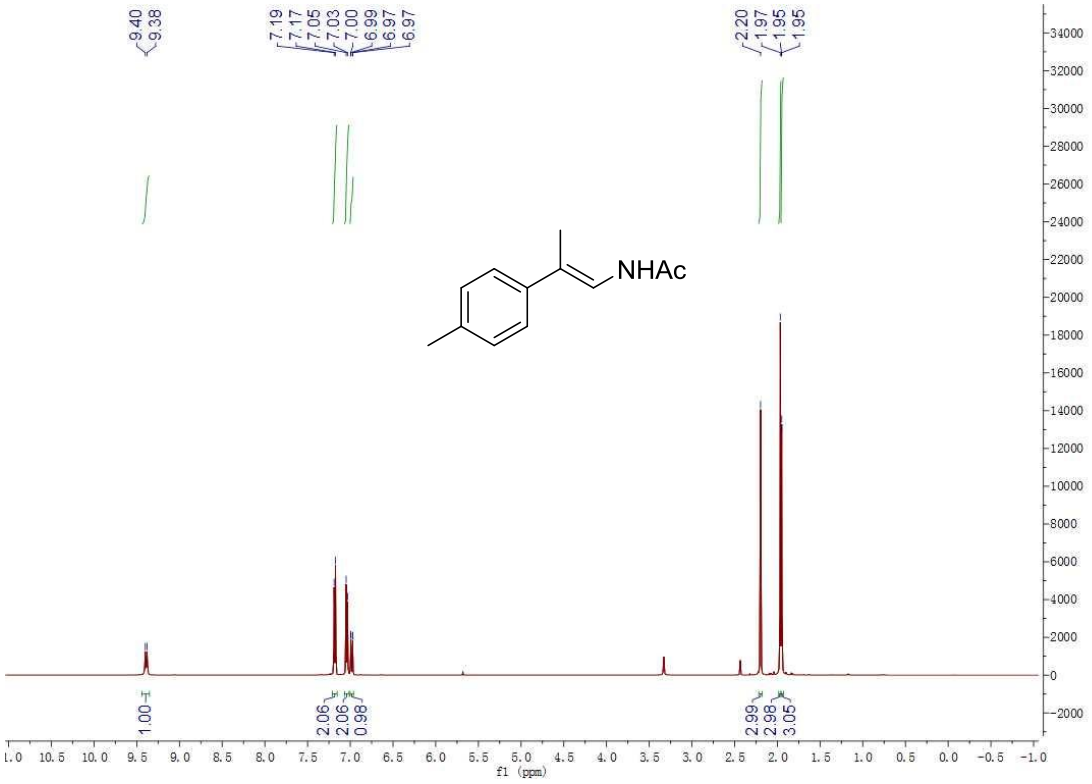


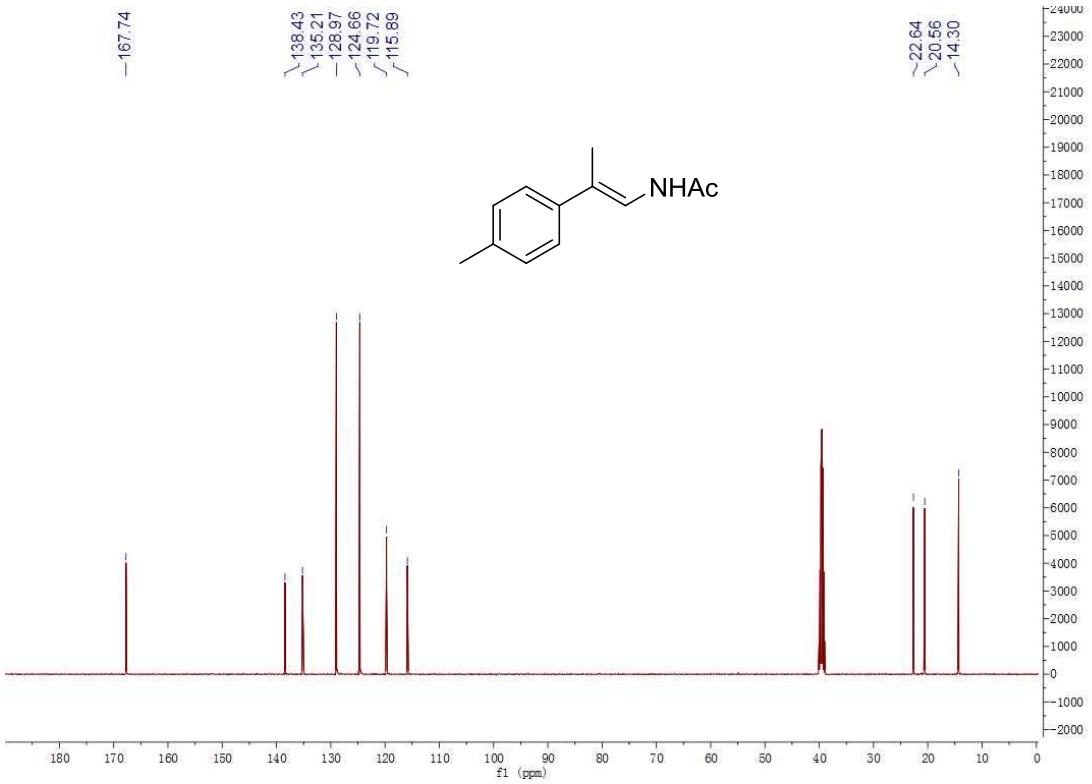
(*Z*)-*N*-(2-(*p*-tolyl)prop-1-en-1-yl)acetamide (1l)



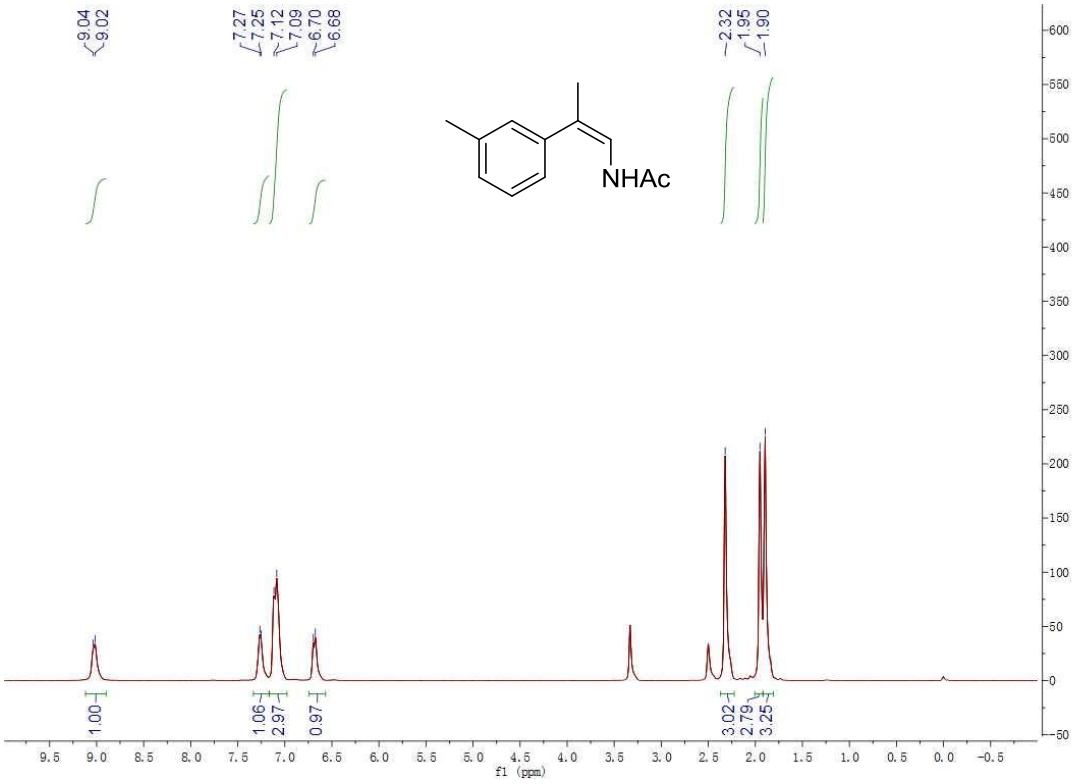


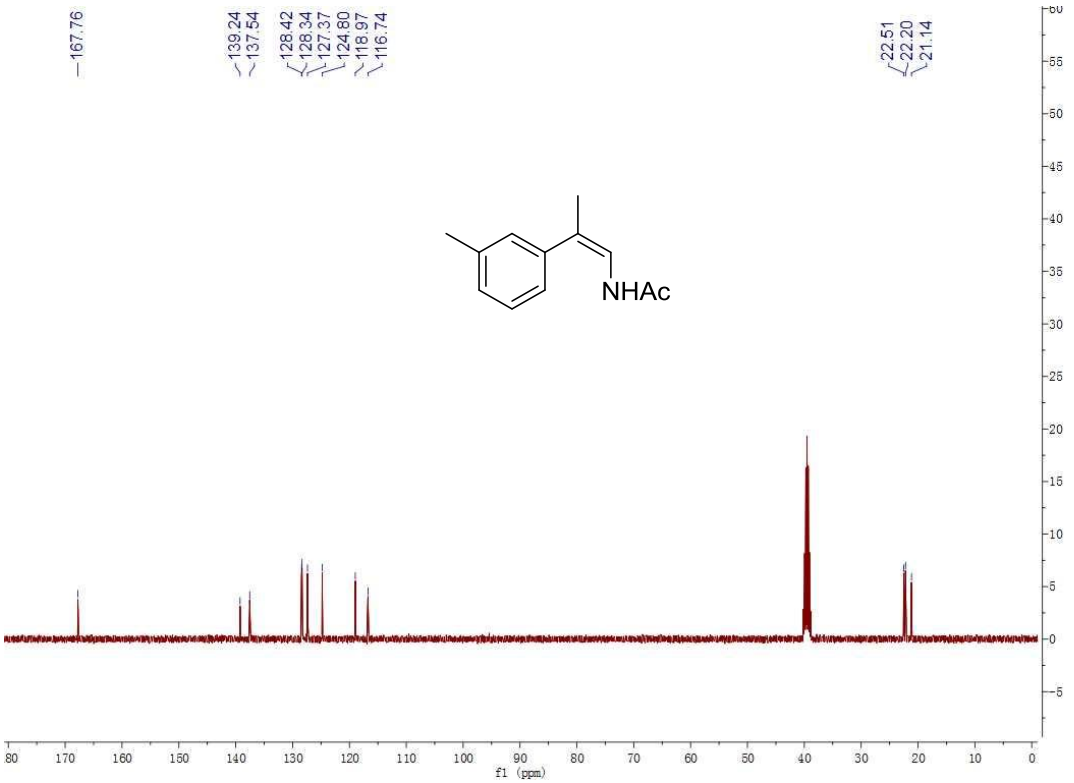
(*E*)-*N*-(2-(*p*-tolyl)prop-1-en-1-yl)acetamide (1l')



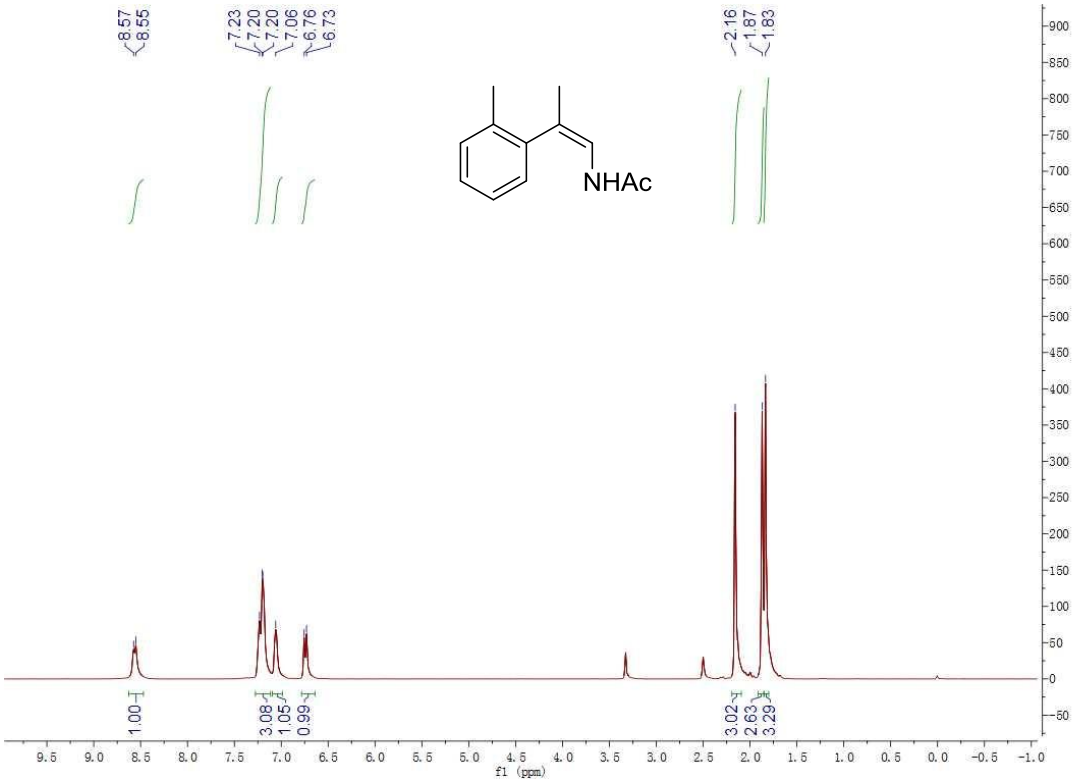


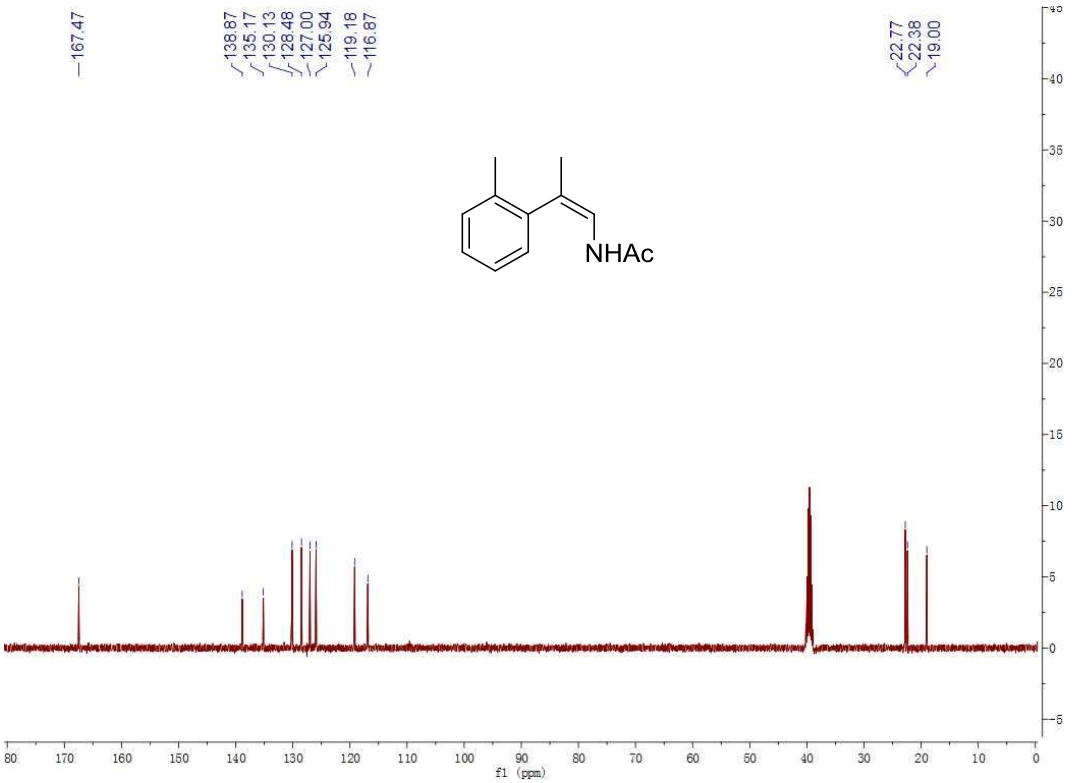
(*Z*)-*N*-(2-(*m*-tolyl)prop-1-en-1-yl)acetamide (1m)



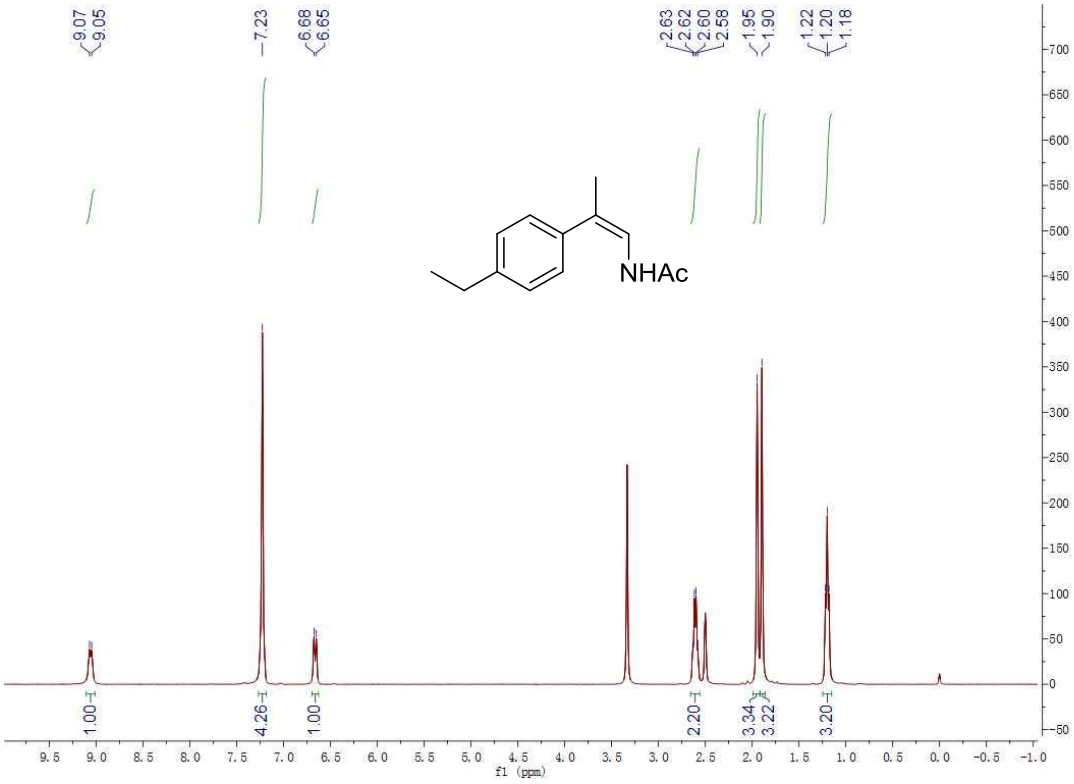


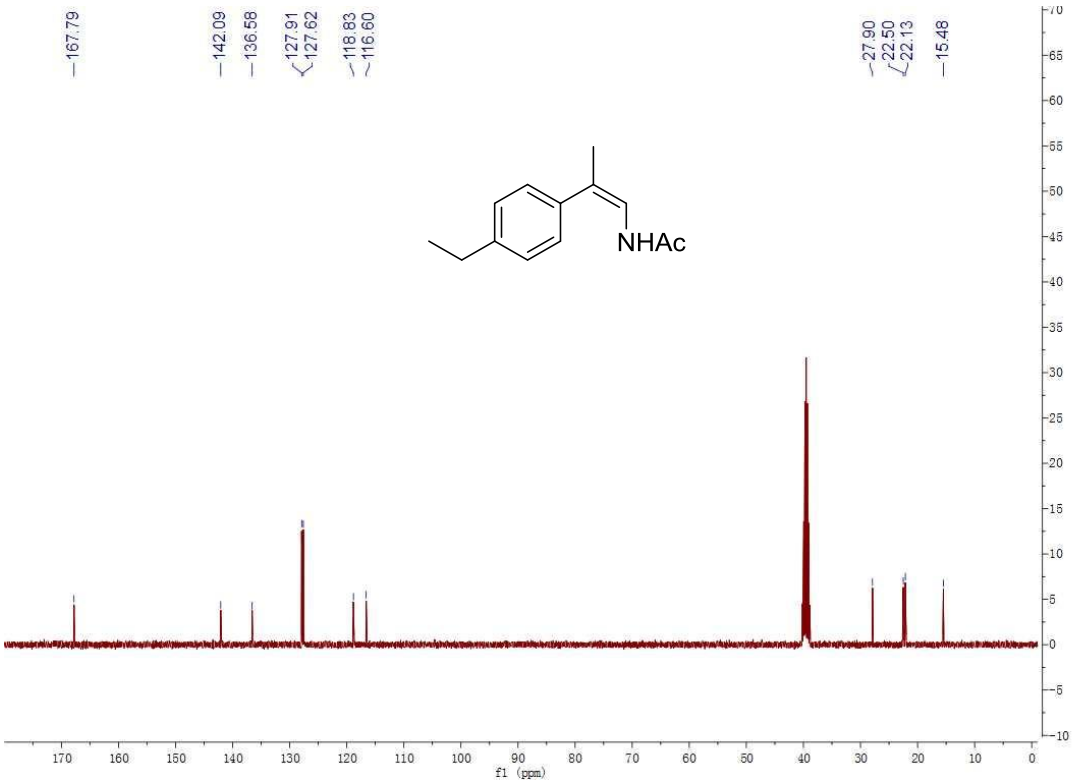
(*Z*)-*N*-(2-(*o*-tolyl)prop-1-en-1-yl)acetamide (1n)



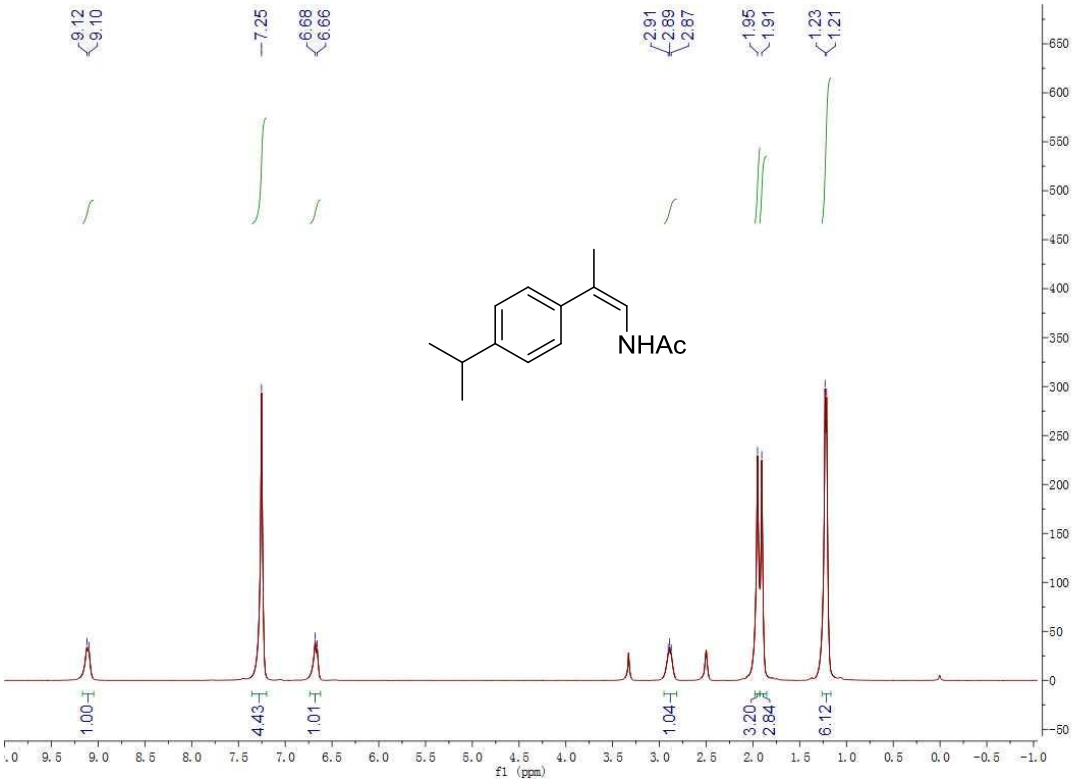


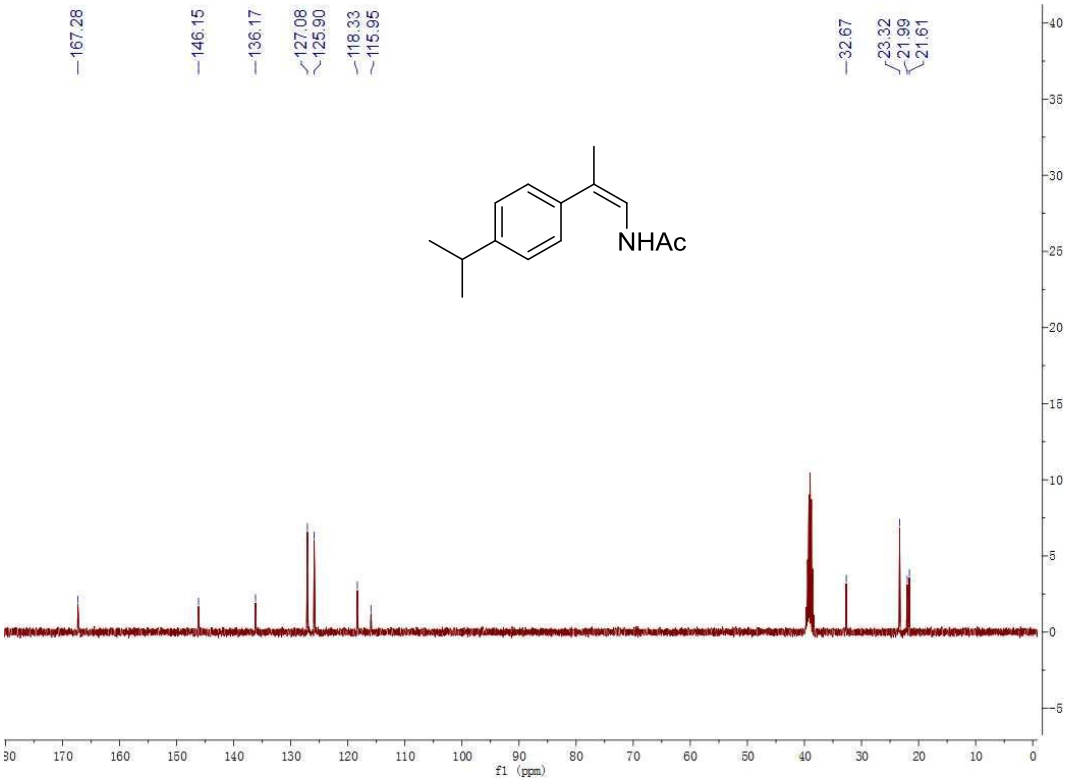
(*Z*)-*N*-(2-(4-ethylphenyl)prop-1-en-1-yl)acetamide (1o)



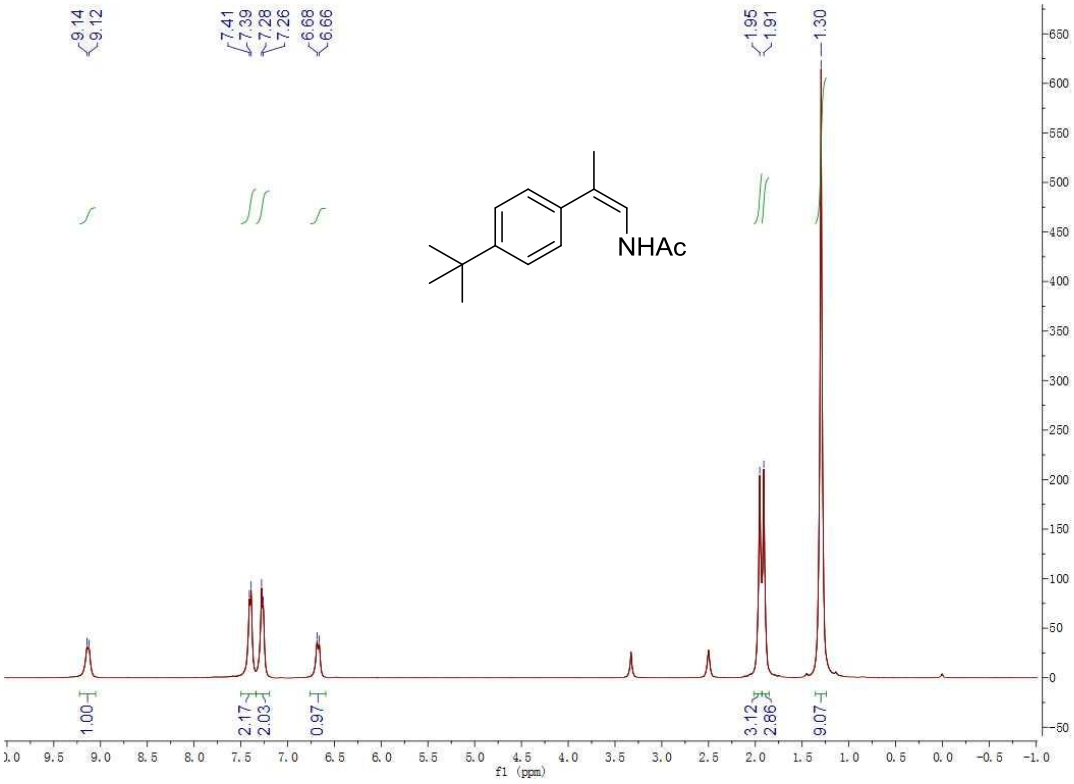


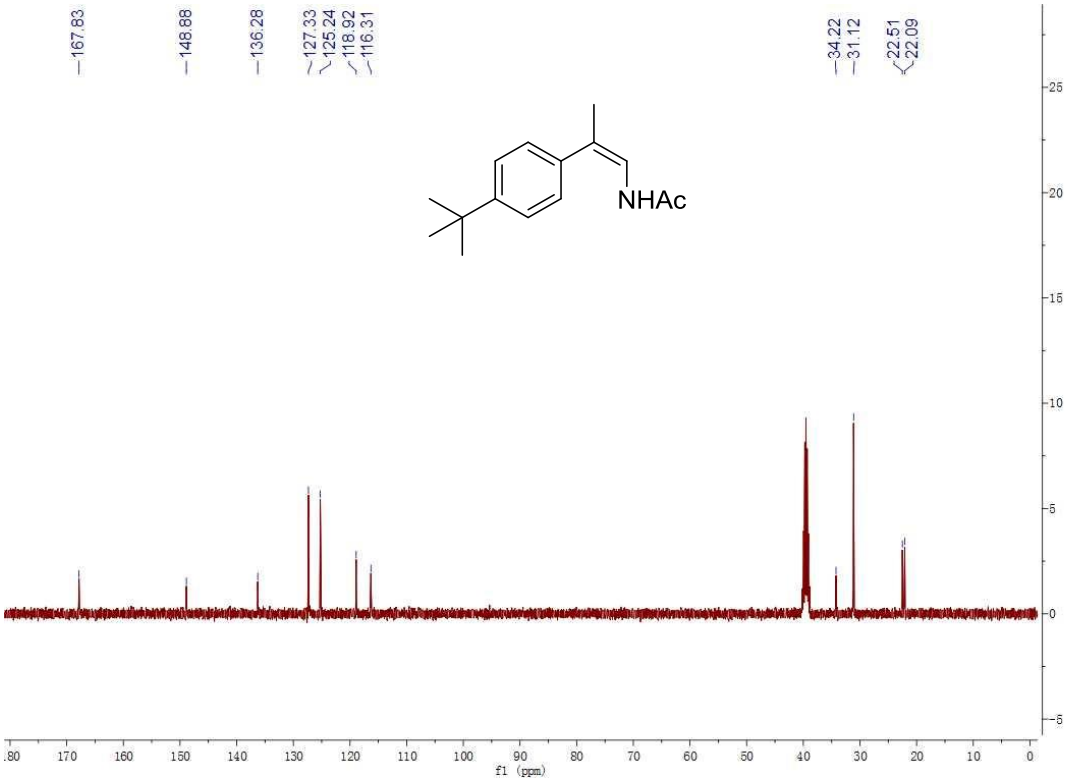
(*Z*)-*N*-(2-(4-isopropylphenyl)prop-1-en-1-yl)acetamide (1p)



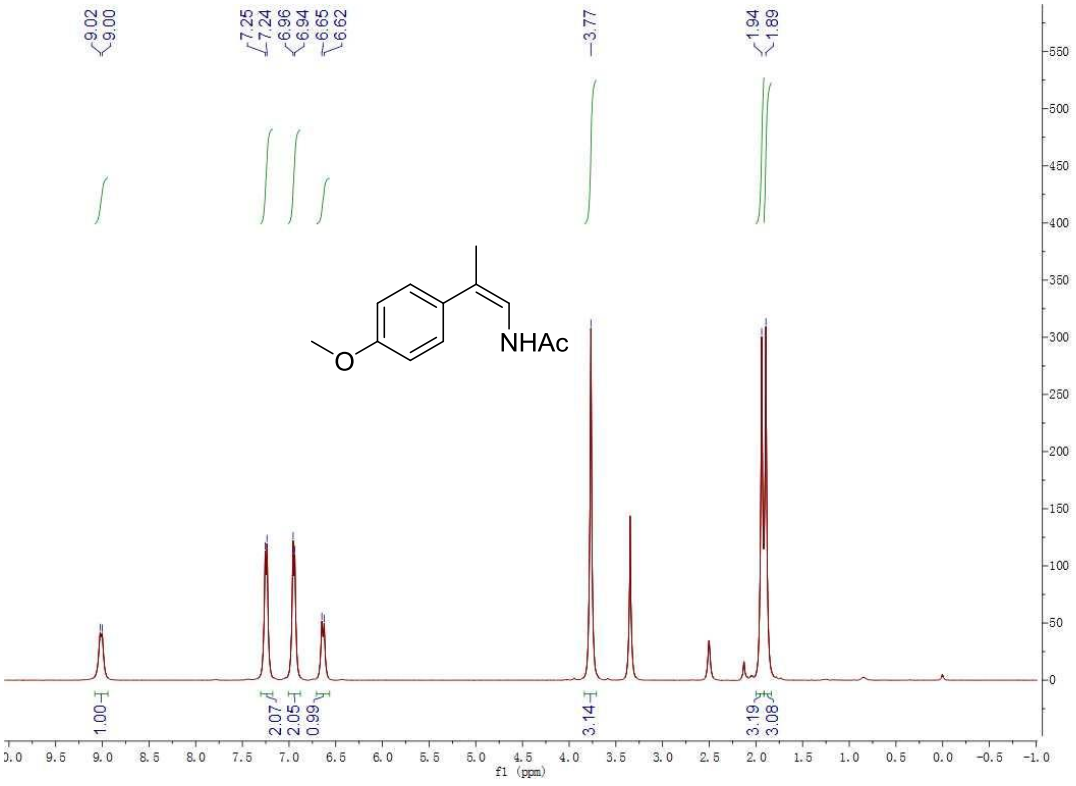


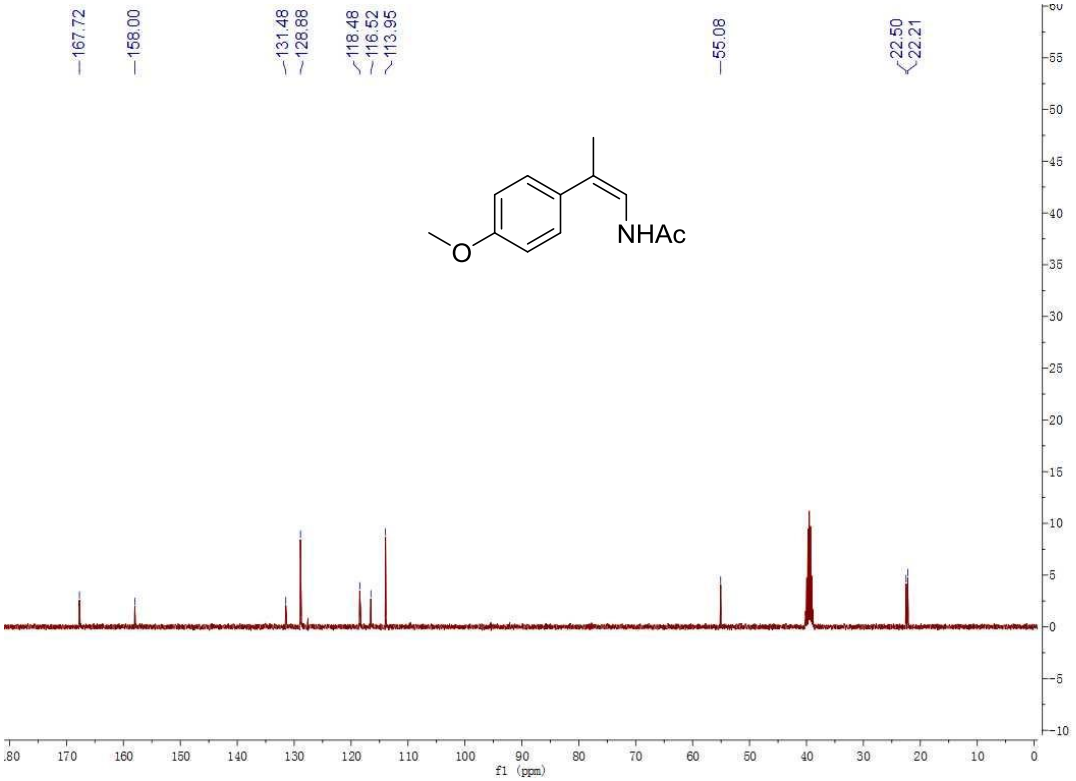
(*Z*)-*N*-(2-(4-(*tert*-butyl)phenyl)prop-1-en-1-yl)acetamide (1q)



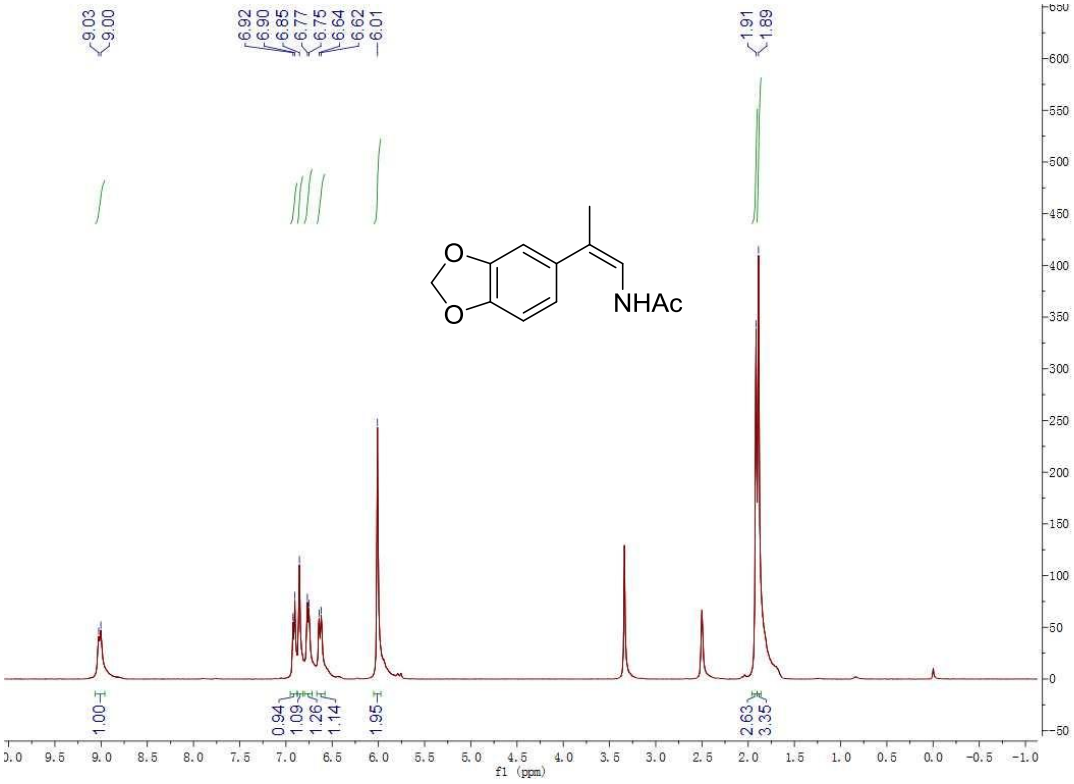


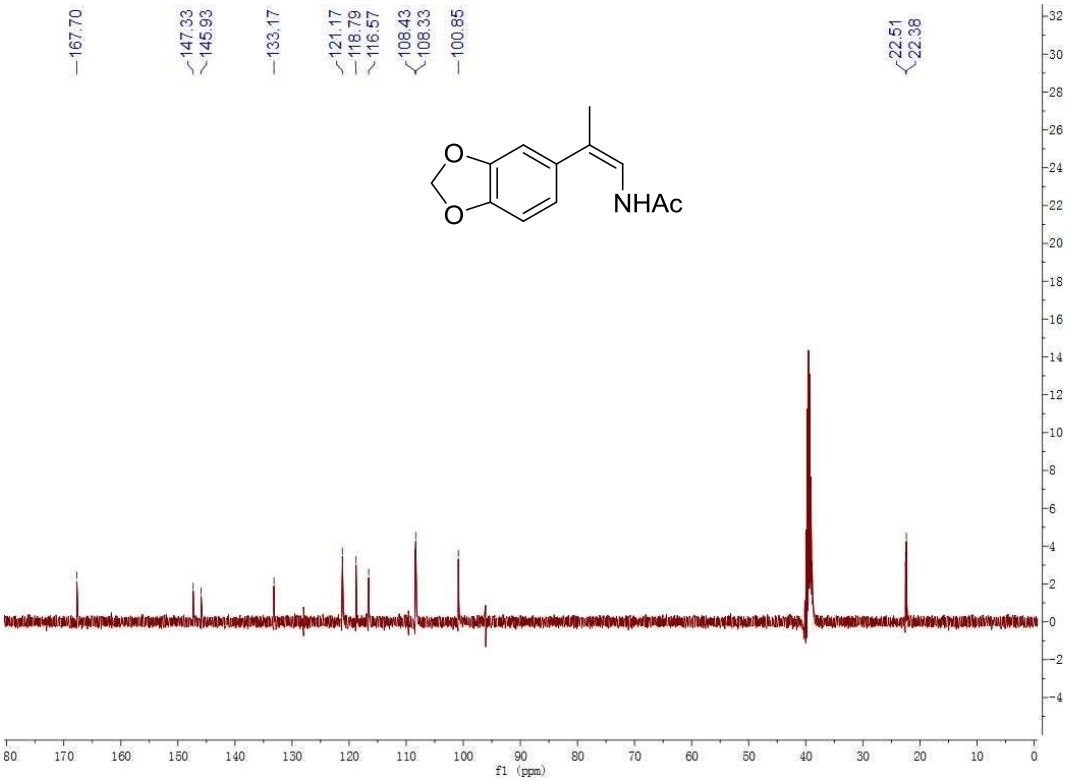
(*Z*)-*N*-(2-(4-methoxyphenyl)prop-1-en-1-yl)acetamide (1r)



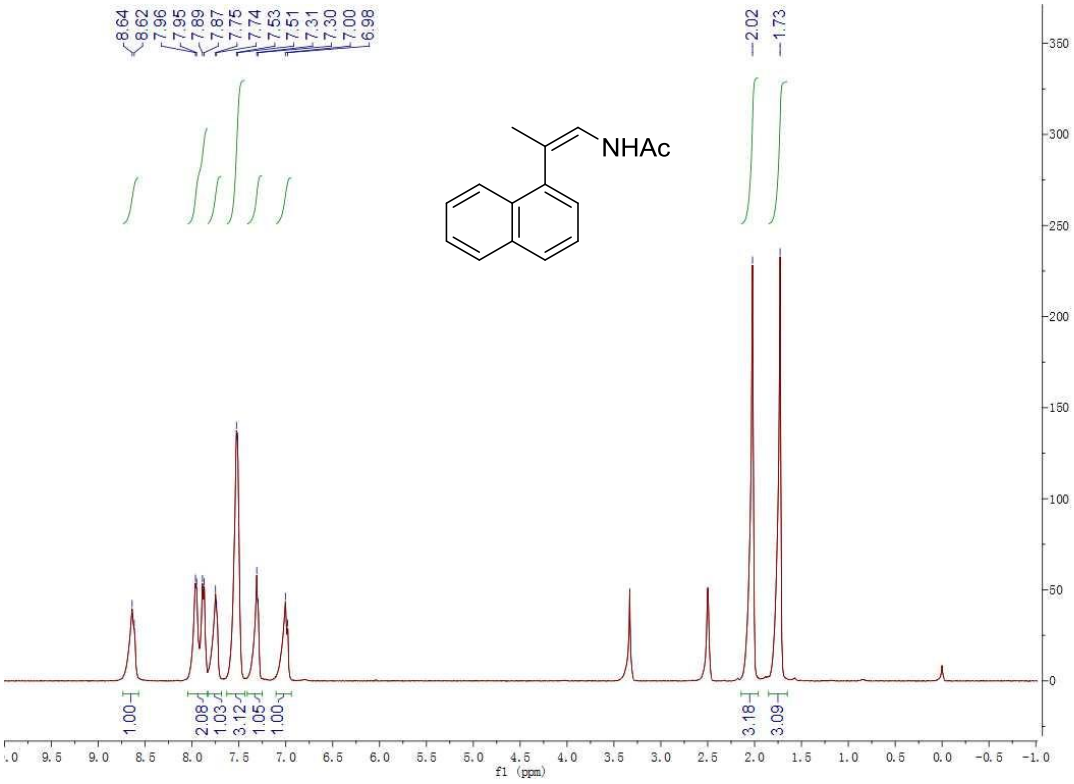


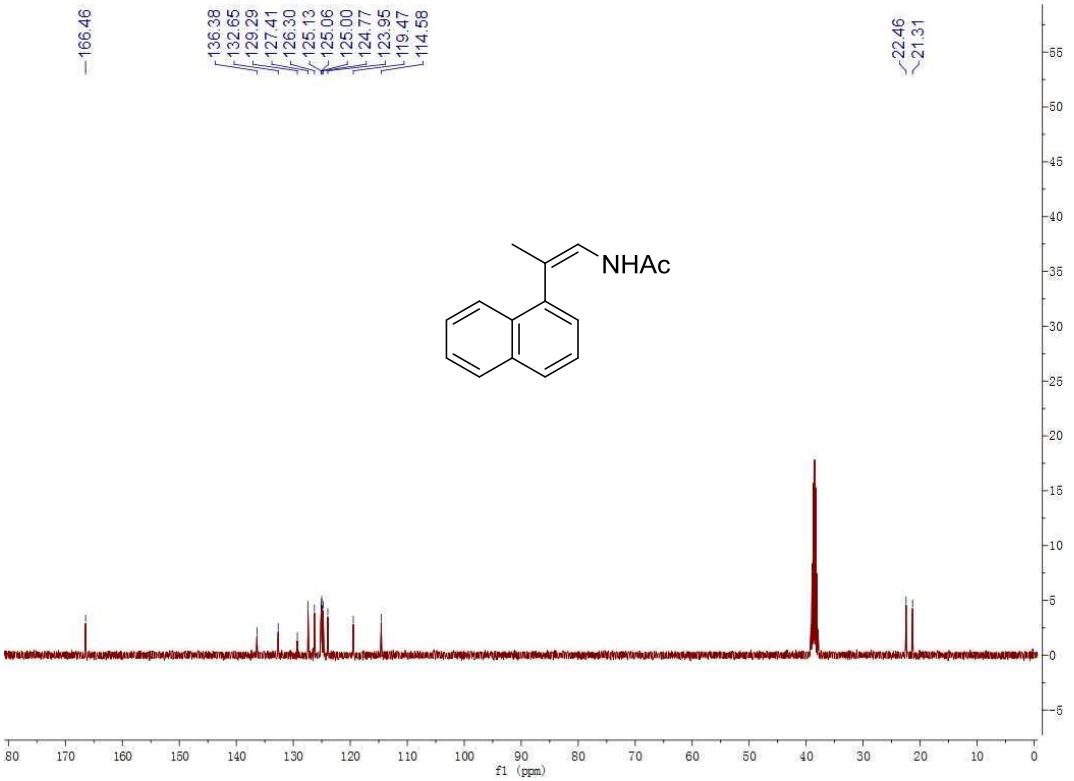
(*Z*)-*N*-(2-(benzo[*d*][1,3]dioxol-5-yl)prop-1-en-1-yl)acetamide (1s)



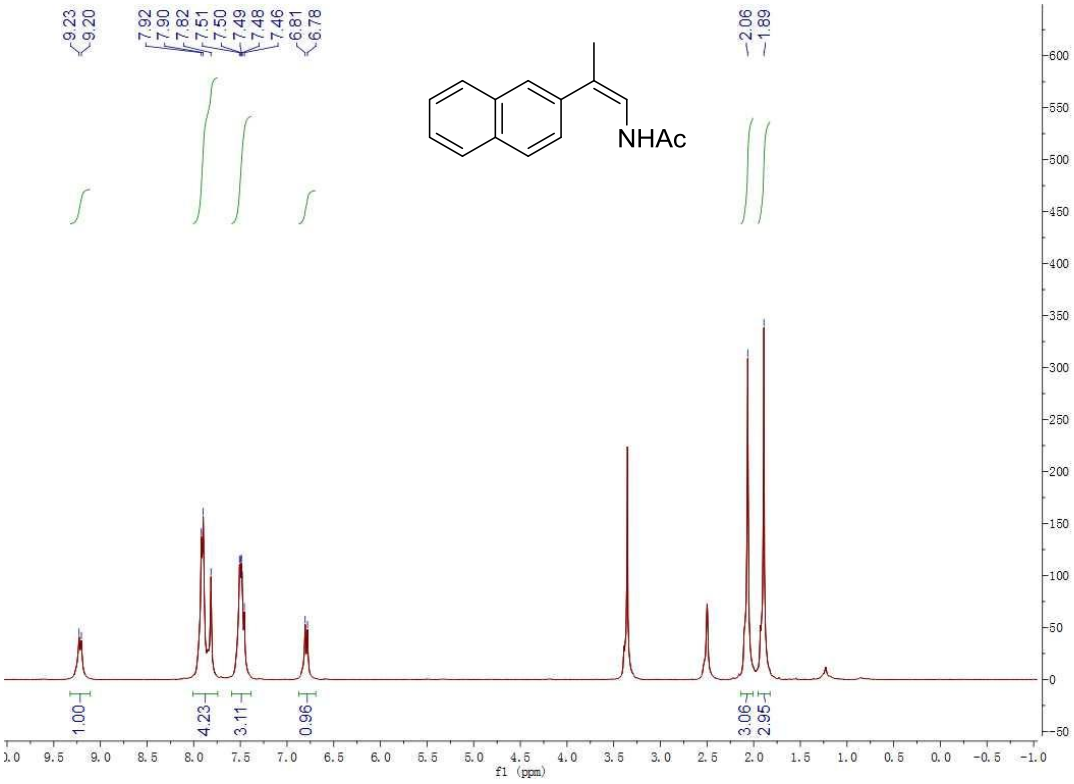


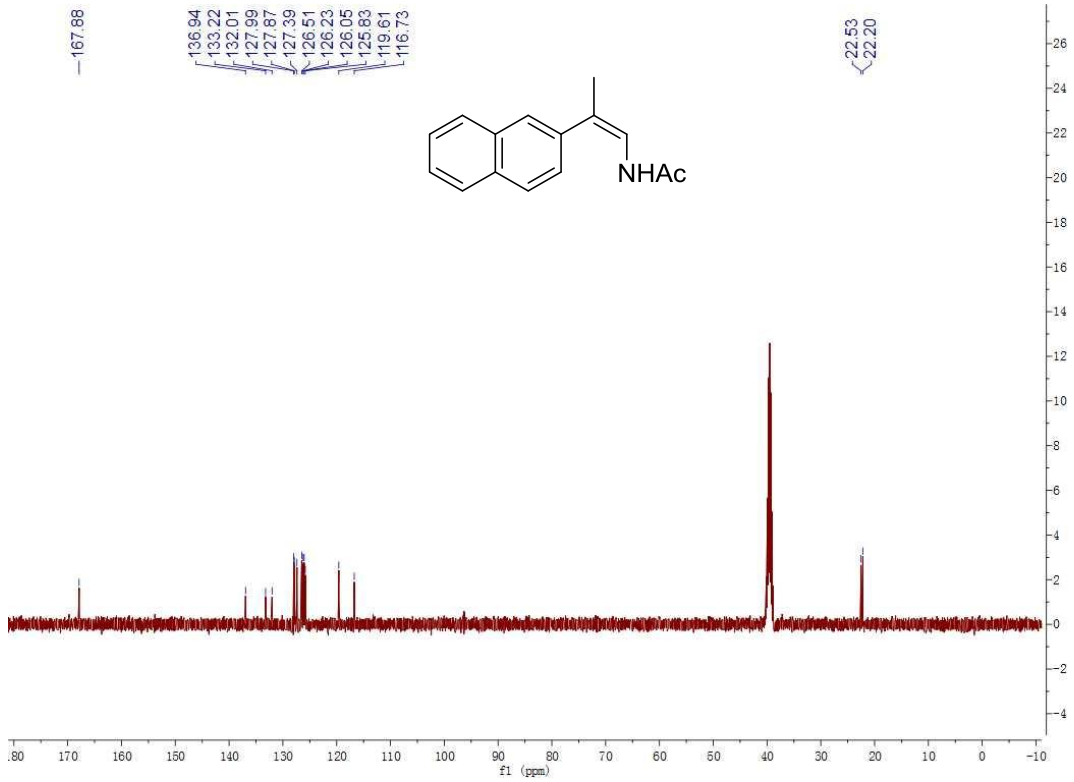
(*Z*)-*N*-(2-(naphthalen-1-yl)prop-1-en-1-yl)acetamide (1t)



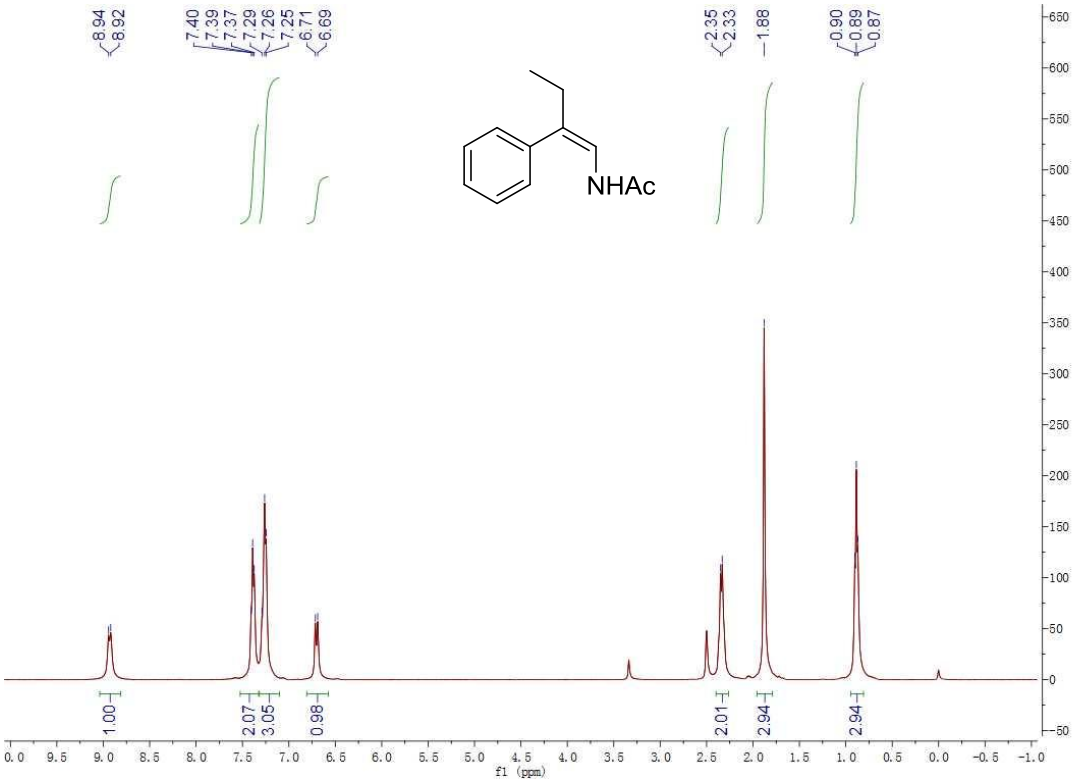


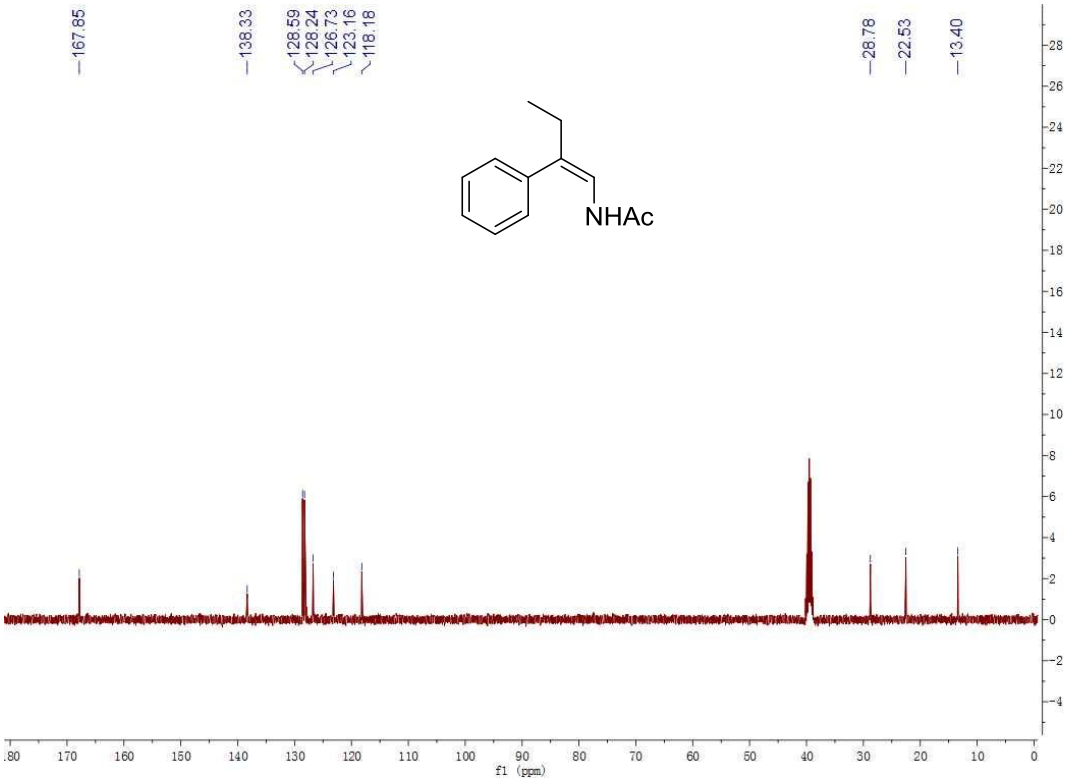
(*Z*)-*N*-(2-(naphthalen-2-yl)prop-1-en-1-yl)acetamide (1u)



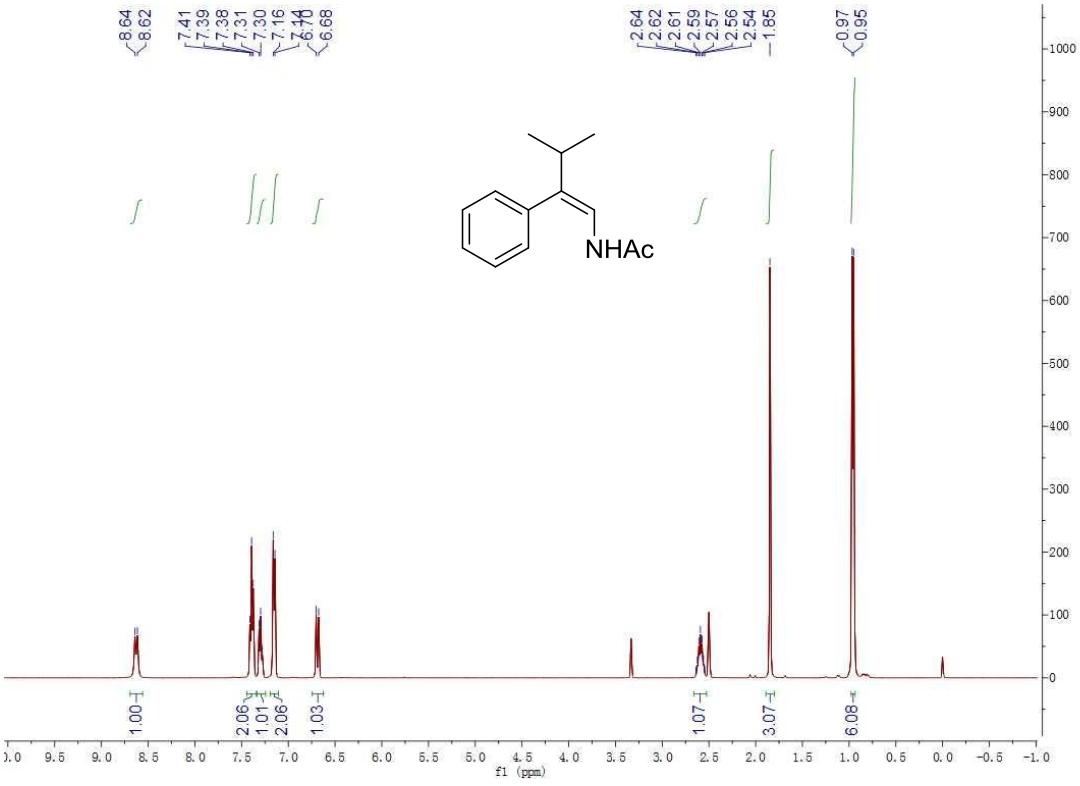


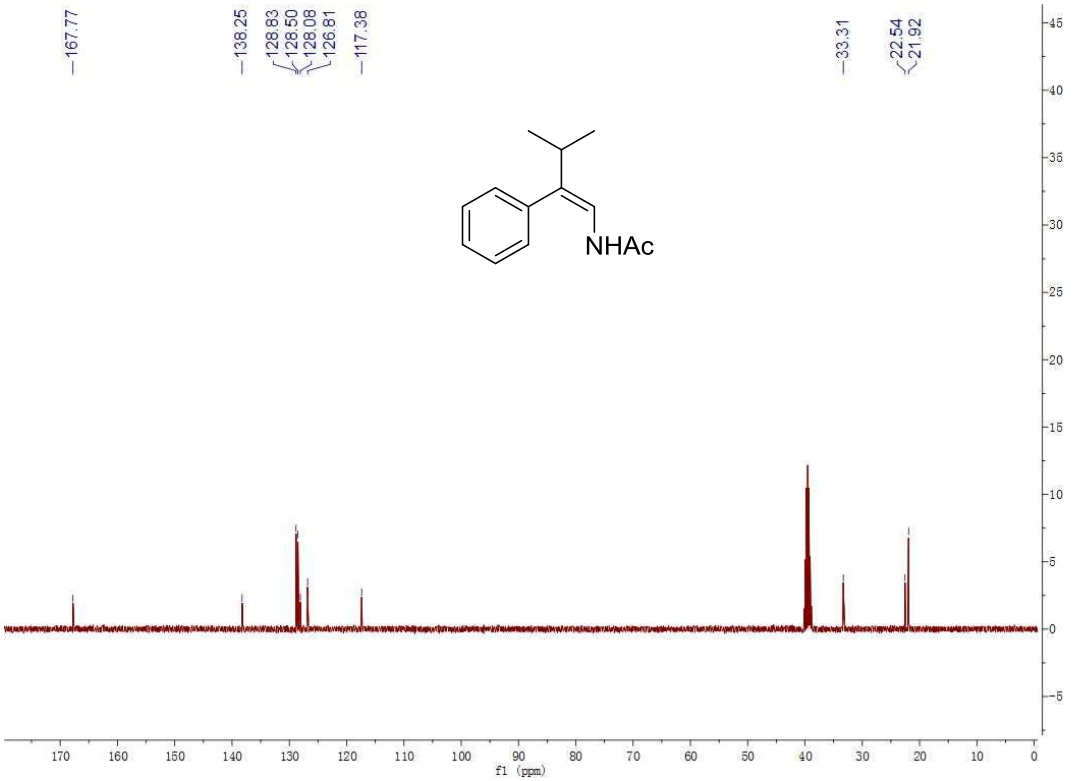
(*Z*)-*N*-(2-phenylbut-1-en-1-yl)acetamide (1v)



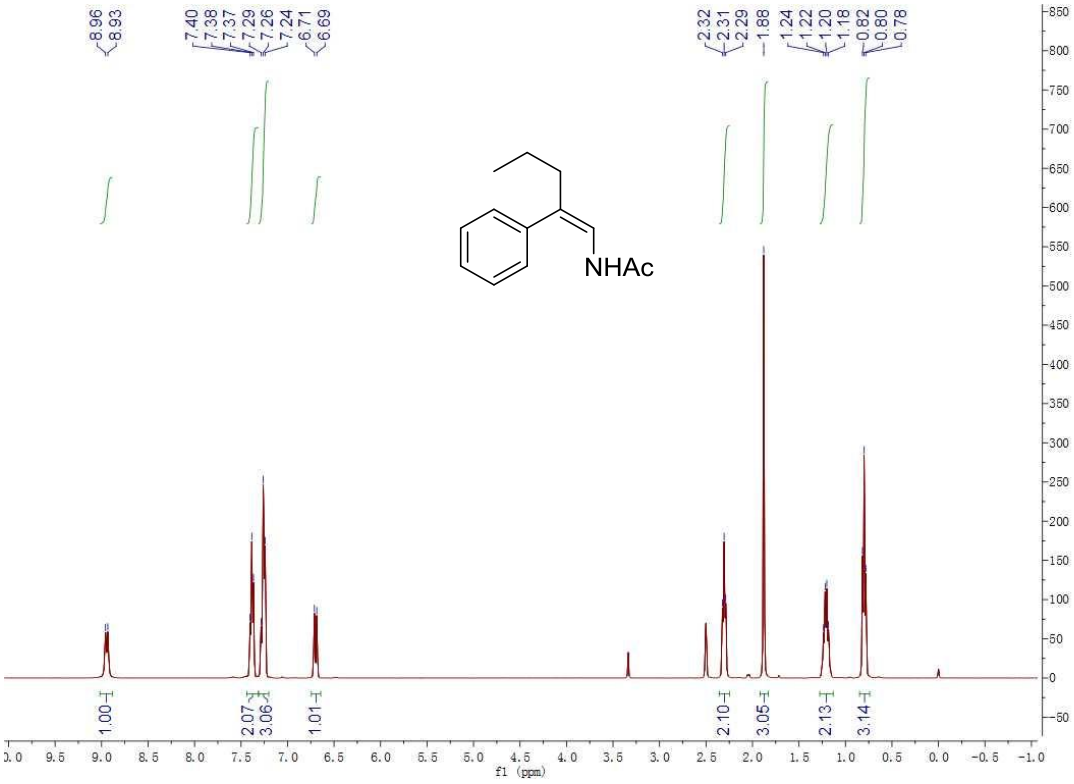


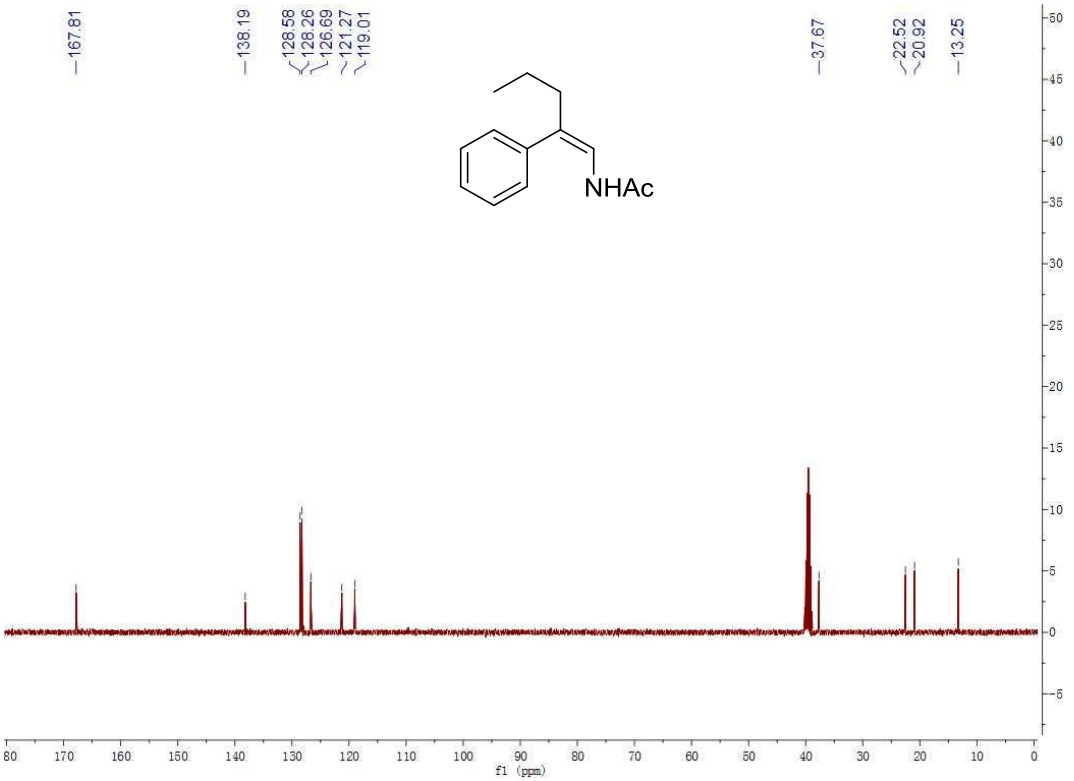
(*Z*)-*N*-(3-methyl-2-phenylbut-1-en-1-yl)acetamide (1w)



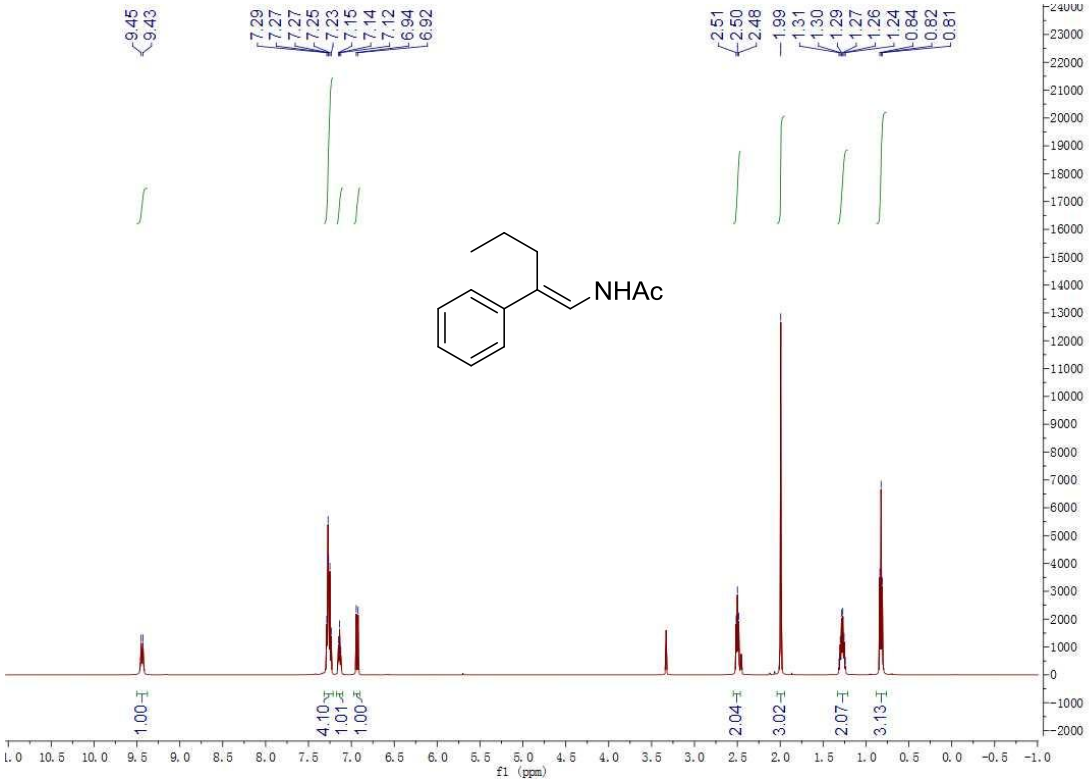


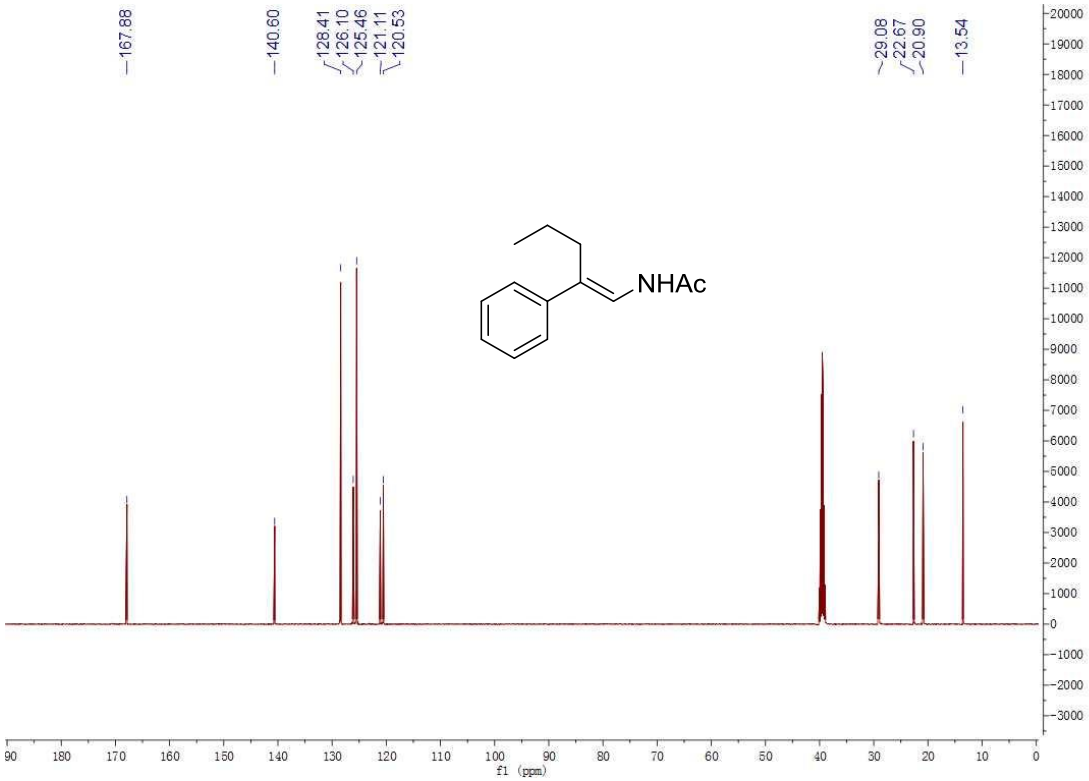
(*Z*)-*N*-(2-phenylpent-1-en-1-yl)acetamide (1x)



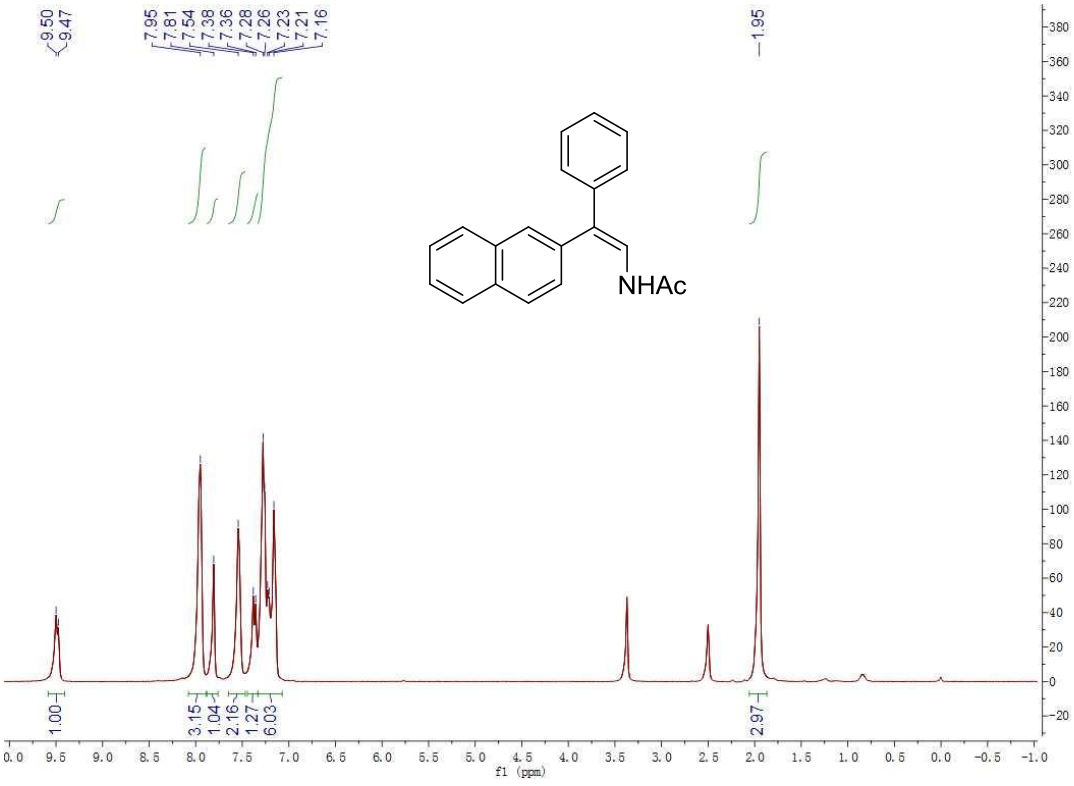


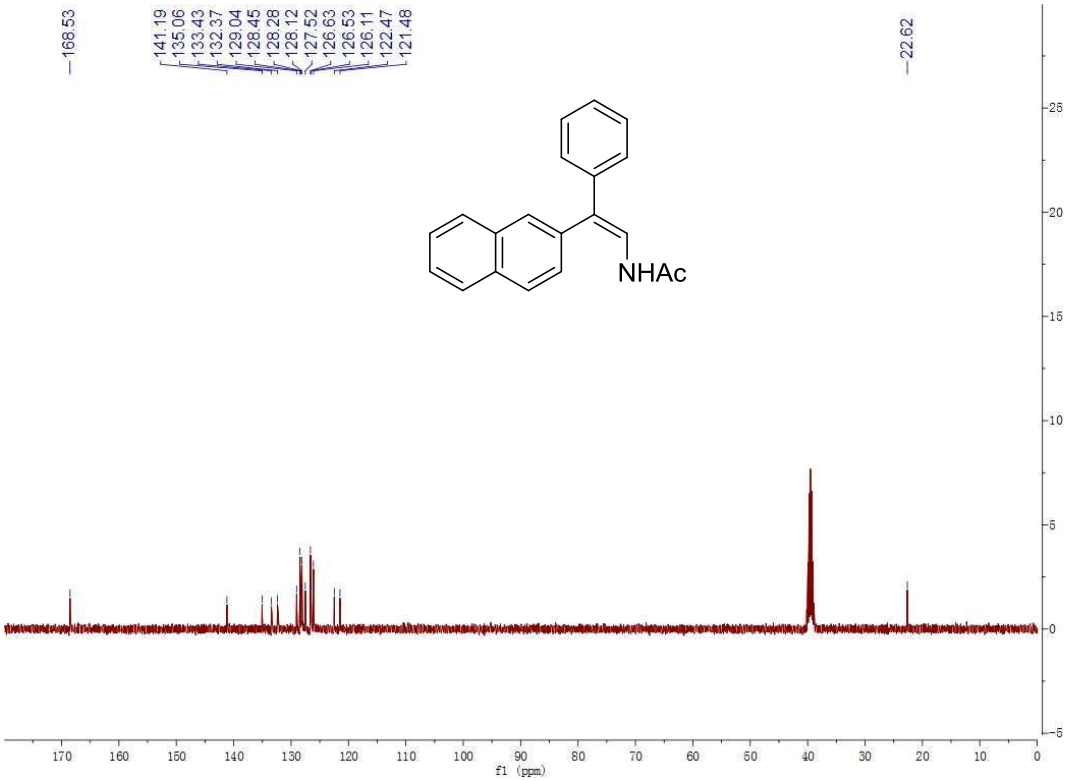
(*E*)-*N*-(2-phenylpent-1-en-1-yl)acetamide (1x')



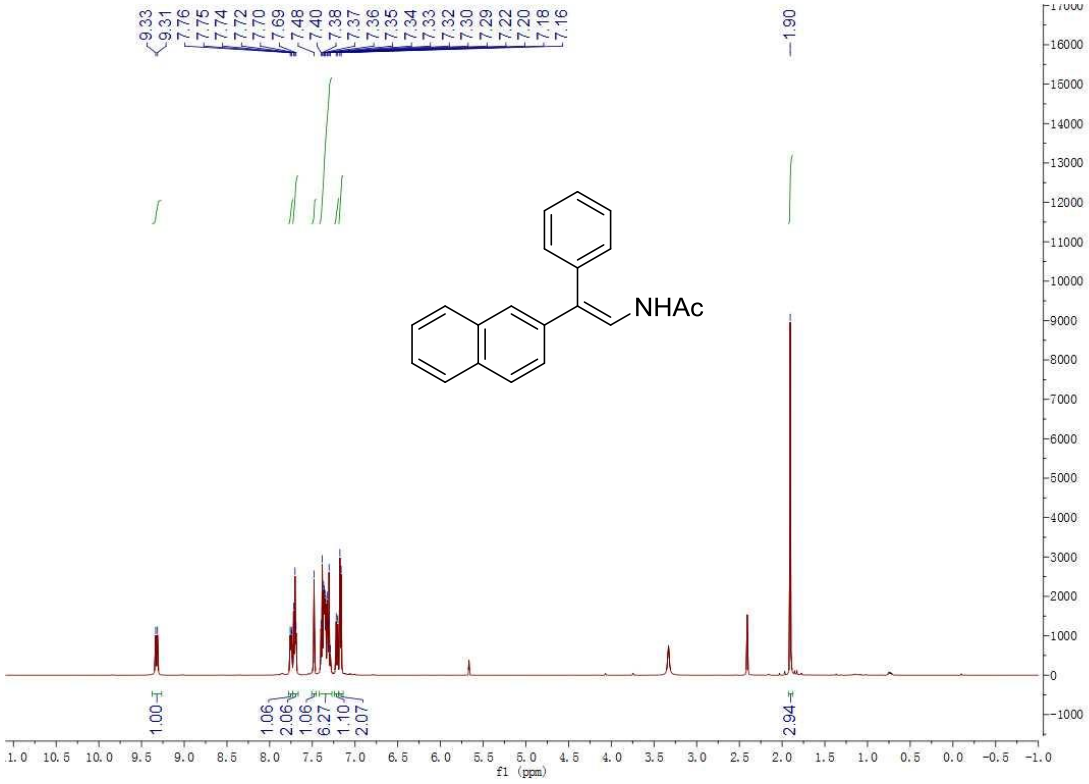


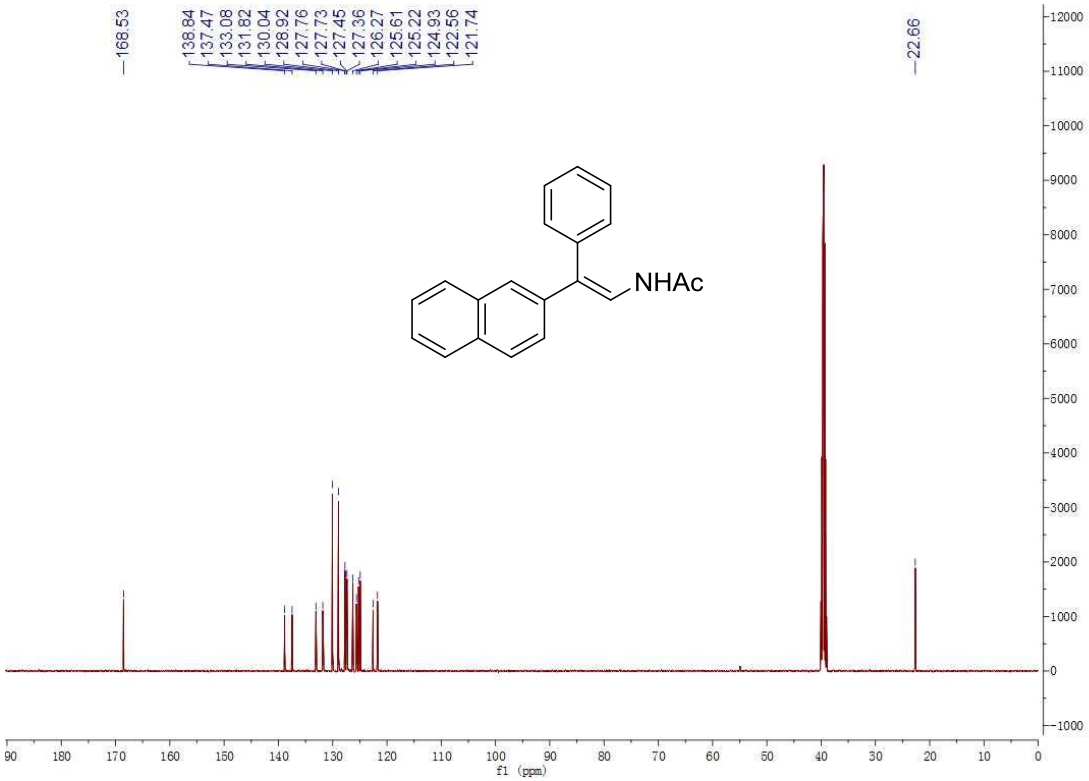
(*Z*)-*N*-(2-(naphthalen-2-yl)-2-phenylvinyl)acetamide (1y)



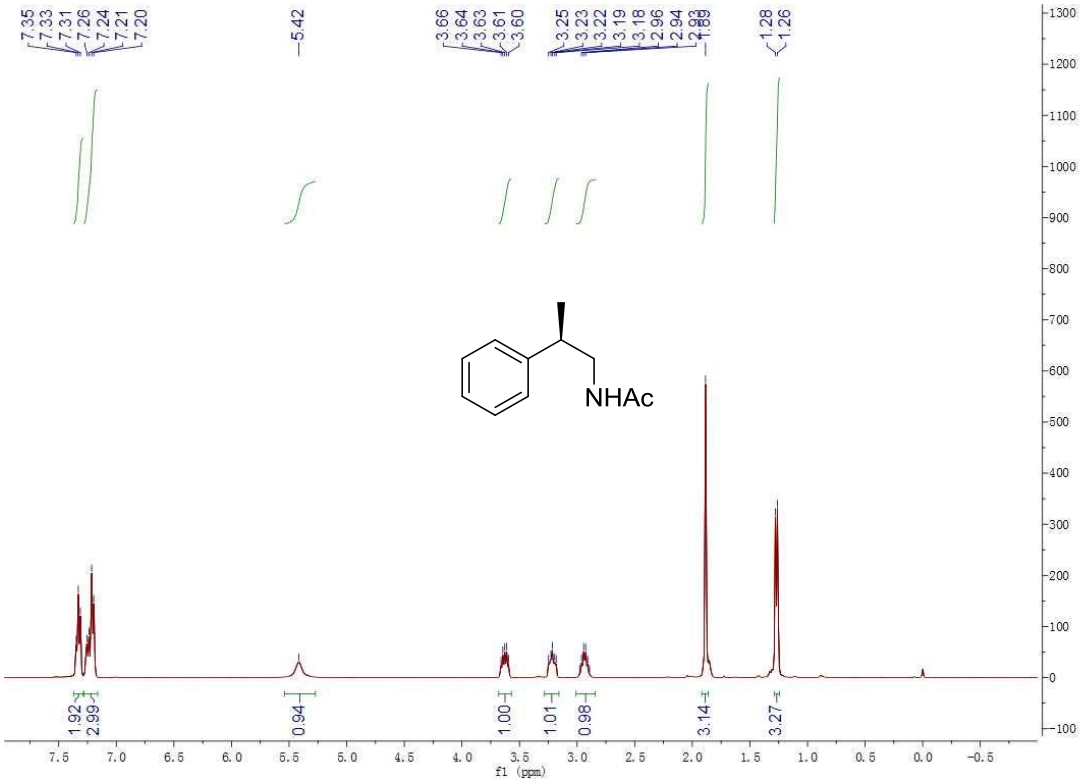


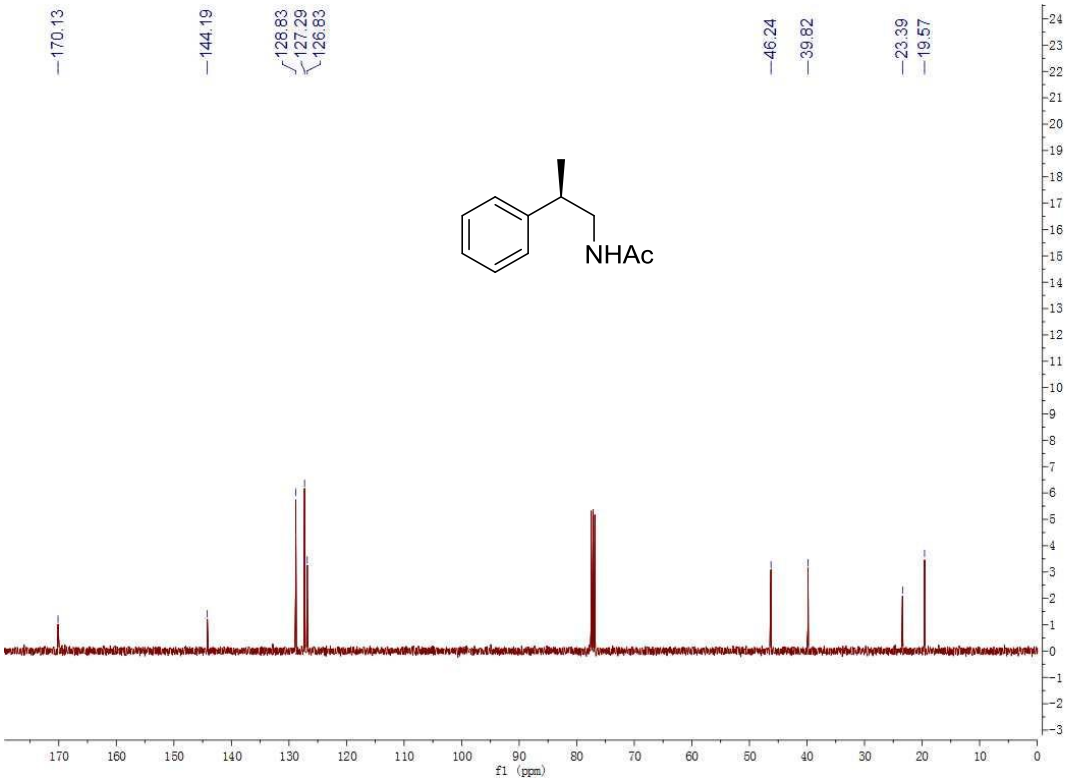
(*E*)-*N*-(2-(naphthalen-2-yl)-2-phenylvinyl)acetamide (1y')



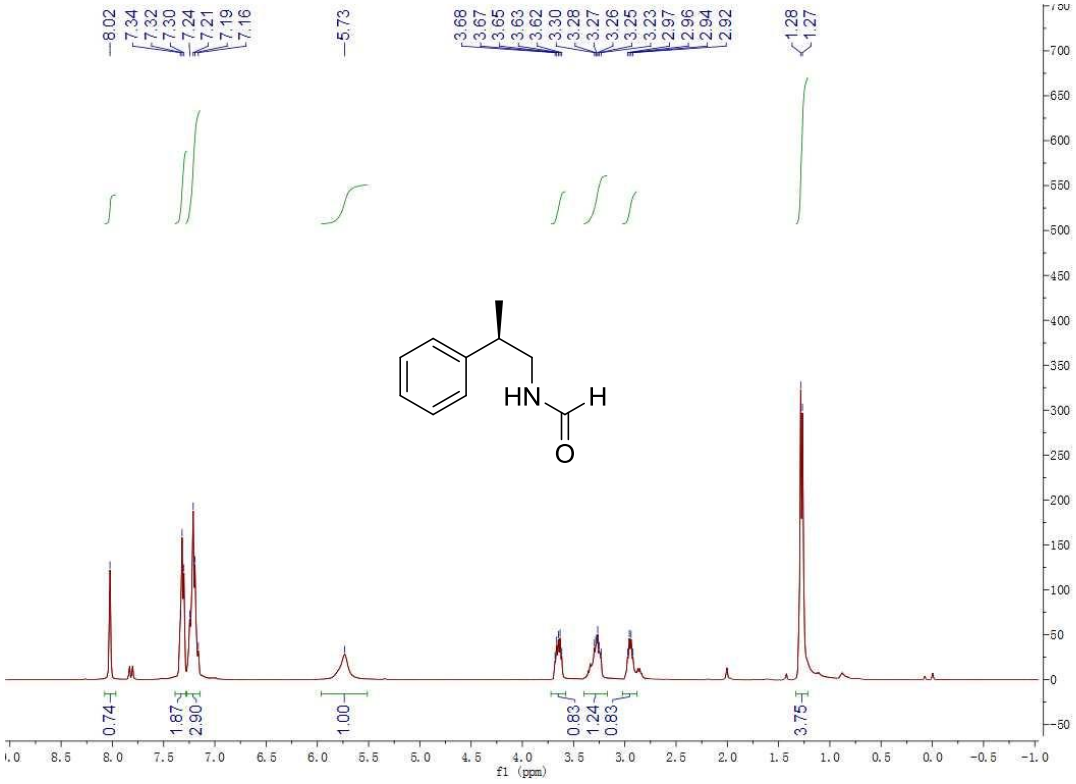


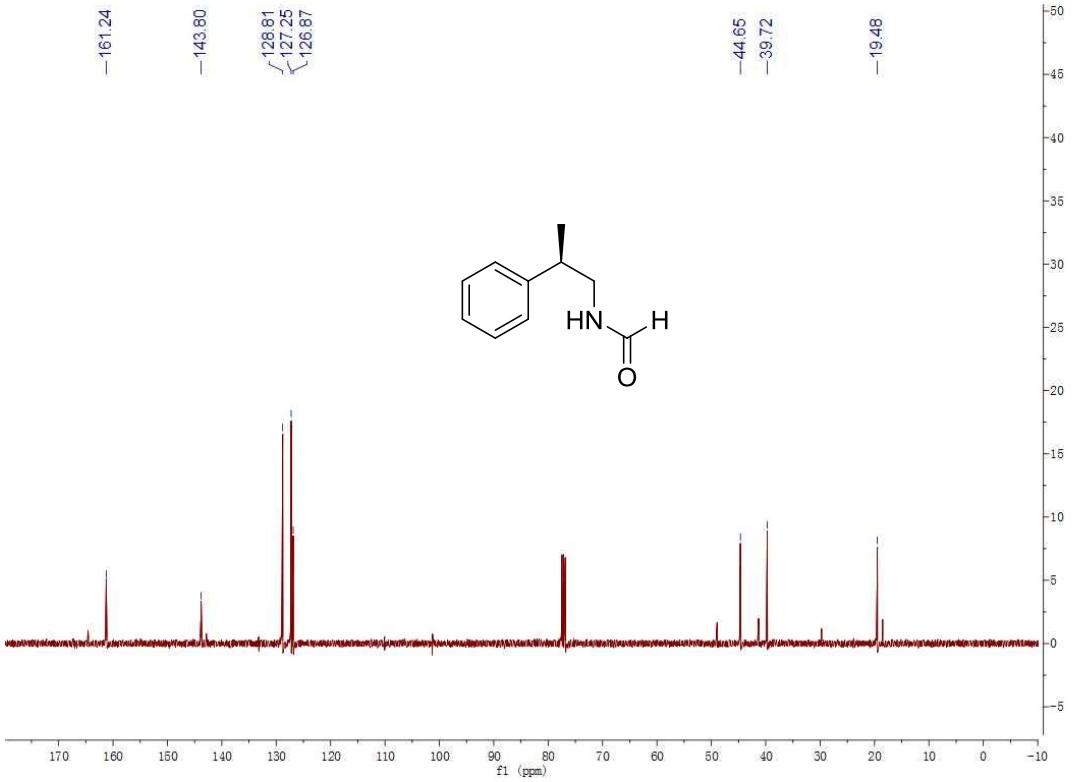
(*R*)-*N*-(2-phenylpropyl)acetamide (2a)



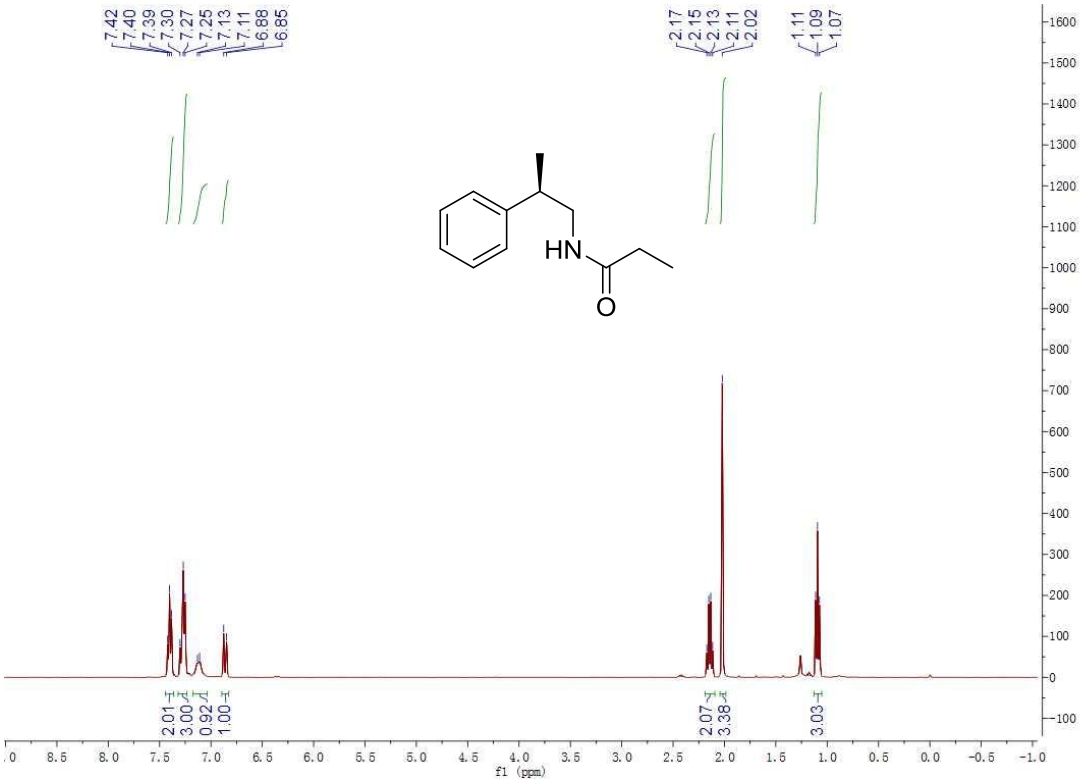


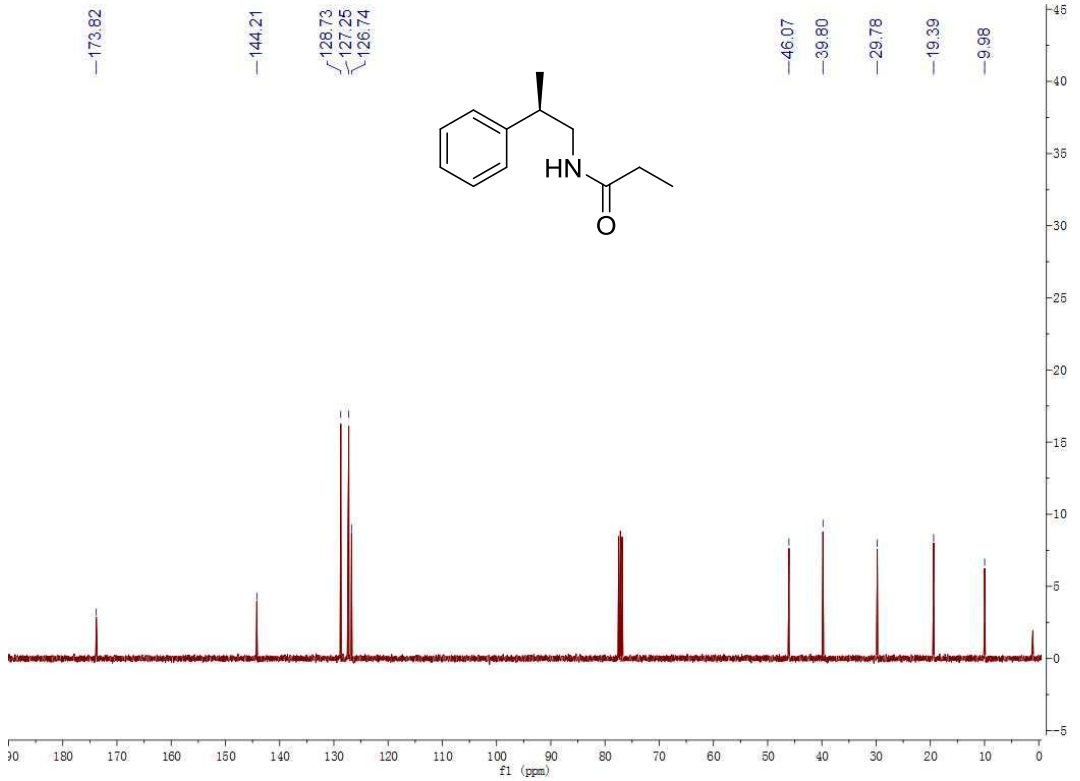
(*R*)-*N*-(2-phenylpropyl)formamide (2b)



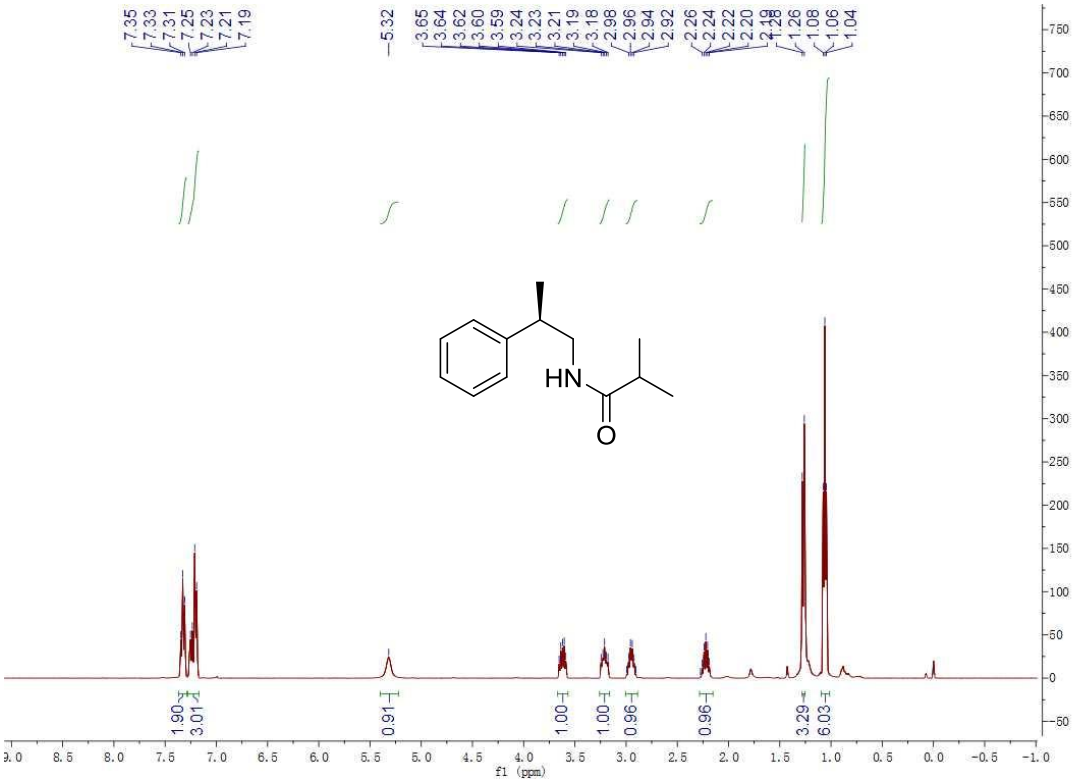


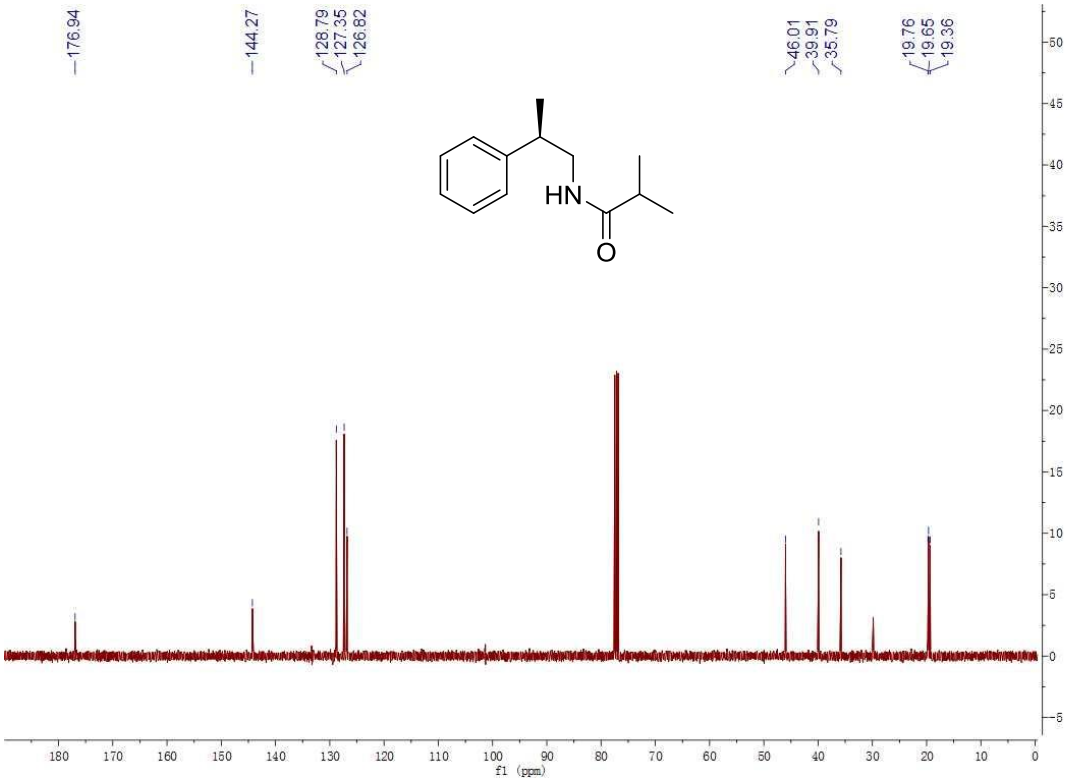
(*R*)-*N*-(2-phenylpropyl)propionamide (2c)



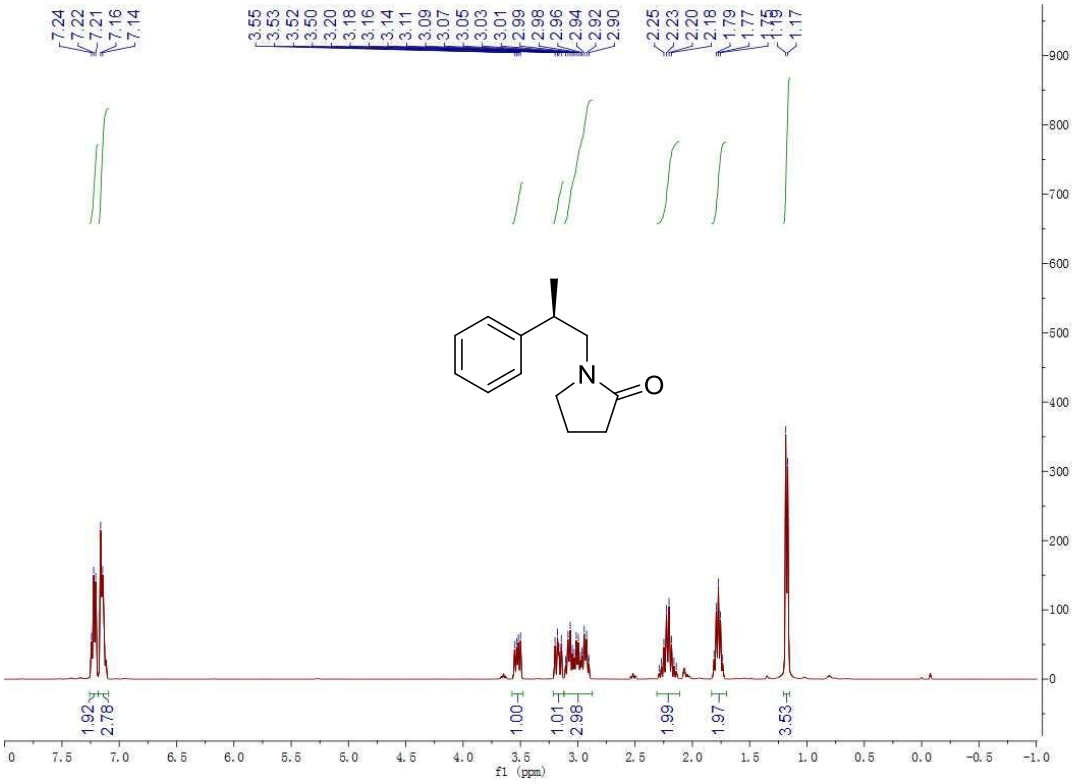


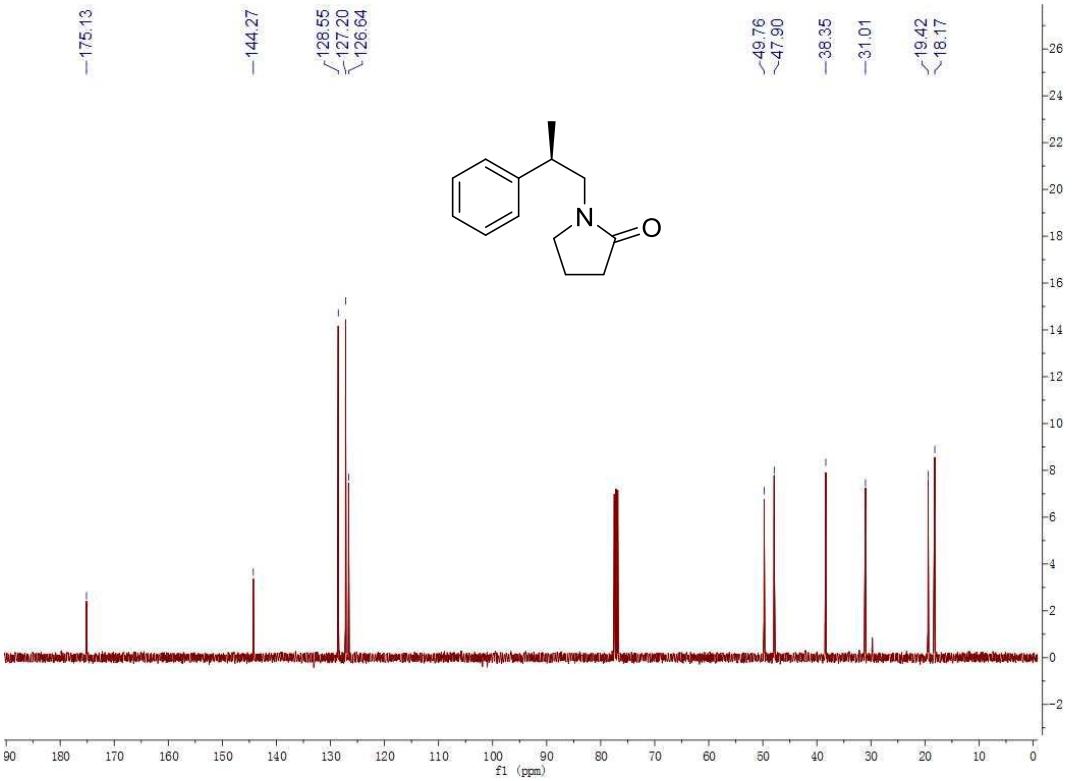
(*R*)-*N*-(2-phenylpropyl)isobutyramide (2d)



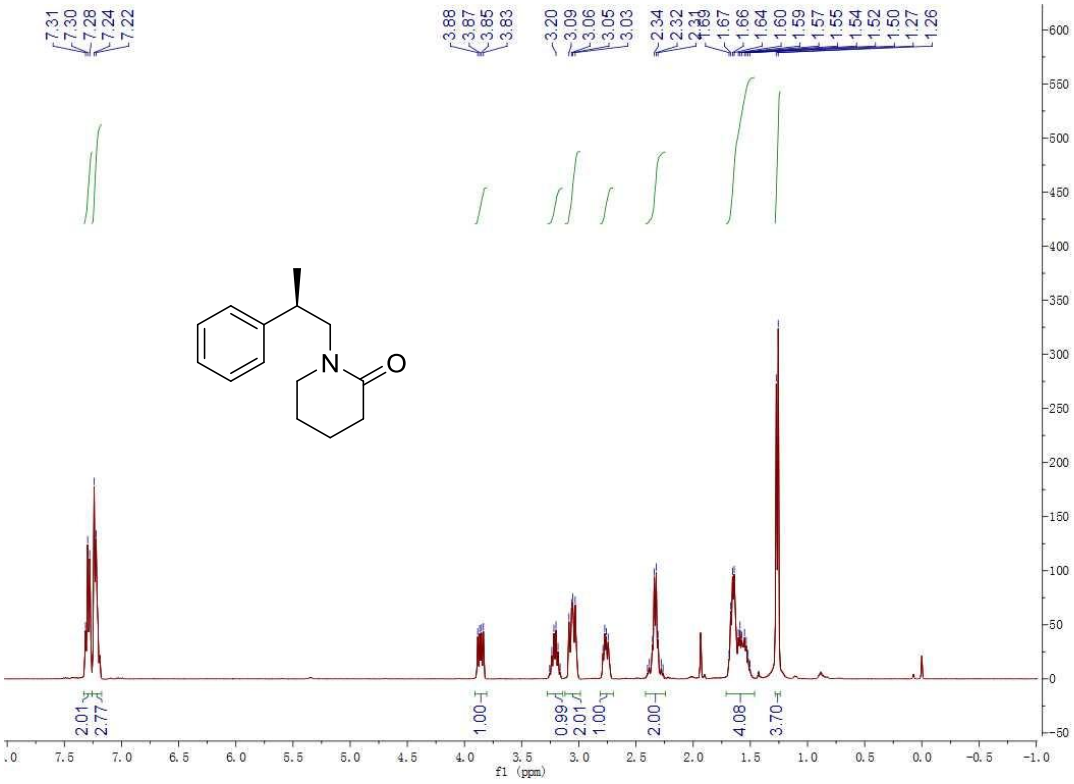


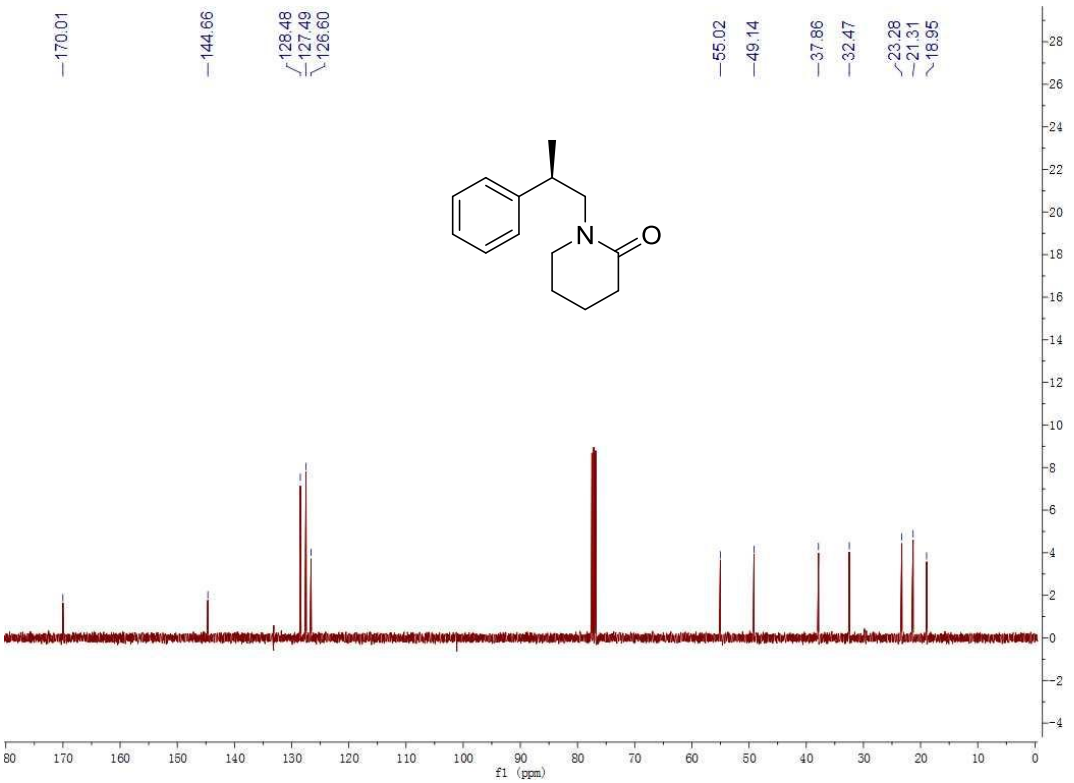
(*R*)-1-(2-phenylpropyl)pyrrolidin-2-one (2e)



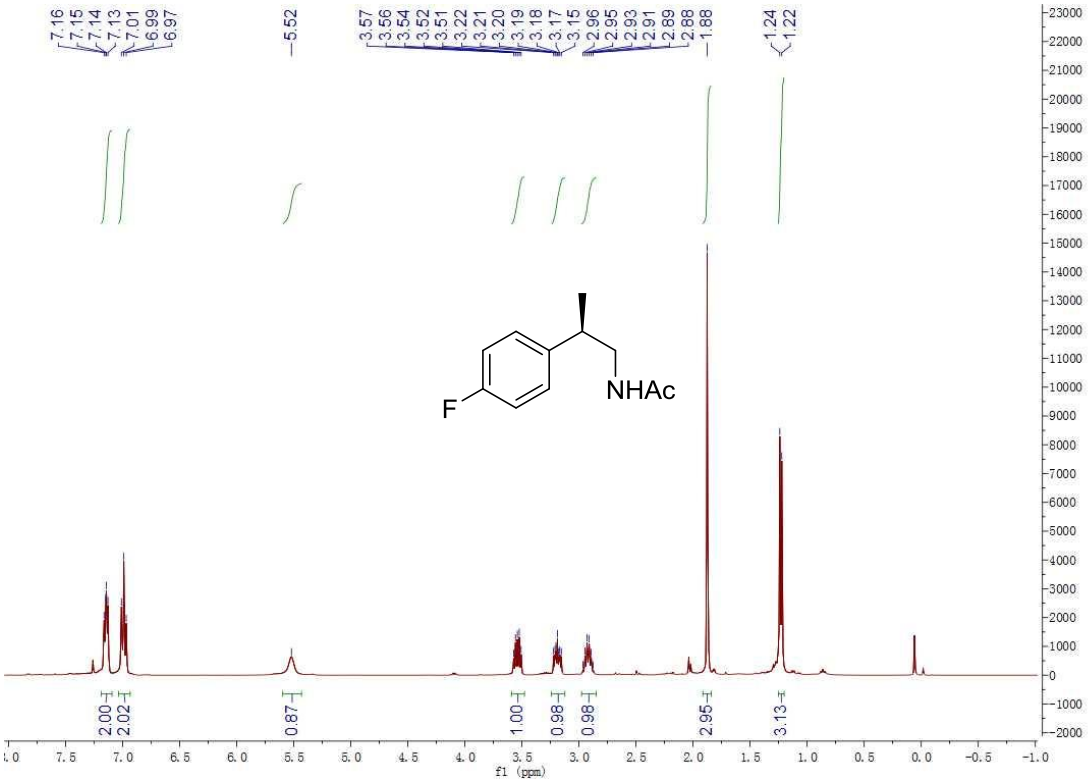


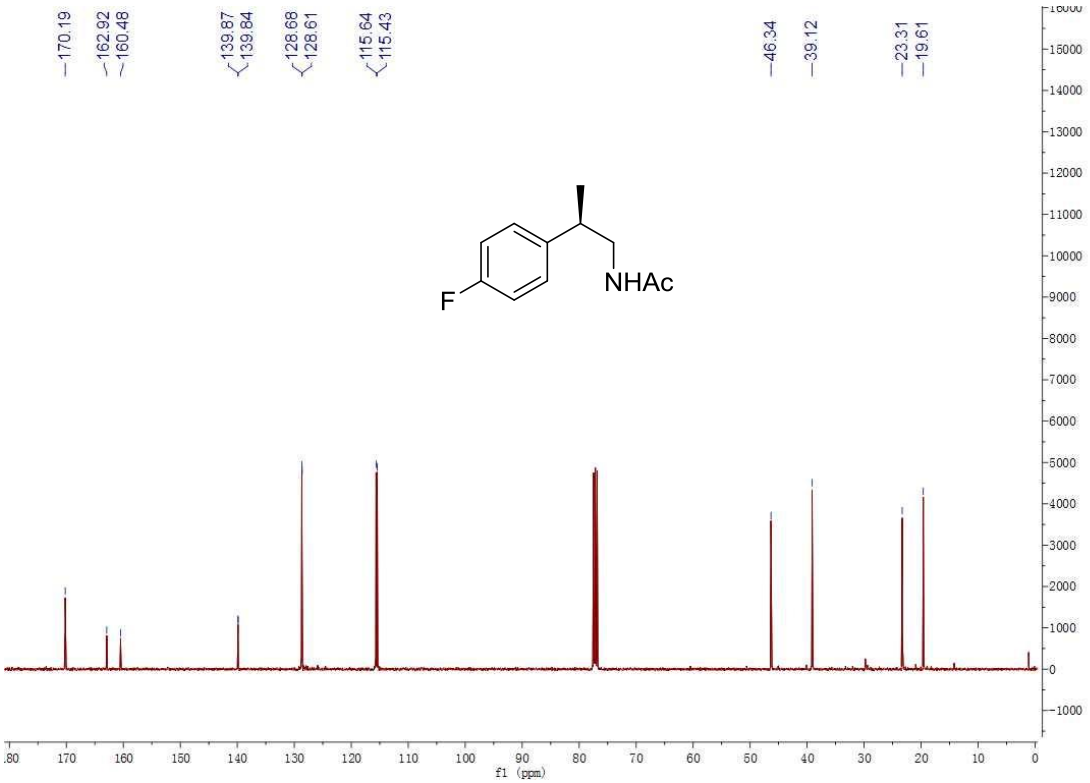
(*R*)-1-(2-phenylpropyl)piperidin-2-one (2f)



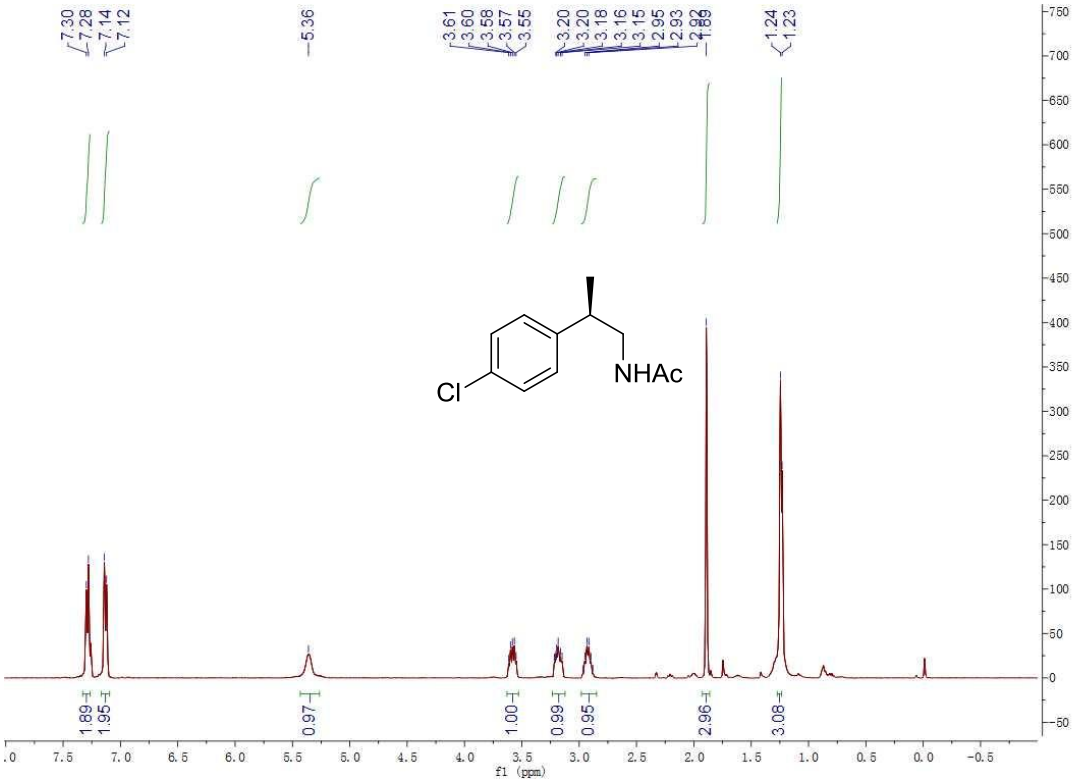


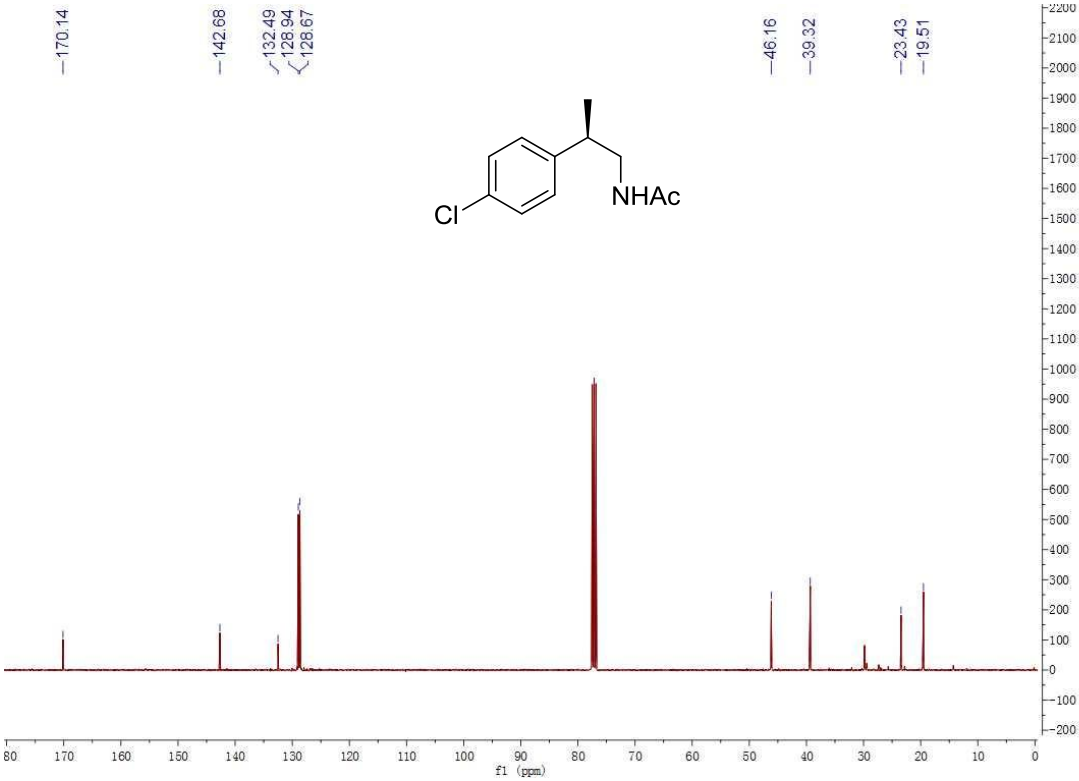
(*R*)-*N*-(2-(4-fluorophenyl)propyl)acetamide (2g)



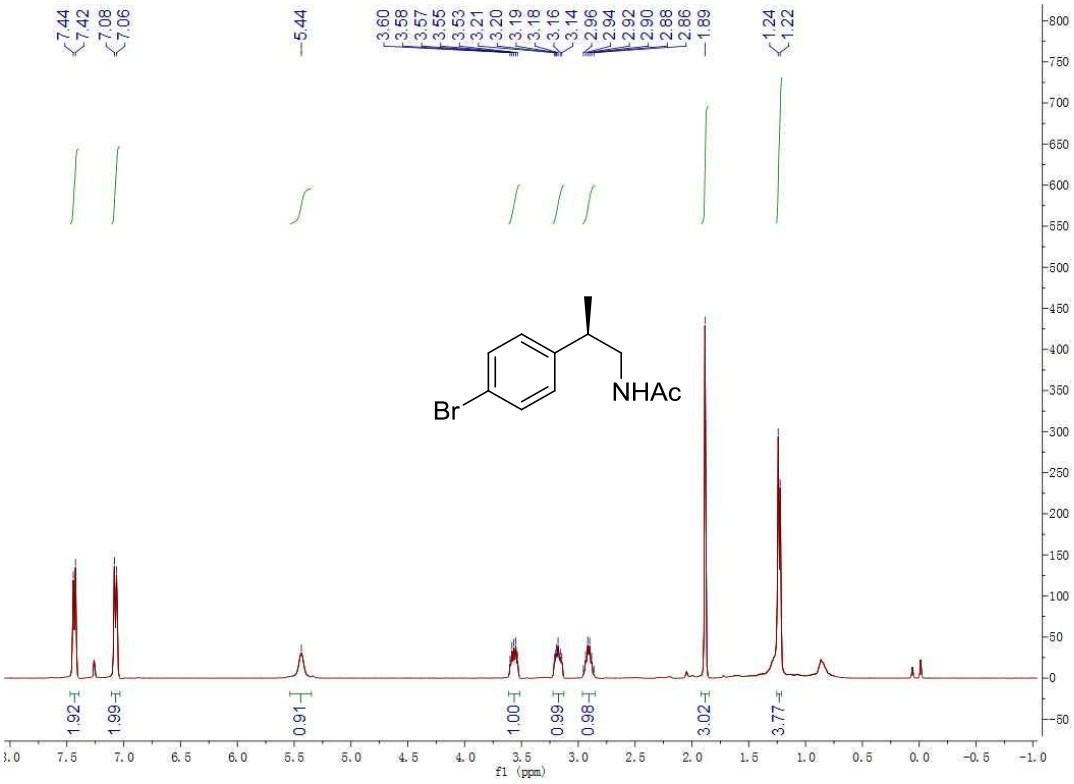


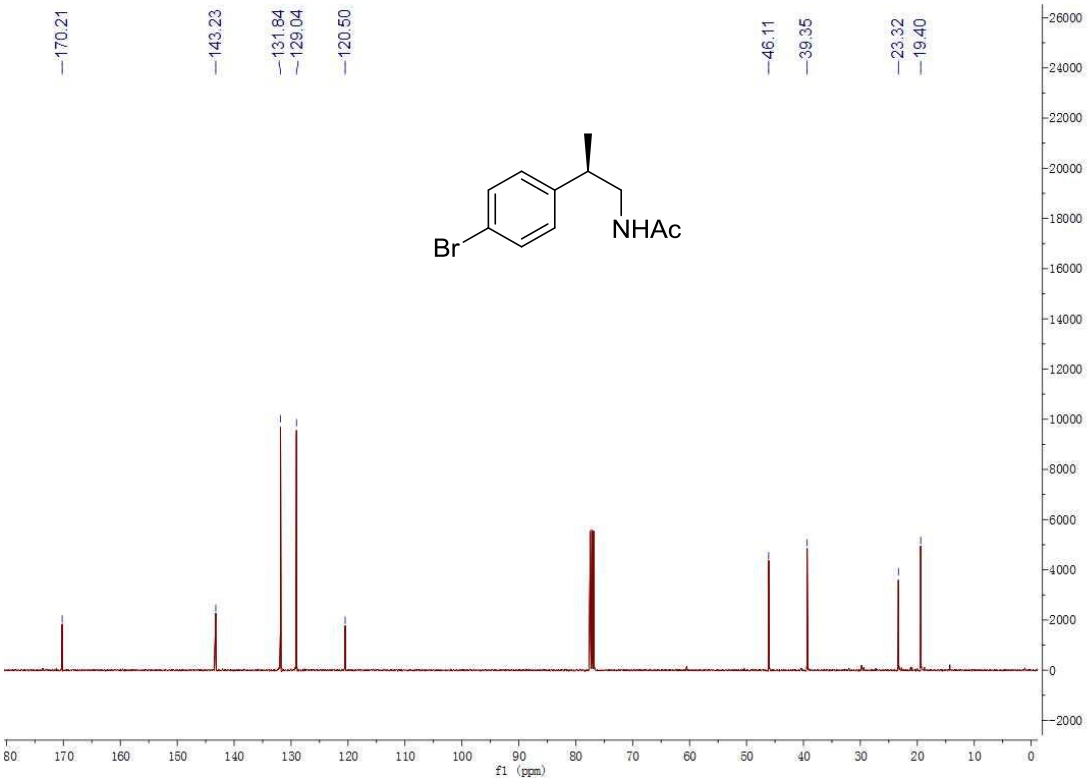
(*R*)-*N*-(2-(4-chlorophenyl)propyl)acetamide (2h)



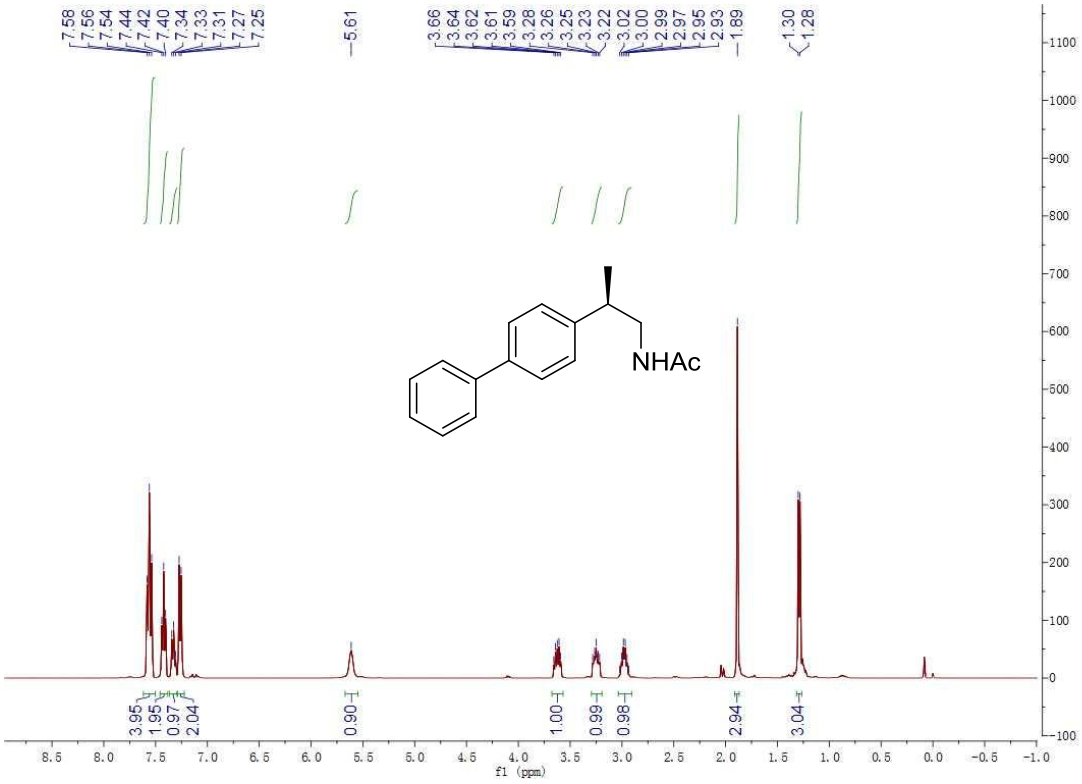


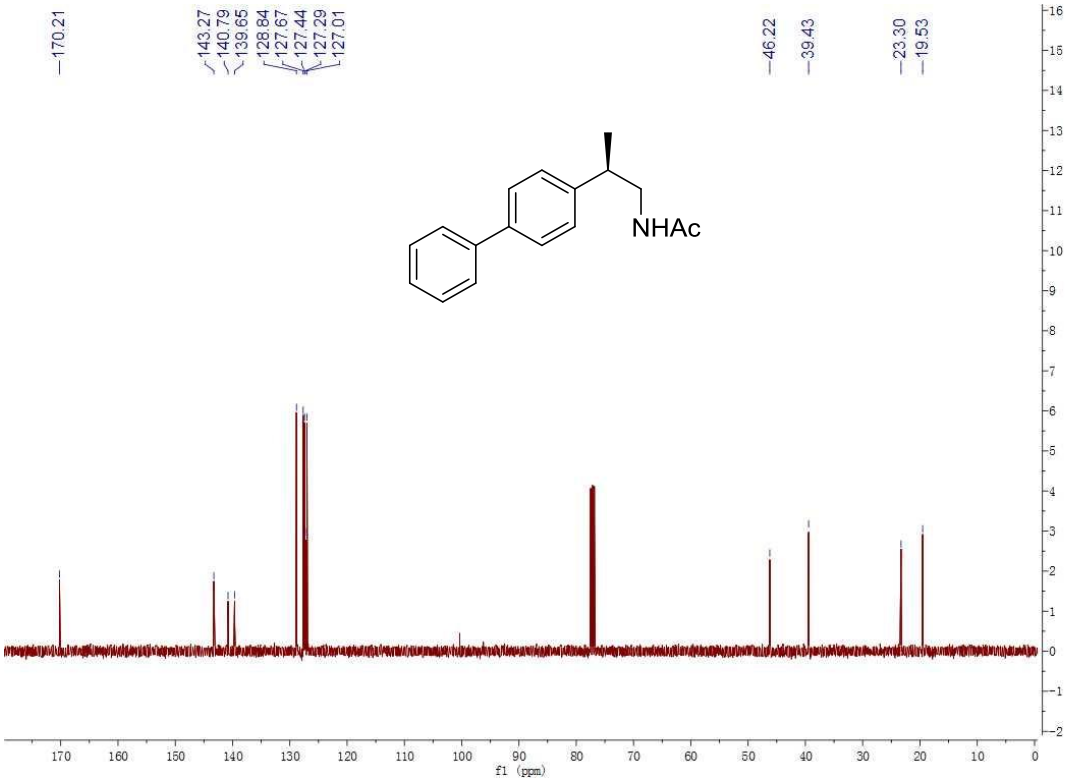
(*R*)-*N*-(2-(4-bromophenyl)propyl)acetamide (2i)



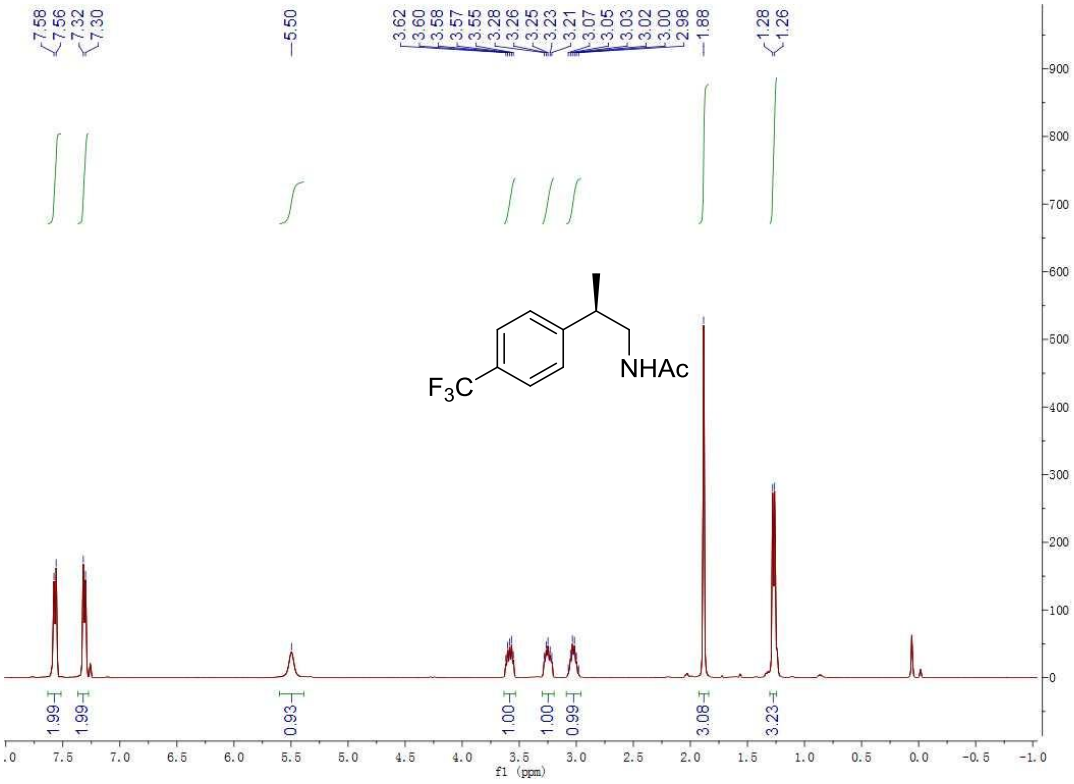


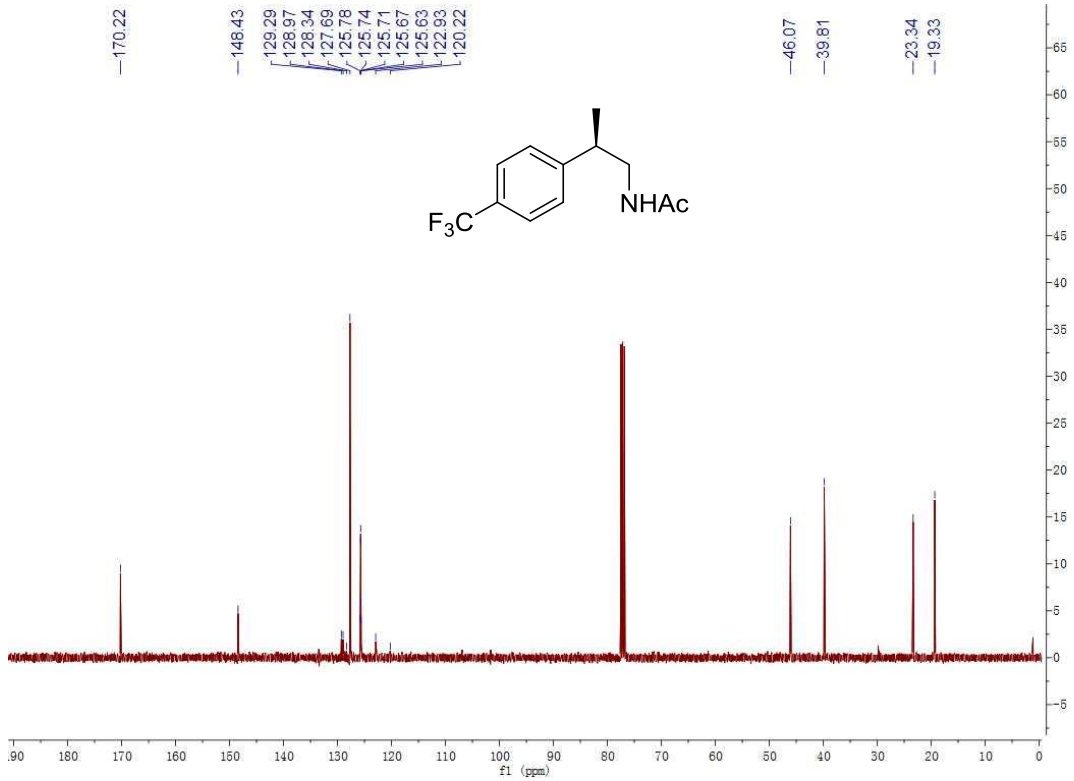
(*R*)-*N*-(2-([1,1'-biphenyl]-4-yl)propyl)acetamide (2j)



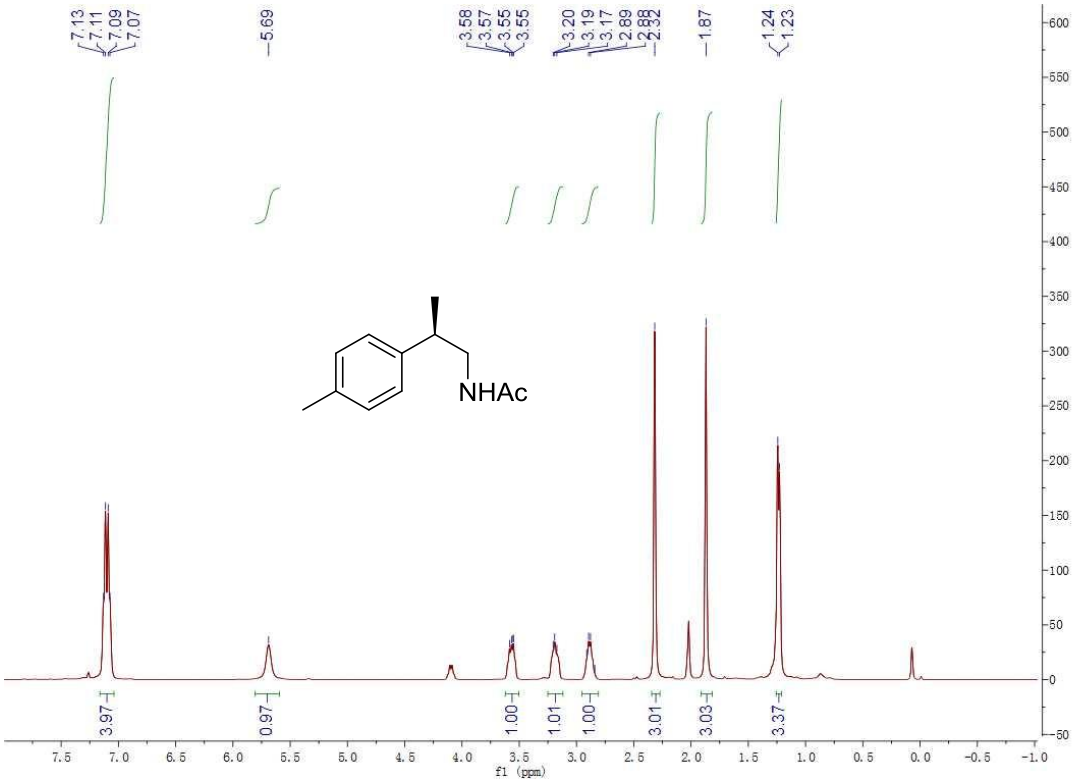


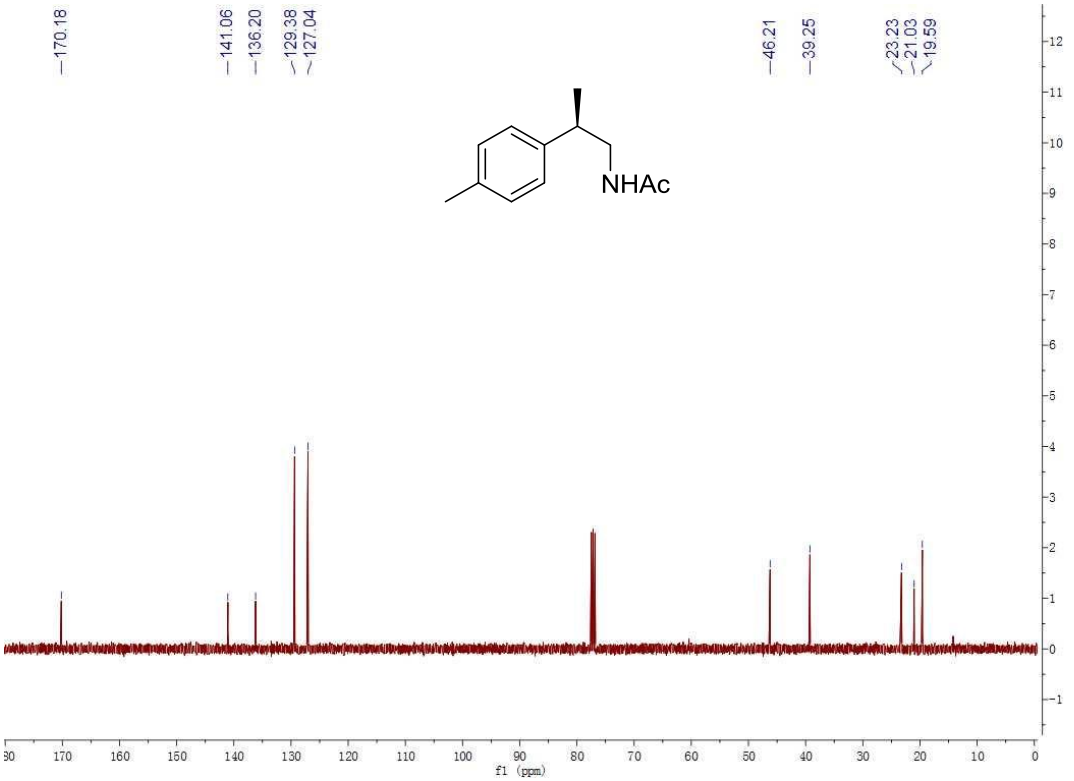
(*R*)-*N*-(2-(4-(trifluoromethyl)phenyl)propyl)acetamide (2k)



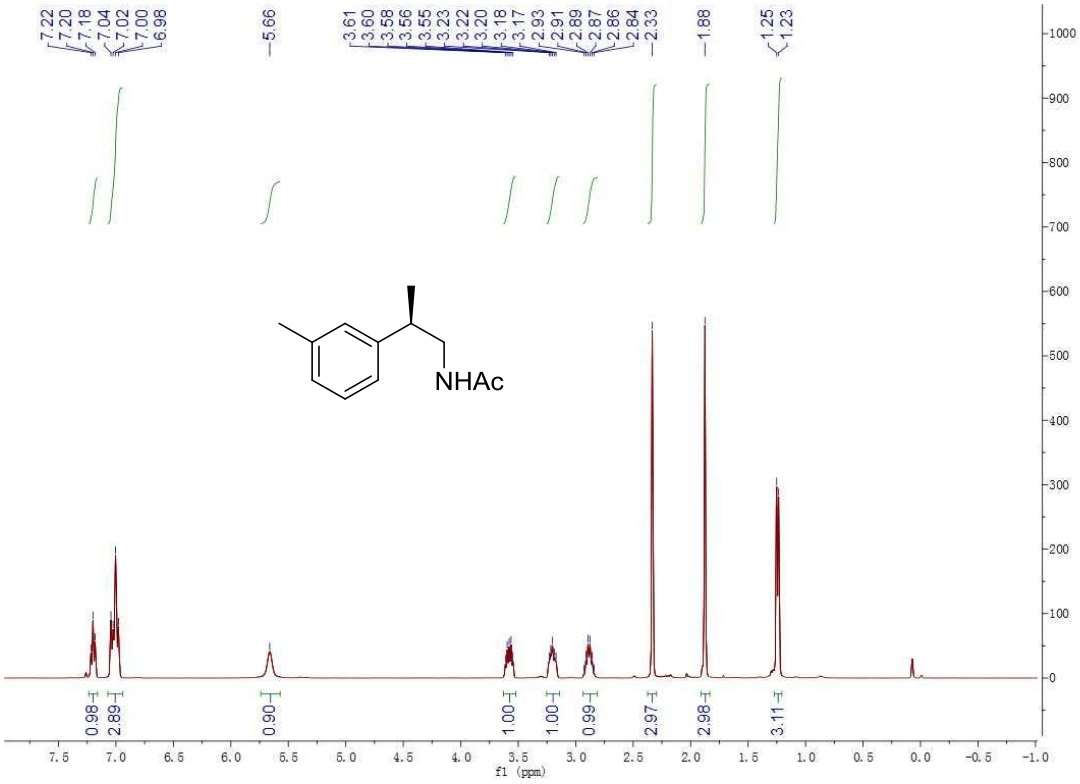


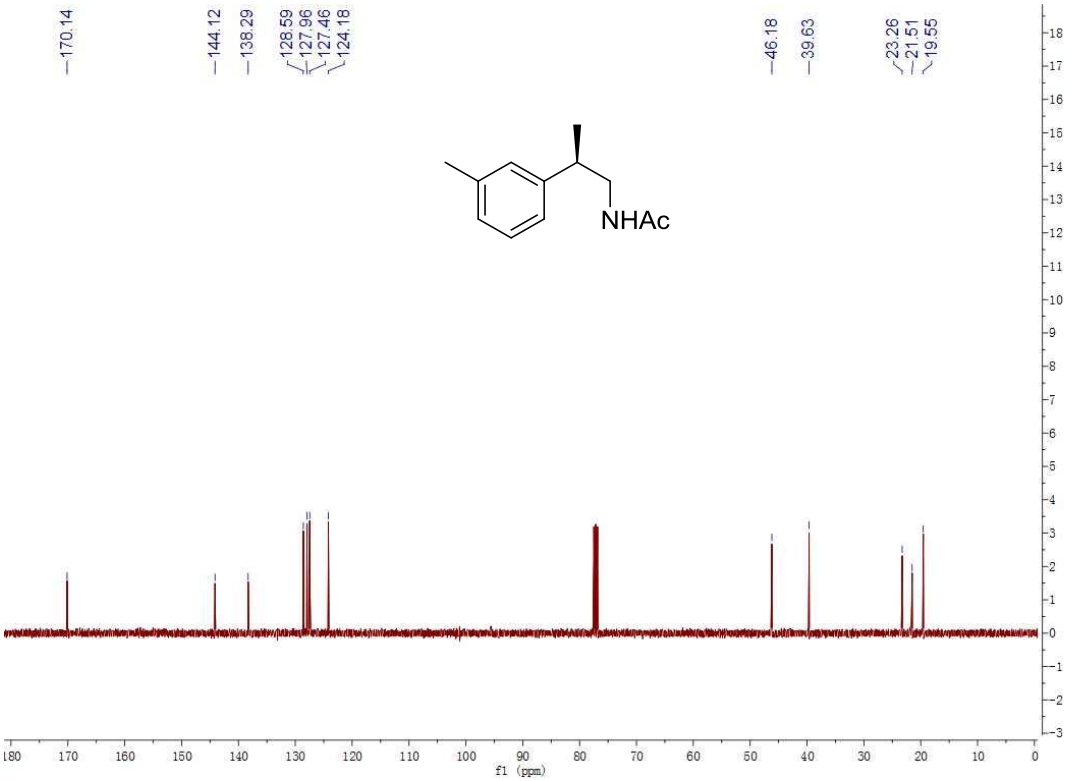
(*R*)-*N*-(2-(*p*-tolyl)propyl)acetamide (2l)



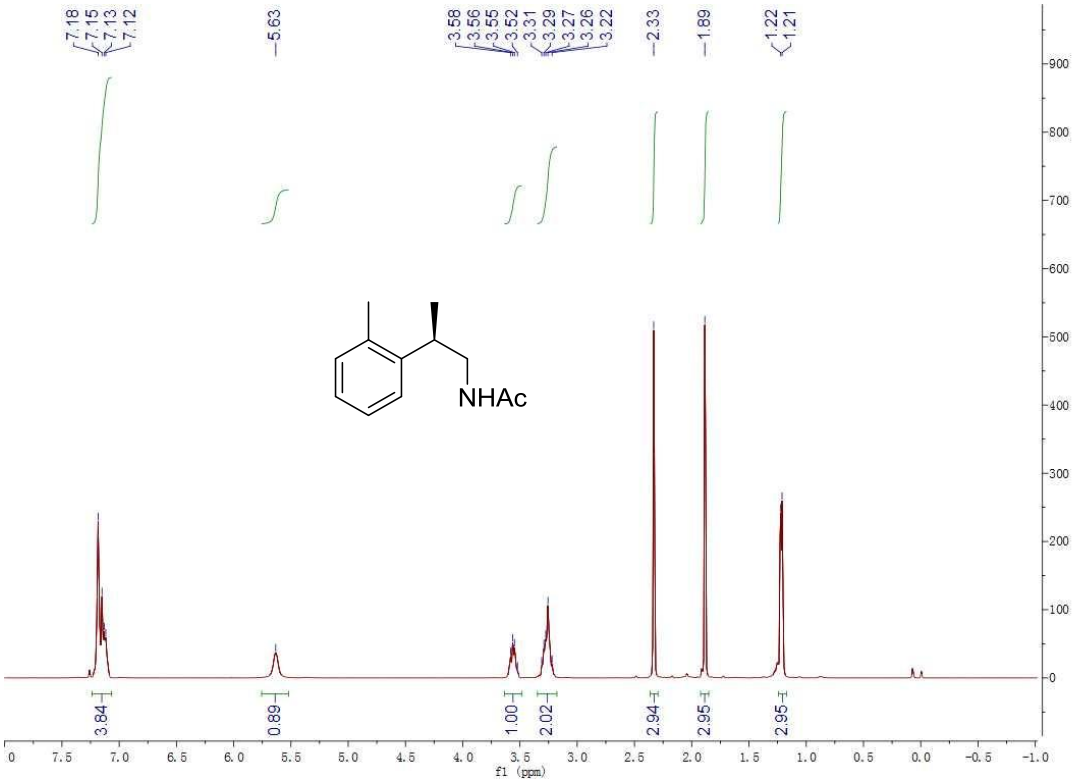


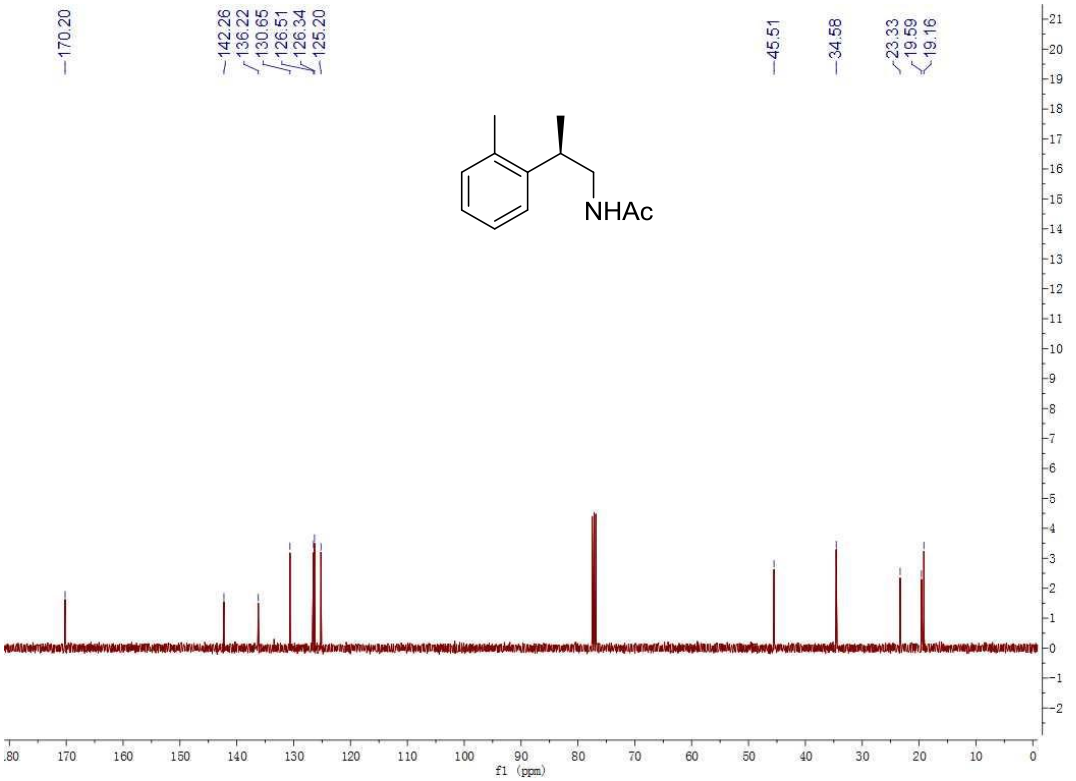
(*R*)-*N*-(2-(*m*-tolyl)propyl)acetamide (2m)



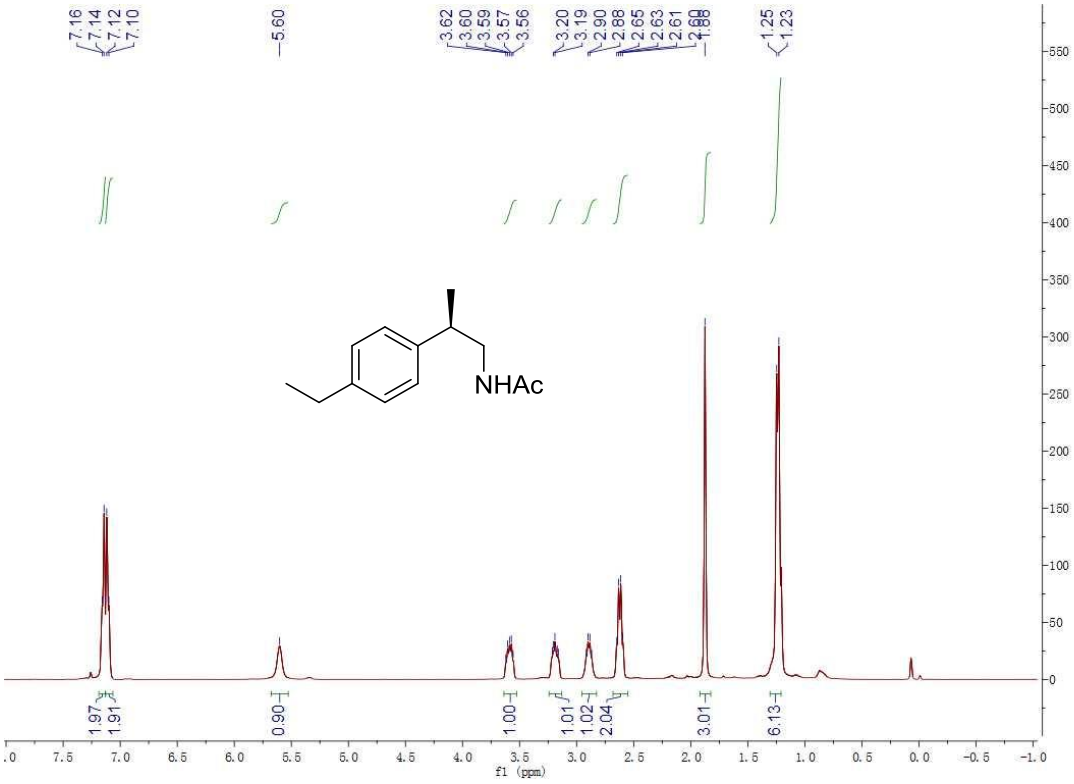


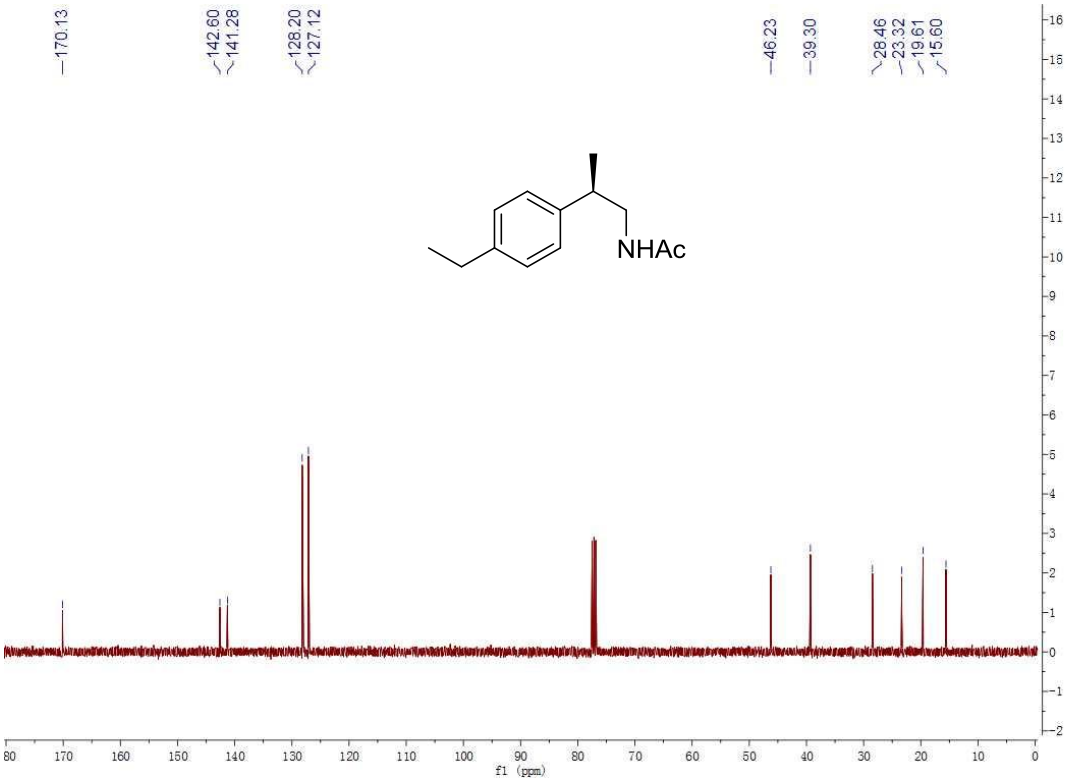
(*R*)-*N*-(2-(*o*-tolyl)propyl)acetamide (2n)



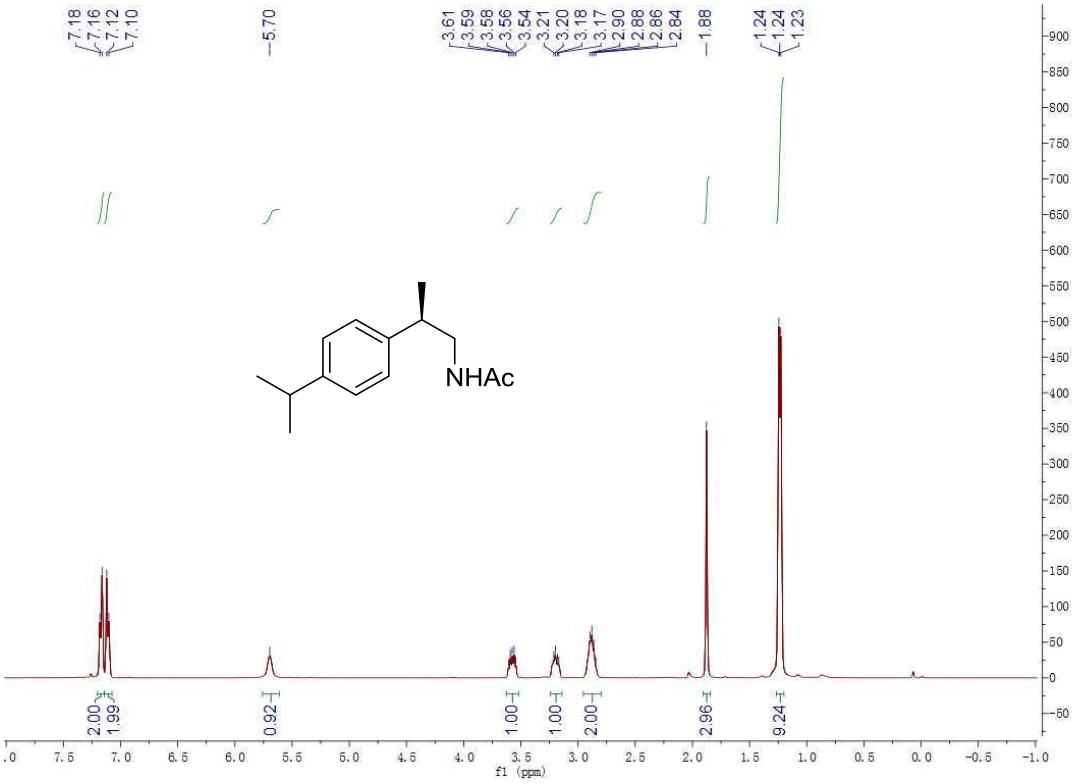


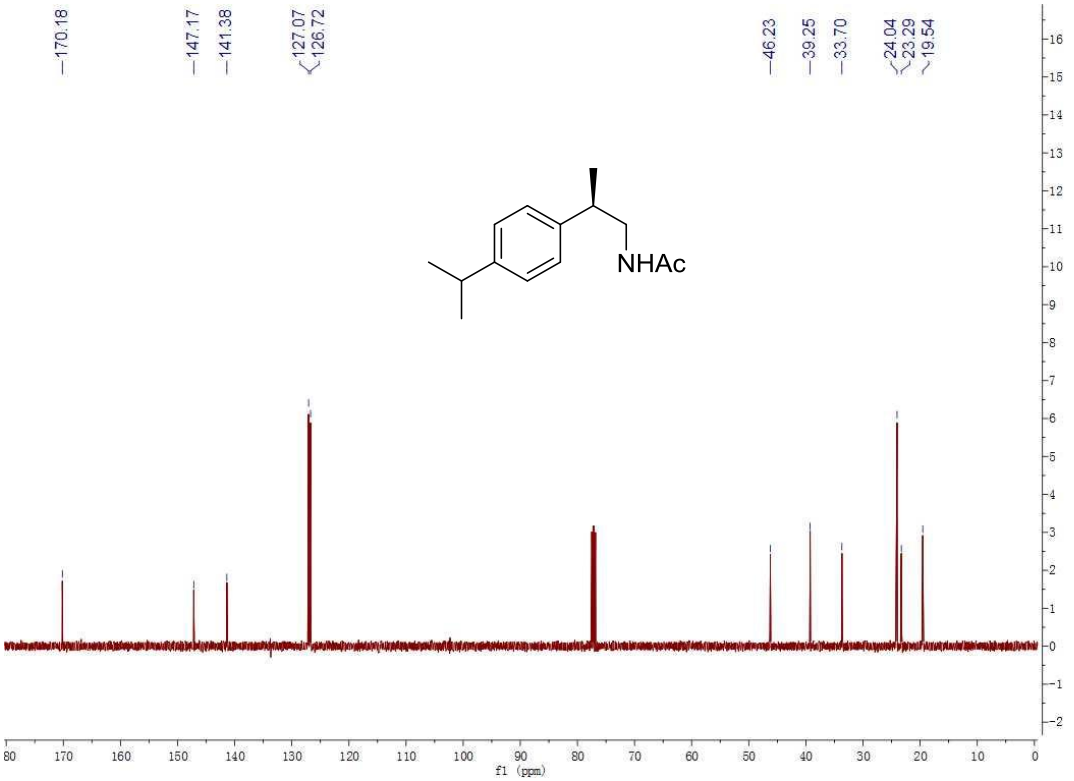
(*R*)-*N*-(2-(4-ethylphenyl)propyl)acetamide (2o)



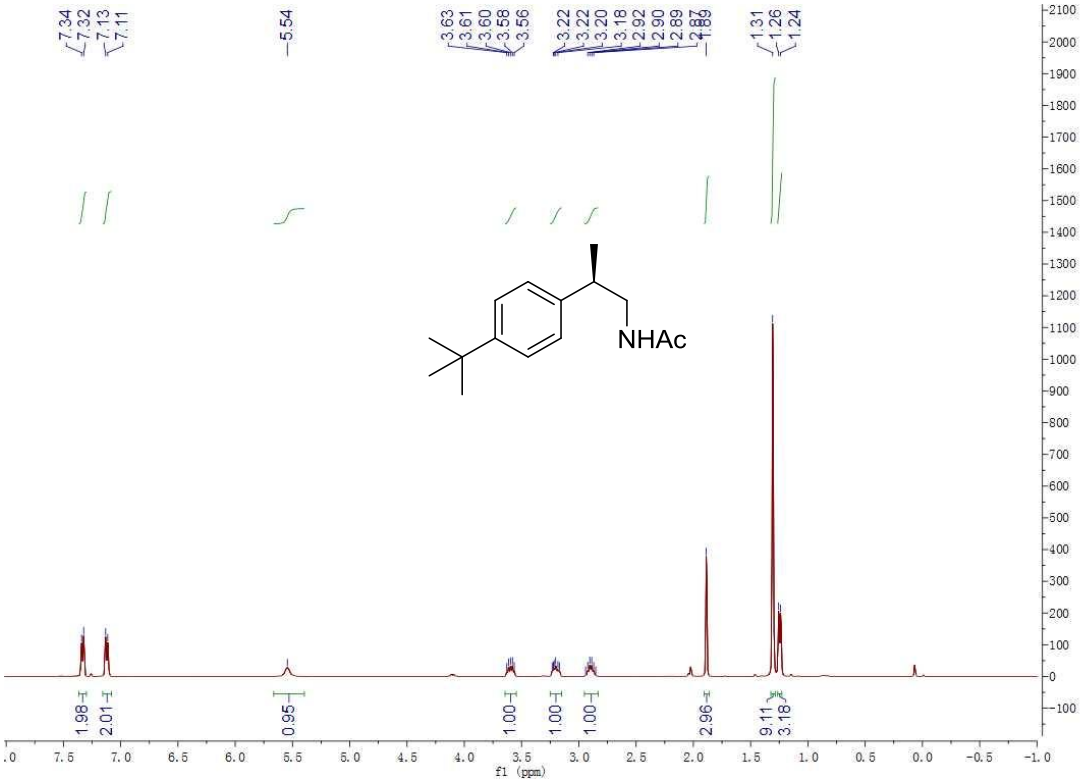


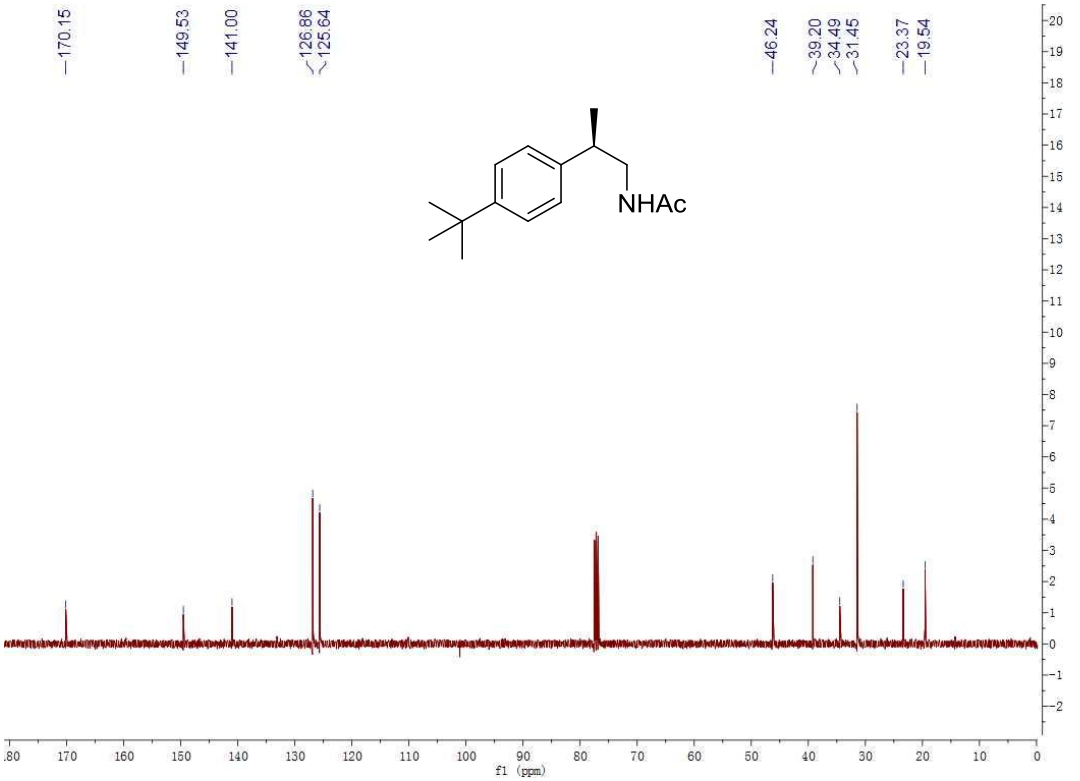
(*R*)-*N*-(2-(4-isopropylphenyl)propyl)acetamide (2p)



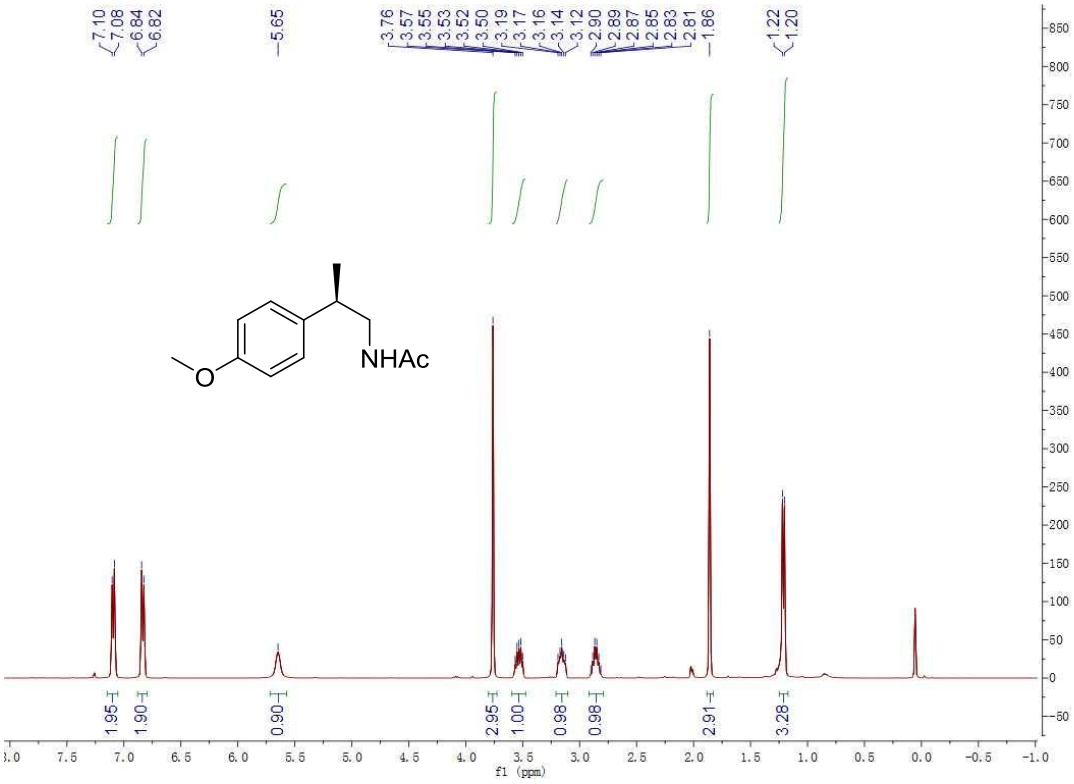


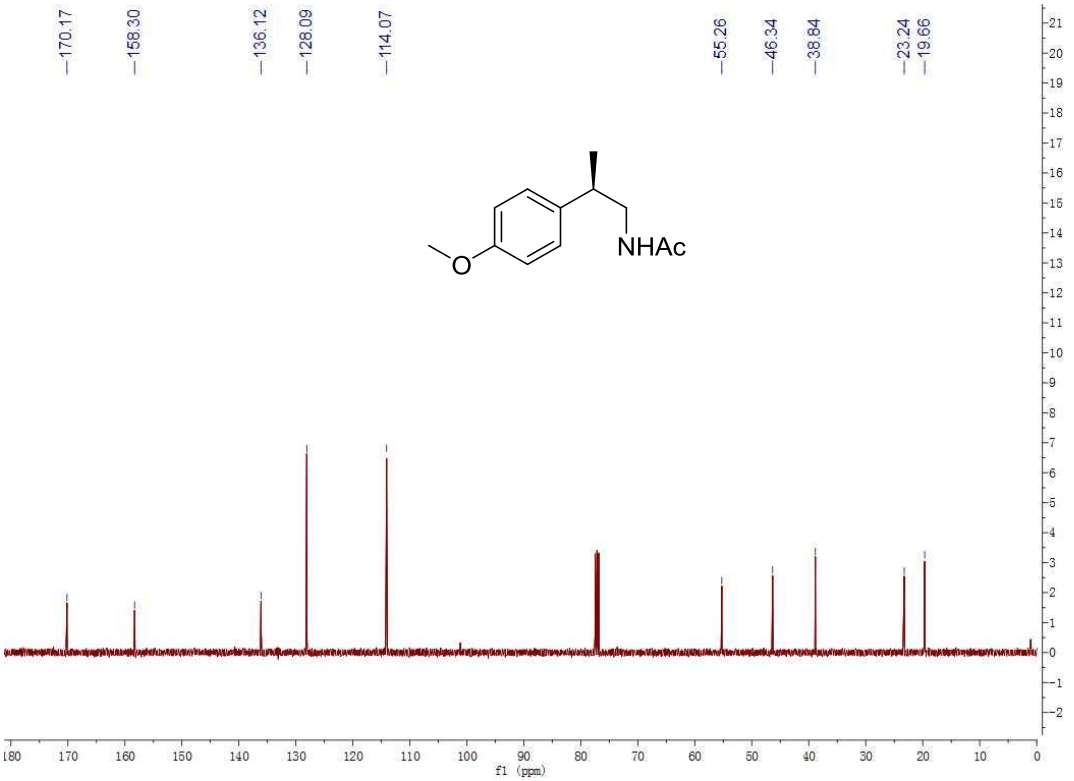
(*R*)-*N*-(2-(4-(*tert*-butyl)phenyl)propyl)acetamide (2q)



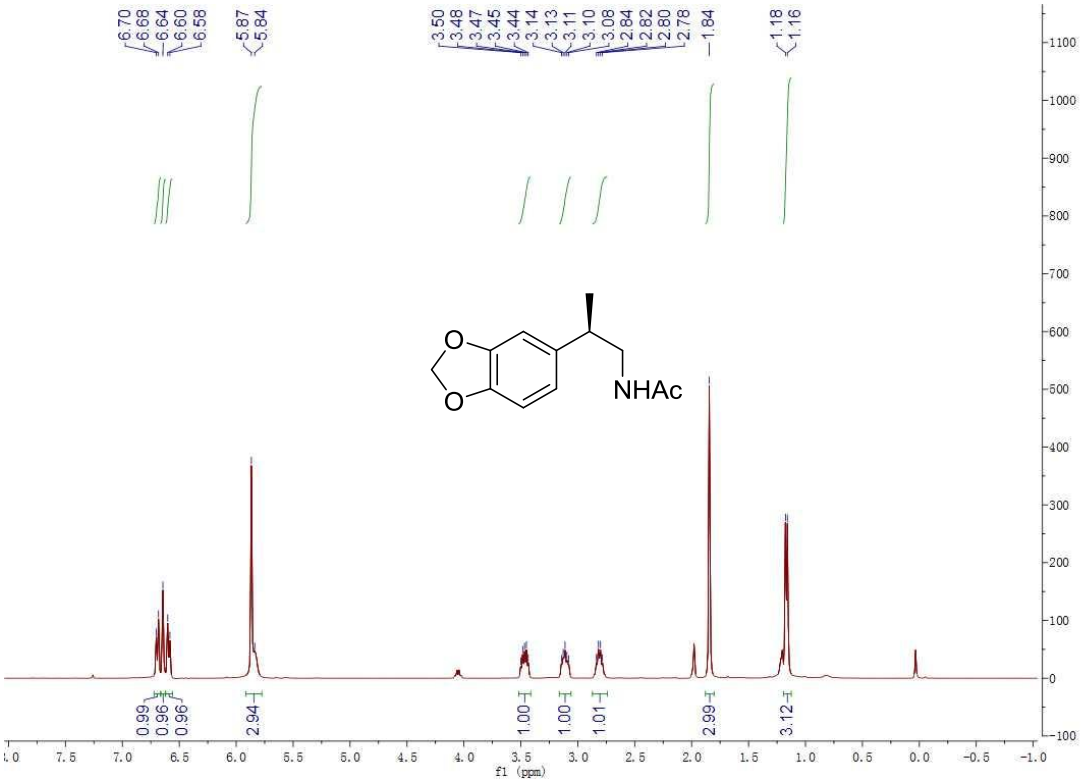


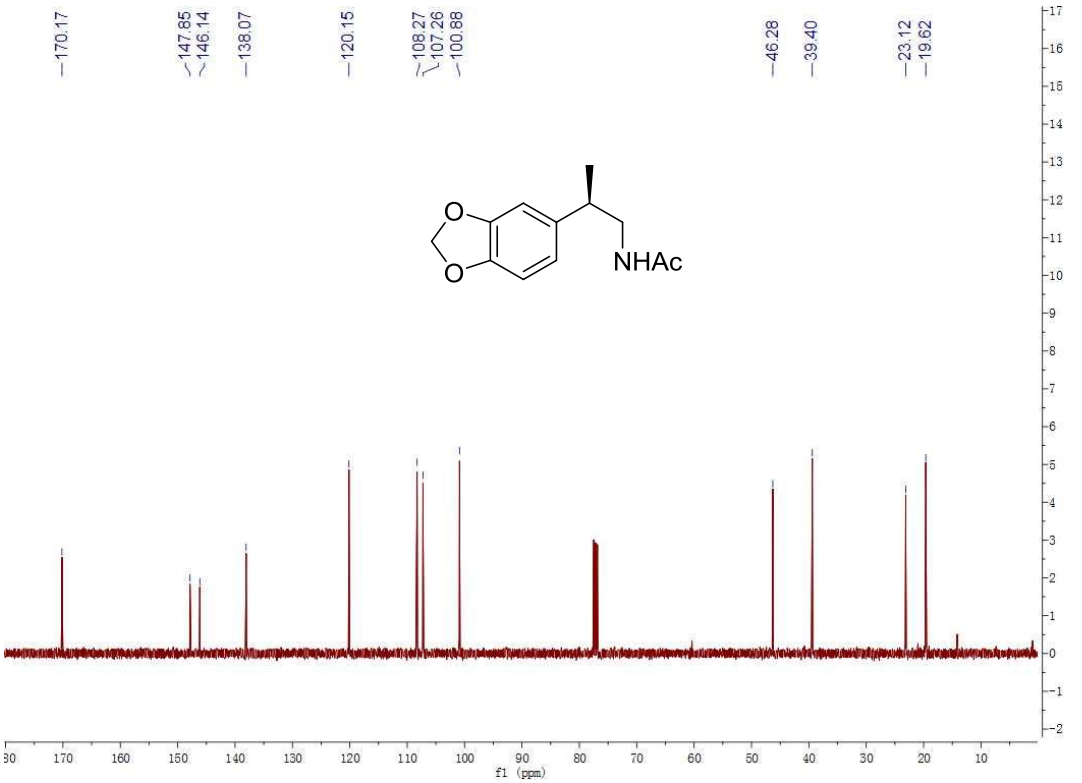
(*R*)-*N*-(2-(4-methoxyphenyl)propyl)acetamide (2r)



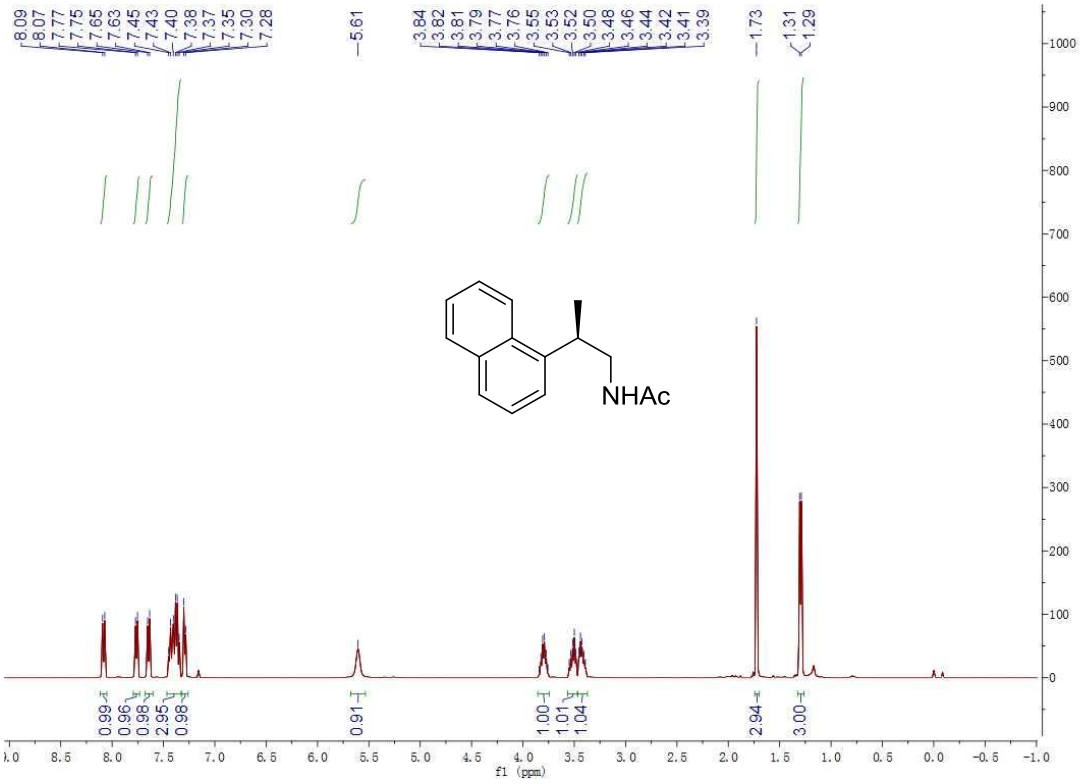


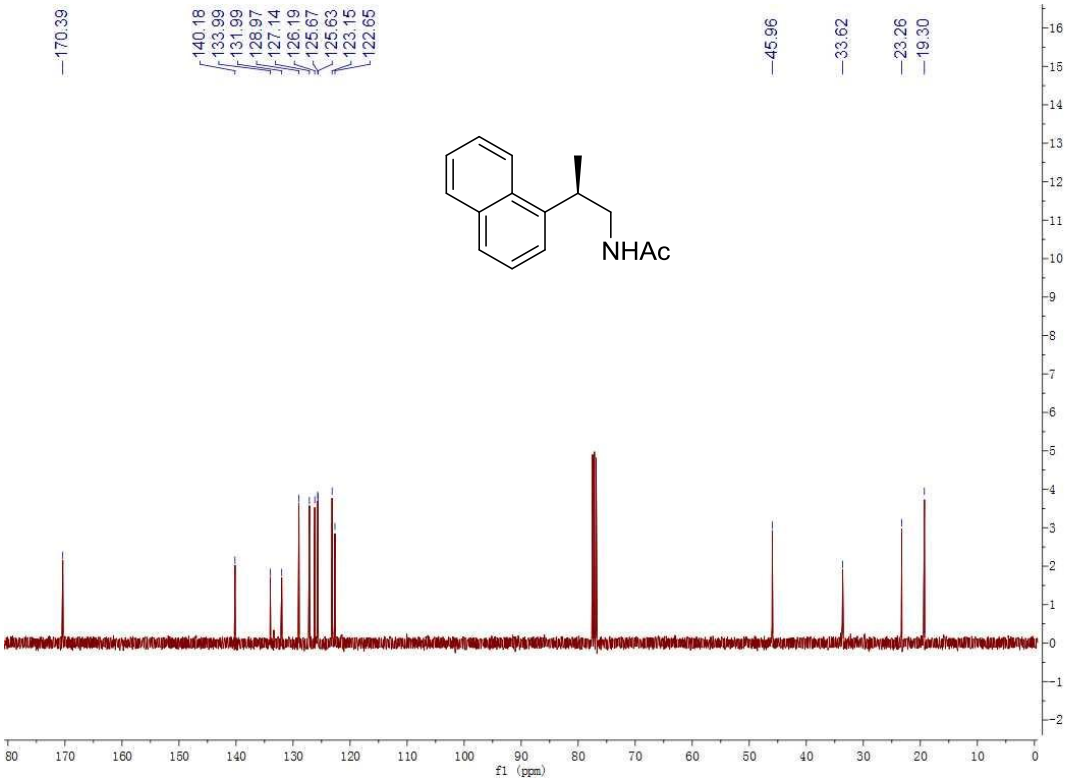
(*R*)-*N*-(2-(benzo[*d*][1,3]dioxol-5-yl)propyl)acetamide (2s)



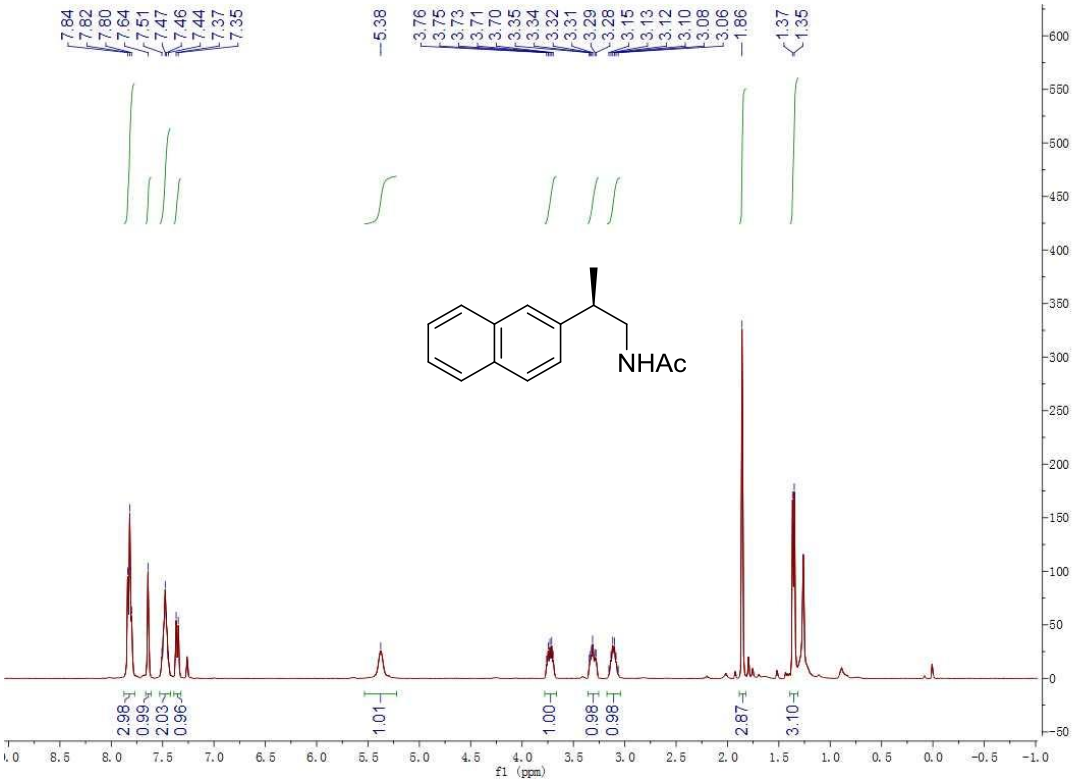


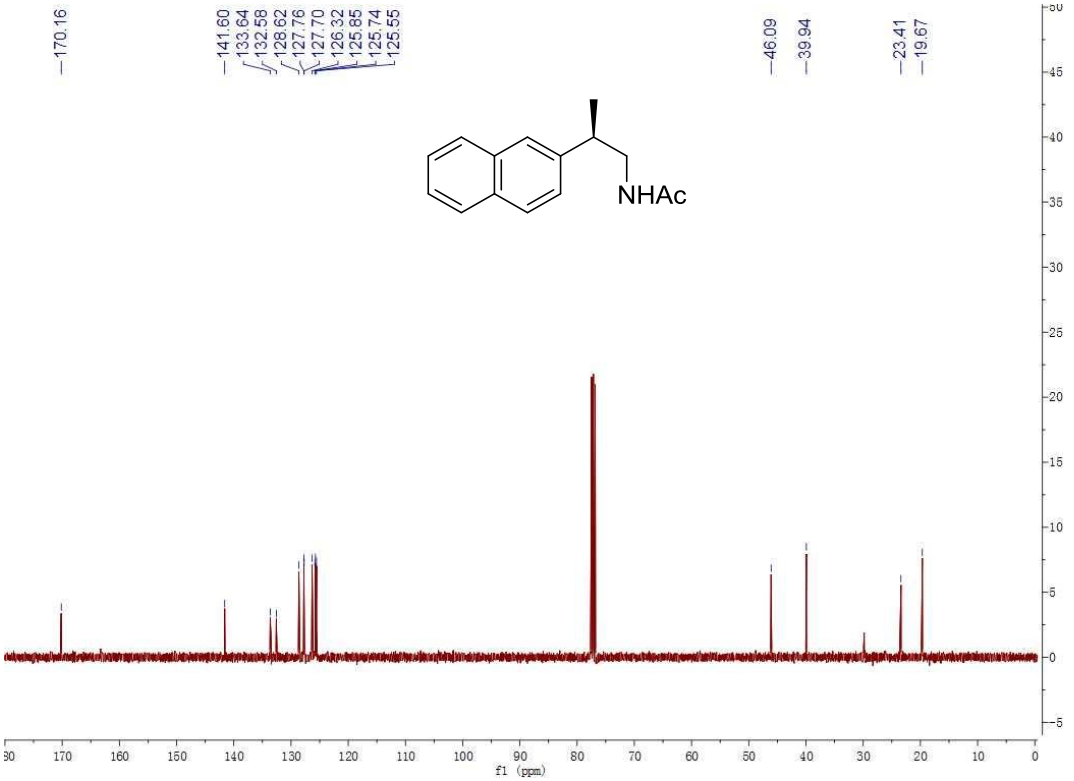
(*R*)-*N*-(2-(naphthalen-1-yl)propyl)acetamide (2t)



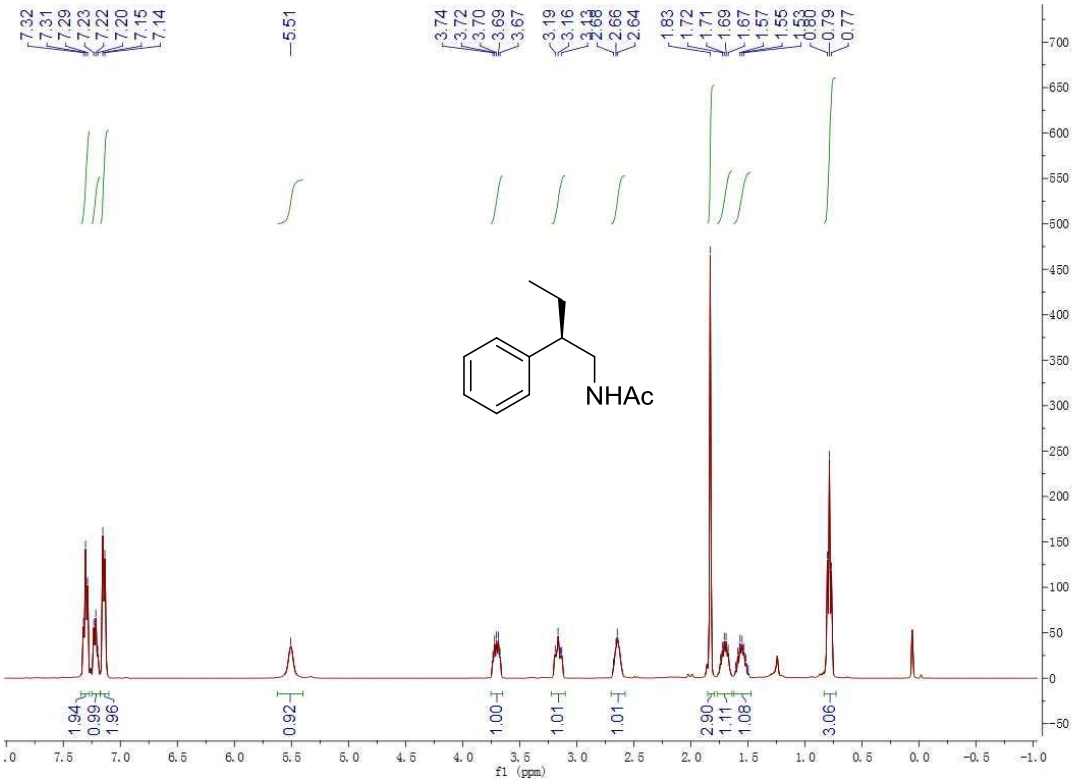


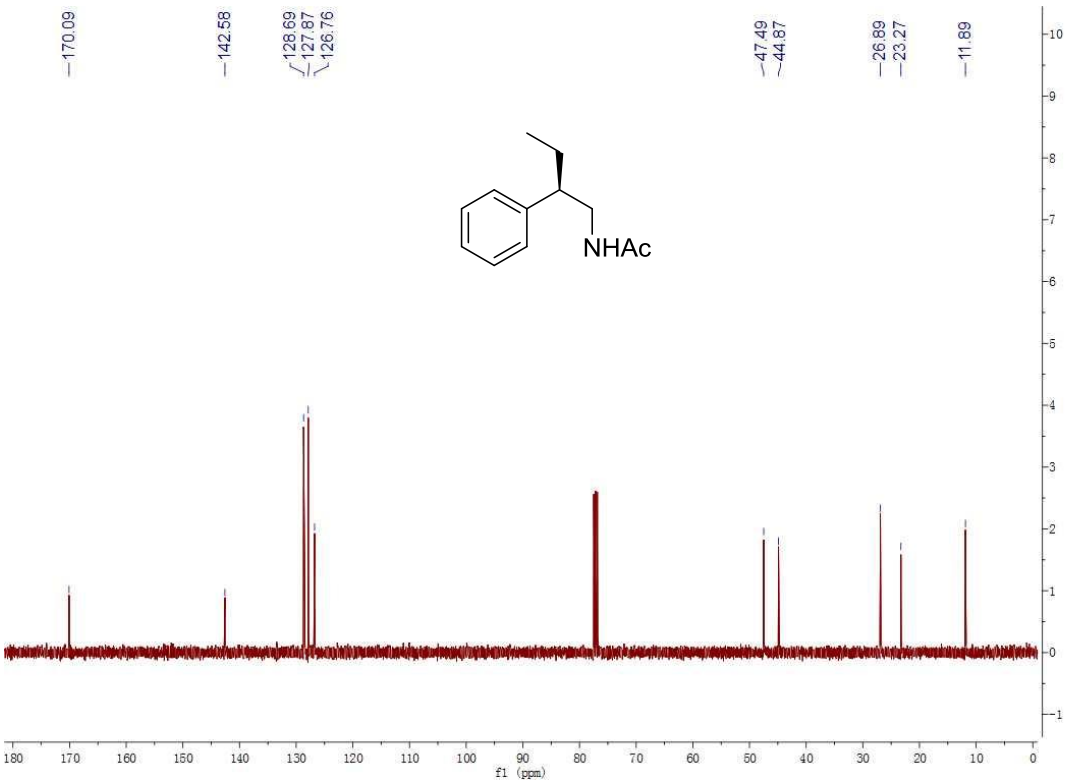
(*R*)-*N*-(2-(naphthalen-2-yl)propyl)acetamide (2u)



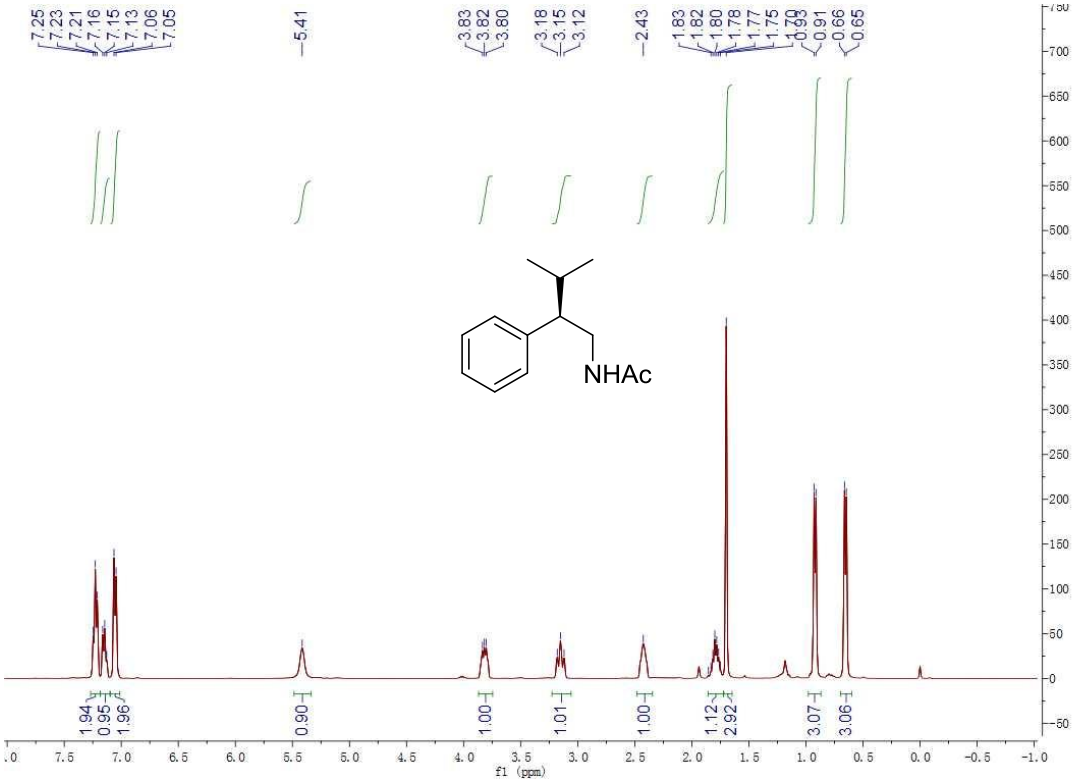


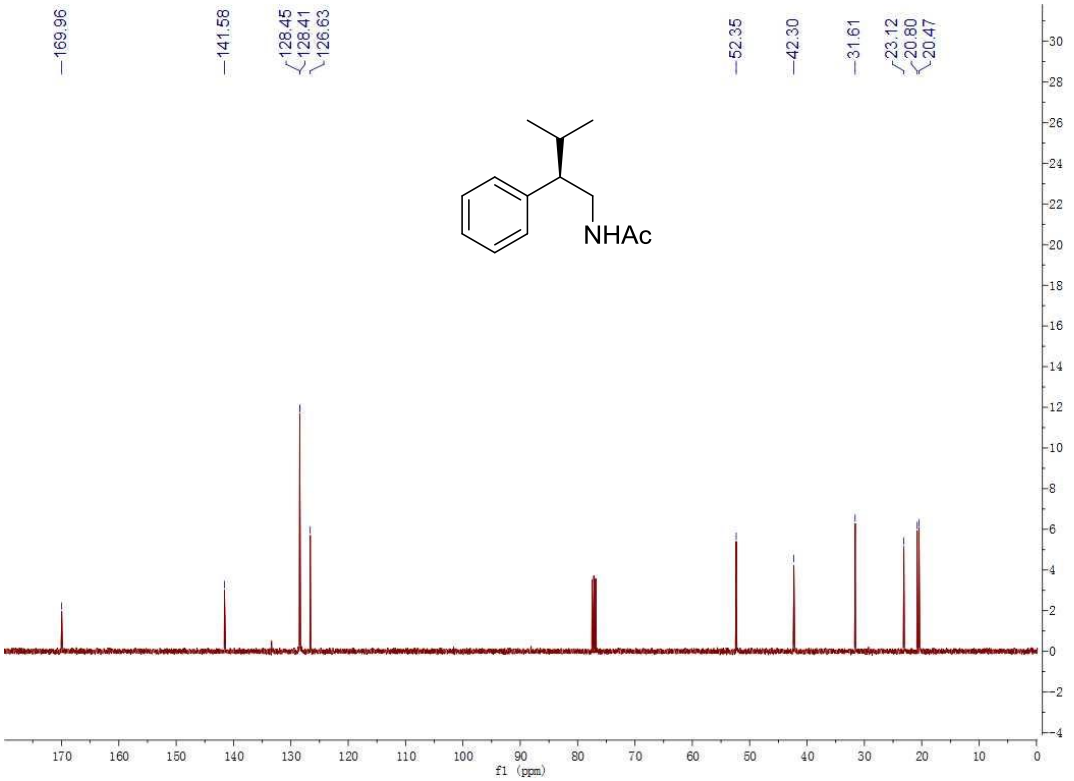
(*R*)-*N*-(2-phenylbutyl)acetamide (2v)



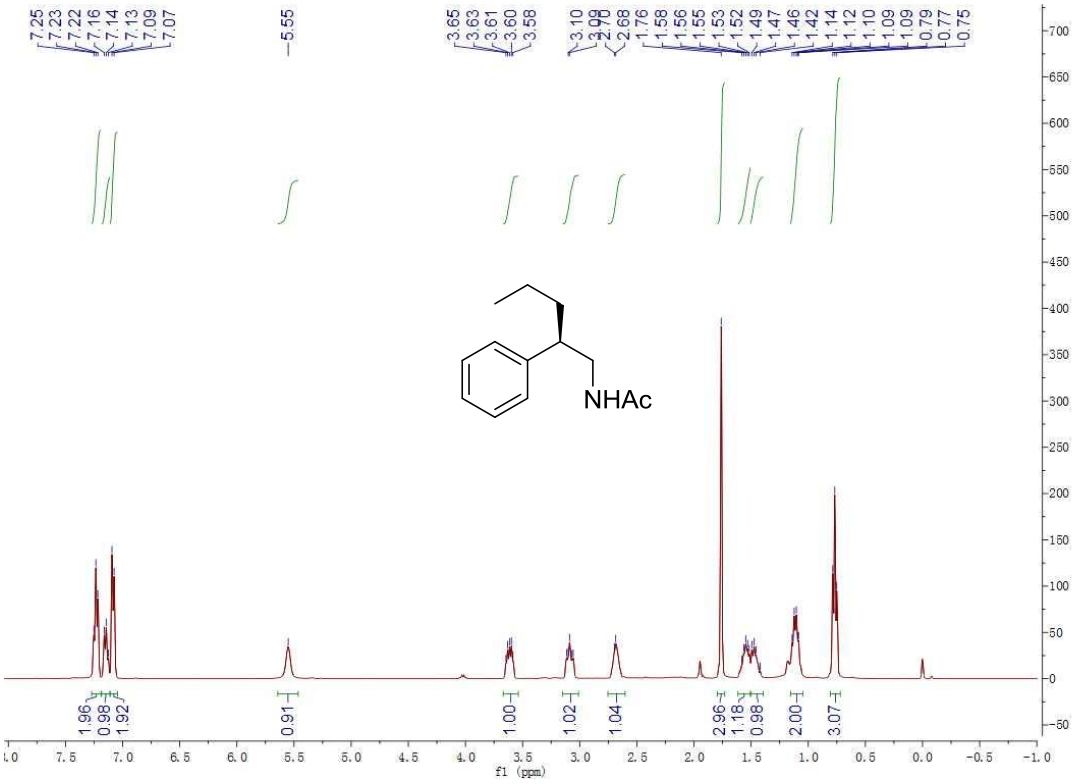


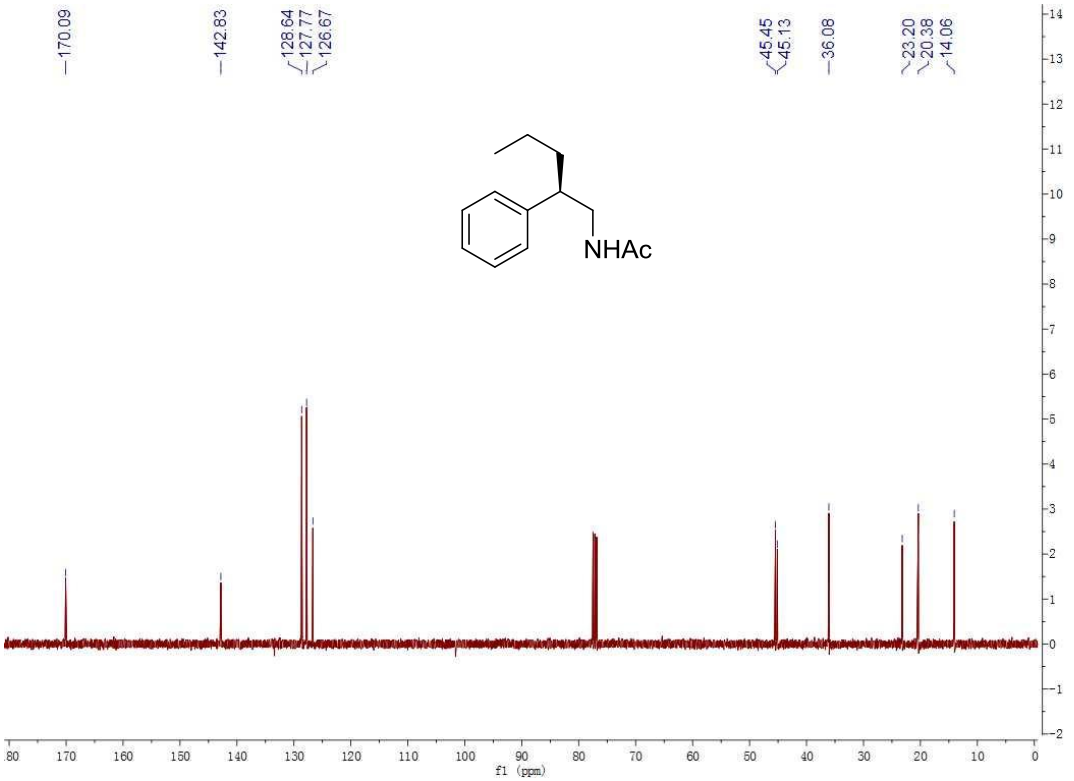
(*R*)-*N*-(3-methyl-2-phenylbutyl)acetamide (2w)



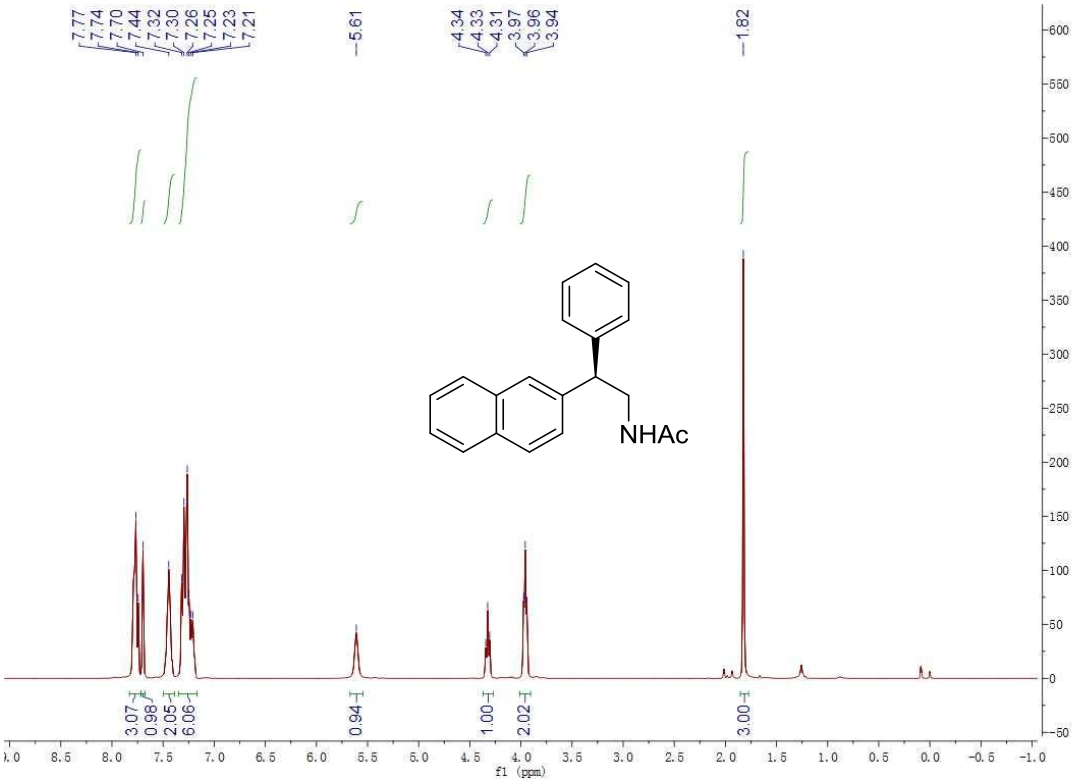


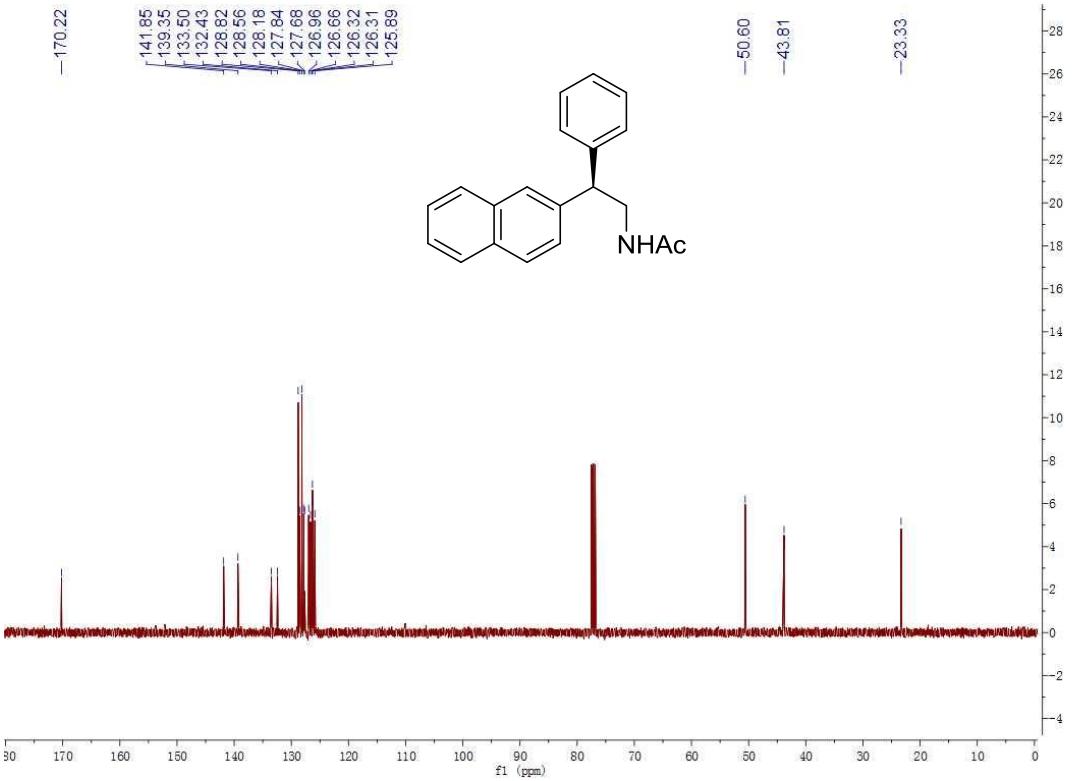
(*R*)-*N*-(2-phenylpentyl)acetamide (2x)



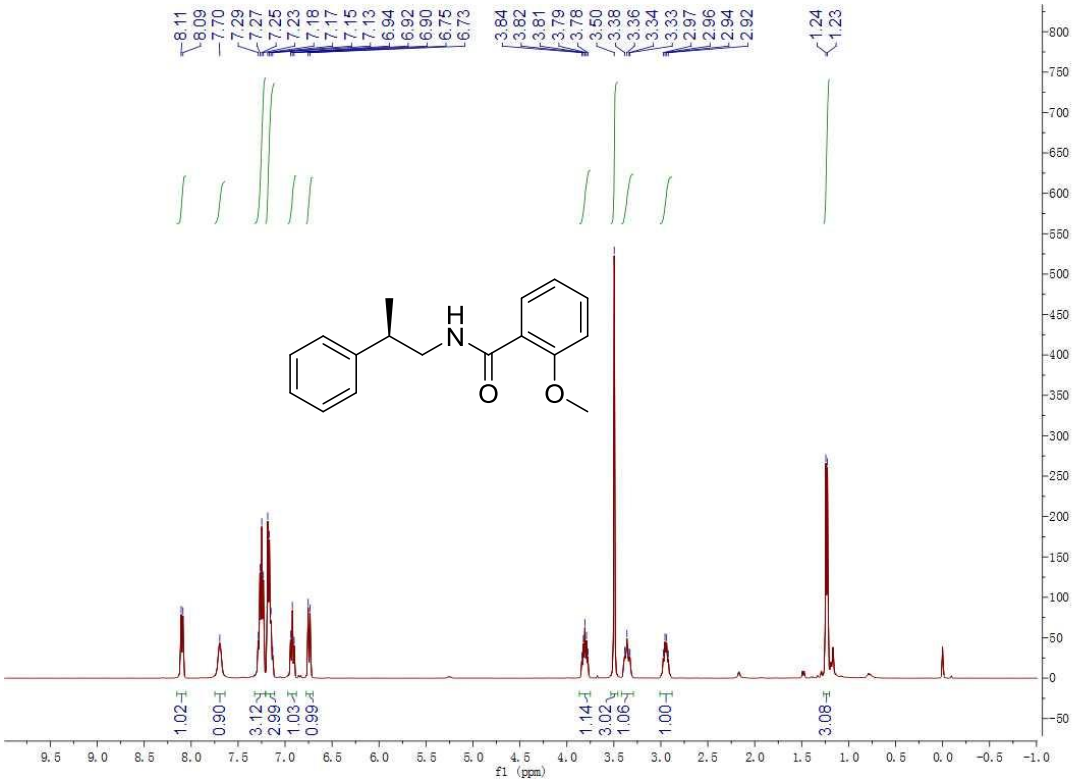


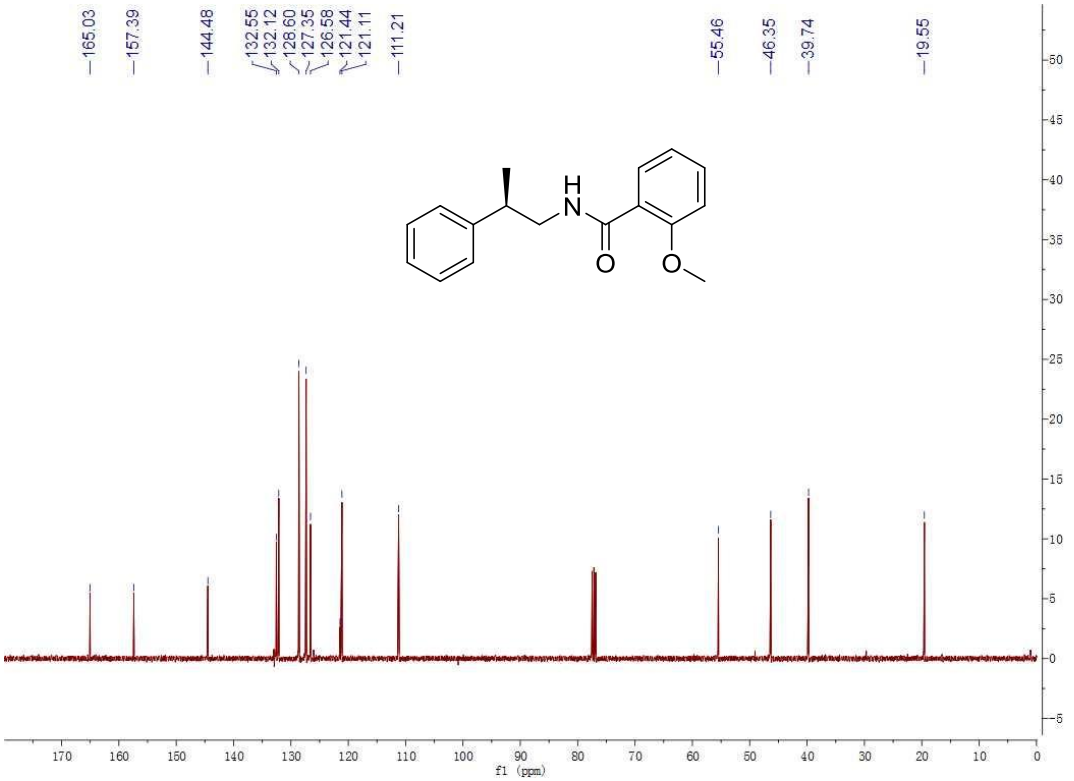
(*R*)-*N*-(2-(naphthalen-2-yl)-2-phenylethyl)acetamide (2y)



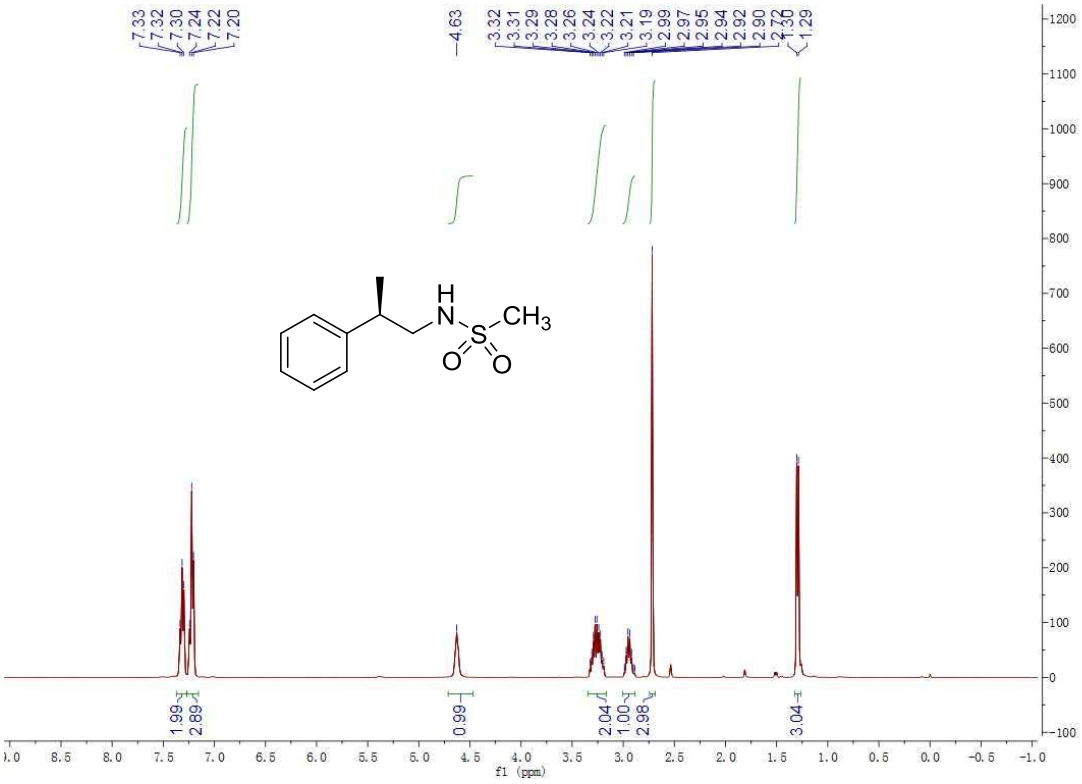


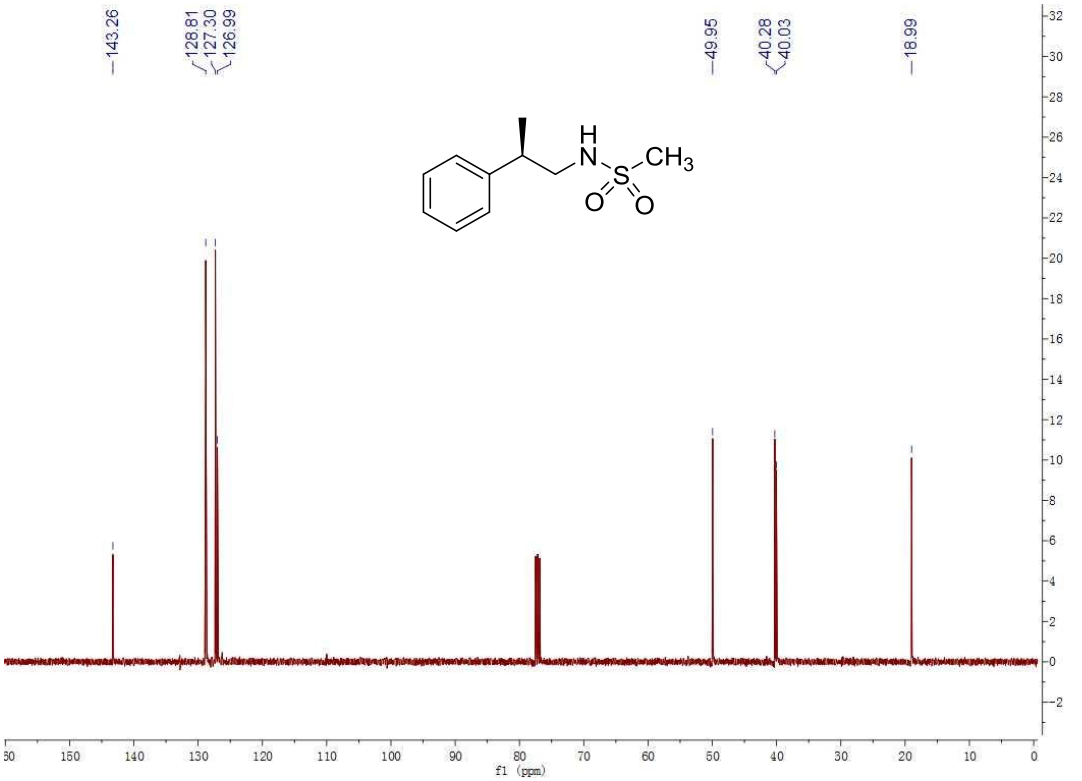
(*R*)-2-methoxy-*N*-(2-phenylpropyl)benzamide (4a)



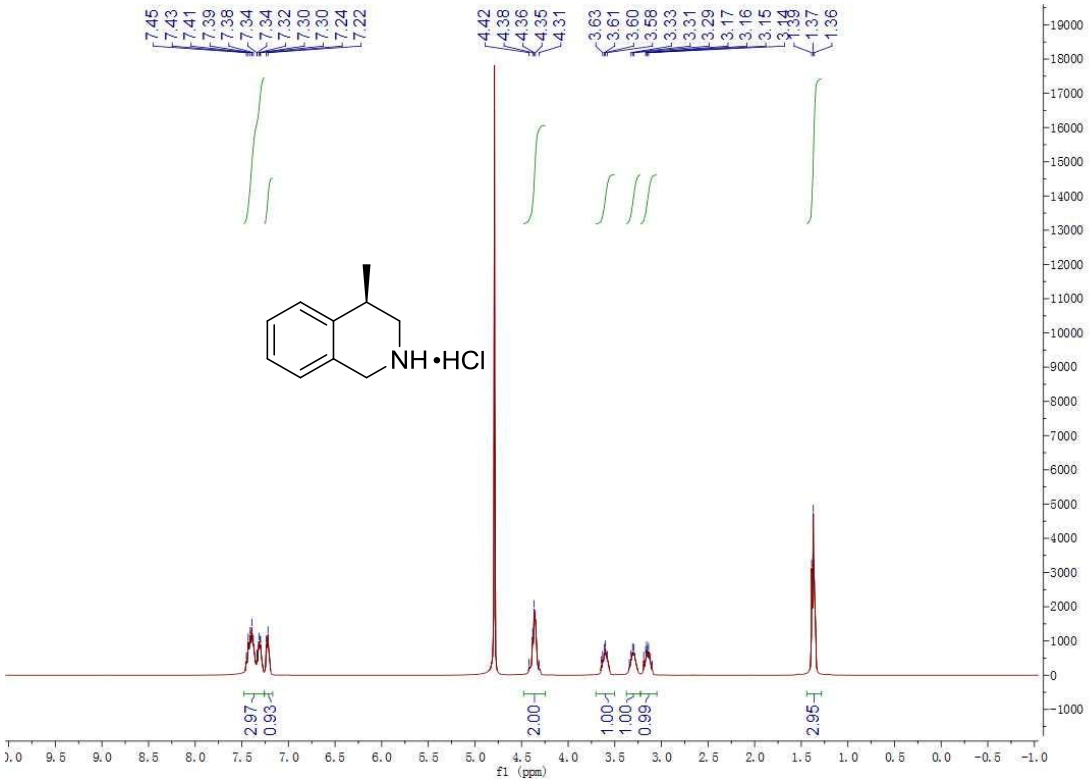


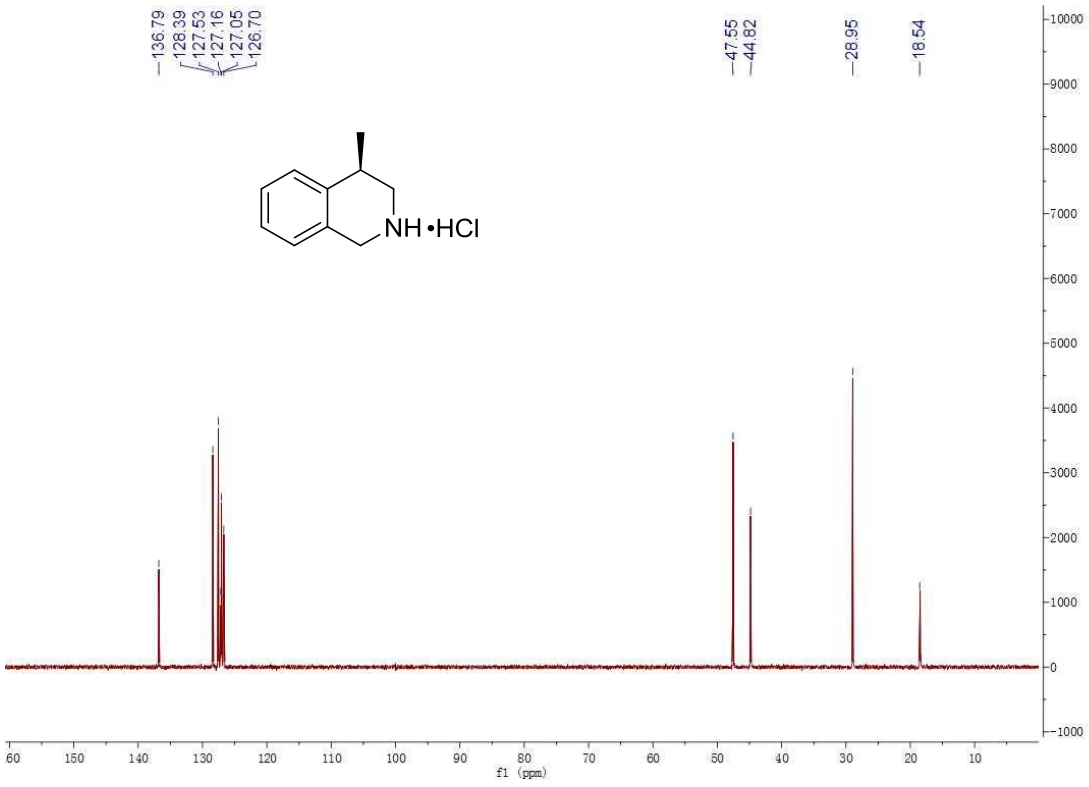
(*R*)-*N*-(2-phenylpropyl)methanesulfonamide (5a)





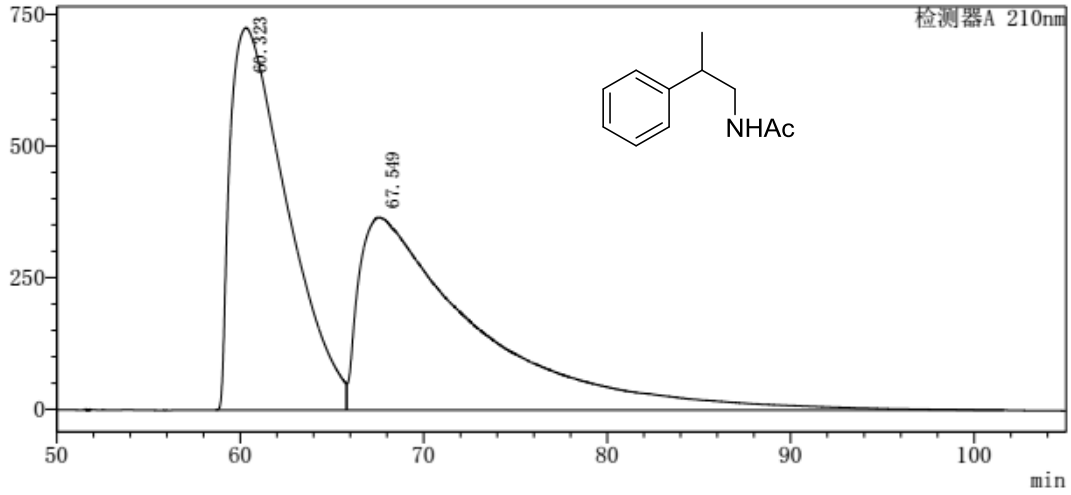
(*R*)-4-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (7a)

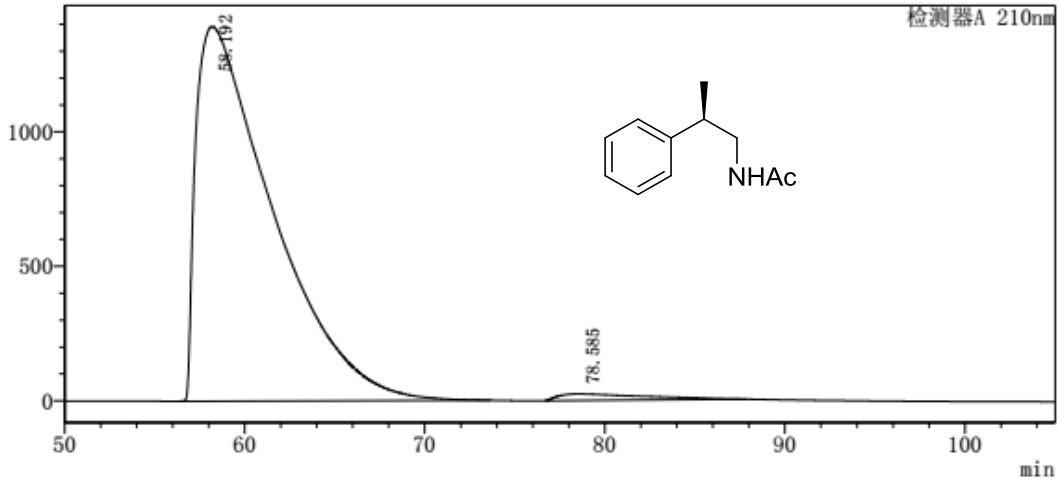




6. HPLC Chromatograms

(*R*)-*N*-(2-phenylpropyl)acetamide (2a)





Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
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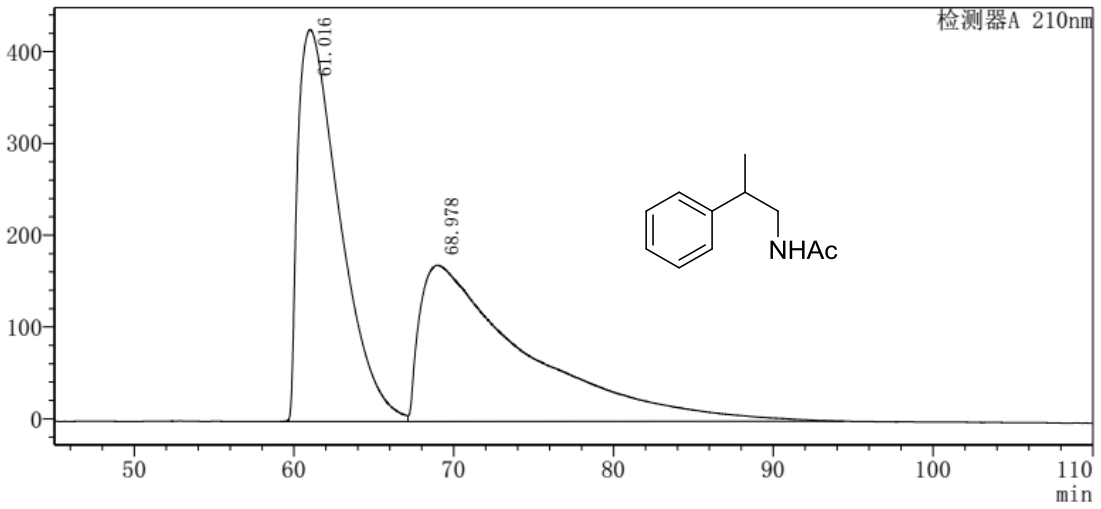
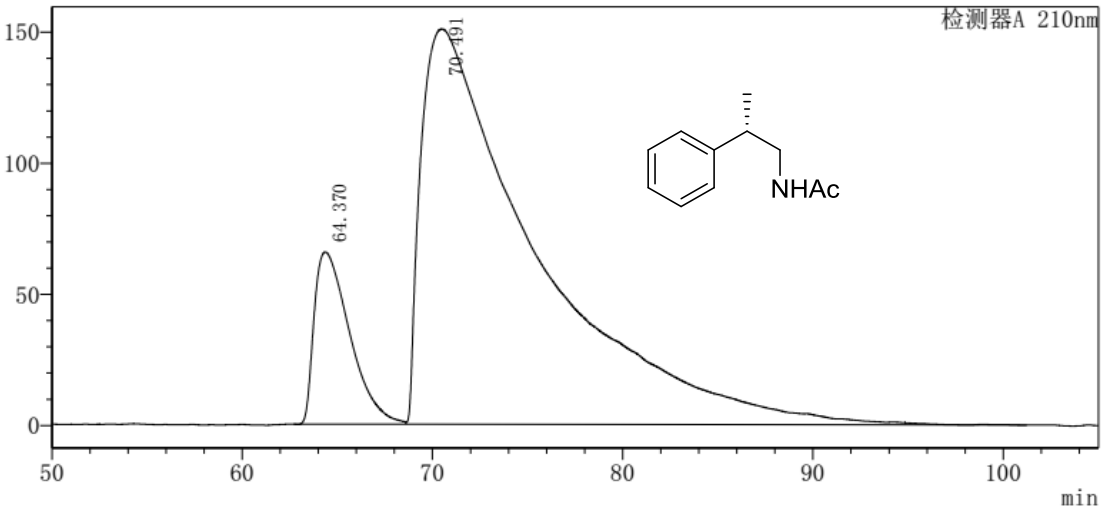
2	78.585	8273891	24461	1.967

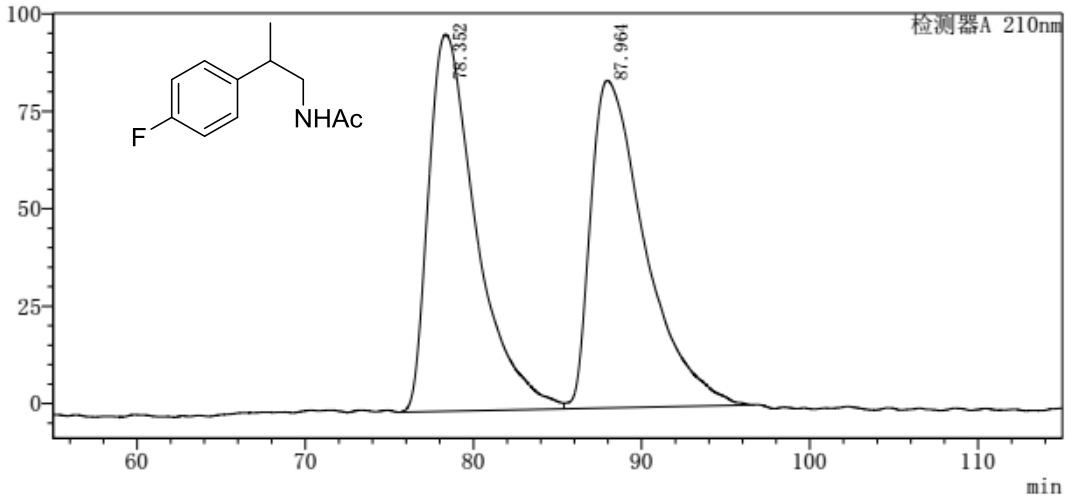
(*S*)-*N*-(2-phenylpropyl)acetamide (2a')

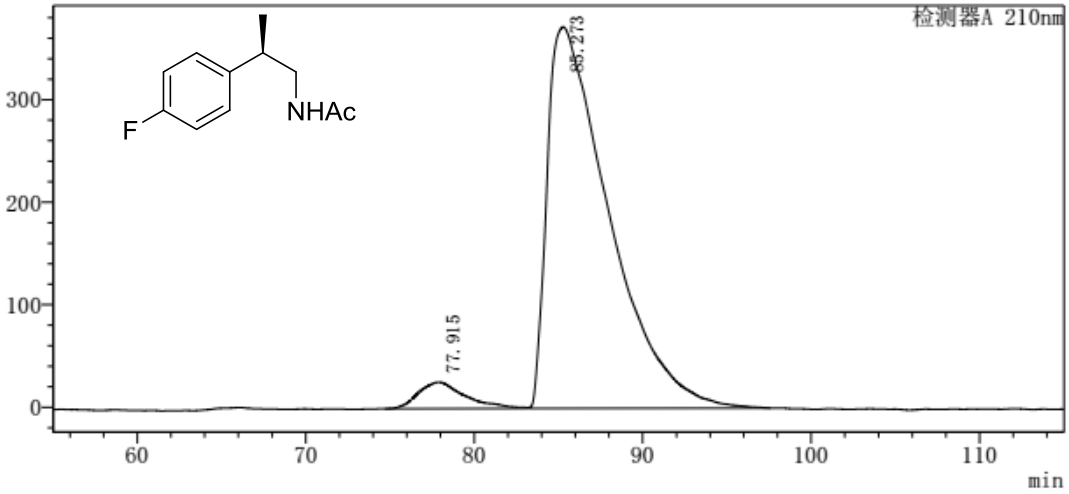




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	64.370	8548844	65643	11.848
2	70.491	63605417	150762	88.152

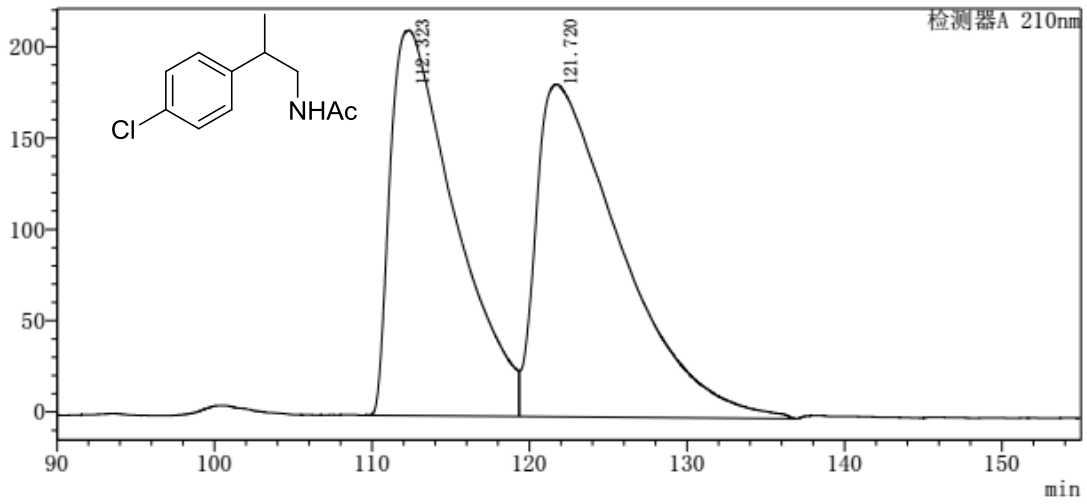
(*R*)-*N*-(2-(4-fluorophenyl)propyl)acetamide (2g)

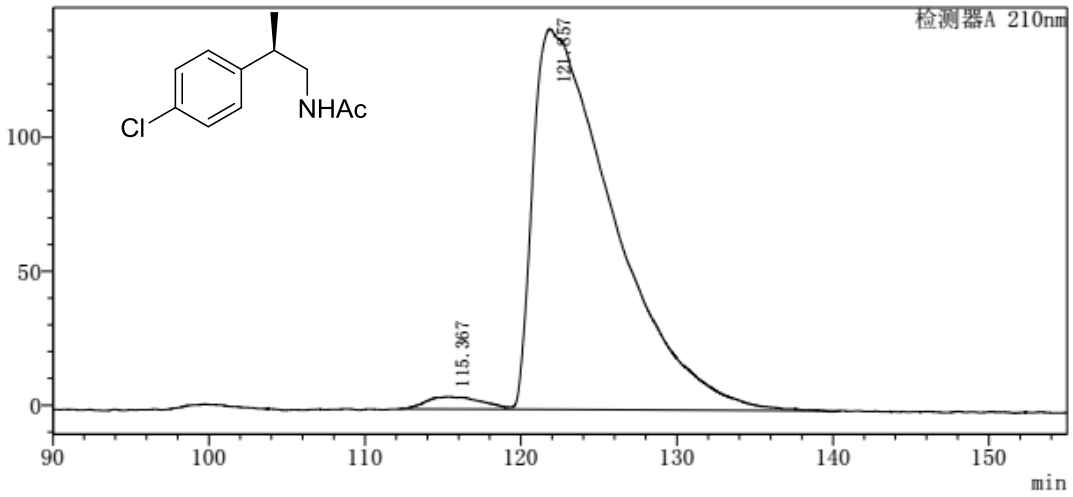




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	77.915	4989881	25737	4.995
2	85.273	94907198	372037	95.005

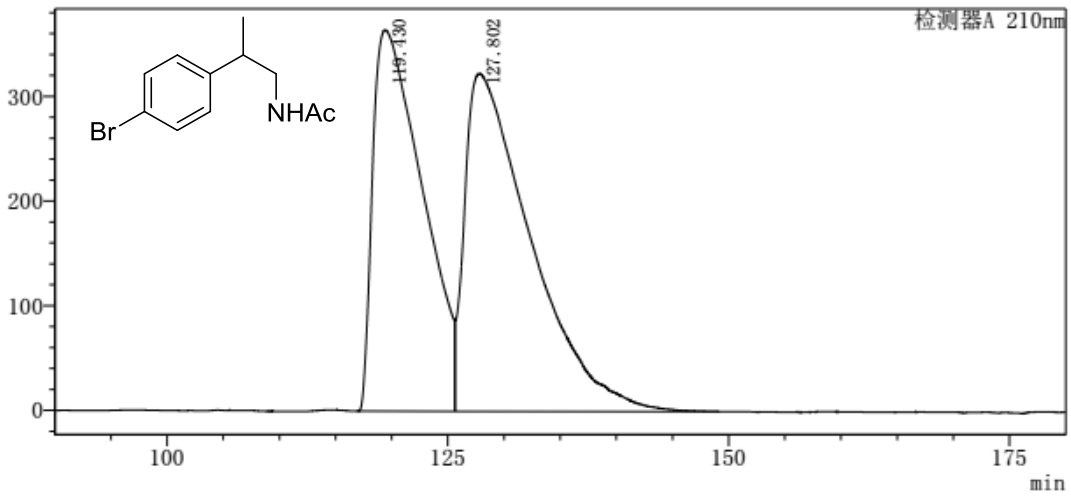
(*R*)-*N*-(2-(4-chlorophenyl)propyl)acetamide (2h)

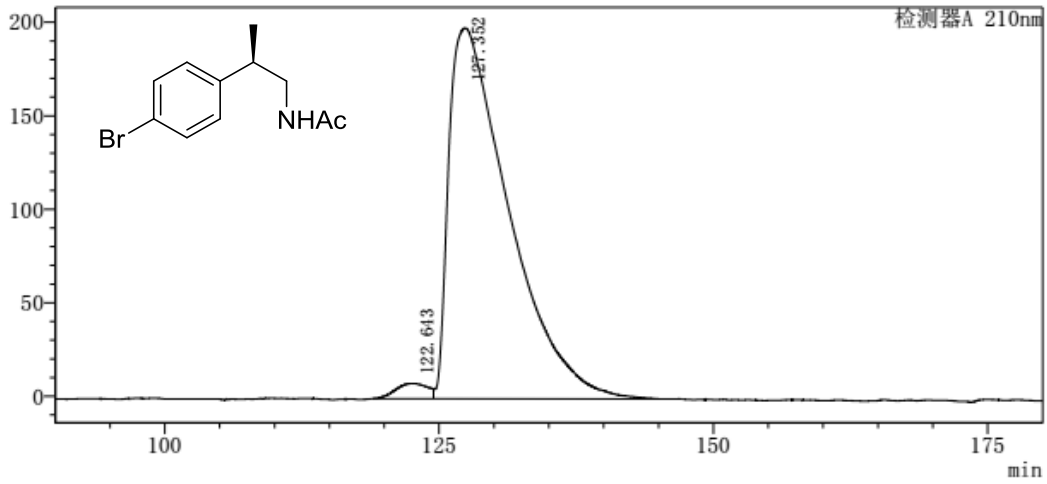




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	115.367	1125950	4590	2.156
2	121.857	51104912	142074	97.844

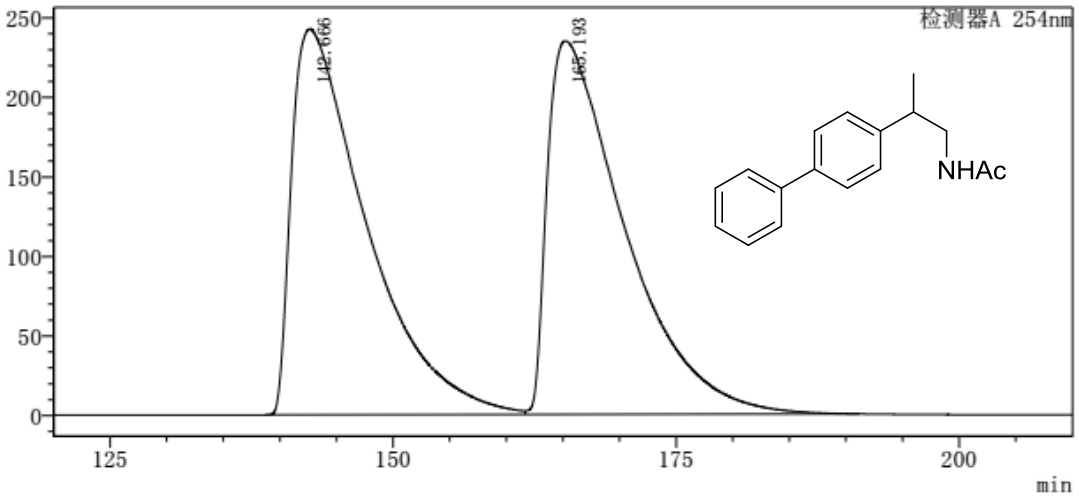
(*R*)-*N*-(2-(4-bromophenyl)propyl)acetamide (1i)

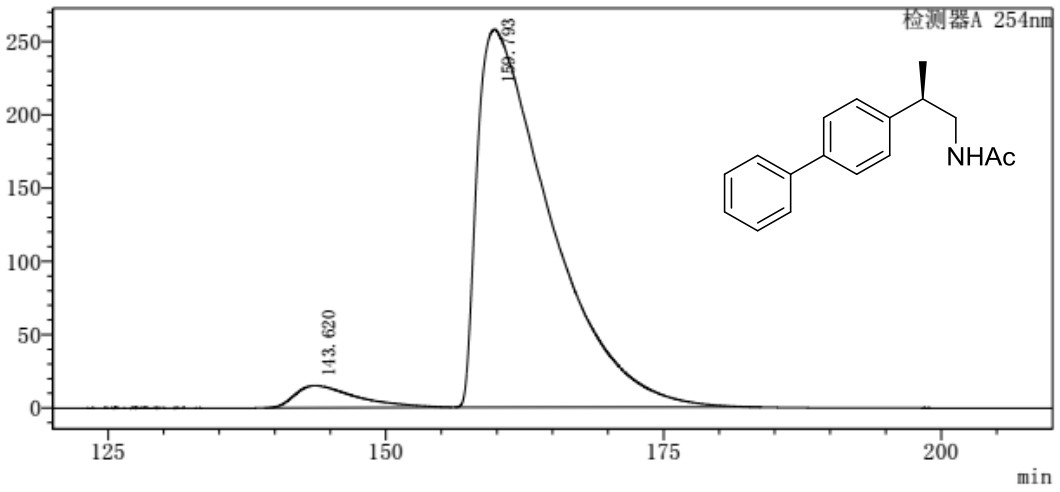




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	122.643	1662263	8141	2.158
2	127.352	75375613	198095	97.842

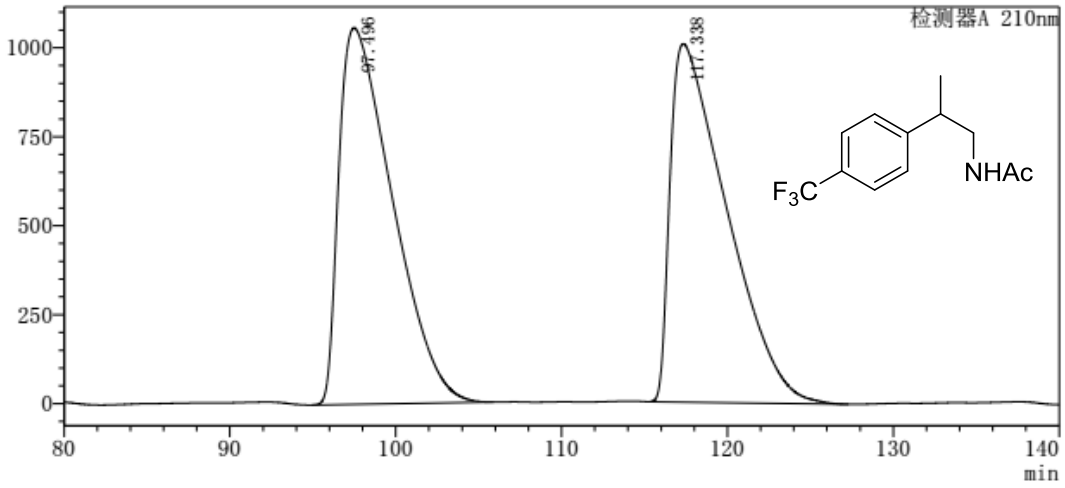
(*R*)-*N*-(2-([1,1'-biphenyl]-4-yl)propyl)acetamide (2j)

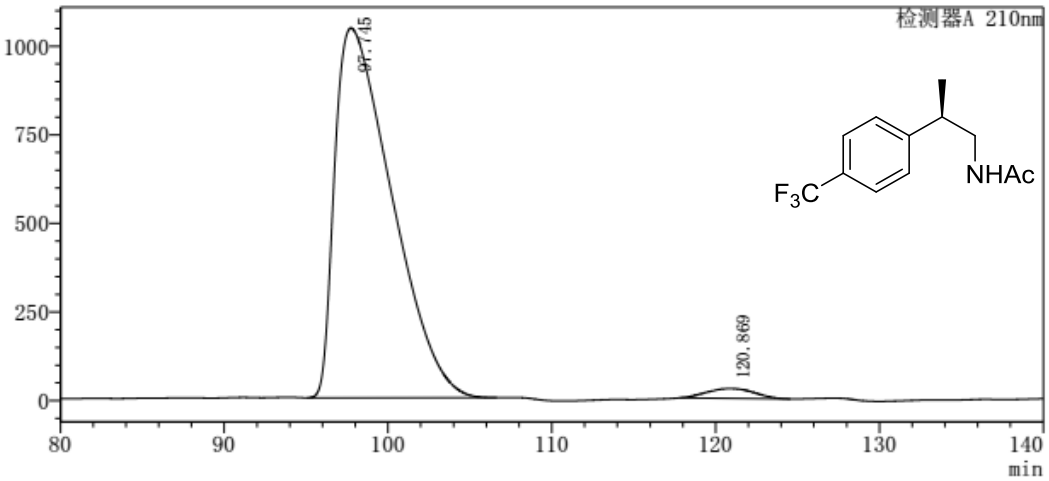




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	143.620	5776025	15062	4.652
2	159.793	118388533	257812	95.348

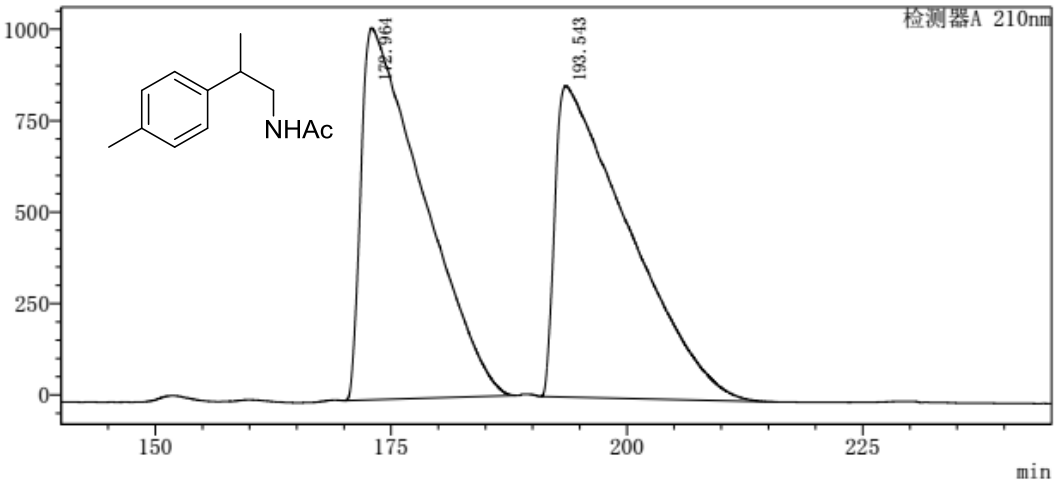
(*R*)-*N*-(2-(4-(trifluoromethyl)phenyl)propyl)acetamide (2k)

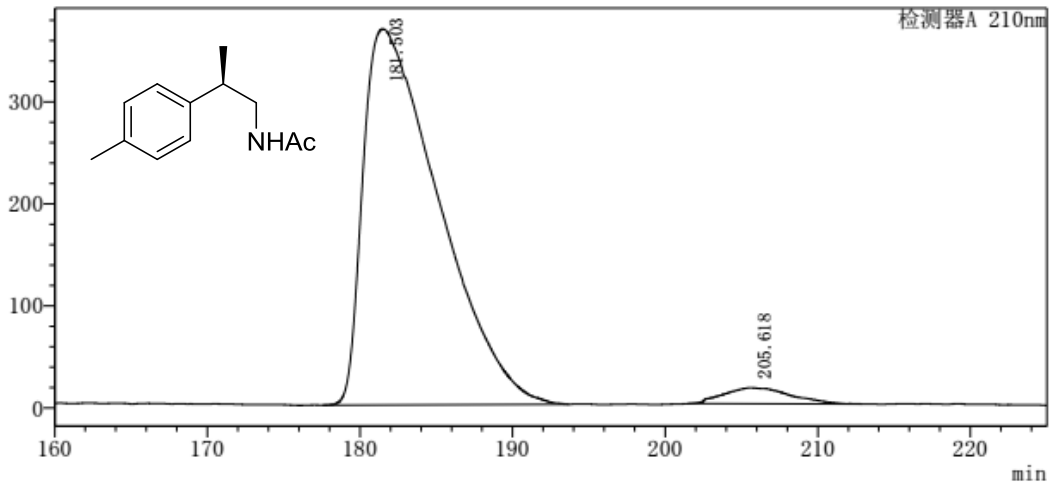




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	97.745	252004755	1043255	97.842
2	120.869	5558192	27593	2.158

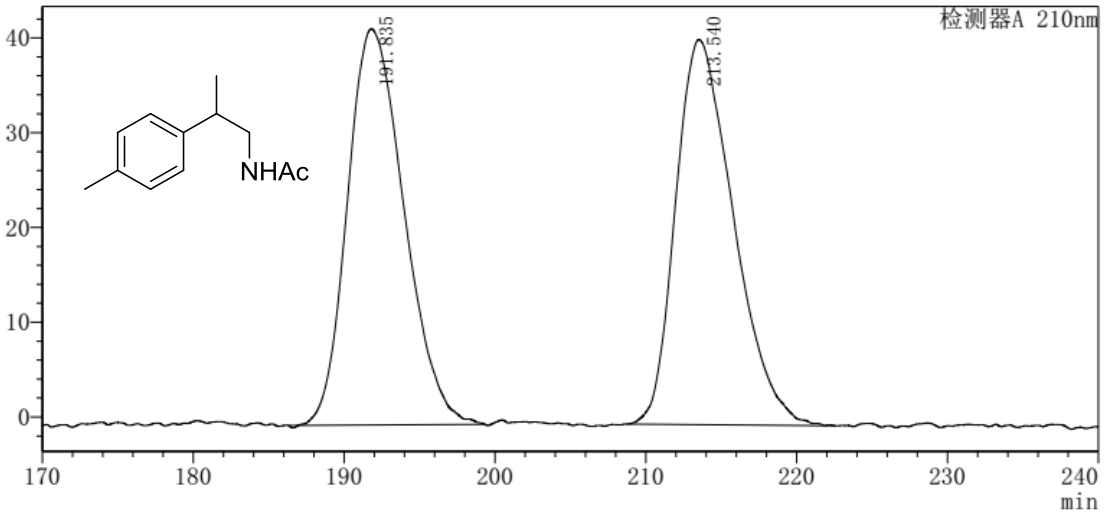
(*R*)-*N*-(2-(*p*-tolyl)propyl)acetamide (2l)

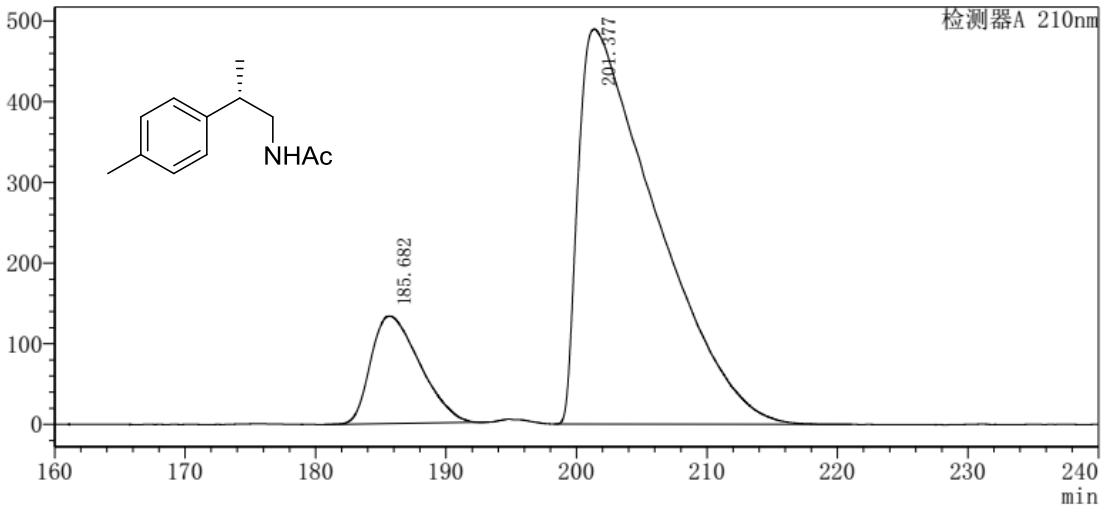




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	181.503	127103249	368061	96.400
2	205.618	4746936	15657	3.600

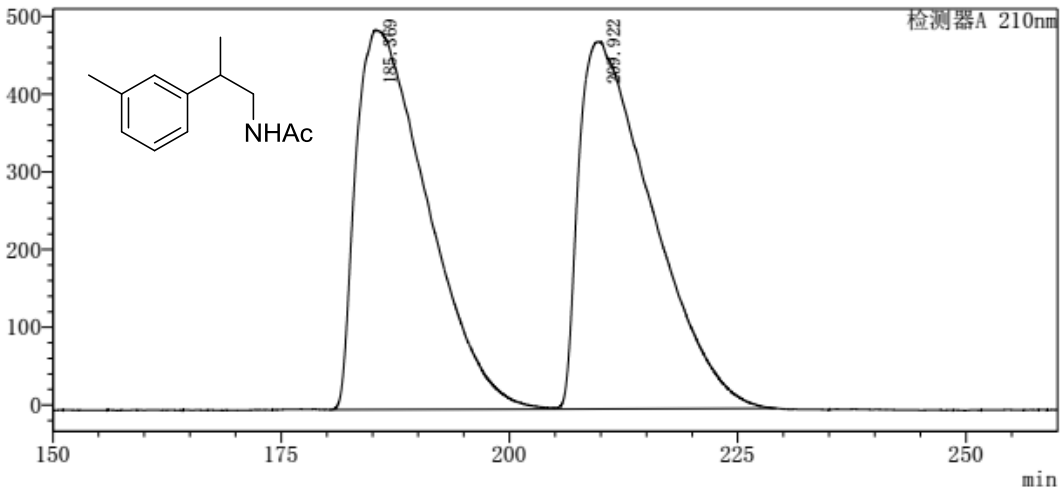
(*S*)-*N*-(2-(*p*-tolyl)propyl)acetamide (2l')

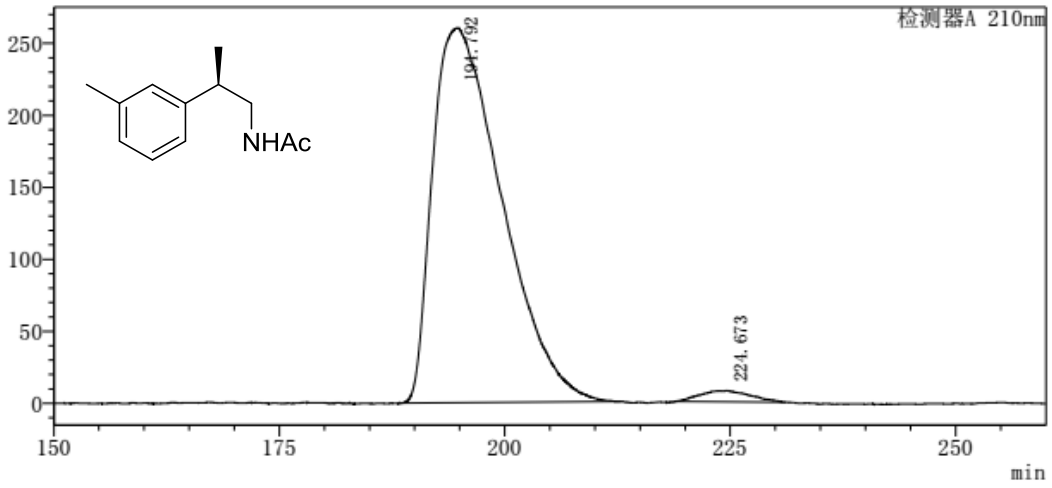




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	185.682	34706067	133073	14.552
2	201.377	203790630	489513	85.448

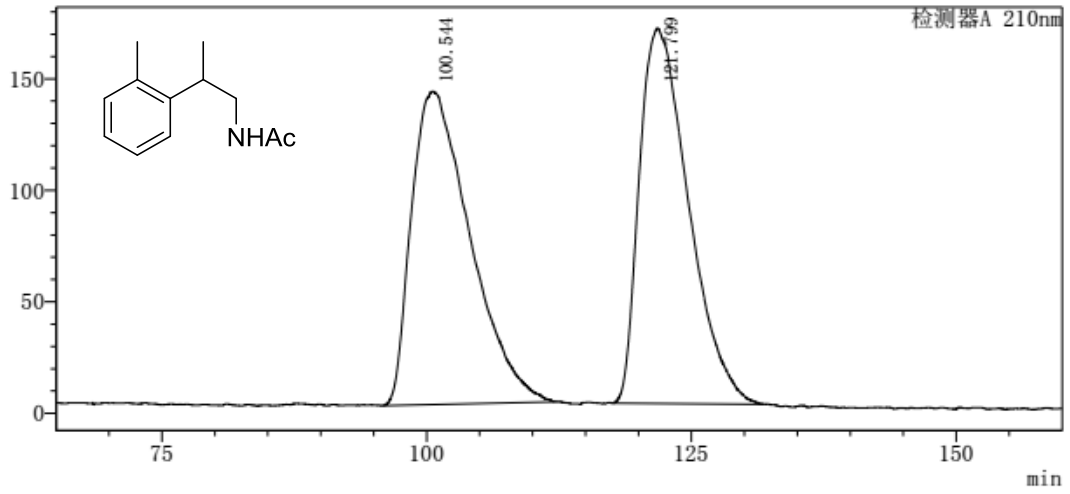
(*R*)-*N*-(2-(*m*-tolyl)propyl)acetamide (2m)

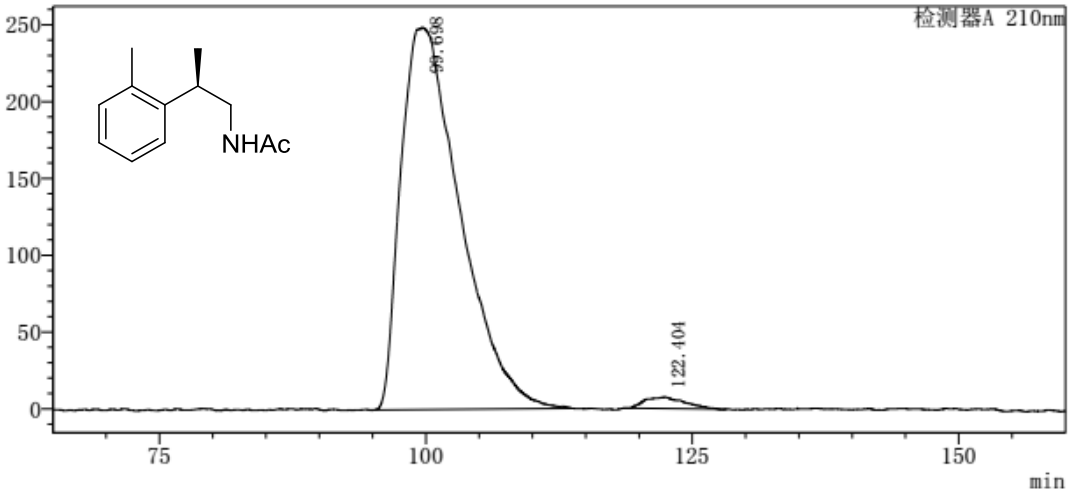




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	194.792	139160639	260084	97.929
2	224.673	2942707	7659	2.071

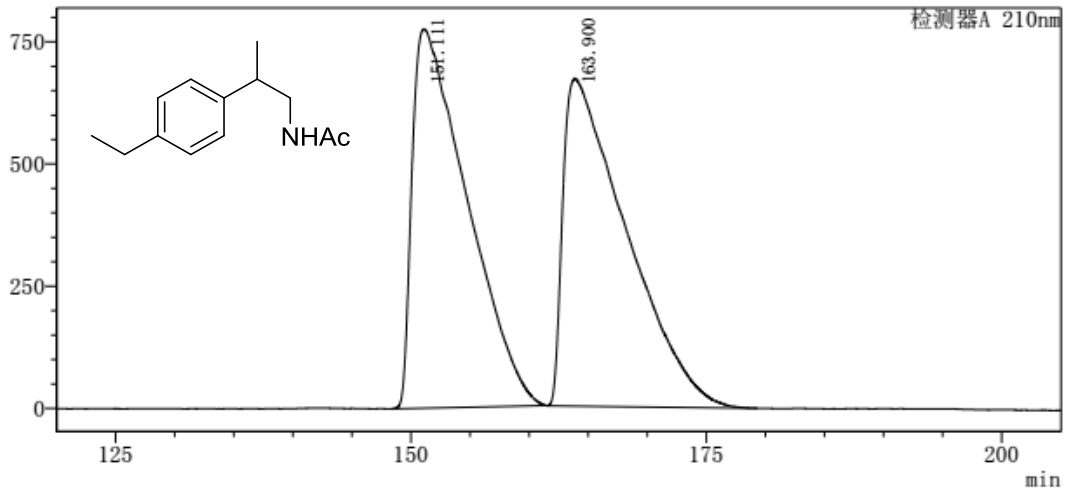
(*R*)-*N*-(2-(*o*-tolyl)propyl)acetamide (2n)

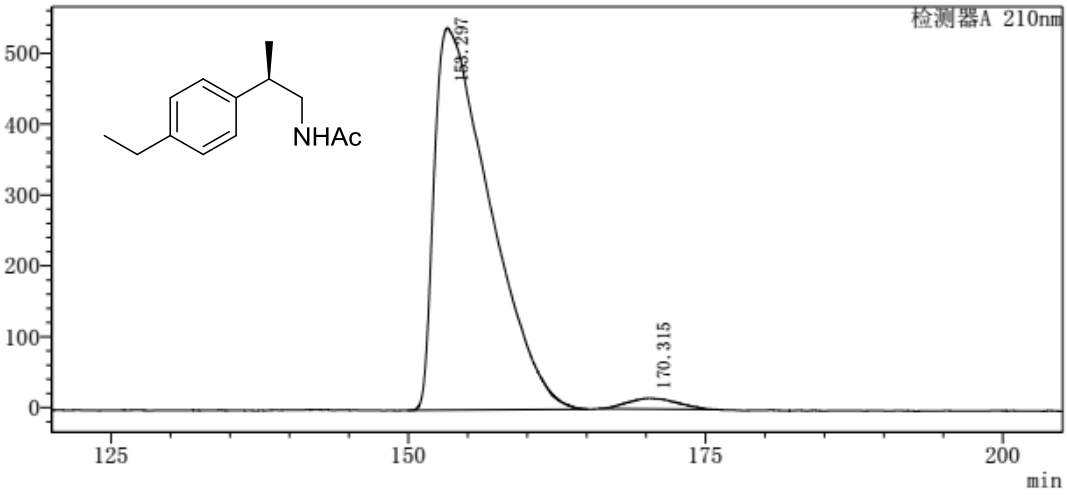




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	99.698	96032559	248616	98.037
2	122.404	1923364	7392	1.963

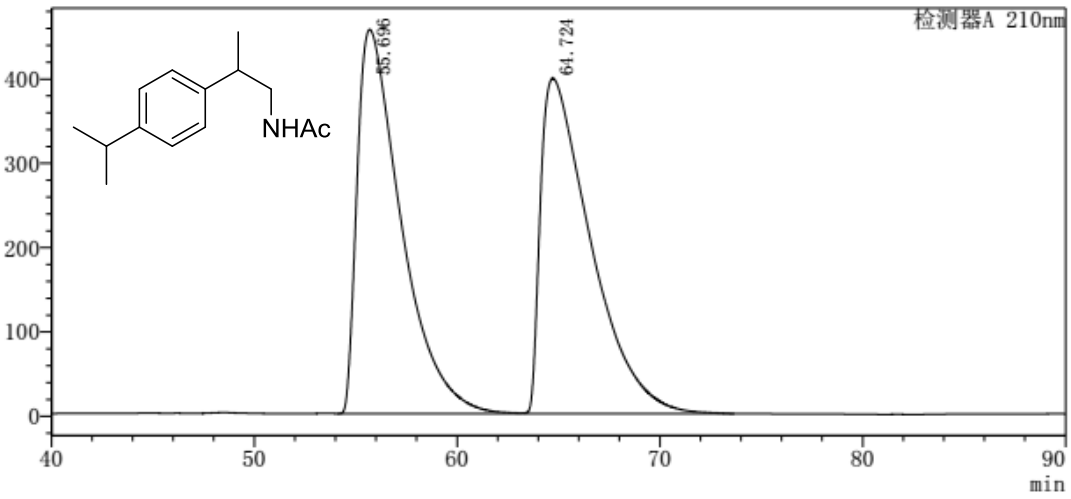
(*R*)-*N*-(2-(4-ethylphenyl)propyl)acetamide (2o)

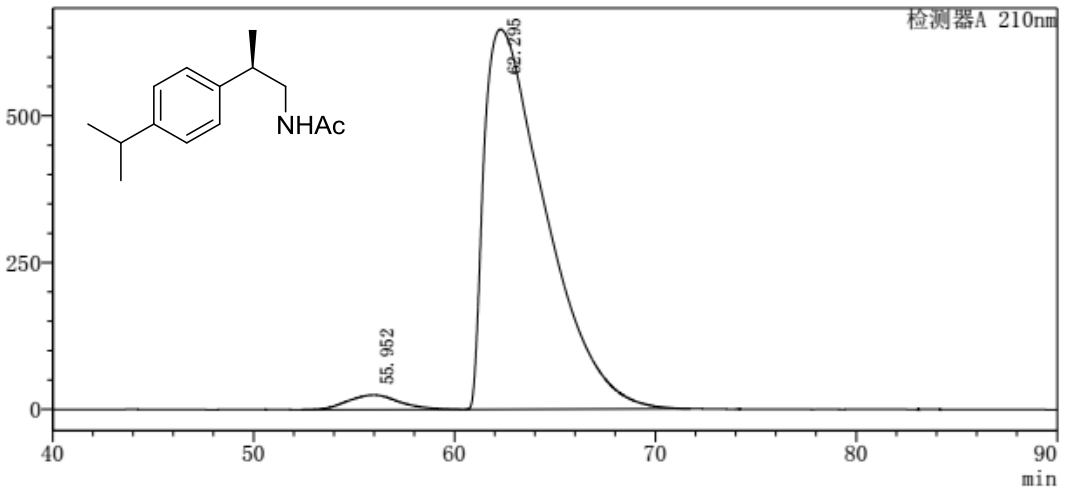




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	153.297	175373172	538933	97.537
2	170.315	4429058	15137	2.463

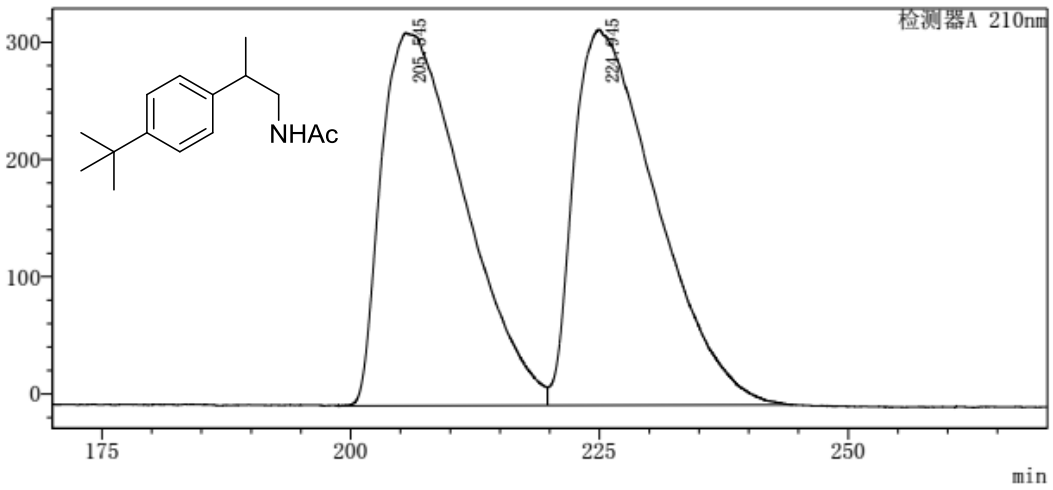
(*R*)-*N*-(2-(4-isopropylphenyl)propyl)acetamide (2p)

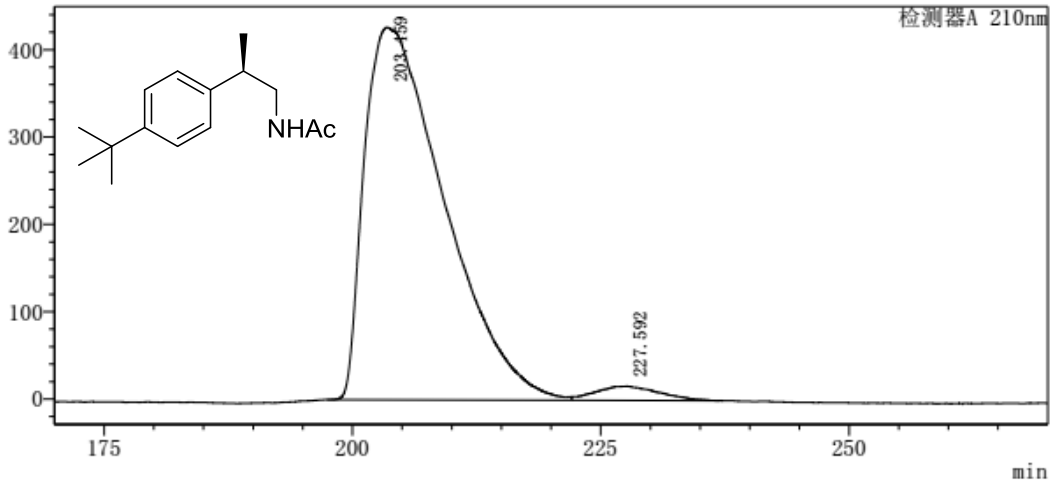




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	55.952	4468914	24801	3.140
2	62.295	137870381	647244	96.860

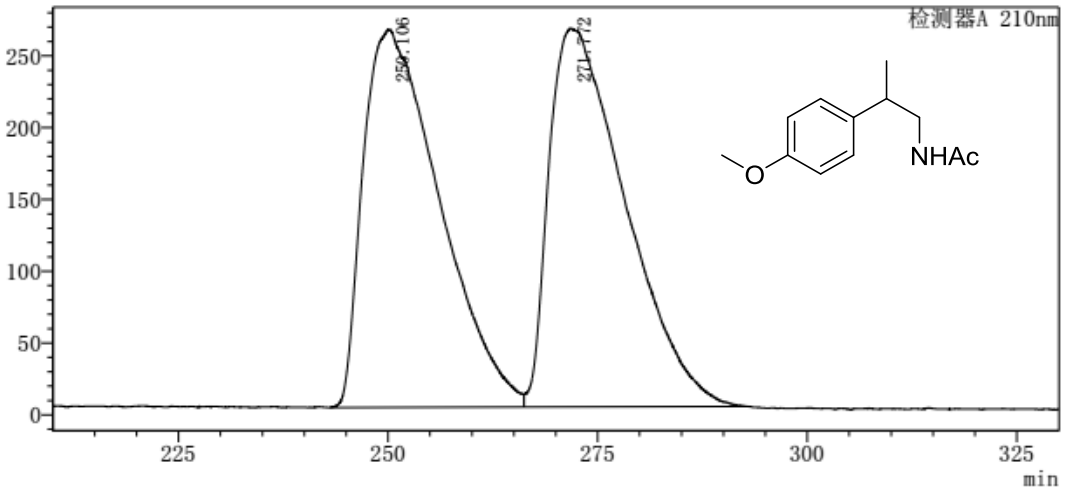
(*R*)-*N*-(2-(4-(*tert*-butyl)phenyl)propyl)acetamide (2q)

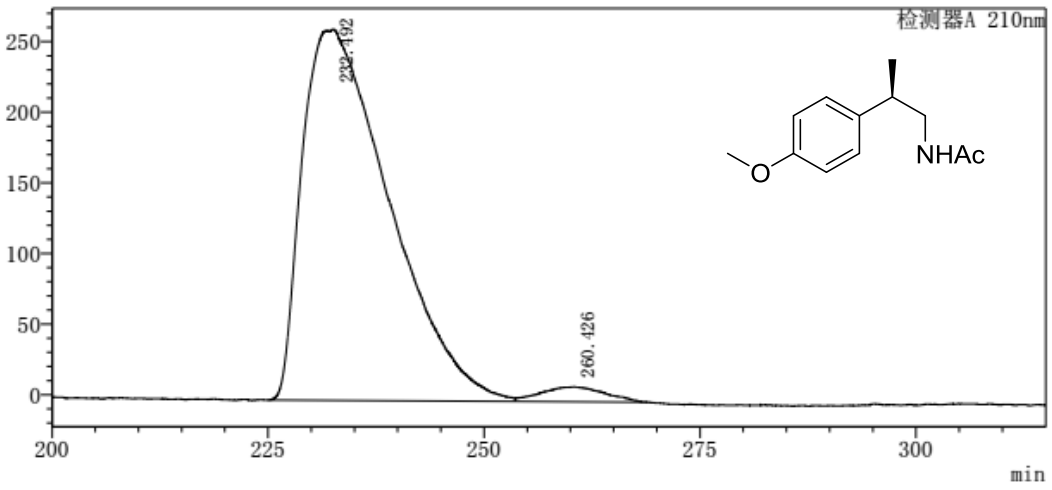




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	203.459	238821161	426225	97.048
2	227.592	7265672	16254	2.952

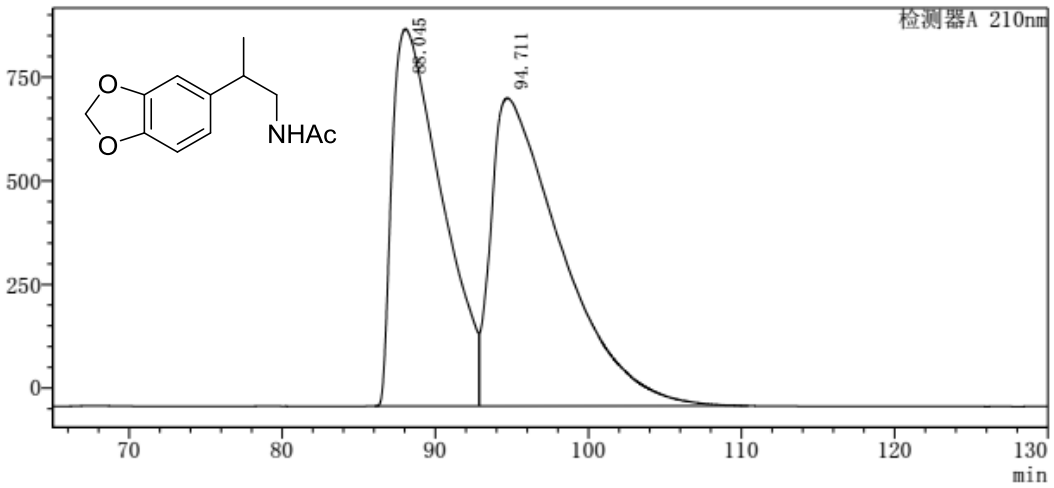
(*R*)-*N*-(2-(4-methoxyphenyl)propyl)acetamide (2r)

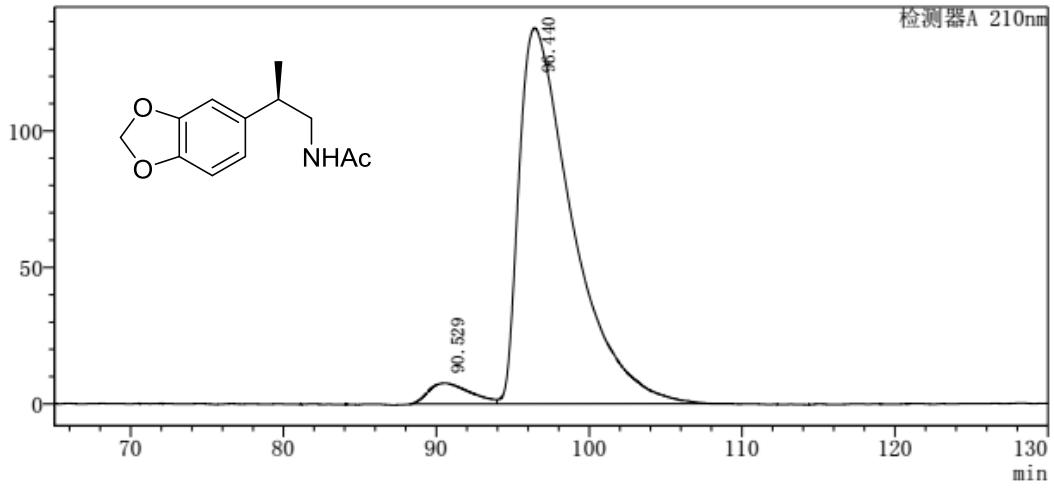




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	232.492	184510212	262671	97.136
2	260.426	5440129	10587	2.864

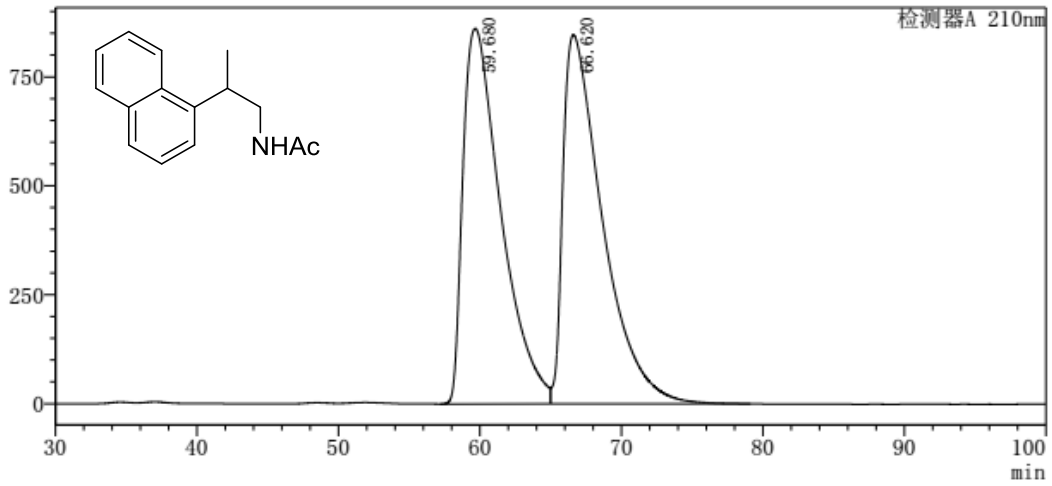
(*R*)-*N*-(2-(benzo[*d*][1,3]dioxol-5-yl)propyl)acetamide (2s)

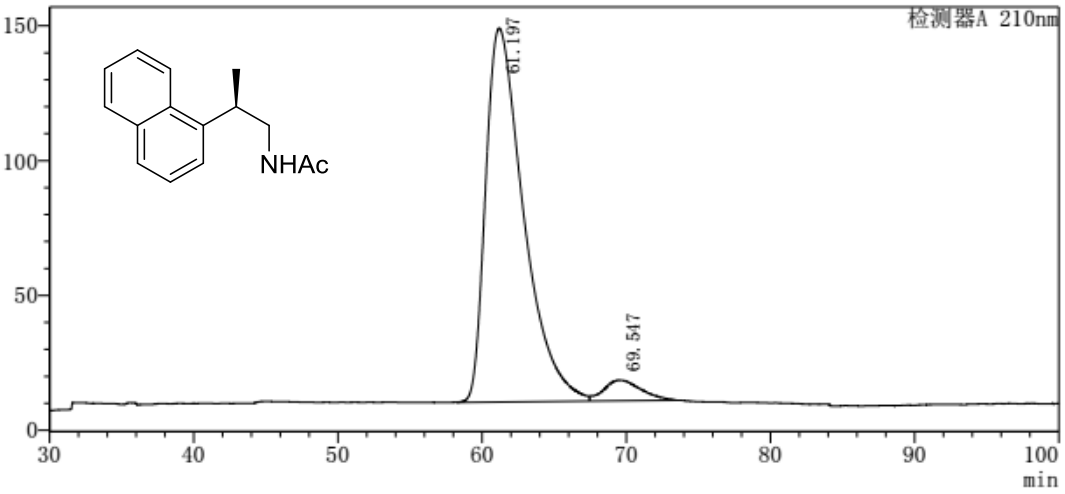




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	90.529	1454392	7652	4.178
2	96.440	33352820	137646	95.822

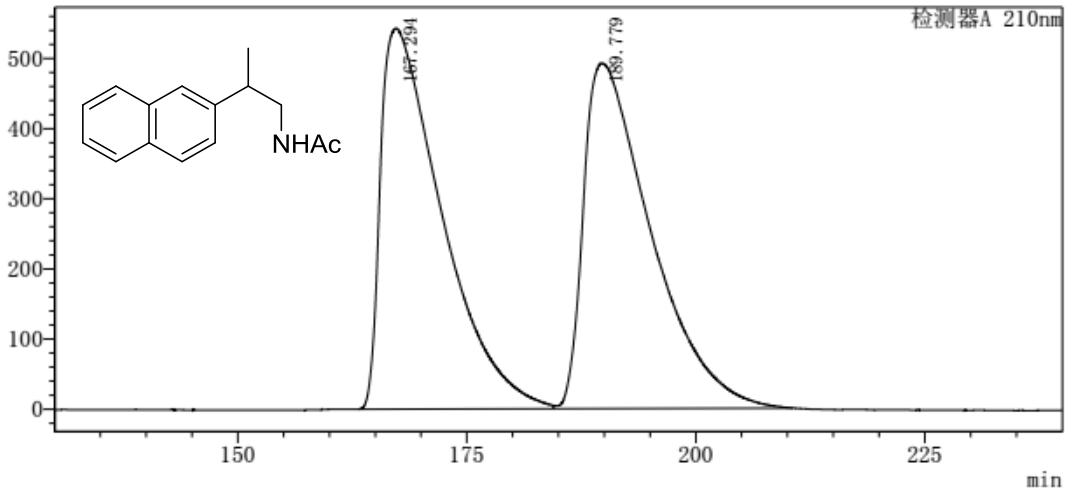
(*R*)-*N*-(2-(naphthalen-1-yl)propyl)acetamide (2t)

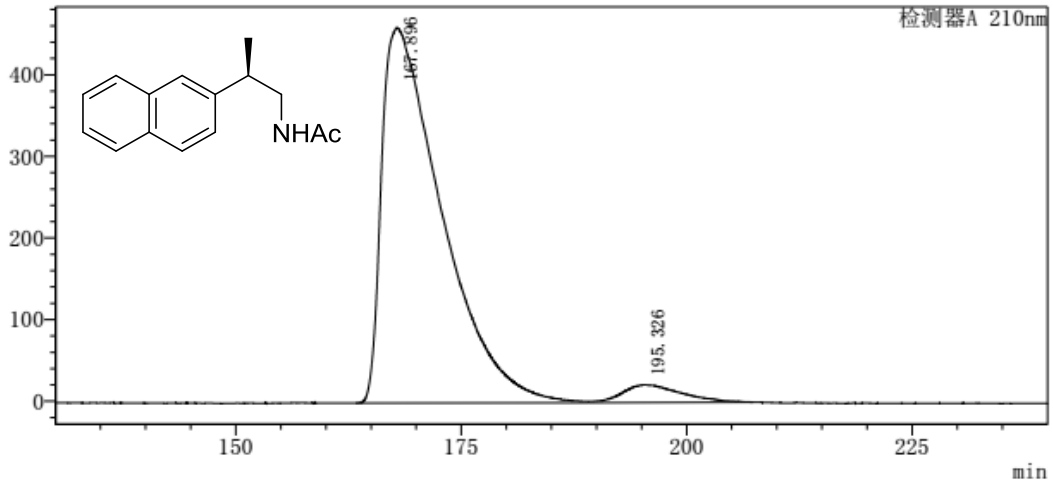




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	61.197	25391870	138580	94.877
2	69.547	1371115	7648	5.123

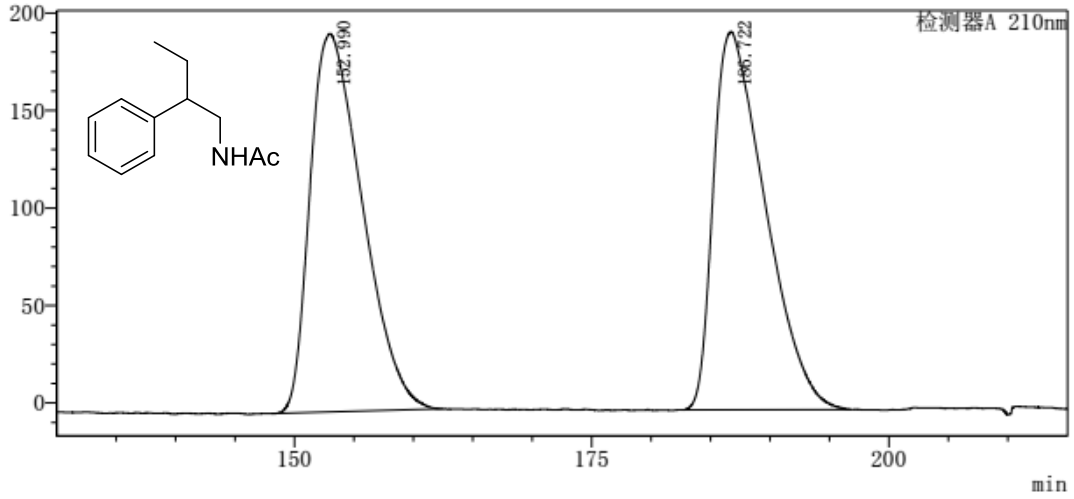
(*R*)-*N*-(2-(naphthalen-2-yl)propyl)acetamide (2u)

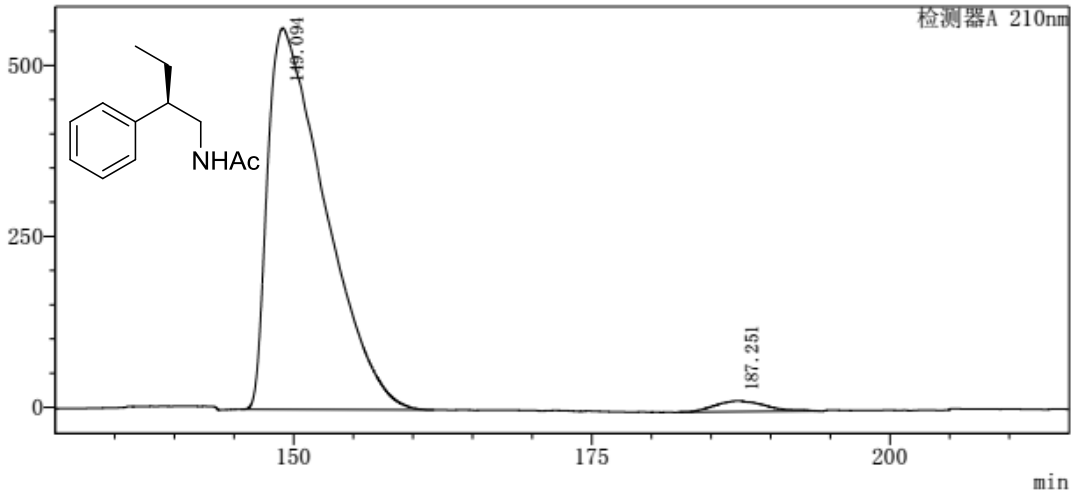




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	167.896	213165877	459647	95.574
2	195.326	9870619	21709	4.426

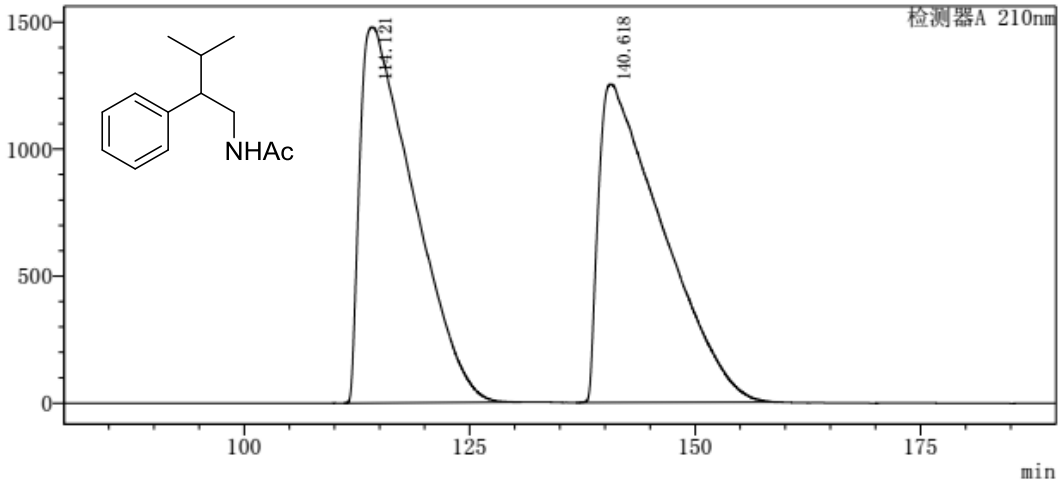
(*R*)-*N*-(2-phenylbutyl)acetamide (2v)

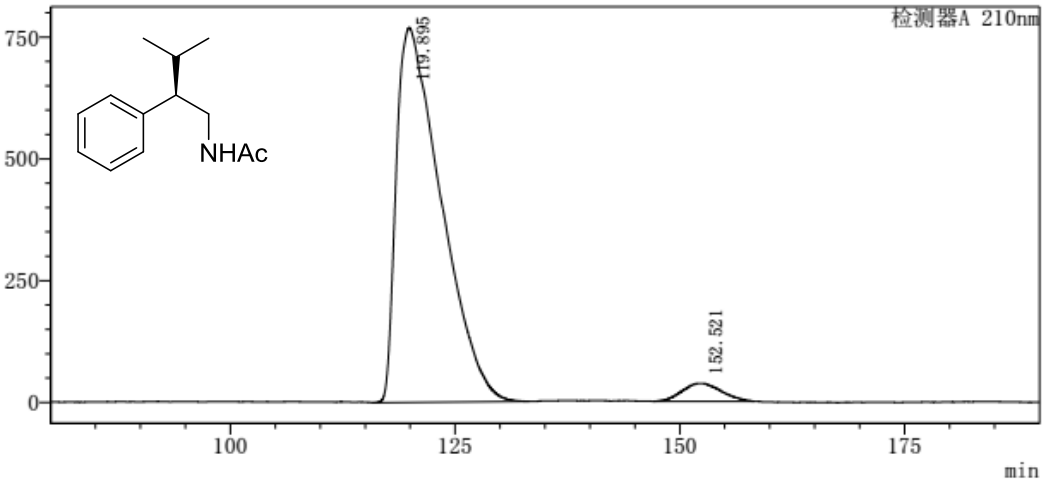




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	149.094	186916779	557725	97.583
2	187.251	4629916	15918	2.417

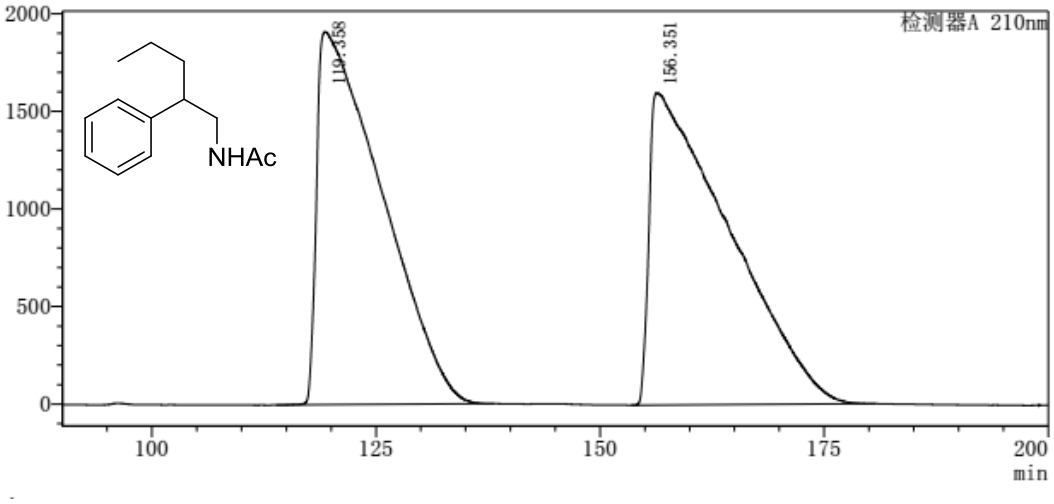
(*R*)-*N*-(3-methyl-2-phenylbutyl)acetamide (2w)

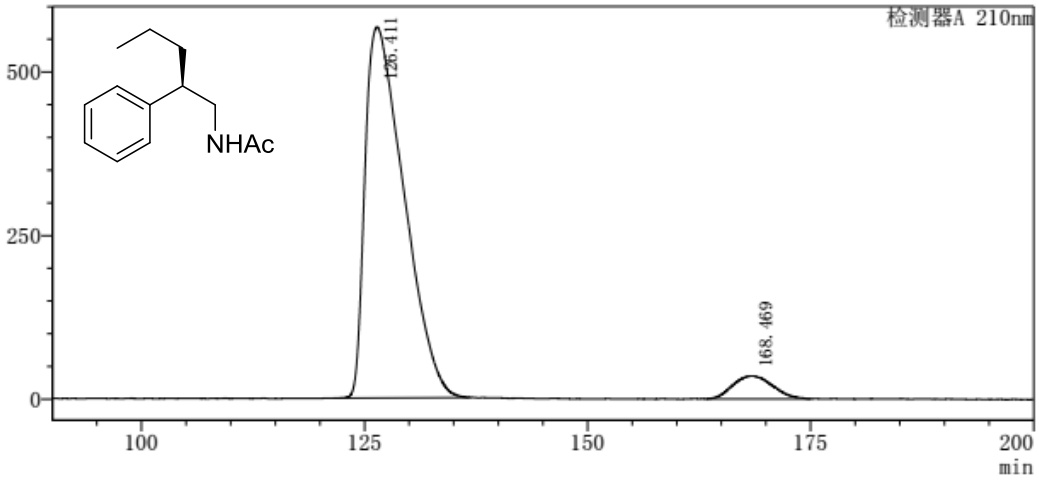




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	119.895	266616368	769339	96.008
2	152.521	11087309	36674	3.992

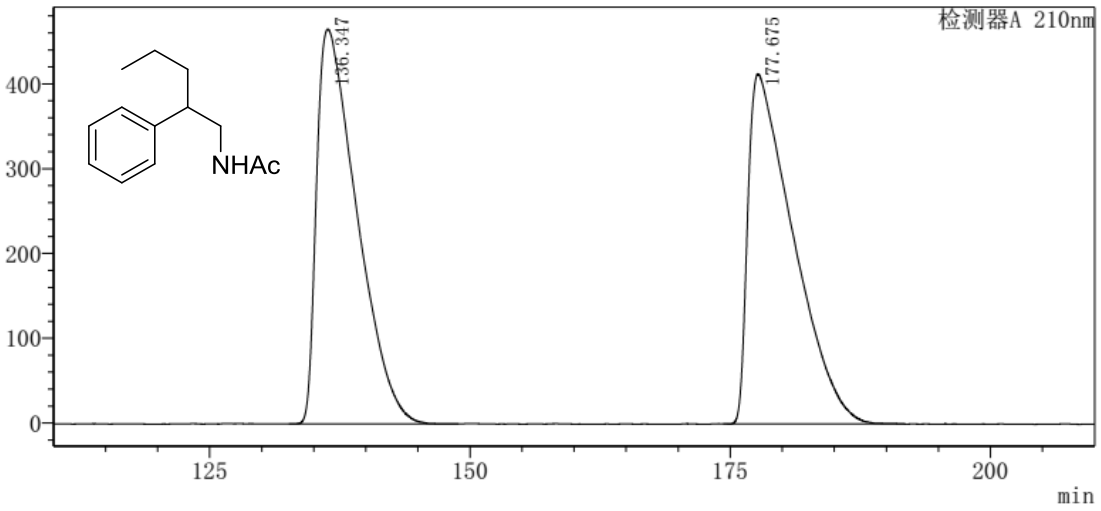
(*R*)-*N*-(2-phenylpentyl)acetamide (2x)

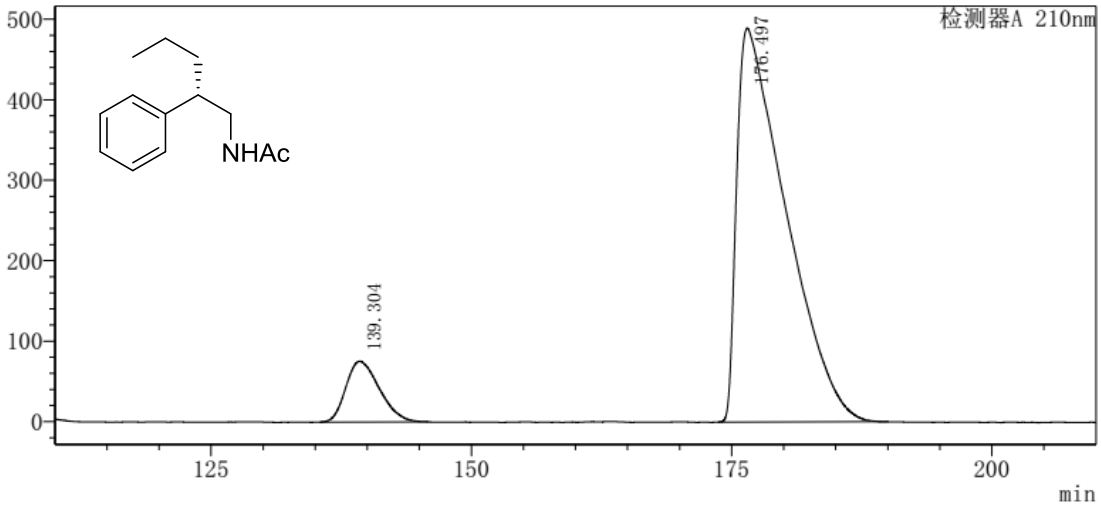




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	126.411	172092400	566575	94.091
2	168.469	10807003	34999	5.909

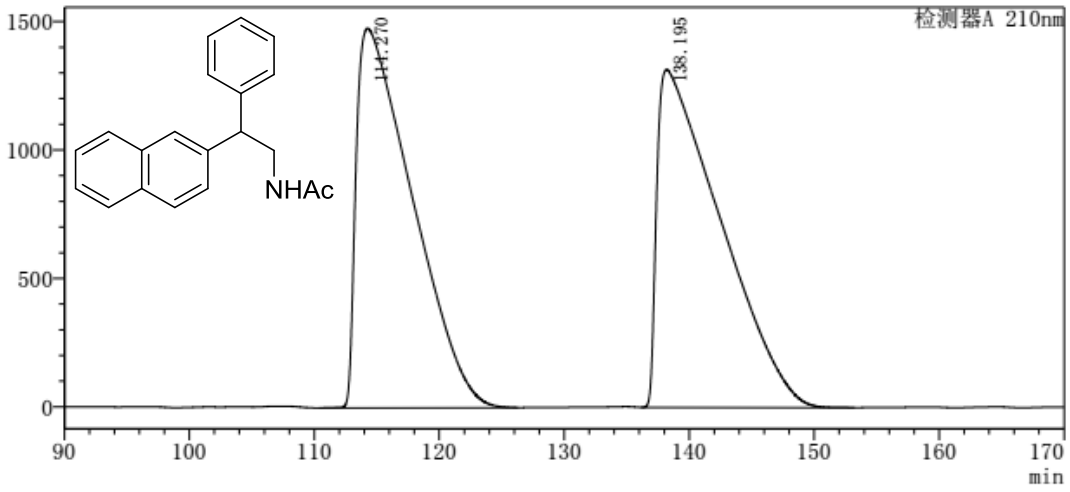
(*S*)-*N*-(2-phenylpentyl)acetamide (2x')

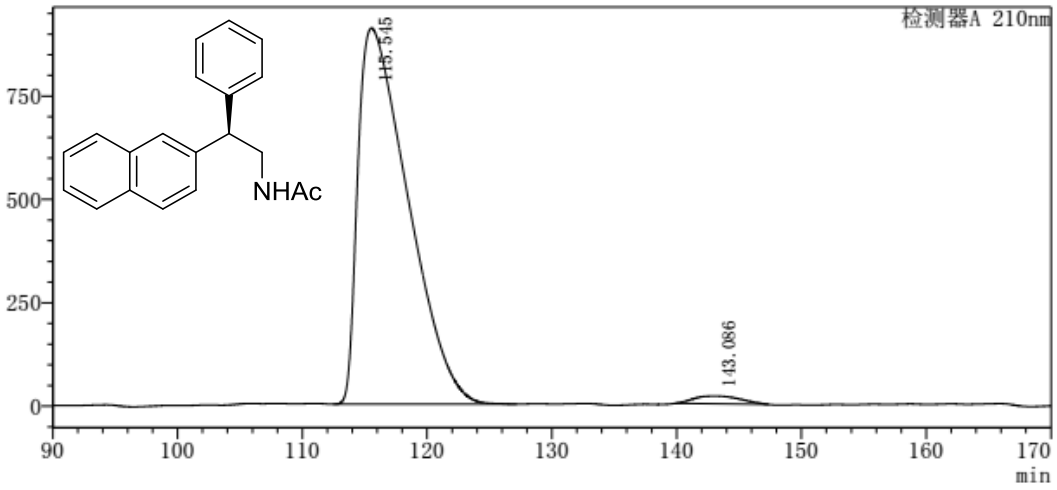




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	139.304	16899021	75504	9.513
2	176.497	160735444	489386	90.487

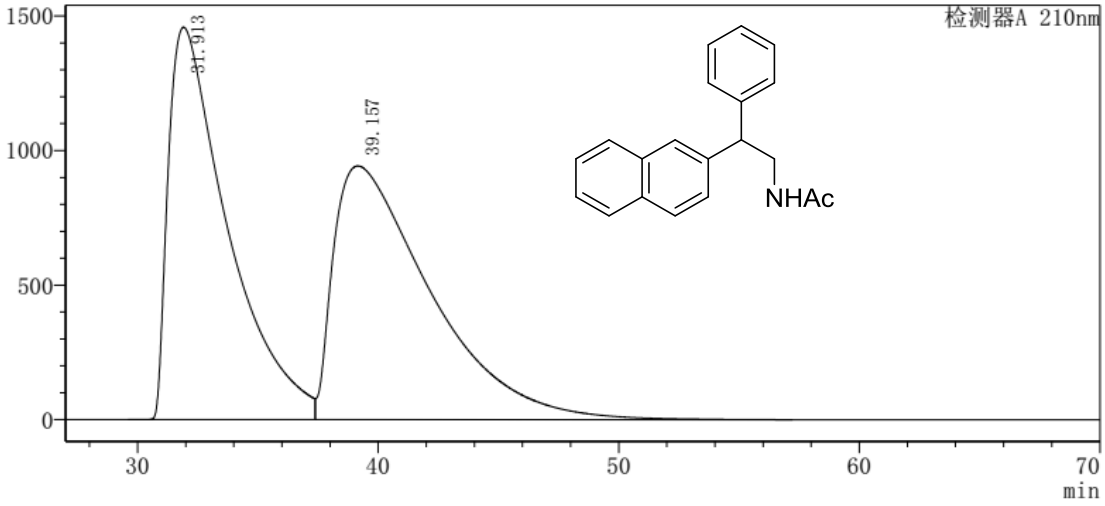
(*R*)-*N*-(2-(naphthalen-2-yl)-2-phenylethyl)acetamide (2y)

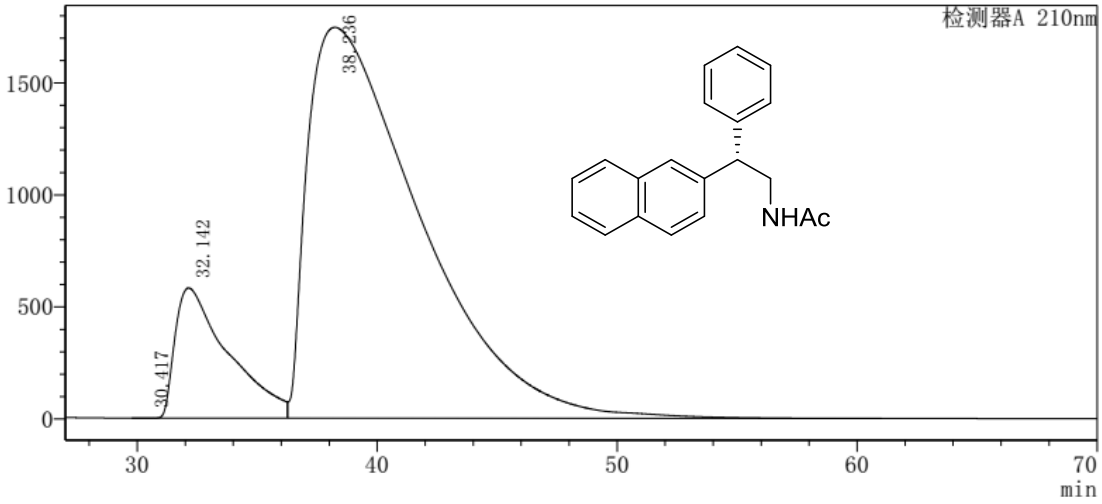




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	115.545	253816079	909720	98.091
2	143.086	4940713	18762	1.909

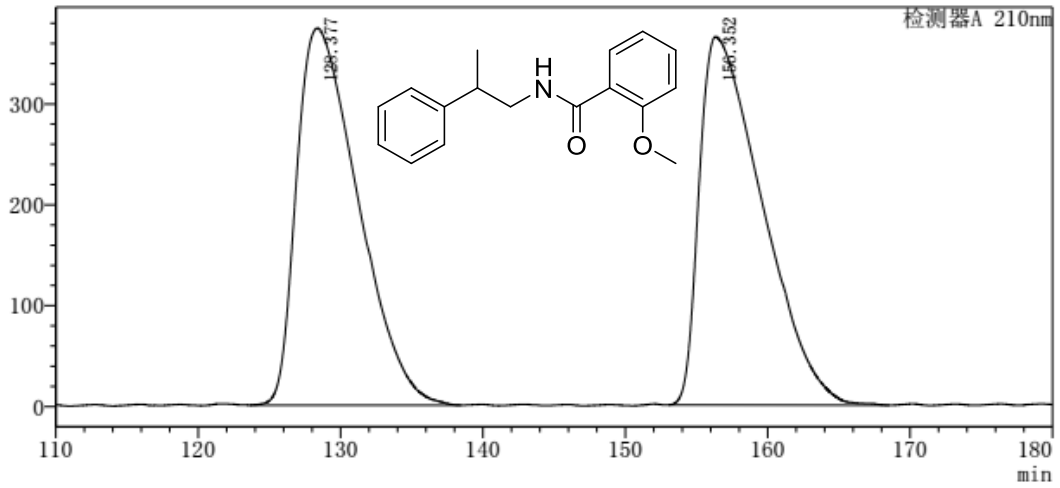
(*S*)-*N*-(2-(naphthalen-2-yl)-2-phenylethyl)acetamide (2y')

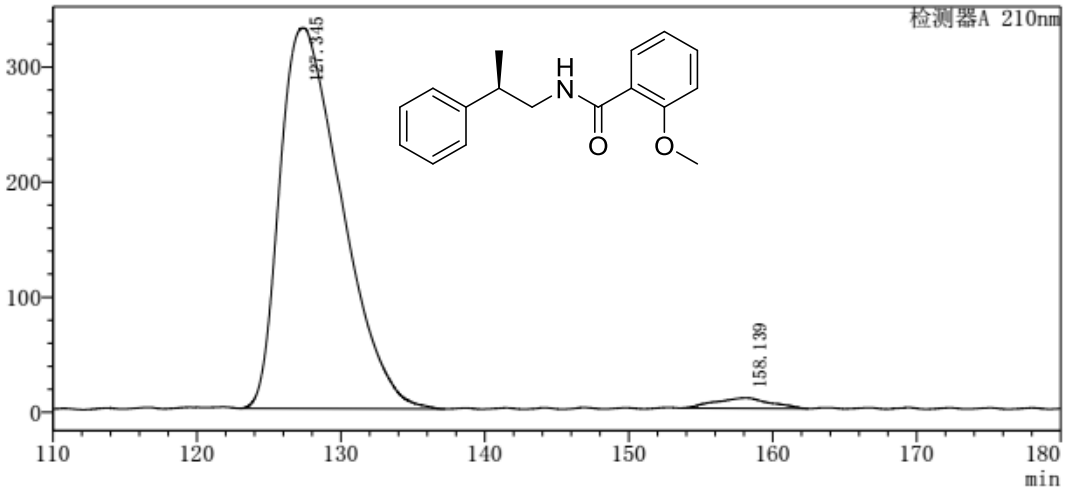




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	32.142	89790988	581101	13.582
2	38.236	571404437	1744418	86.418

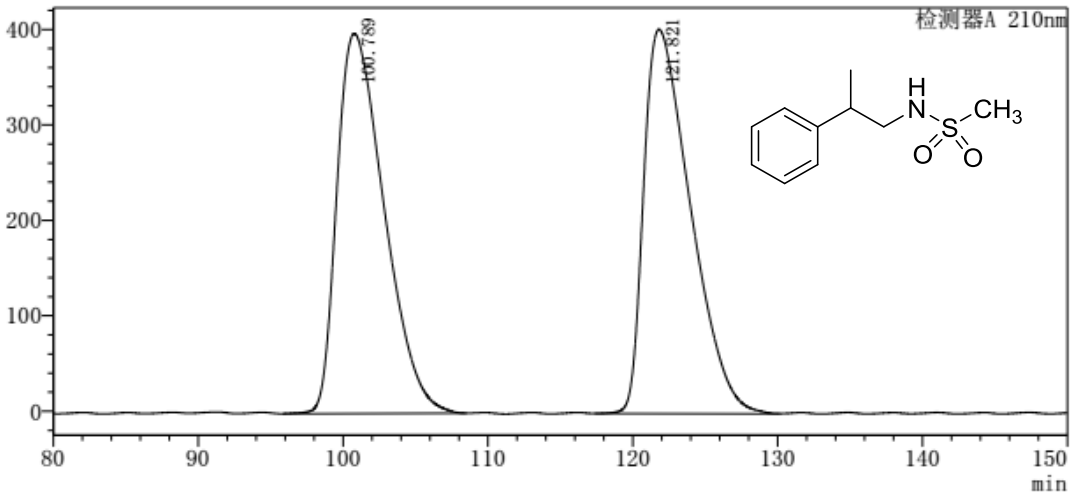
(*R*)-2-methoxy-*N*-(2-phenylpropyl)benzamide (4a)

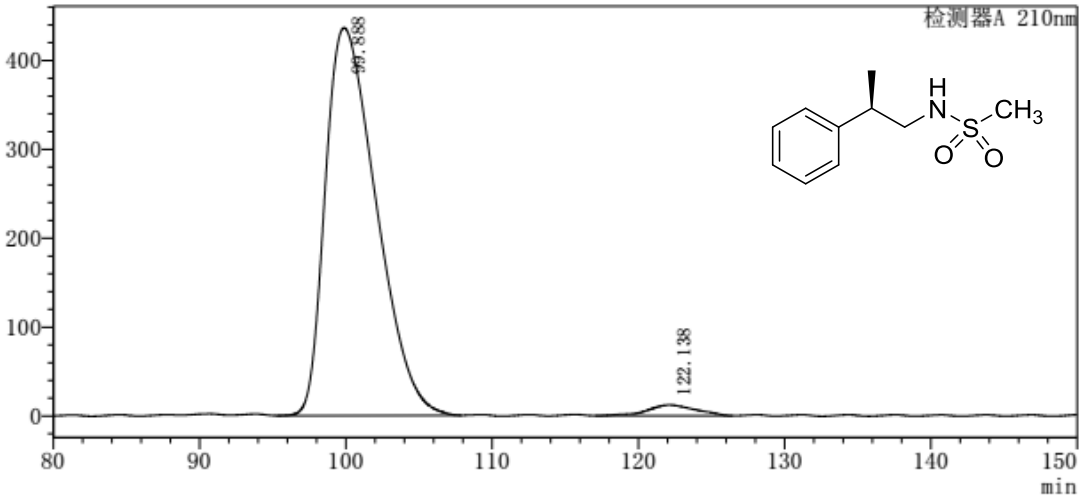




Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	127.345	98598792	330560	97.640
2	158.139	2383223	8985	2.360

(*R*)-*N*-(2-phenylpropyl)methanesulfonamide (5a)

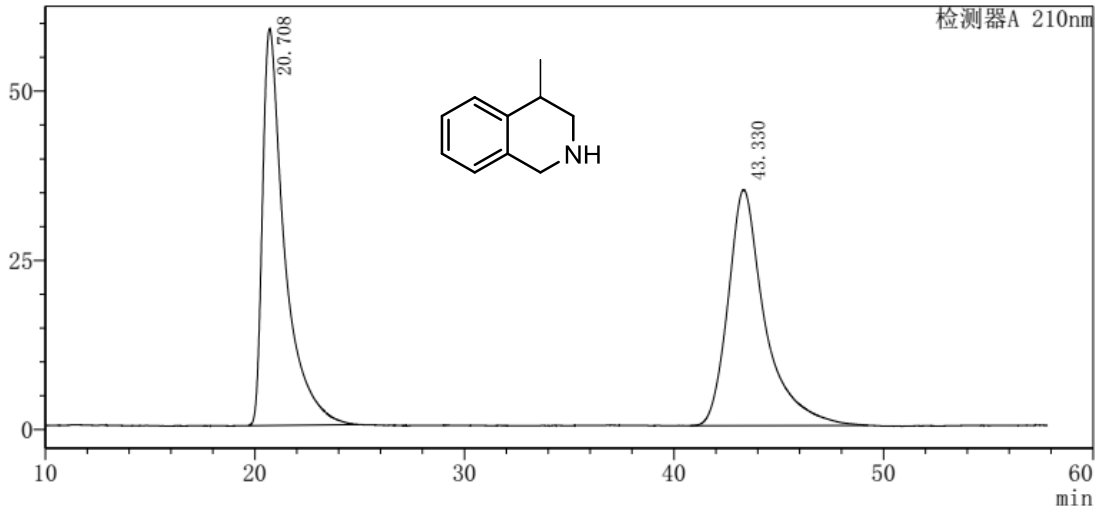


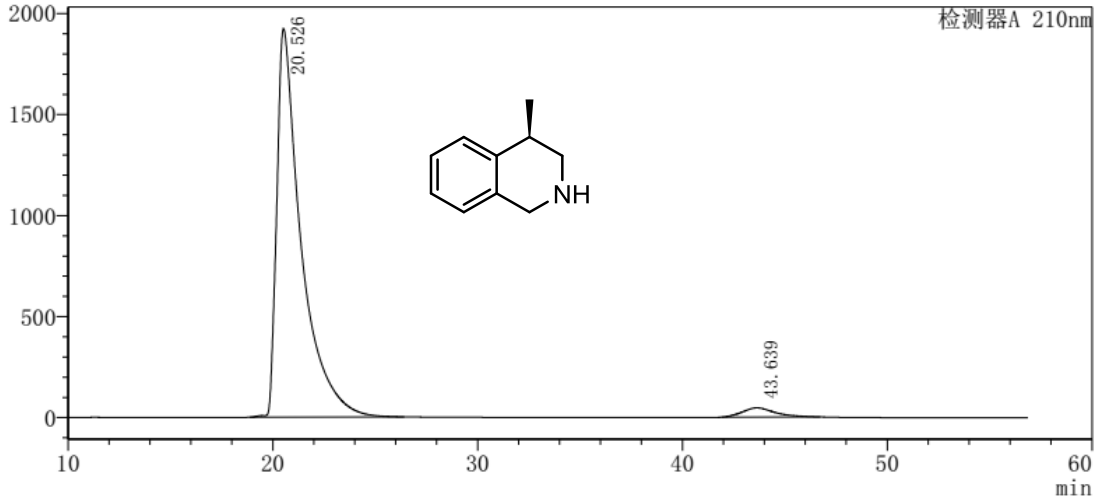


Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	99.888	105551070	436093	97.425
2	122.138	2789474	12166	2.575

(*R*)-4-methyl-1,2,3,4-tetrahydroisoquinoline hydrochloride (7a)

After neutralization





Peak #	RetTime [min]	Area [mAU]	Height [mAU]	Area %
1	20.526	158279939	1922997	96.885
2	43.639	5088245	45915	3.115