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Electronic Supplementary Material (ESI) for

Selective C-N coupling reaction of diaryliodonium salts and dinucleophiles

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General Information

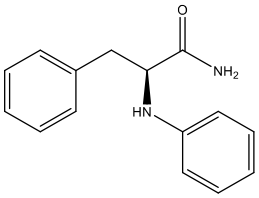
All reactions were carried out under argon atmosphere in dried glassware. The glassware used was dried in an electric oven at 120 °C. Chemicals were purchased from Aladdin, Adamas, Aldrich, Alfa Aesar, and Kelong Chemical Co. and used as received. Petroleum ether refers to the fraction boiling in the 60–90 °C range. ^{1}H NMR spectra were determined on a Bruker Avance 300MHz instrument or on a Bruker Avance III 400 MHz instrument. ^{1}H NMR data are reported in δ units (ppm), and were measured relative to the signals for residual chloroform (7.26 ppm), DMSO (2.50 ppm) or acetone (2.05 ppm) in the deuterated solvent, unless otherwise stated. ^{13}C NMR spectra are reported in δ (ppm) relative to deuterochloroform (77.2 ppm), DMSO-d_6 (39.5 ppm) or acetone-d_6 (206.7 ppm for C=O) unless otherwise stated, and all were obtained with ^{1}H decoupling. IR spectra were taken on a Bruker Tensor-27 infrared spectrometer using an OPUS workstation. Electrospray ionization-mass spectra (ESI-MS) were obtained on a LC-MS spectrometer. High-resolution mass spectra are recorded on a Shimadzu LCMS-IT-TOF instrument in the ESI mode. High-resolution mass spectra are recorded on a Shimadzu LCMS-IT-TOF instrument. All chiral HPLC analyses were performed on a Shimadzu LC-10ATVP liquid chromatography with a Daicel Chiralcel OD-H chiral column (4.6 mm × 250 mm × 5 μm). All rotation data are recorded on a Rudolph Research Analytical Autopol IV auto rotation (Na D line, cell long 10 cm, λ = 589 nm). Melting points were determined using a Shanghai Jingke SGW X-4 microscope melting point apparatus.

General Procedure

Typical experimental procedure for copper-catalyzed selective C-N coupling reaction of diaryliodonium salts and dinucleophiles

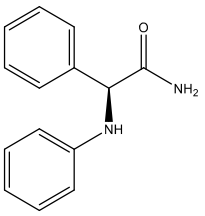
To an oven-dried 25 mL ground mouth test tube equipped with a stir bar was added 0.5 mmol phenylalaninamide, 1 mmol diphenyliodonium triflate,[1] 0.1 mmol anhydrous $Cu(OAc)_2$, 1 mmol K_3PO_4, 5 mL dioxane. The test tube was sealed with a sleeve rubber stopper and evacuated and refilled with argon for three cycles. The mixture was stirred under room temperature for 24 hours. And then the reaction mixture was quenched with water, added with 2 mL saturated NaCl solution, and extracted with ethyl acetate (20 mL) for three times. The combined organic layer was dried with anhydrous $MgSO_4$, and condensed in vacuum on a rotary evaporator. The residual was purified on a silica gel chromatograph column by means of gradient elution (eluent: petroleum ether / ethyl acetate) to give the desired product.

Characterization Data of Compounds 3a-3y



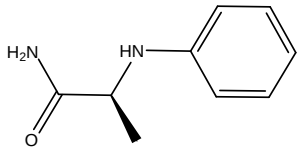
(S)-3-phenyl-2-(phenylamino)propanamide[2] (L-3a)

Yield=95%. Yellow solid. Mp: 151-152 ºC. $[\alpha]_D^{13}$ +13º (c 0.02, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 (s, 1H), 7.29 (ddd, *J* = 18.8, 10.6, 4.7 Hz, 4H), 7.19 (d, *J* = 7.0 Hz, 1H), 7.09 – 6.99 (m, 3H), 6.55 (dd, *J* = 9.0, 8.1 Hz, 3H), 5.75 (d, *J* = 8.8 Hz, 1H), 3.98 (s, 1H), 2.93 (dd, *J* = 36.0, 6.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.28 (s), 148.31 (s), 139.05 (s), 129.63 (s), 129.25 (s), 128.52 (s), 126.64 (s), 116.70 (s), 113.10 (s), 58.66 (s). HPLC (Chiracel OD-H, 254 nm, n-hexane: 2-propanol = 80:20, flow rate: 1 mL/min) retention time: 8.3 min (S form), 12.9 min (R form), 99%ee (S form).



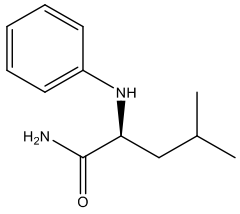
(S)-2-phenyl-2-(phenylamino)acetamide[2] (L-3b)

Yield=94%. White solid. Mp: 125-126 ºC. $[\alpha]_D^{13}$ +106º (c 0.005, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.71 (s, 1H), 7.53 (dd, *J* = 6.4, 5.0 Hz, 2H), 7.34 (dd, *J* = 8.0, 6.6 Hz, 2H), 7.28 (dd, *J* = 4.9, 3.6 Hz, 1H), 7.20 (s, 1H), 7.04 (dd, *J* = 8.5, 7.3 Hz, 2H), 6.62 (dd, *J* = 8.5, 0.8 Hz, 2H), 6.54 (t, *J* = 7.3 Hz, 1H), 6.09 (d, *J* = 7.3 Hz, 1H), 4.91 (d, *J* = 7.1 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 173.18 (s), 147.57 (s), 140.16 (s), 129.21 (s), 128.74 (s), 127.90 (s), 127.66 (s), 116.90 (s), 113.52 (s), 60.83 (s). HPLC (Chiracel OD-H, 254 nm, n-hexane: 2-propanol = 80:20, flow rate: 1 mL/min) retention time: 11.6 min (S form), 16.3 min (R form), 97%ee (S form).



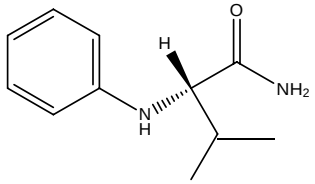
(S)-2-(phenylamino)propanamide[3] (L-3c)

Yield=92%. Yellow solid. Mp: 73-74 ºC. $[\alpha]_D^{13}$ +21º (c 0.006, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 (s, 1H), 7.07 (dd, *J* = 8.3, 7.5 Hz, 2H), 6.99 (s, 1H), 6.55 (td, *J* = 8.0, 4.3 Hz, 3H), 5.71 (d, *J* = 7.1 Hz, 1H), 3.72 (t, *J* = 7.0 Hz, 1H), 1.30 (d, *J* = 6.9 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.76 (s), 148.30 (s), 129.25 (s), 116.74 (s), 113.05 (s), 52.91 (s), 19.40 (s). HPLC (Chiracel OD-H, 254 nm, n-hexane: 2-propanol = 80:20, flow rate: 1 mL/min) retention time: 7.9 min (S form), 12.8 min (R form), 94%ee (S form).



(S)-4-methyl-2-(phenylamino)pentanamide (3d)

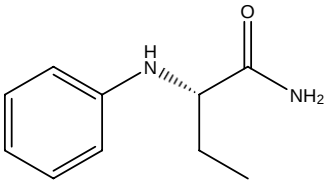
Yield=89%. Yellow solid. Mp: 106-107 ºC. $[\alpha]_D^{13}$ +36º (c 0.009, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (s, 1H), 7.02 – 6.94 (m, 2H), 6.89 (s, 1H), 6.54 – 6.44 (m, 3H), 5.54 (d, *J* = 7.9 Hz, 1H), 3.60 (d, *J* = 5.9 Hz, 1H), 1.68 (tt, *J* = 13.1, 6.6 Hz, 1H), 1.44 (ddd, *J* = 11.9, 8.2, 5.9 Hz, 2H), 0.86 (d, *J* = 6.6 Hz, 3H), 0.79 (d, *J* = 6.6 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 148.61 (s), 129.24 (s), 116.60 (s), 112.99 (s), 55.94 (s), 24.81 (s), 23.39 (s), 22.39 (s). HRMS (ESI-TOF) m/z calcd for $C_{12}H_{18}N_2NaO$ [M+Na^+] 229. 1311; found 229.1294.



(S)-3-methyl-2-(phenylamino)butanamide (3e)

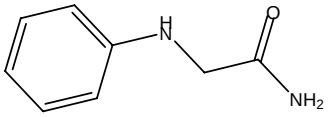
Yield=65%. Yellow solid. Mp: 102-103 ºC. $[\alpha]_D^{13}$ -10º (c 0.005, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.27 (s, 1H), 7.09 – 6.87 (m, 3H), 6.64 – 6.39 (m, 3H), 5.41 (d, *J* = 8.4 Hz, 1H), 3.37 (s,

1H), 1.90 (d, *J* = 6.8 Hz, 1H), 0.89 (dd, *J* = 10.1, 6.8 Hz, 6H).^{13}C NMR (101 MHz, DMSO-d_6 δ 175.31 (s), 148.96 (s), 129.19 (s), 116.58 (s), 113.20 (s), 63.35 (s), 31.13 (s), 19.95 (s), 19.52 (s). IR (KBr) ν (cm^{-1}) 3457, 3392, 3344, 3303, 3170, 2964, 1684, 1607, 1315, 753, 692, 507. HRMS (ESI-TOF) m/z calcd for $C_{11}H_{16}N_2NaO$ [M+Na^+] 215.1155; found 215.1130.



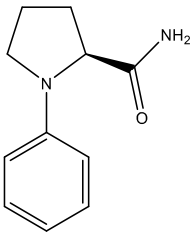
(S)-2-(phenylamino)butanamide[2] (3f)

Yield=80%. White solid. Mp: 93-94 ºC. $[\alpha]_D^{13}$+6 (c 0.008, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.33 (s, 1H), 7.05 (dt, *J* = 22.3, 13.9 Hz, 3H), 6.64 – 6.49 (m, 3H), 5.61 (d, *J* = 7.7 Hz, 1H), 3.58 (d, *J* = 6.3 Hz, 1H), 1.79 – 1.53 (m, 2H), 0.95 (t, *J* = 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.88 (s), 148.60 (s), 129.23 (s), 116.62 (s), 113.08 (s), 58.91 (s), 26.28 (s), 11.13 (s).



2-(phenylamino)acetamide[2] (3g)

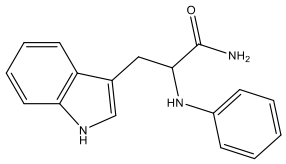
Yield=52%. Yellow solid. Mp: 110-112 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.34 (s, 1H), 7.17 – 7.00 (m, 3H), 6.62 – 6.45 (m, 3H), 5.85 (t, *J* = 5.8 Hz, 1H), 3.56 (d, *J* = 5.9 Hz, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 172.90 (s), 148.80 (s), 129.31 (s), 116.74 (s), 112.70 (s).



(S)-1-phenylpyrrolidine-2-carboxamide[4] (3h)

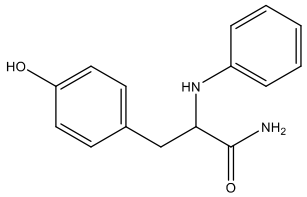
Yield=52%. Yellow solid. Mp: 138-139 ºC. $[\alpha]_D^{13}$ +66º (c 0.005, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (s, 1H), 7.22 (dd, *J* = 8.6, 7.3 Hz, 2H), 7.10 (s, 1H), 6.68 (t, *J* = 7.3 Hz, 1H), 6.53

(d, *J* = 7.8 Hz, 2H), 3.97 – 3.80 (m, 1H), 3.60 (s, 1H), 3.22 (d, *J* = 8.1 Hz, 1H), 2.25 (s, 1H), 2.08 – 1.95 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 176.25 (s), 147.44 (s), 129.33 (s), 116.30 (s), 112.39 (s), 62.64 (s), 48.68 (s), 31.53 (s), 24.04 (s). HRMS (ESI-TOF) m/z calcd for $C_{11}H_{14}N_2NaO$ [M+Na^+] 213.0998; found 213.0978.



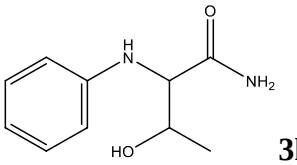
3-(1H-indol-3-yl)-2-(phenylamino)propanamide (3i)

Yield=80%. Yellow solid. Mp: 125-126 ºC. $[\alpha]_D^{13}$ -5º (c 0.01, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.83 (s, 1H), 7.61 (d, *J* = 7.8 Hz, 1H), 7.45 (s, 1H), 7.32 (d, *J* = 8.0 Hz, 1H), 7.20 (d, *J* = 2.3 Hz, 1H), 7.08 – 6.95 (m, 5H), 6.59 – 6.49 (m, 3H), 5.64 (d, *J* = 7.9 Hz, 1H), 3.98 (d, *J* = 5.2 Hz, 1H), 3.13 (d, *J* = 5.1 Hz, 1H), 3.02 (d, *J* = 8.4 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.85 (s), 136.52 (s), 129.25 (s), 127.80 (s), 124.20 (s), 121.28 (s), 118.77 (d, *J* = 12.3 Hz), 116.61 (s), 113.01 (s), 111.77 (s), 58.20 (s). IR (KBr) ν (cm^{-1}) 3406, 3295, 3153, 3052, 2922, 2852, 1689, 1601, 1499, 1320, 750, 691, 505, 423. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{17}N_3NaO$ [M+Na^+] 302.1264; found 302.1250.



3-(4-hydroxyphenyl)-2-(phenylamino)propanamide (3j)

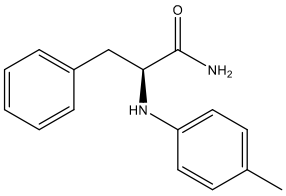
Yield=93%. Yellow oil. $[\alpha]_D^{13}$ +21º (c 0.005, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.22 (s, 1H), 7.44 (s, 1H), 7.17 – 7.00 (m, 5H), 6.74 – 6.67 (m, 2H), 6.59 (dd, *J* = 13.6, 7.5 Hz, 3H), 5.67 (d, *J* = 8.6 Hz, 1H), 3.93 (d, *J* = 5.4 Hz, 1H), 2.92 (d, *J* = 5.3 Hz, 1H), 2.83 (d, *J* = 8.5 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ 175.43 (s), 156.19 (s), 148.34 (s), 130.50 (s), 129.23 (s), 128.98 (s), 116.66 (s), 115.31 (s), 113.10 (s), 59.06 (s). IR (KBr) ν (cm^{-1}) 3351, 2923, 1665, 1602, 1509, 1238, 831, 753,692. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{16}N_2NaO_2$ [M+Na^+] 279.1104; found 279.1082.



3k

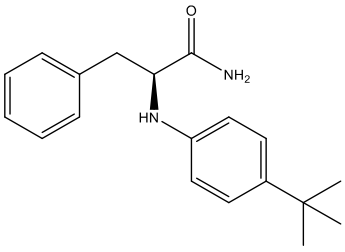
3-hydroxy-2-(phenylamino)butanamide (3k)

Yield=35%. Yellow oil. $[\alpha]_D^{13}$ +1.5° (c 0.003, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.26 (s, 1H), 7.12 – 7.03 (m, 3H), 6.64 – 6.52 (m, 3H), 5.41 (d, *J* = 7.4 Hz, 1H), 4.96 (d, *J* = 5.3 Hz, 1H), 3.96 (d, *J* = 6.2 Hz, 1H), 3.52 (dd, *J* = 7.4, 4.7 Hz, 1H), 1.14 (d, *J* = 6.3 Hz, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 174.58 (s), 148.63 (s), 129.29 (s), 116.84 (s), 113.20 (s), 67.33 (s), 63.89 (s), 20.82 (s). IR (KBr) ν (cm^{-1}) 3483, 3362, 1668, 1287, 1252, 1178, 1039, 750, 643, 579, 516. HRMS(ESI-TOF) m/z calcd for $C_{10}H_{14}N_2NaO_2$ [M+Na^+] 217.0947; found 217.0922.



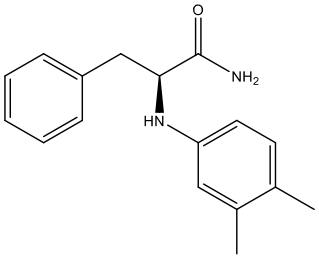
(S)-2-(p-toluidino)-3-phenylpropanamide (3l)

Yield=92%. Yellow solid. Mp: 101-102 ºC. $[\alpha]_D^{13}$ +26° (c 0.01, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.39 (s, 1H), 7.33 – 7.22 (m, 4H), 7.22 – 7.14 (m, 1H), 7.02 (s, 1H), 6.86 (d, *J* = 8.2 Hz, 2H), 6.48 (d, *J* = 8.4 Hz, 2H), 5.48 (d, *J* = 8.9 Hz, 1H), 3.94 (d, *J* = 5.4 Hz, 1H), 3.08 – 2.75 (m, 2H), 2.12 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 175.38 (s), 146.00 (s), 139.08 (s), 129.64 (d, *J* = 6.1 Hz), 128.50 (s), 126.60 (s), 125.18 (s), 113.33 (s), 59.01 (s), 20.51 (s). IR (KBr) ν (cm^{-1}) 3276, 3080, 2920, 1699, 1515, 1450, 831, 734, 695, 524. HRMS (ESI-TOF) m/z calcd for $C_{16}H_{18}N_2NaO$ [M+Na^+] 277.1311; found 277.1297.



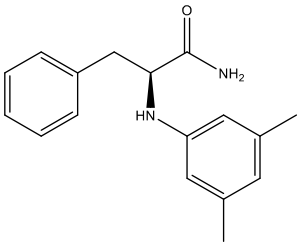
(S)-2-(4-tert-butylphenylamino)-3-phenylpropanamide (3m)

Yield=75%. Yellow solid. Mp. 146-148 ºC. $[\alpha]_D^{13}$ +19º (c 0.01, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.40 (s, 1H), 7.34 – 7.23 (m, 4H), 7.21 – 7.14 (m, 1H), 7.09 – 6.97 (m, 3H), 6.54 – 6.43 (m, 2H), 5.52 (d, *J* = 8.8 Hz, 1H), 3.93 (d, *J* = 5.1 Hz, 1H), 2.97 (d, *J* = 5.0 Hz, 1H), 2.87 (d, *J* = 8.8 Hz, 1H), 1.19 (d, *J* = 6.8 Hz, 9H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.48 (s), 145.85 (s), 139.07 (d, *J* = 15.3 Hz), 129.60 (s), 128.50 (s), 126.60 (s), 125.84 (s), 112.88 (s), 58.98 (s), 33.90 (s), 31.90 (s). IR (KBr) ν (cm^{-1}) 3290, 3091, 2960, 1699, 1454, 1296, 840, 736, 697, 573, 528. HRMS (ESI-TOF) m/z calcd for $C_{19}H_{24}N_2NaO$ [M+Na^+] 319.1781; found 319.1764.



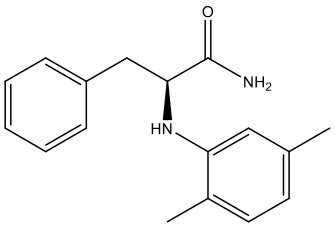
(S)-2-(3,4-dimethylphenylamino)-3-phenylpropanamide (3n)

Yield=89%. Yellow solid. Mp: 122-123 ºC. $[\alpha]_D^{13}$ +32º (c 0.005, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.41 (s, 1H), 7.33 – 7.24 (m, 4H), 7.19 (dt, *J* = 9.3, 4.3 Hz, 1H), 7.05 (d, *J* = 1.0 Hz, 1H), 6.79 (d, *J* = 8.1 Hz, 1H), 6.39 (d, *J* = 2.1 Hz, 1H), 6.30 (dd, *J* = 8.1, 2.3 Hz, 1H), 5.41 (d, *J* = 8.9 Hz, 1H), 3.93 (d, *J* = 5.2 Hz, 1H), 2.92 (ddd, *J* = 22.4, 13.7, 6.9 Hz, 2H), 2.06 (d, *J* = 14.7 Hz, 6H).^{113}C NMR (101 MHz, DMSO-d_6) δ 175.54 (s), 146.31 (s), 139.13 (s), 136.59 (s), 130.21 (s), 129.62 (s), 128.51 (s), 126.60 (s), 124.11 (s), 114.97 (s), 110.69 (s), 59.03 (s), 20.21 (s), 18.83 (s). IR (KBr) ν (cm^{-1}) 3378, 3197, 2922, 1640, 1505, 1449, 1308, 1083, 803, 726, 701, 465, 440. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{20}N_2NaO$ [M+Na^+] 291.1468; found 291.1442.



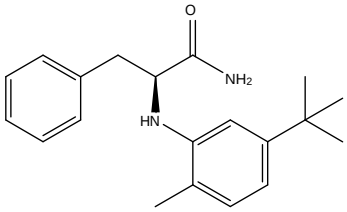
(S)-2-(3,5-dimethylphenylamino)-3-phenylpropanamide (3o)

Yield=91%. Yellow oil. $[\alpha]_D^{13}$ +36° (c 0.009, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.50 (s, 1H), 7.34 – 7.24 (m, 4H), 7.20 (dt, *J* = 9.3, 4.3 Hz, 1H), 7.12 (s, 1H), 6.78 (d, *J* = 6.0 Hz, 2H), 6.35 (d, *J* = 8.7 Hz, 1H), 4.49 (d, *J* = 8.4 Hz, 1H), 3.95 (d, *J* = 5.0 Hz, 1H), 3.04 (ddd, *J* = 22.2, 13.6, 6.8 Hz, 2H), 2.12 (s, 3H), 2.02 (s, 3H).^{13}C NMR (101 MHz, DMSO-d_6) δ 175.49 (s), 143.44 (s), 138.92 (s), 131.12 (s), 129.70 (s), 128.56 (s), 127.35 (s), 126.73 (s), 125.50 (s), 122.80 (s), 110.77 (s), 59.47 (s), 20.48 (s), 17.76 (s). IR (KBr) ν (cm^{-1}) 3426, 2921, 2858, 1671, 1513, 1449, 1267, 1120, 805, 701, 552. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{20}N_2NaO$ [M+Na^+] 291.1468; found 291.1444.



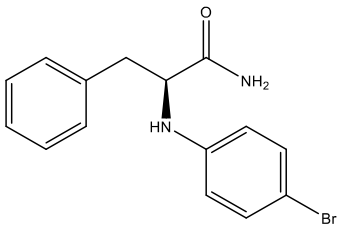
(S)-2-(2,5-dimethylphenylamino)-3-phenylpropanamide (3p)

Yield=89%. Yellow oil. $[\alpha]_D^{13}$ +34° (c 0.006, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.46 (s, 1H), 7.38 – 6.91 (m, 6H), 6.74 (s, 2H), 6.30 (d, *J* = 7.1 Hz, 1H), 4.45 (d, *J* = 7.6 Hz, 1H), 3.89 (s, 1H), 2.99 (dd, *J* = 26.3, 11.3 Hz, 2H), 2.03 (d, *J* = 39.7 Hz, 6H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.44 (s), 143.38 (s), 138.88 (s), 131.05 (s), 129.65 (s), 128.51 (s), 127.28 (s), 126.67 (s), 125.41 (s), 122.73 (s), 110.66 (s), 59.41 (s), 20.44 (s), 17.74 (s). IR (KBr) ν (cm^{-1}) 3431, 3024, 2921, 2853, 1674, 1617, 1580, 1521, 1300, 1135, 799, 701. HRMS (ESI-TOF) m/z calcd for $C_{17}H_{20}N_2NaO$ [M+Na^+] 291.1468; found 291.1440.



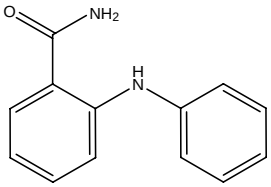
(S)-2-(5-tert-butyl-2-methylphenylamino)-3-phenylpropanamide (3q)

Yield=82%. Yellow solid. Mp: 125-126 °C. $[\alpha]_D^{13}$ +29° (c 0.01, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.53 (s, 1H), 7.20 (dd, *J* = 51.3, 17.2 Hz, 5H), 6.81 (d, *J* = 7.2 Hz, 1H), 6.60 – 6.33 (m, 2H), 4.55 (d, *J* = 7.6 Hz, 1H), 3.94 (s, 1H), 3.12 – 2.82 (m, 2H), 1.97 (s, 3H), 1.15 (s, 8H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 175.53 (s), 149.43 (s), 145.20 (s), 138.95 (s), 129.72 (s), 128.53 (s), 126.69 (s), 119.81 (s), 113.76 (s), 108.08 (s), 59.33 (s), 34.58 (s), 31.67 (s), 17.26 (s). IR (KBr) ν (cm^{-1}) 3435, 3130, 2958, 1691, 1577, 1418, 852, 813, 702, 591, 561. HRMS (ESI-TOF) m/z calcd for $C_{20}H_{26}N_2NaO$ [M+Na^+] 333.1937; found 333.1915.



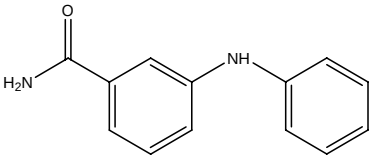
(S)-2-(4-bromophenylamino)-3-phenylpropanamide (3r)

Yield=83%. Pale yellow solid. Mp: 182-183 ºC. $[\alpha]_D^{13}$ +22º (c 0.01, acetone). ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.47 (s, 1H), 7.38 – 6.89 (m, 8H), 6.49 (d, *J* = 8.2 Hz, 2H), 6.01 (d, *J* = 8.3 Hz, 1H), 3.94 (s, 1H), 3.06 – 2.73 (m, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 174.81 (s), 147.62 (s), 138.80 (s), 131.69 (s), 129.57 (s), 128.48 (s), 126.64 (s), 114.97 (s), 107.24 (s), 58.49 (s). IR (KBr) ν (cm^{-1}) 3397, 3371, 3181, 2924, 2861, 1632, 1495, 1307, 1256, 1125, 815, 716, 695, 631, 468. HRMS (ESI-TOF) m/z calcd for $C_{15}H_{15}BrN_2NaO$ [M+Na^+] 341.0260; found 341.0235.



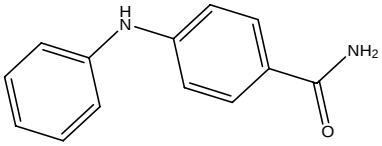
2-(phenylamino)benzamide[5] (3s)

Yield=70%. Yellow solid. Mp: 101-102 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 1H), 8.08 (s, 1H), 7.71 (dd, *J* = 7.9, 1.4 Hz, 1H), 7.49 (s, 1H), 7.36 – 7.25 (m, 4H), 7.19 – 7.13 (m, 2H), 7.02 – 6.95 (m, 1H), 6.79 (ddd, *J* = 8.1, 7.0, 1.4 Hz, 1H).^{13}C NMR (101 MHz, DMSO-d_6) δ 171.79 (s), 145.41 (s), 141.85 (s), 132.61 (s), 129.86 (d, *J* = 7.4 Hz), 122.38 (s), 120.21 (s), 118.19 (s), 117.90 (s), 115.10 (s).



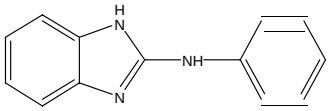
3-(phenylamino)benzamide[6] (3t)

Yield=73%. Yellow solid. Mp: 153-154 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.31 (s, 1H), 7.90 (s, 1H), 7.59 – 7.53 (m, 1H), 7.32 – 7.23 (m, 5H), 7.21 – 7.15 (m, 1H), 7.09 (dd, *J* = 8.6, 1.0 Hz, 2H), 6.86 (t, *J* = 7.3 Hz, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 144.03 (s), 135.94 (s), 129.70 (s), 129.46 (s), 120.54 (s), 119.60 (s), 118.83 (s), 117.56 (s), 115.91 (s).



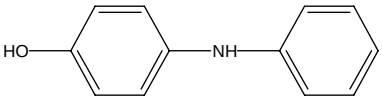
4-(phenylamino)benzamide[6] (3u)

Yield=74%. White solid. Mp: 129-130 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 8.56 (s, 1H), 7.79 – 7.68 (m, 3H), 7.33 – 7.25 (m, 2H), 7.15 (dd, *J* = 8.6, 1.0 Hz, 2H), 7.08 – 7.00 (m, 3H), 6.97 – 6.88 (m, 1H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 146.99 (s), 129.67 (d, *J* = 16.9 Hz), 124.84 (s), 121.51 (s), 118.83 (s), 114.69 (s).



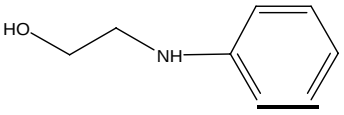
N-phenyl-1H-benzo[d]imidazol-2-amine[7] (3v)

Yield=82%. Yellow solid. Mp: 188-190 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.63 (dt, *J* = 10.0, 1.9 Hz, 2H), 7.56 – 7.45 (m, 3H), 7.24 (d, *J* = 7.8 Hz, 1H), 7.03 (td, *J* = 7.5, 1.5 Hz, 1H), 6.95 – 6.81 (m, 2H), 6.42 (s, 2H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 154.39 (s), 142.46 (s), 135.16 (d, *J* = 8.9 Hz), 130.62 (s), 128.77 (s), 127.13 (s), 121.87 (s), 119.52 (s), 115.36 (s), 108.24 (s).



4-anilinophenol[8] (3w)

Yield=62%. Yellow solid. Mp: 67-68 ºC. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.00 (s, 1H), 7.63 (s, 1H), 7.06 (d, *J* = 25.0 Hz, 2H), 6.99 – 6.77 (m, 4H), 6.65 (dd, *J* = 17.4, 7.4 Hz, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 152.49 (s), 146.22 (s), 134.71 (s), 129.45 (s), 121.86 (s), 118.09 (s), 116.12 (s), 114.62 (s).

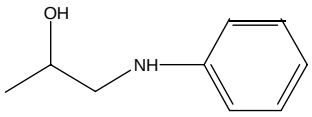


3x

2-Anilinoethanol[9] (3x)

Yield=60%. Yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.14 – 7.00 (m, 2H), 6.63 – 6.46 (m, 3H),

5.43 (t, *J* = 5.4 Hz, 1H), 4.69 (t, *J* = 5.5 Hz, 1H), 3.55 (q, *J* = 6.0 Hz, 2H), 3.08 (q, *J* = 6.0 Hz, 2H).^{13}C NMR (101 MHz, DMSO-d_6) δ 149.38 (s), 129.33 (s), 116.02 (s), 112.47 (s), 60.10 (s), 46.00 (s).



1-anilino-propan-2-ol[10] (**3y**)

Yield=50%. Yellow oil. ^{1}H NMR (400 MHz, DMSO-d_6) δ 7.11 – 6.97 (m, 2H), 6.62 – 6.44 (m, 3H), 5.43 (t, *J* = 5.7 Hz, 1H), 4.71 (d, *J* = 4.7 Hz, 1H), 3.85 – 3.70 (m, 1H), 3.03 – 2.83 (m, 2H), 1.19 – 1.02 (m, 3H). ^{13}C NMR (101 MHz, DMSO-d_6) δ 149.44 (s), 129.31 (s), 115.93 (s), 112.74 (s), 112.46 (s), 72.42 (s), 65.19 (s), 51.36 (s), 21.93 (s).

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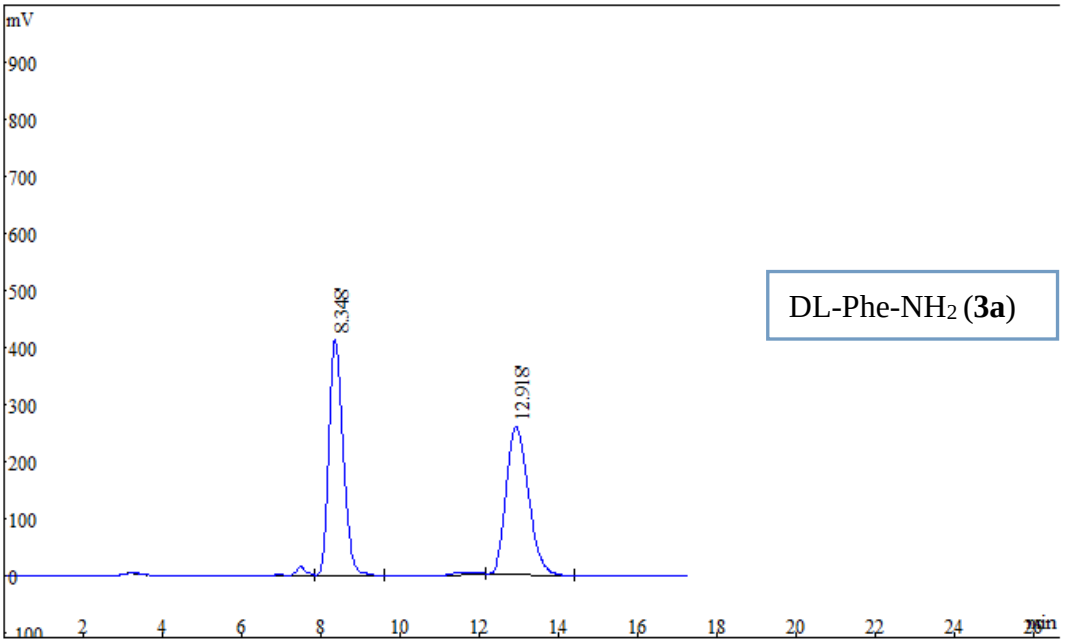
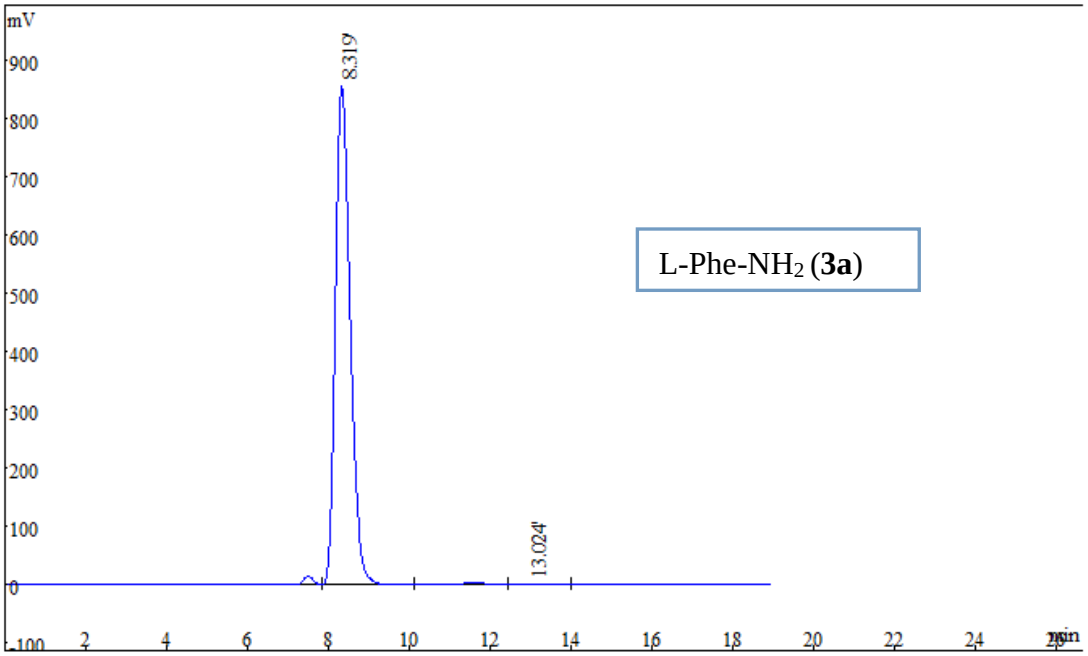
Copies of chiral HPLC traces for Compounds 3a-3c



DL-Phe-NH_2 (**3a**)

Rank	Time	Conc.	Area	Height
1	8.348	50.19	9973195	411274
2	12.918	49.81	9897316	258298
Total		100	19870511	669572



L-Phe-NH_2 (**3a**)

Rank	Time	Conc.	Area	Height
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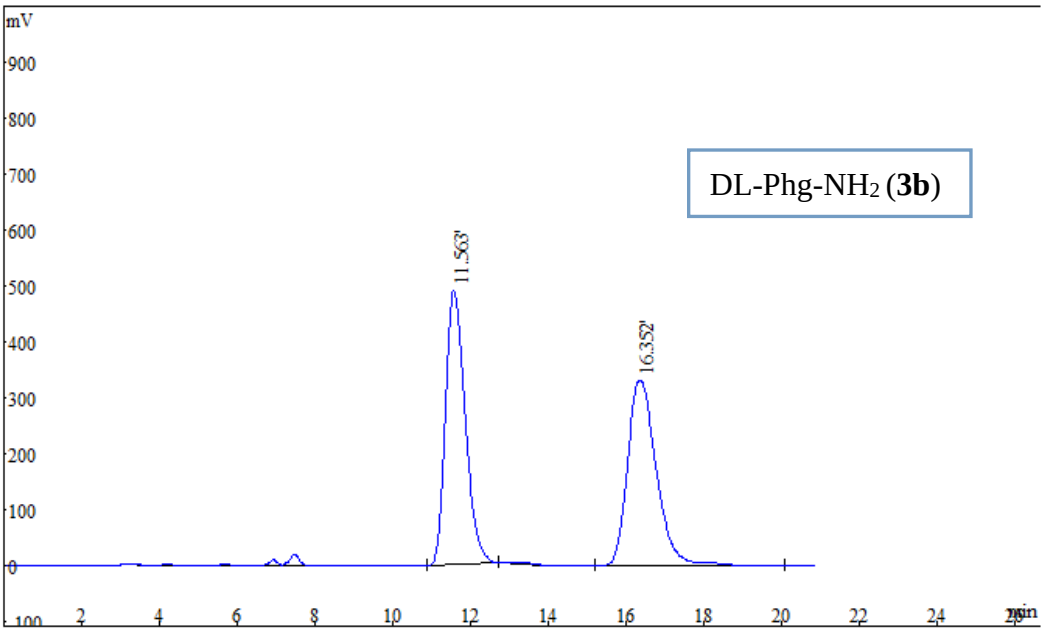
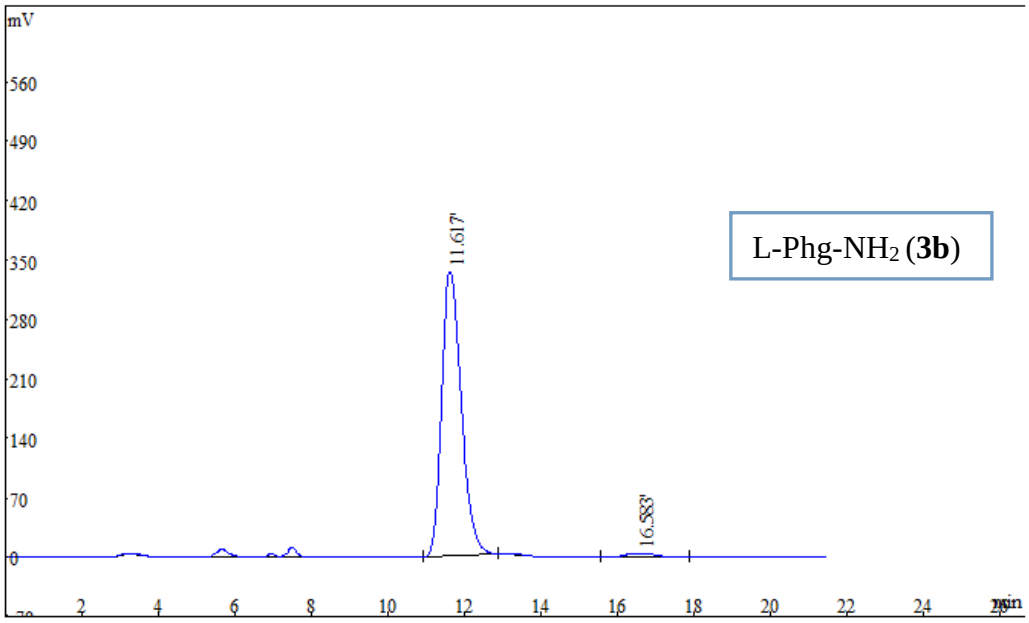
2	13.024	0.5078	107238	2903
Total		100	21117784	856980



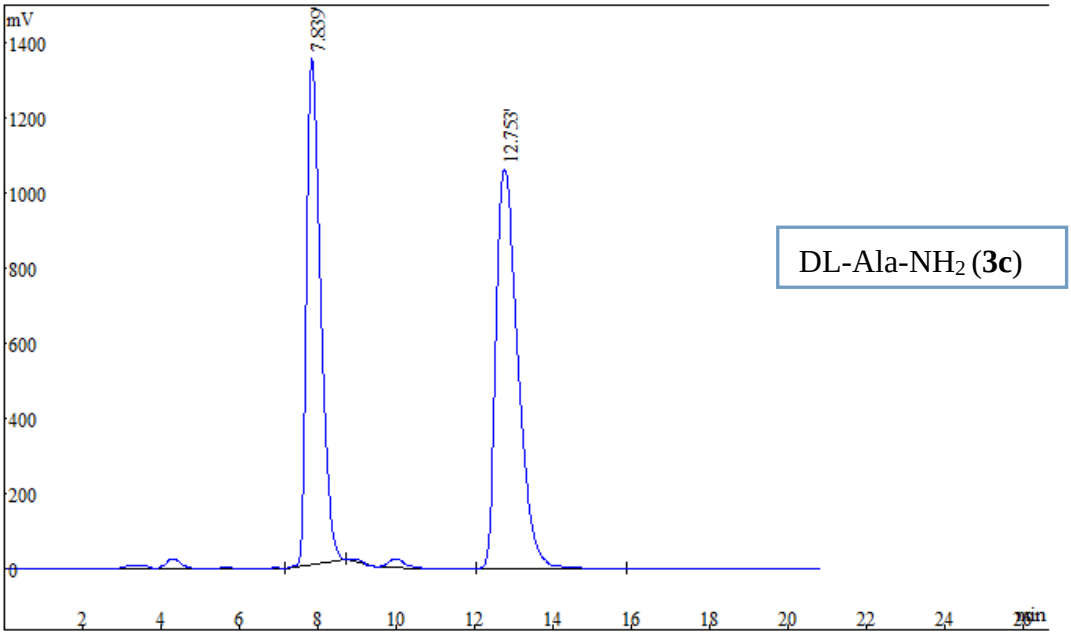
DL-Phg-NH_2 (**3b**)

Rank	Time	Conc.	Area	Height
1	11.563	49.98	16683864	487714
2	16.352	50.02	16699688	331533
Total		100	33383552	819247



L-Phg-NH_2 (**3b**)

Rank	Time	Conc.	Area	Height
1	11.617	98.13	11525287	334307
2	16.583	1.874	220156	4471
Total		100	11745443	338778



DL-Ala-NH_2 (**3c**)

Rank	Time	Conc.	Area	Height
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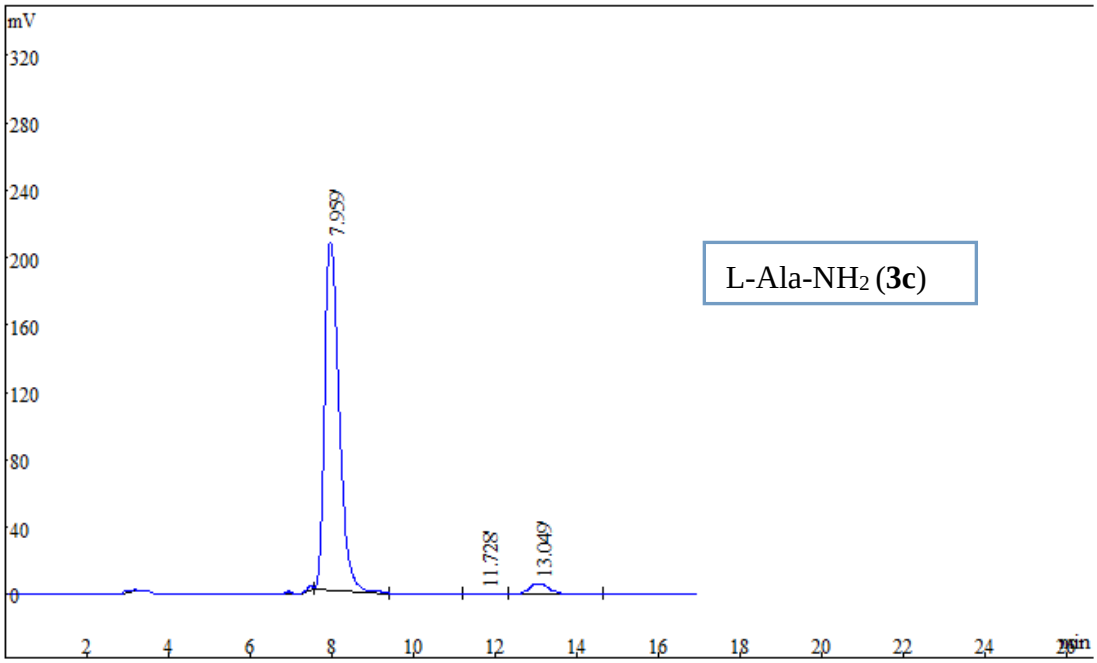
2	12.753	55.13	39967018	1059590
Total		100	72498976	2402729

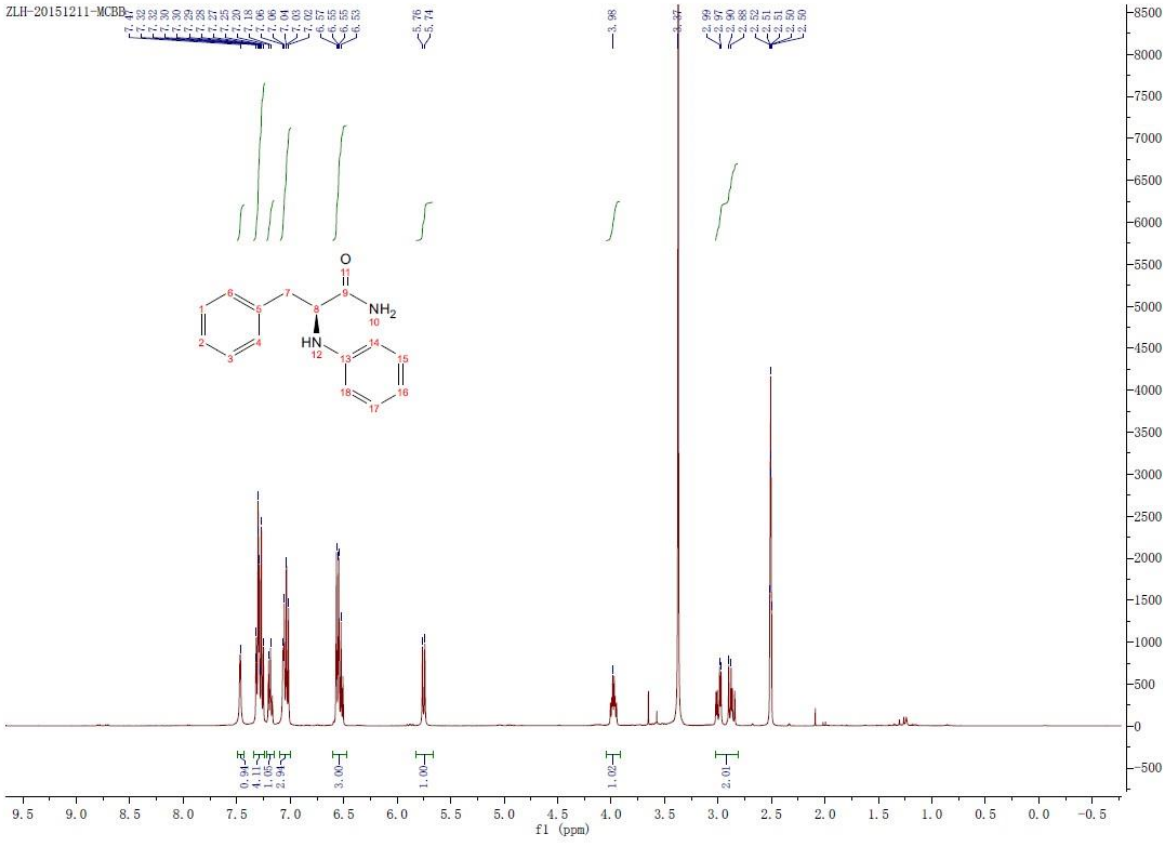


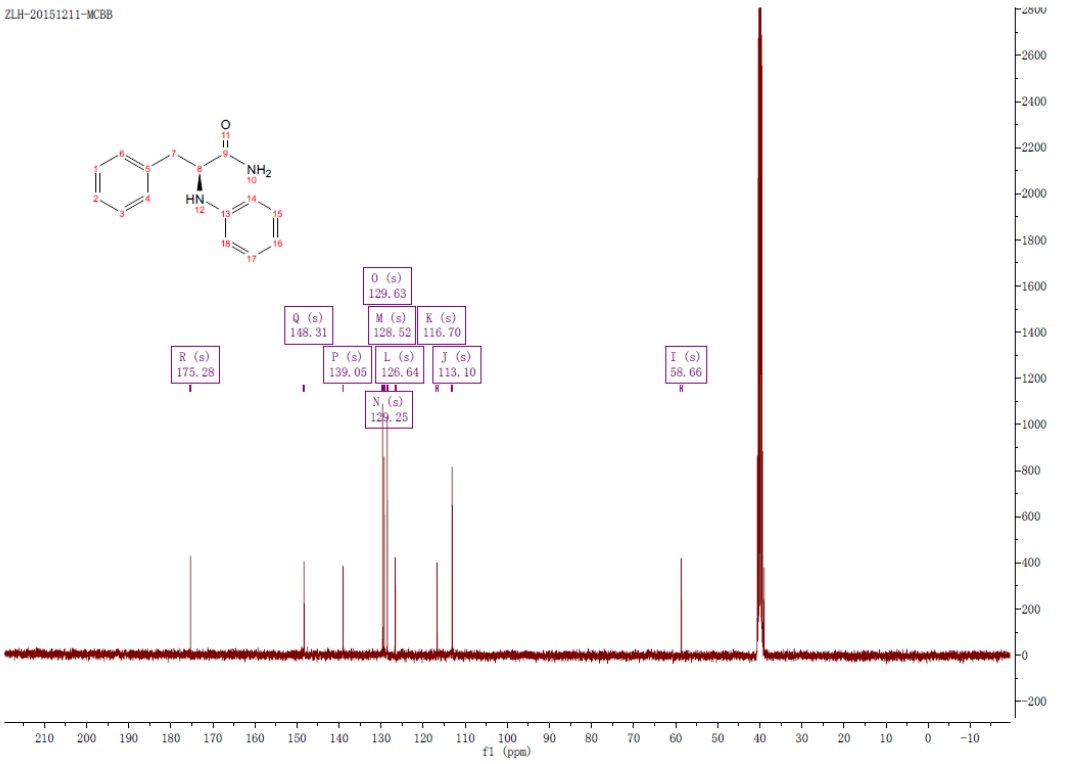
L-Ala-NH_2 (**3c**)

Rank	Time	Conc.	Area	Height
1	7.959	94.57	4867165	206297
2	11.728	0.4745	24422	750
3	13.049	4.957	255107	6695
Total		100	5146694	213742

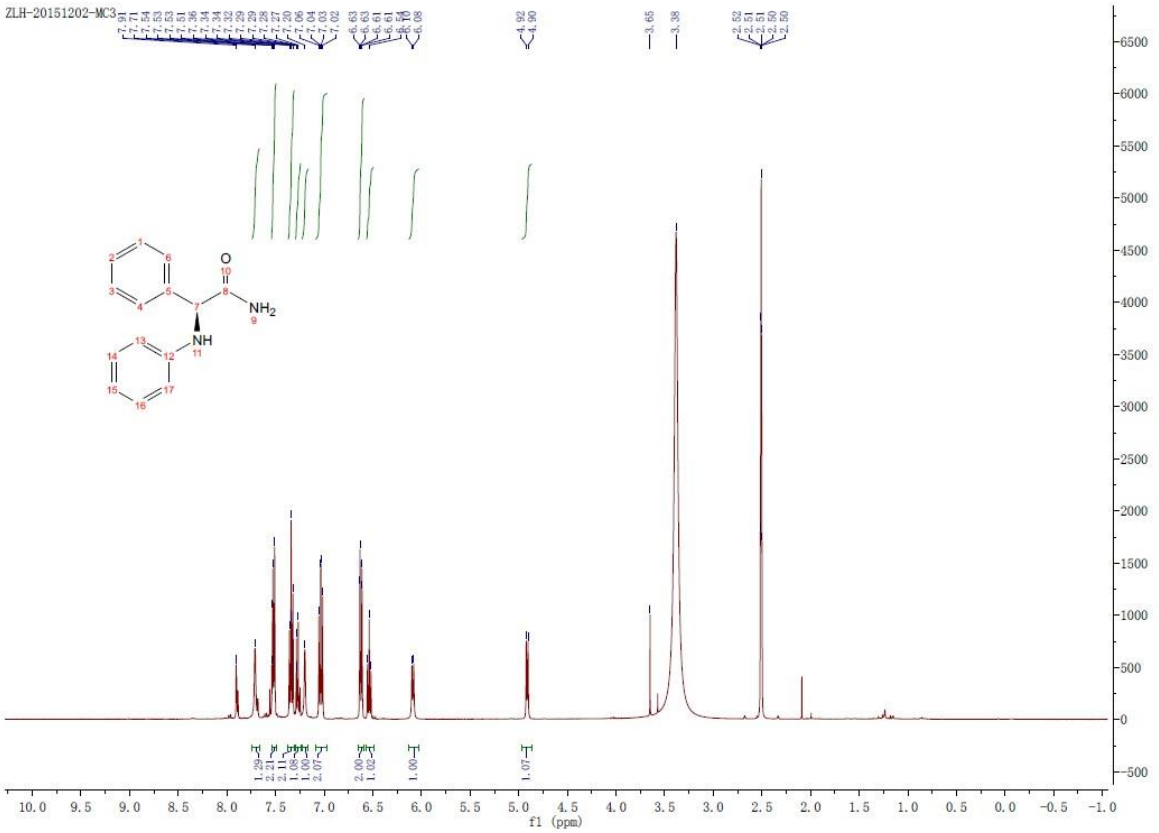
Copies of ^{1}H and ^{13}C NMR Spectra for Compounds 3a-3y

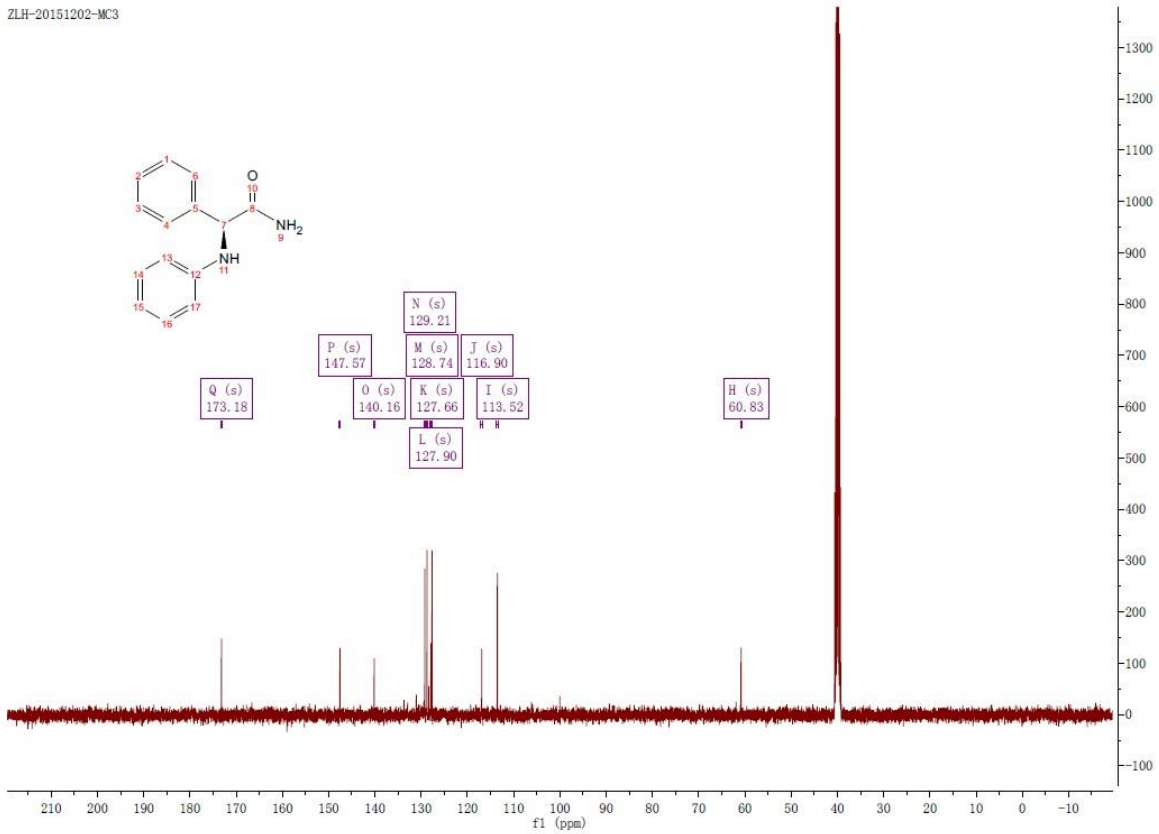
(S)-3-phenyl-2-(phenylamino)propanamide[2] (L-3a)



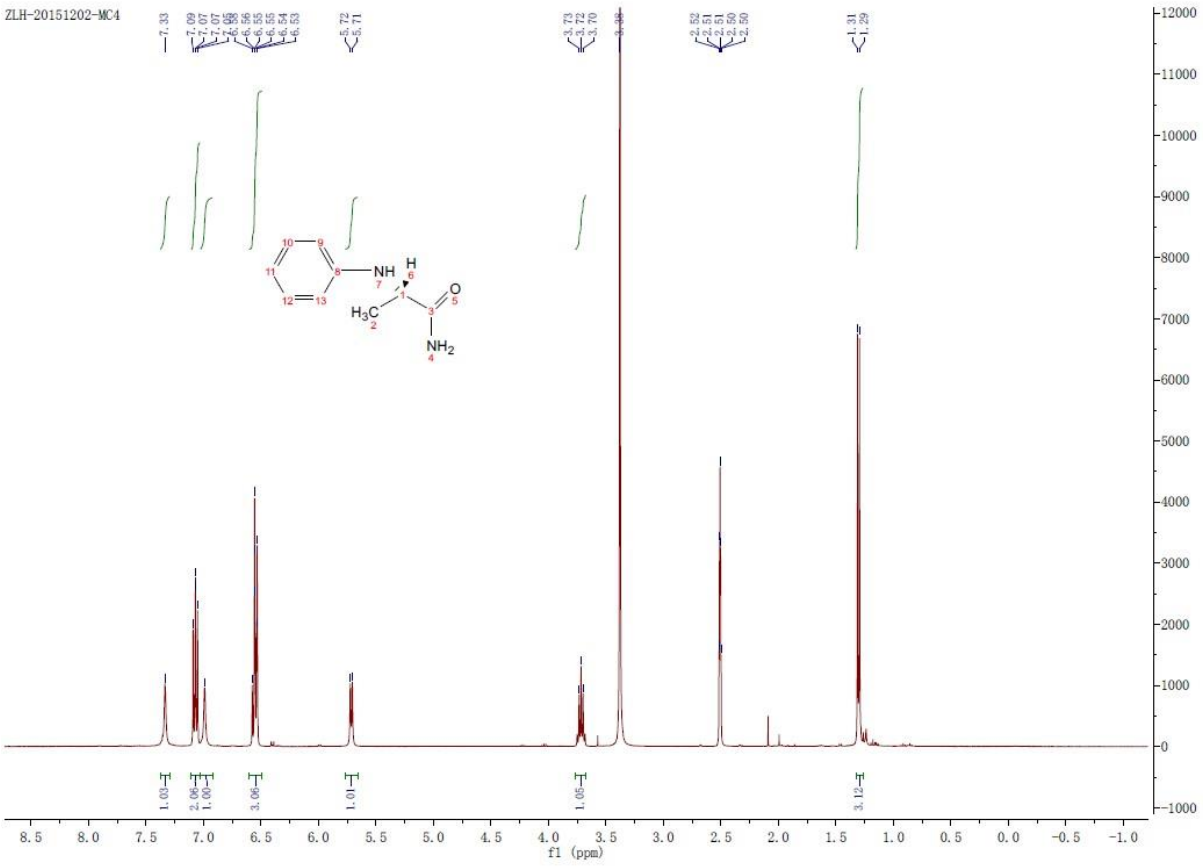


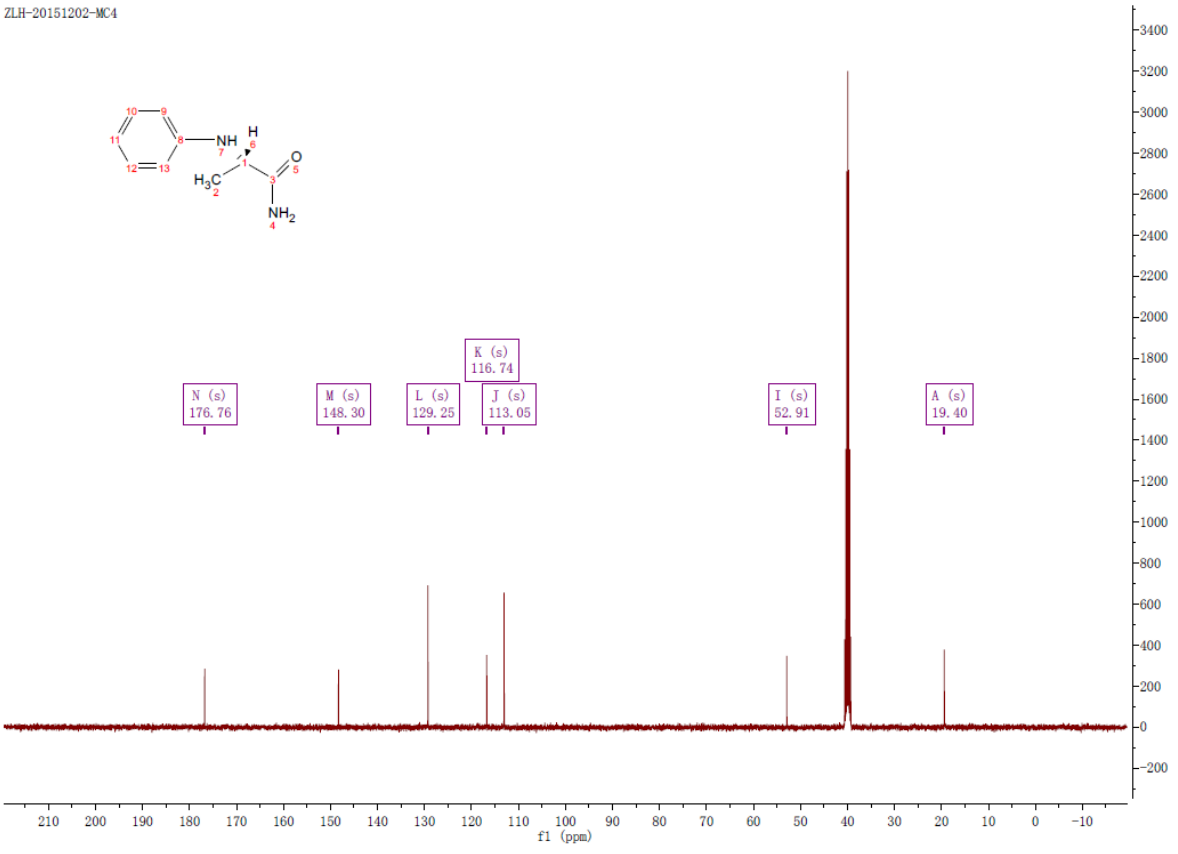
(S)-2-phenyl-2-(phenylamino)acetamide[2](L-3b)



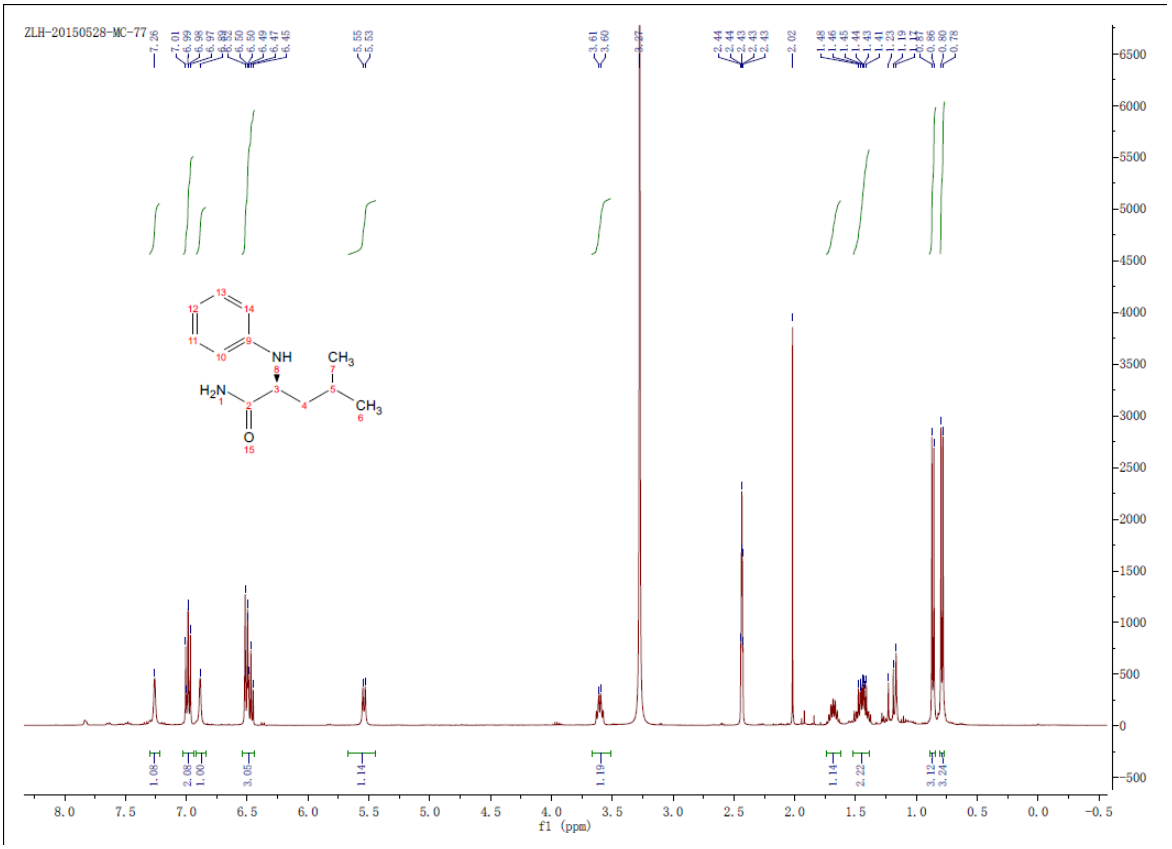


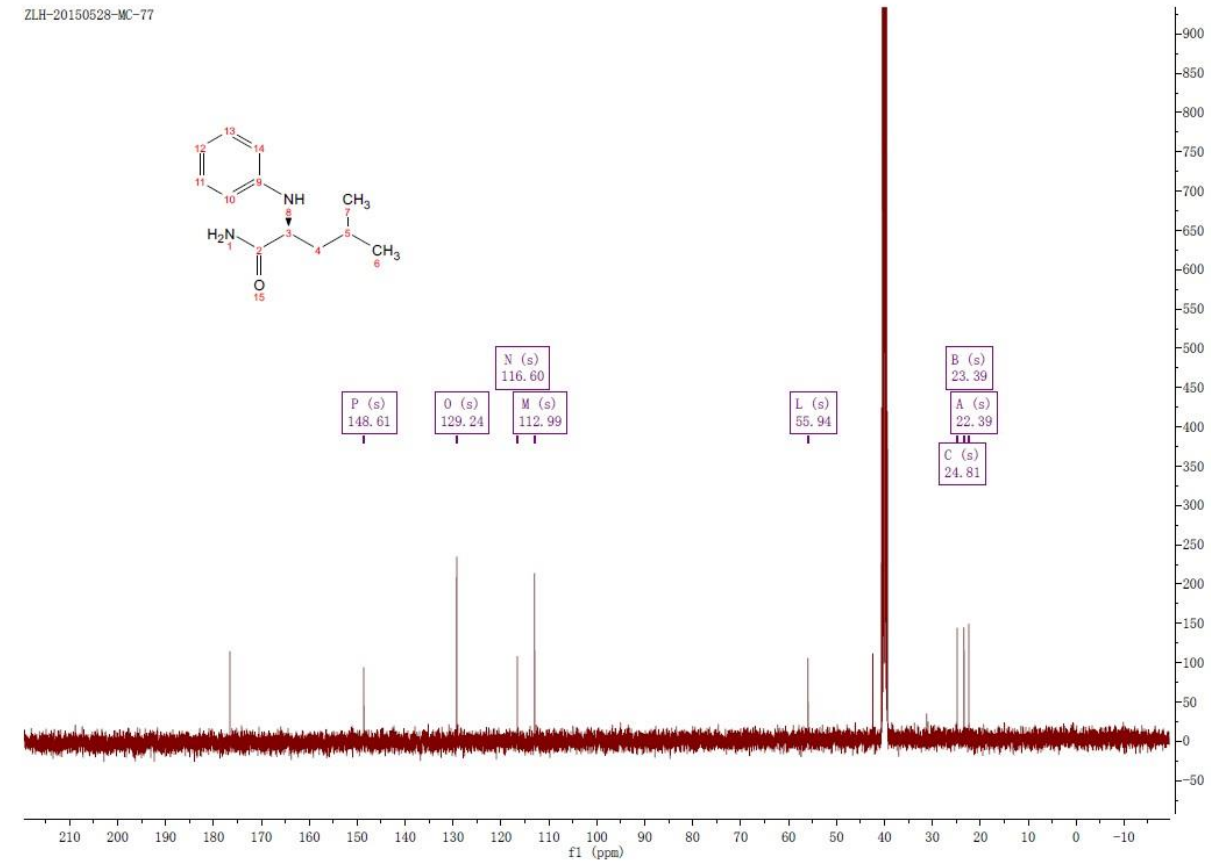
(S)-2-(phenylamino)propanamide[2] (L-3c)



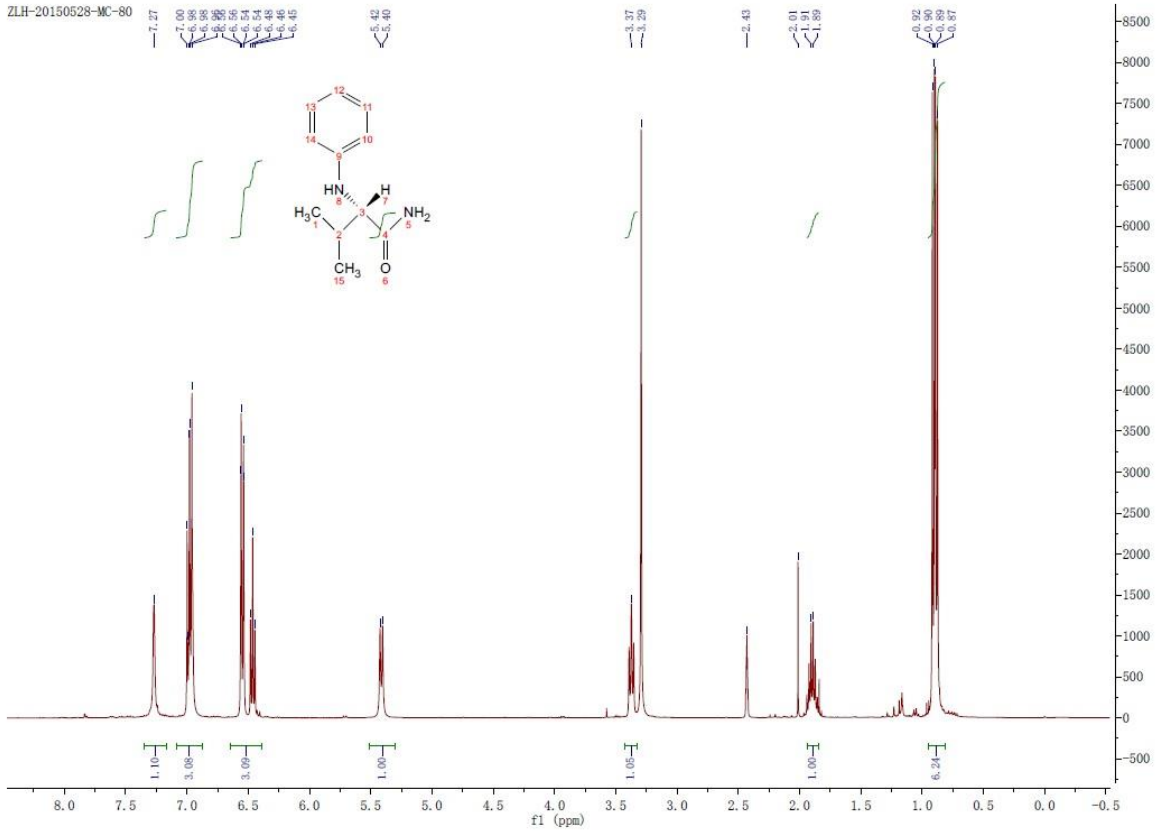


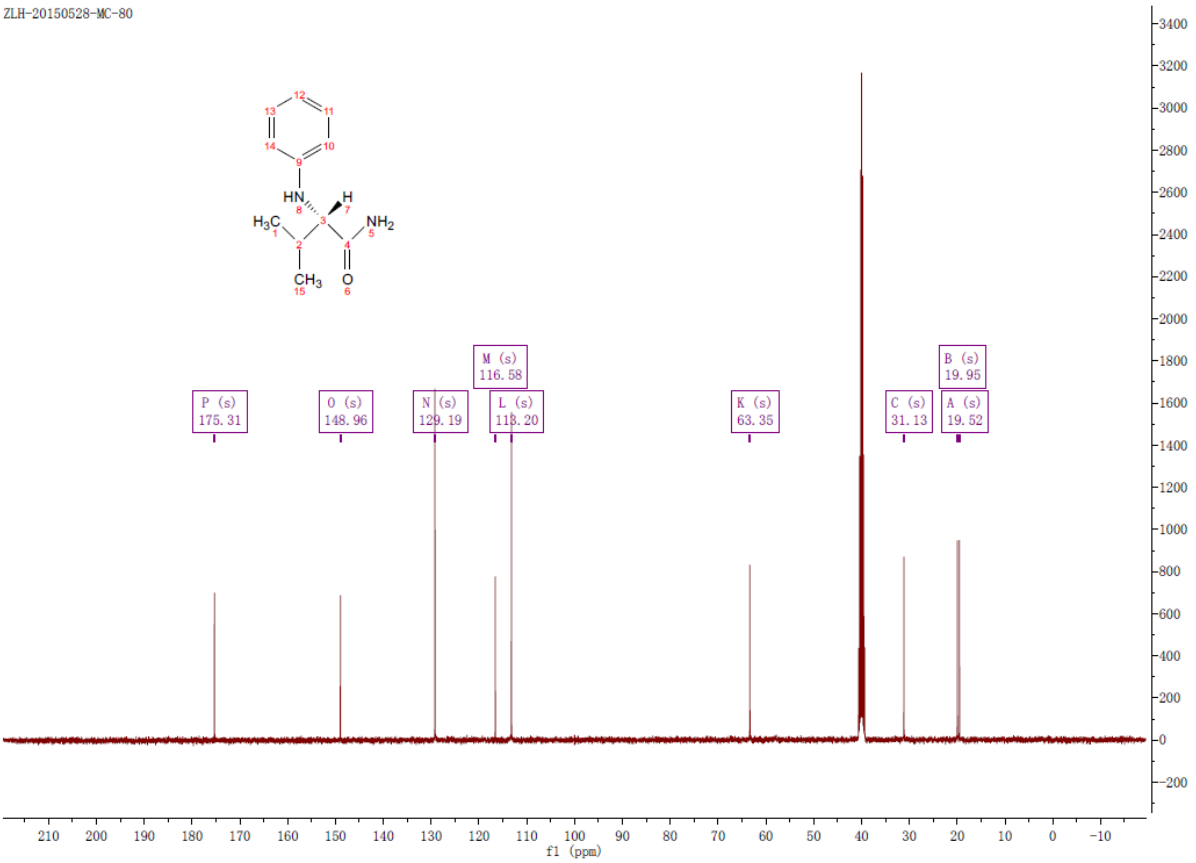
(S)-4-methyl-2-(phenylamino)pentanamide (3d)



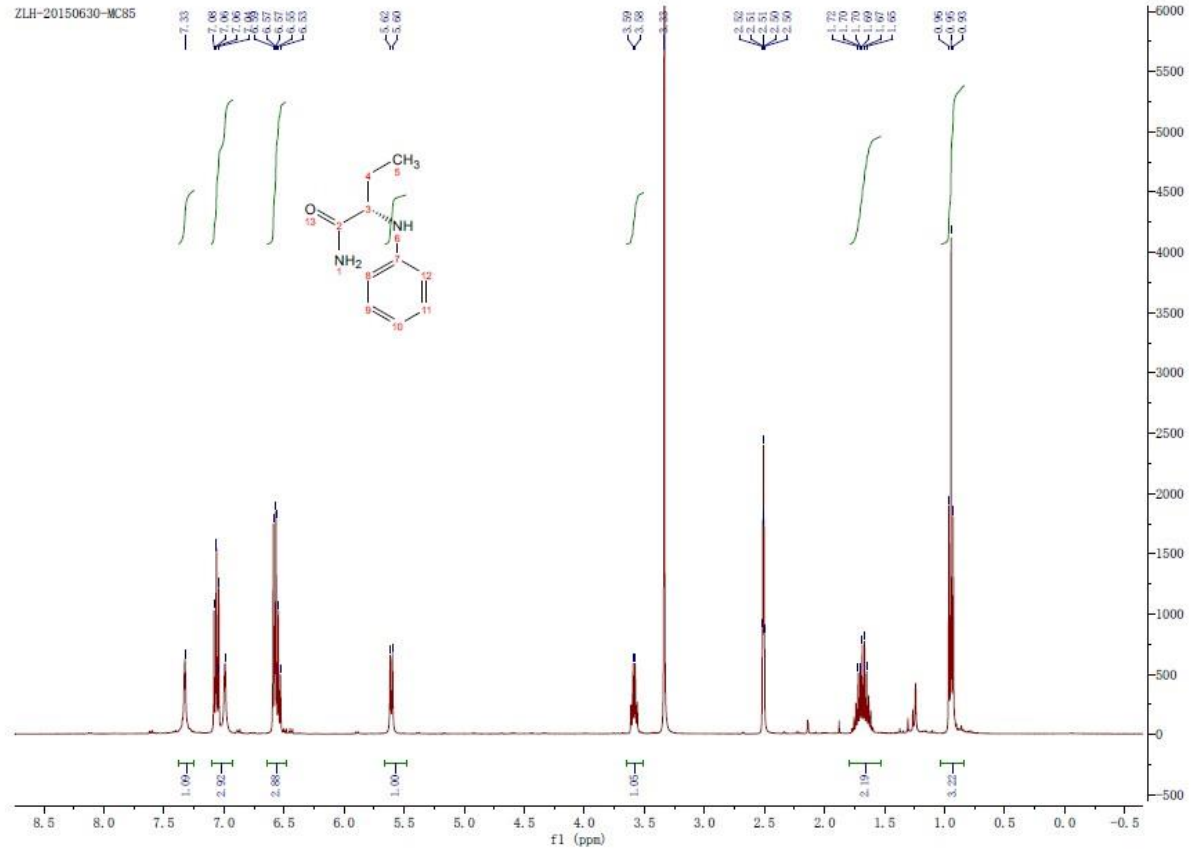


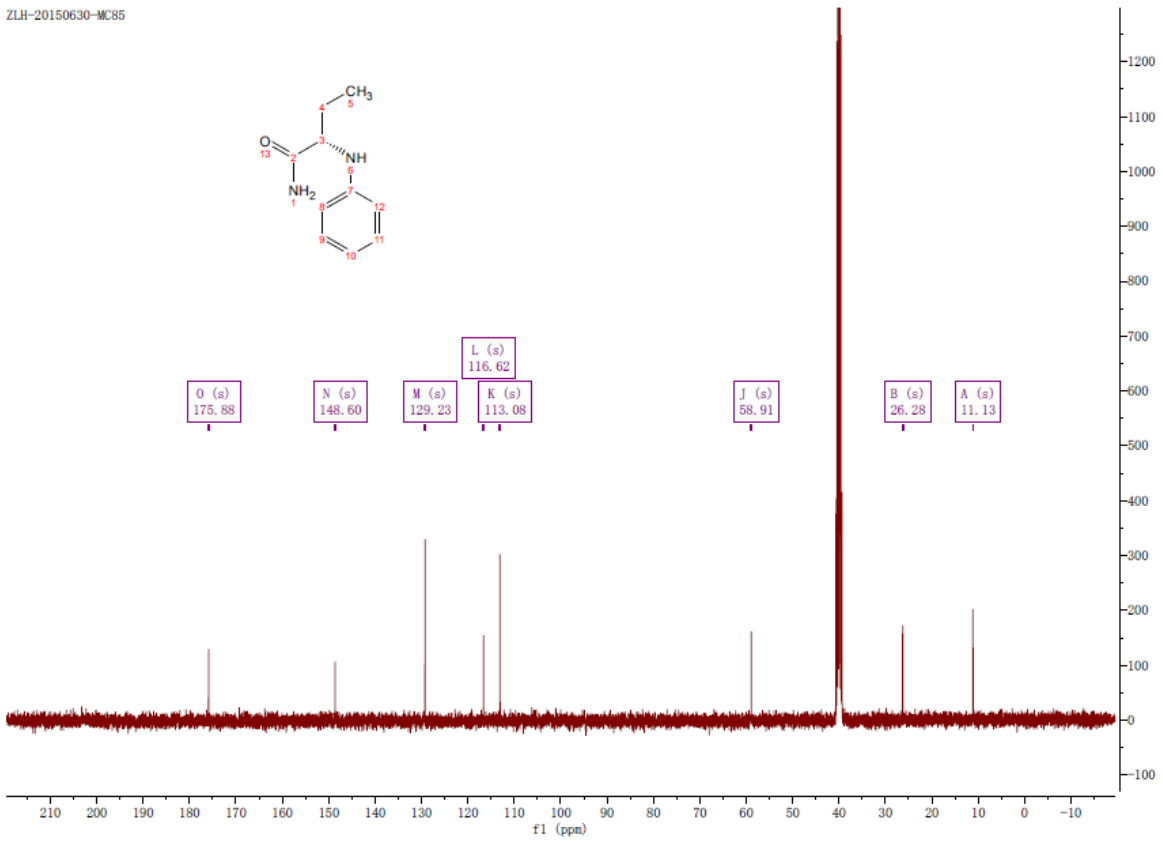
(S)-3-methyl-2-(phenylamino)butanamide (3e)



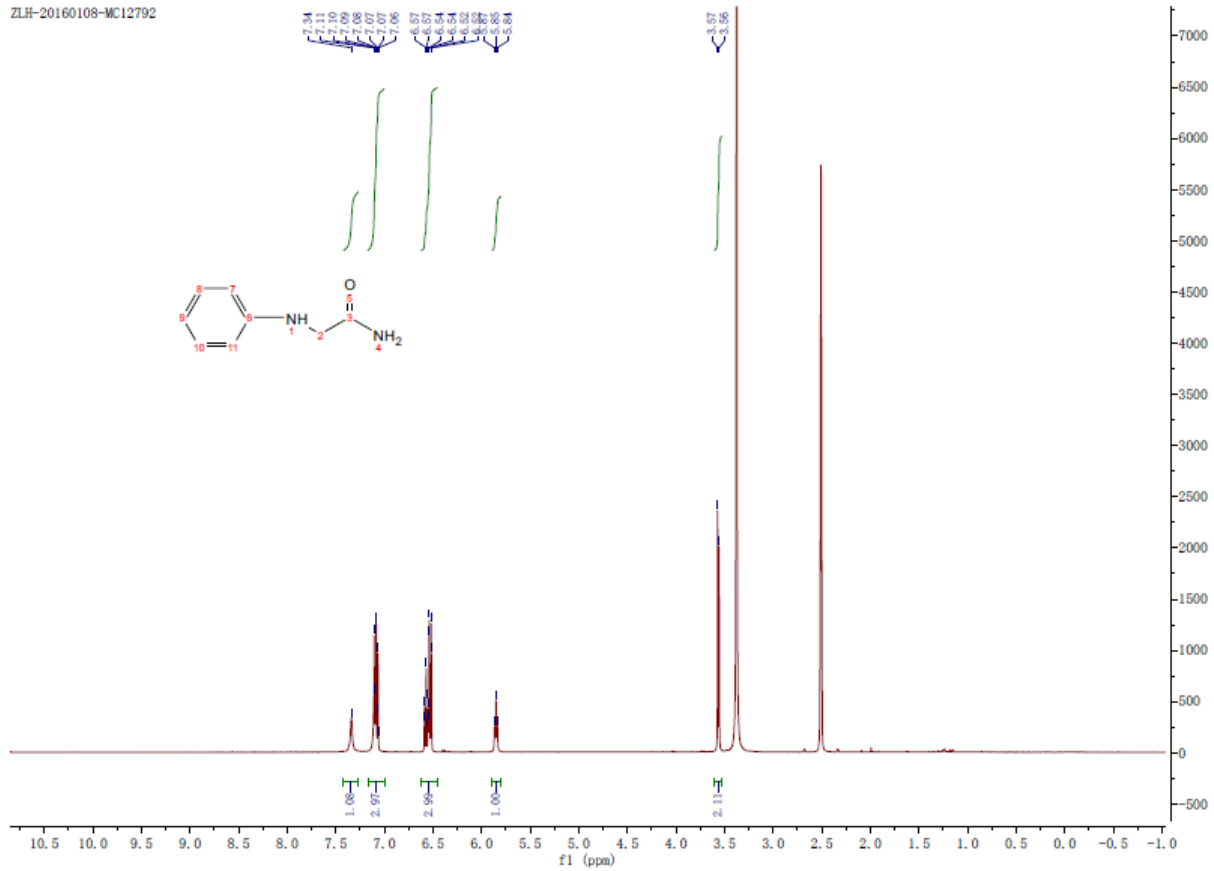


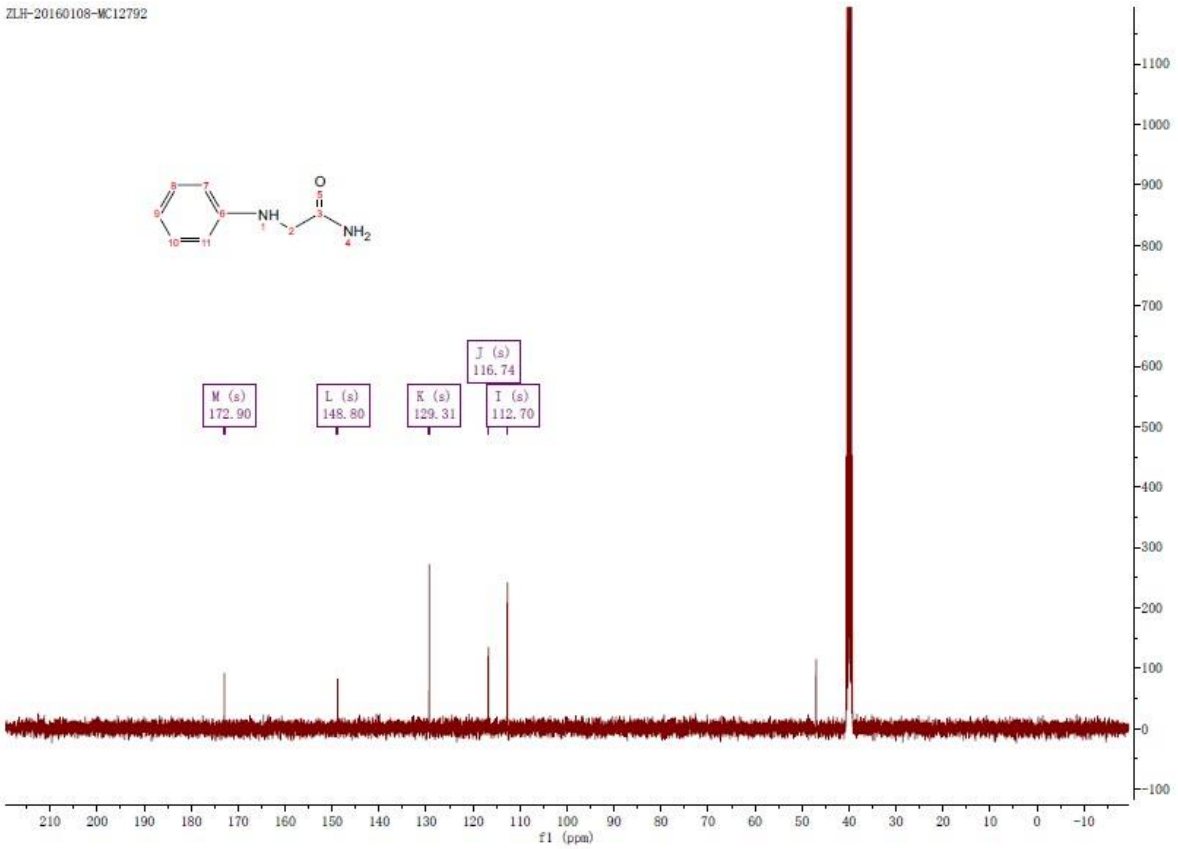
(S)-2-(phenylamino)butanamide[2] (3f)



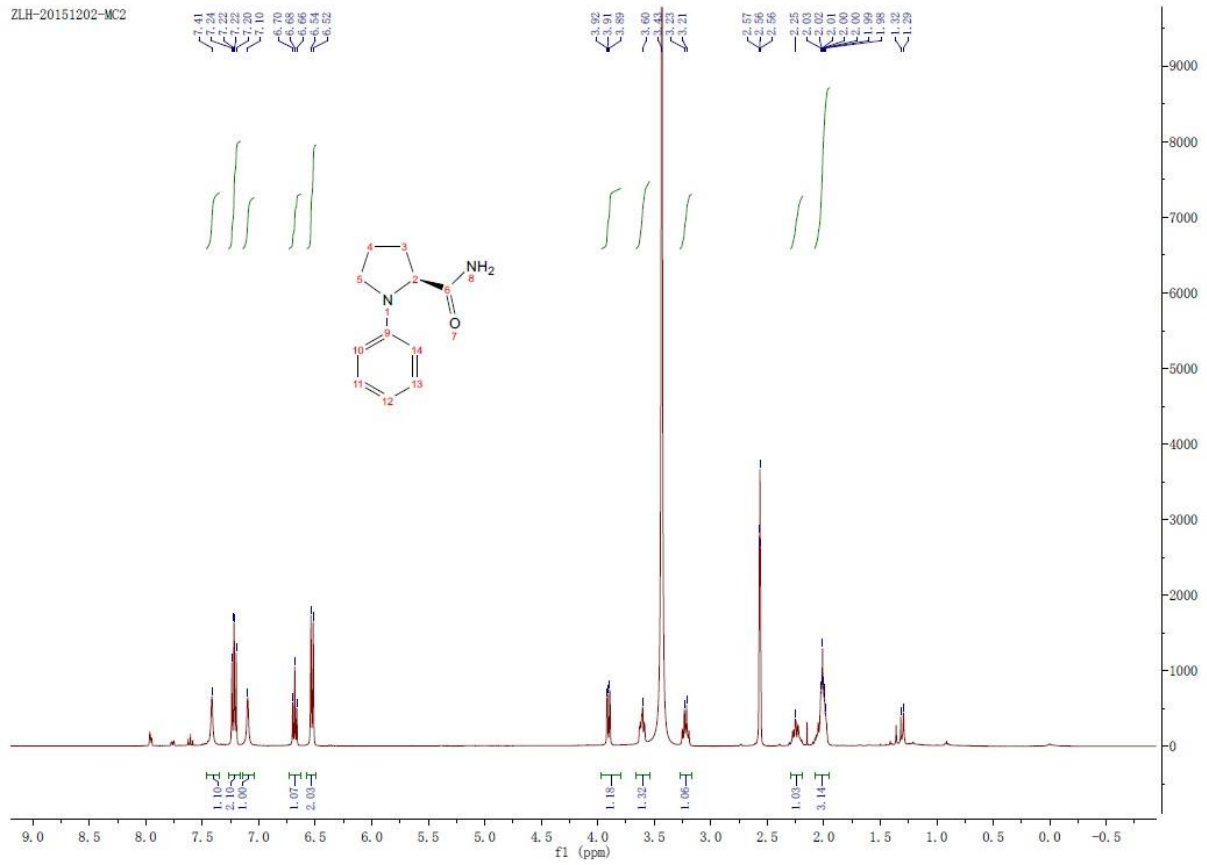


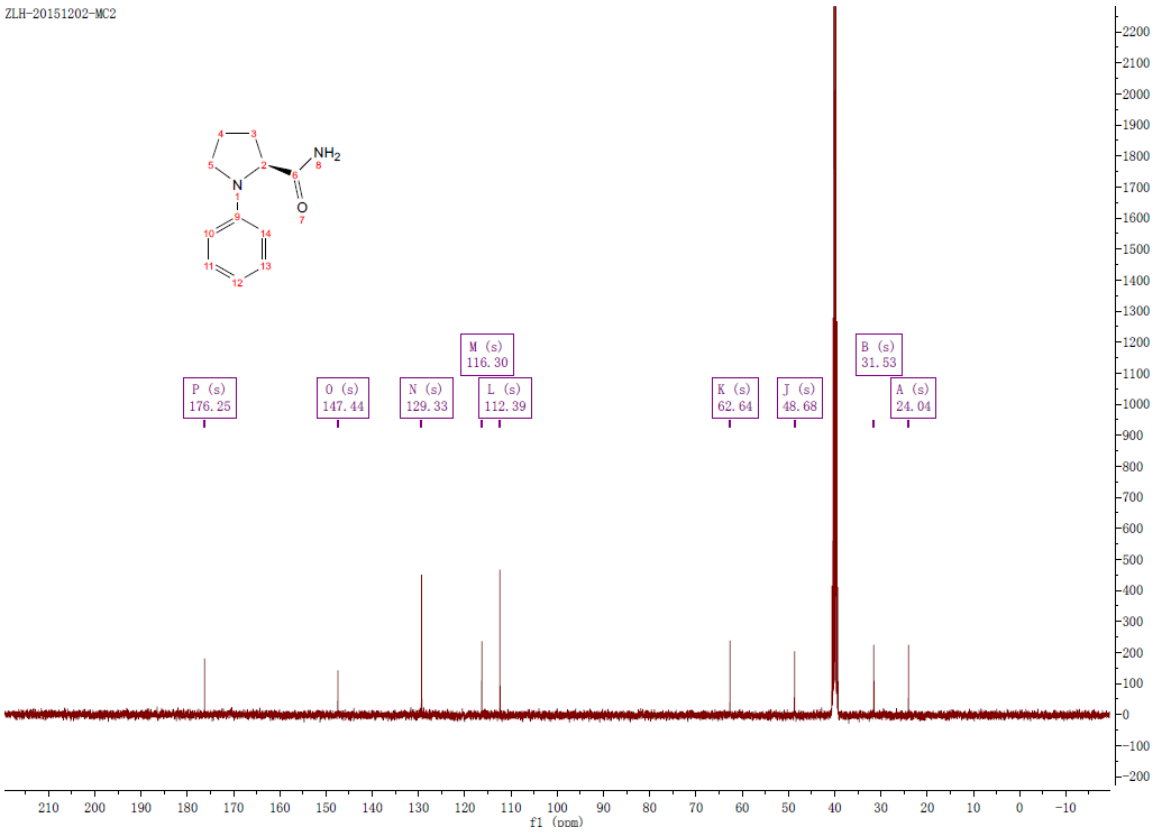
2-(phenylamino)acetamide[2] (3g)



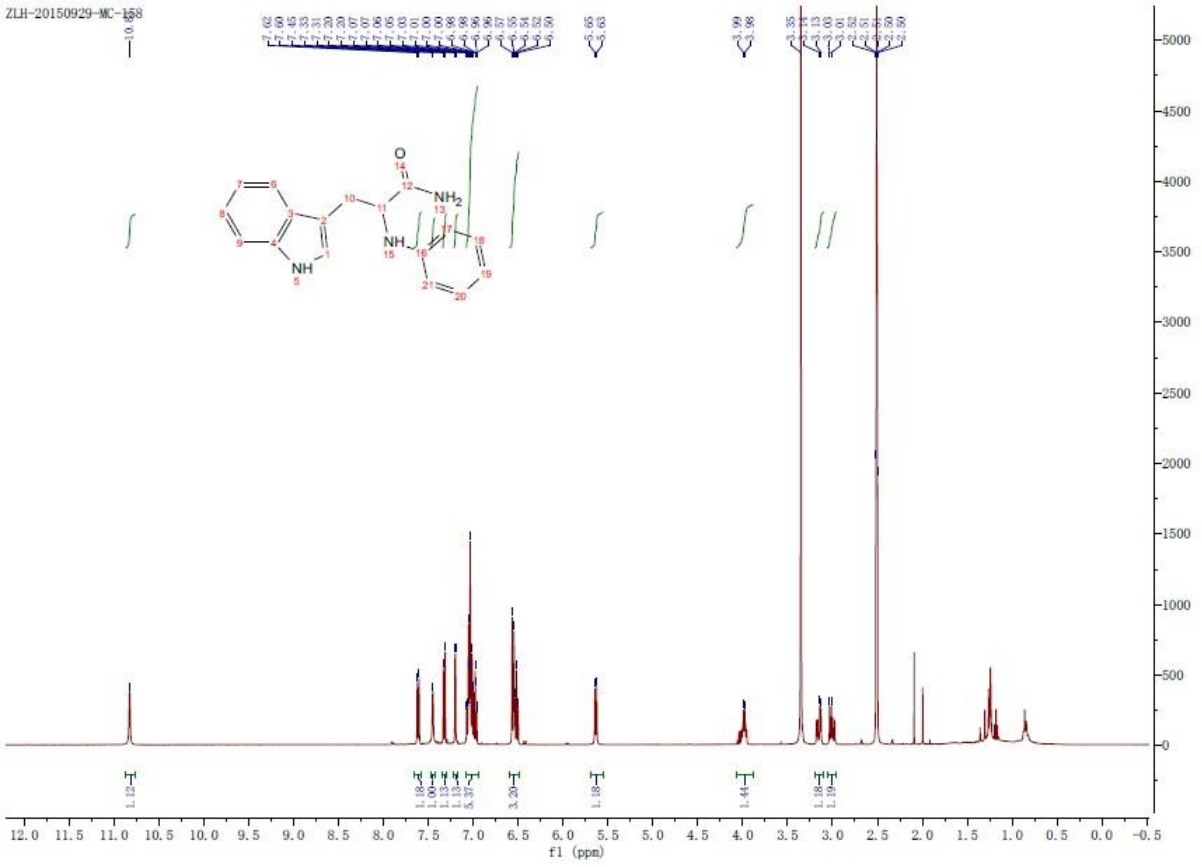


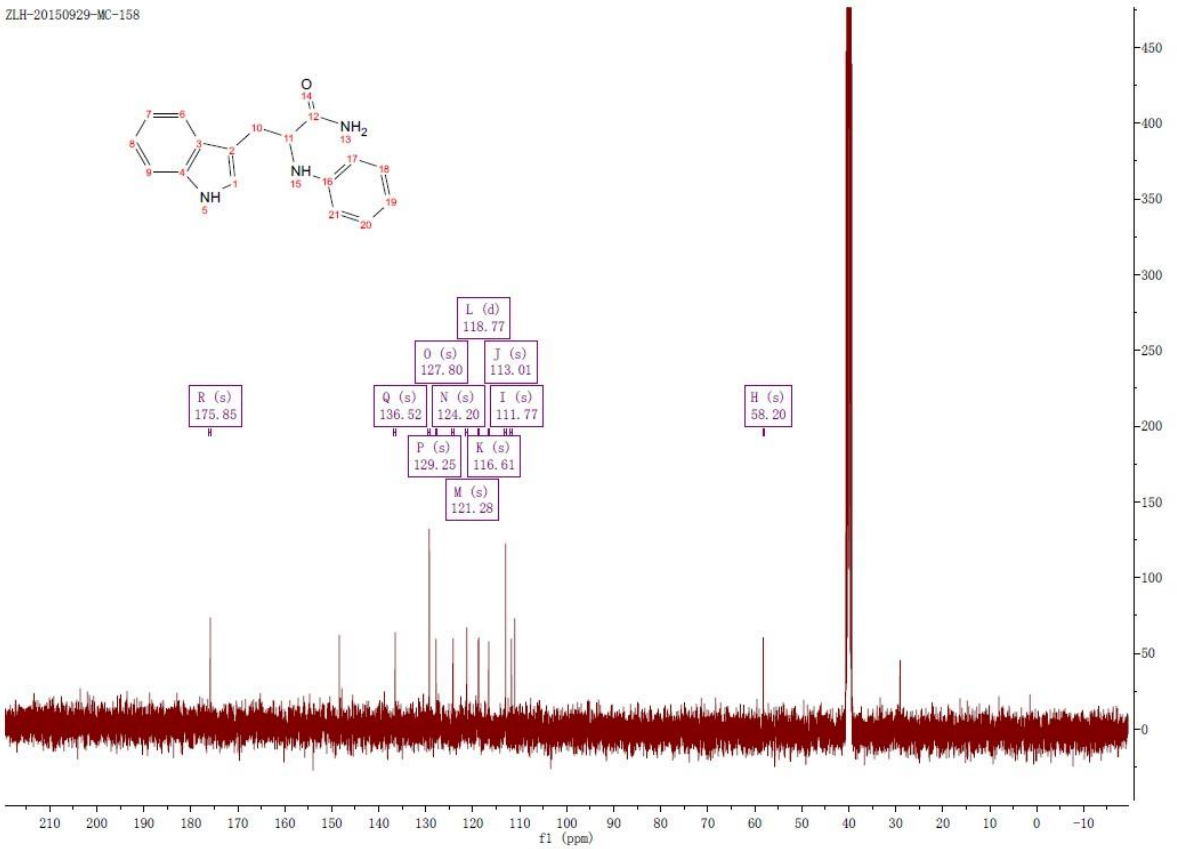
(S)-1-phenylpyrrolidine-2-carboxamide[3] (3h)



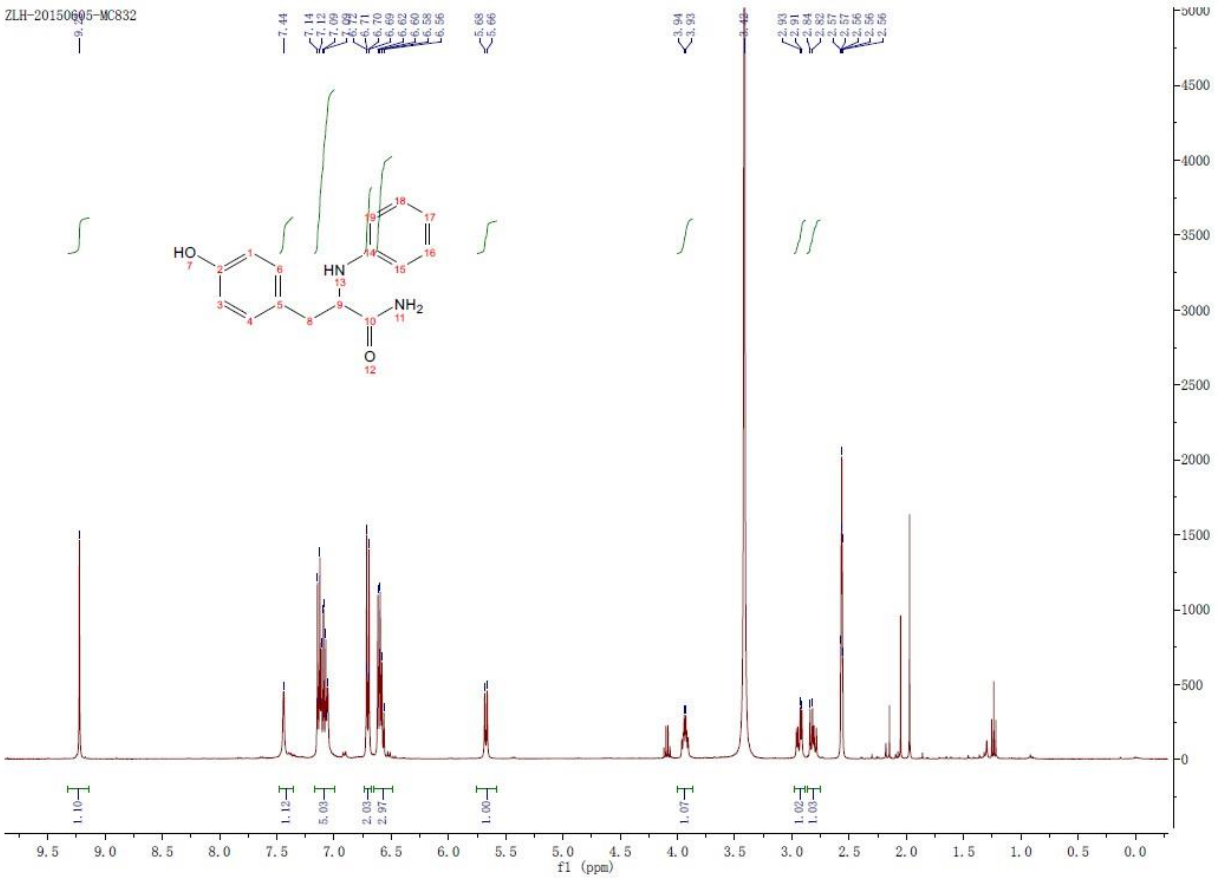


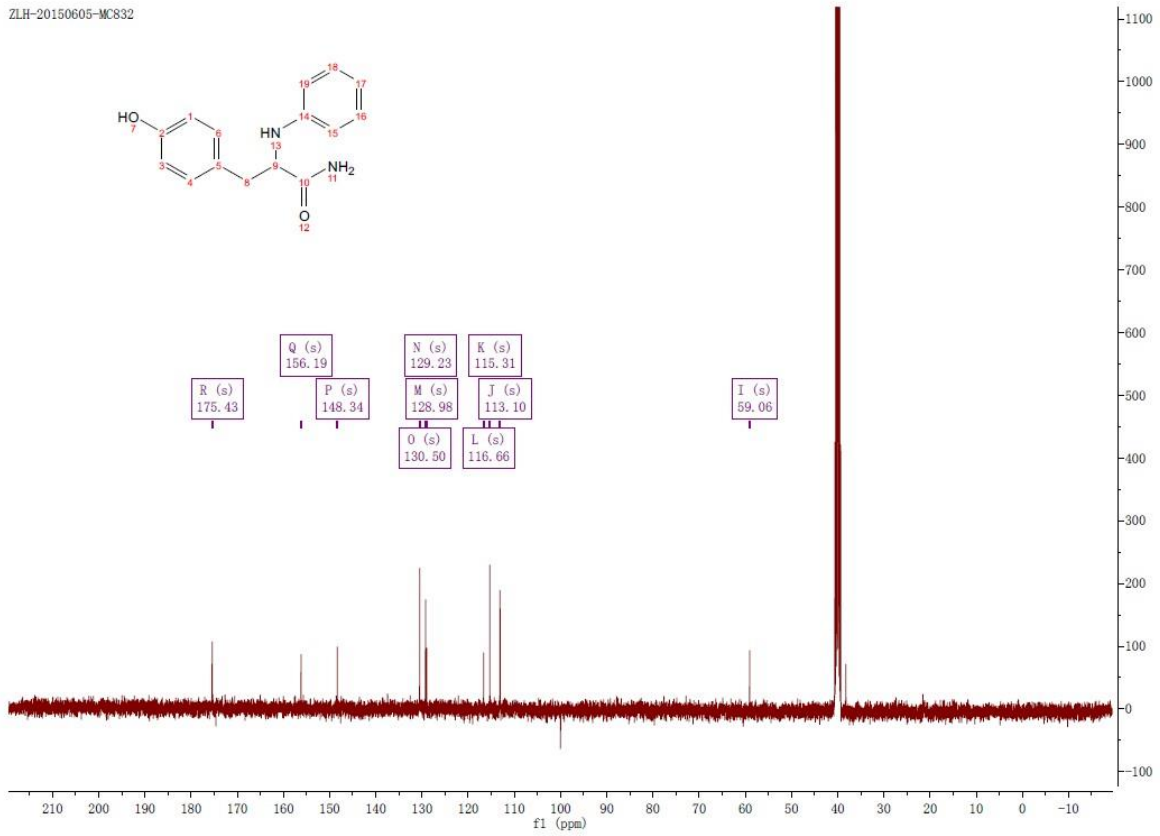
3-(1H-indol-3-yl)-2-(phenylamino)propanamide (3i)



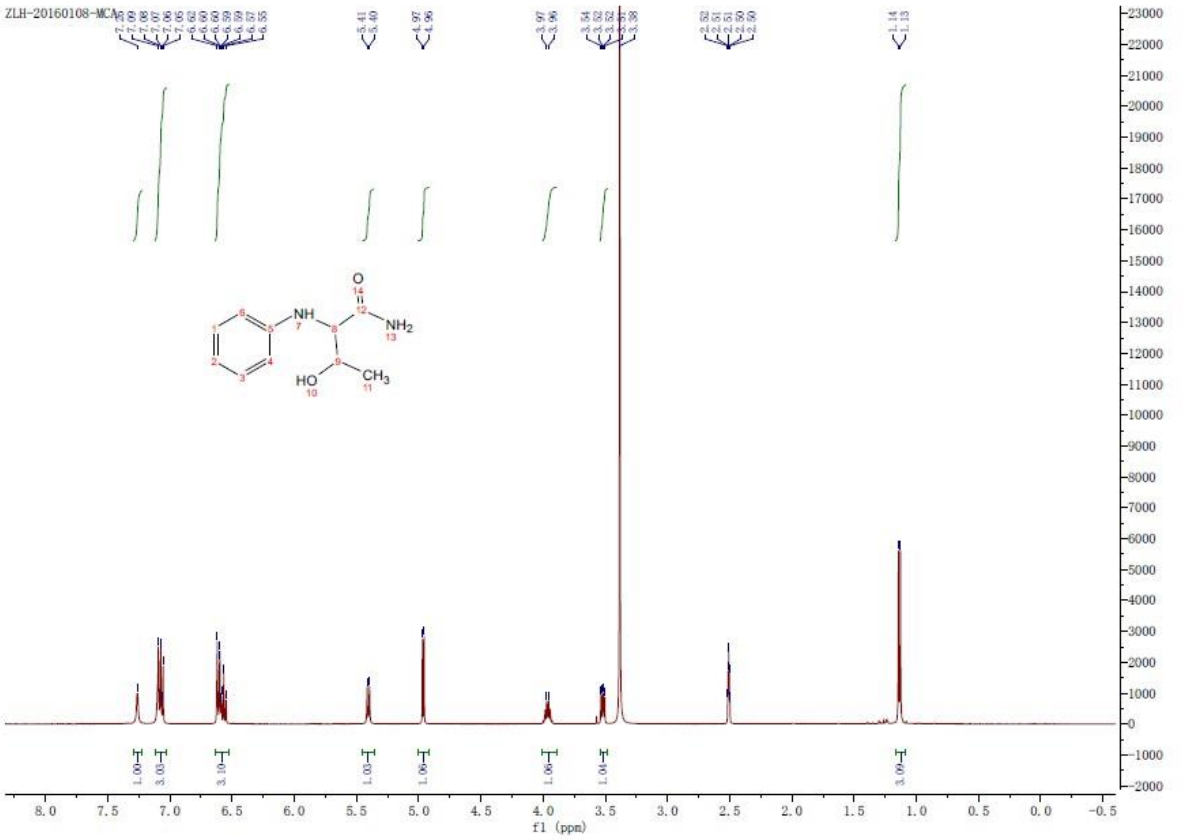


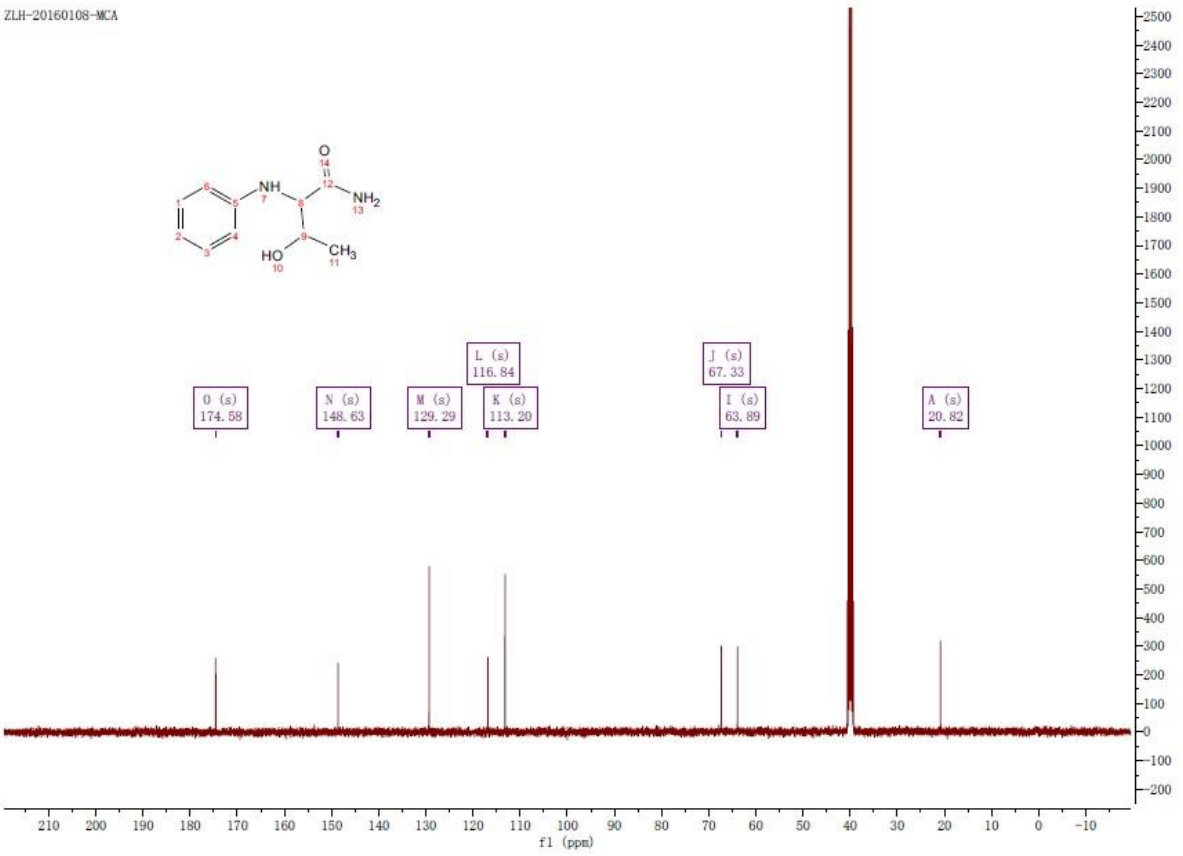
3-(4-hydroxyphenyl)-2-(phenylamino)propanamide (3j)



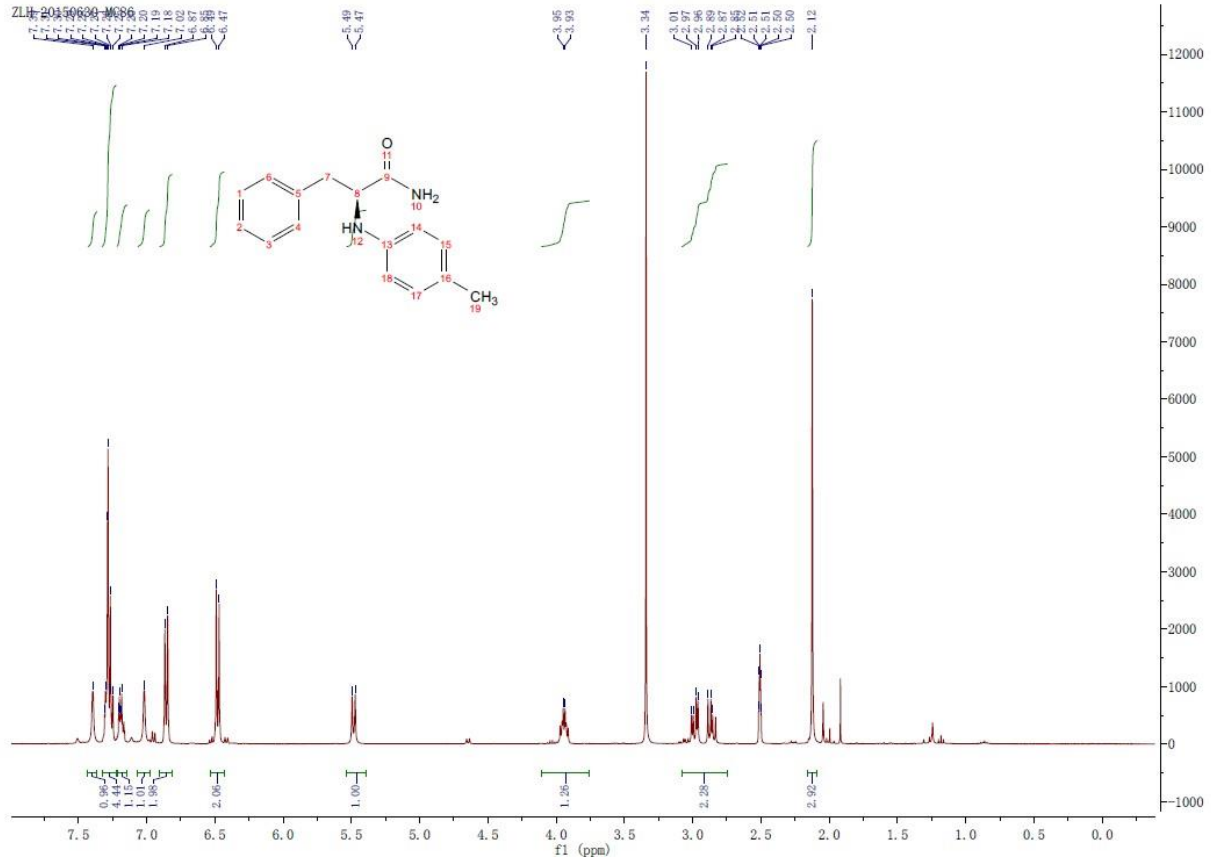


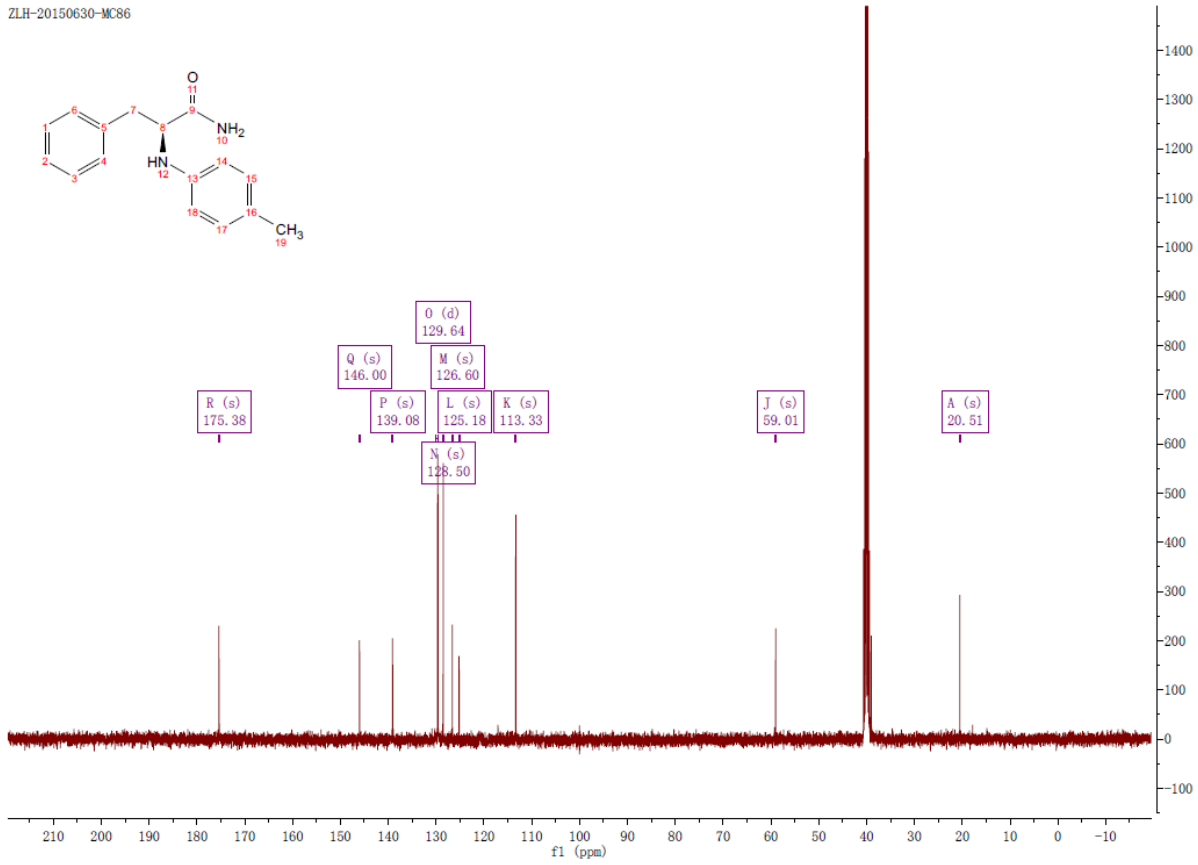
3-hydroxy-2-(phenylamino)butanamide (3k)



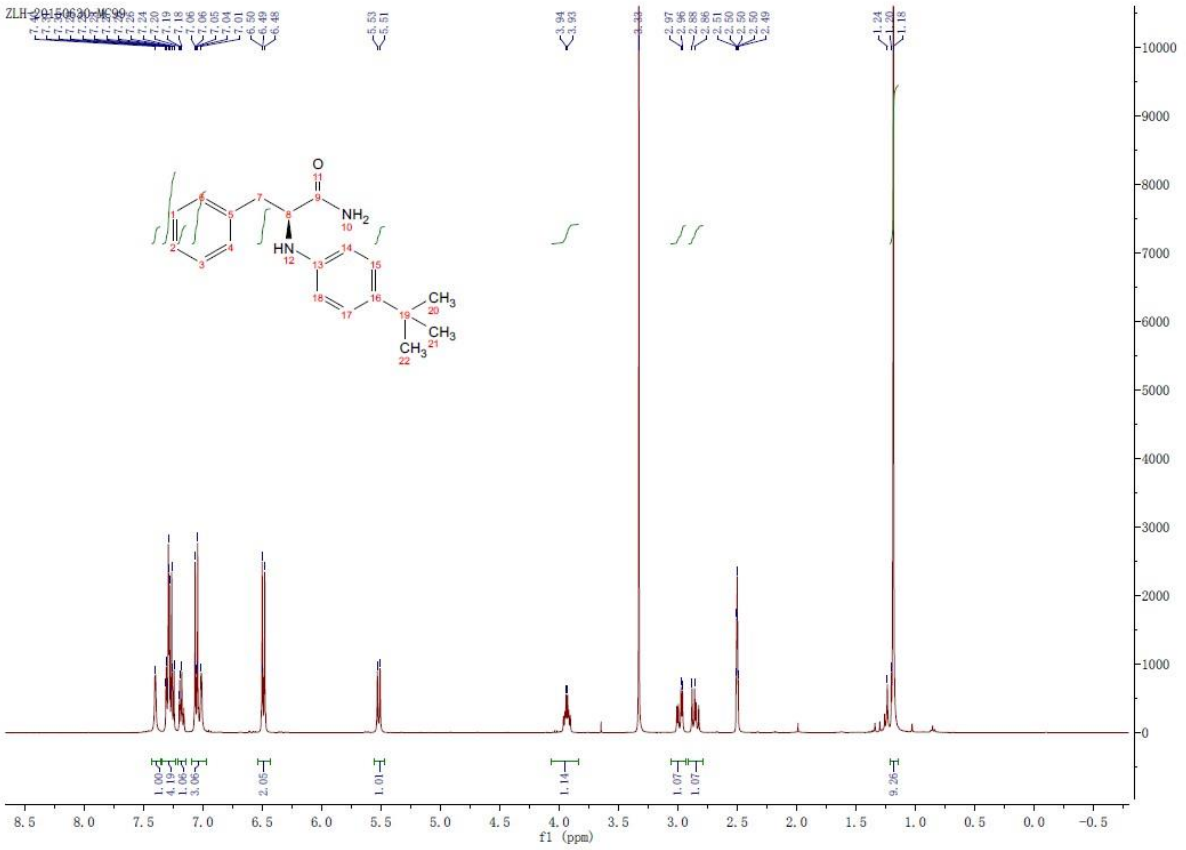


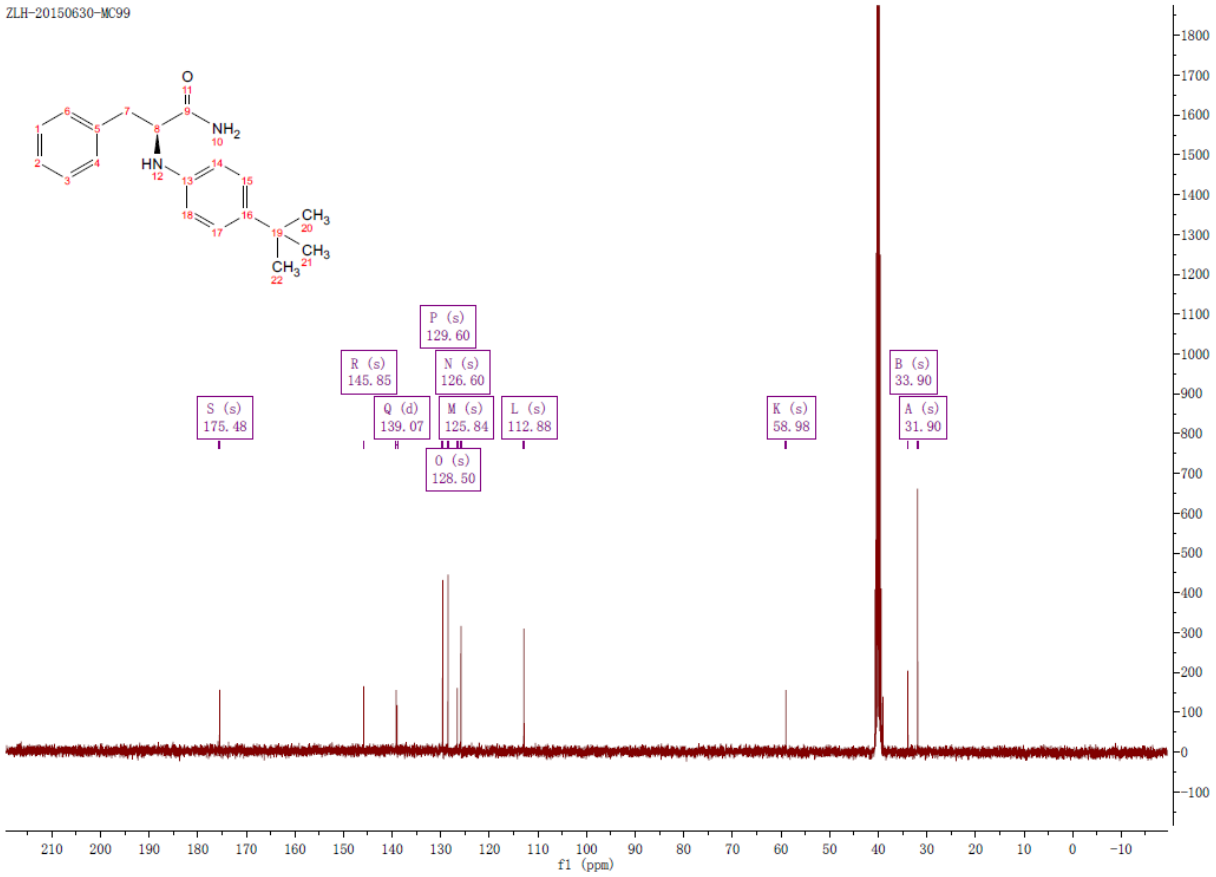
(S)-2-(p-toluidino)-3-phenylpropanamide (3l)



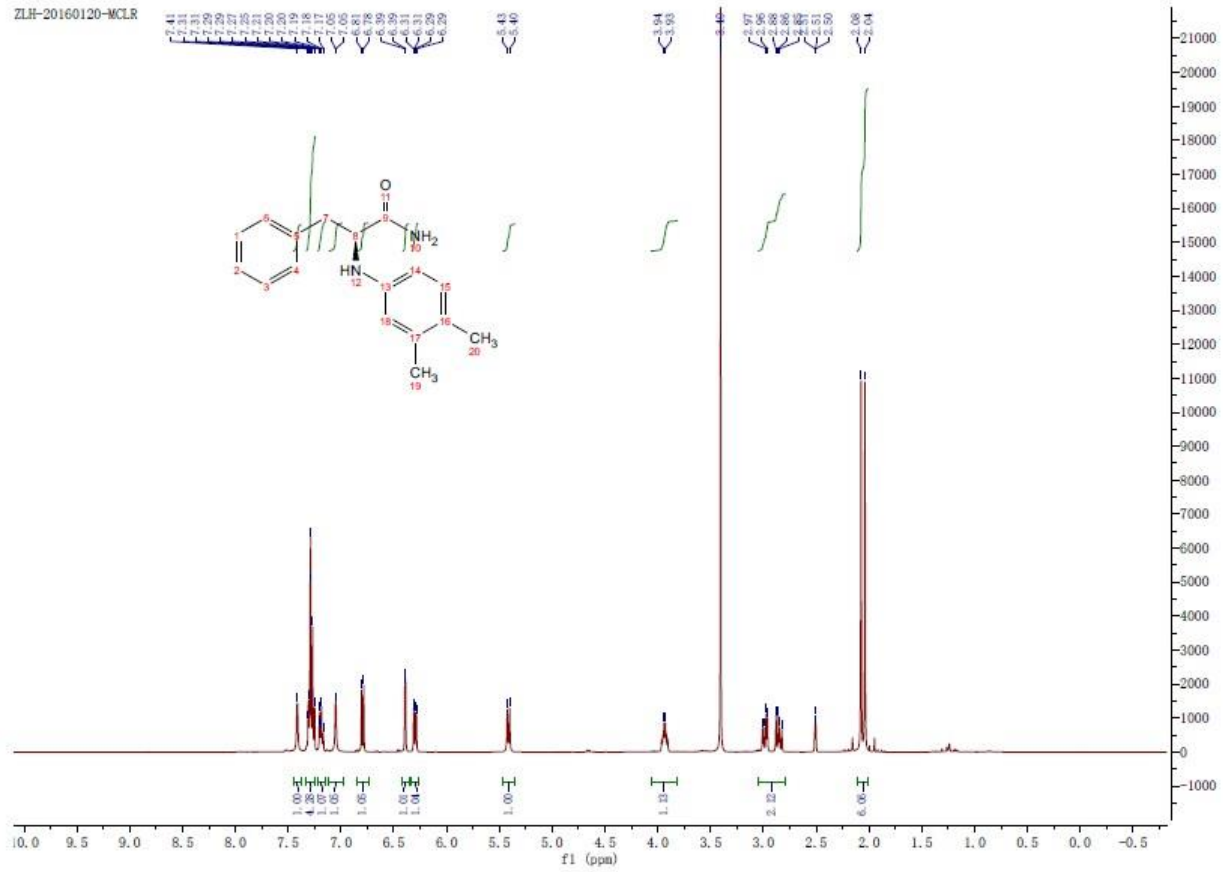


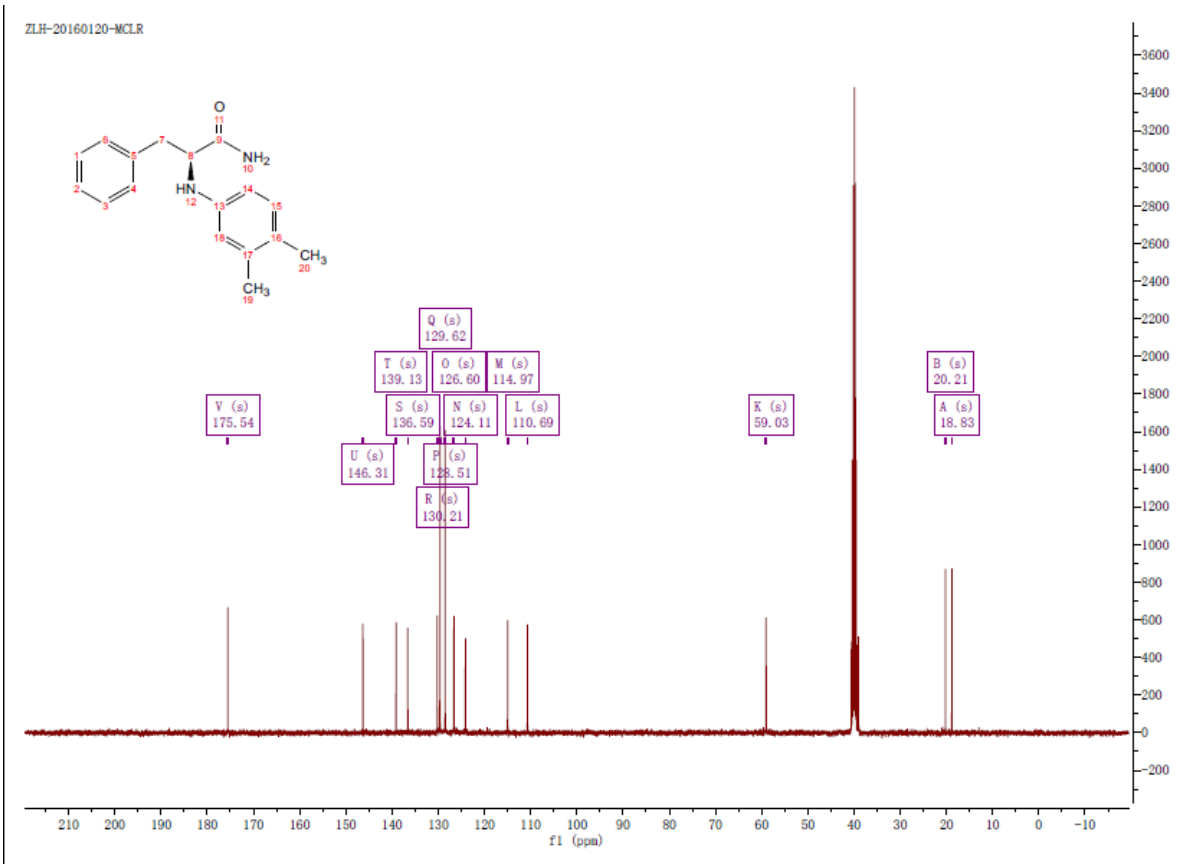
(S)-2-(4-tert-butylphenylamino)-3-phenylpropanamide (3m)



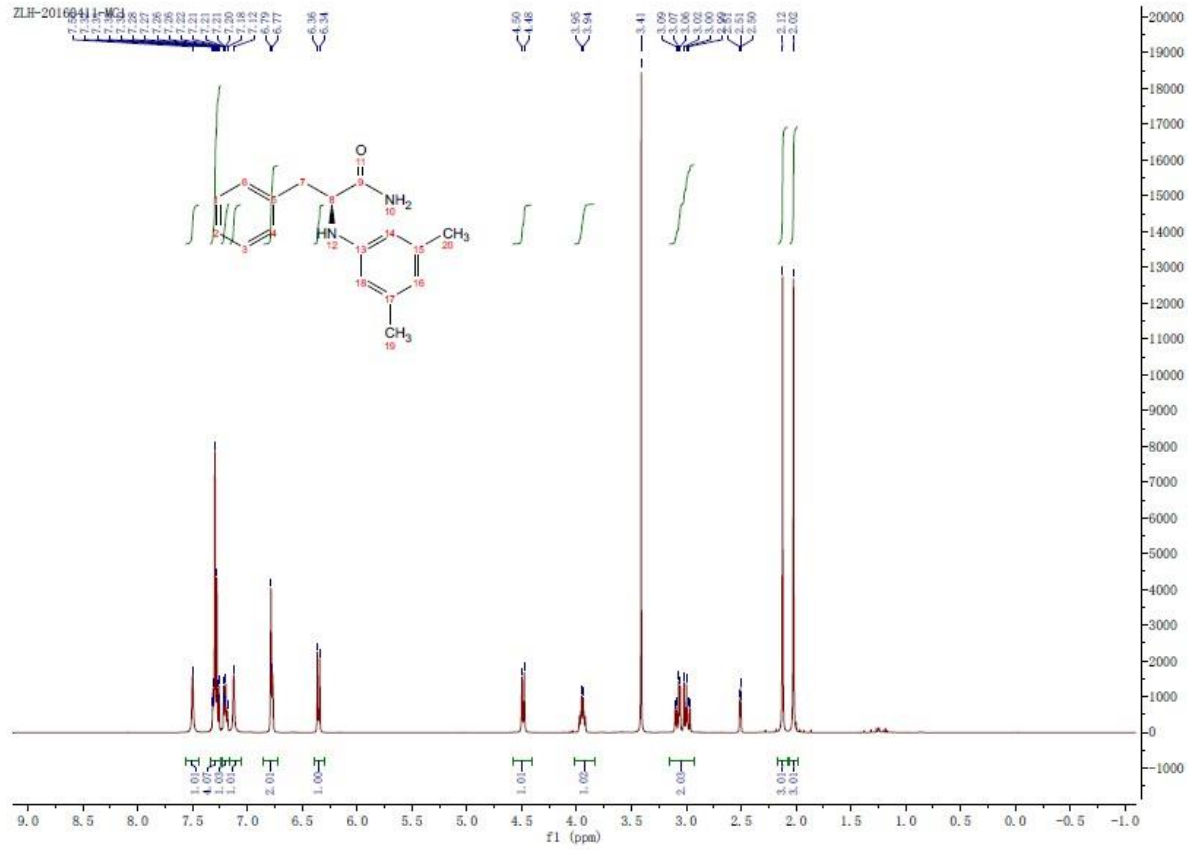


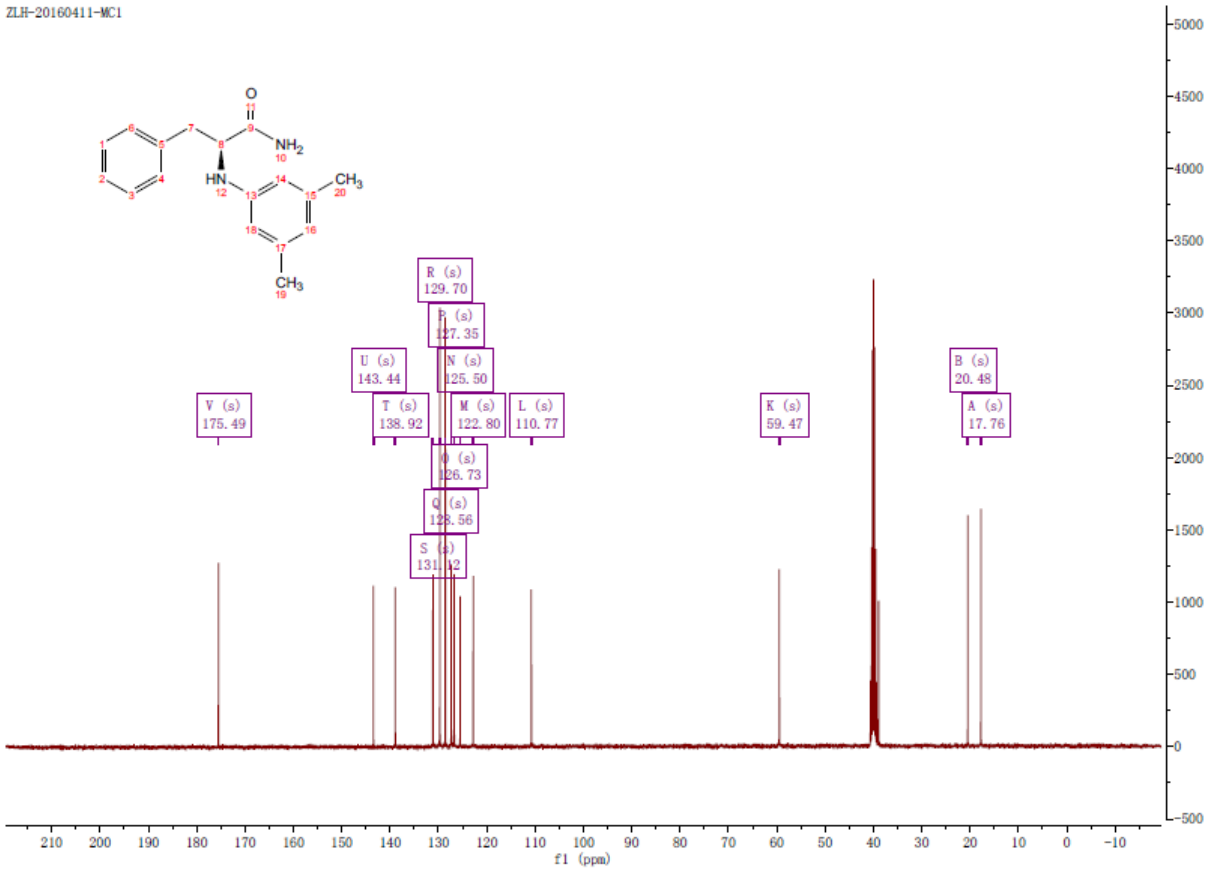
(S)-2-(3,4-dimethylphenylamino)-3-phenylpropanamide (3n)



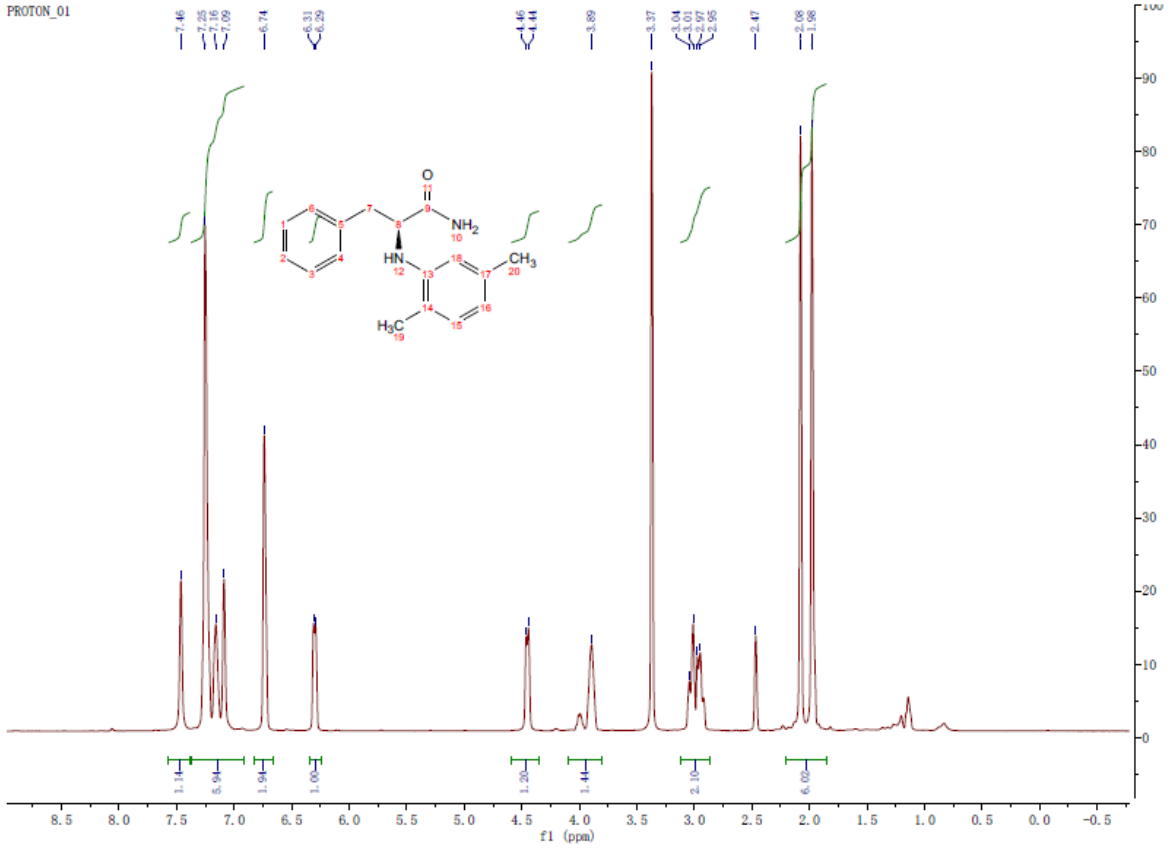


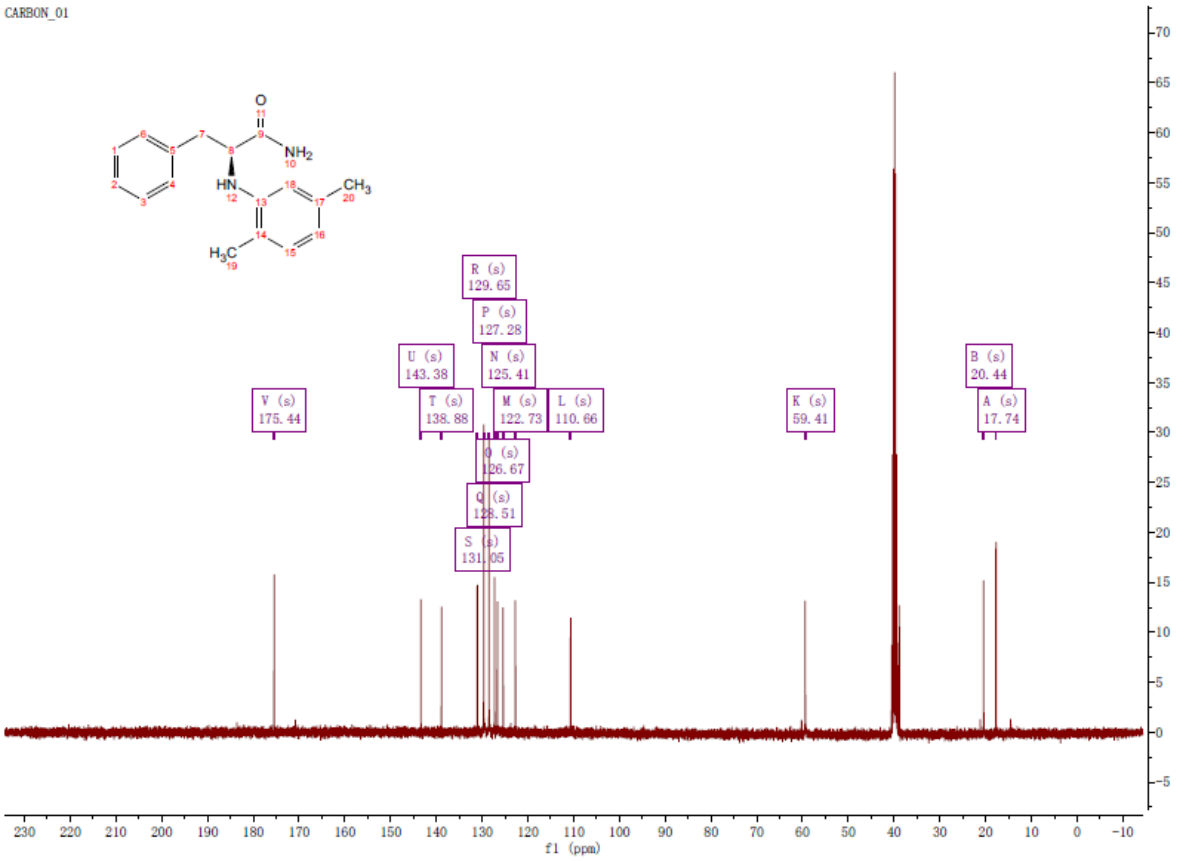
(S)-2-(3,5-dimethylphenylamino)-3-phenylpropanamide (3o)



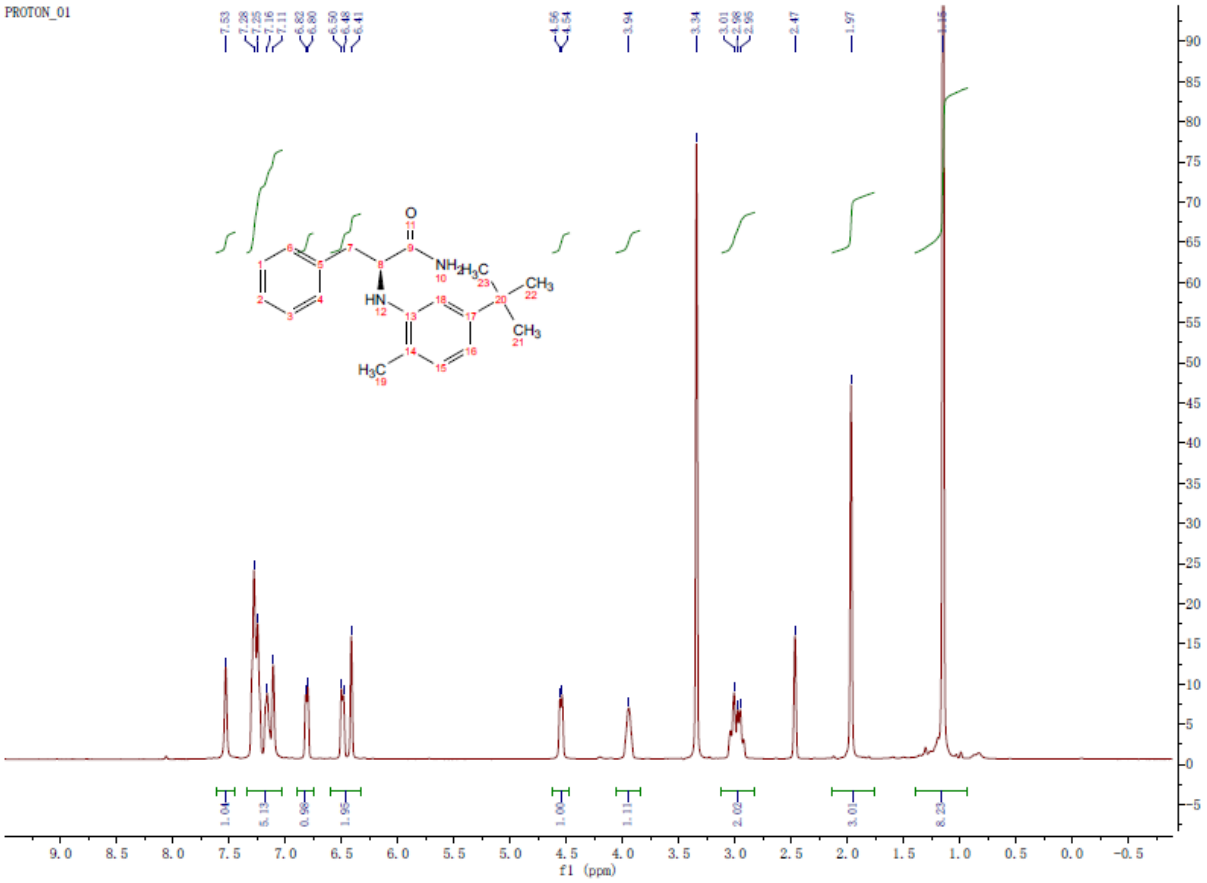


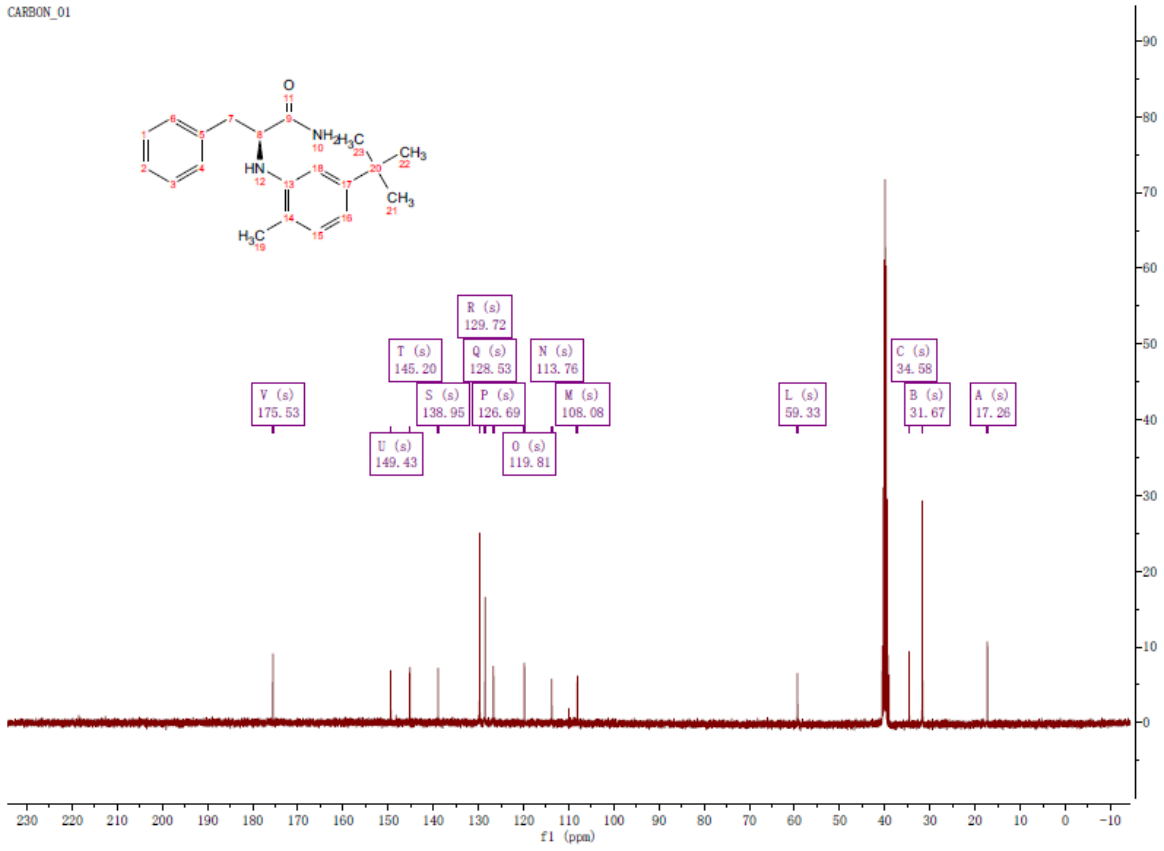
(S)-2-(2,5-dimethylphenylamino)-3-phenylpropanamide (3p)



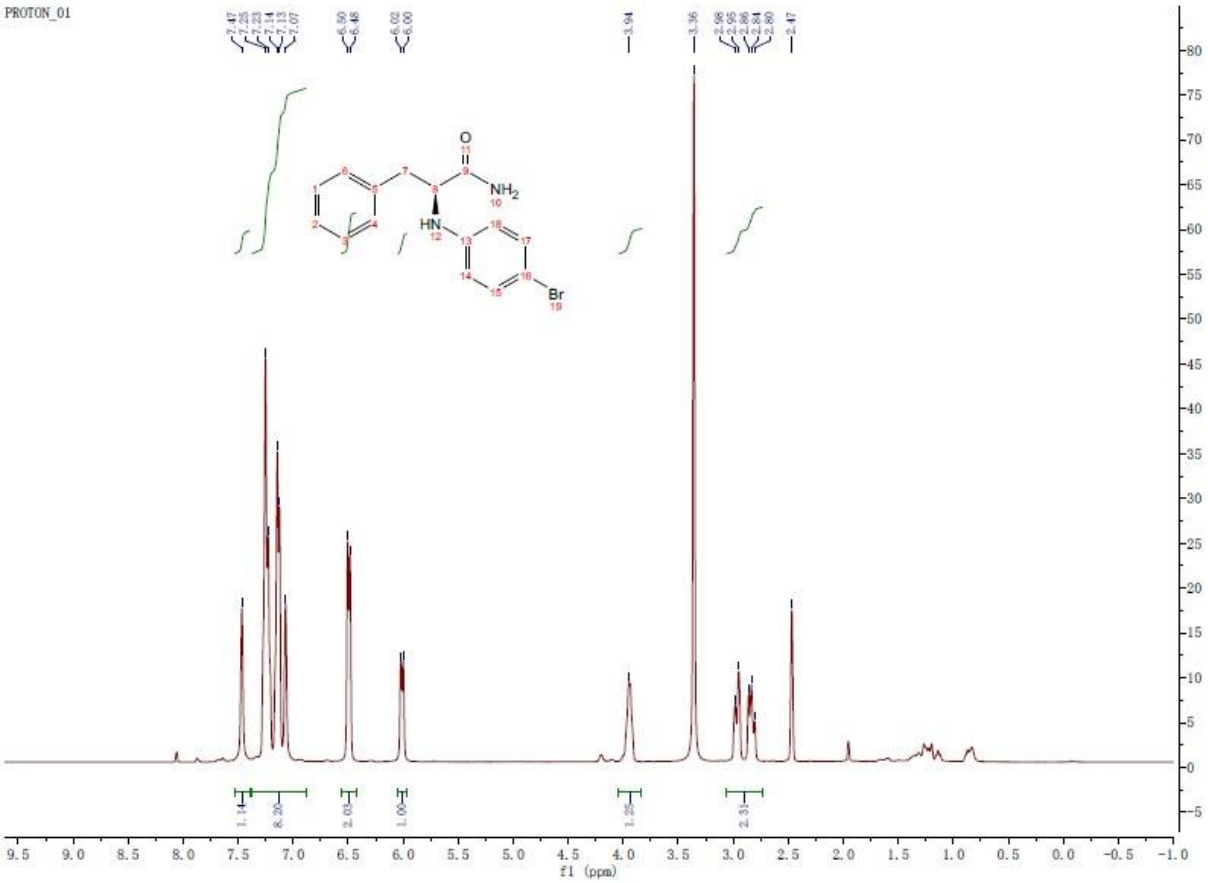


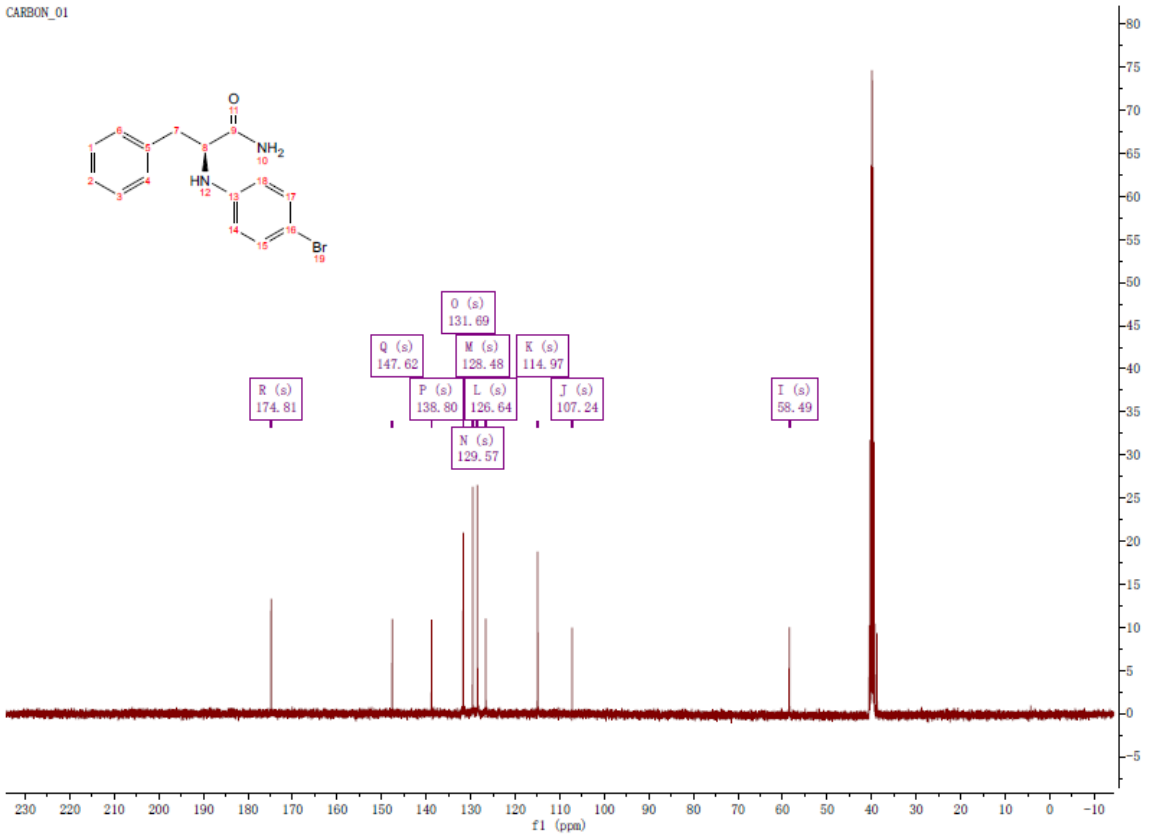
(S)-2-(5-tert-butyl-2-methylphenylamino)-3-phenylpropanamide (3q)



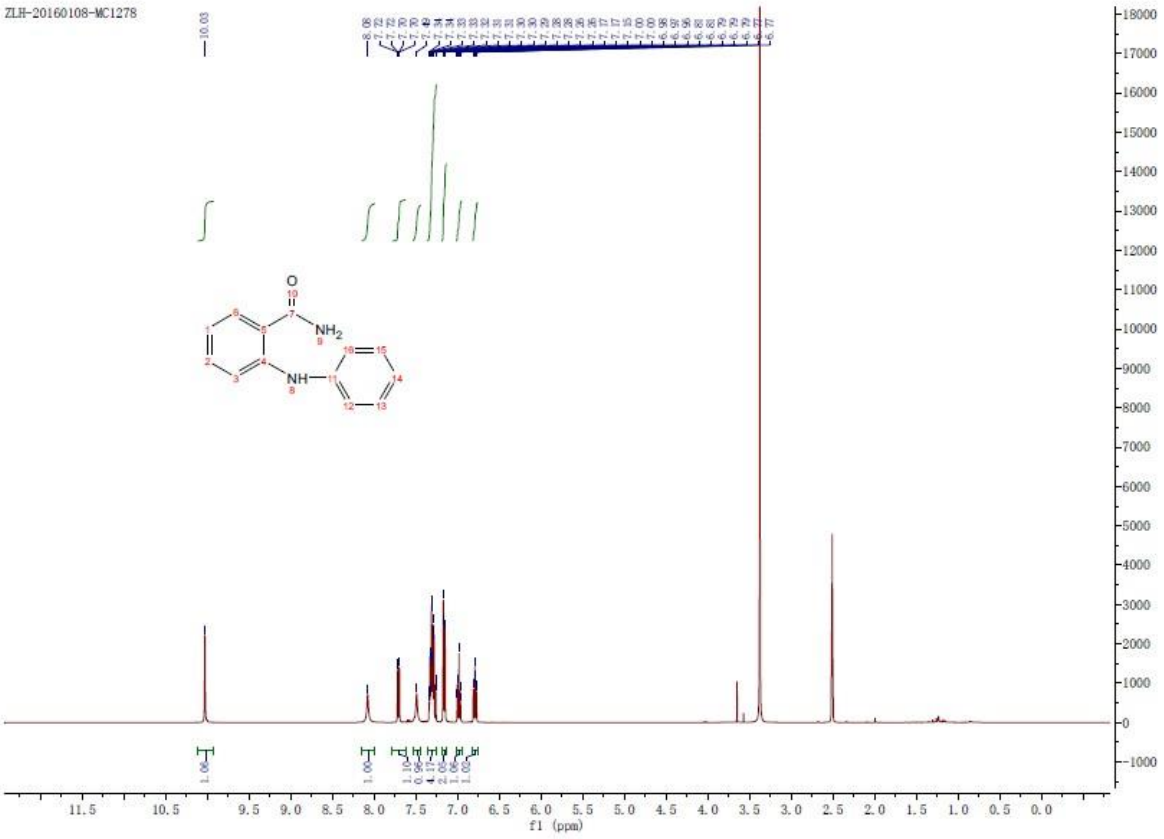


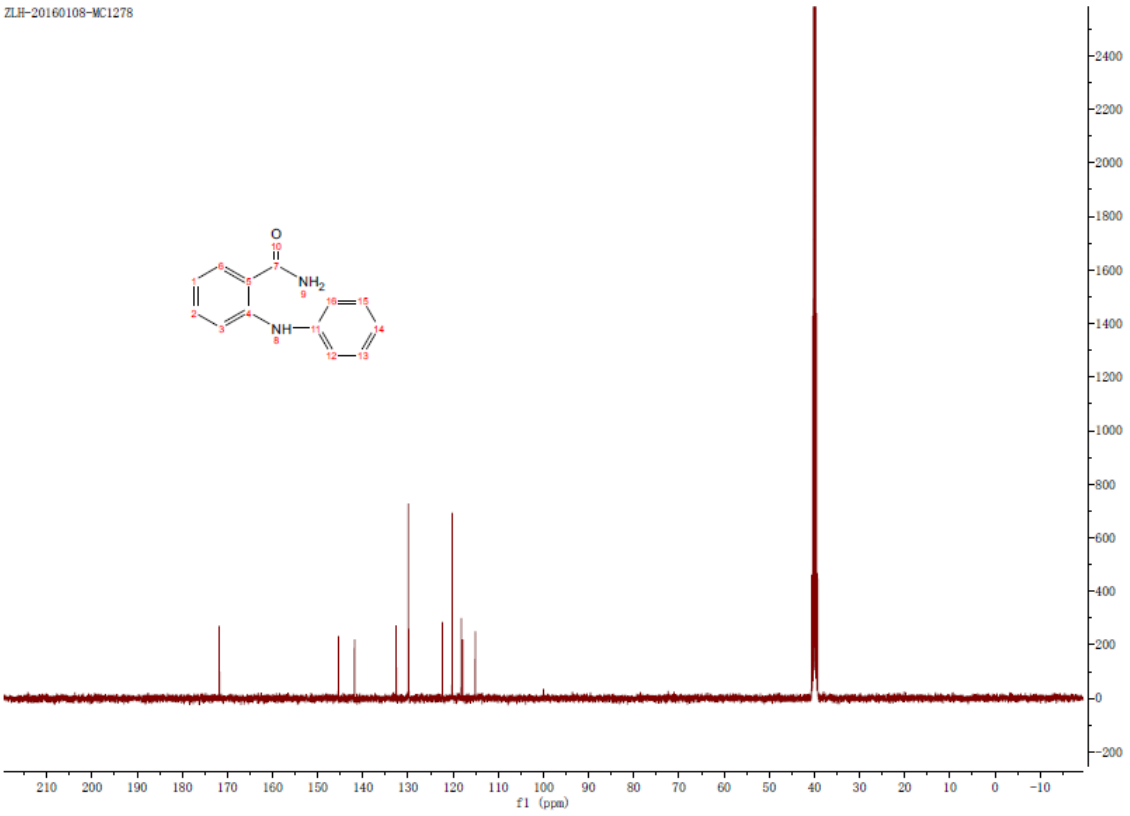
(S)-2-(4-bromophenylamino)-3-phenylpropanamide (3r)



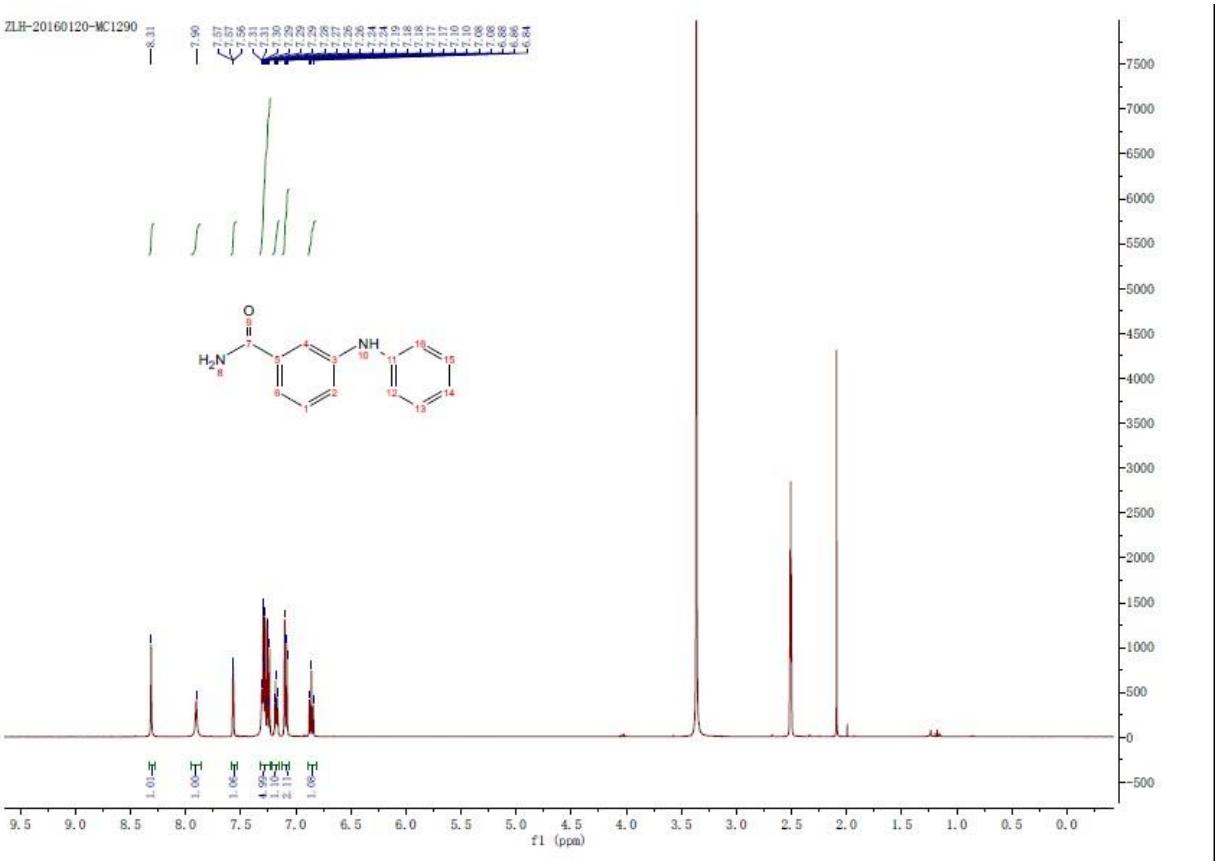


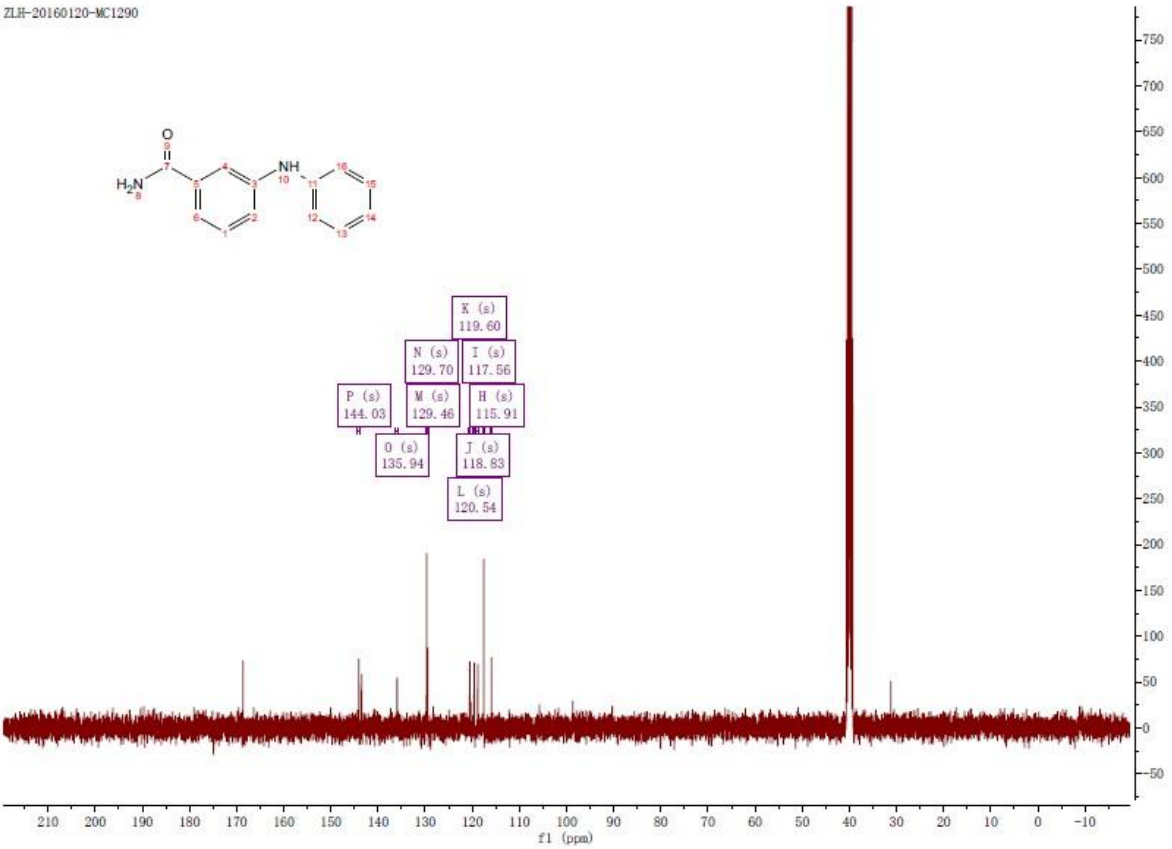
2-(phenylamino)benzamide[4] (3s)



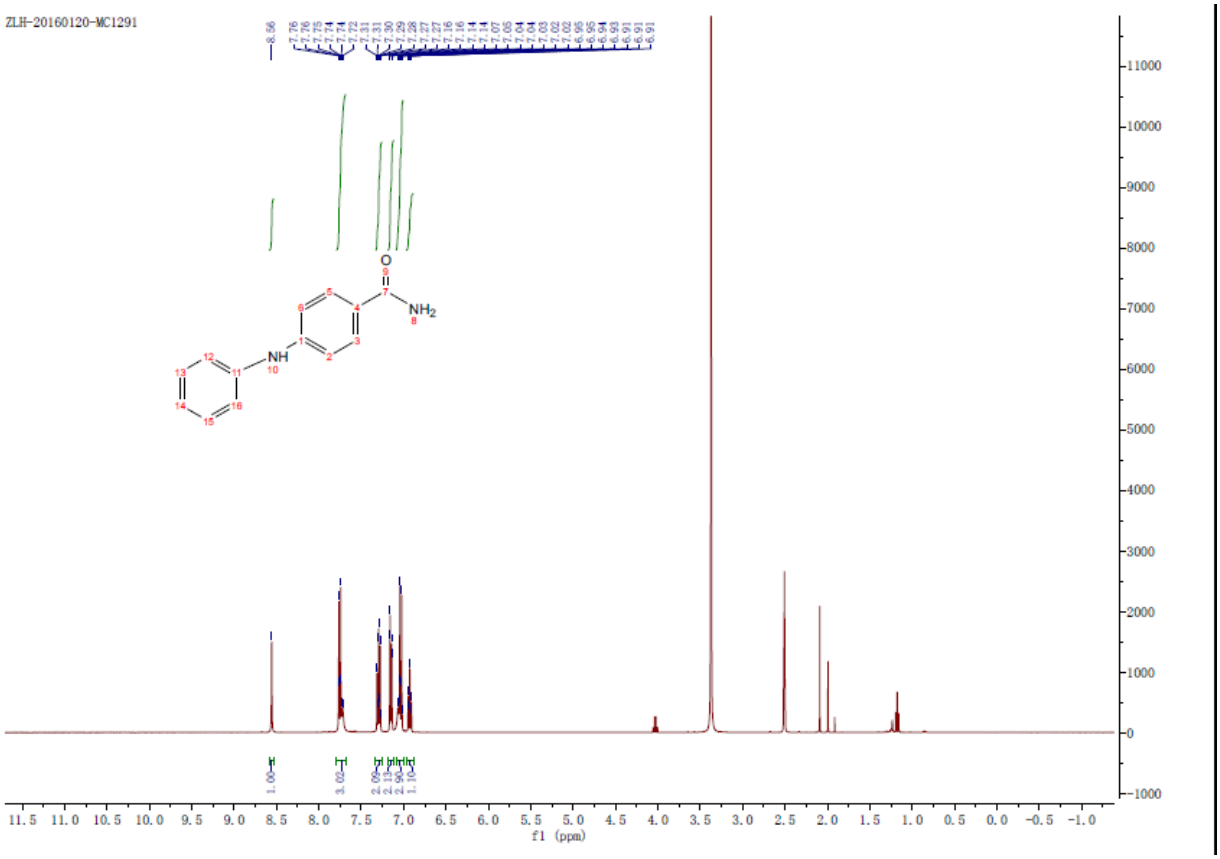


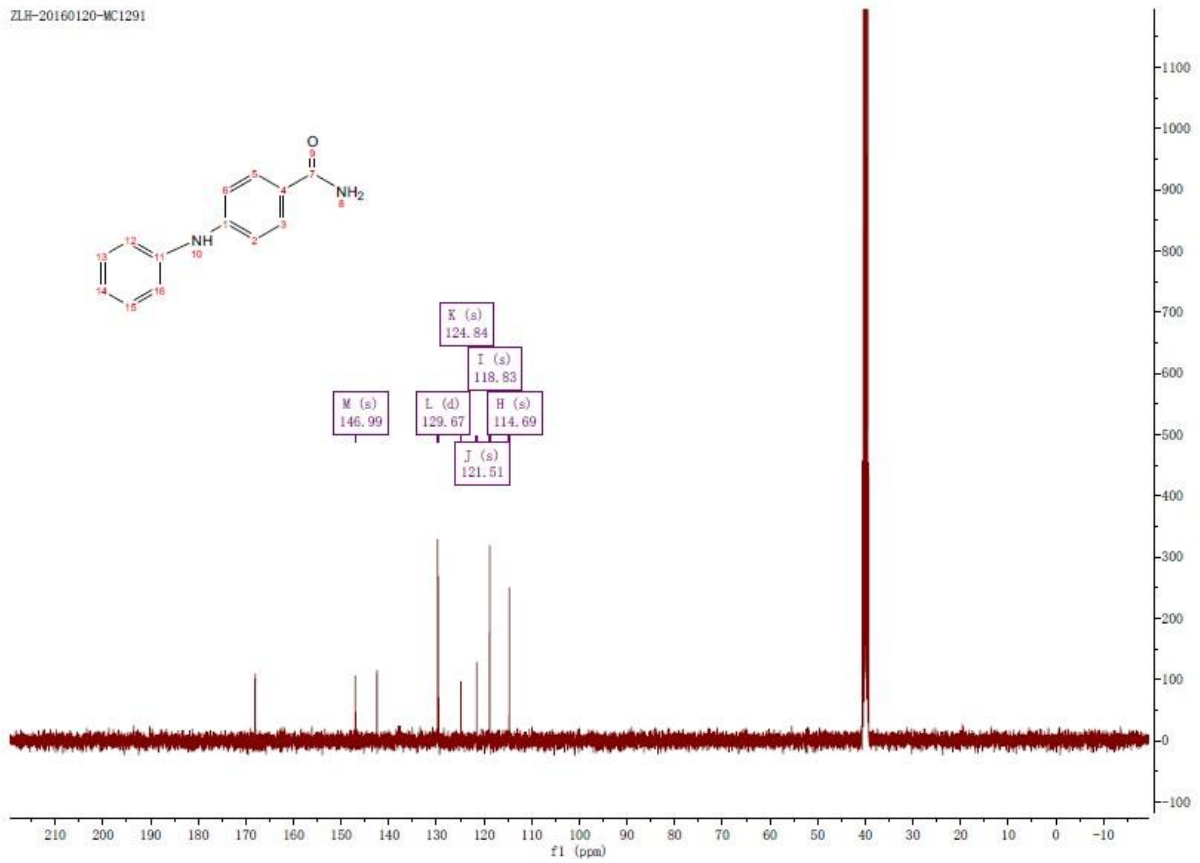
3-(phenylamino)benzamide (3t)



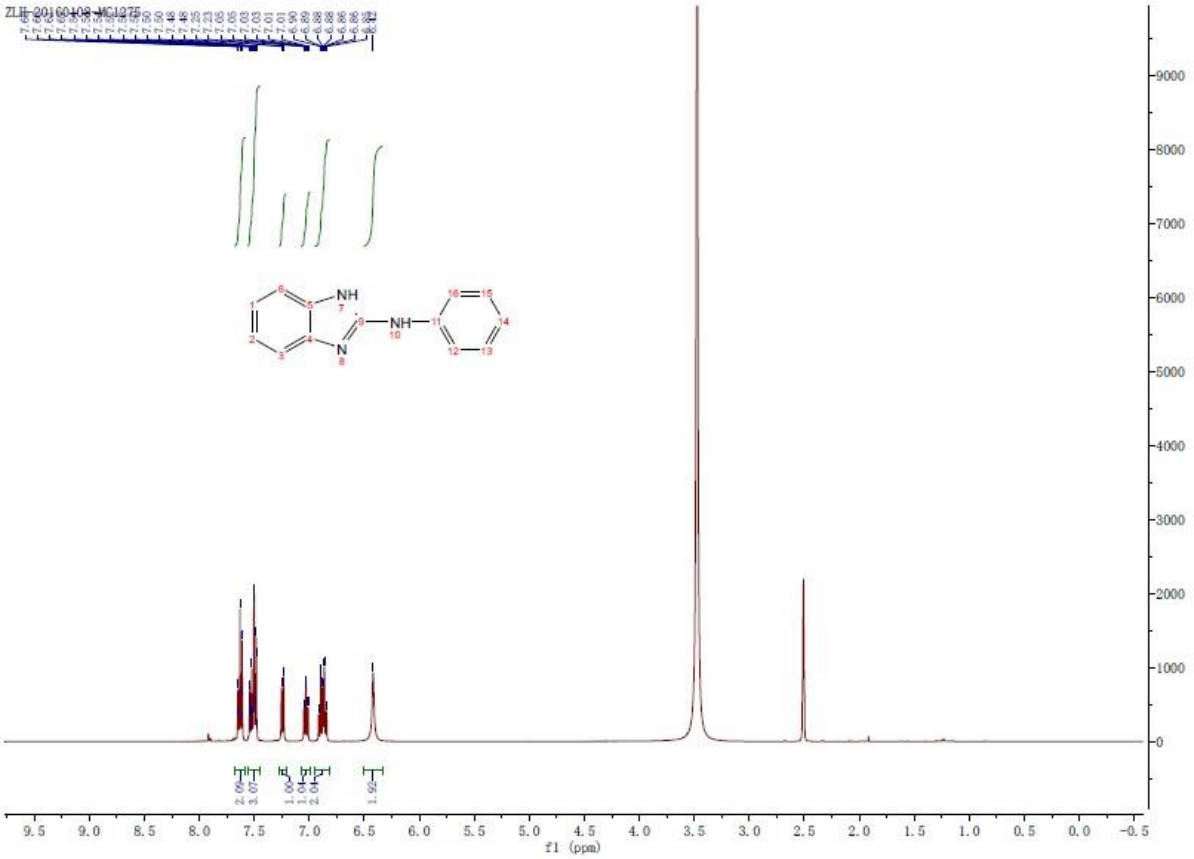


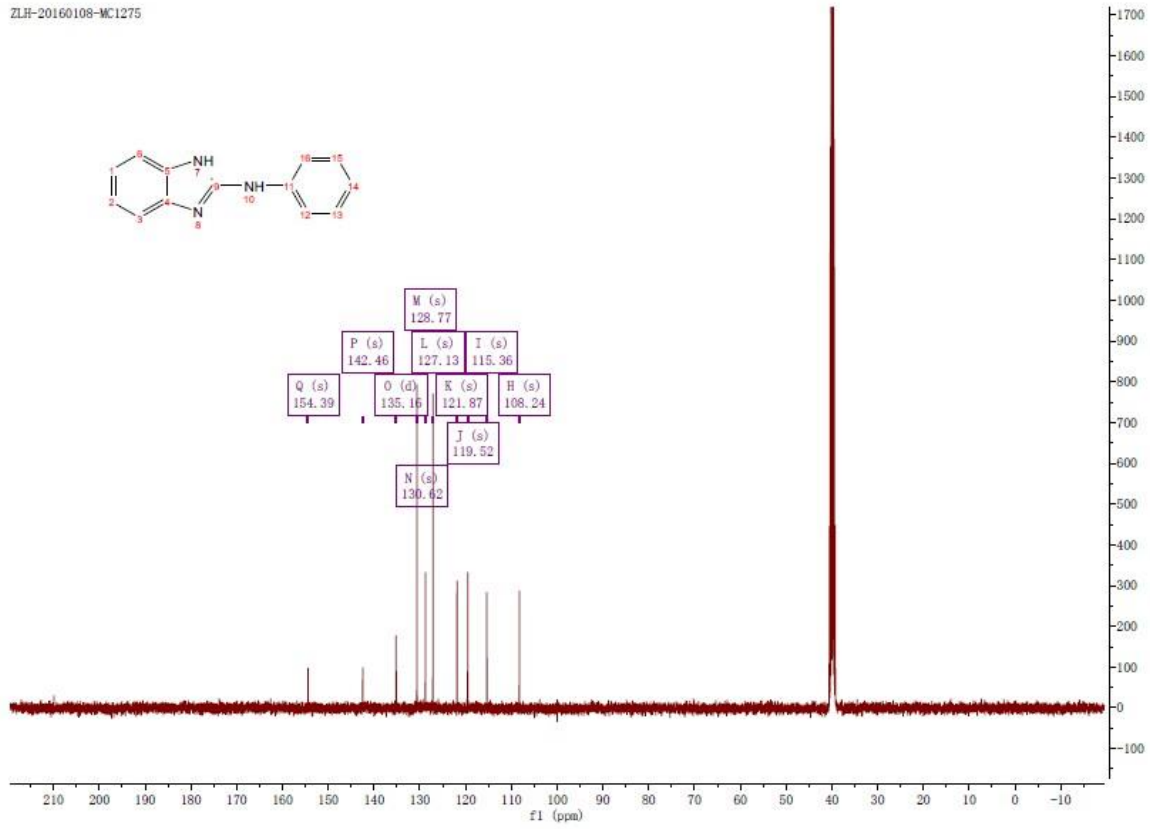
4-(phenylamino)benzamide[5] (3u)



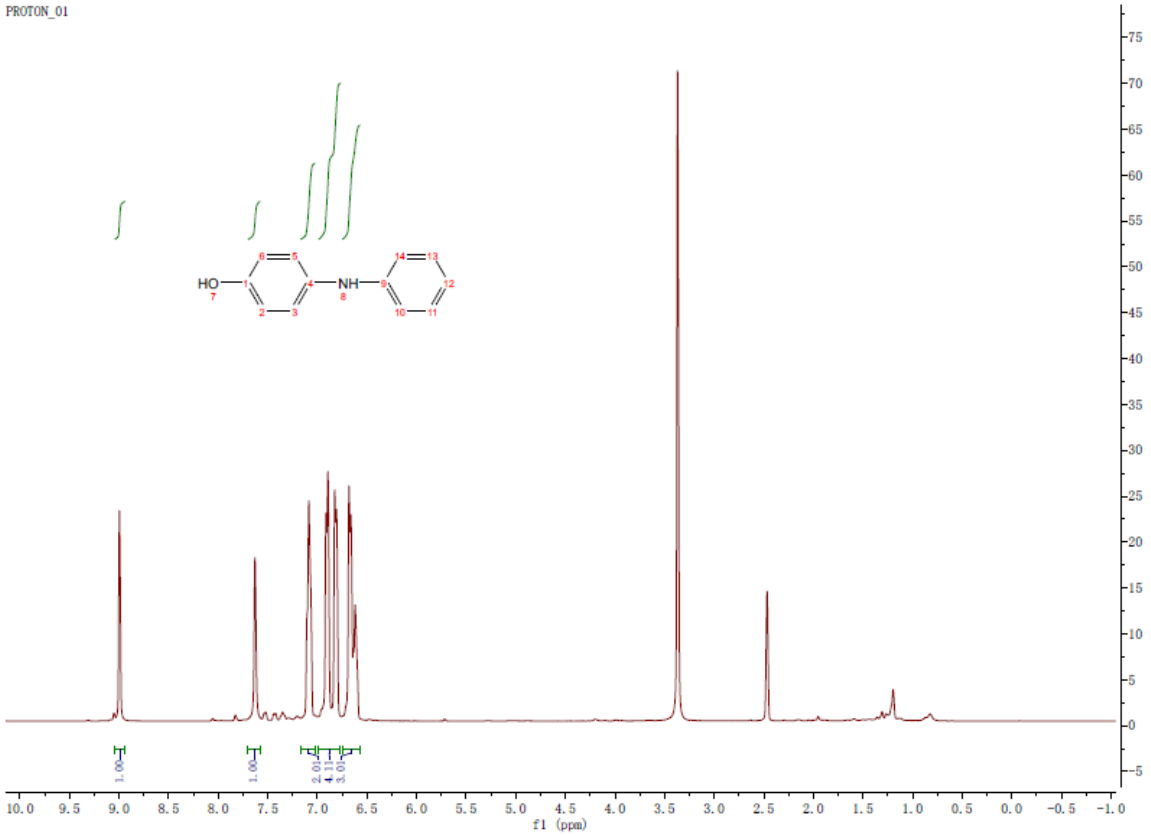


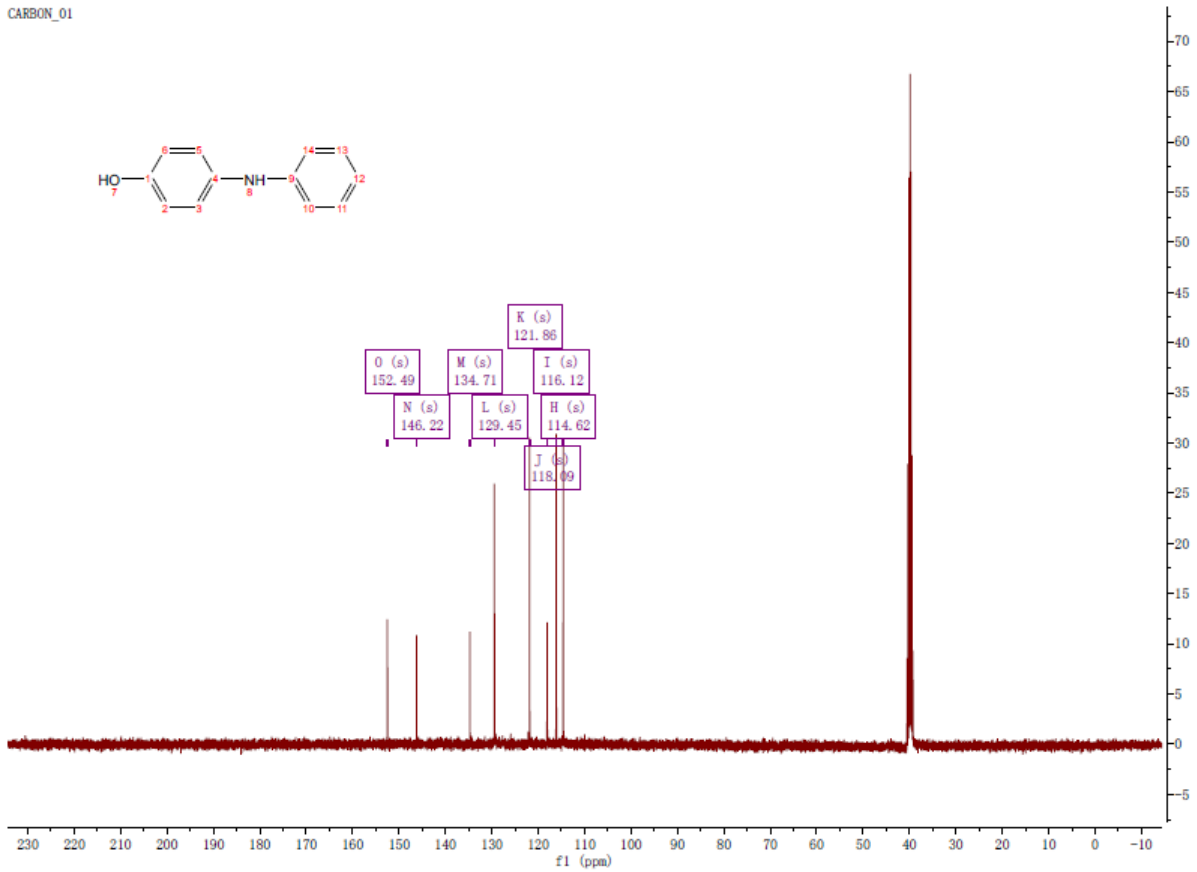
N-phenyl-1H-benzo[d]imidazol-2-amine[6] (3v)



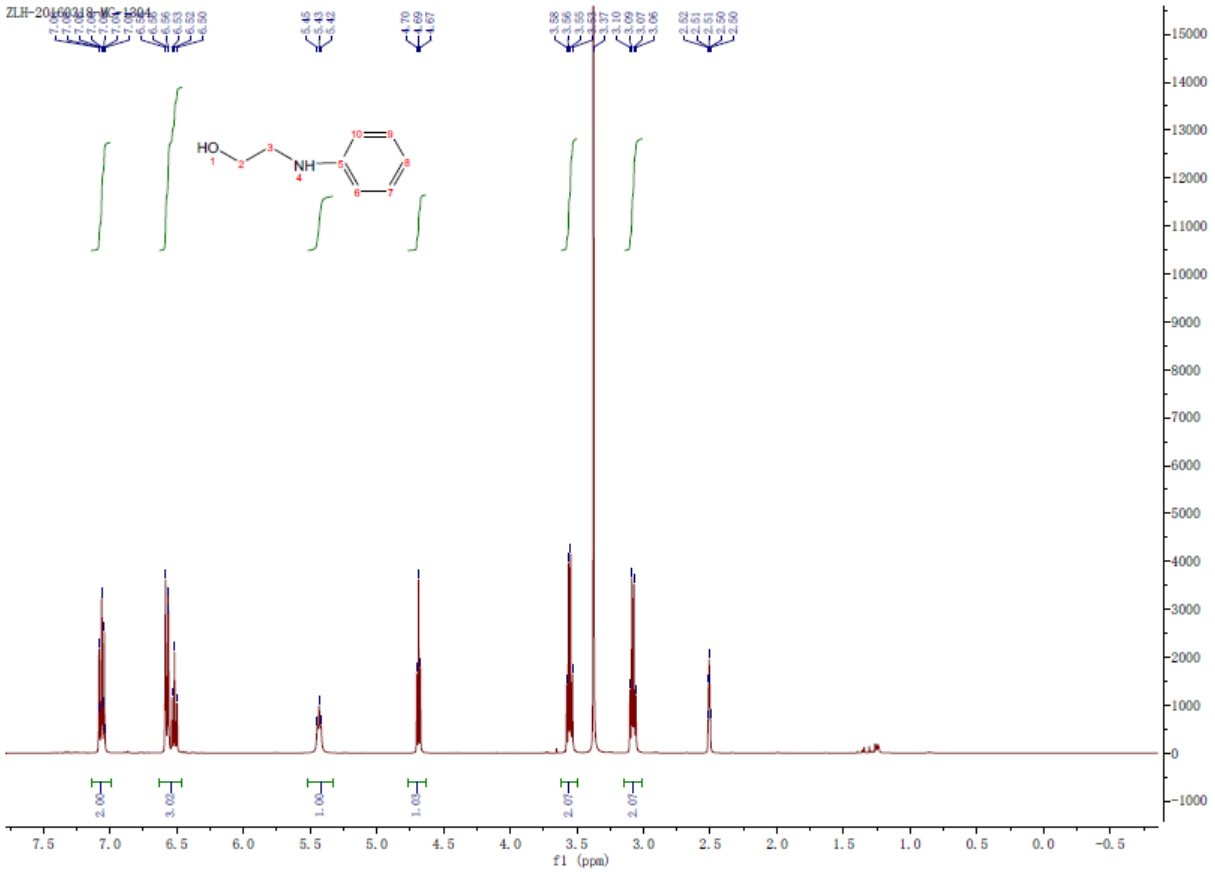


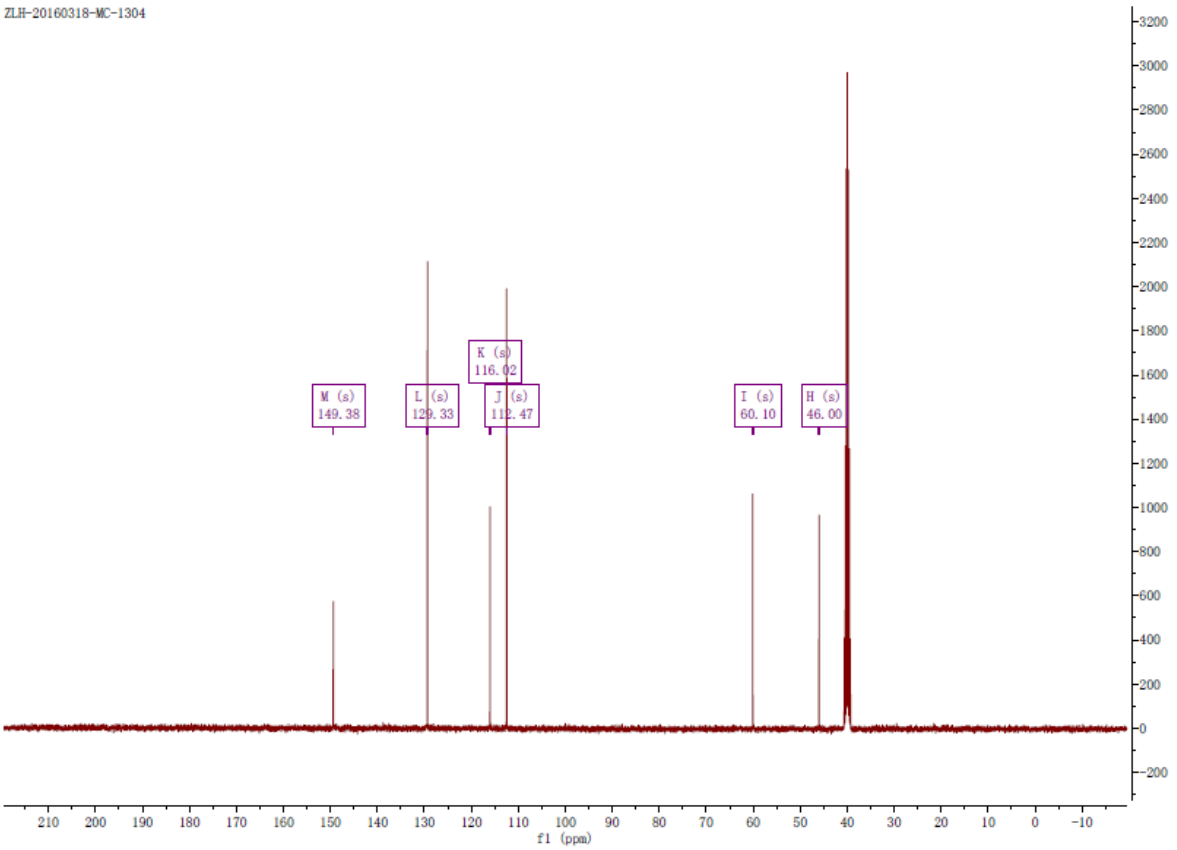
4-anilinophenol[7] **(3w)**





2-Anilinoethanol[8] (3x)





1-anilino-propan-2-ol[9] **(3y)**