Supporting Information

Iridium-catalyzed Asymmetric, Complete Hydrogenation of Pyrimidinium Salts under Batch and Flow

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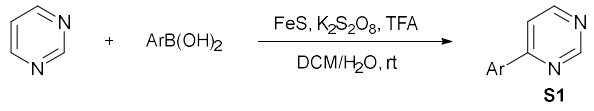
1. General Information

All commercially available reagents were used without further purification. Chromatography was conducted by using 300−400 mesh silica gel. Oil bath served as the heat source. All new compounds gave satisfactory spectroscopic analyses (^{1}H NMR, ^{13}C NMR, HRMS, melting point (mp, for solid)). NMR spectra were recorded on a 400 MHz NMR spectrometer. Reference values for residual solvents were taken as δ = 7.26 (Chloroform-*d*) ppm, δ = 2.50 (DMSO-d_6) ppm for ^{1}H NMR and δ = 77.0 (Chloroform-*d*) ppm, δ = 39.5 (DMSO-d_6) ppm for ^{13}C NMR. Abbreviations for signal coupling are as follows: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = double doublet, and td = double triplet. Coupling constants were taken from the spectra directly and are uncorrected. Optical rotations were determined using a Rudolph Research Analytical Autopol VI automatic polarimeter. High-resolution mass spectra (HRMS) were recorded on Bruker microTOF Q III by the ESI method. Melting point (mp) was recorded on an SRS-optic melting point apparatus. HPLC analyses were performed using Agilent Technologies 1260 Infinity II with Daicel Chiralpak AD-H column, Chiralpak IC column and Chiralcel OD-H column. Single-Crystal X-Ray diffraction was recorded at Bruker APEX-II CCD diffractometer.

2. Experimental Procedures

2.1 General procedure for the synthesis of 4-substituted pyrimidines

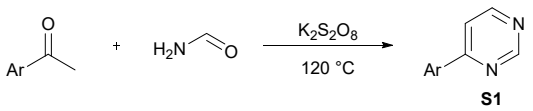
2.1.1 General procedure A: preparation of 4-substituted pyrimidines[1]



S1

To a solution of pyrimidine (5.0 mmol, 1.0 equiv.) in solvent (50 mL, DCM/H_2O = 1/1) were added TFA (5.0 mmol, 1.0 equiv.), FeS (5.0 mmol, 1.0 equiv.), arylboronic acids (7.5 mmol, 1.5 equiv.) and $K_2S_2O_8$ (15.0 mmol, 3.0 equiv.). The mixture was stirred for 48 h at room temperature. After completion of reaction (confirmed by TLC), the resulting solution was directly filtered through a pad of celite and washed with DCM. The filtrate was added with saturated aqueous $NaHCO_3$ solution, and the combined aqueous layers were extracted with DCM. Then the combined organic layers were washed with brine, over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica gel flash column chromatography to give 4-substituted pyrimidines.

2.1.2 General procedure B: preparation of 4-substituted pyrimidines[2]

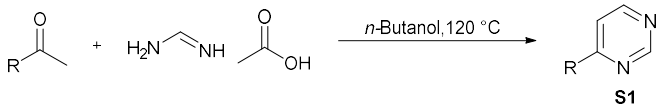


S1

To a solution of substituted acetophenone (5.0 mmol, 1.0 equiv.) in formamide (16.0 mL) was added $K_2S_2O_8$ (15.0 mmol, 3.0 equiv.). The mixture was sparged with argon for 10 min and the reaction mixture was stirred at 120 ℃ for 36 h. After completion of reaction (confirmed by TLC), reaction mixture was cooled to room temperature. The resulting solution was directly filtered through a pad of celite and washed with DCM. The

filtrate was added with water and extracted with DCM. The combined organic layers were washed with brine, over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica gel flash column chromatography to give 4-substituted pyrimidines.

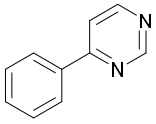
2.1.3 General procedure C: preparation of 4-substituted pyrimidines



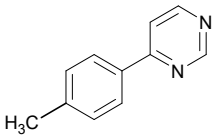
S1

A mixture of substituted acetophenone (10.0 mmol, 1.0 equiv.), formamidine acetate (50.0 mmol, 5.0 equiv.) and *n*-butanol (8.3 mL) was heated at 130 ℃ and stirred for 24 hours. After completion of reaction (confirmed by TLC), reaction mixture was cooled to room temperature and concentrated in vacuo. The crude reaction mixture was purified by silica gel flash column chromatography to give 4-substituted pyrimidines.

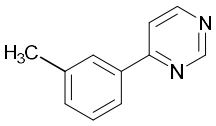
4-phenylpyrimidine (S1a): 336 mg, 43% yield, white solid, mp = 68.5 – 70.9 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (s, 1H), 8.75 (d, *J* = 5.2 Hz, 1H), 8.13 – 8.04 (m, 2H), 7.74 – 7.68 (m, 1H), 7.58 – 7.44 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 159.3, 157.6, 136.7, 131.2, 129.2, 127.3, 117.1. HRMS (ESI) m/z: calcd for $C_{10}H_9N_2$ $[M + H]^+$, 157.0760; found, 157.0763.



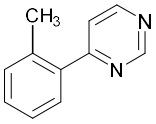
4-(*p*-tolyl)pyrimidine (S1b): 417 mg, 49% yield, white solid, mp = 69.5 – 73.3 ℃. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.23 (s, 1H), 8.71 (d, *J* = 5.2 Hz, 1H), 7.98 (d, *J* = 8.0 Hz, 2H), 7.70 – 7.64 (m, 1H), 7.30 (d, *J* = 8.0 Hz, 2H), 2.42 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.0, 159.2, 157.4, 141.7, 133.8, 129.9, 127.2, 116.8, 21.5. HRMS (ESI) m/z: calcd for $C_{11}H_{11}N_2$ $[M + H]^+$, 171.0917; found, 171.0919.



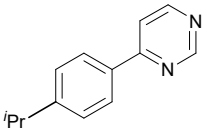
4-(*m*-tolyl)pyrimidine (S1c): 366 mg, 43% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.72 (d, *J* = 7.2 Hz, 1H), 7.90 (s, 1H), 7.83 (d, *J* = 8.0 Hz, 1H), 7.67 (d, *J* = 8.8 Hz, 1H), 7.42 – 7.27 (m, 1H), 7.30 (d, *J* = 7.6 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 159.1, 157.4, 138.9, 136.5, 131.9, 129.0, 127.8, 124.3, 117.1, 21.5. HRMS (ESI) m/z: calcd for $C_{11}H_{11}N_2$ $[M + H]^+$, 171.0917; found, 171.0912.



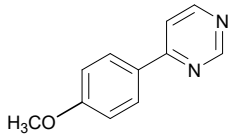
4-(*o*-tolyl)pyrimidine (S1d): 349 mg, 41% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (s, 1H), 8.76 (d, *J* = 5.2 Hz, 1H), 7.48 – 7.41 (m, 2H), 7.39 – 7.27 (m, 3H), 2.43 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.2, 158.6, 156.8, 137.6, 136.1, 131.2, 129.7, 129.6, 126.2, 121.3, 20.4. HRMS (ESI) m/z: calcd for $C_{11}H_{11}N_2$ $[M + H]^+$, 171.0917; found, 171.0916.



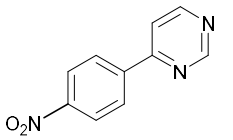
4-(4-isopropylphenyl)pyrimidine (S1e): 446 mg, 45% yield, yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.72 (d, *J* = 5.6 Hz, 1H), 8.05 – 7.99 (m, 2H), 7.68 (d, *J* = 5.6 Hz, 1H), 7.37 (d, *J* = 8.4 Hz, 2H), 3.05 – 2.91 (m, 1H), 1.29 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.1, 159.2, 157.4, 152.6, 134.2, 127.3, 127.3, 116.9, 34.2, 23.9. HRMS (ESI) m/z: calcd for $C_{13}H_{15}N_2O$ $[M + H]^+$, 199.1230; found, 199.1227.



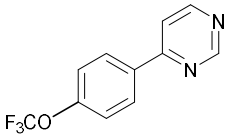
4-(4-methoxyphenyl)pyrimidine (S1f): 344 mg, 37% yield, white solid, mp = 87.9 – 90.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.17 (s, 1H), 8.65 (d, *J* = 5.6 Hz, 1H), 8.03 (d, *J* = 8.8 Hz, 2H), 7.59 (d, *J* = 5.2 Hz, 1H), 6.97 (d, *J* = 8.8 Hz, 2H), 3.83 (s, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.4, 162.2, 159.1, 157.2, 128.9, 128.7, 116.1, 114.4, 55.5. HRMS (ESI) m/z: calcd for $C_{11}H_{10}N_2O$ $[M + H]^+$, 187.0866; found, 187.0865.



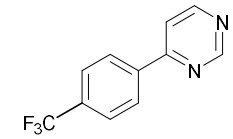
4-(4-nitrophenyl)pyrimidine (S1g): 362 mg, 36% yield, white solid, mp = 92.5 – 97.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.34 (s, 1H), 8.88 (d, *J* = 5.6 Hz, 1H), 8.39 – 8.24 (m, 4H), 7.80 (dd, *J* = 5.2, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.6, 159.5, 158.3, 149.56, 142.4, 128.3, 124.3, 117.7. HRMS (ESI) m/z: calcd for $C_{10}H_8N_3O_2$ $[M + H]^+$, 202.0611; found, 202.0610.



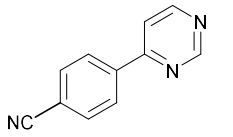
4-(4-(trifluoromethoxy)phenyl)pyrimidine (S1h): 672 mg, 56% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.32 (d, *J* = 1.2 Hz, 1H), 8.84 (d, *J* = 5.2 Hz, 1H), 8.21 (d, *J* = 8.0 Hz, 2H), 7.80 – 7.74 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.6, 159.4, 58.1, 140.0, 132.9 (q, *J* = 32.5 Hz), 127.7, 126.1 (q, *J* = 3.8 Hz), 124.0 (q, *J* = 270.8 Hz), 117.5. HRMS (ESI) m/z: calcd for $C_{11}H_8F_3N_2O$ $[M + H]^+$, 241.0583; found, 241.0580.



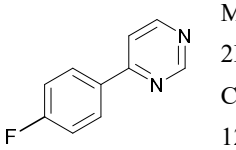
4-(4-(trifluoromethyl)phenyl)pyrimidine (S1i): 358 mg, 32% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.27 (d, *J* = 1.2 Hz, 1H), 8.79 (d, *J* = 5.2 Hz, 1H), 8.16 – 8.10 (m, 2H), 7.70 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.39 – 7.33 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.6, 159.3, 157.8, 151.5 (q, *J* = 1.8 Hz), 135.1, 129.0, 121.3, 151.5 (q, *J* = 256.7 Hz), 117.0. HRMS (ESI) m/z: calcd for $C_{11}H_8F_3N_2$ $[M + H]^+$, 225.0634; found, 225.0633.



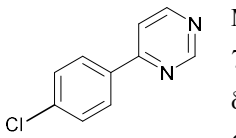
4-(pyrimidin-4-yl)benzonitrile (S1j): 280 mg, 31% yield, yellow solid, mp = 91.5 – 95.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.31 (d, *J* = 1.6 Hz, 1H), 8.85 (d, *J* = 5.6 Hz, 1H), 8.24 – 8.16 (m, 2H), 7.84 – 7.78 (m, 2H), 7.75 (dd, *J* = 5.2, 1.2 Hz, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 161.9, 159.4, 158.2, 140.7, 132.9, 127.8, 118.4, 117.5, 114.7. HRMS (ESI) m/z: calcd for $C_{11}H_8N_3$ $[M + H]^+$, 182.0713; found, 182.0714.



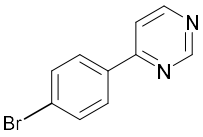
4-(4-fluorophenyl)pyrimidine (S1k): 331 mg, 38% yield, white solid, mp = 65.4 – 69.3 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (d, *J* = 1.6 Hz, 1H), 8.74 (d, *J* = 5.2 Hz, 1H), 8.12 – 8.05 (m, 2H), 7.66 (dd, *J* = 5.6, 1.6 Hz, 1H), 7.22 – 7.14 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.9 (d, *J* = 250.5 Hz), 162.9, 159.2, 157.6, 132.8 (d, *J* = 3.1 Hz), 129.4 (d, *J* = 8.7 Hz), 116.7, 116.2 (d, *J* = 21.7 Hz). HRMS (ESI) m/z: calcd for $C_{10}H_8FN_2$ $[M + H]^+$, 175.0666; found, 175.0669.



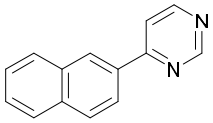
4-(4-chlorophenyl)pyrimidine (S1l): 390 mg, 41% yield, white solid, mp = 69.4 – 73.4 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.75 (d, *J* = 5.2 Hz, 1H), 8.01 (d, *J* = 8.4 Hz, 2H), 7.65 (d, *J* = 5.2 Hz, 1H), 7.46 (d, *J* = 8.4 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.8, 159.2, 157.7, 137.6, 135.0, 129.4, 128.5, 116.9. HRMS (ESI) m/z: calcd for $C_{10}H_8ClN_2$ $[M + H]^+$, 191.0371; found, 191.0376.



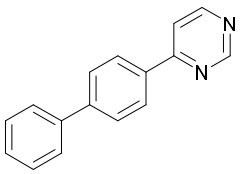
4-(4-bromophenyl)pyrimidine (S1m): 433 mg, 37% yield, white solid, mp = 69.9 – 72.2 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (d, *J* = 1.2 Hz, 1H), 8.75 (d, *J* = 5.2 Hz, 1H), 7.98 – 7.91 (m, 2H), 7.67 – 7.59 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.8, 159.3, 157.8, 135.5, 132.4, 128.7, 126.0, 116.8. HRMS (ESI) m/z: calcd for $C_{10}H_8BrN_2$ $[M + H]^+$, 234.9865; found, 234.9863.



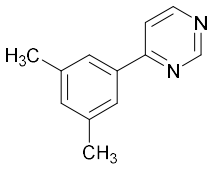
4-(naphthalen-2-yl)pyrimidine (S1n): 484 mg, 47% yield, yellow solid, mp = 122.5 – 126.1 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.30 (s, 1H), 8.72 (d, *J* = 5.2 Hz, 1H), 8.56 (s, 1H), 8.11 (dd, *J* = 8.8, 2.0 Hz, 1H), 7.95 – 7.81 (m, 3H), 7.73 (dd, *J* = 5.2, 1.2 Hz, 1H), 7.55 – 7.46 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.7, 159.1, 157.5, 134.7, 133.7, 133.2, 129.0, 128.8, 127.8, 127.6, 127.5, 126.7, 123.7, 117.1. HRMS (ESI) m/z: calcd for $C_{14}H_{11}N_2$ $[M + H]^+$, 207.0917; found, 207.0916.



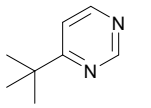
4-([1,1'-biphenyl]-4-yl)pyrimidine (S1o): 534 mg, 46% yield, yellow solid, mp = 184.5 – 188.7 °C. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.29 (d, *J* = 1.2 Hz, 1H), 8.76 (d, *J* = 5.2 Hz, 1H), 8.20 – 8.14 (m, 2H), 7.78 – 7.71 (m, 3H), 7.69 – 7.61 (m, 2H), 7.52 – 7.37 (m, 3H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 163.6, 159.5, 157.6, 144.0, 140.2, 135.4, 129.0, 128.1, 127.8, 127.7, 127.5, 116.9. HRMS (ESI) m/z: calcd for $C_{16}H_{12}N_2$ $[M + H]^+$, 233.1073; found, 233.1072.



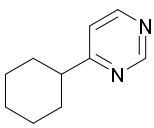
4-(3,5-dimethylphenyl)pyrimidine (S1p): 221 mg, 24% yield, pale yellow oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.24 (s, 1H), 8.72 (d, *J* = 5.2 Hz, 1H), 7.62 – 7.74 (m, 3H), 7.14 (s, 1H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 164.4, 159.1, 157.4, 138.8, 136.6, 132.9, 125.1, 117.5, 21.4. HRMS (ESI) m/z: calcd for $C_{12}H_{13}N_2$ $[M + H]^+$, 185.1073; found, 185.1075.



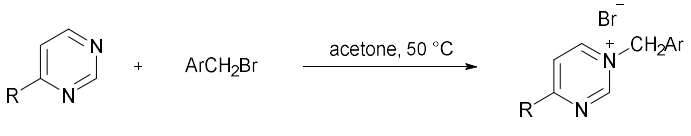
4-(*tert*-butyl)pyrimidine (S1q): 218 mg, 16% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.14 (d, *J* = 1.2 Hz, 1H), 8.62 (d, *J* = 5.2 Hz, 1H), 7.33 (dd, *J* = 5.2, 1.2 Hz, 1H), 1.35 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 177.9, 158.4, 157.0, 117.0, 37.6, 29.5. HRMS (ESI) m/z: calcd for $C_8H_{13}N_2$ $[M + H]^+$, 137.1073; found, 137.1074.



4-cyclohexylpyrimidine (S1r): 454 mg, 28% yield, colorless oil. ^{1}H NMR (400 MHz, Chloroform-*d*) δ 9.10 (d, *J* = 1.6 Hz, 1H), 8.59 (d, *J* = 5.6 Hz, 1H), 7.16 (dd, *J* = 5.2, 1.2 Hz, 1H), 2.70 – 2.56 (m, 1H), 1.97 – 1.90 (m, 2H), 1.90 – 1.87 (m, 2H), 1.79 – 1.71 (m, 1H), 1.55 – 1.45 (m, 2H), 1.44 – 1.33 (m, 2H), 1.32 – 1.25 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 174.7, 158.7, 156.9, 118.9, 46.1, 32.1, 26.3, 26.0. HRMS (ESI) m/z: calcd for $C_{10}H_{15}N_2$ $[M + H]^+$, 163.1230; found, 163.1234.



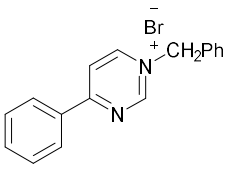
2.2 General procedure for the synthesis of 4-subsituted pyrimidinium salts



1

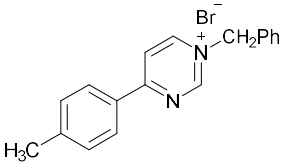
To a solution of 4-substituted pyrimidines (0.5 mmol, 1.0 equiv.) in acetone (1.0 mL) was added different substituted benzyl bromide (0.75 mmol, 1.5 equiv.). The resulted mixture was heated at reflux for 48 h. After completion of reaction (confirmed by TLC), the resulting precipitate was collected and rinsed with acetone and diethyl ether to give the solid product which was directly used for the hydrogenation.

1-benzyl-4-phenylpyrimidin-1-ium bromide (1a): 152 mg, 93% yield, white solid, mp = 175.1 – 177.9 ℃.



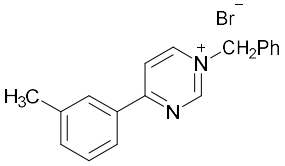
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 9.50 (d, J = 6.8 Hz, 1H), 8.85 (d, J = 6.8 Hz, 1H), 8.43 (d, J = 7.6 Hz, 2H), 7.81 – 7.59 (m, 5H), 7.51 – 7.42 (m, 3H), 5.84 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.2, 154.0, 152.0, 135.1, 134.1, 133.5, 130.2, 129.9, 129.7, 129.6, 129.5, 119.4, 60.2. HRMS (ESI) m/z: calcd for $C_{17}H_{15}N_2$ [M – Br]$^+$, 247.1230; found, 247.1233.

1-benzyl-4-(*p*-tolyl)pyrimidin-1-ium bromide (1b): 155 mg, 91% yield, white solid, mp = 171.4.1 – 173.5 ℃.



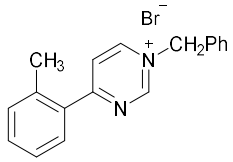
^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 9.43 (d, J = 6.8 Hz, 1H), 8.79 (d, J = 6.8 Hz, 1H), 8.34 (d, J = 8.0 Hz, 2H), 7.65 – 7.58 (m, 2H), 7.53 – 7.42 (m, 5H), 5.81 (s, 2H), 2.45 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 153.5, 151.1, 145.8, 133.7, 130.4, 130.3, 129.3, 129.2, 129.2, 129.0, 118.3, 59.5, 21.3. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2$ [M – Br]$^+$, 261.1386; found, 261.1385.

1-benzyl-4-(*m*-tolyl)pyrimidin-1-ium bromide (1c): 153 mg, 90% yield, white solid, mp = 170.6 – 172.3 ℃.



^{1}H NMR (400 MHz, DMSO-d_6) δ 10.04 (s, 1H), 9.49 (d, J = 5.6 Hz, 1H), 8.83 (d, J = 6.8 Hz, 1H), 8.29 – 8.19 (m, 2H), 7.66 – 7.53 (m, 4H), 7.50 – 7.41 (m, 3H), 5.83 (s, 2H), 2.44 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 153.5, 151.4, 139.2, 135.3, 133.6, 133.0, 129.6, 129.4, 129.3, 129.2, 129.0, 126.4, 118.8, 59.6, 20.9. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2$ [M – Br]$^+$, 261.1386; found, 261.1387.

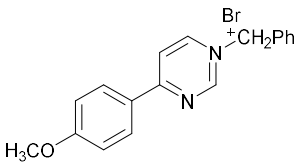
1-benzyl-4-(*o*-tolyl)pyrimidin-1-ium bromide (1d): 157 mg, 92% yield, white solid, mp = 171.6 – 174.4 ℃.



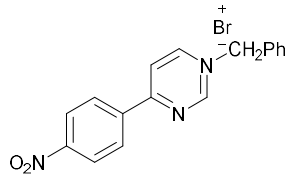
^{1}H NMR (400 MHz, DMSO-d_6) δ 10.14 (s, 1H), 9.55 (dd, J = 6.8, 1.6 Hz, 1H), 8.53 (dd, J = 6.8, 1.2 Hz, 1H), 7.80 – 7.65 (m, 3H), 7.60 – 7.53 (m, 1H), 7.52 – 7.42 (m, 5H), 5.91 (s, 2H), 2.53 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 172.3, 152.9, 151.0, 137.9, 134.3, 133.5, 132.3, 131.9, 131.1, 129.4, 129.3, 129.2, 126.7, 123.0, 59.7, 20.4. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2$ [M – Br]$^+$, 261.1386; found, 261.1384.

1-benzyl-4-(4-isopropylphenyl)pyrimidin-1-ium bromide (1e): 166 mg, 90% yield, white solid, mp = 191.3 – 195.4 ℃. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 9.45 (s, 1H), 8.80 (s, 1H), 8.36 (d, J = 7.0 Hz, 2H), 7.63 (s, 2H), 7.56 (d, J = 7.2 Hz, 2H), 7.50 – 7.42 (m, 3H), 5.82 (s, 2H), 3.10 – 2.95 (m, 1H), 1.25 (d, J = 5.6 Hz, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.5, 156.1, 153.5, 151.1, 133.7, 130.7, 129.4, 129.4, 129.2, 129.1, 127.8, 118.4, 59.5, 33.6, 23.3. HRMS (ESI) m/z: calcd for $C_{20}H_{21}N_2$ [M – Br]$^+$, 289.1699; found, 289.1701.

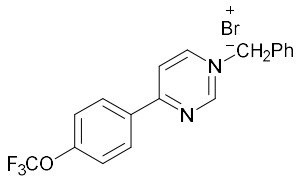
1-benzyl-4-(4-methoxyphenyl)pyrimidin-1-ium bromide (1f): 170 mg, 95% yield, pale yellow solid, mp = 178.6 – 180.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.91 (s, 1H), 9.34 (s, 1H), 8.72 (s, 1H), 8.43 (d, J = 8.0 Hz, 2H), 7.67 – 7.40 (m, 5H), 7.22 (d, J = 7.6 Hz, 2H), 5.77 (s, 2H), 3.92 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.8, 164.9, 153.3, 150.4, 133.8, 131.6, 129.3, 129.1, 128.9, 125.2, 117.4, 115.3, 59.2, 55.9. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2O$ $[M - Br]^+$, 277.1335; found, 277.1335.



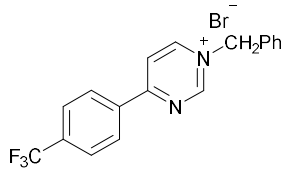
1-benzyl-4-(4-nitrophenyl)pyrimidin-1-ium bromide (1g): 127 mg, 68% yield, white solid, mp = 165.3 – 168.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.22 (s, 1H), 9.71 (d, J = 6.8 Hz, 1H), 9.02 (d, J = 6.8 Hz, 1H), 8.65 (d, J = 8.8 Hz, 2H), 8.47 (d, J = 8.4 Hz, 2H), 7.73 – 7.39 (m, 5H), 5.92 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 166.8, 153.7, 152.5, 150.5, 138.5, 133.5, 130.5, 129.4, 129.16, 129.2, 124.4, 120.5, 60.0. HRMS (ESI) m/z: calcd for $C_{17}H_{14}N_3O_2$ $[M - Br]^+$, 292.1081; found, 292.1085.



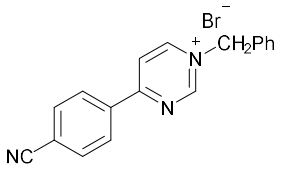
1-benzyl-4-(4-(trifluoromethoxy)phenyl)pyrimidin-1-ium bromide (1h): 169 mg, 82% yield, white solid, mp = 181.3 – 184.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H), 9.56 (d, J = 6.4 Hz, 1H), 8.88 (d, J = 6.8 Hz, 1H), 8.56 (d, J = 8.0 Hz, 2H), 7.72 – 7.59 (m, 4H), 7.51 – 7.40 (m, 3H), 5.85 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.4, 153.6, 152.5 (q, J = 1.6 Hz), 151.8, 133.6, 132.0, 131.7, 129.4, 129.2, 129.1, 121.6, 119.9 (q, J = 256.6 Hz), 119.3, 59.8. HRMS (ESI) m/z: calcd for $C_{18}H_{14}F_3N_2O$ $[M - Br]^+$, 331.1053; found, 331.1056.

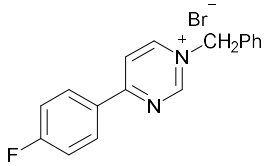


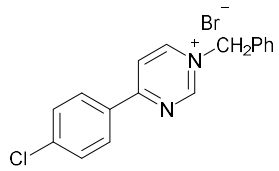
1-benzyl-4-(4-(trifluoromethyl)phenyl)pyrimidin-1-ium bromide (1i): 172 mg, 87% yield, white solid, mp = 189.3 – 192.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.16 (s, 1H), 9.64 (dd, J = 6.8, 1.6 Hz, 1H), 8.98 (d, J = 6.8 Hz, 1H), 8.61 (d, J = 8.4 Hz, 2H), 8.06 (d, J = 8.4 Hz, 2H), 7.69 – 7.63 (m, 2H), 7.52 – 7.43 (m, 3H), 5.90 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.4, 153.7, 152.3, 136.8, 133.5, 133.2, 129.9, 129.4, 129.2, 129.1, 126.4 (q, J = 4.0 Hz), 123.6 (q, J = 271.2 Hz), 120.0, 59.9. HRMS (ESI) m/z: calcd for $C_{18}H_{14}F_3N_2$ $[M - Br]^+$, 315.1104; found, 315.1106.

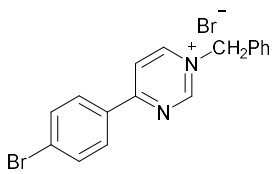


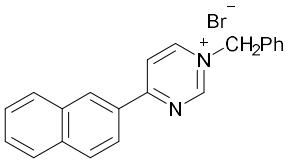
1-benzyl-4-(4-cyanophenyl)pyrimidin-1-ium bromide (1j): 111 mg, 63% yield, white solid, mp = 183.2 – 185.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.13 (s, 1H), 9.62 (dd, J = 6.8, 1.6 Hz, 1H), 8.95 (d, J = 6.8 Hz, 1H), 8.56 (d, J = 8.8 Hz, 2H), 8.17 (d, J = 8.4 Hz, 2H), 7.68 – 7.58 (m, 2H), 7.51 – 7.41 (m, 3H), 5.87 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.1, 153.7, 152.3, 137.0, 133.4, 133.4, 129.6, 129.4, 129.2, 129.1, 120.1, 117.9, 116.0, 60.0. HRMS (ESI) m/z: calcd for $C_{18}H_{14}N_3$ $[M - Br]^+$, 272.1182; found, 272.1184.

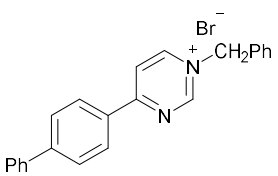


1-benzyl-4-(4-fluorophenyl)pyrimidin-1-ium bromide (1k): 159 mg, 92% yield, white solid, mp = 186.3 – 188.7 °C.  ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 9.52 (d, J = 6.8 Hz, 1H), 8.85 (d, J = 6.8 Hz, 1H), 8.57 – 8.47 (m, 2H), 7.67 – 7.50 (m, 4H), 7.49 – 7.39 (m, 3H), 5.85 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6, 166.0 (d, J = 253.2 Hz), 153.5, 151.5, 133.6, 132.2 (d, J = 9.9 Hz), 129.7 (d, J = 2.8 Hz), 129.3, 129.1, 129.0, 118.7, 116.9 (d, J = 22.0 Hz), 59.6. HRMS (ESI) m/z: calcd for $C_{17}H_{14}FN_2$ [M – Br]$^+$, 265.1163; found, 265.1163.

1-benzyl-4-(4-chlorophenyl)pyrimidin-1-ium bromide (1l): 166 mg, 92% yield, white solid, mp = 176.3 – 179.1 °C.  ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 9.53 (dd, J = 6.8, 2.0 Hz, 1H), 8.86 (dd, J = 6.8, 1.2 Hz, 1H), 8.48 – 8.42 (m, 2H), 7.80 – 7.74 (m, 2H), 7.66 – 7.60 (m, 2H), 7.50 – 7.42 (m, 3H), 5.84 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.6, 153.5, 151.7, 139.7, 133.6, 131.9, 130.9, 129.8, 129.3, 129.1, 129.0, 119.0, 59.7. HRMS (ESI) m/z: calcd for $C_{17}H_{14}ClN_2$ [M – Br]$^+$, 281.0840; found, 281.0842.

1-benzyl-4-(4-bromophenyl)pyrimidin-1-ium bromide (1m): 191 mg, 94% yield, white solid, mp = 173.4 – 175.6 °C.  ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H), 9.56 (dd, J = 6.8, 2.0 Hz, 1H), 8.88 (dd, J = 6.8, 1.2 Hz, 1H), 8.39 – 8.31 (m, 2H), 7.94 – 7.85 (m, 2H), 7.69 – 7.60 (m, 2H), 7.51 – 7.39 (m, 3H), 5.87 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 167.7, 153.5, 151.7, 133.6, 132.8, 132.2, 130.9, 129.3, 129.1, 129.1, 129.0, 119.0, 59.7. HRMS (ESI) m/z: calcd for $C_{17}H_{14}BrN_2$ [M – Br]$^+$, 325.0335; found, 325.0338.

1-benzyl-4-(naphthalen-2-yl)pyrimidin-1-ium bromide (1n): 181 mg, 96% yield, yellow solid, mp = 203.4 – 205.7 °C.  ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.12 (s, 1H), 9.57 (dd, J = 6.8, 1.6 Hz, 1H), 9.17 (d, J = 1.6 Hz, 1H), 8.99 (dd, J = 6.8, 1.2 Hz, 1H), 8.42 (dd, J = 8.8, 1.6 Hz, 1H), 8.22 – 8.14 (m, 2H), 8.05 (d, J = 8.0 Hz, 1H), 7.76 – 7.63 (m, 4H), 7.52 – 7.42 (m, 3H), 5.89 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 153.5, 151.3, 135.6, 133.7, 132.5, 131.4, 130.3, 129.8, 129.6, 129.4, 129.3, 129.2, 129.0, 127.8, 127.5, 124.0, 119.0, 59.5. HRMS (ESI) m/z: calcd for $C_{21}H_{17}N_2$ [M – Br]$^+$, 297.1386; found, 297.1387.

4-([1,1'-biphenyl]-4-yl)-1-benzylpyrimidin-1-ium bromide (1o): 190 mg, 94% yield, yellow solid, mp = 190.8 – 193.2 °C.  ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.08 (s, 1H), 9.53 (dd, J = 6.8, 2.0 Hz, 1H), 8.90 (dd, J = 6.8, 1.2 Hz, 1H), 8.54 – 8.49 (m, 2H), 8.02 – 7.97 (m, 2H), 7.85 – 7.81 (m, 2H), 7.69 – 7.64 (m, 2H), 7.56 – 7.43 (m, 6H), 5.87 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.1, 153.5, 151.3, 145.8, 138.3, 133.7, 131.8, 129.8, 129.3, 129.2, 129.1, 128.9, 127.7, 127.0, 118.6, 59.5. HRMS (ESI) m/z: calcd for $C_{23}H_{19}N_2$ [M – Br]$^+$, 323.1543; found, 323.1542.

1-benzyl-4-(3,5-dimethylphenyl)pyrimidin-1-ium bromide (1p): 167 mg, 94% yield, white solid, mp = 225.2 – 227.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 9.46 (d, J = 6.8 Hz, 1H), 8.79 (d, J = 6.8 Hz, 1H), 8.06 (s, 2H), 7.67 – 7.36 (m, 6H), 5.82 (s, 2H), 2.40 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.9, 153.4, 151.3, 139.1, 136.2, 133.7, 133.0, 129.3, 129.2, 129.0, 126.8, 118.7, 59.6, 20.8. HRMS (ESI) m/z: calcd for $C_{19}H_{19}N_2$ [M – Br]$^+$, 275.1543; found, 275.1544.

1-benzyl-4-(*tert*-butyl)pyrimidin-1-ium bromide (1q): 100 mg, 65% yield, white solid, mp = 173.1 – 176.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 9.42 (d, J = 5.6 Hz, 1H), 8.33 (d, J = 6.8 Hz, 1H), 7.67 – 7.37 (m, 5H), 5.82 (s, 2H), 1.38 (s, 9H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 186.5, 153.5, 151.5, 134.0, 129.9, 129.7, 120.6, 60.2, 39.7, 29.0. HRMS (ESI) m/z: calcd for $C_{15}H_{19}N_2$ [M – Br]$^+$, 227.1543; found, 227.1540.

1-benzyl-4-cyclohexylpyrimidin-1-ium bromide (1r): 108 mg, 65% yield, white solid, mp = 168.2 – 171.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.96 (s, 1H), 9.36 (dd, J = 6.8, 2.0 Hz, 1H), 8.19 (dd, J = 6.8, 1.2 Hz, 1H), 7.62 – 7.57 (m, 2H), 7.49 – 7.41 (m, 3H), 5.79 (s, 2H), 3.05 – 2.96 (m, 1H), 1.97 – 1.88 (m, 2H), 1.86 – 1.77 (m, 2H), 1.76 – 1.66 (m, 1H), 1.59 – 1.46(m, 2H), 1.44 – 1.31 (m, 2H), 1.30 – 1.17 (m, 1H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 182.8, 153.2, 150.8, 133.4, 129.4, 129.2, 121.7, 59.8, 45.5, 30.7, 25.2, 25.1. HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_2$ [M – Br]$^+$, 253.1699; found, 253.1703.

1-(4-methylbenzyl)-4-phenylpyrimidin-1-ium bromide (3a): 160 mg, 94% yield, white solid, mp = 172.6 – 173.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.04 (s, 1H), 9.48 (dd, J = 7.2, 2.0 Hz, 1H), 8.84 (dd, J = 7.2, 1.2 Hz, 1H), 8.44 – 8.40 (m, 2H), 7.80 – 7.74 (m, 1H), 7.71 – 7.65 (m, 2H), 7.54 (d, J = 8.4 Hz, 2H), 7.27 (d, J = 8.0 Hz, 2H), 5.80 (s, 2H), 2.31 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 153.4, 151.4, 139.0, 134.6, 133.0, 130.6, 129.7, 129.7, 129.1, 129.1, 118.8, 59.5, 20.7. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2$ [M – Br]$^+$, 261.1386; found, 261.1389.

1-(4-methoxybenzyl)-4-phenylpyrimidin-1-ium bromide (3b): 166 mg, 93% yield, white solid, mp = 189.4 – 191.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 9.50 (dd, J = 6.8, 1.6 Hz, 1H), 8.84 (dd, J = 6.8, 1.2 Hz, 1H), 8.44 – 8.38 (m, 2H), 7.80 – 7.73 (m, 1H), 7.70 – 7.61 (m, 4H), 7.05 – 6.98 (m, 2H), 5.79 (s, 2H), 3.76 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 160.1, 153.3, 151.2, 134.5, 133.0, 131.0, 129.7, 129.1, 125.4, 118.8, 114.5, 59.2, 55.3. HRMS (ESI) m/z: calcd for $C_{18}H_{17}N_2O$ [M – Br]$^+$, 277.1335; found, 277.1334.

1-(4-cyanobenzyl)-4-phenylpyrimidin-1-ium bromide (3c): 162 mg, 92% yield, white solid, mp = 185.4 – 187.6 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 9.54 (dd, J = 6.8, 2.0 Hz, 1H), 8.89 (d, J = 6.8 Hz, 1H), 8.44 (d, J = 7.2 Hz, 2H), 7.96 (d, J = 8.4 Hz, 2H), 7.88 – 7.76 (m, 3H), 7.69 (t, J = 7.6 Hz, 2H), 5.97 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 153.8, 151.8, 138.8, 134.7, 133.0, 132.9, 129.9, 129.7, 129.2, 118.9, 118.4, 111.9, 58.8. HRMS (ESI) m/z: calcd for $C_{18}H_{14}N_3$ [M – Br]$^+$, 272.1182; found, 272.1184.

4-phenyl-1-(4-(trifluoromethyl)benzyl)pyrimidin-1-ium bromide (3d): 184 mg, 93% yield, white solid, mp = 183.5 – 186.7 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.06 (s, 1H), 9.53 (d, J = 6.8 Hz, 1H), 8.88 (d, J = 6.8 Hz, 1H), 8.47 – 8.38 (m, 2H), 7.90 – 7.76 (m, 5H), 7.73 – 7.66 (m, 2H), 5.96 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 153.7, 151.7, 138.1, 134.7, 133.0, 129.9, 129.7, 129.5, 129.1, 126.7 (q, J = 270.6 Hz), 125.9 (q, J = 3.8 Hz), 118.9, 58.8. HRMS (ESI) m/z: calcd for $C_{18}H_{14}F_3N_2$ [M – Br]$^+$, 315.1104; found, 315.1105.

1-(4-(methoxycarbonyl)benzyl)-4-phenylpyrimidin-1-ium bromide (3e): 183 mg, 95% yield, white solid, mp = 193.2 – 195.5 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (s, 1H), 9.54 (dd, J = 6.8, 1.6 Hz, 1H), 8.89 (dd, J = 7.2, 1.2 Hz, 1H), 8.47 – 8.41 (m, 2H), 8.04 – 7.99 (m, 2H), 7.81 – 7.64 (m, 5H), 5.96 (s, 2H), 3.86 (s, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.8, 165.7, 153.8, 151.8, 138.7, 134.7, 133.0, 130.2, 129.7, 129.3, 129.2, 118.9, 59.0, 52.4. HRMS (ESI) m/z: calcd for $C_{19}H_{17}N_2O_2$ [M – Br]$^+$, 305.1285; found, 305.1290.

1-(4-fluorobenzyl)-4-phenylpyrimidin-1-ium bromide (3f): 162 mg, 94% yield, white solid, mp = 183.4 – 186.9 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.07 (s, 1H), 9.53 (dd, J = 6.8, 2.0 Hz, 1H), 8.86 (dd, J = 6.8, 1.2 Hz, 1H), 8.45 – 8.40 (m, 2H), 7.80 – 7.73 (m, 3H), 7.71 – 7.65 (m, 2H), 7.35 – 7.28 (m, 2H), 5.86 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.65, 162.60 (d, J = 244.8 Hz), 153.5, 151.4, 134.6, 133.0, 131.8 (d, J = 8.6 Hz), 129.8 (d, J = 3.0 Hz), 129.7, 129.1, 118.8, 116.0 (d, J = 21.6 Hz), 58.7. HRMS (ESI) m/z: calcd for $C_{17}H_{14}BrFN_2$ [M – Br]$^+$, 265.1136; found, 265.1141.

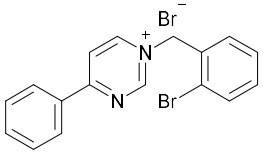
1-(4-chlorobenzyl)-4-phenylpyrimidin-1-ium bromide (3g): 168 mg, 93% yield, white solid, mp = 178.4 – 181.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.01 (s, 1H), 9.47 (dd, J = 7.2, 2.0 Hz, 1H), 8.84 (d, J = 6.8 Hz, 1H), 8.46 – 8.40 (m, 2H), 7.82 – 7.75 (m, 1H), 7.72 – 7.64 (m, 4H), 7.58 – 7.52 (m, 2H), 5.82 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 153.6, 151.5, 134.6, 134.2, 133.0, 132.5, 131.1, 129.7, 129.1, 129.1, 118.8, 58.8. HRMS (ESI) m/z: calcd for $C_{17}H_{14}ClN_2$ [M – Br]$^+$, 281.0840; found, 281.0844.

1-(4-bromobenzyl)-4-phenylpyrimidin-1-ium bromide (3h): 190 mg, 94% yield, white solid, mp = 175.4 – 178.3 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.09 (s, 1H), 9.55 (dd, J = 6.8, 1.6 Hz, 1H), 8.87 (d, J = 6.8 Hz, 1H), 8.42 (d, J = 7.6 Hz, 2H), 7.81 – 7.61 (m, 7H), 5.87 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 153.5, 151.5, 134.6, 132.9, 132.9, 132.0, 131.4, 129.7, 129.1, 122.9, 118.8, 58.7. HRMS (ESI) m/z: calcd for $C_{17}H_{14}BrN_2$ [M – Br]$^+$, 325.0335; found, 325.0335.

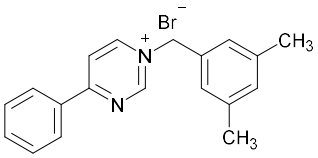
1-(3-bromobenzyl)-4-phenylpyrimidin-1-ium bromide (3i): 194 mg, 95% yield, white solid, mp = 174.3 – 176.1 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.05 (s, 1H), 9.52 (dd, J = 7.2, 2.0 Hz, 1H), 8.86 (dd, J = 6.8, 0.8 Hz, 1H), 8.47 – 8.40 (m, 2H), 7.94 (t, J = 2.0 Hz, 1H), 7.82 – 7.74 (m, 1H), 7.72 – 7.62 (m, 4H), 7.43 (t, J = 8.0 Hz, 1H), 5.84 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 153.6, 151.5, 136.0, 134.7, 133.0,

132.2, 131.9, 131.2, 129.7, 129.1, 128.3, 122.2, 118.9, 58.7. HRMS (ESI) m/z: calcd for $C_{17}H_{14}BrN_2$ [M – Br]$^+$, 325.0335; found, 325.0335.

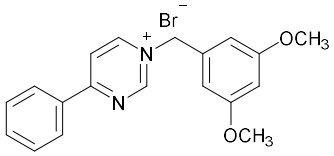
1-(2-bromobenzyl)-4-phenylpyrimidin-1-ium bromide (3j): 194 mg, 95% yield, white solid, mp = 173.4 – 176.8 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 9.98 (s, 1H), 9.40 (dd, J = 6.8, 1.6 Hz, 1H), 8.90 (dd, J = 6.8, 0.8 Hz, 1H), 8.50 – 8.42 (m, 2H), 7.83 – 7.75 (m, 2H), 7.75 – 7.66 (m, 2H), 7.51 – 7.39 (m, 3H), 5.95 (s, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 169.0, 154.0, 151.9, 134.8, 133.2, 132.9, 132.8, 131.3, 131.0, 129.7, 129.2, 128.5, 123.1, 118.8, 59.7. HRMS (ESI) m/z: calcd for $C_{17}H_{14}BrN_2$ [M – Br]$^+$, 325.0335; found, 325.0336.



1-(3,5-dimethylbenzyl)-4-phenylpyrimidin-1-ium bromide (3k): 167 mg, 94% yield, white solid, mp = 170.3 – 173.4 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.03 (s, 1H), 9.48 (dd, J = 6.8, 1.6 Hz, 1H), 8.84 (d, J = 6.8 Hz, 1H), 8.50 – 8.39 (m, 2H), 7.82 – 7.74 (m, 1H), 7.72 – 7.63 (m, 2H), 7.24 (s, 2H), 7.07 (s, 1H), 5.75 (s, 2H), 2.28 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 153.5, 151.5, 138.4, 134.6, 133.4, 133.0, 130.6, 129.7, 129.1, 126.6, 118.8, 59.6, 20.8. HRMS (ESI) m/z: calcd for $C_{19}H_{19}N_2$ [M – Br]$^+$, 275.1543; found, 275.1546.



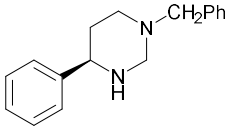
1-(3,5-dimethoxybenzyl)-4-phenylpyrimidin-1-ium bromide (3l): 182 mg, 94% yield, white solid, mp = 187.2 – 189.2 °C. ^{1}H NMR (400 MHz, DMSO-d_6) δ 10.10 (s, 1H), 9.56 (dd, J = 6.8, 1.6 Hz, 1H), 8.85 (d, J = 6.8 Hz, 1H), 8.43 (d, J = 7.6 Hz, 2H), 7.81 – 7.63 (m, 3H), 6.90 (d, J = 2.4 Hz, 2H), 6.55 (t, J = 2.4 Hz, 1H), 5.75 (s, 2H), 3.76 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.6, 161.0, 153.5, 151.4, 135.5, 134.6, 133.0, 129.7, 129.1, 118.8, 107.3, 100.9, 59.6, 55.5. HRMS (ESI) m/z: calcd for $C_{19}H_{19}N_2O_2$ [M – Br]$^+$, 307.1441; found, 307.1445.

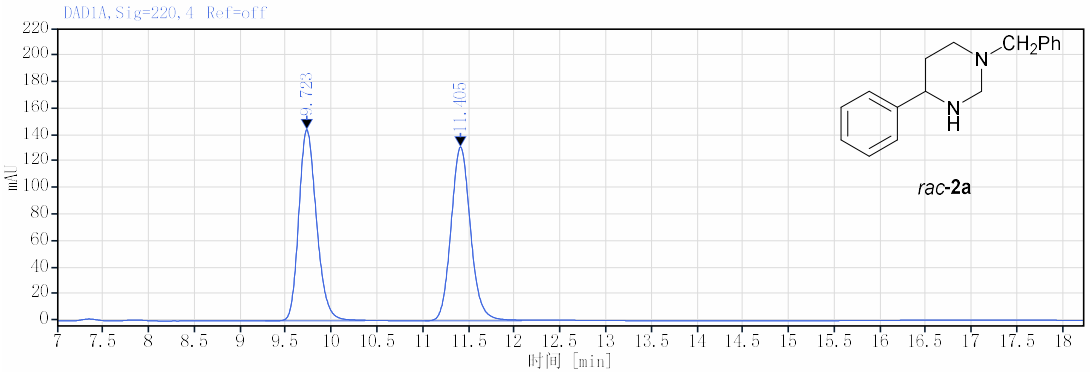


2.3 Asymmetric hydrogenation of 4-subsituted pyrimidinium salts

A mixture of $[Ir(COD)Cl]_2$ (0.13 mg, 0.002 mmol, 1.0 mol%) and (*S*,*S*)-f-Binaphane (3.5 mg, 0.0044 mmol, 2.2 mol%) was dissolved in a degassed solvent DCM (3.0 mL) at argon atmosphere, and the resulting solution was allowed to be stirred at room temperature for 30 min. Then, 4-subsituted pyrimidinium salts (0.2 mmol, 1.0 equiv.) was added. The mixture was transferred to an autoclave, which was purged (3 × 10 atm) and charged with H_2 (60 atm); then the reaction mixture was stirred at −20 °C for 72 h. The hydrogen gas was released slowly, and the solution was concentrated and purified by silica gel flash column chromatography to afford the desired chiral product.

(*R*)-1-benzyl-4-phenylhexahydropyrimidine (2a): 46 mg, 91% yield, colorless oil, 96% *ee*, $[\alpha]_D^{20}$ = −8.3 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 9.7 min (minor), t_{R2} = 11.3 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.42 – 7.08 (m, 10H), 3.99 (dd, J = 10.8, 2.0 Hz, 1H), 3.72 – 3.65 (m, 1H), 3.64 – 3.41 (m, 2H), 3.29 (d, J = 10.8 Hz, 1H), 3.64 – 3.41 (m, 1H), 2.37 – 2.27 (m, 1H), 1.87 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 138.1, 129.3, 128.6, 128.4, 127.2, 127.2, 126.5, 70.0, 59.8, 59.7, 52.9, 33.5. HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_2$ [M + H]$^+$, 253.1699; found, 253.1700.





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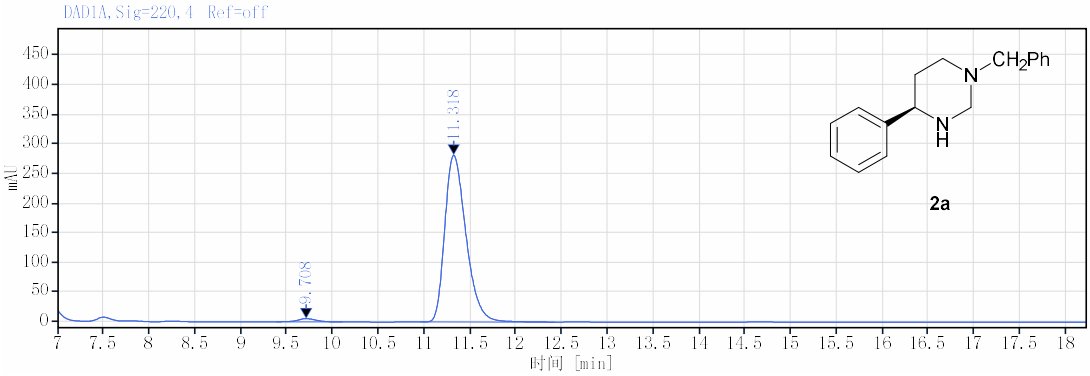
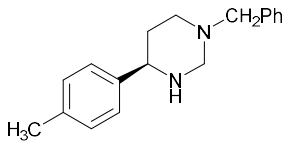
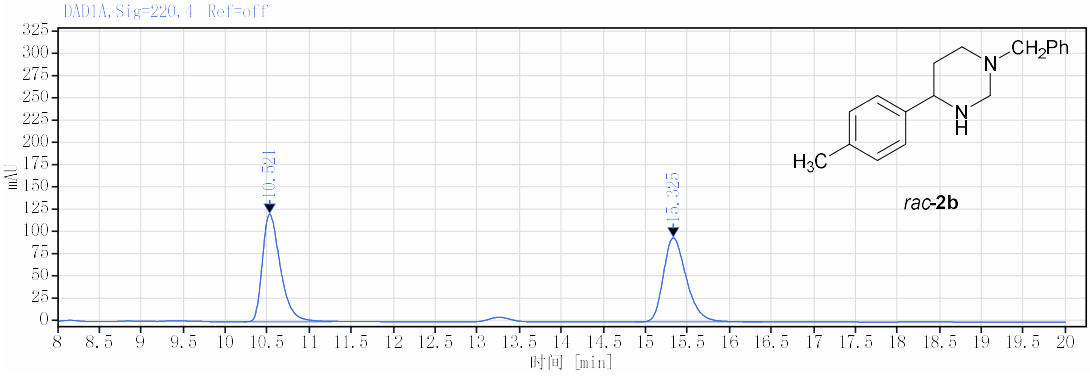
11.405	BM m	0.23	1944.18	131.22	49.94



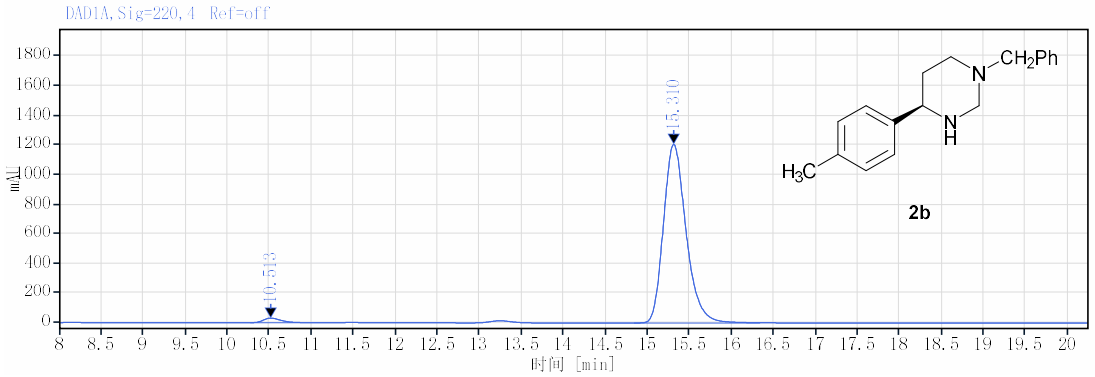
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.708	MM m	0.23	86.87	5.72	1.88
11.318	BB	1.47	4533.92	281.63	98.12

(*R*)-1-benzyl-4-(*p*-tolyl)hexahydropyrimidine (2b): 49 mg, 92% yield, colorless oil, 96% *ee*, $[\alpha]_D^{20} = -12.8$ (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 10.5 min (minor), t_{R2} = 15.3 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.11 (m, 9H), 3.98 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.68 – 3.38 (m, 3H), 3.28 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.03 (m, 1H), 2.36 – 2.26 (m, 4H), 1.86 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 140.8, 138.2, 136.8, 129.3, 129.2, 128.4, 127.2, 126.4, 70.0, 59.9, 59.4, 53.0, 33.5, 21.2. HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_2$ $[M + H]^+$, 267.1856; found, 267.1854.



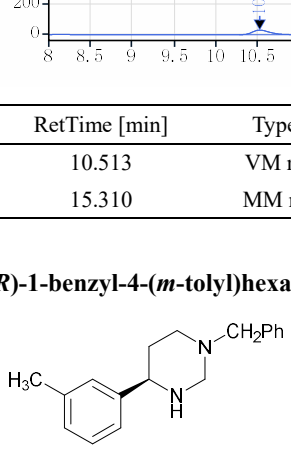


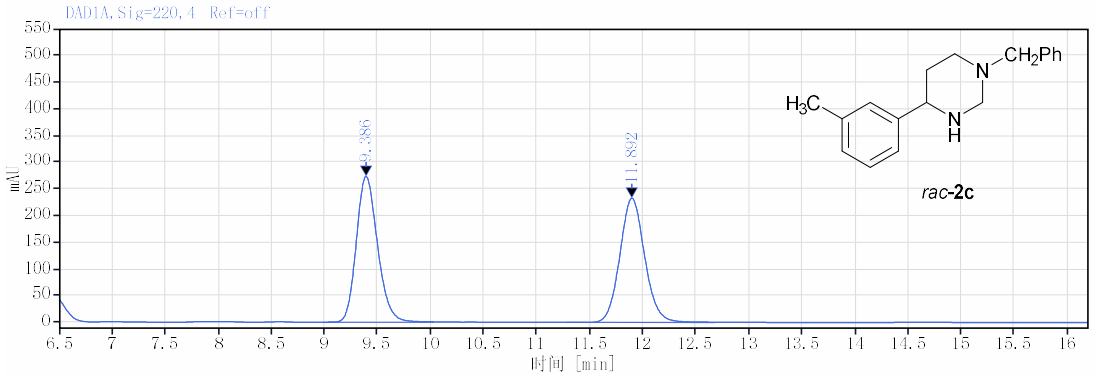
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.521	BM m	0.23	1808.41	121.08	50.13
15.325	BM m	0.29	1798.70	94.58	49.87



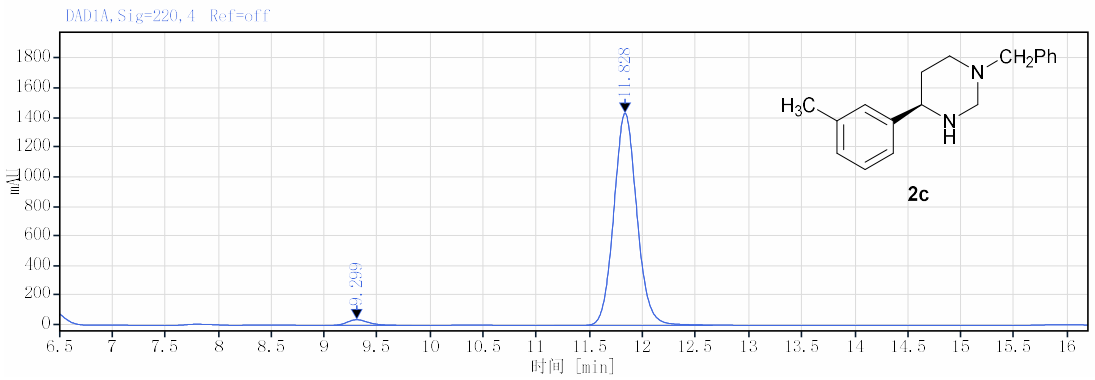
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.513	VM m	0.22	441.19	31.02	1.91
15.310	MM m	0.29	22611.44	1206.10	98.09

(*R*)-1-benzyl-4-(*m*-tolyl)hexahydropyrimidine (2c): 48 mg, 90% yield, colorless oil, 95% *ee*, $[\alpha]_D^{20} = -10.8$ (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 9.3 min (minor), t_{R2} = 11.8 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.04 (m, 9H), 3.99 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.68 – 3.41 (m, 3H), 3.28 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.39 – 2.25 (m, 4H), 1.91 – 1.79 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.7, 138.2, 138.2, 129.3, 128.5, 128.4, 128.0, 127.3, 127.2, 123.5, 70.1, 59.8, 59.7, 53.0, 33.5, 21.6. HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_2$ $[M + H]^+$, 267.1856; found, 267.1858.



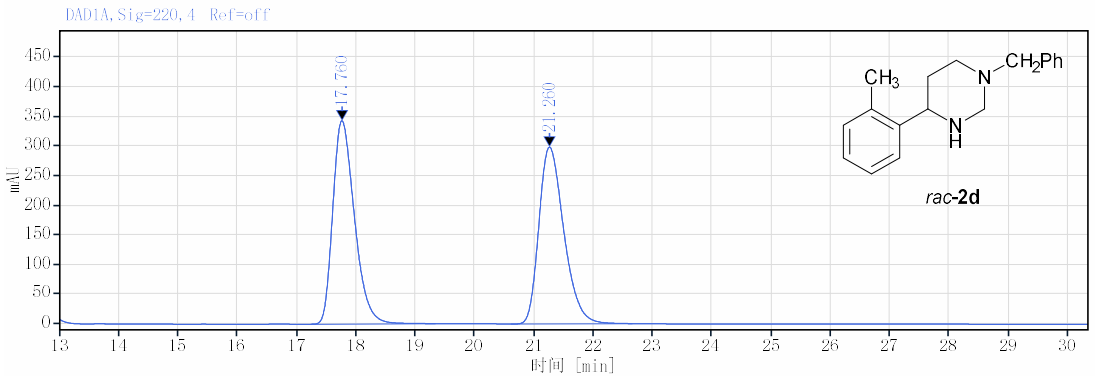


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.386	MM m	0.21	3809.12	273.71	50.03
11.892	BM m	0.25	3805.04	233.17	49.97

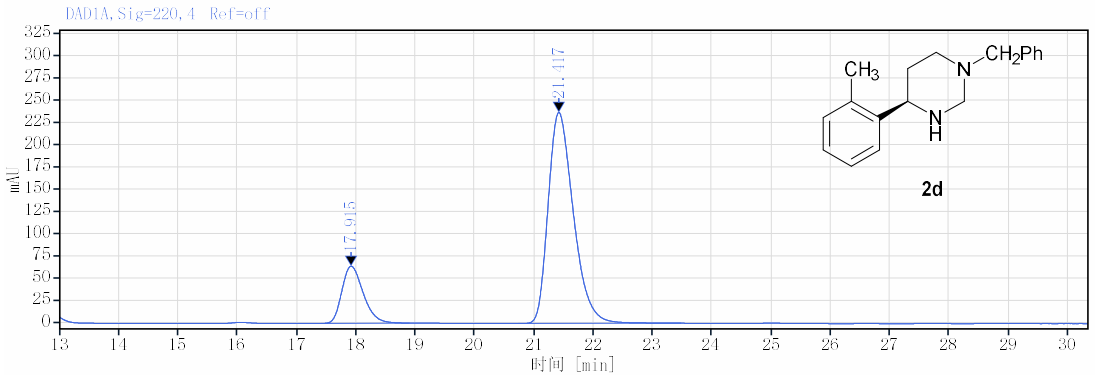


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.299	BV	0.84	556.86	38.51	2.51
11.828	BM m	0.23	21657.62	1433.45	97.49

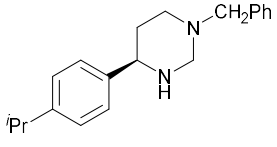
(*R*)-1-benzyl-4-(*o*-tolyl)hexahydropyrimidine (2d): 47 mg, 88% yield, colorless oil, 63% *ee*, $[\alpha]_D^{20}$ = −4.6 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 17.9 min (minor), t_{R2} = 21.4 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.12 (m, 9H), 4.00 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.83 (dd, *J* = 11.6, 3.2 Hz, 1H), 3.66 – 3.41 (m, 2H), 3.30 (d, *J* = 10.8 Hz, 1H), 3.17 – 3.07 (m, 1H), 2.43 – 2.28 (m, 4H), 1.93 – 1.80 (m, 1H), 1.76 – 1.71 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.7, 138.2, 135.7, 130.6, 129.3, 128.4, 127.2, 127.0, 126.3, 125.0, 70.3, 59.9, 56.5, 53.2, 32.5, 19.28. HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_2$ $[M + H]^+$, 267.1856; found, 267.1852.



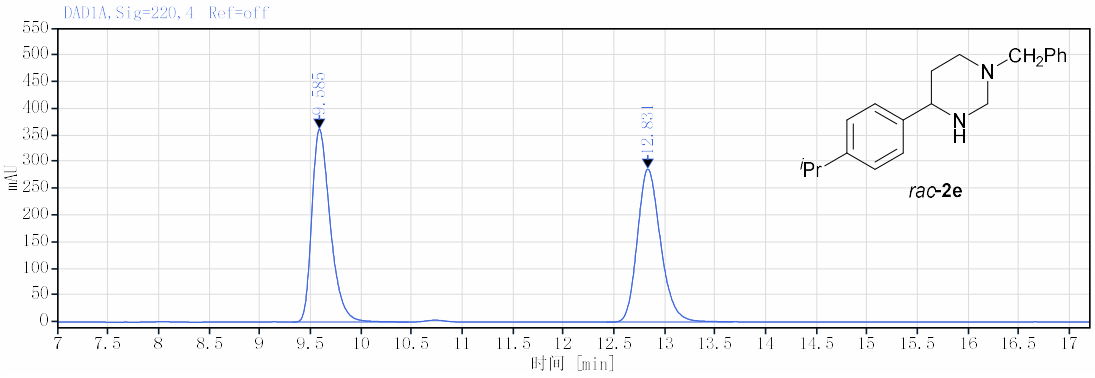
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
17.760	BB	2.11	8702.82	343.08	49.99
21.260	BM m	0.45	8706.75	298.28	50.01



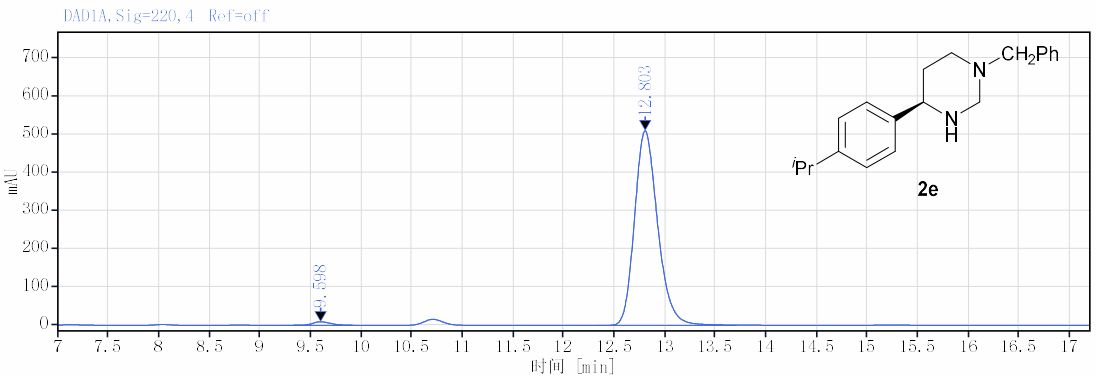
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
17.915	BM m	0.39	1610.03	64.21	18.67
21.417	BM m	0.45	7014.72	237.35	81.33

(*R*)-1-benzyl-4-(4-isopropylphenyl)hexahydropyrimidine (2e): 54 mg, 92% yield, colorless oil, 97% *ee*, 

$[\alpha]_D^{20}$ = −8.7 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 9.6 min (minor), t_{R2} = 12.8 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.26 (m, 7H), 7.20 – 7.16 (m, 2H), 3.99 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.67 – 3.41 (m, 3H), 3.28 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.04 (m, 1H), 2.93 – 2.84 (m, 1H), 2.35 – 2.25 (m, 1H), 1.88 – 1.82 (m, 2H), 1.23 (d, *J* = 7.2 Hz, 6H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.8, 141.2, 138.2, 129.3, 128.4, 127.2, 126.6, 126.5, 70.1, 59.8, 59.5, 53.0, 33.9, 33.4, 24.1. HRMS (ESI) m/z: calcd for $C_{20}H_{26}N_2$ $[M + H]^+$, 295.2169; found, 295.2168.

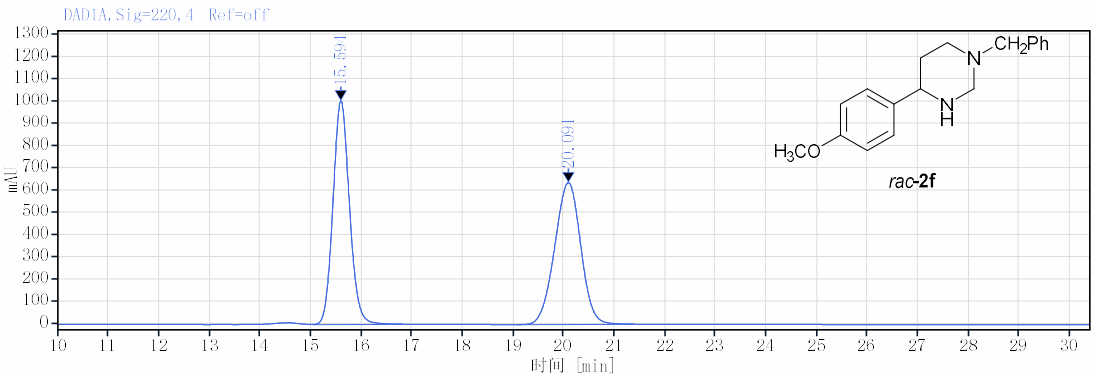


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.585	VV	1.15	4588.48	361.53	49.99
12.831	BM m	0.25	4590.30	286.71	50.01

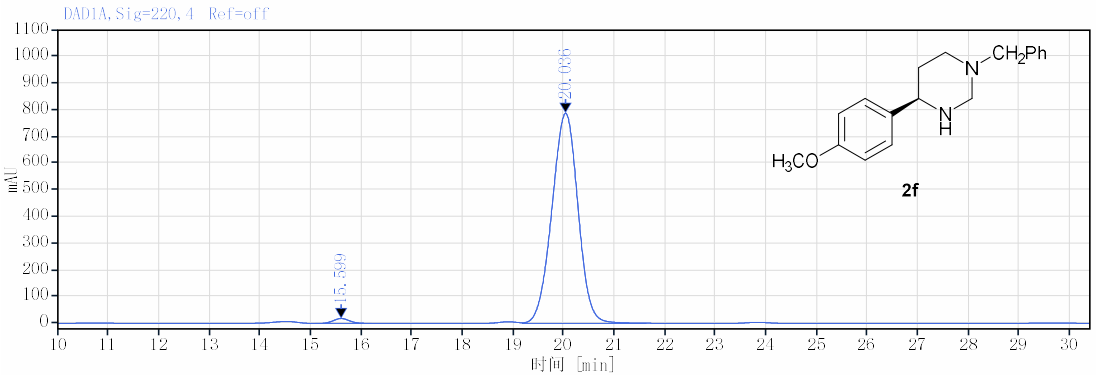


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.598	MM m	0.19	119.14	9.38	1.44
12.803	BM m	0.24	8138.14	510.78	98.56

(*R*)-1-benzyl-4-(4-methoxyphenyl)hexahydropyrimidine (2f): 52 mg, 92% yield, colorless oil, 97% *ee*, $[\alpha]_D^{20}$ = −11.5 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 15.6 min (minor), t_{R2} = 20.0 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.22 (m, 7H), 6.90 – 6.81 (m, 2H), 3.97 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.78 (s, 3H), 3.66 – 3.41 (m, 3H), 3.28 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.04 (m, 1H), 2.34 – 2.25 (m, 1H), 1.90 – 1.78 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 138.2, 136.1, 129.3, 128.4, 127.6, 127.2, 113.9, 70.1, 59.8, 59.1, 55.4, 53.0, 33.4. HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_2O$ $[M + H]^+$, 283.1805; found, 283.1804.

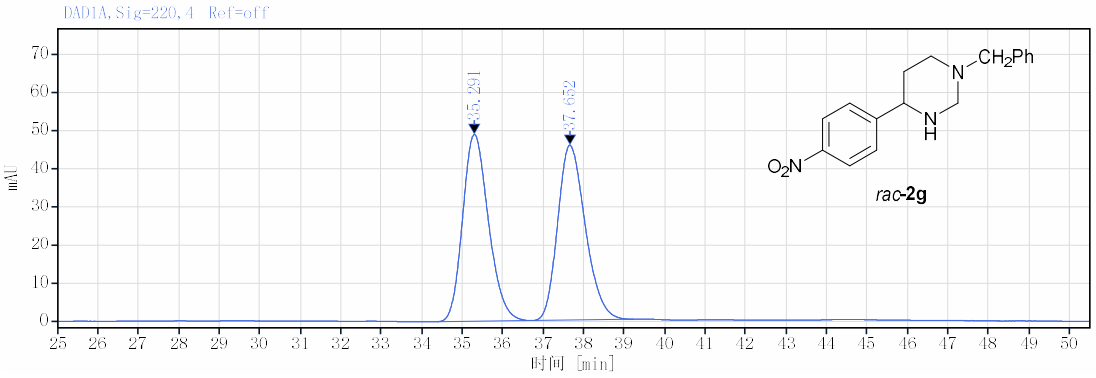


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
15.594	VM m	0.35	22889.60	1006.51	49.99
20.091	BM m	0.56	22895.18	638.19	50.01

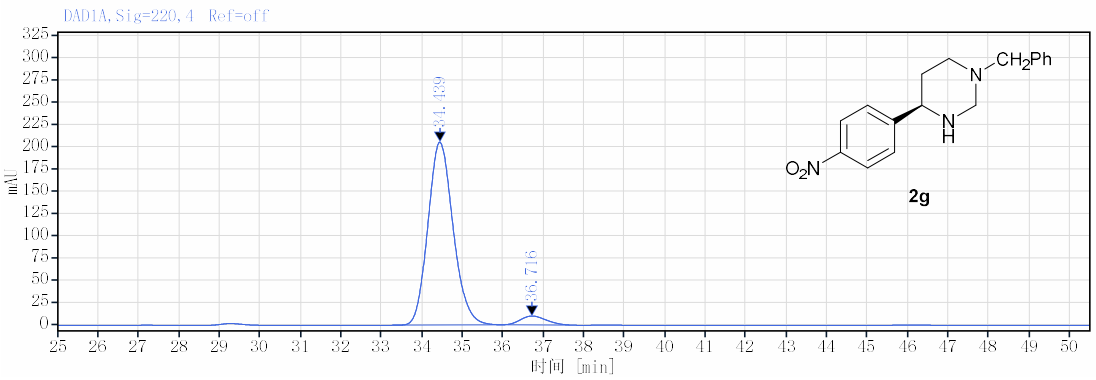


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
15.599	VM m	0.35	419.45	18.72	1.46
20.036	VM m	0.56	28259.87	788.16	98.54

(*R*)-1-benzyl-4-(4-nitrophenyl)hexahydropyrimidine (2g): 53 mg, 89% yield, colorless oil, 91% *ee*, $[\alpha]_D^{20}$ = −5.8 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 34.4 min (major), t_{R2} = 36.7 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.19 (d, *J* = 8.8 Hz, 2H), 7.54 (d, *J* = 8.8 Hz, 2H), 7.39 – 7.27 (m, 5H), 4.07 – 3.98 (m, 1H), 3.80 (dd, *J* = 10.8, 3.6 Hz, 1H), 3.67 – 3.44 (m, 2H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.12 (d, *J* = 11.6 Hz, 1H), 2.44 – 2.32 (m, *J* = 11.6, 3.2 Hz, 1H), 1.95 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 150.8, 147.1, 129.2, 128.4, 127.3, 127.2, 123.7, 69.6, 59.5, 59.0, 52.4, 33.1. HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_3O_2$ $[M + H]^+$, 298.1550; found, 298.1549.

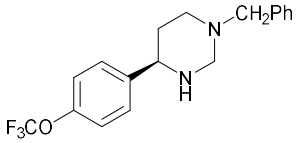


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
35.291	MM m	0.68	2169.85	49.03	49.95
37.652	MM m	0.73	2174.51	45.88	50.05

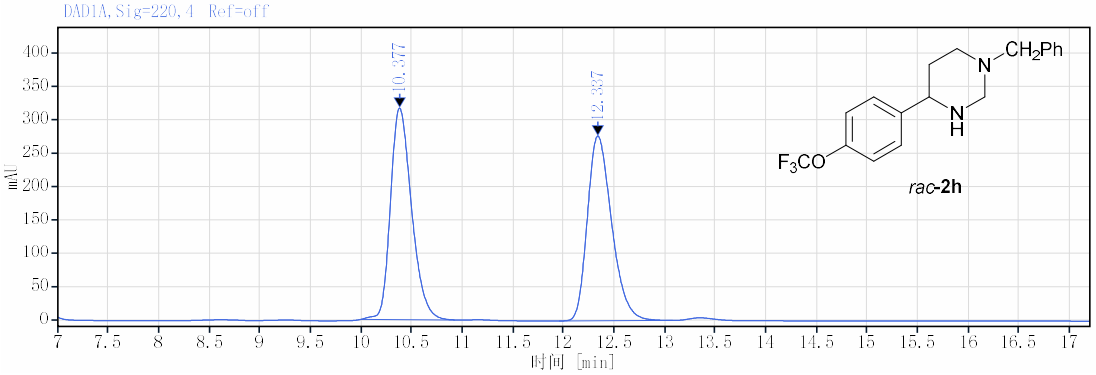


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
34.439	MM m	0.67	8908.19	205.68	95.40
36.716	MM m	0.65	429.99	9.92	4.60

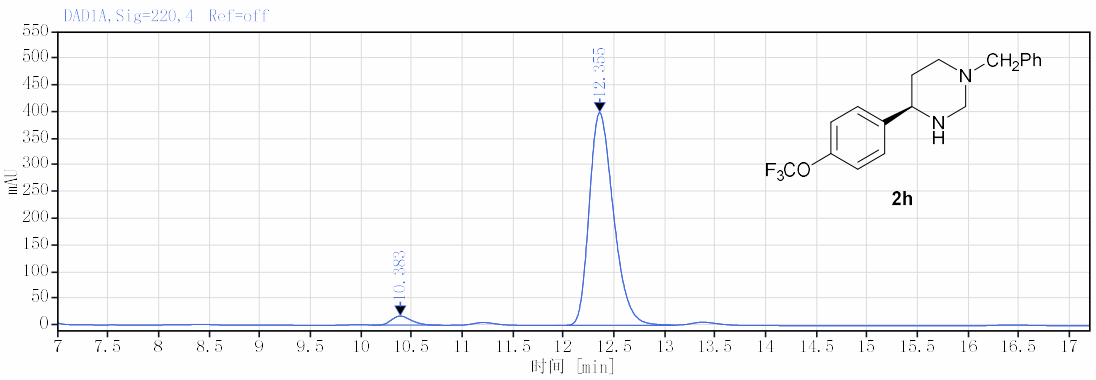
(*R*)-1-benzyl-4-(4-(trifluoromethoxy)phenyl)hexahydropyrimidine (2h): 60 mg, 90% yield, colorless oil,



93% *ee*, $[\alpha]_D^{20}$ = −6.3 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 10.4 min (minor), t_{R2} = 12.4 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.43 – 7.26 (m, 7H), 7.17 (d, *J* = 8.4 Hz, 2H), 3.99 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.73 – 3.66 (m, 1H), 3.65 – 3.41 (m, 2H), 3.29 (d, *J* = 10.8 Hz, 1H), 3.15 – 3.05 (m, 1H), 2.38 – 2.26 (m, 1H), 1.88 – 1.79 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.4 (d, *J* = 1.9 Hz), 142.5, 138.0, 129.3, 128.5, 127.9, 127.3, 121.1, 120.6 (q, *J* = 255.3 Hz), 69.9, 59.8, 59.0, 52.8, 33.4. HRMS (ESI) m/z: calcd for $C_{18}H_{20}F_3N_2O$ $[M + H]^+$, 337.1522; found, 337.1523.

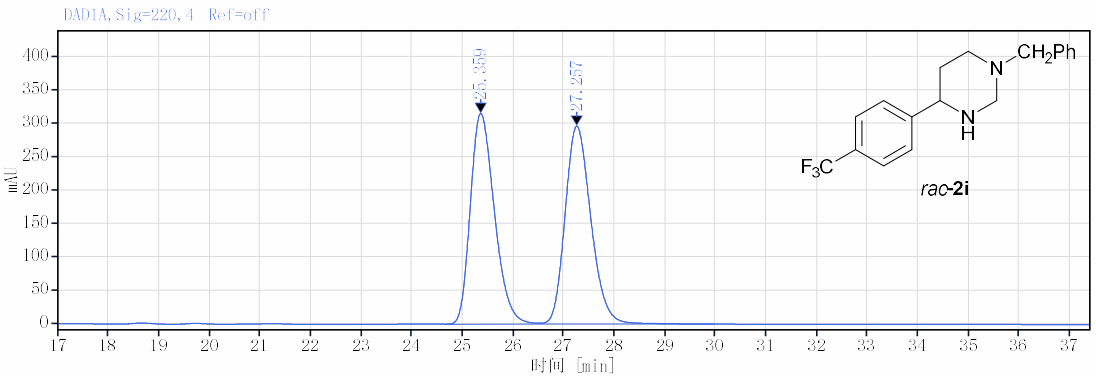


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.377	MM m	0.22	4617.65	317.56	49.95
12.337	BM m	0.26	4626.55	277.01	50.05

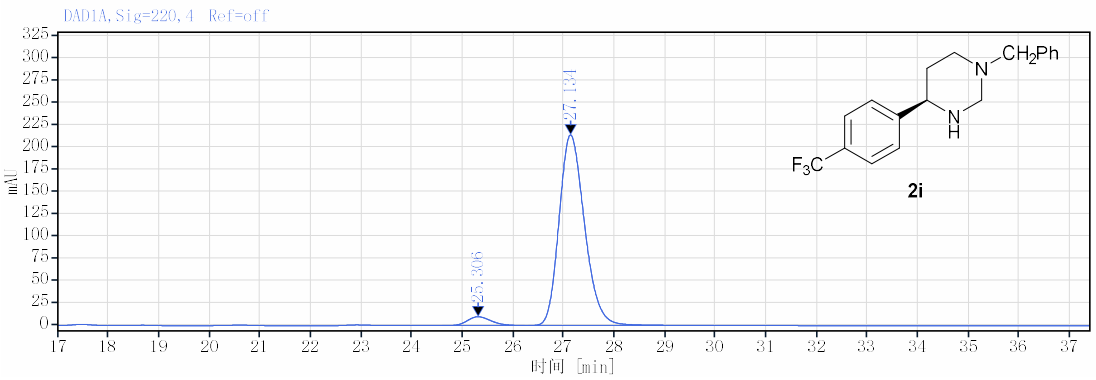


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.383	MM m	0.21	233.09	16.92	3.38
12.355	BV	1.18	6655.04	398.75	96.62

(*R*)-1-benzyl-4-(4-(trifluoromethyl)phenyl)hexahydropyrimidine (2i): 59 mg, 92% yield, colorless oil, 92% *ee*, $[\alpha]_D^{20} = -6.3$ (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 25.3 min (minor), t_{R2} = 27.1 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.4 Hz, 2H), 7.39 – 7.25 (m, 5H), 4.01 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.78 – 3.71 (m, 1H), 3.66 – 3.43 (m, 2H), 3.30 (d, *J* = 10.8 Hz, 1H), 3.16 – 3.06 (m, 1H), 2.39 –2.28 (m, 1H), 1.90 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 147.7, 138.0, 129.7, 129.3, 128.5, 127.3, 126.8, 125.5 (q, *J* = 3.8 Hz), 124.3 (q, *J* = 270.4 Hz), 69.9, 59.8, 59.3, 52.8, 33.4. HRMS (ESI) m/z: calcd for $C_{18}H_{20}F_3N_2$ $[M + H]^+$, 321.1573; found, 321.1575.

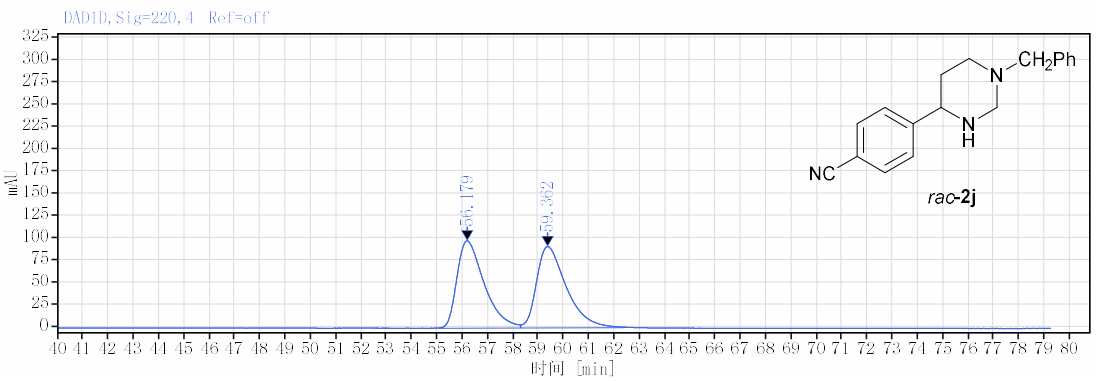


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
25.359	BV	1.86	10454.89	316.05	49.77
27.257	VB	3.44	10552.20	297.14	50.23

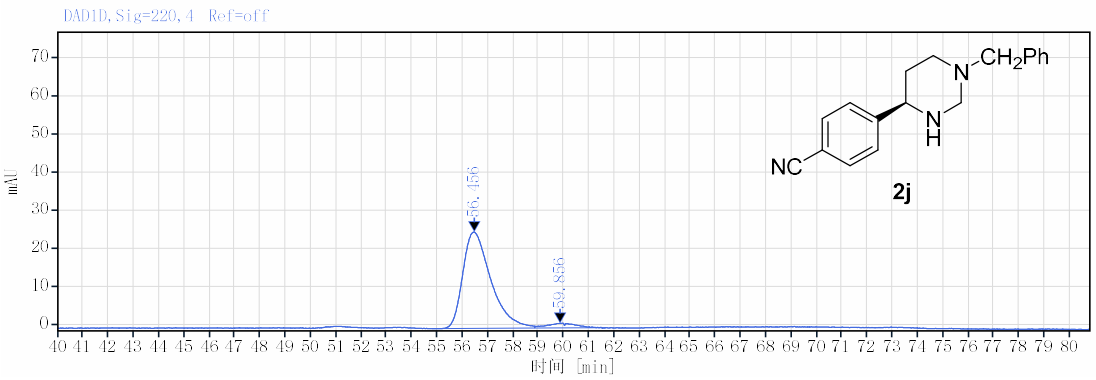


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
25.306	BB	1.63	315.48	9.85	4.05
27.134	BB	3.67	7482.79	214.33	95.95

(*R*)-1-benzyl-4-(4-nitrophenyl)hexahydropyrimidine (2j): 49 mg, 88% yield, colorless oil, 90% *ee*, $[\alpha]_D^{20}$ = −6.5 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.4 mL/min; UV detection at 220 nm; t_{R1} = 56.5 min (major), t_{R2} = 59.9 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.66 – 7.59 (m, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.37 – 7.25 (m, 5H), 4.00 (d, *J* = 10.8 Hz, 1H), 3.79 – 3.70 (m, 1H), 3.66 – 3.43 (m, 2H), 3.30 (d, *J* = 10.8 Hz, 1H), 3.16 – 3.05 (m, 1H), 2.41 –2.30 (m, 1H), 1.92 – 1.75 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3, 143.5, 132.3, 129.6, 128.6, 127.4, 126.4, 119.1, 111.1, 69.9, 59.6, 59.1, 53.0, 33.3. HRMS (ESI) m/z: calcd for $C_{19}H_{20}N_3$ $[M + H]^+$, 278.1652; found, 278.1647.

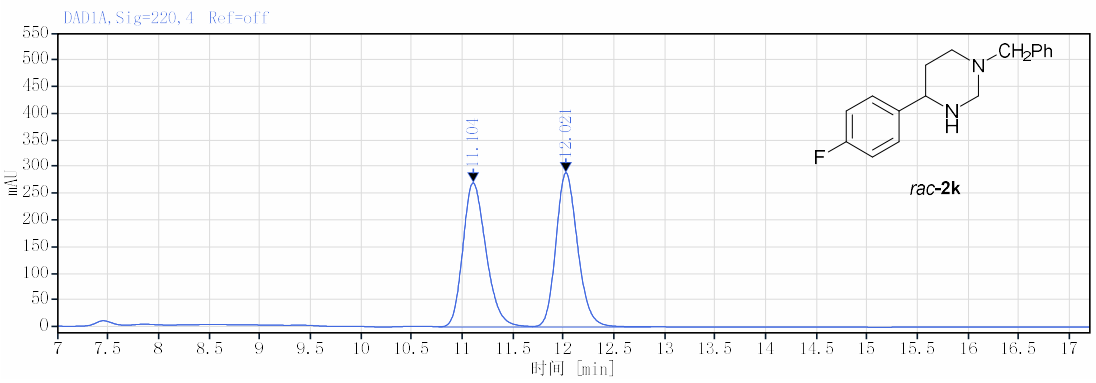


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
56.179	VV	3.22	7345.69	98.12	49.54
59.362	VV	4.11	7481.92	91.44	50.46

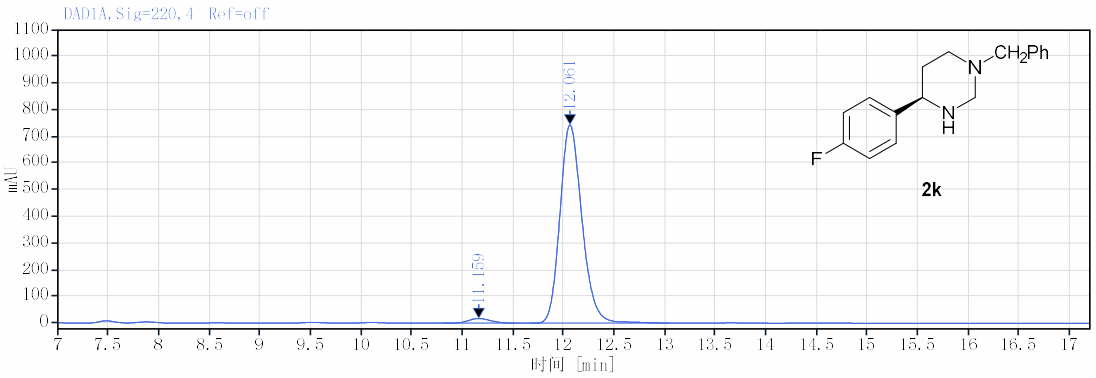


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
56.456	MM m	0.91	1947.54	25.29	95.13
59.856	MM m	0.94	99.62	1.25	4.87

(*R*)-1-benzyl-4-(4-fluorophenyl)hexahydropyrimidine (2k): 50 mg, 92% yield, colorless oil, 95% *ee*, $[\alpha]_D^{20}$ = −8.2 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 11.2 min (minor), t_{R2} = 12.0 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.23 (m, 7H), 7.06 – 6.93 (m, 2H), 3.98 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.70 – 3.42 (m, 3H), 3.28 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.37 – 2.25 (m, 1H), 1.87 – 1.78 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.0 (d, *J* = 243.4 Hz), 139.6 (d, *J* = 3.1 Hz), 138.1, 129.3, 128.4, 128.1 (d, *J* = 7.9 Hz), 127.3, 115.3 (d, *J* = 21.0 Hz), 70.0, 59.8, 59.0, 52.9, 33.5. HRMS (ESI) m/z: calcd for $C_{17}H_{20}FN_2$ $[M + H]^+$, 271.1605; found, 271.1608.

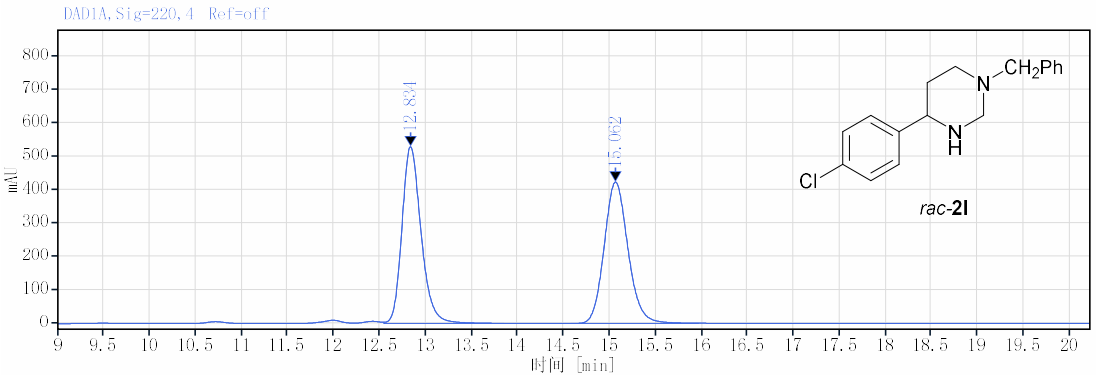


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.104	VV	0.93	4315.17	270.39	49.97
12.021	VM m	0.23	4320.08	289.45	50.03

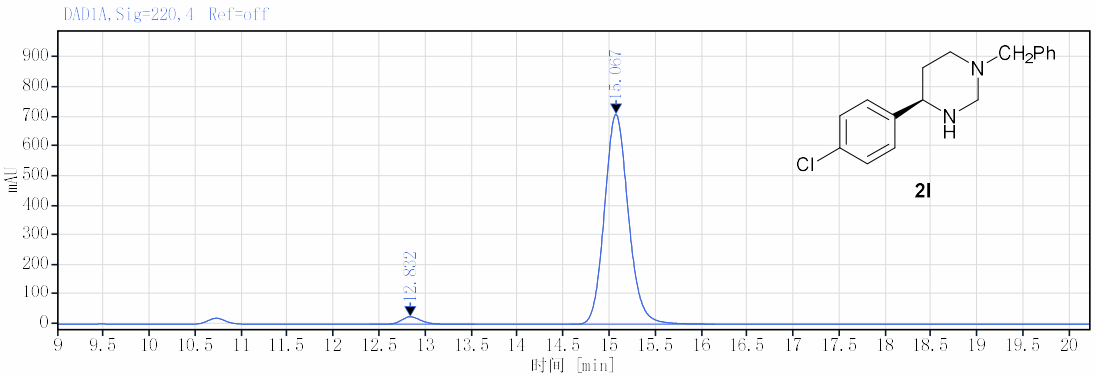


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.159	BM m	0.24	276.47	17.75	2.39
12.061	BM m	0.23	11267.29	743.26	97.61

(*R*)-1-benzyl-4-(4-chlorophenyl)hexahydropyrimidine (2l): 52 mg, 91% yield, colorless oil, 94% *ee*, $[\alpha]_D^{20}$ = −6.2 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 12.8 min (minor), t_{R2} = 15.0 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.23 (m, 9H), 3.98 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.69 – 3.42 (m, 3H), 3.27 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.03 (m, 1H), 2.35 – 2.24 (m, 1H), 1.86 – 1.77 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.3, 138.1, 132.9, 129.3, 128.7, 128.4, 127.9, 127.3, 69.9, 59.8, 59.0, 52.8, 33.4. HRMS (ESI) m/z: calcd for $C_{17}H_{20}ClN_2$ $[M + H]^+$, 287.1301; found, 287.1296.

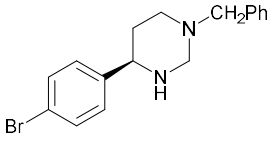


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
12.834	VM m	0.22	7665.05	530.49	50.03
15.062	BM m	0.28	7657.18	424.56	49.97

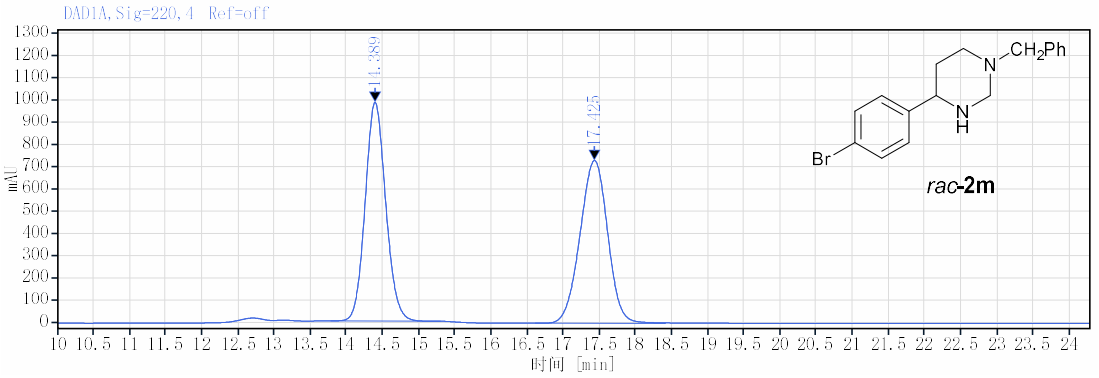


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
12.832	MM m	0.23	378.80	25.42	2.88
15.067	BM m	0.28	12772.64	708.34	97.12

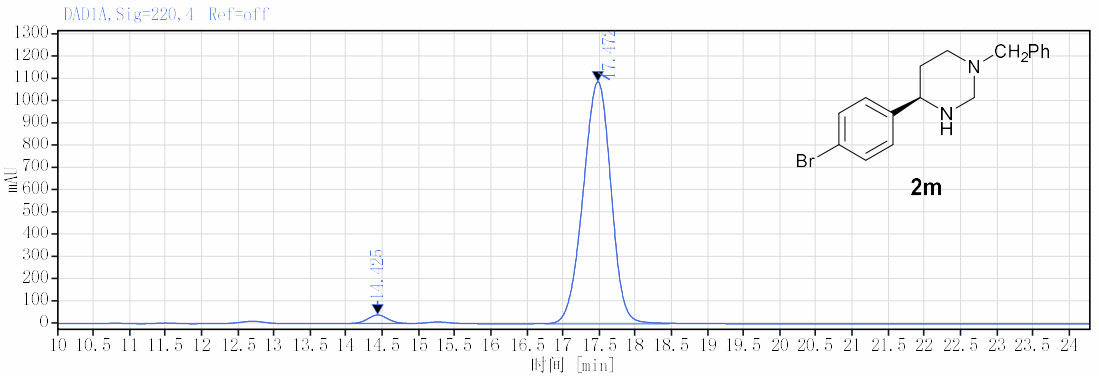
(*R*)-1-benzyl-4-(4-bromophenyl)hexahydropyrimidine (2m): 61 mg, 93% yield, colorless oil, 95% *ee*,



$[\alpha]_D^{20}$ = −5.9 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 14.4 min (minor), t_{R2} = 17.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.47 – 7.20 (m, 9H), 3.97 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.67 – 3.41 (m, 3H), 3.27 (d, *J* = 10.8 Hz, 1H), 3.14 – 3.02 (m, 1H), 3.37 – 3.24 (m, 1H), 1.84 – 1.78 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 138.1, 131.6, 129.2, 128.4, 128.3, 127.3, 121.0, 69.9, 59.8, 59.0, 52.8, 33.3. HRMS (ESI) m/z: calcd for $C_{17}H_{20}BrN_2$ $[M + H]^+$, 331.0804; found, 331.0807.

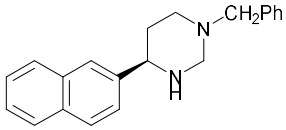


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
14.389	MM m	0.30	19471.62	983.96	49.97
17.425	BM m	0.42	19495.39	732.56	50.03



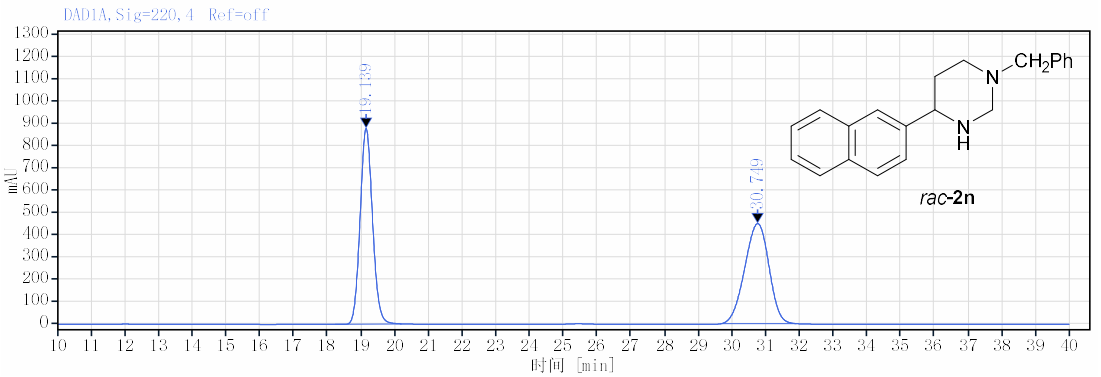
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
14.425	MM m	0.30	736.93	38.27	2.47
17.472	MM m	0.42	29151.46	1088.87	97.53

(*R*)-1-benzyl-4-(naphthalen-2-yl)hexahydropyrimidine (2n): 57 mg, 94% yield, white solid, 95% *ee*, mp =

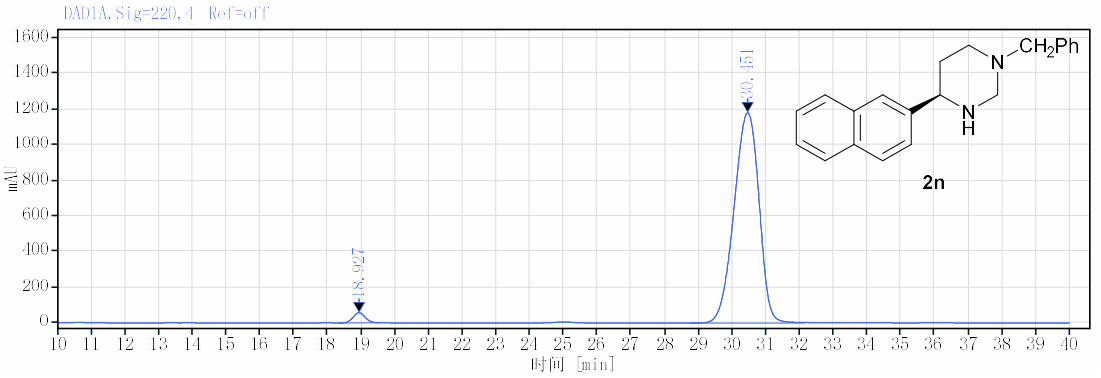


83.3 – 87.5 °C. $[\alpha]_D^{20}$ = −7.2 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 18.9 min (minor), t_{R2} = 30.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.80 (d, *J* = 8.8 Hz, 4H), 7.51 – 7.24 (m, 8H), 4.03 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.89 – 3.79 (m, 1H), 3.68 – 3.44 (m, 2H), 3.34 (d, *J*

= 10.8 Hz, 1H), 3.18 – 3.07 (m, 1H), 2.43 –2.29 (m, 1H), 1.97 – 1.91 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 141.2, 138.2, 133.6, 132.8, 129.3, 128.4, 128.2, 128.0, 127.7, 127.2, 126.1, 125.8, 125.3, 124.6, 70.1, 59.8, 59.7, 53.0, 33.5. HRMS (ESI) m/z: calcd for $C_{21}H_{23}N_2$ $[M + H]^+$, 303.1856; found, 303.1857.

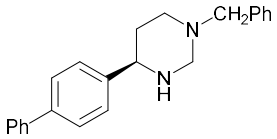


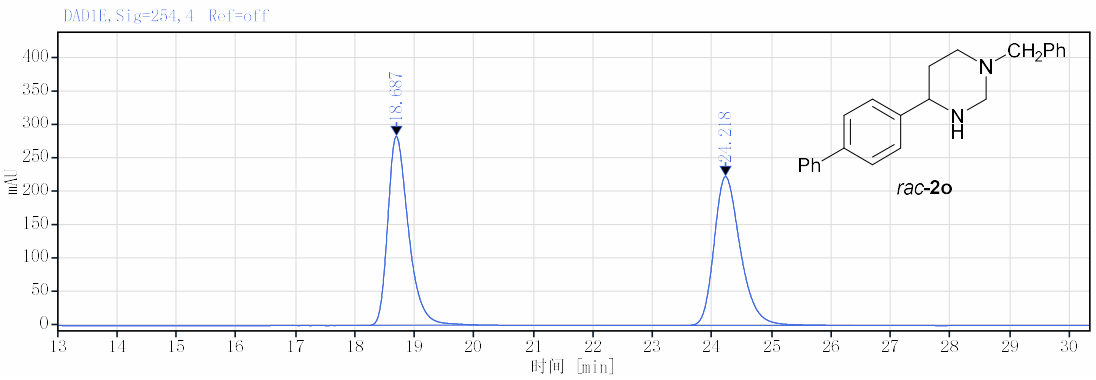
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
19.139	MM m	0.39	22469.50	880.71	49.99
30.749	MM m	0.79	22482.76	450.21	50.01



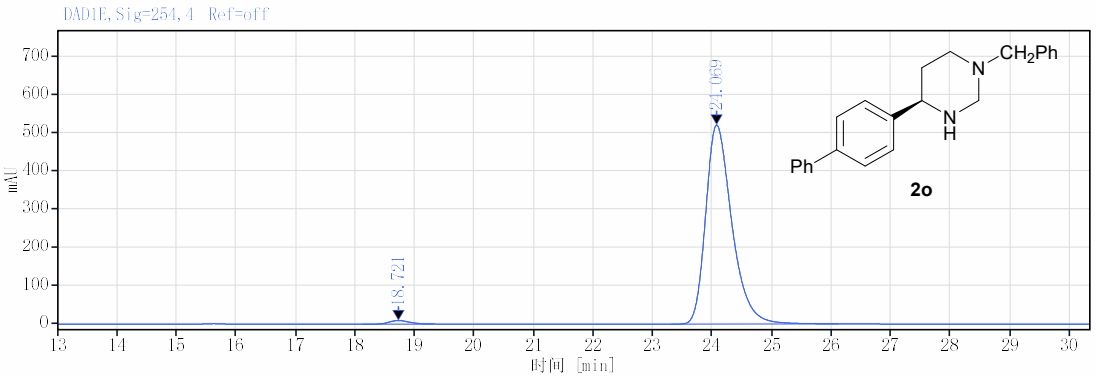
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
18.927	VM m	0.38	1423.48	57.53	2.29
30.451	BM m	0.82	60666.04	1182.14	97.71

(*R*)-4-([1,1'-biphenyl]-4-yl)-1-benzylhexahydropyrimidine (2o): 62 mg, 95% yield, white solid, 97% *ee*, mp = 78.2 – 81.0 °C. $[\alpha]_D^{20}$ = −8.9 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 254 nm; t_{R1} = 18.7 min (minor), t_{R2} = 24.1 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.61 – 7.52 (m, 4H), 7.47 – 7.25 (m, 10H), 4.02 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.77 – 3.69 (m, 1H), 3.66 – 3.42 (m, 2H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.16 – 3.06 (m, 1H), 2.40 –2.27 (m, 1H), 1.95 – 1.86 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 142.8, 141.0, 140.2, 138.1, 129.3, 128.9, 128.5, 127.3, 127.3, 127.2, 126.9, 70.0, 59.9, 59.4, 52.9, 33.4. HRMS (ESI) m/z: calcd for $C_{23}H_{25}N_2$ $[M + H]^+$, 329.2012; found, 329.2015.



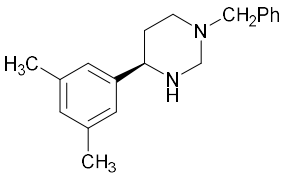


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
18.687	BM m	0.37	6851.83	283.48	50.02
24.218	BM m	0.47	6846.43	223.29	49.98

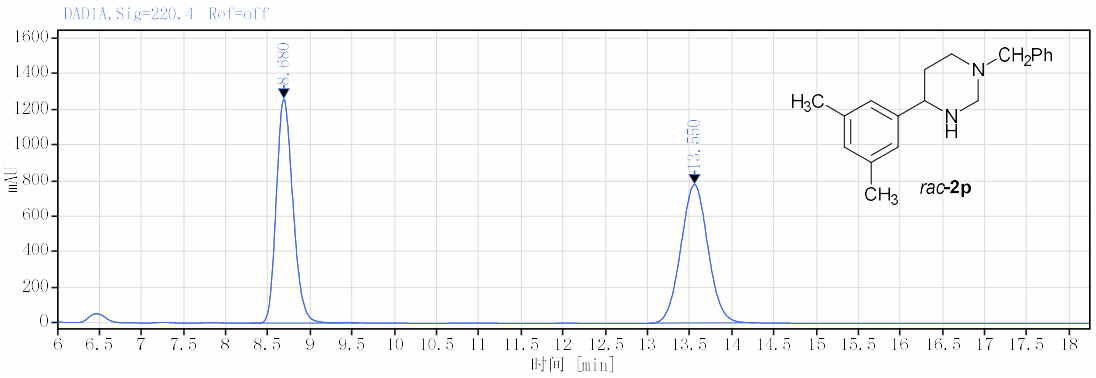


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
18.721	BM m	0.38	235.46	9.56	1.45
24.069	BM m	0.46	15979.32	522.51	98.55

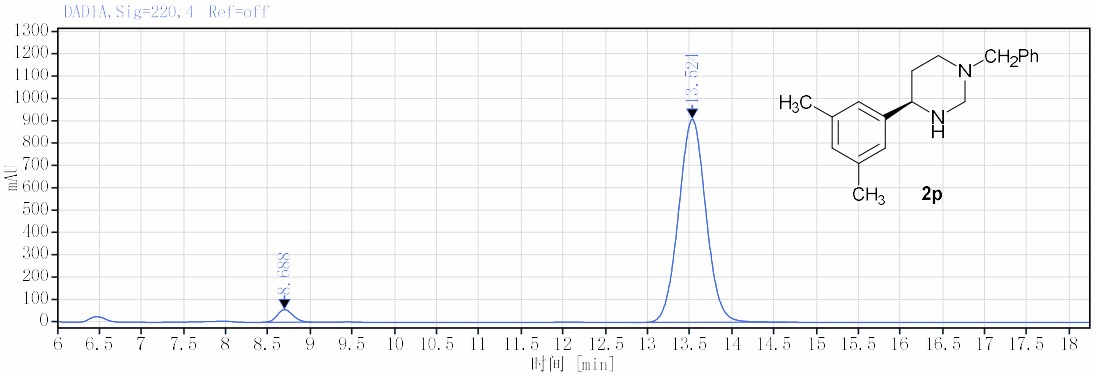
(*R*)-1-benzyl-4-(3,5-dimethylphenyl)hexahydropyrimidine (2p): 53 mg, 94% yield, colorless oil, 93% *ee*.



$[\alpha]_D^{20}$ = −8.4 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 8.7 min (minor), t_{R2} = 13.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.22 (m, 5H), 6.97 (s, 2H), 6.88 (s, 1H), 3.98 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.65 – 3.40 (m, 3H), 3.27 (d, *J* = 10.4 Hz, 1H), 3.13 – 3.04 (m, 1H), 3.35 – 3.25 (m, 7H), 1.91 – 1.78 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 138.3, 138.1, 129.3, 128.8, 128.4, 127.2, 124.3, 70.1, 59.8, 59.7, 53.0, 33.5, 21.5. HRMS (ESI) m/z: calcd for $C_{19}H_{25}N_2$ $[M + H]^+$, 281.2012; found, 281.2014.

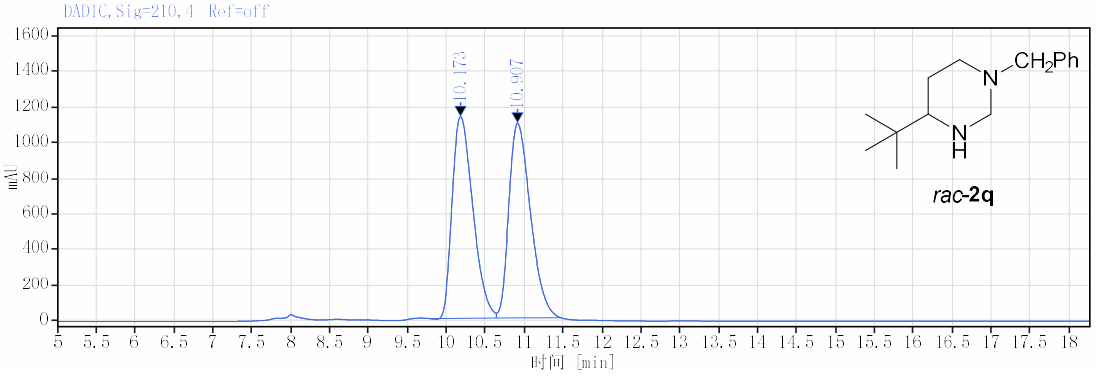


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
8.680	BM m	0.21	17393.18	1260.95	50.02
13.550	MM m	0.35	17377.81	778.49	49.98

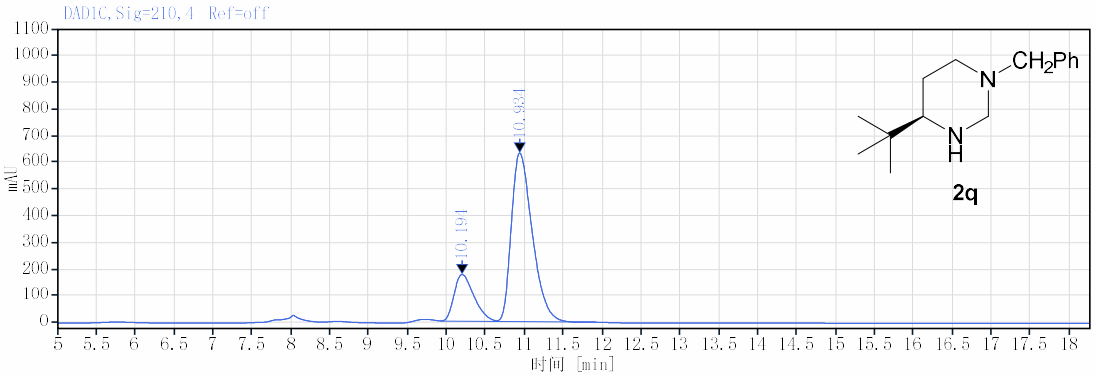


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
8.688	MM m	0.20	741.67	56.84	3.49
13.524	MM m	0.35	20510.01	910.57	96.51

(*R*)-1-benzyl-4-(*tert*-butyl)hexahydropyrimidine (2q): 42 mg, 91% yield, colorless oil, 58% *ee*, $[\alpha]_D^{20}$ = −5.4 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 95/5; flow rate = 0.4 mL/min; UV detection at 210 nm; t_{R1} = 10.2 min (minor), t_{R2} = 10.9 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.34 – 7.21 (m, 5H), 3.93 (dd, *J* = 10.8, 2.4 Hz, 1H), 3.60 – 3.26 (m, 2H), 3.09 – 3.00 (m, 2H), 2.21 – 2.15 (m, 1H), 2.14 – 2.02 (m, 1H), 1.62 – 1.53 (m, 2H), 1.50 – 1.38 (m, 1H), 0.90 (s, 9H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.1, 129.3, 128.4, 127.2, 70.4, 64.9, 59.9, 53.2, 33.3, 27.0, 26.8. HRMS (ESI) m/z: calcd for $C_{15}H_{25}N_2$ $[M + H]^+$, 233.2012; found, 233.2014.

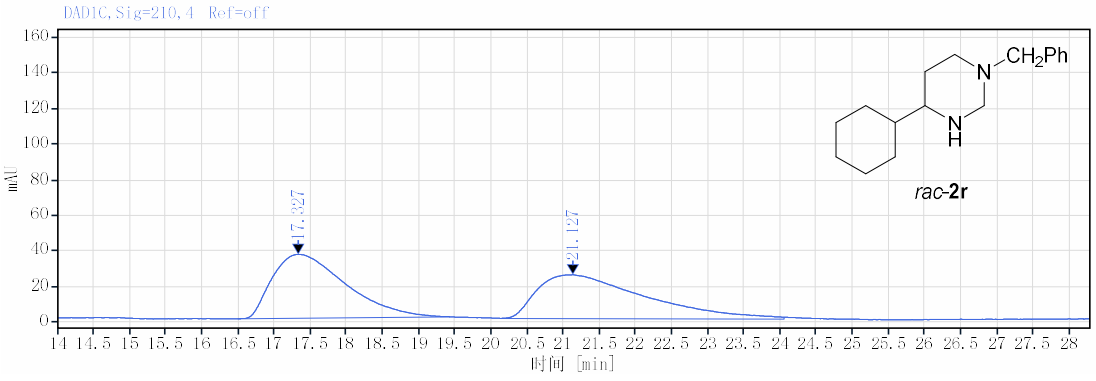


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.173	MM m	0.29	21003.41	1134.46	49.86
10.907	MM m	0.30	21123.16	1095.50	50.14

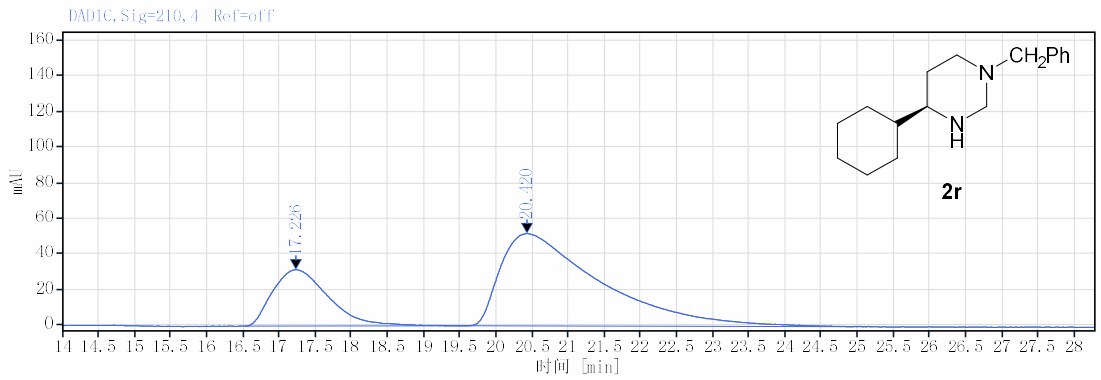


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.194	MM m	0.27	3097.14	174.91	20.77
10.934	MM m	0.29	11814.71	632.32	79.23

(*R*)-1-benzyl-4-cyclohexylhexahydropyrimidine (2r): 46 mg, 90% yield, colorless oil, 49% *ee*, $[\alpha]_D^{20}$ = −7.6 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak IC column, *n*-hexane/*i*-PrOH = 95/5; flow rate = 0.4 mL/min; UV detection at 210 nm; t_{R1} = 17.2 min (minor), t_{R2} = 20.4 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.31 (d, *J* = 4.4 Hz, 4H), 7.26 – 7.21 (m , 1H), 3.89 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.56 – 3.31 (m, 2H), 3.06 (d, *J* = 10.8 Hz, 1H), 3.03 – 2.95 (m, 1H), 2.32 – 2.23 (m, 1H), 2.15 – 2.06 (m, 1H), 1.85 (d, *J* = 12.8 Hz, 1H), 1.73 – 1.56 (m, 6H), 1.46 – 1.35 (m, 1H), 1.23 – 1.14 (m, 3H), 1.05 – 0.90 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 138.2, 129.3, 128.4, 127.2, 70.1, 60.4, 59.9, 53.0, 43.1, 29.7, 29.3, 26.8, 26.5. HRMS (ESI) m/z: calcd for $C_{17}H_{27}N_2$ $[M + H]^+$, 259.2169; found, 259.2171.

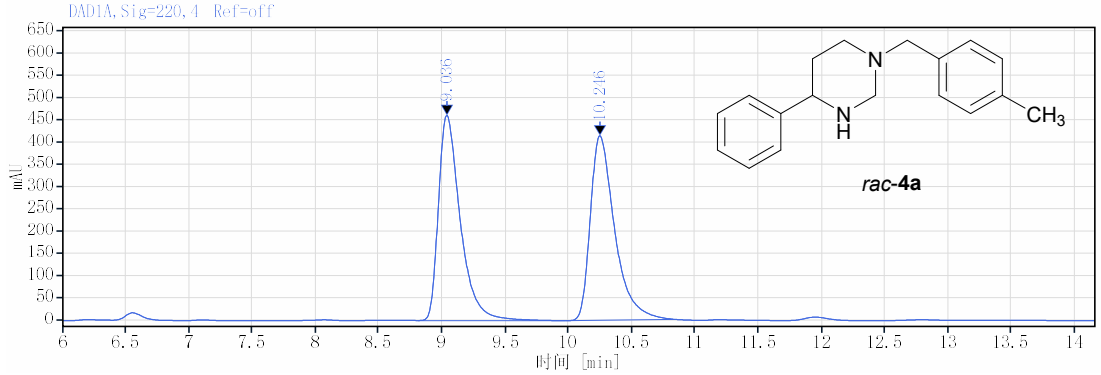


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
17.327	BM m	0.86	2534.22	35.94	49.93
21.127	BM m	1.22	2541.07	24.60	50.07

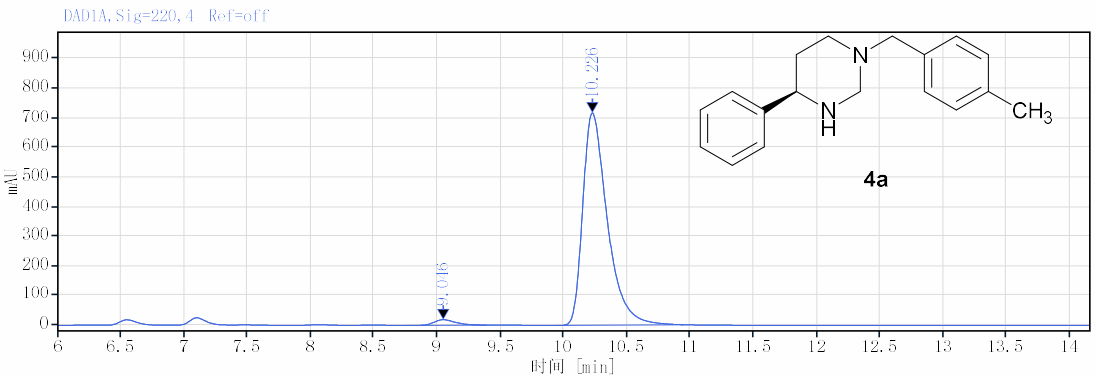


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
17.226	BM m	0.65	1703.56	31.73	25.51
20.420	BM m	1.18	4973.31	51.93	74.49

(*R*)-1-(4-methylbenzyl)-4-phenylhexahydropyrimidine (4a): 50 mg, 94% yield, white solid, 96% *ee*, mp = 81.5 – 84.3 °C. $[\alpha]_D^{20}$ = −9.3 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 9.0 min (minor), t_{R2} = 10.2 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.35 – 7.11 (m, 9H), 3.99 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.71 – 3.63 (m,1H), 3.61 – 3.38 (m, 2H), 3.27 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.05 (m, 1H), 2.37 – 2.26 (m, 4H), 1.87 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 136.8, 135.0, 129.3, 129.1, 128.6, 127.2, 126.5, 70.0, 59.8, 59.6, 52.9, 33.5, 21.2. HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_2$ $[M + H]^+$, 267.1856; found, 267.1857.

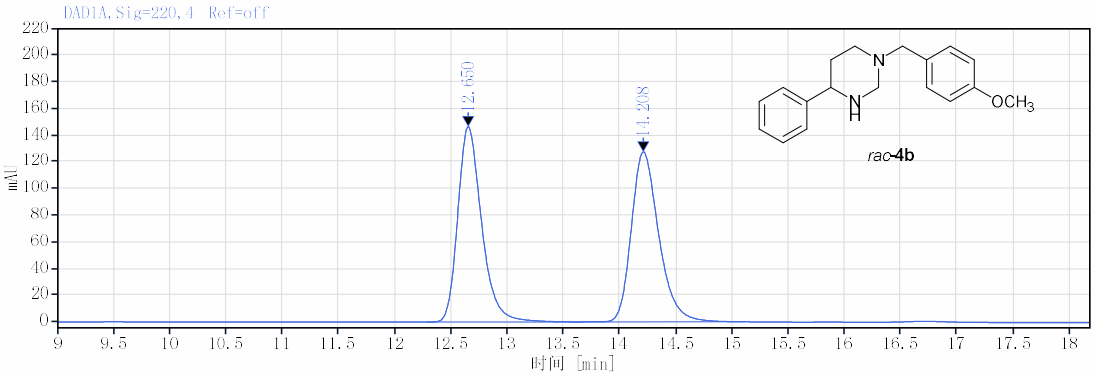


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.036	VB	1.17	5557.02	461.71	50.00
10.246	BM m	0.20	5557.52	415.00	50.00

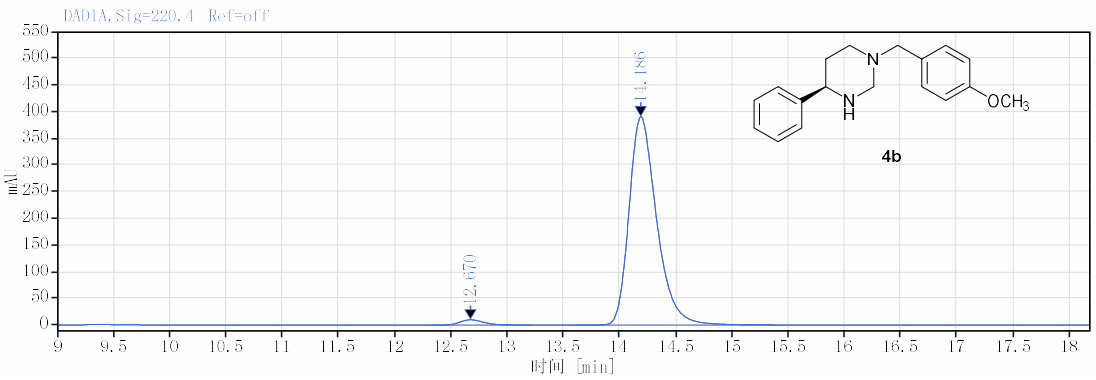


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.046	MM m	0.18	212.25	18.44	2.15
10.226	BM m	0.20	9652.15	716.89	97.85

(*R*)-1-(4-methoxybenzyl)-4-phenylhexahydropyrimidine (4b): 52 mg, 93% yield, white solid, 96% *ee*, mp = 70.3 – 73.5 ℃. $[\alpha]_D^{20}$ = −11.3 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 12.7 min (minor), t_{R2} = 14.2 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.36 – 7.22 (m, 7H), 6.91 – 6.82 (m, 2H), 3.99 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.78 (s, 3H), 3.66 – 3.41 (m, 3H), 3.26 (d, *J* = 10.8 Hz, 1H), 3.13 – 3.04 (m, 1H), 2.34 – 2.21 (m, 1H), 1.89 – 1.80 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.8, 143.6, 130.4, 129.9, 128.5, 127.1, 126.4, 113.7, 69.8, 59.6, 59.0, 55.3, 52.7, 33.4. HRMS (ESI) m/z: calcd for $C_{18}H_{23}N_2O$ $[M + H]^+$, 283.1805; found, 283.1807.

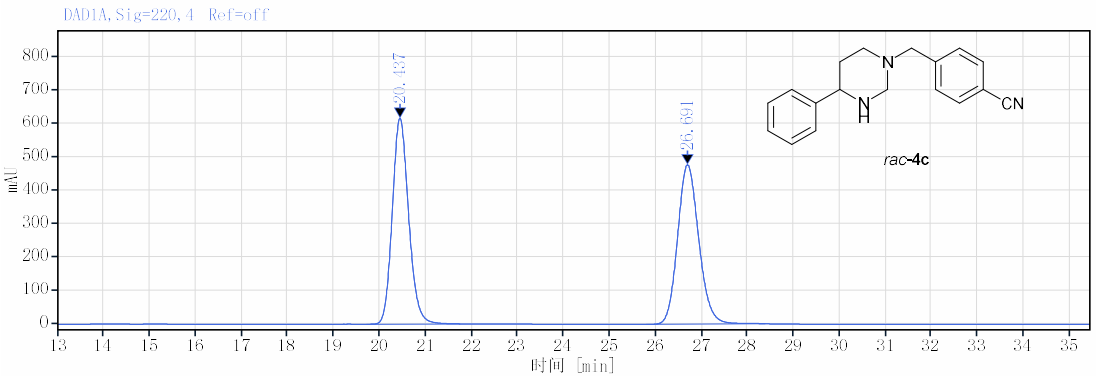


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
12.650	BB	1.34	2162.53	146.49	49.98
14.208	BM m	0.26	2164.04	127.44	50.02

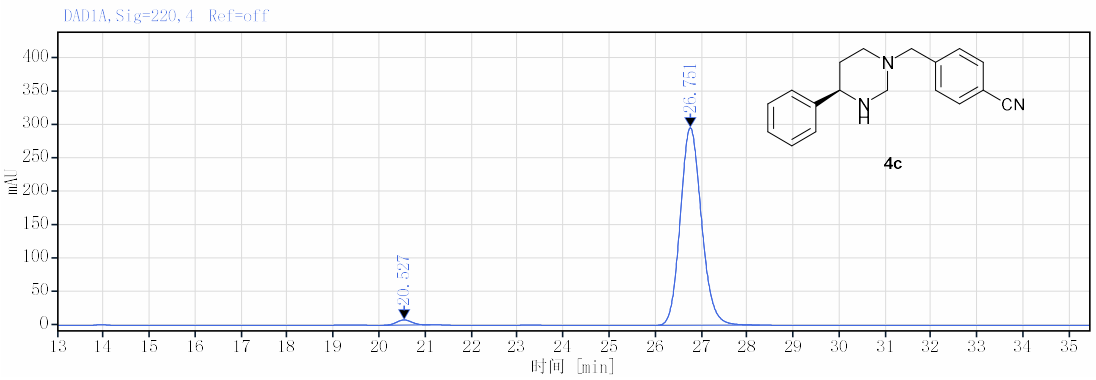


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
12.670	BM m	0.23	149.32	10.03	2.19
14.186	BM m	0.26	6660.61	390.68	97.81

(*R*)-4-((4-phenyltetrahydropyrimidin-1(2*H*)-yl)methyl)benzonitrile (4c): 50 mg, 90% yield, pale yellow oil, 96% *ee*, $[\alpha]_D^{20}$ = −8.0 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.4 mL/min; UV detection at 220 nm; t_{R1} = 20.5 min (major), t_{R2} = 26.8 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.62 (d, *J* = 8.0 Hz, 2H), 7.48 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.30 (m, 4H), 7.29 – 7.23 (m, 1H), 3.94 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.74 – 3.47 (m, 3H), 3.30 (d, *J* = 10.4 Hz, 1H), 3.07 – 2.98 (m, 1H), 2.42 –2.31 (m, 1H), 1.90 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 144.3, 143.5, 132.3, 129.6, 128.6, 127.4, 126.5, 119.1, 111.1, 69.9, 59.6, 59.1, 53.1, 33.3. HRMS (ESI) m/z: calcd for $C_{19}H_{20}N_3$ $[M + H]^+$, 278.1652; found, 278.1655.

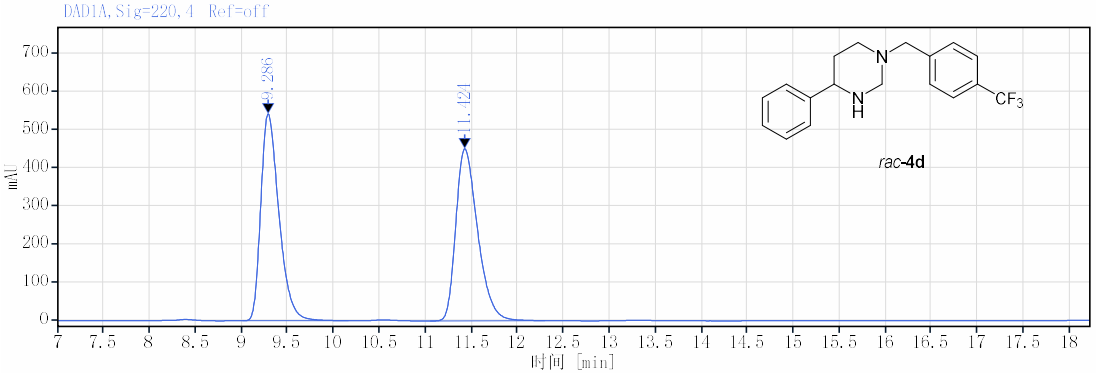


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
20.437	BM m	0.38	15292.59	617.49	50.01
26.691	BM m	0.49	15284.21	477.94	49.99

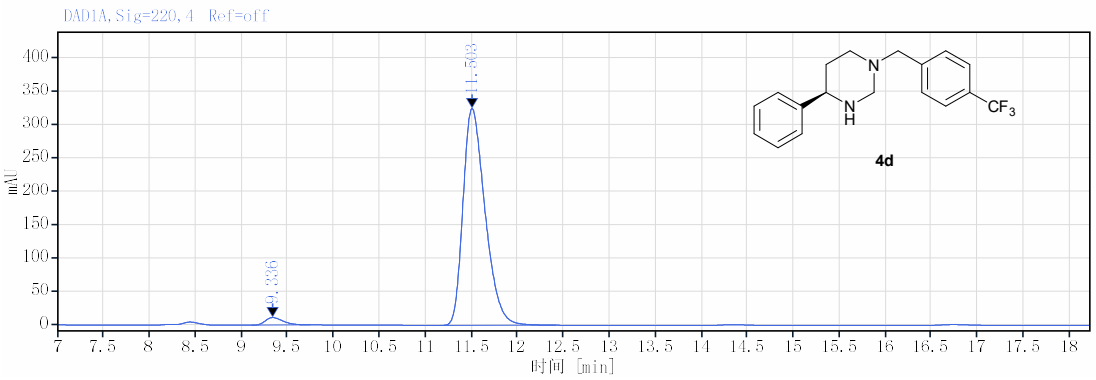


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
20.527	BM m	0.36	177.27	7.73	1.84
26.751	BM m	0.49	9473.03	296.42	98.16

(*R*)-4-phenyl-1-(4-(trifluoromethyl)benzyl)hexahydropyrimidine (4d): 58 mg, 90% yield, white solid, 95% *ee*, mp = 83.2 – 84.7 °C. $[\alpha]_D^{20}$ = −7.6 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 9.3 min (minor), t_{R2} = 11.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.59 (d, *J* = 8.0 Hz, 2H), 7.49 (d, *J* = 8.0 Hz, 2H), 7.39 – 7.31 (m, 4H), 7.27 – 7.23 (m, 1H), 3.97 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.73 – 3.45 (m, 3H), 3.34 (d, *J* = 10.8 Hz, 1H), 3.11 – 3.00 (m, 1H), 2.42 –2.30 (m, 1H), 1.89 – 1.8 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.6, 142.6, 129.7, 129.3, 128.6, 127.3, 126.5, 125.4 (q, *J* = 270.2 Hz), 125.4 (q, *J* = 3.8 Hz), 70.0, 59.7, 59.2, 53.0, 33.4. HRMS (ESI) m/z: calcd for $C_{18}H_{20}F_3N_2$ $[M + H]^+$, 321.1573; found, 321.1570.

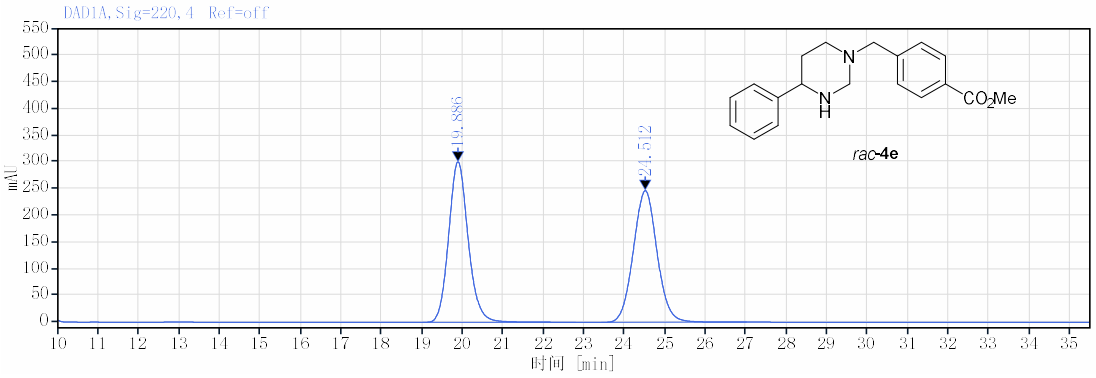


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.286	VB	1.15	7439.06	542.83	49.95
11.424	BM m	0.25	7453.80	451.67	50.05

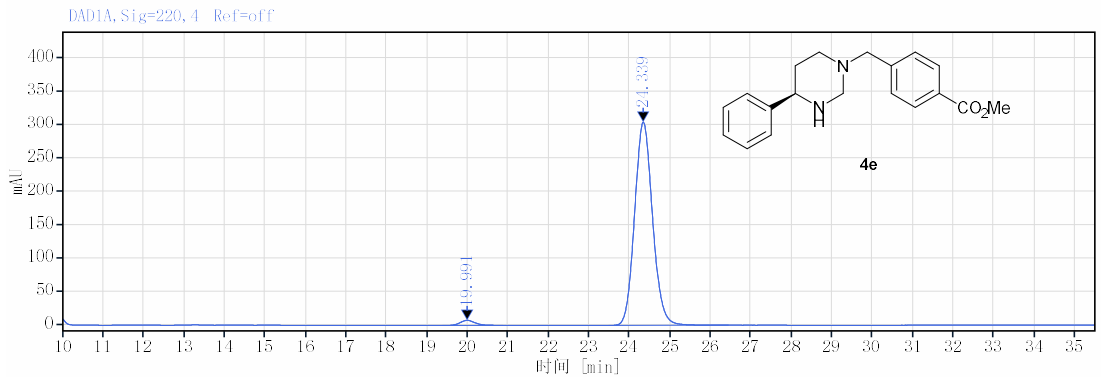


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.336	BM m	0.20	146.99	11.27	2.64
11.503	BM m	0.26	5421.59	325.22	97.36

methyl (*R*)-4-((4-phenyltetrahydropyrimidin-1(2*H*)-yl)methyl)benzoate (4e): 58 mg, 93% yield, white solid, 96% *ee*, mp = 95.8 – 98.9 °C $[\alpha]_D^{20}$ = −9.5 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 20.4 min (minor), t_{R2} = 25.0 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 8.00 (d, *J* = 8.4 Hz, 2H), 7.44 (d, *J* = 8.0 Hz, 2H), 7.38 – 7.22 (m, 5H), 3.97 (dd, *J* = 10.4, 1.6 Hz, 1H), 3.91 (s, 3H), 3.73 – 3.47 (m, 3H), 3.32 (d, *J* = 10.8 Hz, 1H), 3.11 – 3.01 (m, 1H), 2.40 – 2.30 (m, 1H), 1.89 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 167.2, 143.8, 143.6, 129.8, 129.2, 129.0, 128.6, 127.3, 126.5, 70.0, 59.6, 59.4, 53.0, 52.2, 33.4. HRMS (ESI) m/z: calcd for $C_{19}H_{23}N_2O_2$ $[M + H]^+$, 311.1754; found, 311.1754.

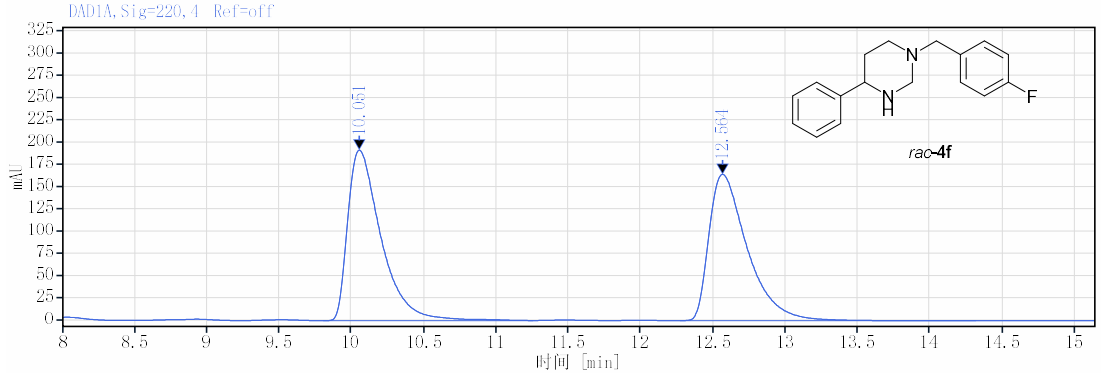


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
19.886	BB	3.80	10083.49	300.63	50.08
24.512	BB	3.59	10049.56	246.90	49.92

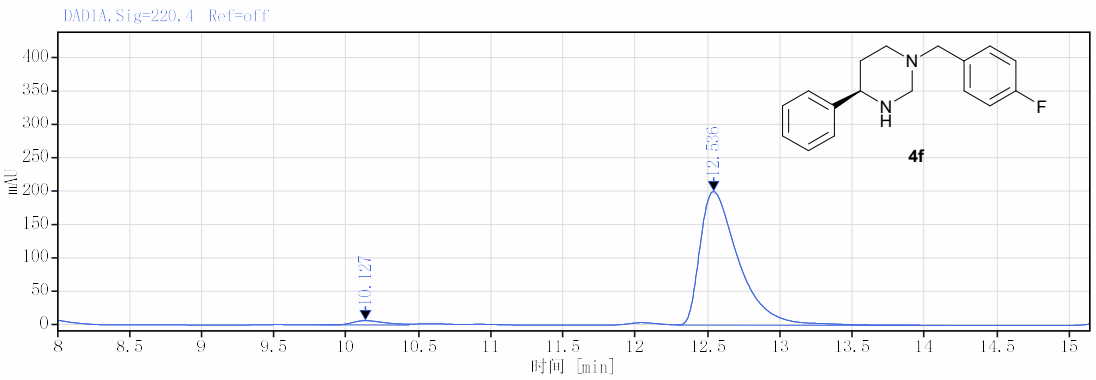


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
19.991	BB	1.49	193.77	7.59	2.02
24.339	BB	2.96	9393.07	304.85	97.98

(*R*)-1-(4-fluorobenzyl)-4-phenylhexahydropyrimidine (4f): 50 mg, 92% yield, white solid, 95% *ee*, mp = 83.5 – 88.1 °C. $[\alpha]_D^{20}$ = −7.5 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 10.1 min (minor), t_{R2} = 12.5 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.21 (m, 7H), 7.01 (t, *J* = 8.8 Hz, 2H), 3.98 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.72 – 3.62 (m, 1H), 3.60 – 3.38 (m, 2H), 3.28 (d, *J* = 10.8 Hz, 1H), 3.12 – 3.00 (m, 1H), 2.38 – 2.25 (m, 1H), 1.87 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 162.2 (d, *J* = 243.4 Hz), 143.7, 133.9 (d, *J* = 3.5 Hz), 130.7 (d, *J* = 7.9 Hz), 128.6, 127.3, 126.5, 115.2 (d, *J* = 21.1 Hz), 69.9, 59.7, 59.0, 52.9, 33.4. HRMS (ESI) m/z: calcd for $C_{17}H_{20}FN_2$ $[M + H]^+$, 271.1605; found, 271.1603.

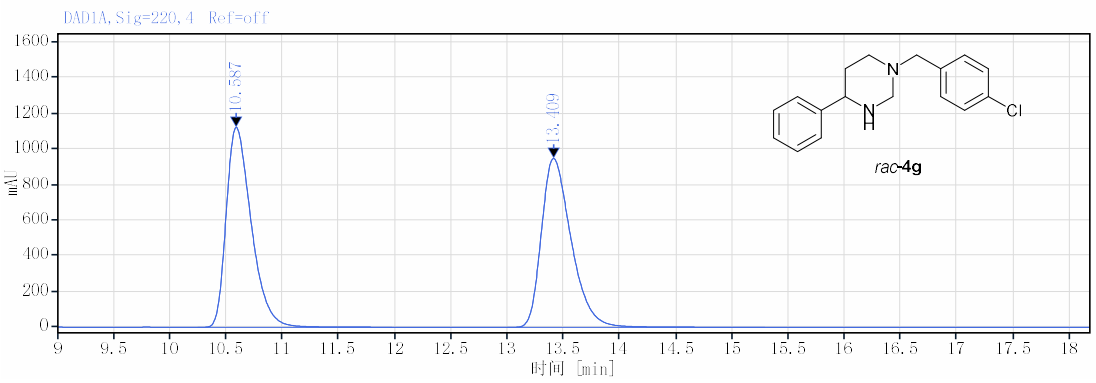


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.051	BV	1.45	3080.45	191.90	50.29
12.564	VB	2.05	3044.43	164.71	49.71

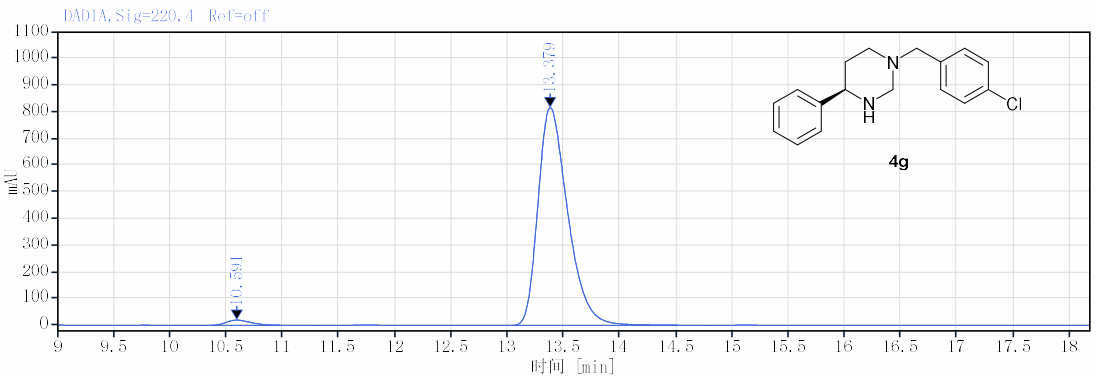


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.127	BM m	0.24	100.74	6.44	2.64
12.536	VB	1.88	3720.84	200.51	97.36

(*R*)-1-(4-chlorobenzyl)-4-phenylhexahydropyrimidine (4g): 53 mg, 92% yield, white solid, 96% *ee*, mp = 95.7 – 99.8 °C. $[\alpha]_D^{20}$ = −7.5 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 10.6 min (minor), t_{R2} = 13.4 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.38 – 7.24 (m, 9H), 3.96 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.74 – 3.64 (m, 1H), 3.62 – 3.38 (m, 2H), 3.29 (d, *J* = 10.8 Hz, 1H), 3.11 – 2.98 (m, 1H), 2.38 – 2.25 (m, 1H), 1.88 – 1.80 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 168.7, 153.6, 151.5, 134.6, 134.2, 133.0, 132.5, 131.1, 129.7, 129.1, 129.1, 118.8, 58.8. HRMS (ESI) m/z: calcd for $C_{17}H_{20}ClN_2$ $[M + H]^+$, 287.1310; found, 287.1309.

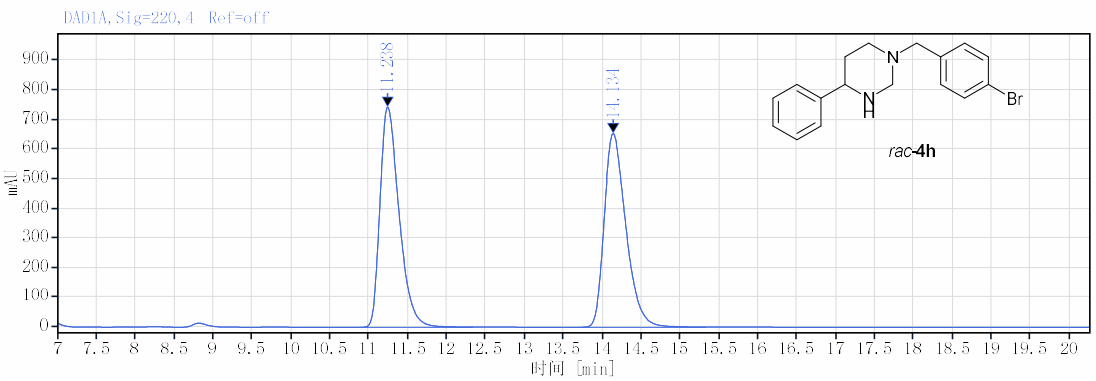


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.587	BB	1.73	17466.72	1124.80	49.99
13.409	BB	2.30	17472.74	949.87	50.01

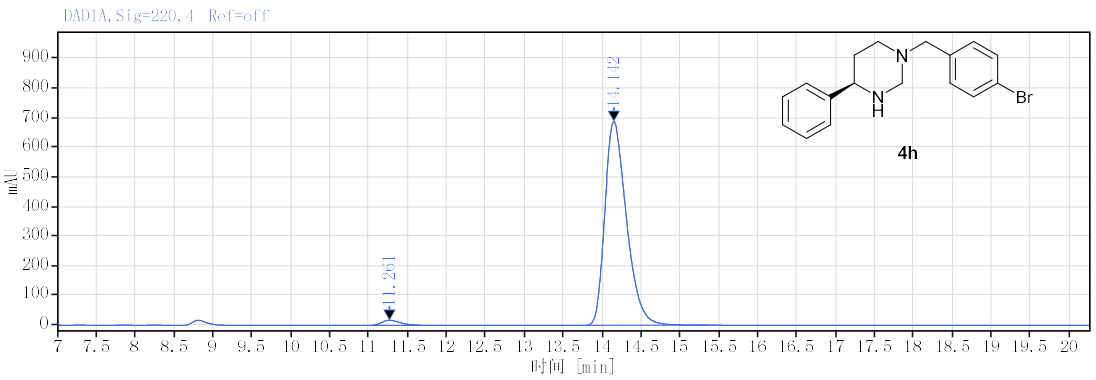


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
10.591	BB	1.02	315.82	19.93	2.06
13.379	BB	1.85	15024.01	816.74	97.94

(*R*)-1-(4-bromobenzyl)-4-phenylhexahydropyrimidine (4h): 60 mg, 91% yield, white solid, 96% *ee*, mp = 97.5 – 100.3 ℃. $[\alpha]_D^{20}$ = −10.1 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 11.3 min (minor), t_{R2} = 14.1 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.48 – 7.22 (m, 9H), 3.95 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.60 – 3.36 (m, 3H), 3.29 (d, *J* = 10.4 Hz, 1H), 3.10 – 3.00 (m, 1H), 2.27 – 2.26 (m, 1H), 1.87 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.7, 137.4, 131.5, 130.9, 128.6, 127.3, 126.5, 121.0, 69.9, 59.7, 59.0, 52.9, 33.4. HRMS (ESI) m/z: calcd for $C_{17}H_{20}BrN_2$ $[M + H]^+$, 331.0804; found, 331.0803.

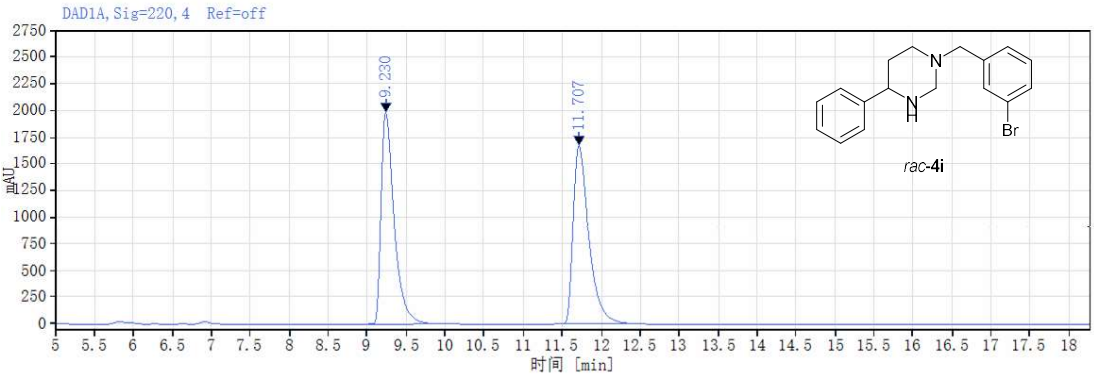


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.238	BV	1.46	12665.05	742.40	50.00
14.134	BV	1.63	12663.52	653.71	50.00

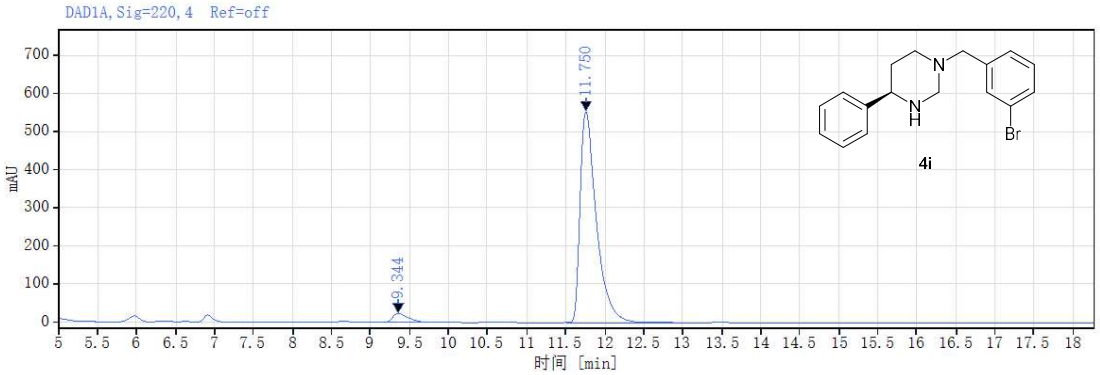


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.261	BM m	0.26	294.89	17.49	2.16
14.142	BM m	0.30	13328.12	687.99	97.84

(*R*)-1-(3-bromobenzyl)-4-phenylhexahydropyrimidine (4i): 61 mg, 92% yield, colorless oil, 93% *ee*. $[\alpha]_D^{20}$ = −9.31 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, hexane: isopropanol = 90:10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 9.3 min (minor), t_{R2} = 11.7 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.53 (t, *J* = 2.0 Hz, 1H), 7.41 – 7.15 (m, 8H), 3.96 (dd, *J* = 10.4, 2.0 Hz, 1H), 3.71 – 3.64 (m, 1H), 3.59 – 3.37 (m, 2H), 3.30 (d, *J* = 10.4 Hz, 1H), 3.12 – 3.02 (m, 1H), 2.39 – 2.25 (m, 1H), 1.91 – 1.82 (m, 2H). ^{13}C NMR (101 MHz, Chloroform-*d*) δ 143.6, 140.8, 132.0, 130.3, 123.0, 128.6, 127.7, 127.3, 126.5, 122.6, 69.9, 59.7, 59.1, 53.0, 33.4. HRMS (ESI) m/z: calcd for $C_{17}H_{20}BrN_2$ $[M + H]^+$, 331.0804; found, 331.0802.

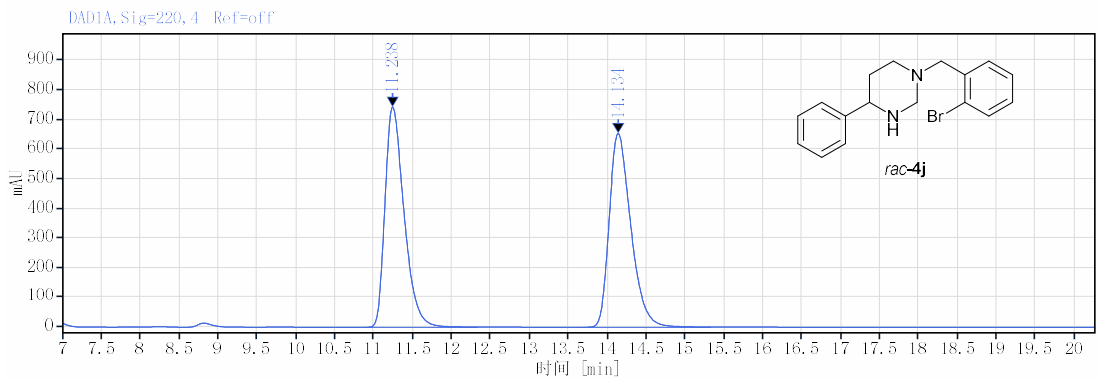


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.230	VM m	0.18	23295.34	1983.57	49.96
11.707	MM m	0.21	23330.06	1670.97	50.04

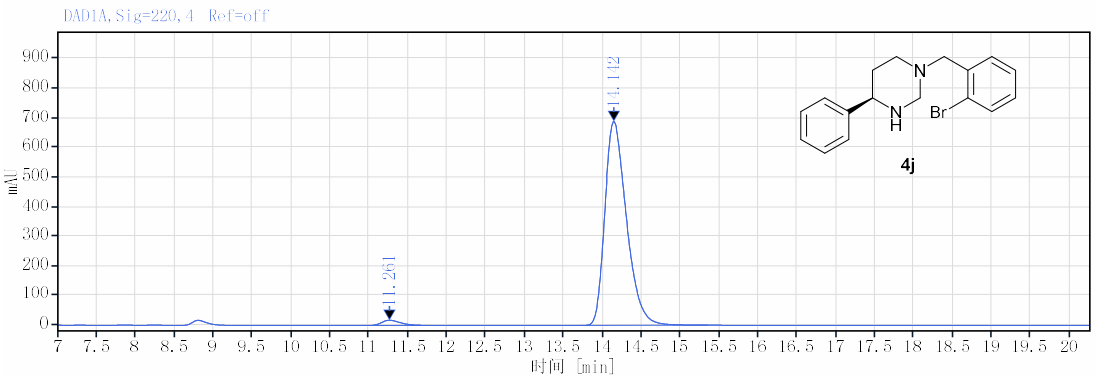


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.344	MM m	0.20	303.54	22.79	3.65
11.750	MM m	0.22	8018.52	554.36	96.35

(*R*)-1-(2-bromobenzyl)-4-phenylhexahydropyrimidine (4j): 60 mg, 91% yield, colorless oil, 95% *ee*, $[\alpha]_D^{20}$ = −9.7 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 11.3 min (minor), t_{R2} = 14.1 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.58 – 7.48 (m, 2H), 7.39 – 7.22 (m, 6H), 7.15 – 7.07 (m, 1H), 4.00 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.75 – 3.40 (m, 4H), 3.18 – 3.09 (m, 1H), 2.54 – 2.44 (m, 1H), 1.95 – 1.83 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 137.8, 132.9, 130.9, 128.7, 128.6, 127.4, 127.2, 126.5, 124.8, 69.8, 59.6, 58.5, 53.1, 33.4. HRMS (ESI) m/z: calcd for $C_{17}H_{20}BrN_2$ $[M + H]^+$, 331.0804; found, 331.0803.

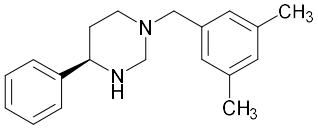


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.238	BV	1.46	12665.05	742.40	50.00
14.134	BV	1.63	12663.52	653.71	50.00

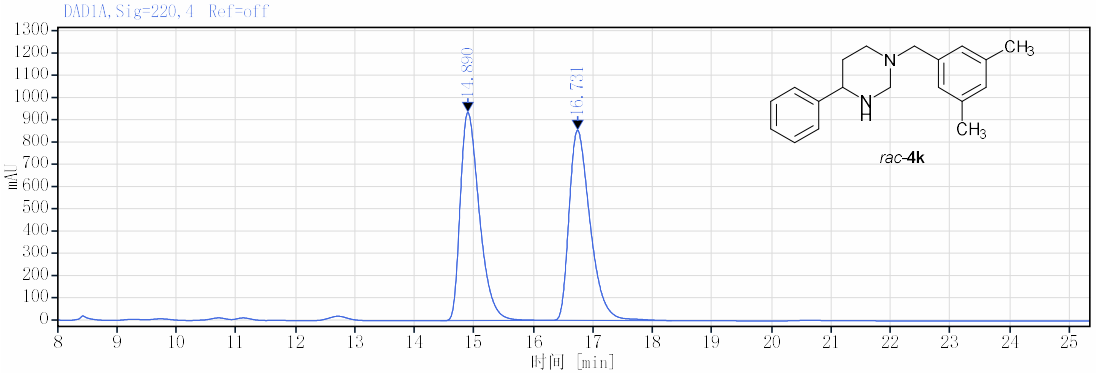


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.261	BM m	0.26	294.89	17.49	2.16
14.142	BM m	0.30	13328.12	687.99	97.84

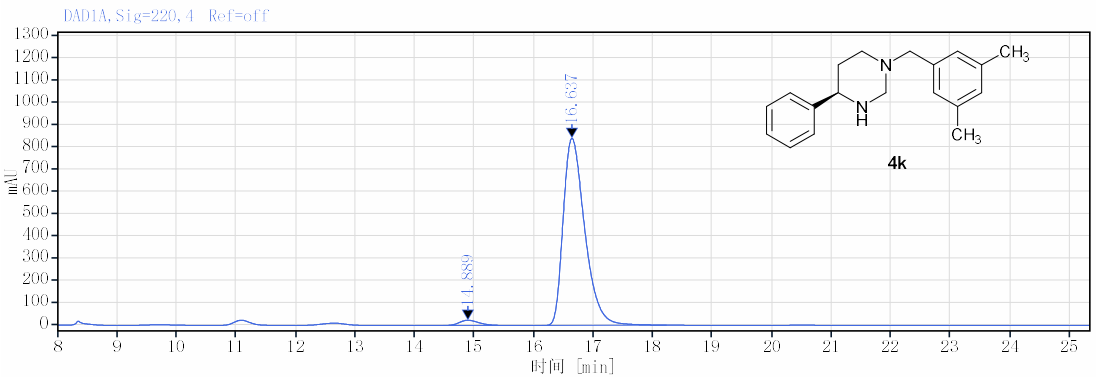
(*R*)-1-(3,5-dimethylbenzyl)-4-phenylhexahydropyrimidine (4k): 53 mg, 94% yield, colorless oil, 95% *ee*,



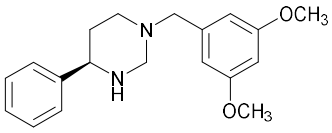
$[\alpha]_D^{20}$ = −7.9 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 14.9 min (minor), t_{R2} = 16.6 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.22 (m, 5H), 6.96 (s, 2H), 6.90 (s, 1H), 4.00 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.72 – 3.63 (m, 1H), 3.57 – 3.34 (m, 2H), 3.27 (d, *J* = 10.8 Hz, 1H), 3.16 – 3.06 (m, 1H), 3.38 – 3.25 (m, 7H), 1.92 – 1.80 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 137.9, 137.9, 128.9, 128.6, 127.2, 127.2, 126.5, 70.1, 59.8, 59.7, 53.0, 33.4, 21.4. HRMS (ESI) m/z: calcd for $C_{19}H_{25}N_2$ $[M + H]^+$, 281.2012; found, 281.2011.

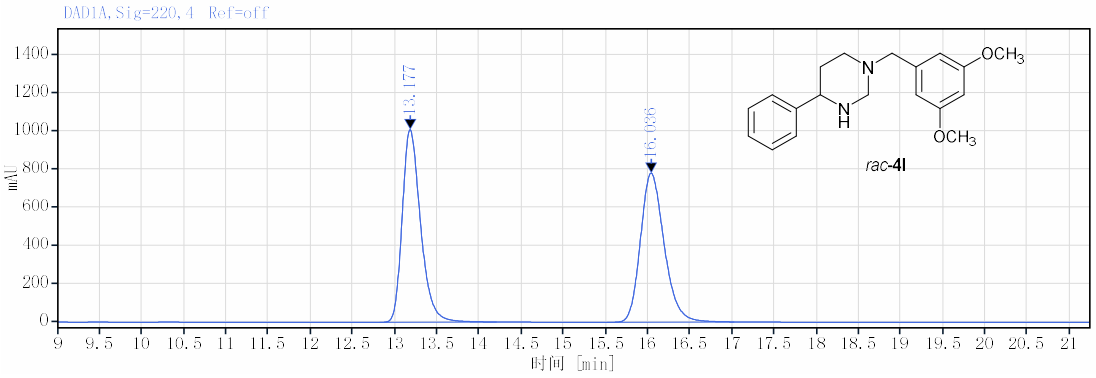


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
14.890	BB	1.86	20858.74	936.85	49.91
16.731	BM m	0.38	20935.34	855.30	50.09

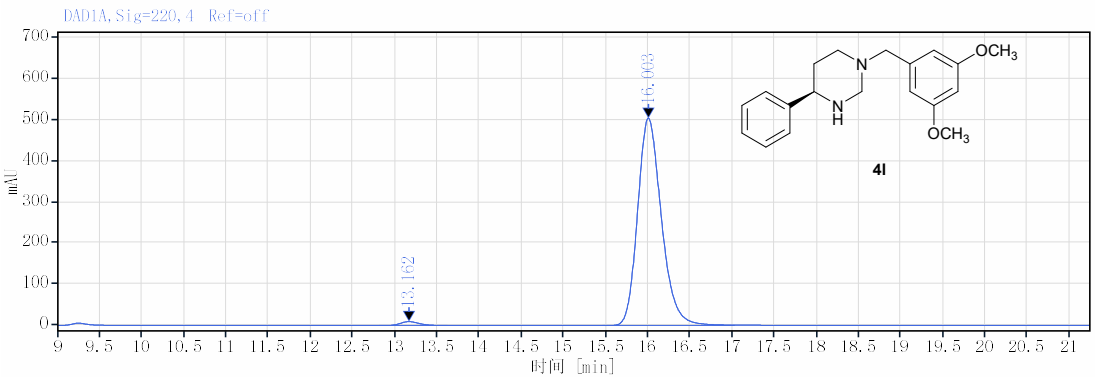


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
14.889	MM m	0.34	518.70	23.25	2.39
16.637	VM m	0.39	21156.19	841.66	97.61

(*R*)-1-(3,5-dimethoxybenzyl)-4-phenylhexahydropyrimidine (4l): 57 mg, 92% yield, colorless oil, 97% *ee*,  $[\alpha]_D^{20}$ = −11.3 (*c* = 0.5, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 13.2 min (minor), t_{R2} = 16.0 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.21 (m, 5H), 6.96 (s, 2H), 6.90 (s, 1H), 4.00 (dd, *J* = 10.8, 2.0 Hz, 1H), 3.72 – 3.64 (m, 1H), 3.57 – 3.34 (m, 2H), 3.27 (d, *J* = 10.8 Hz, 1H), 3.15 – 3.06 (m, 1H), 3.36 – 3.25 (m, 7H), 1.92 – 1.82 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 143.8, 137.9, 137.9, 128.9, 128.6, 127.2, 127.2, 126.5, 70.1, 59.8, 59.7, 53.0, 33.4, 21.4. HRMS (ESI) m/z: calcd for $C_{19}H_{25}N_2O_2$ $[M + H]^+$, 313.1911; found, 313.1910.



RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
13.177	BM m	0.23	15299.29	1011.21	49.98
16.036	BM m	0.30	15311.18	782.33	50.02



RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
13.162	BM m	0.24	149.89	9.64	1.49
16.003	BM m	0.30	9914.59	504.82	98.51

2.4 General procedure for asymmetric hydrogenation under continuous flow

All process parts, including fittings, tubes, valves and junctions that hold pressure were purchased from SHENZHEN INSFTECH CO,. Ltd. The specification of the reaction coil is 0.5 ml/m. The information of other main components is summarized in Table S1.

Table S1 Components details of reactor system

Name	Information
Pump	Sanotac high pressure HPLC pump AP0030 (0-10 mL/min; 20 MPa)
MFC	SHENZHEN INSFTECH CO,. Ltd. FCM-1050 (0-500sccm,10MPa)
BPR	SHENZHEN INSFTECH CO,. Ltd. FAV-1500B (0-500mL/min, 10MPa)
Mixer	SHENZHEN INSFTECH CO,. Ltd. MGL-2000（200*250μm，2000Psi）

A mixture of $[Ir(COD)Cl]_2$ (1.0 mol%) and (*S*,*S*)-f-Binaphane (2.2 mol%) was dissolved in a degassed solvent DCM/$CHCl_3$ at argon atmosphere, and the resulting solution was allowed to be stirred at room temperature for 30 min. Then, N-benzyl-4-phenylpyrimidinium bromide **1a** (1.0 equiv.) was added. The process was washed by DCM/$CHCl_3$ at a liquid flow rate of 5 mL/min and gas flow rate of 10 sccm (avoid back flow of liquid to gas flow meter) for 10 minutes and then pressurized the BPR. After the reactor was pressurized to 8 MPa, the aforehand reaction medium was pumped instead of solvent. Liquid flow rate was set at 0.5 mL/min and gas flow rate was keeping 120 sccm. The liquid holding capacity of the reaction coil can be adjusted according to the needs. The conversion and *ee* value were analyzed by NMR and HPLC. When reaction finished, system was depressurized by releasing the gas of Equilibar BPR slowly, and washed the whole system by pumping ethanol for 10 minutes.

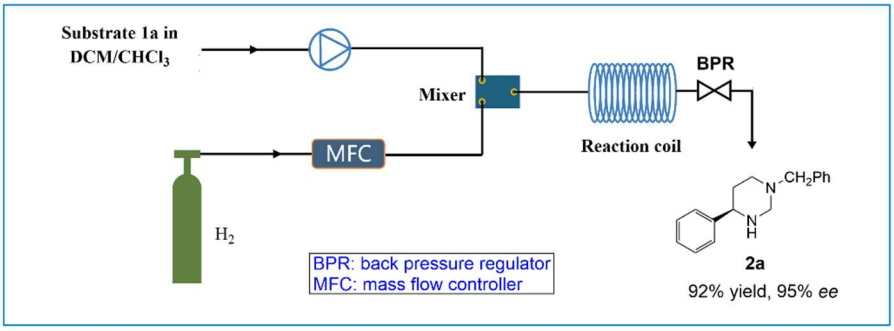
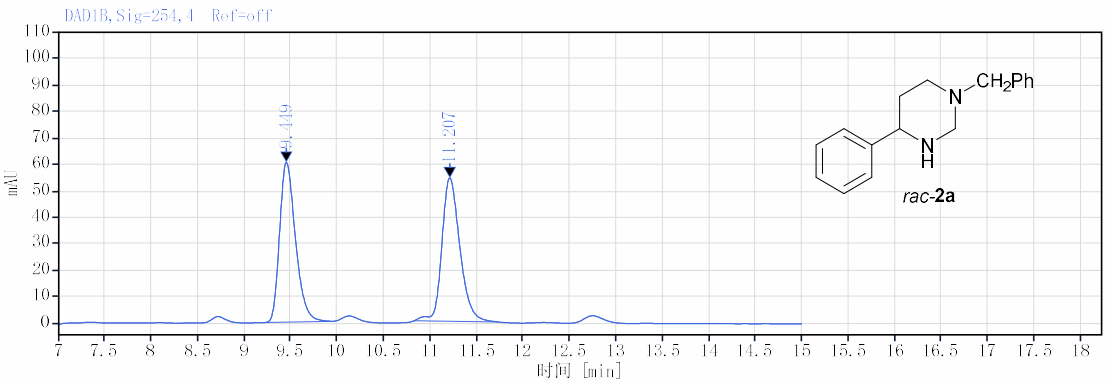
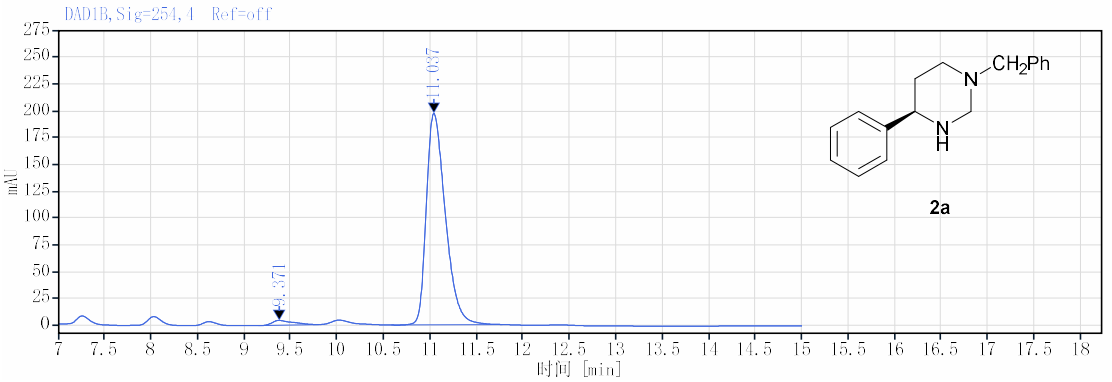


Figure S1 AH of **1a** under continuous flow.



RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.449	MM m	0.18	716.46	60.33	49.57
11.207	MM m	0.20	728.86	54.18	50.43



RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
9.371	MM m	0.22	68.63	4.48	2.38
11.037	MM.m	0.22	2809.91	197.25	97.62

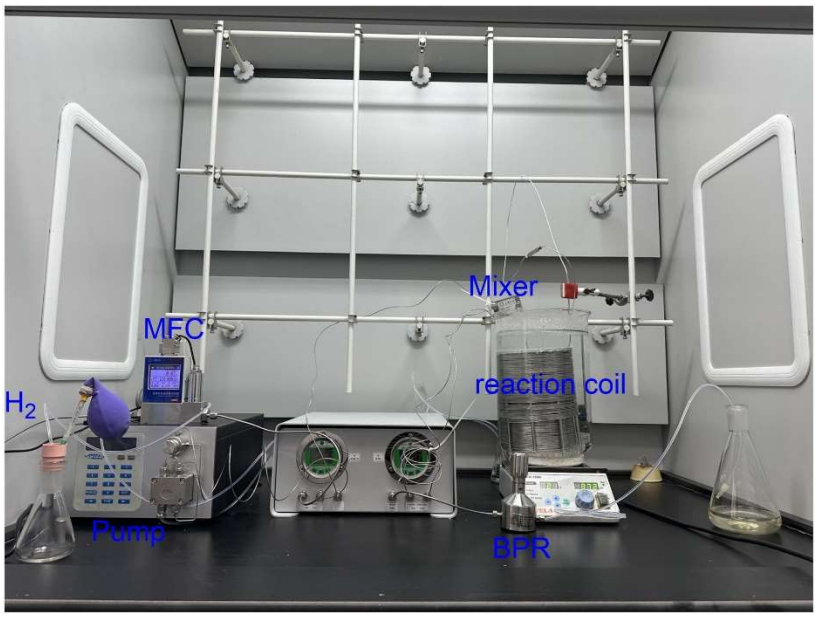
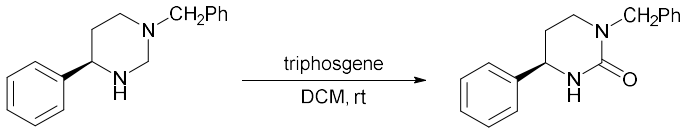


Figure S2 Set-up for asymmetric hydrogenation under continuous flow.

1-benzyl-4-phenyl-1,6-dihydropyrimidine (9): ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.67 – 7.64 (m, 2H), 7.40 – 7.23 (m, 9H), 5.35 – 5.34 (m, 1H), 4.20 (s, 2H), 4.05 (d, *J* = 3.6 Hz, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 151.4, 142.3, 138.4, 134.8, 129.0, 128.3, 128.3, 128.0, 127.8, 125.2, 99.8, 56.9, 45.4. HRMS (ESI) m/z: calcd for $C_{17}H_{17}N_2$ [M + H]$^+$, 249.3365.; found, 249.3364.

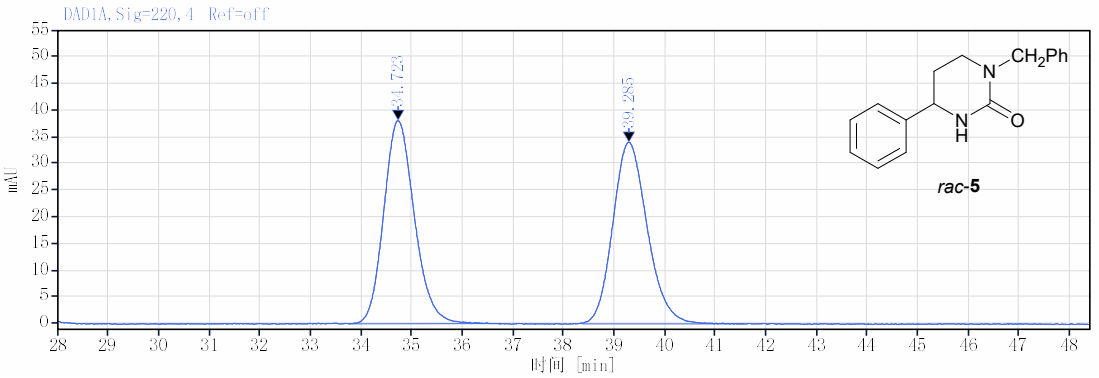
2.5 Product thansformations



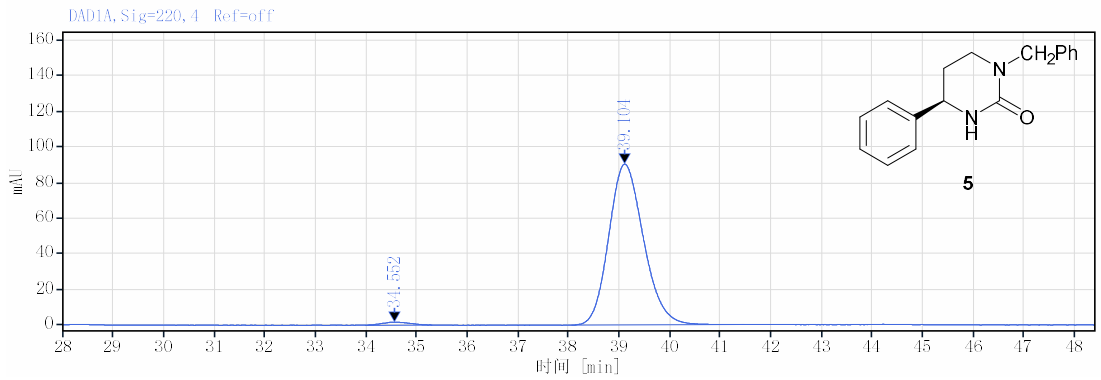
2a **5**

To a solution of **2a** (0.2 mmol, 1.0 equiv.) in DCM (1.0 mL) was added triphosgene (0.12 mmol, 0.6 equiv.). After stirring 15 min at room temperature, the reaction was quenched with saturated aqueous Na_2CO_3 solution, and the combined aqueous layers were extracted with DCM. The combined organic portions were washed with brine, dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica gel flash chromatography using dichloromethane/methanol as eluent to give **5**.

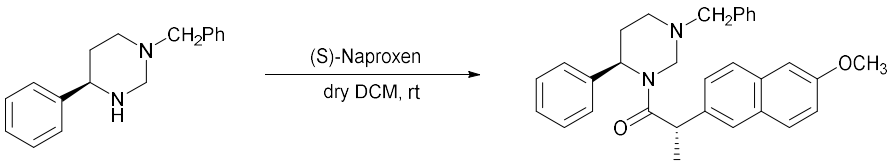
(*R*)-1-benzyl-4-phenyltetrahydropyrimidin-2(1*H*)-one (5): 49 mg, 85% yield, white solid, 97% *ee*, mp = 155.2 – 157.3 °C $[\alpha]_D^{20}$ = −3.3 (*c* = 0.17, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 34.6 min (minor), t_{R2} = 39.1 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.45 – 7.26 (m, 10H), 4.90 (s, 1H), 4.67 – 4.49 (m, 3H), 3.27 – 3.18 (m, 1H), 3.16 – 3.05 (m, 1H), 2.19 – 2.06 (m, 1H), 2.00 – 1.86 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 156.4, 142.4, 138.1, 128.9, 128.7, 128.08, 128.06, 127.4, 126.2, 55.5, 50.8, 43.2, 31.2. HRMS (ESI) m/z: calcd for $C_{17}H_{19}N_2O$ [M + Na]$^+$, 289.1311; found, 289.1307.



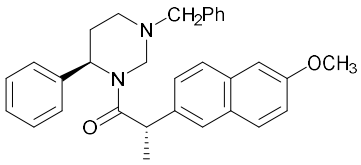
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [2mAu]	Area%
34.723	BM m	0.62	1607.20	38.09	49.96
39.285	VM m	0.68	1609.52	34.04	50.04

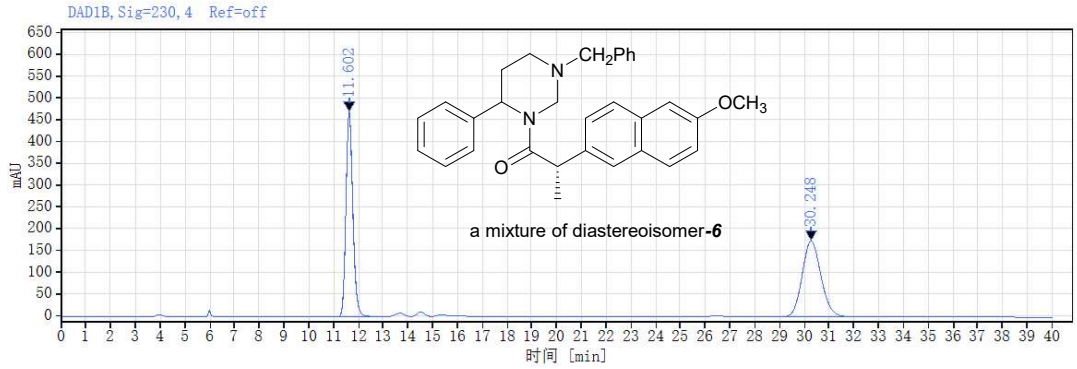


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
34.552	VM m	0.46	66.13	1.70	1.51
39.104	MM m	0.71	4310.06	90.39	98.49

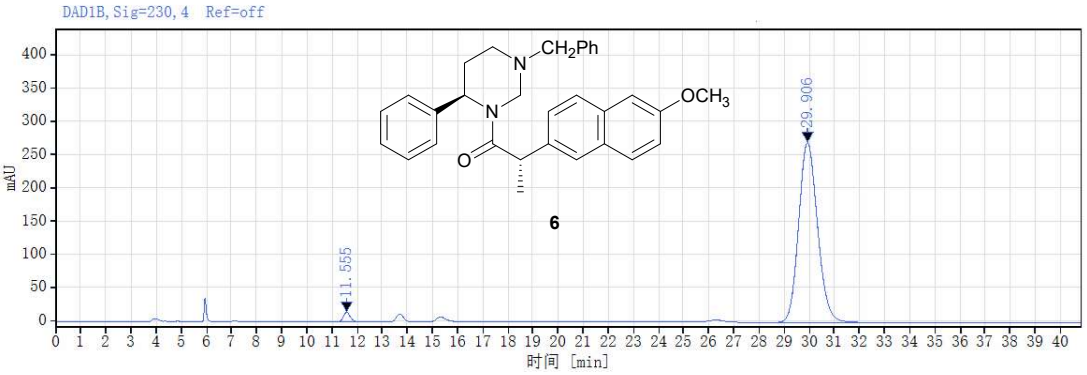


To a solution of **2a** (0.2 mmol, 1.0 equiv.) in dryDCM (1.0 mL) was added a solution of **10** (0.24 mmol, 1.2 equiv.)[3] in dryDCM (1.0 mL) via syringe. After stirring 12 h at room temperature, the resulting mixture was quenched by water and then extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica gel flash chromatography using petroleum ether as eluent to give **6**.

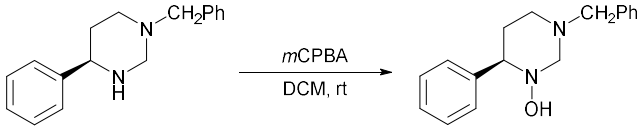
(*S*)-1-((*R*)-3-benzyl-6-phenyltetrahydropyrimidin-1(2*H*)-yl)-2-(6-methoxynaphthalen-2-yl)propan-1-one (6):  75 mg, 81% yield, white solid, HPLC analysis of the crude mixture revealed that the *dr* value was >20:1, mp = 115.8 – 118.5 ℃. $[\alpha]_D^{20}$ = 19.30 (*c* = 0.43, $CHCl_3$). The diastereomeric excess was determined by HPLC on Chiralpak IC column, hexane: isopropanol = 80:20; flow rate = 0.8 mL/min; UV detection at 230 nm; t_{R1} = 11.6 min (minor), t_{R2} = 29.9 min (major)). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.98 – 6.57 (m, 16H), 6.27 – 5.56 (m, 1H), 4.85– 4.30 (m, 1H), 4.20 – 4.02 (m, 1H), 3.92 (s, 3H), 3.70 – 2.80 (s, 3H), 2.75 – 2.50 (m, 1H), 2.49 – 2.04 (m, 3H), 1.59 (d, *J* = 6.0 Hz, 3H). ^{13}C NMR (100 MHz, DMSO-d_6) δ 173.7, 157.6, 139.1, 137.7, 137.0, 133.7, 129.4, 129.6, 128.9, 128.7, 128.3, 127.4, 127.1, 127.0, 126.8, 126.6, 126.0, 118.9, 105.7, 63.6, 58.4, 55.5, 50.0, 47.3, 43.2, 25.4, 20.8. HRMS (ESI) m/z: calcd for $C_{31}H_{33}N_2O_2$ $[M + H]^+$, 464.2464; found, 464.2463.



RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.602	BB	2.34	9134.69	470.37	49.86
30.248	BM m	0.82	9187.16	174.37	50.14

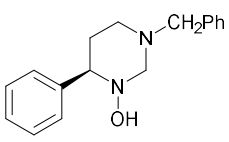


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
11.555	VB	1.35	292.27	14.81	2.02
29.906	BB	5.43	14185.19	270.88	97.98



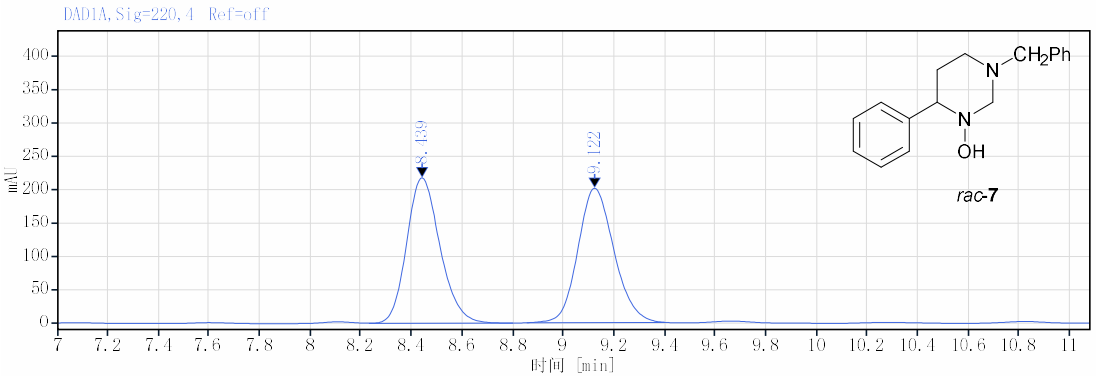
2a **7**

To a solution of **2a** (0.2 mmol, 1.0 equiv.) in DCM (1.0 mL) was added 3-chloroperoxybenzoic acid (0.22 mmol, 1.1 equiv.). After stirring 10 min at room temperature, the reaction was quenched with 1.0 M NaOH solution. The resulting mixture was extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica gel flash chromatography using dichloromethane/methanol as eluent to give **7**.



(*R*)-3-benzyl-6-phenyltetrahydropyrimidin-1(2*H*)-ol (7): 49 mg, 91% yield, colorless oil, 96% *ee*. $[\alpha]_D^{20}$ = 25.9 (*c* = 0.24, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralpak AD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 8.3 min (minor), t_{R2} = 8.9 min (major). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.40 – 7.29 (m, 10H), 4.33 (s, 2H), 4.20 – 4.12 (m, 1H), 4.03 – 3.84 (m, 2H), 3.14 – 3.06 (m, 1H), 2.97 – 2.85 (m, 1H), 2.13 – 2.04 (m, 1H), 1.88 – 1.74 (m, 1H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 145.9, 137.9, 129.3, 128.6, 128.4, 127.4, 126.7, 126.1, 82.3, 64.2, 57.8, 57.7, 40.2.

HRMS (ESI) m/z: calcd for $C_{17}H_{21}N_2O$ $[M + H]^+$, 269.1648; found, 269.1644.



RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
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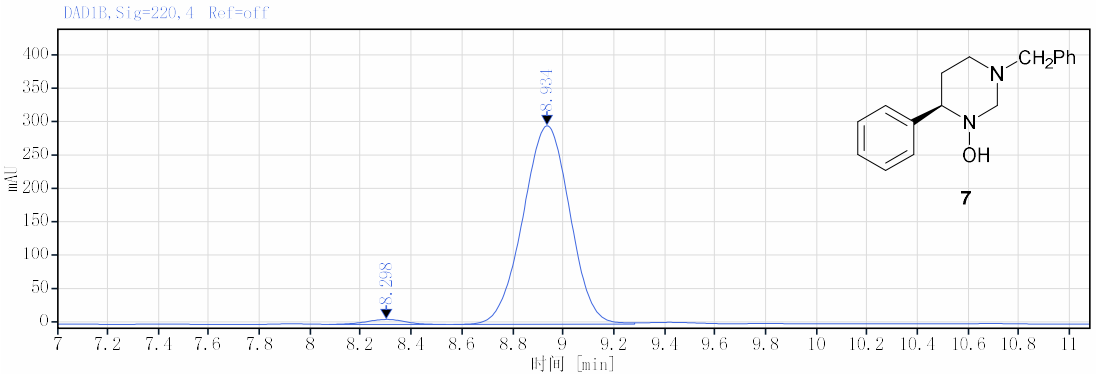
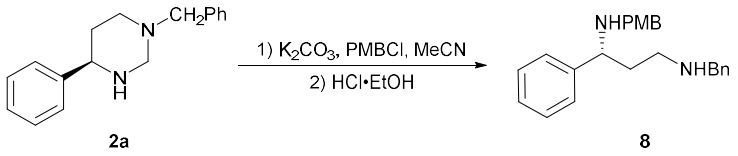
9.122	MM m	0.15	1996.30	201.63	49.97



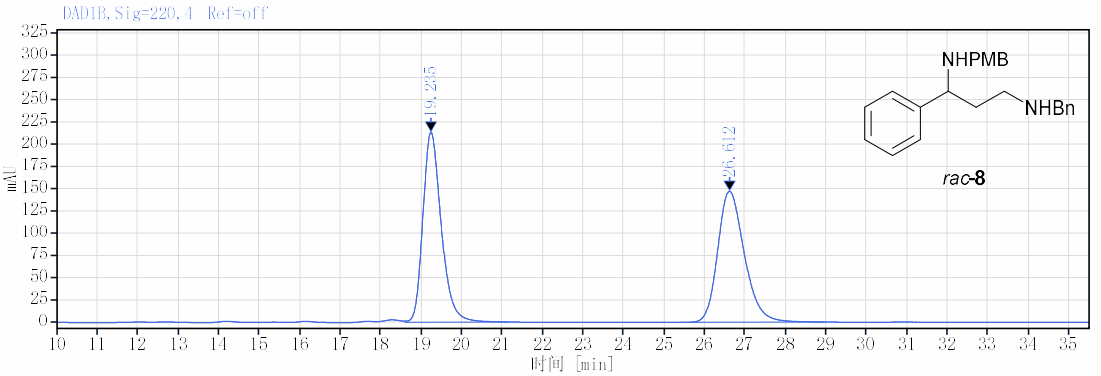
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
8.298	VB	0.46	80.01	7.49	2.05
8.934	BV	0.72	3831.22	297.80	97.95



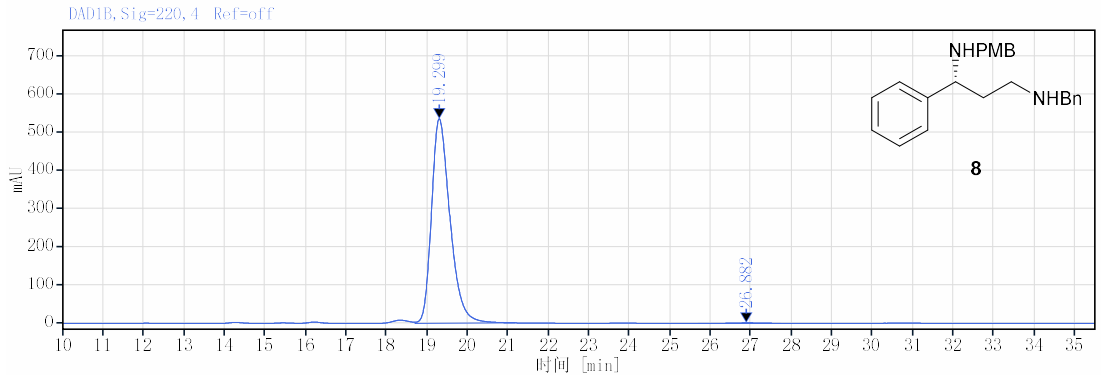
2a **8**

To a solution of **2a** (0.2 mmol, 1.0 equiv.) in MeCN (2.0 mL) was added potassium carbonate (0.4 mmol, 2 equiv.) and 4-methoxybenzylchloride (0.3 mmol, 1.5 equiv.). After stirring 2 h at 60 ℃, the mixture was cooled and filtered. The solvent was evaporated from the filtrate. The residue was dissolved in EtOH (1.0 mL) and added 2.0 M HCl ethanol solution (1.0 mL, 5.0 equiv.). The mixture was stirring 12 h at 75 ℃ and then the mixture was cooled. The volatiles was removed under reduced pressure. The residue was slurried with Et_2O at room temperature for 12 h and then filtered. The residue was added DCM and saturated aqueous $NaHCO_3$ solution and then extracted with DCM. The combined organic layers were washed with brine, dried over Na_2SO_4, filtered, and evaporated in vacuo. The residue was purified by silica gel flash chromatography using dichloromethane/methanol as eluent to give **8**.

(*R*)-N^3-benzyl-N^1-(4-methoxybenzyl)-1-phenylpropane-1,3-diamine (8): 29 mg, 65% yield, colorless oil, 99% *ee*, $[\alpha]_D^{20}$ = 16.5 (*c* = 0.20, $CHCl_3$). The enantiomeric excess was determined by HPLC on Chiralcel OD-H column, *n*-hexane/*i*-PrOH = 90/10; flow rate = 0.6 mL/min; UV detection at 220 nm; t_{R1} = 19.3 min (major), t_{R2} = 26.9 min (minor). ^{1}H NMR (400 MHz, Chloroform-*d*) δ 7.37 – 7.23 (m, 10H), 7.15 (d, *J* = 8.4 Hz, 2H), 6.82 (d, *J* = 8.4 Hz, 2H), 3.79 (s, 3H), 3.76 – 3.66 (m, 3H), 3.61 – 3.40 (m, 2H), 2.68 – 2.67 (m, 2H), 1.88 – 1.81 (m, 2H). ^{13}C NMR (100 MHz, Chloroform-*d*) δ 158.7, 144.2, 140.4, 132.9, 129.4, 128.6, 128.5, 128.3, 127.3, 127.2, 127.0, 113.9, 61.6, 55.4, 54.2, 50.9, 47.3, 38.2. HRMS (ESI) m/z: calcd for $C_{24}H_{29}N_2O$ $[M + H]^+$, 361.2274; found, 361.2269.



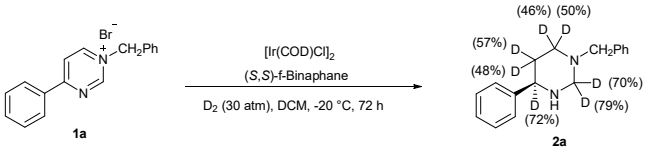
RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
19.235	VM m	0.48	6750.39	213.99	50.01
26.612	BM m	0.70	6746.90	147.39	49.99

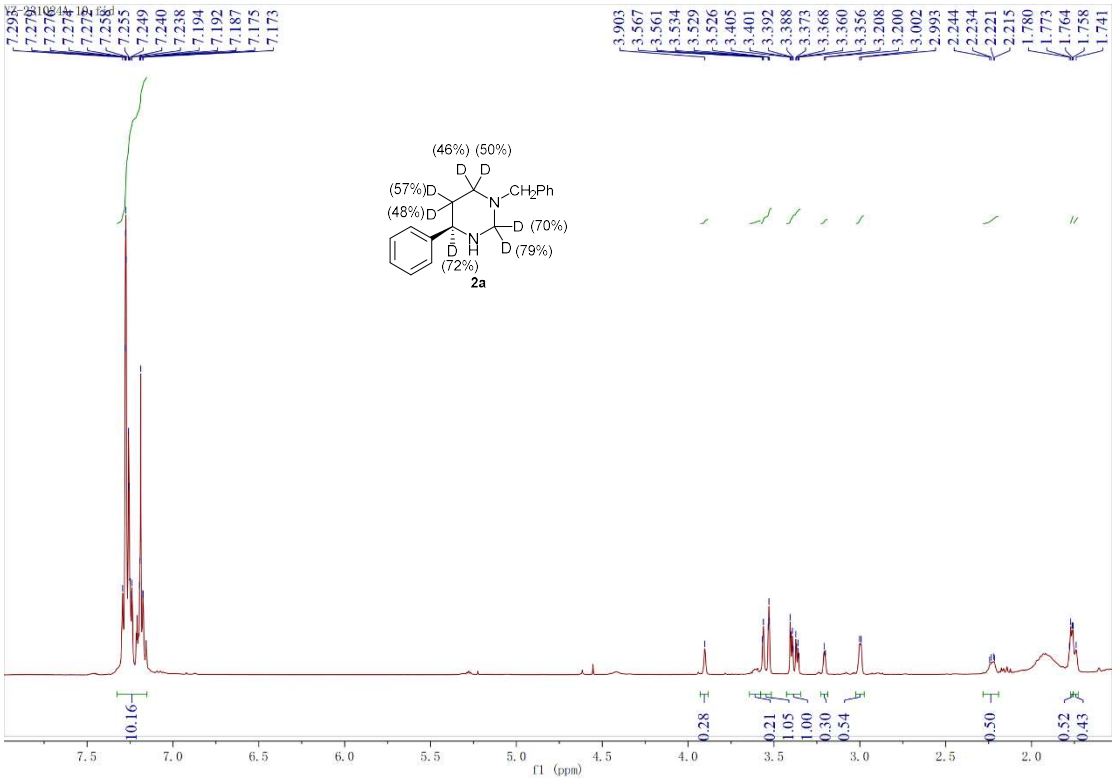


RetTime [min]	Type	Wide [min]	Area [mAu * s]	Height [mAu]	Area%
19.299	VM m	0.49	17098.76	536.75	99.72
26.882	MM m	0.51	48.15	1.12	0.28

2.6 Result of deuterium labeling experiments

Following standard hydrogenation procedure, deuterium labeling experiments were conducted with specific modification.





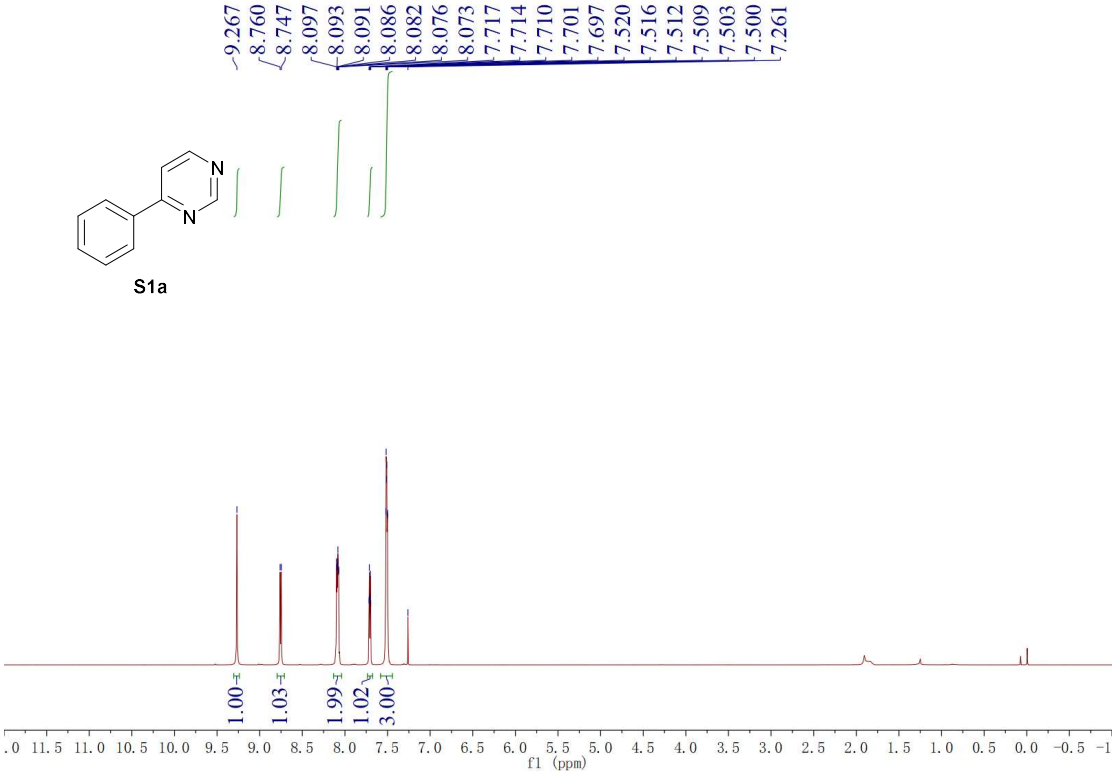
3. References

(1) J. Wang, S. Wang, G. Wang, J. Zhang and X.-Q. Yu, *Chem. Commun.*, 2012, **48**, 11769–11771.

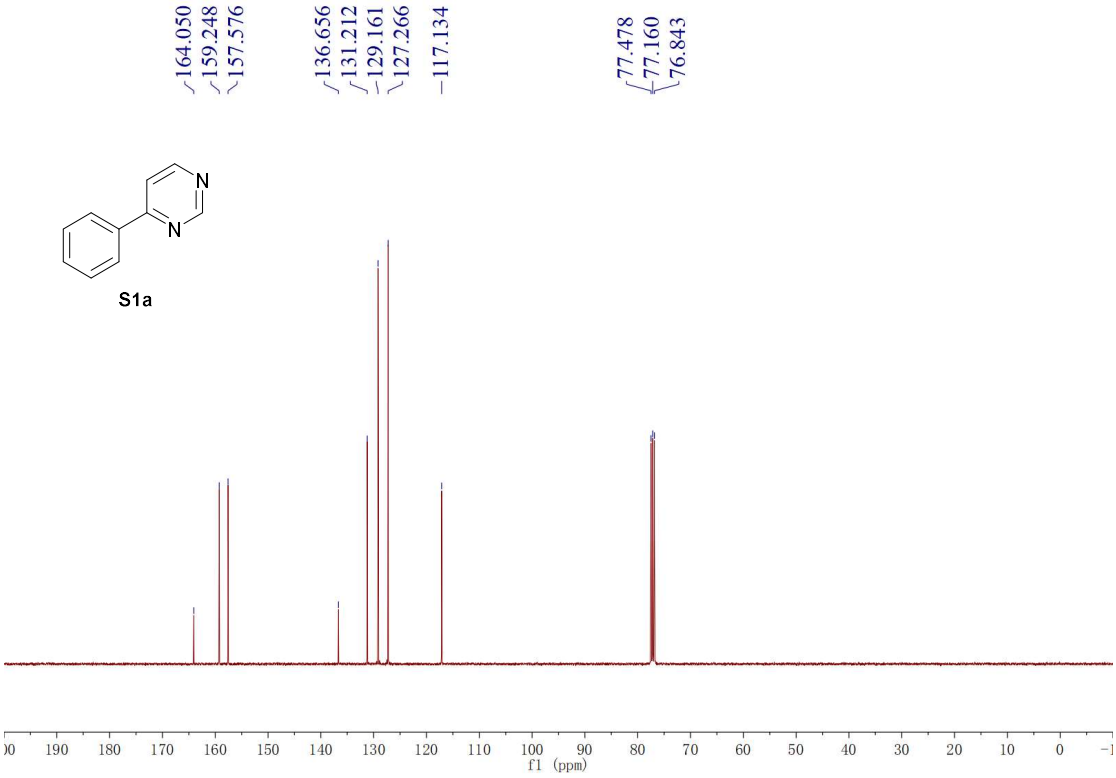
(2) S. D. Jadhav and A. Singh, *Org. Lett.*, 2017, **19**, 5673–5676.

(3) M. J. Stefanko, Y. K. Gun'ko, D. K. Rai and P. Evans, *Tetrahedron*, 2008, **64**, 10132–10139.

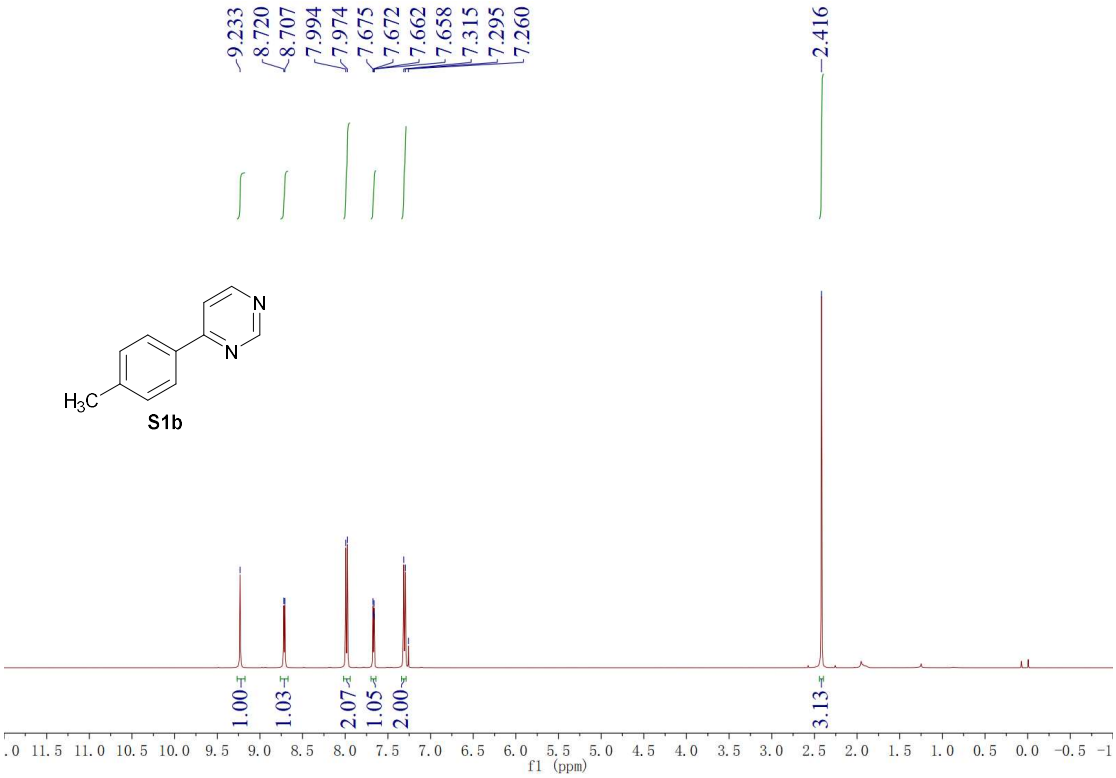
4. NMR Spectrum



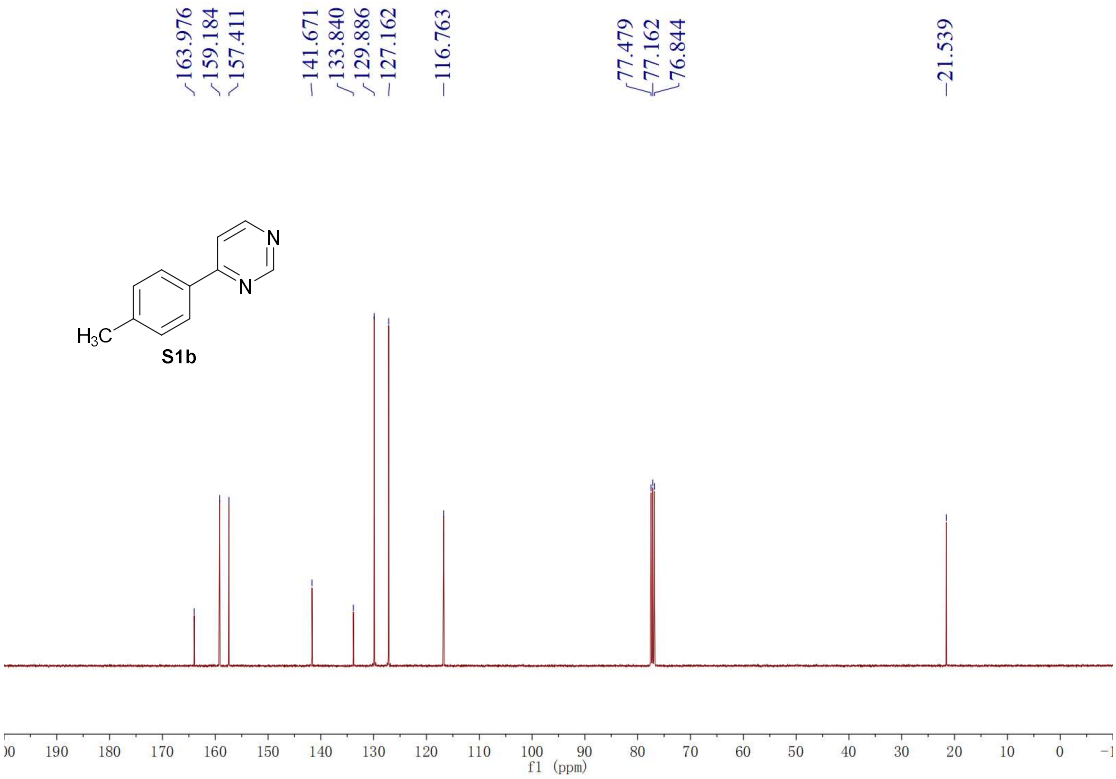
^{1}H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1a



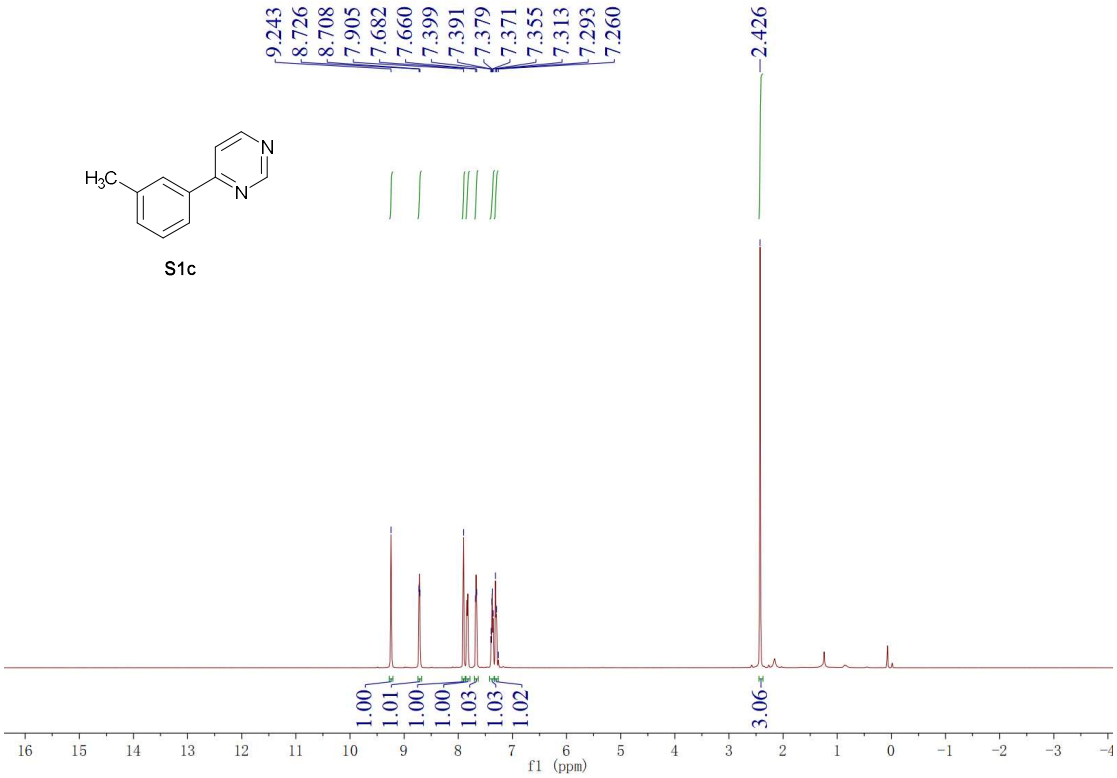
^{13}C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1a



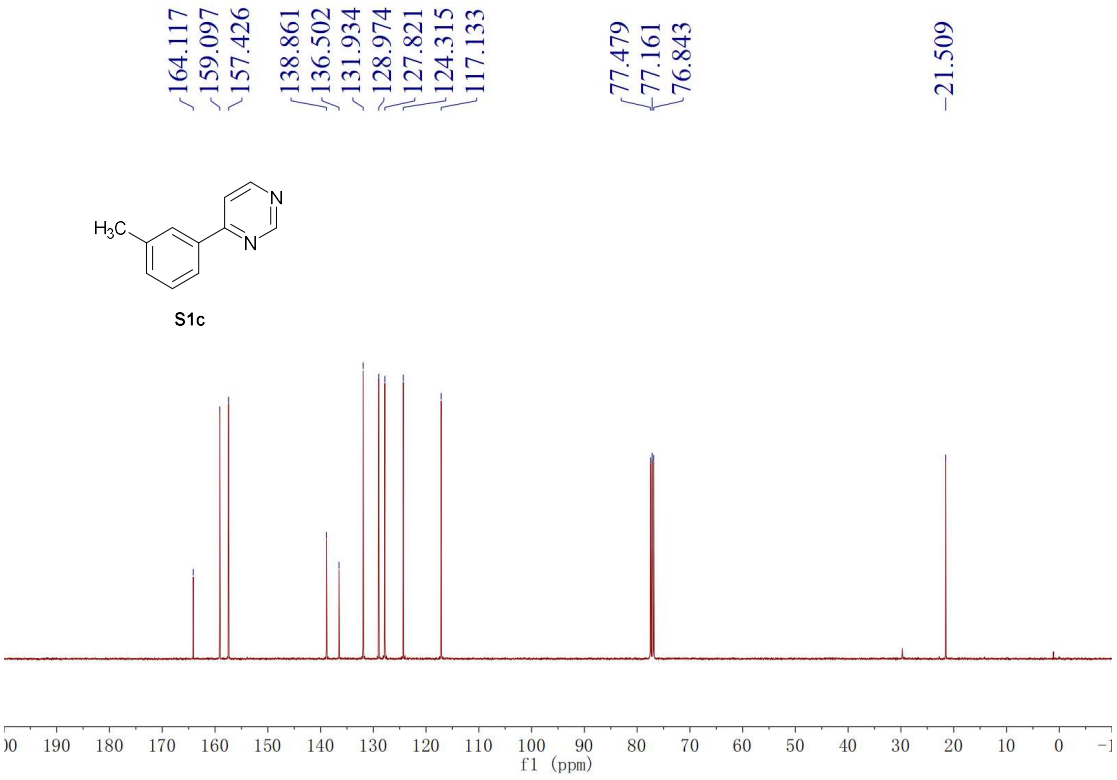
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1b



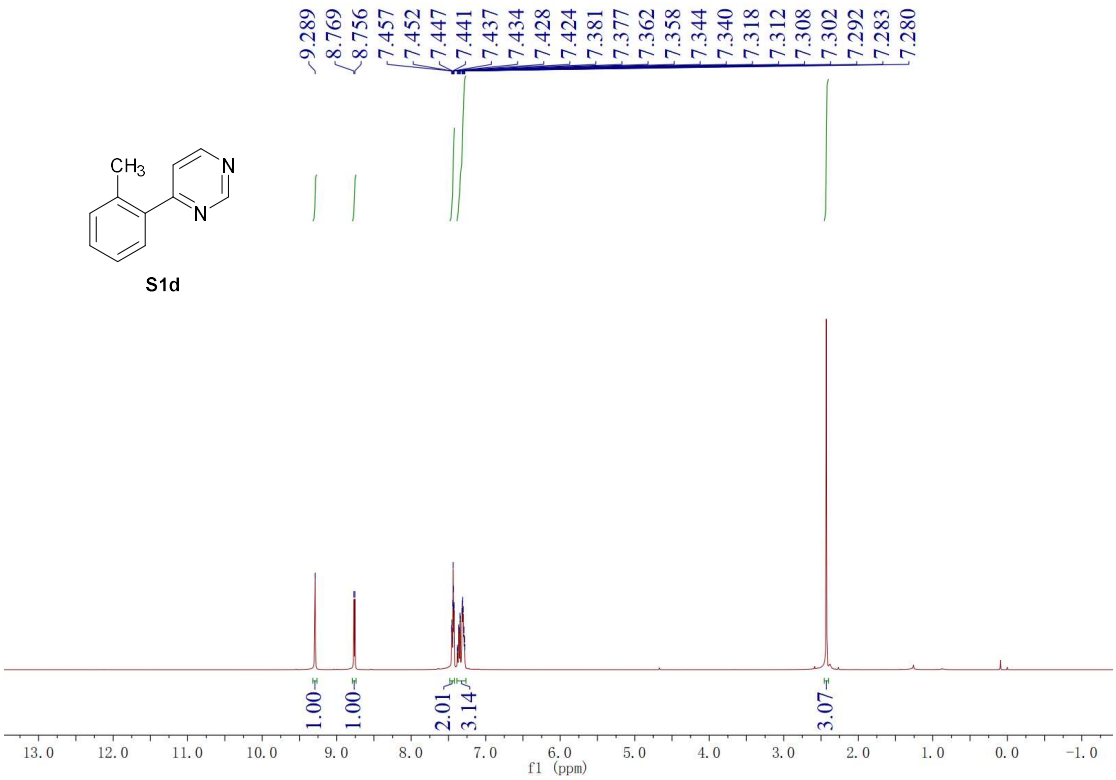
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1b



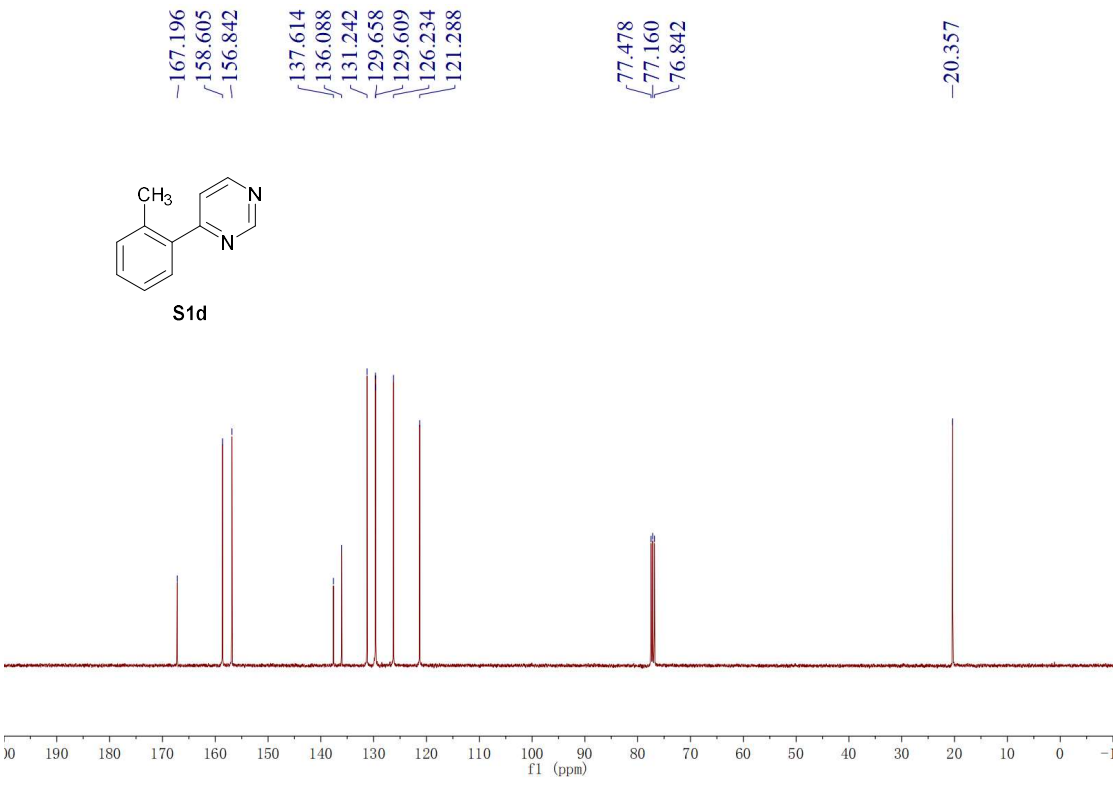
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1c



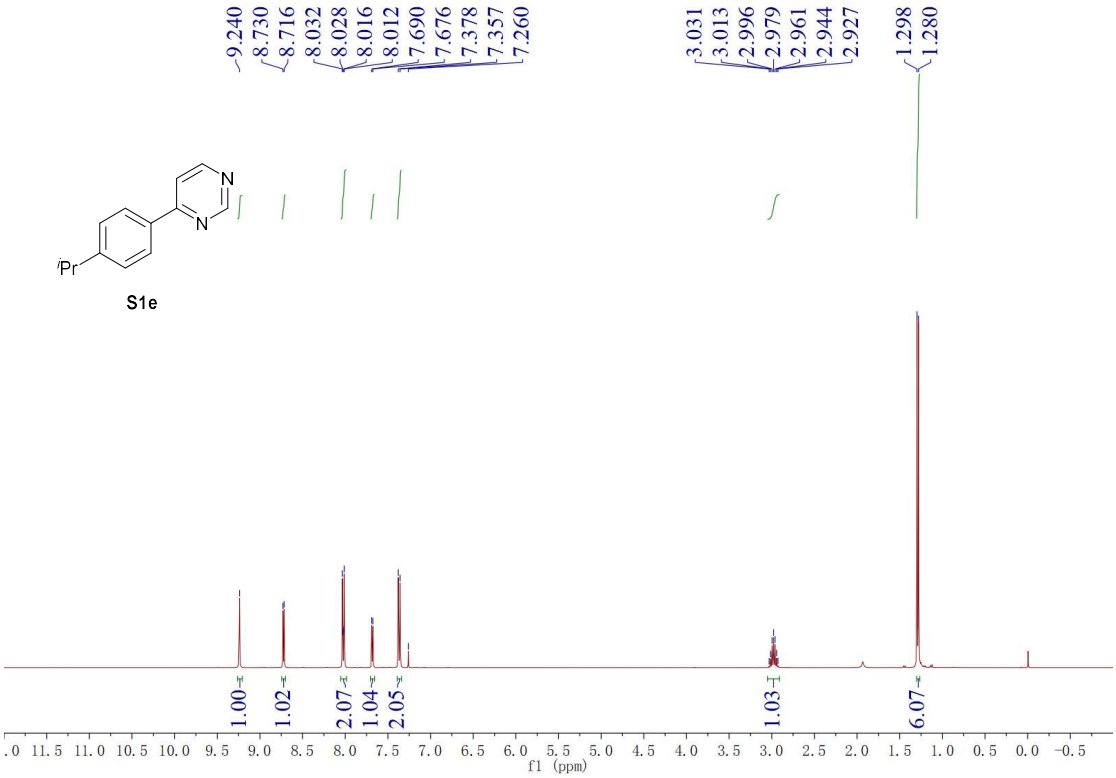
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1c



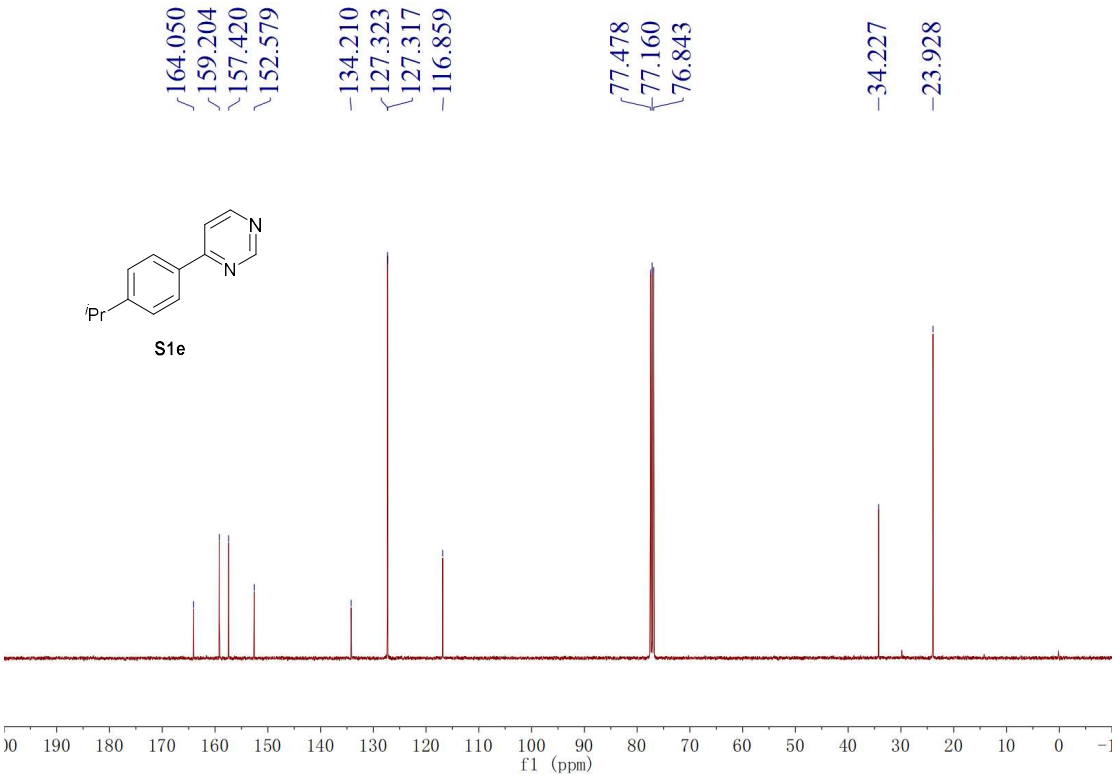
^{1}H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1d



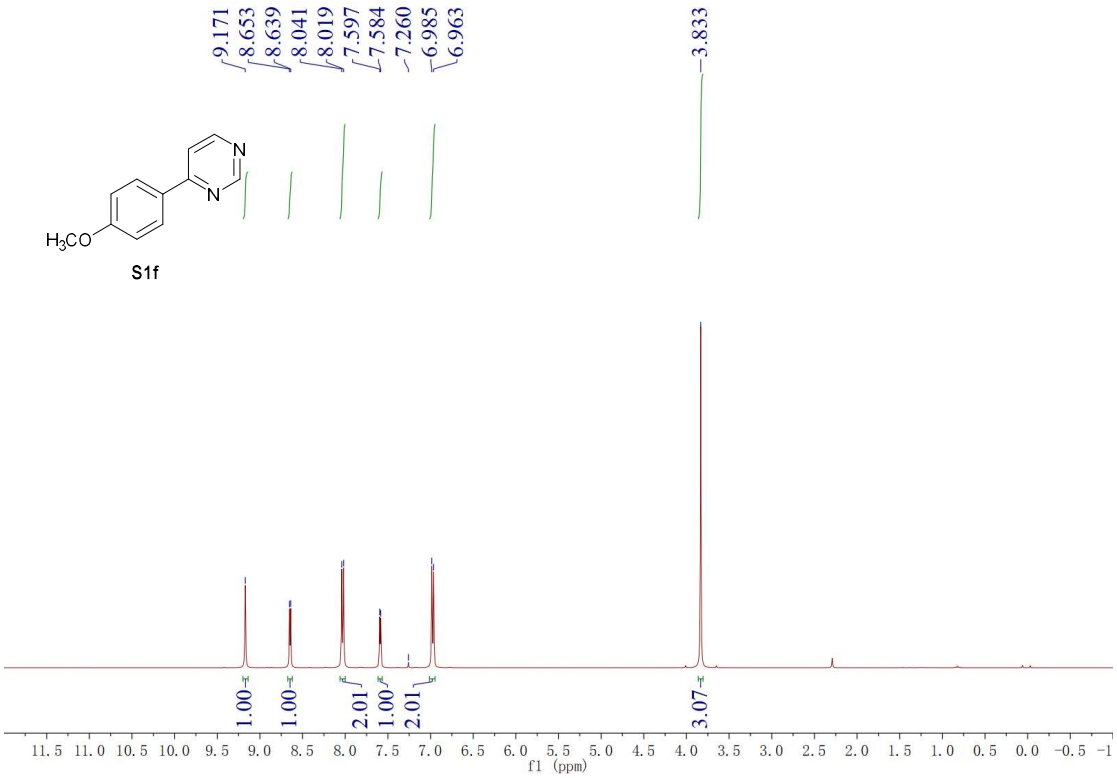
^{13}C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1d



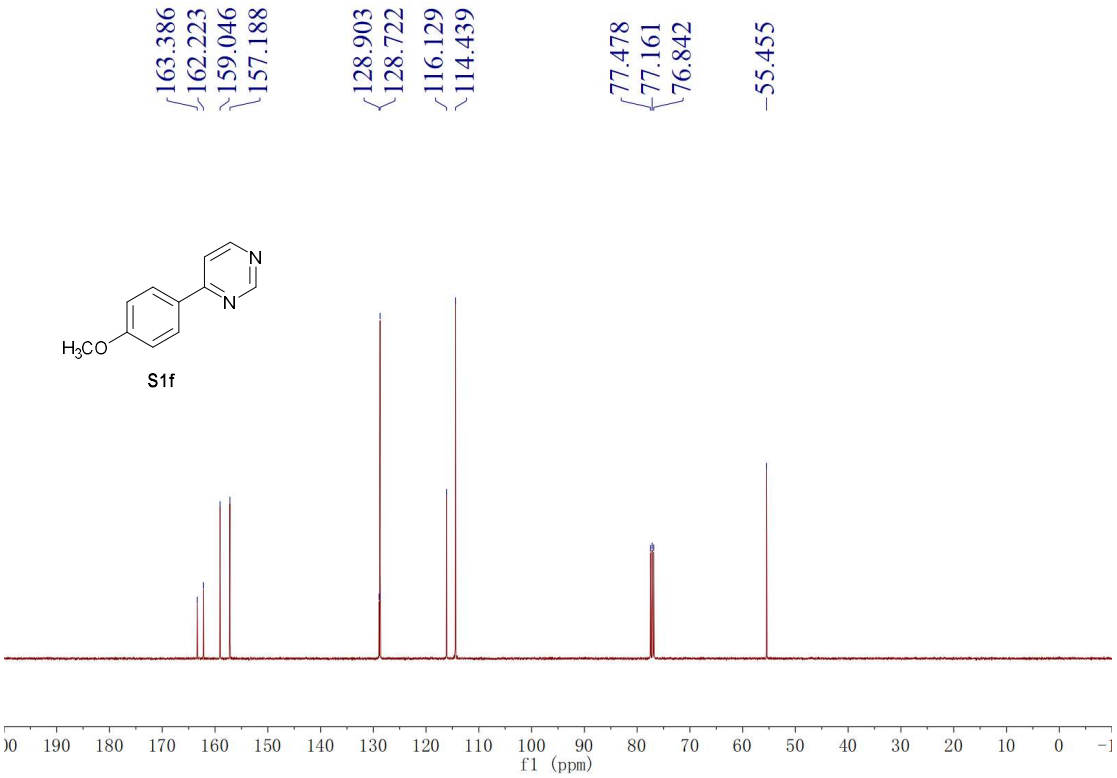
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1e



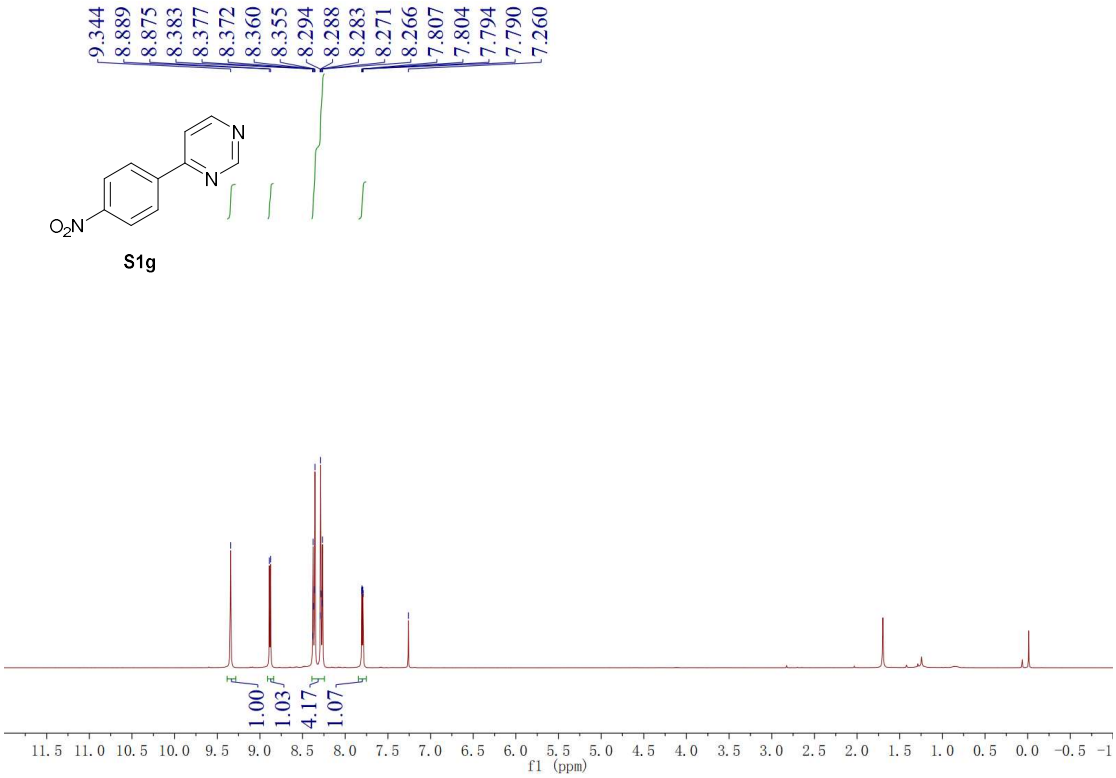
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1e



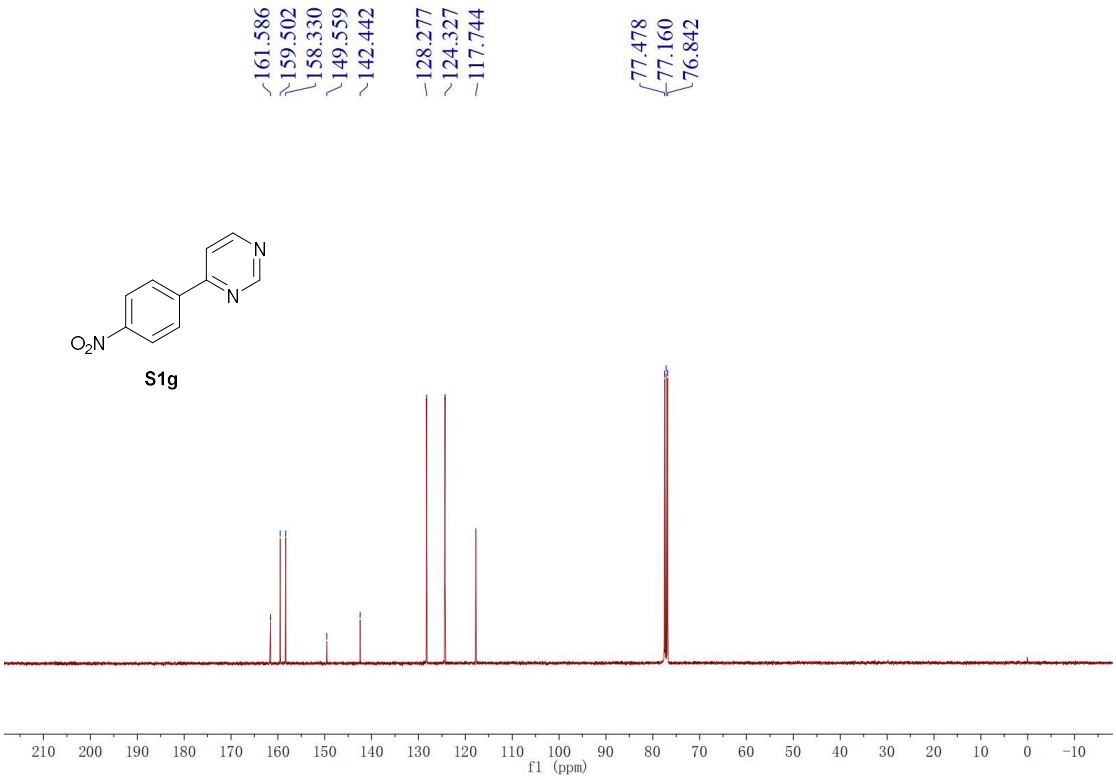
^{1}H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1f



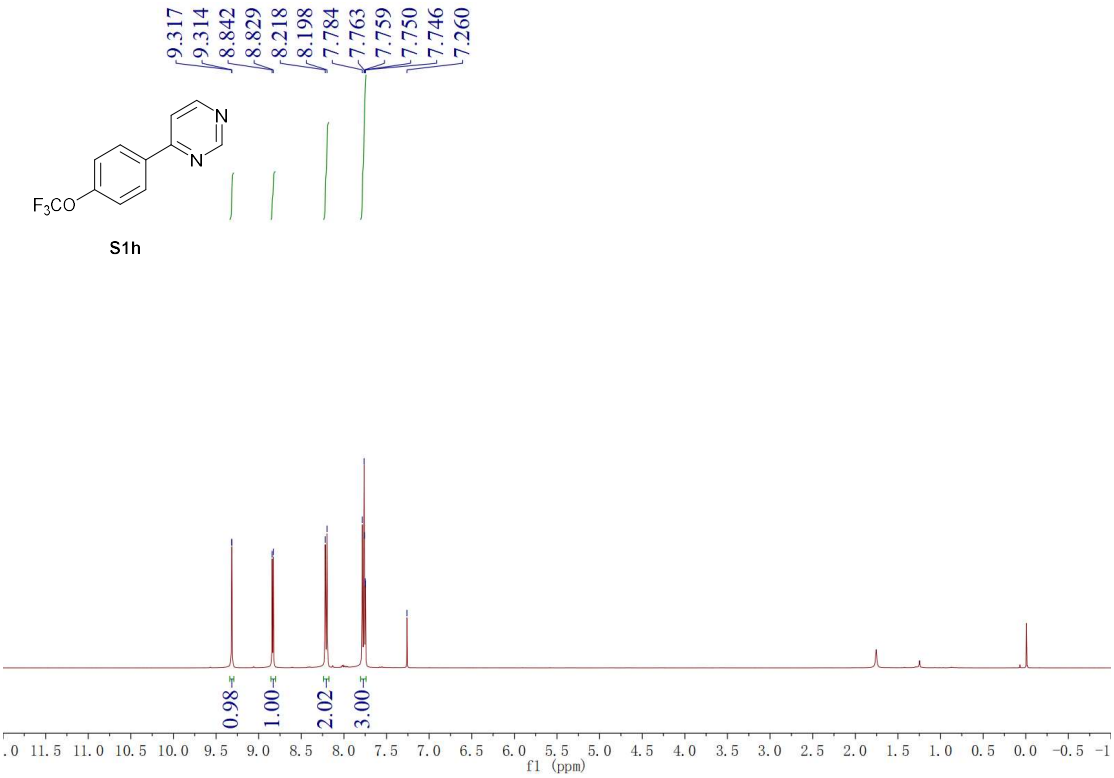
^{13}C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1f



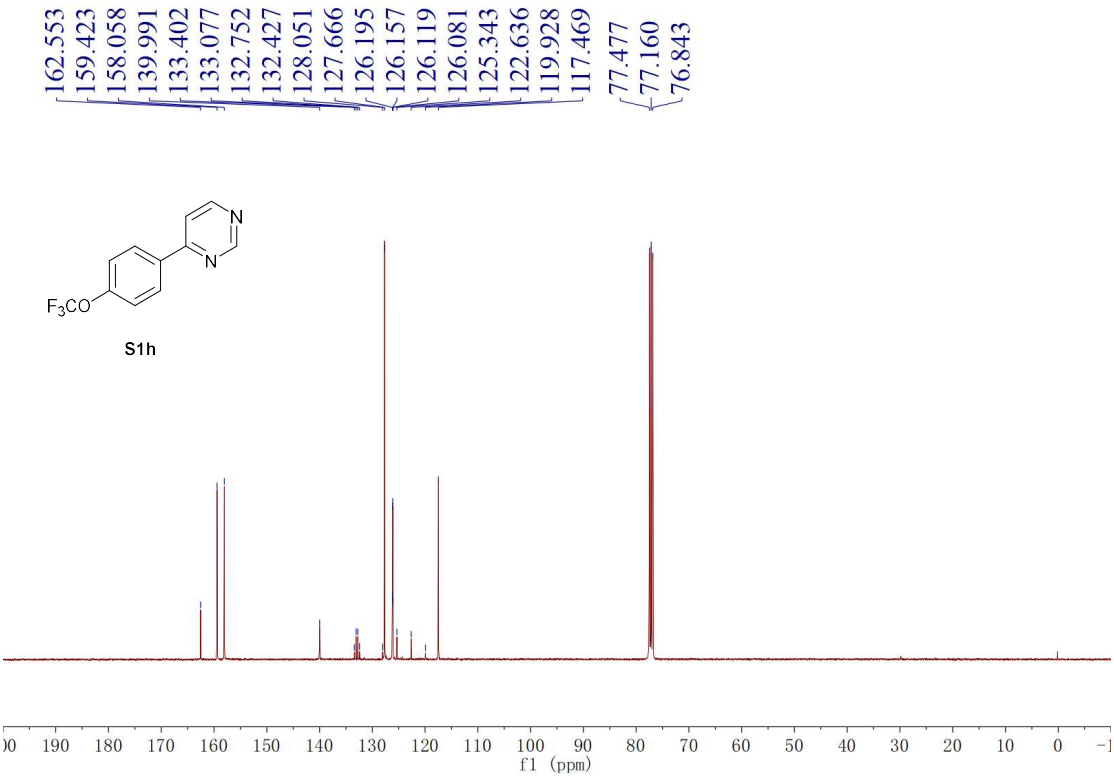
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1g



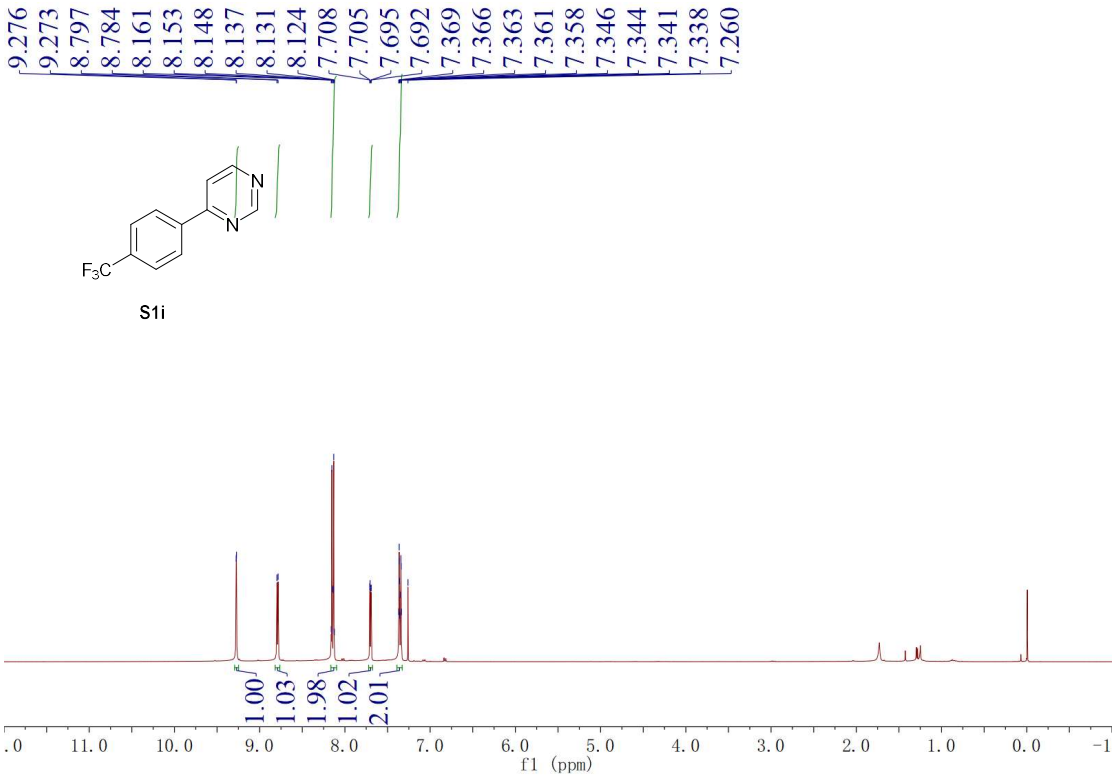
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1g



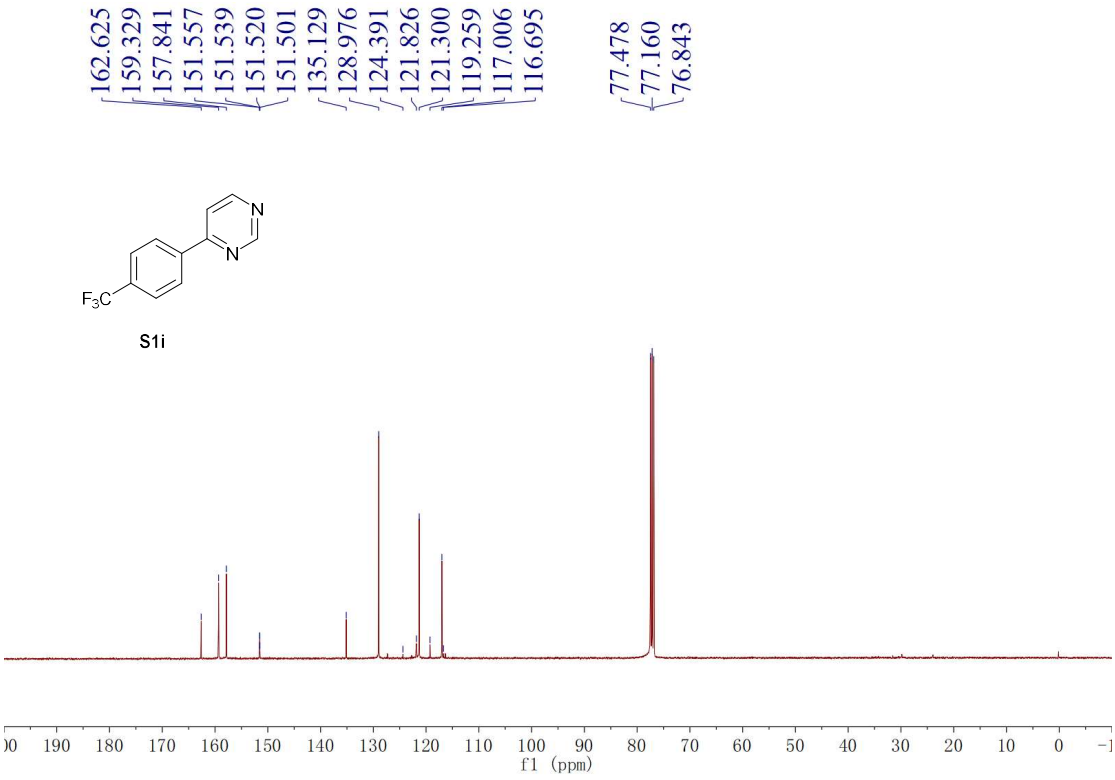
^{1}H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1h



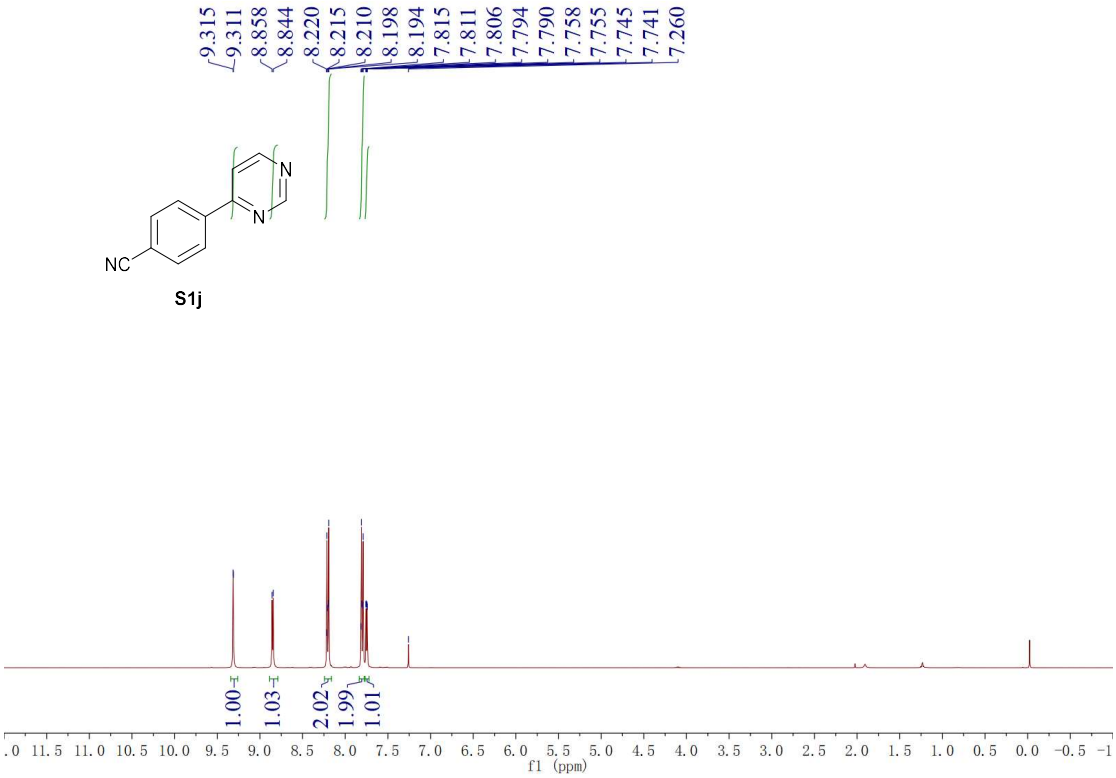
^{13}C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1h



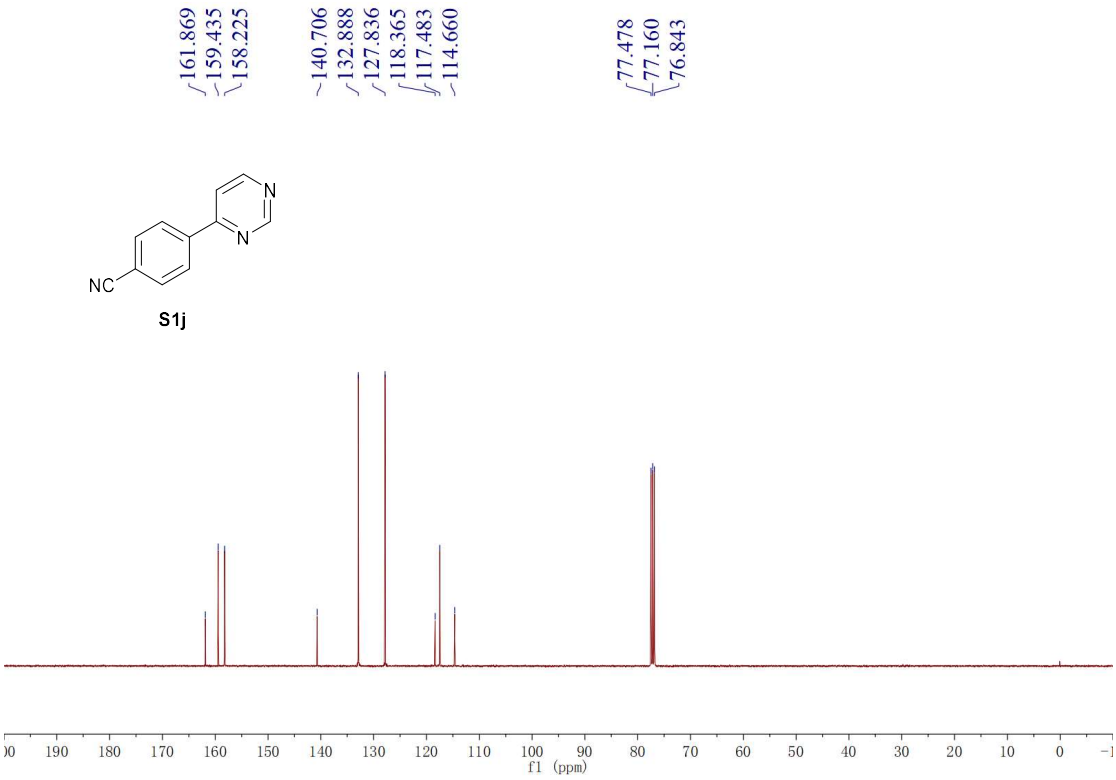
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1i



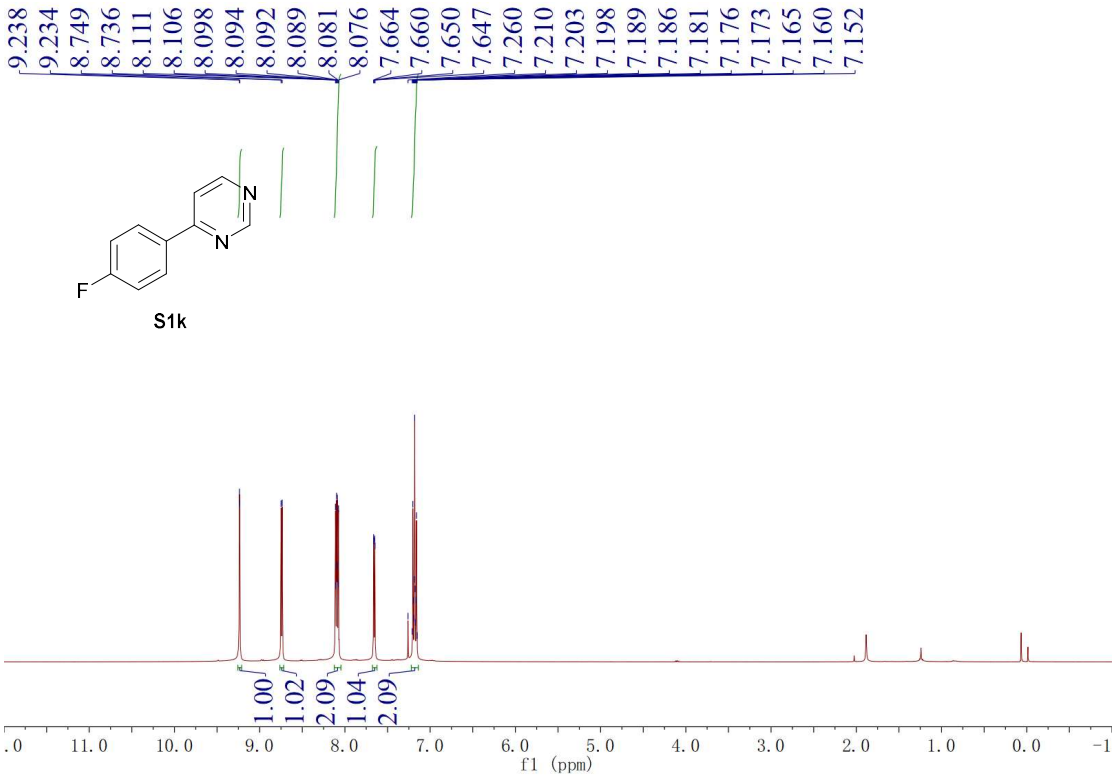
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1i



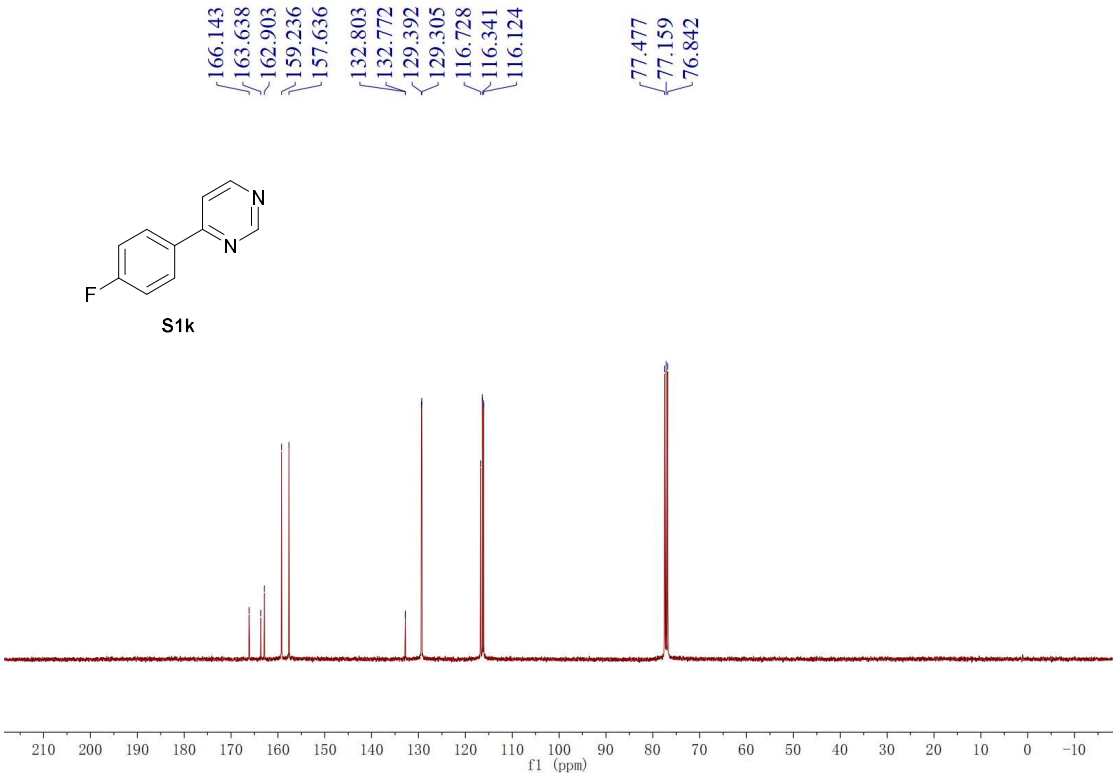
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1j



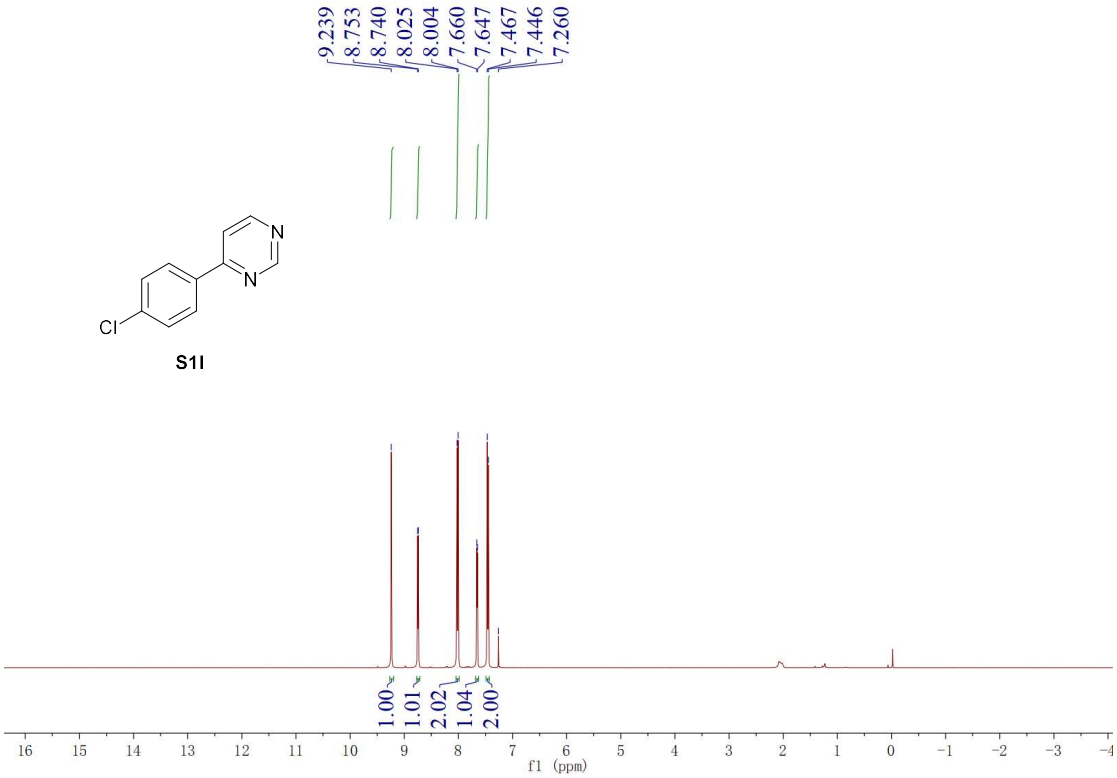
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1j



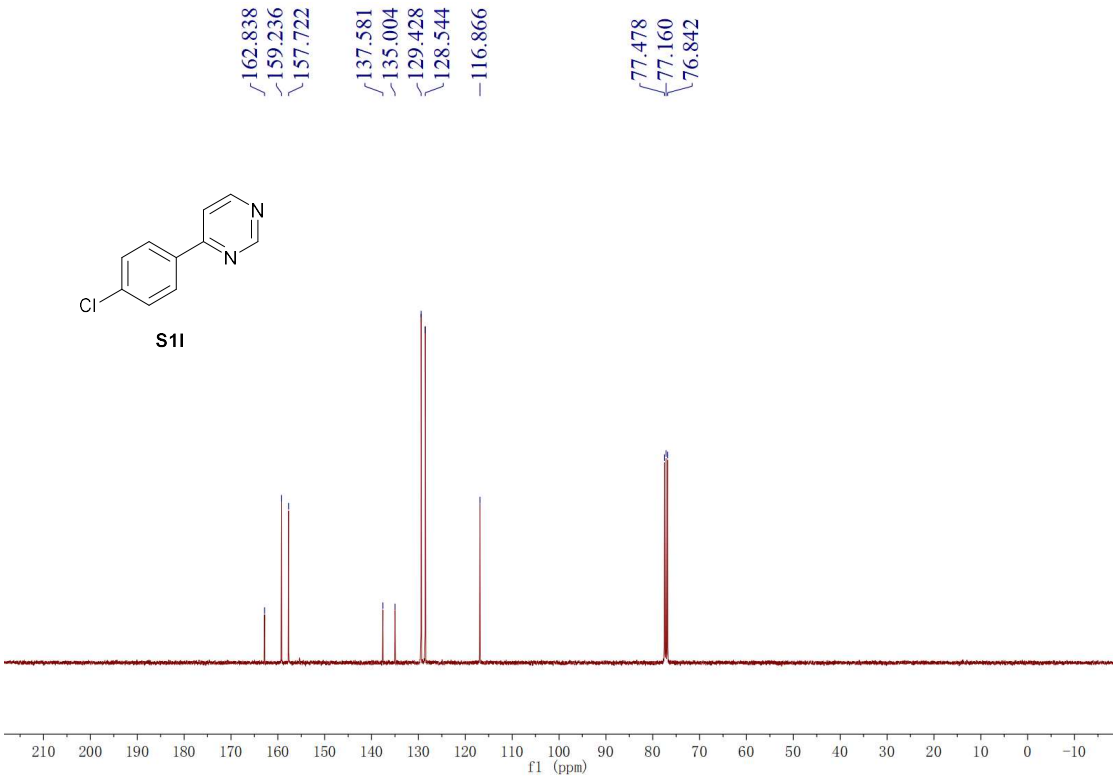
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1k



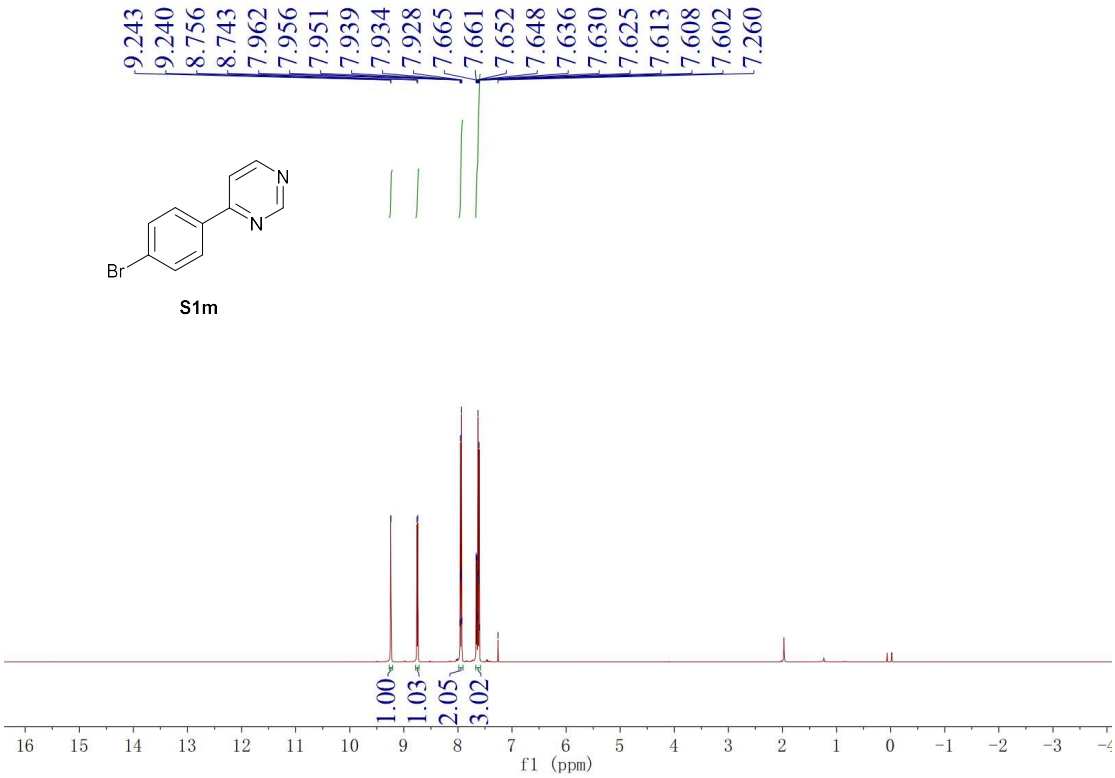
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1k



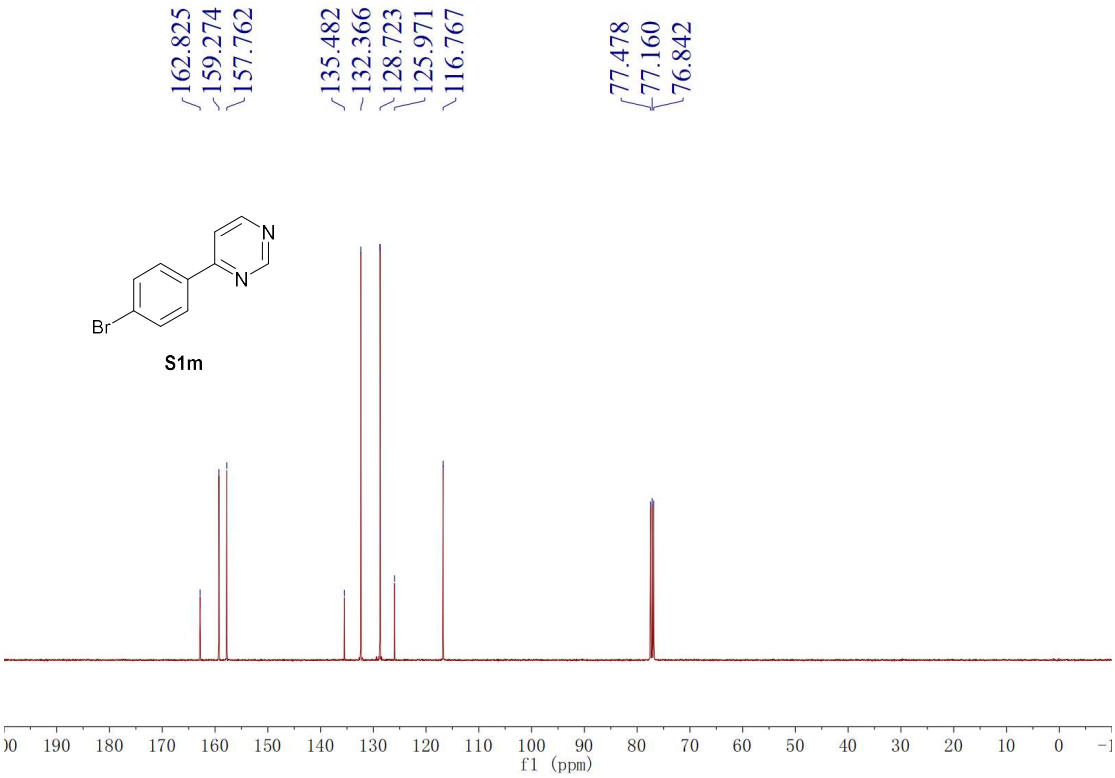
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1l



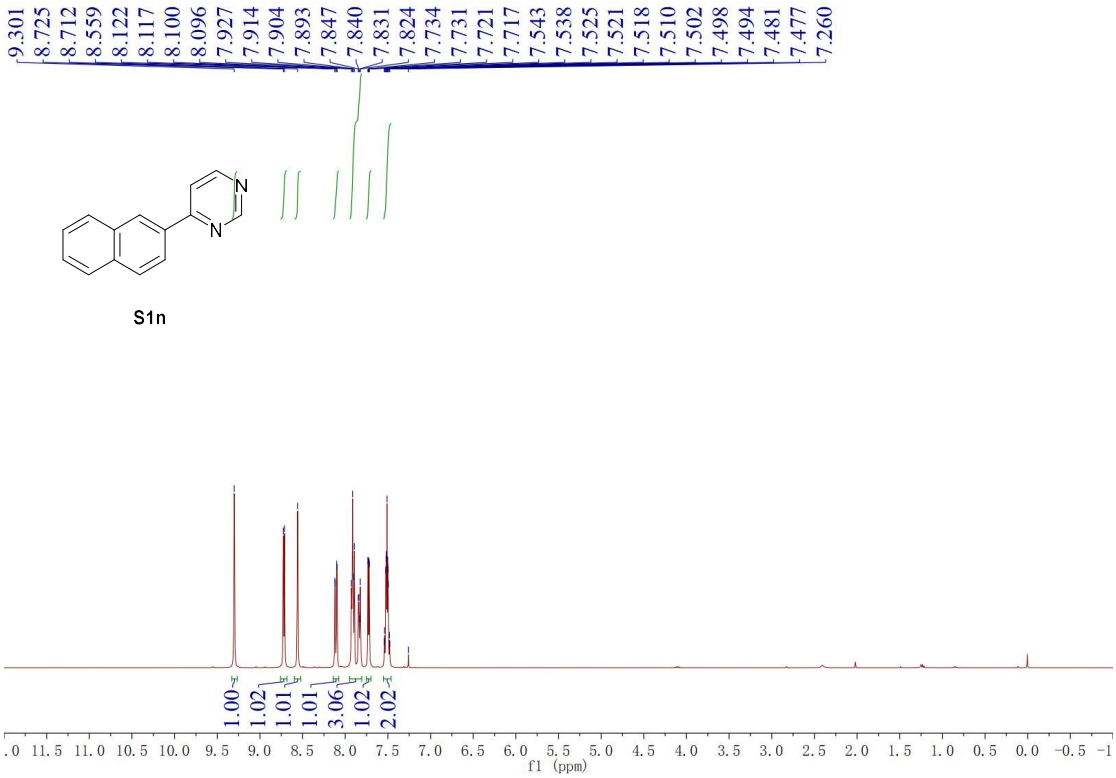
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1l



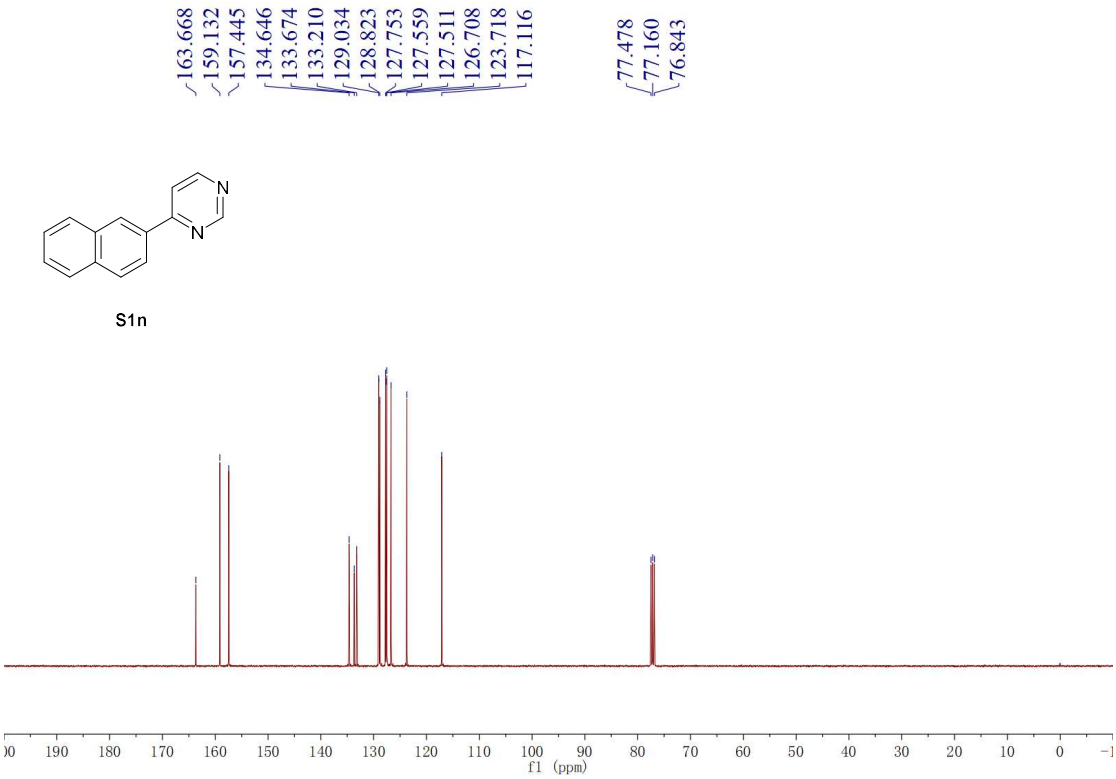
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1m



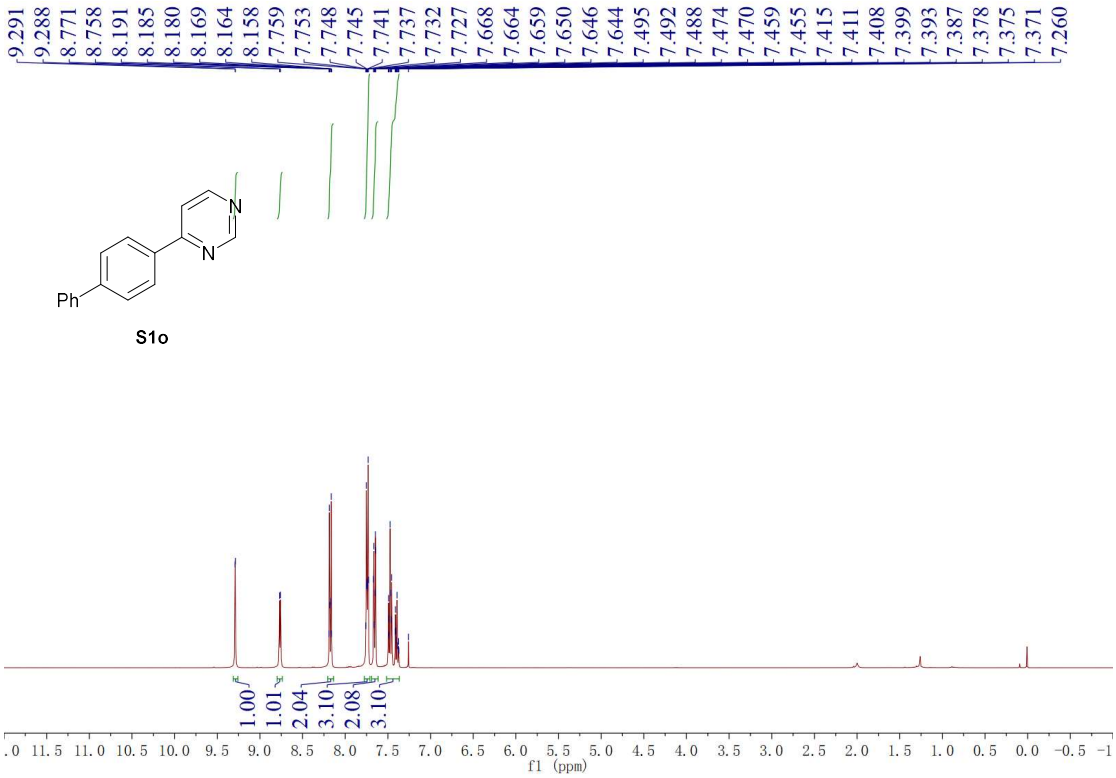
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1m



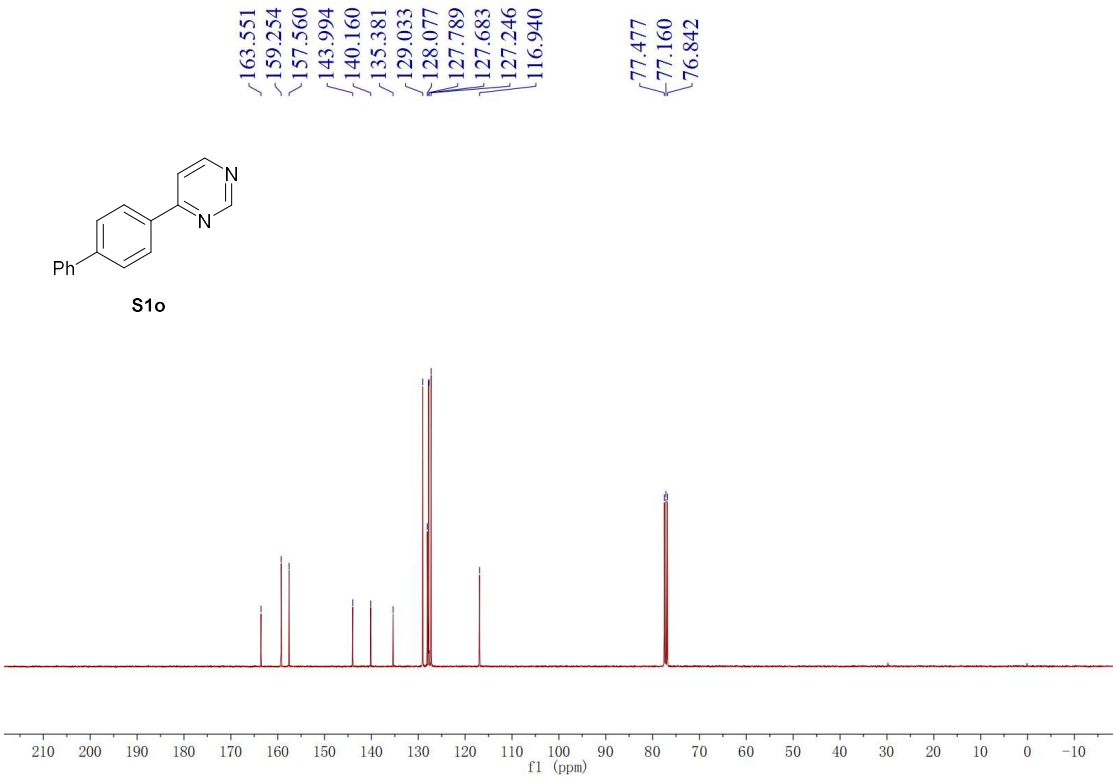
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1n



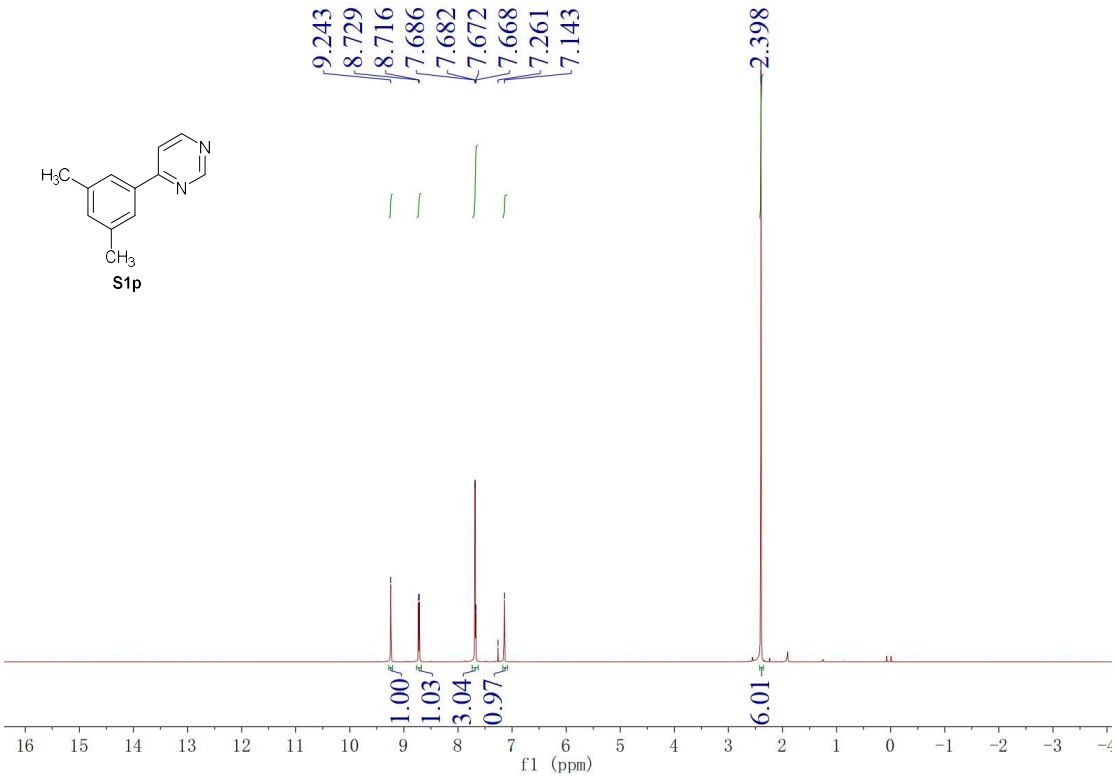
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1n



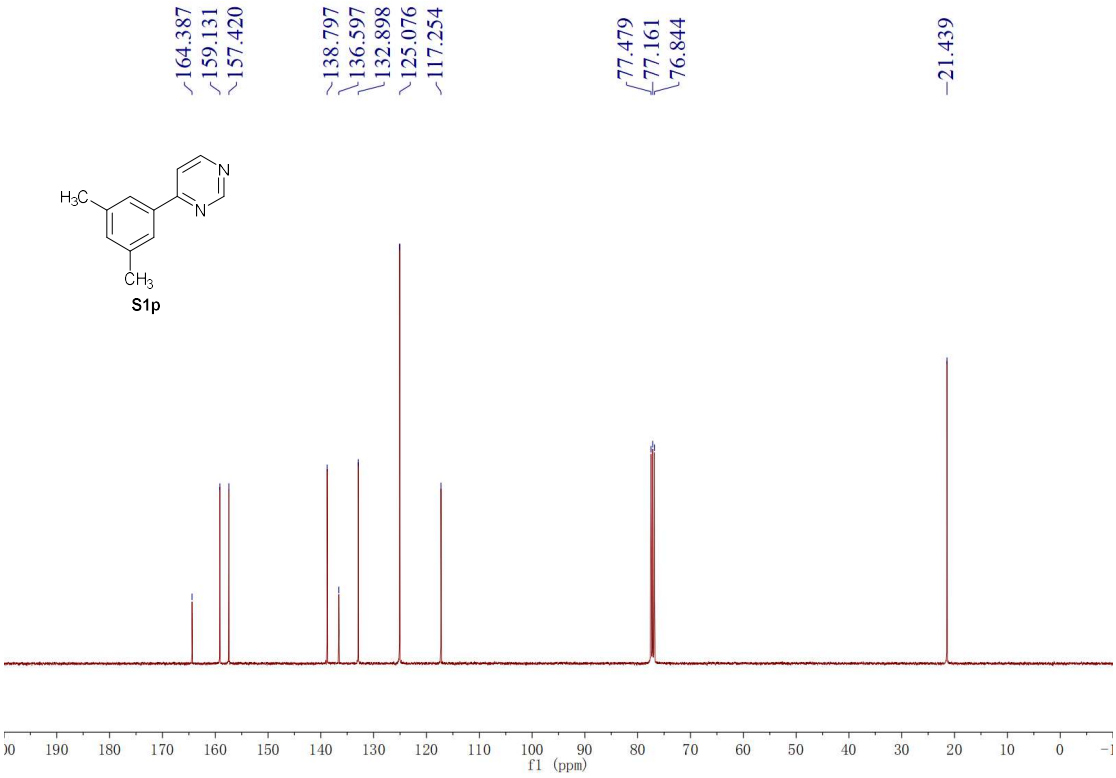
^{1}H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1o



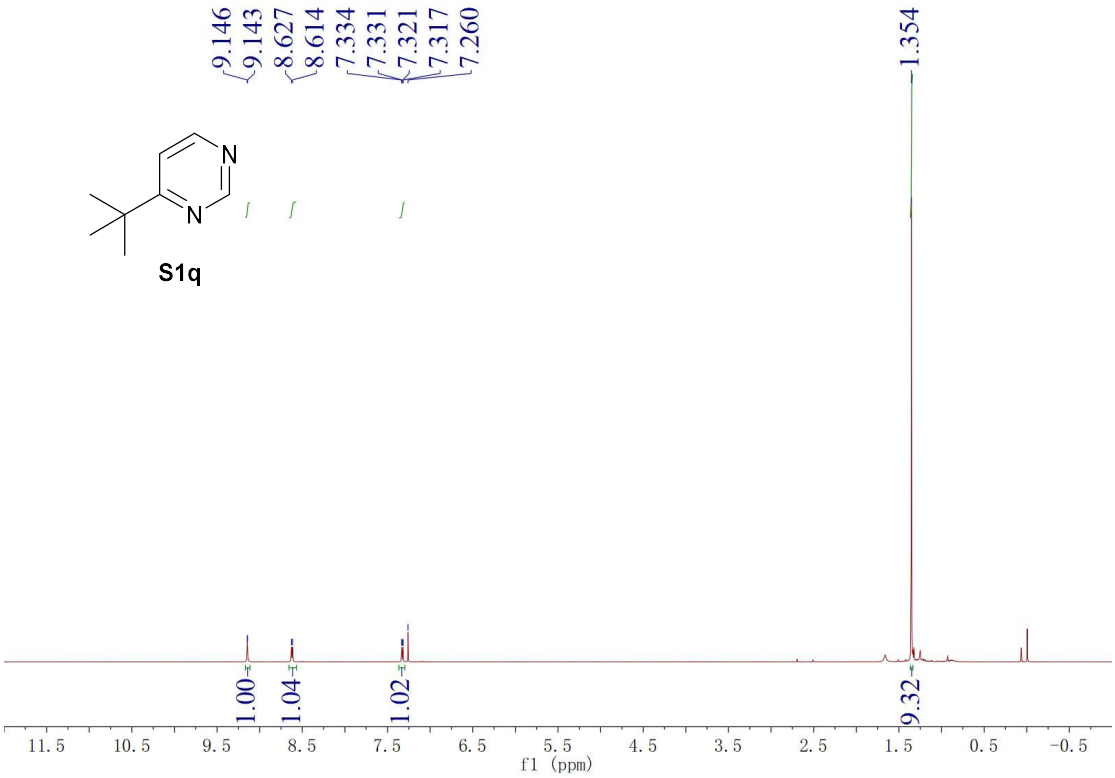
^{13}C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1o



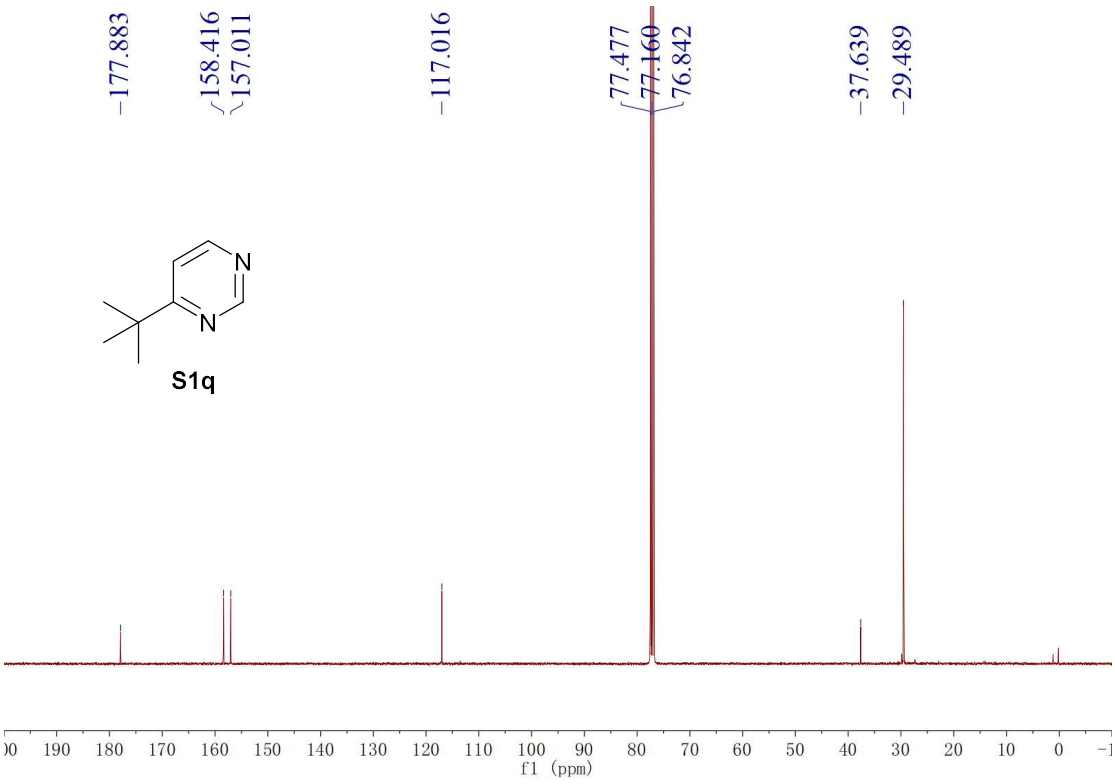
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1p



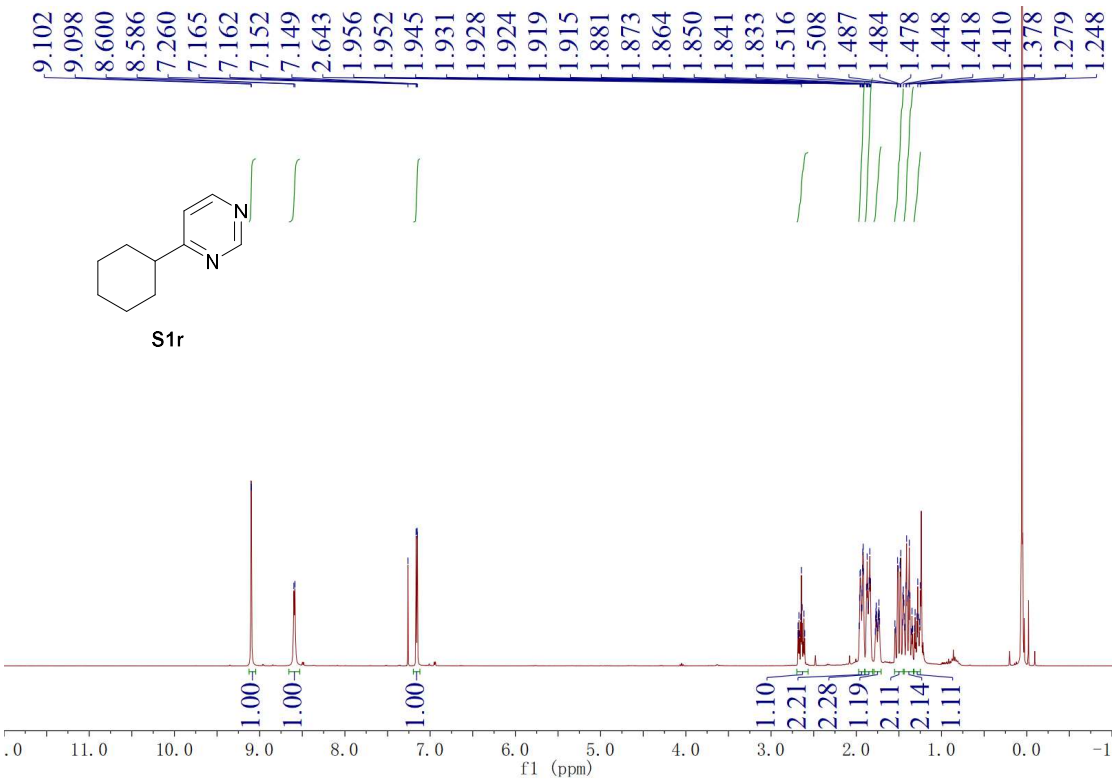
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1p



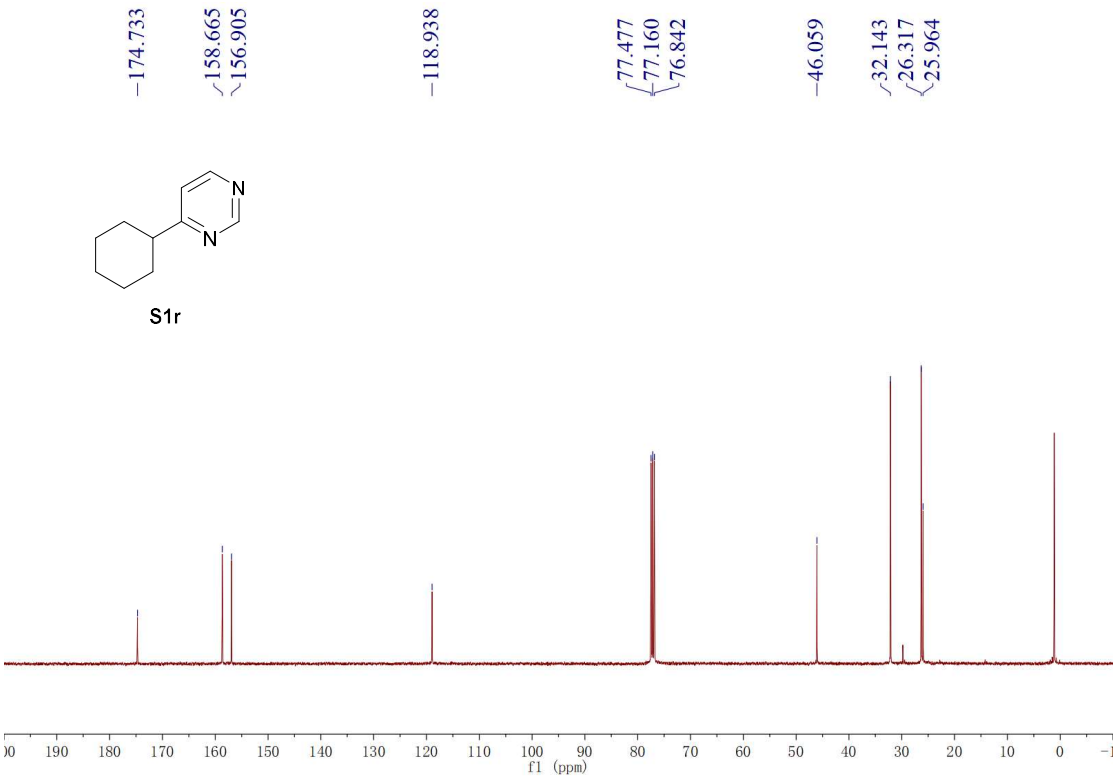
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1q



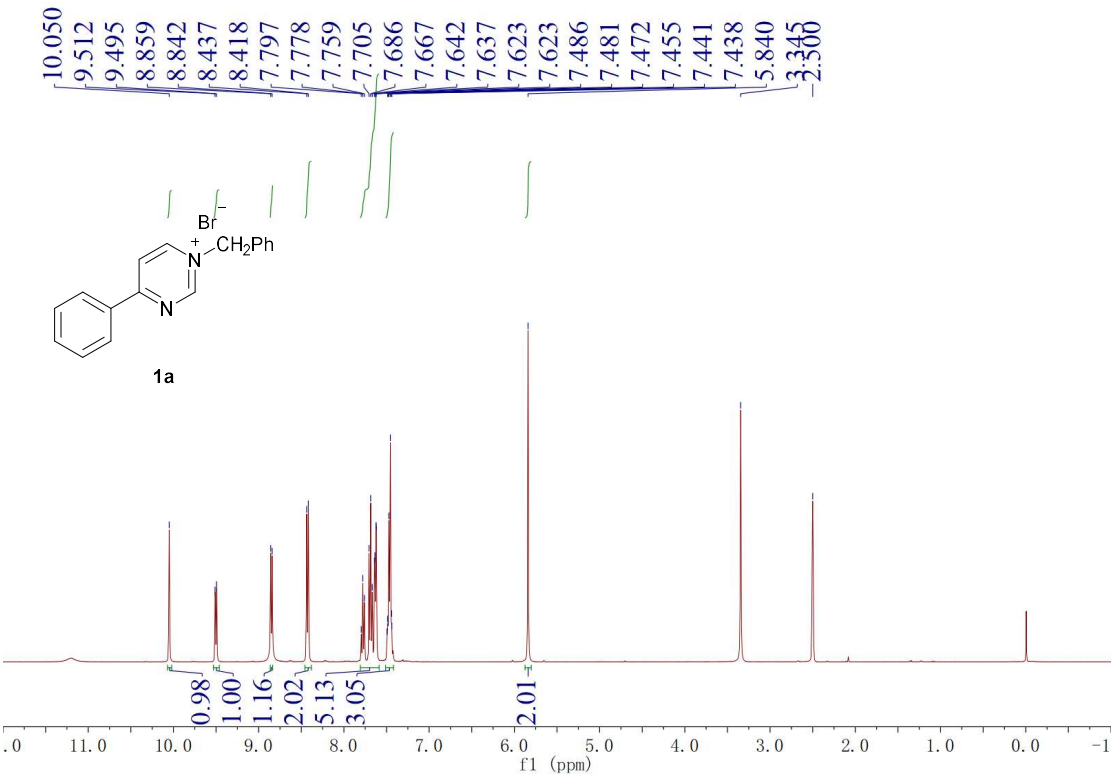
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1q



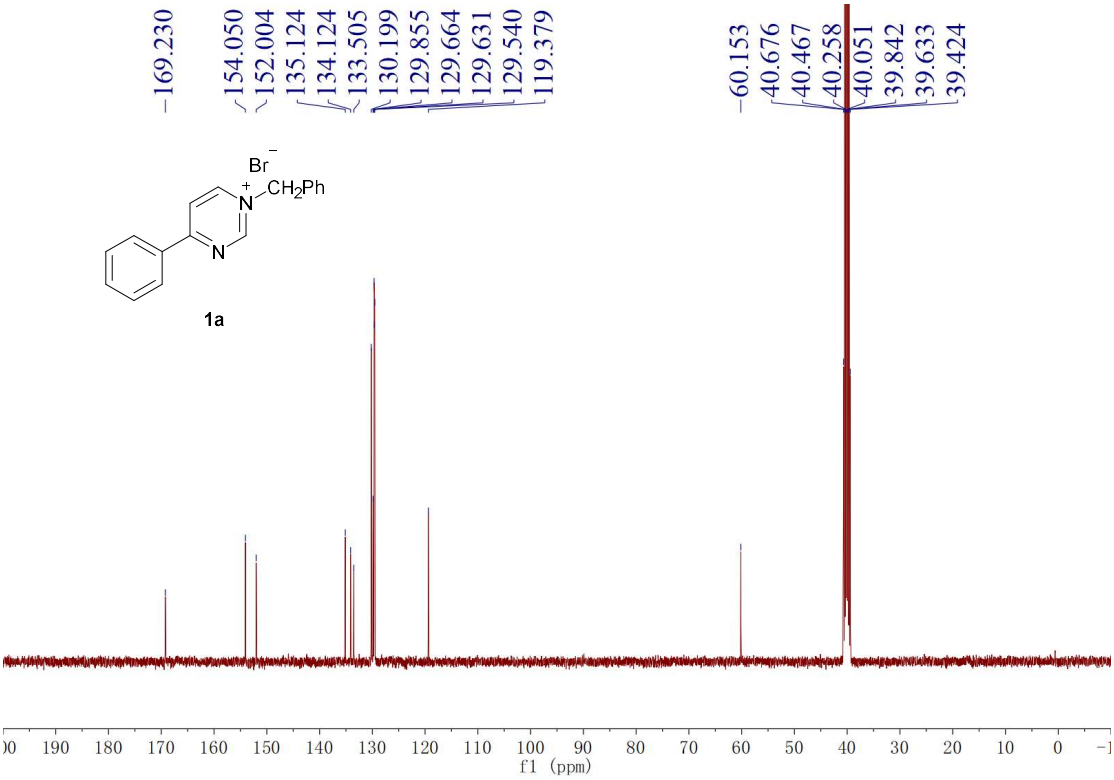
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound S1r



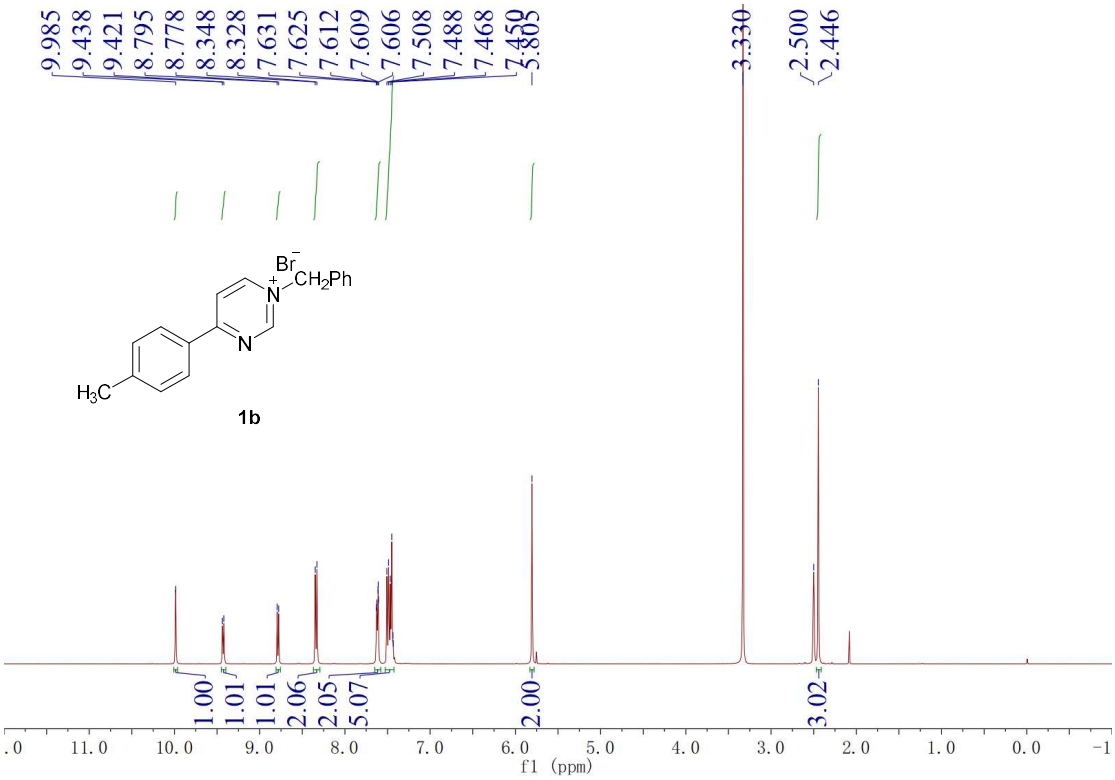
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound S1r



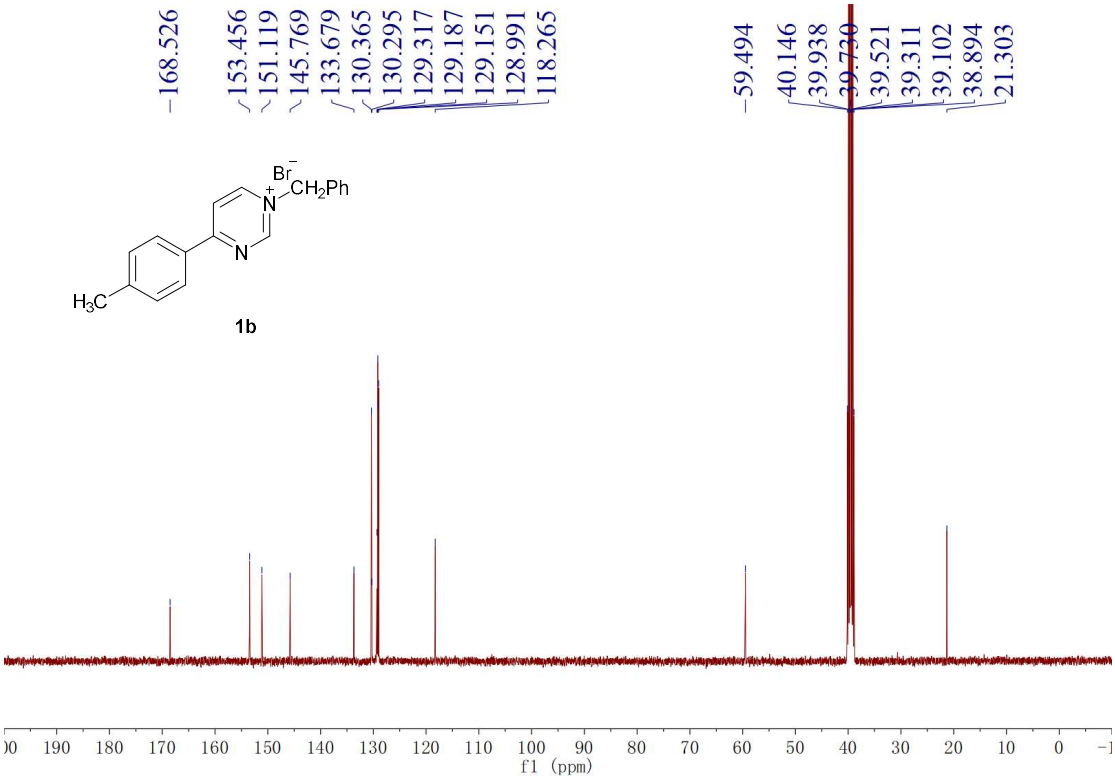
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1a



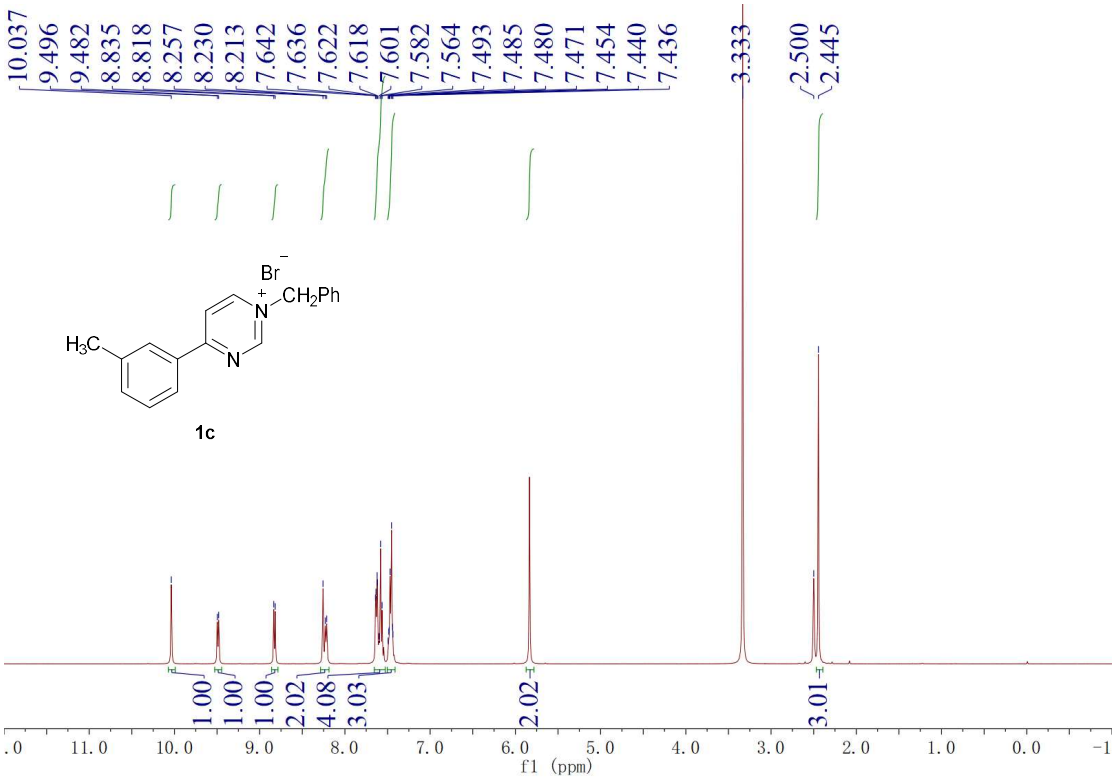
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1a



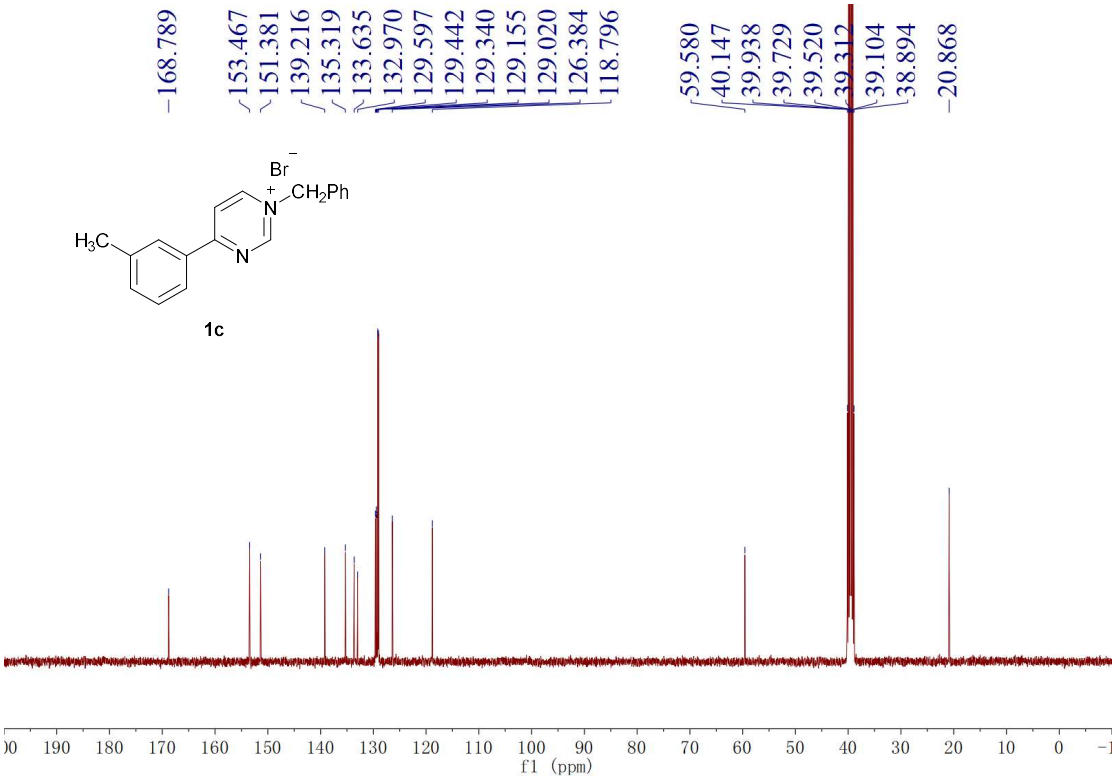
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1b



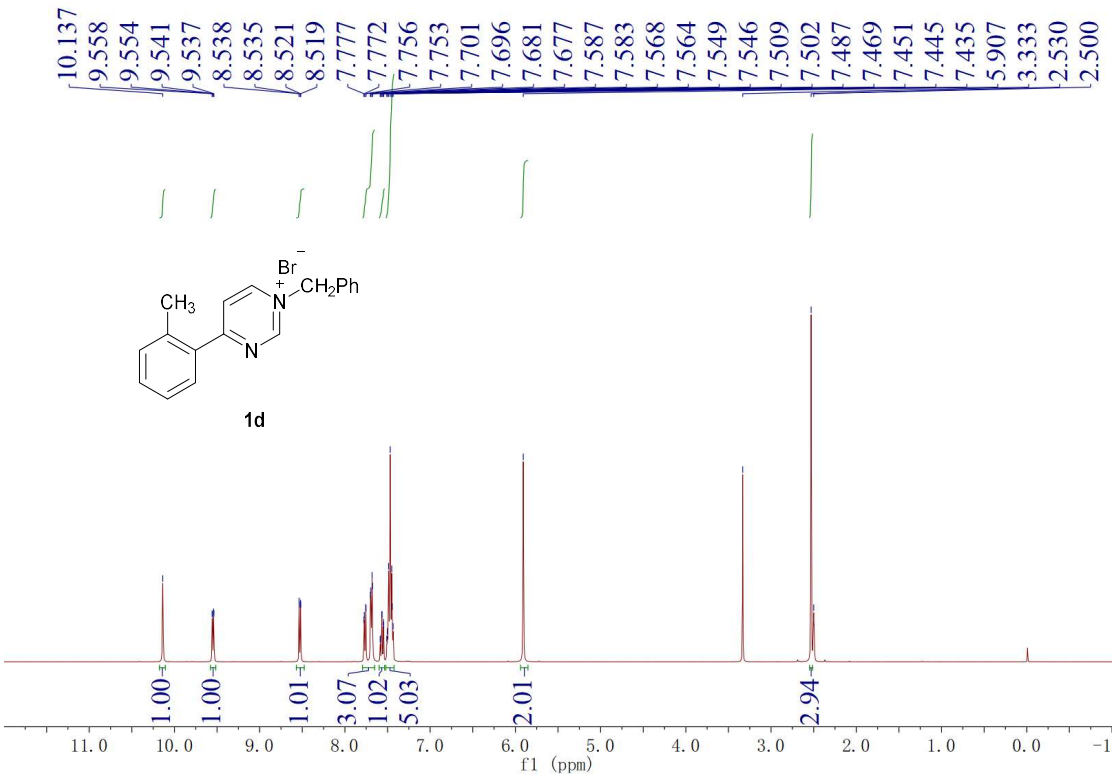
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1b



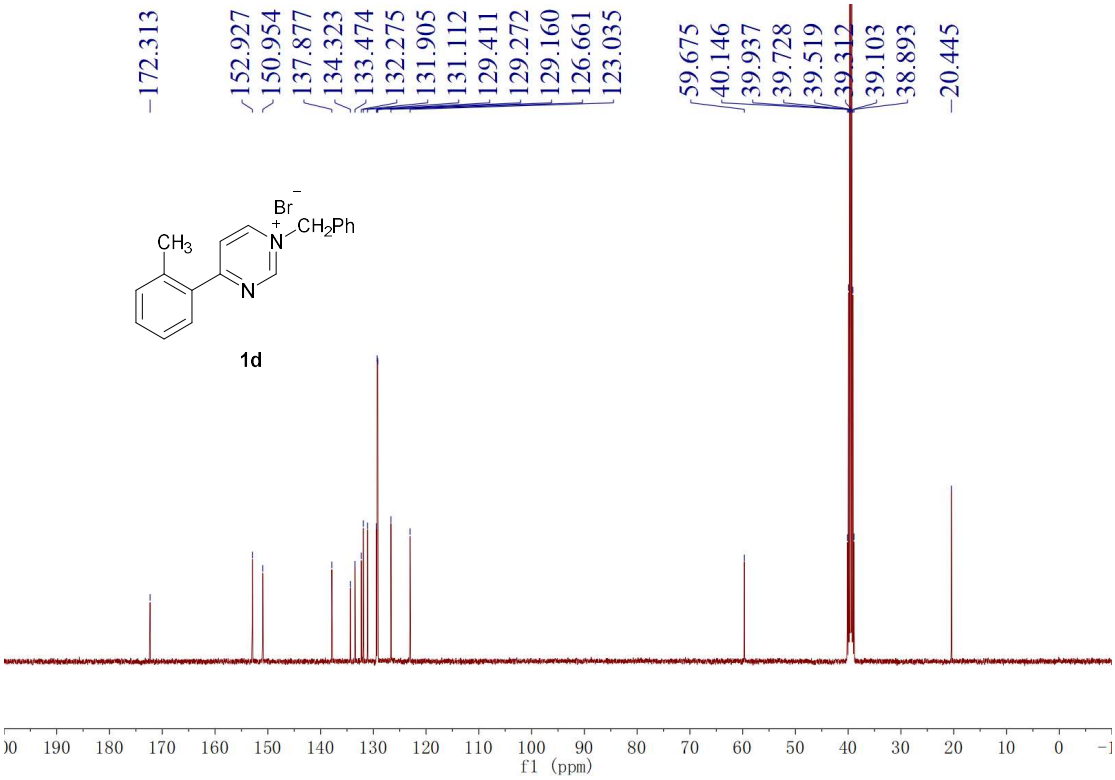
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1c



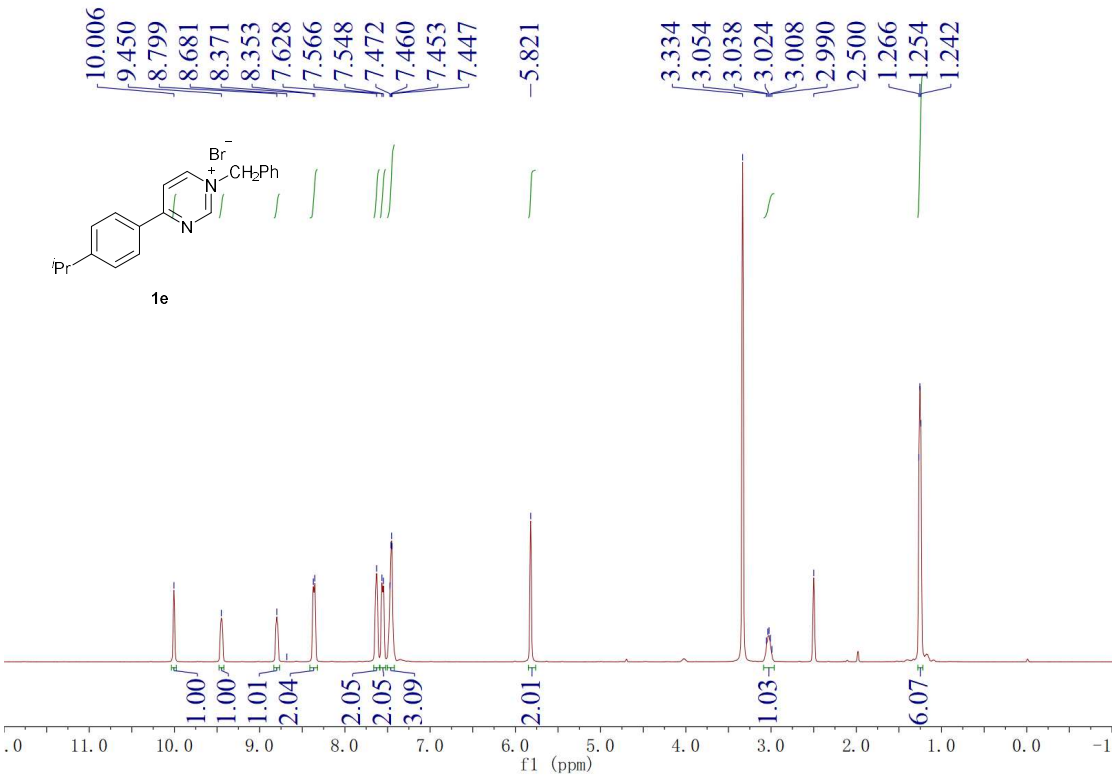
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1c



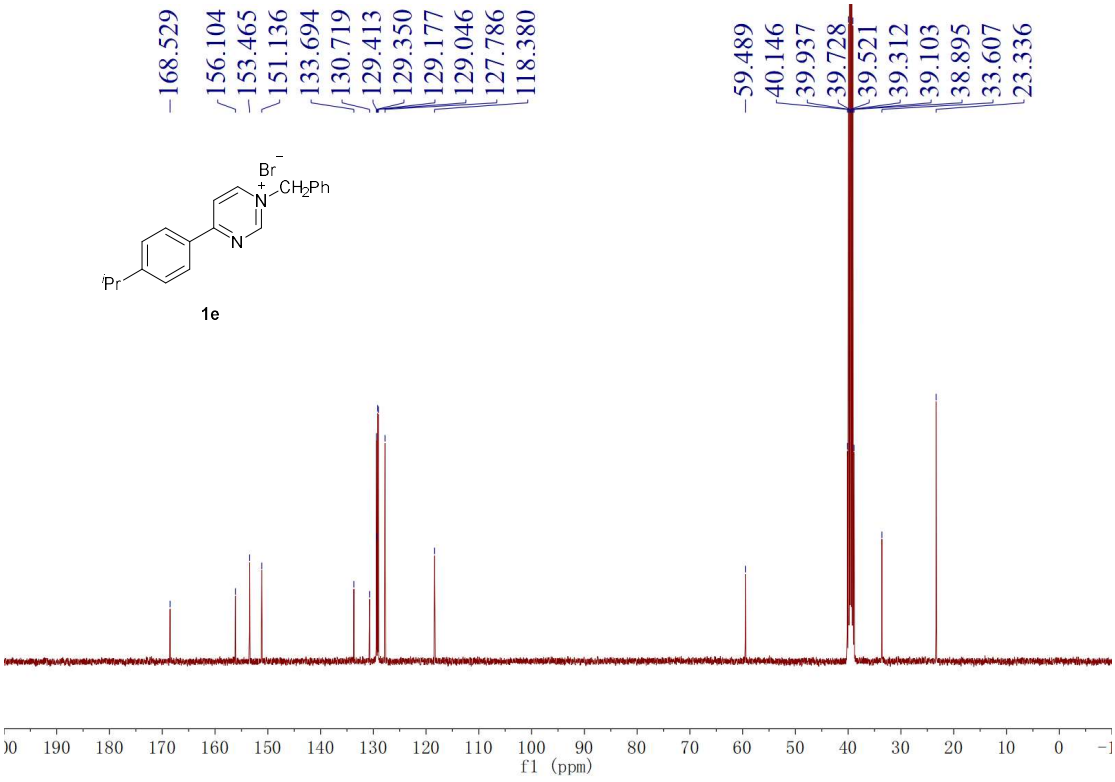
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1d



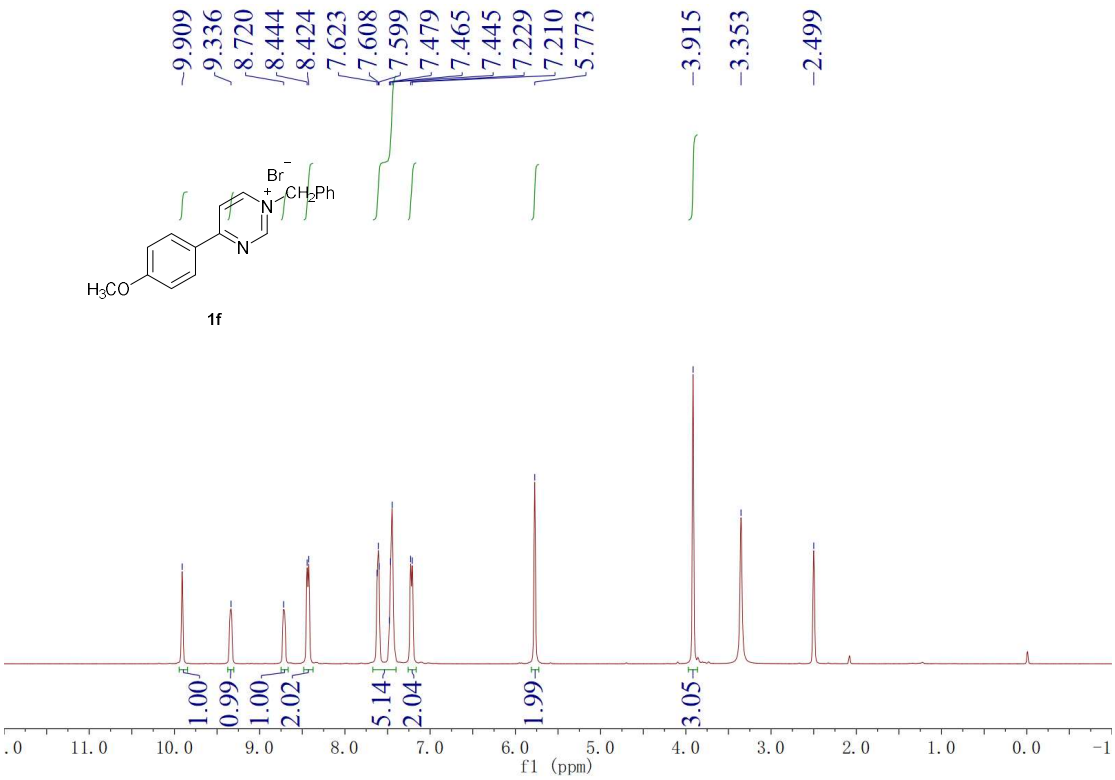
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1d



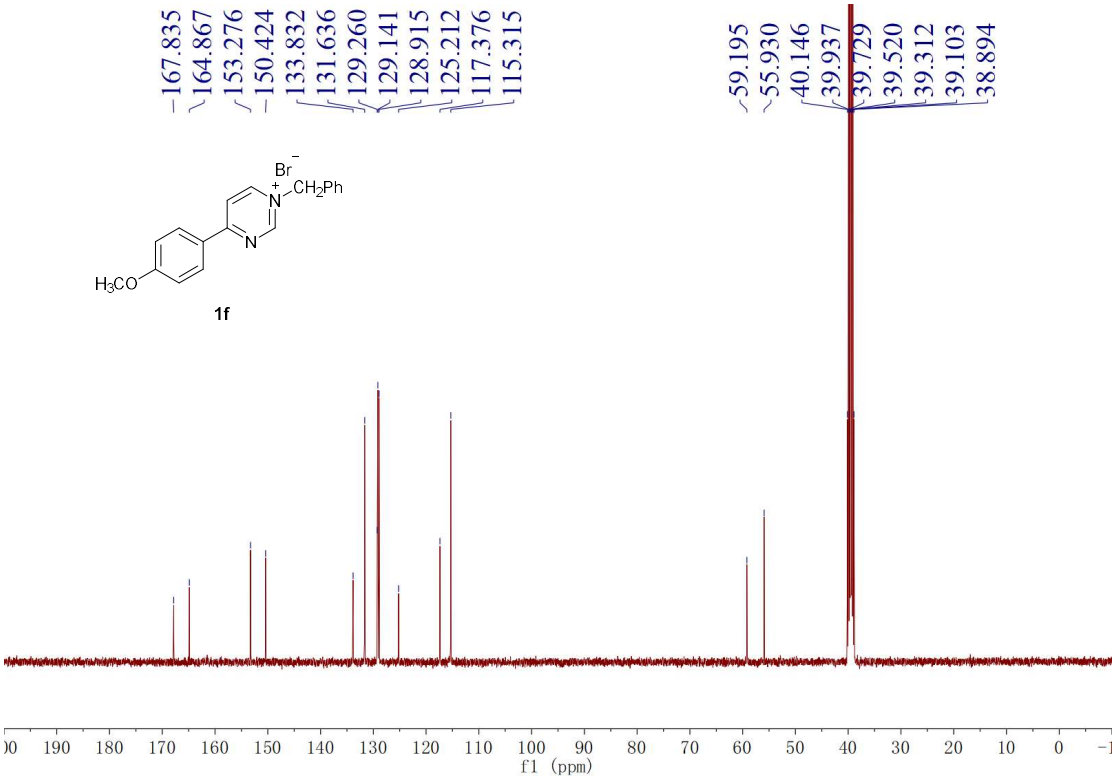
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1e



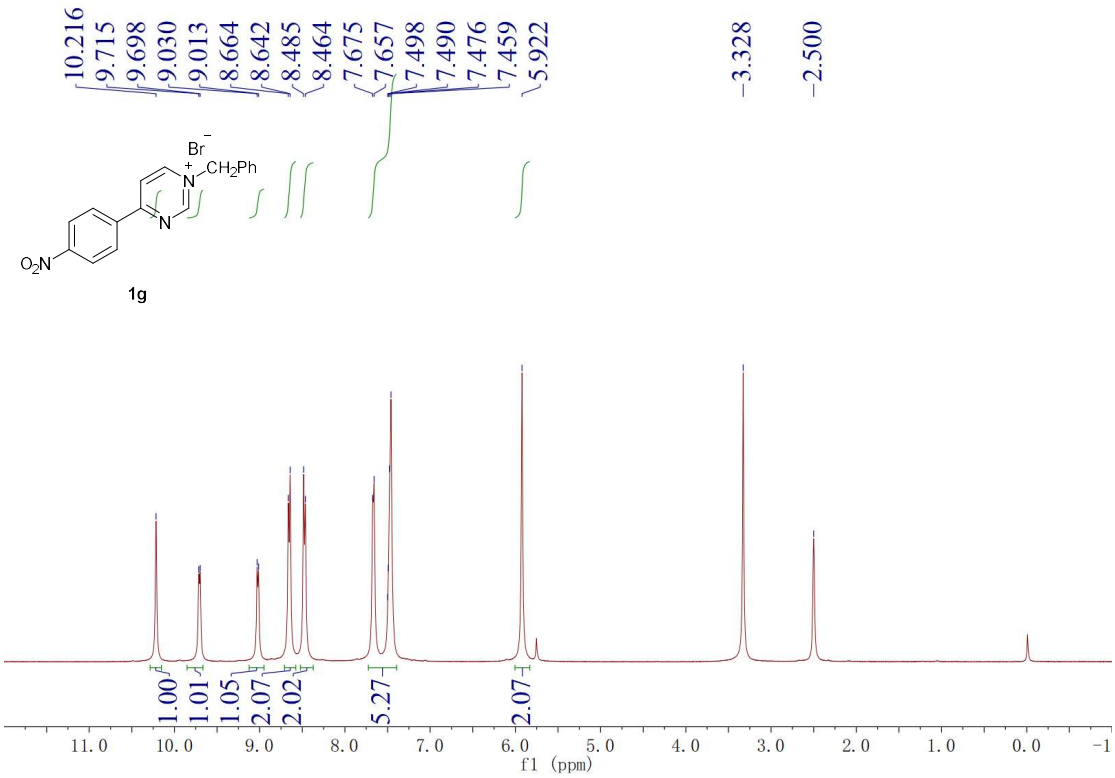
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1e



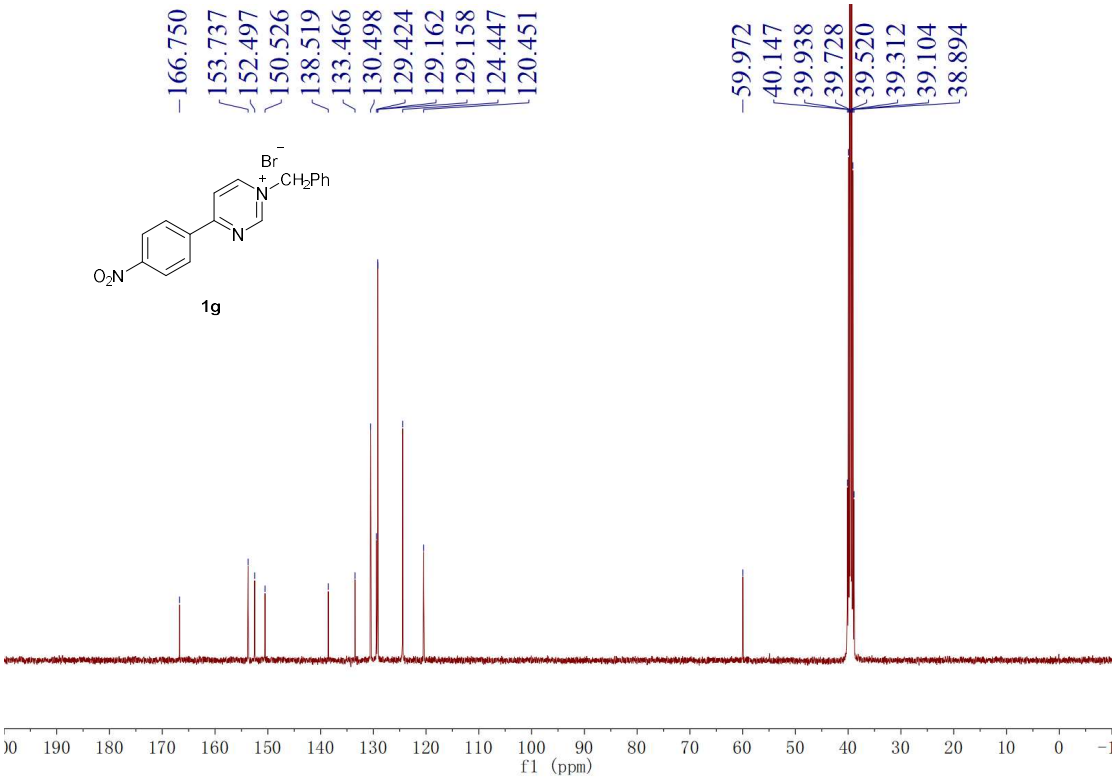
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1f



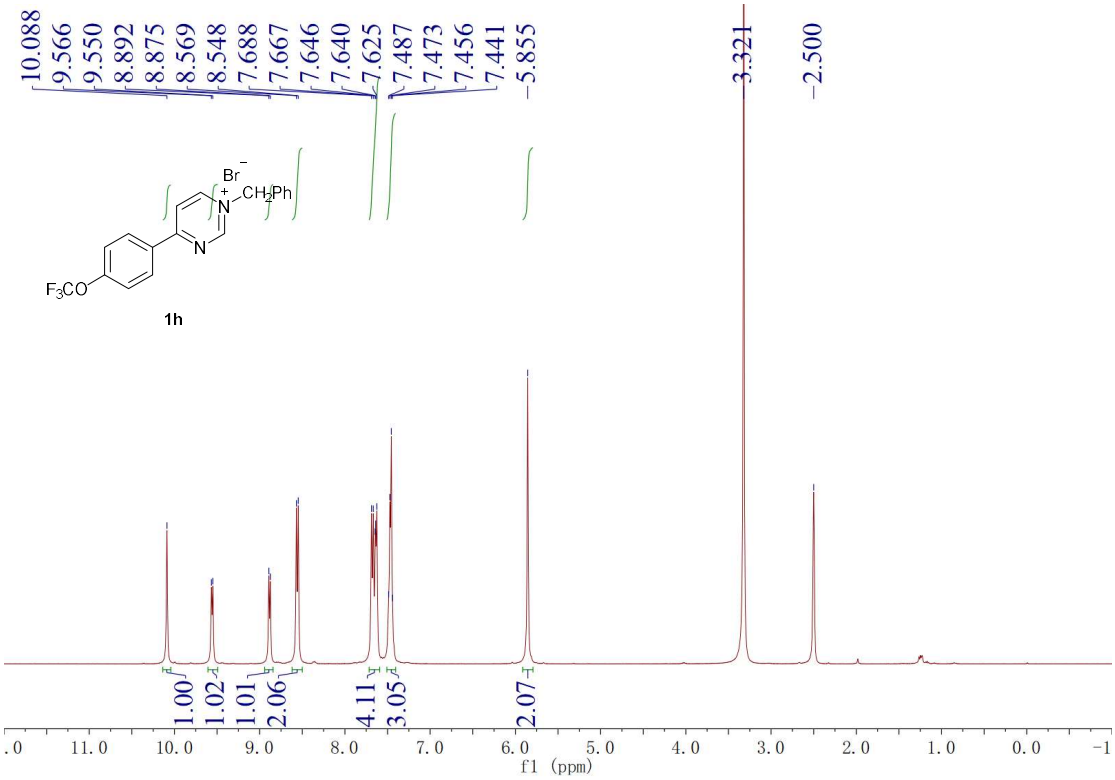
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1f



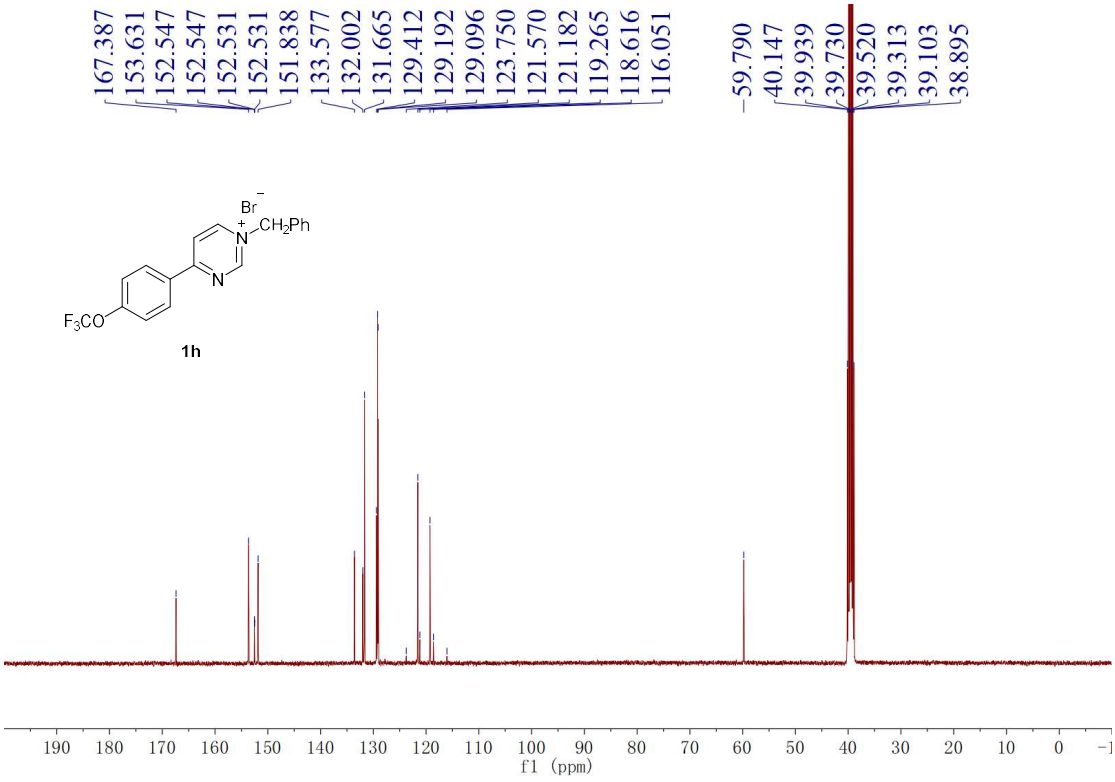
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1g



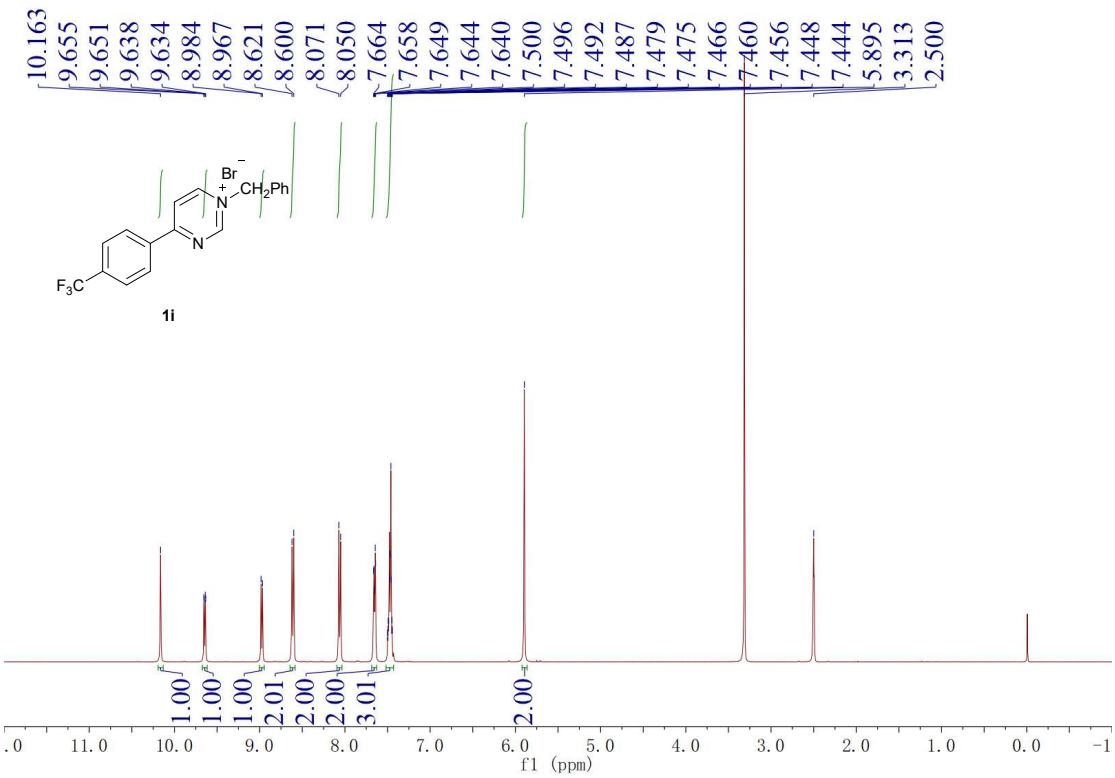
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1g



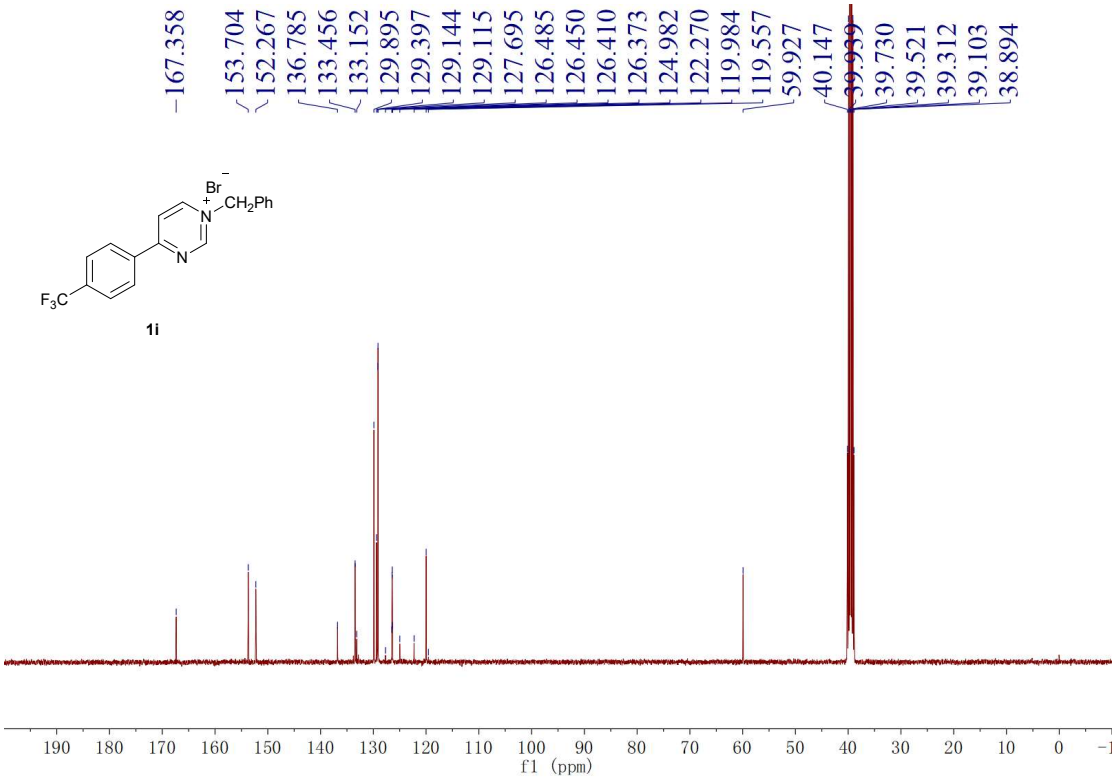
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1h



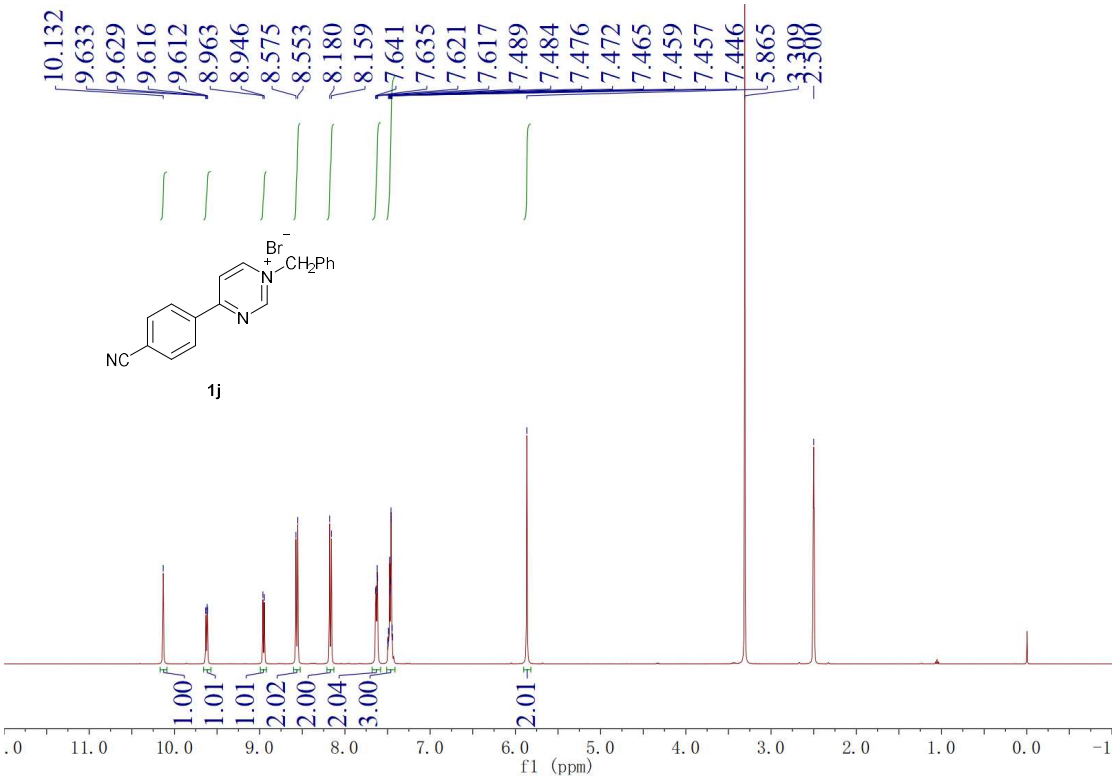
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1h



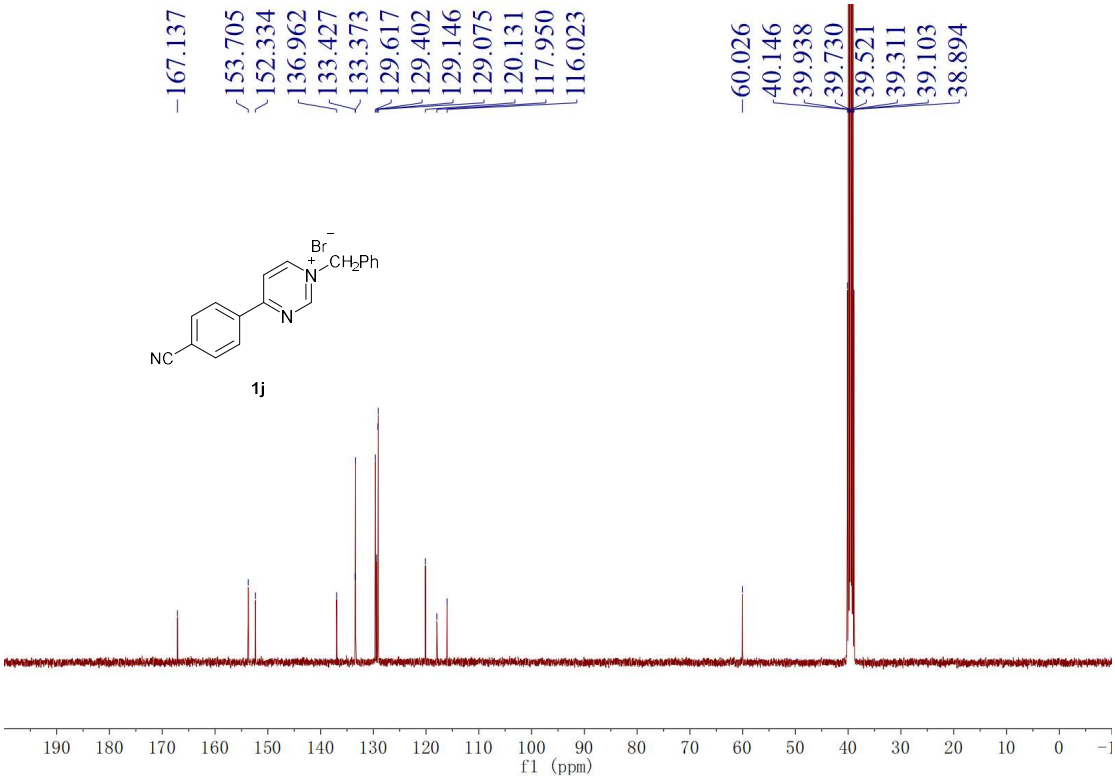
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1i



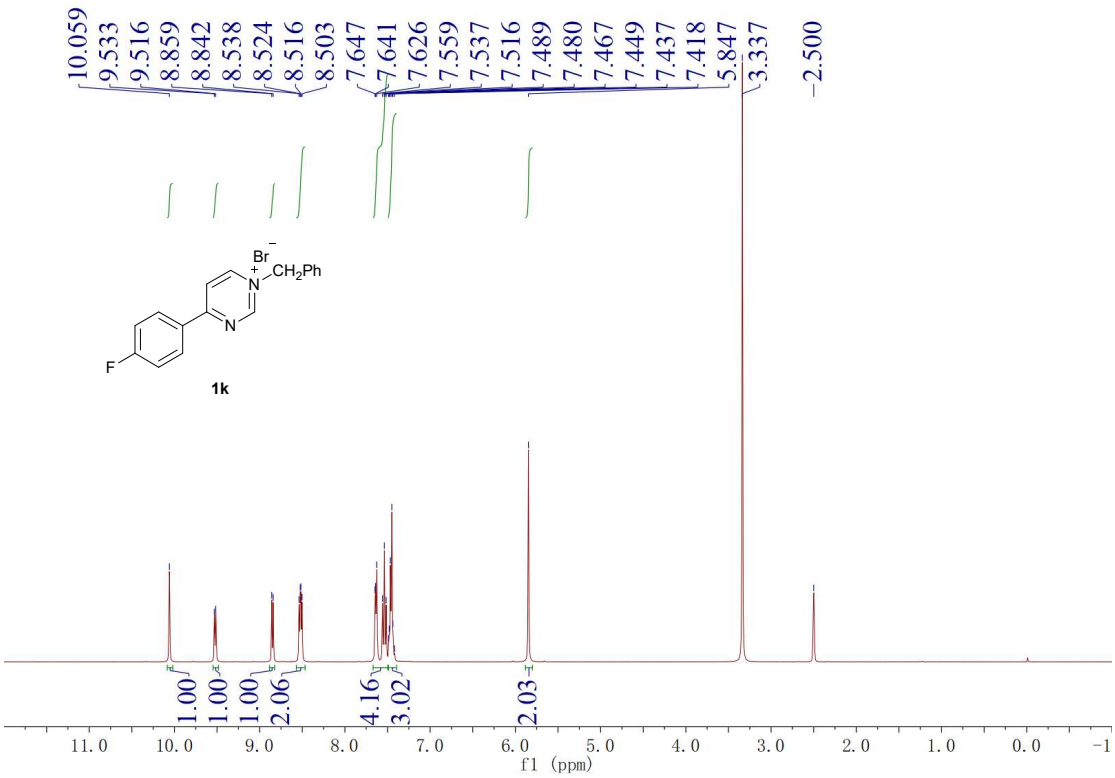
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1i



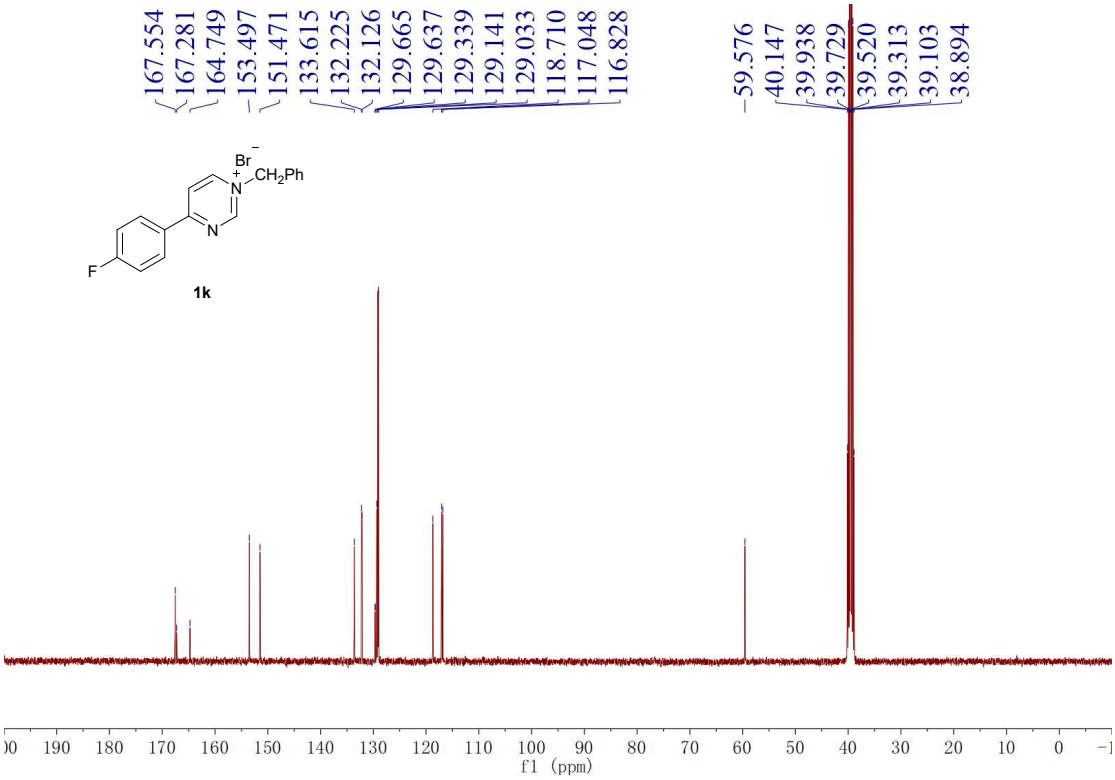
^{1}H-NMR Spectrum (400 MHz, DMSO-d_6) of Compound 1j



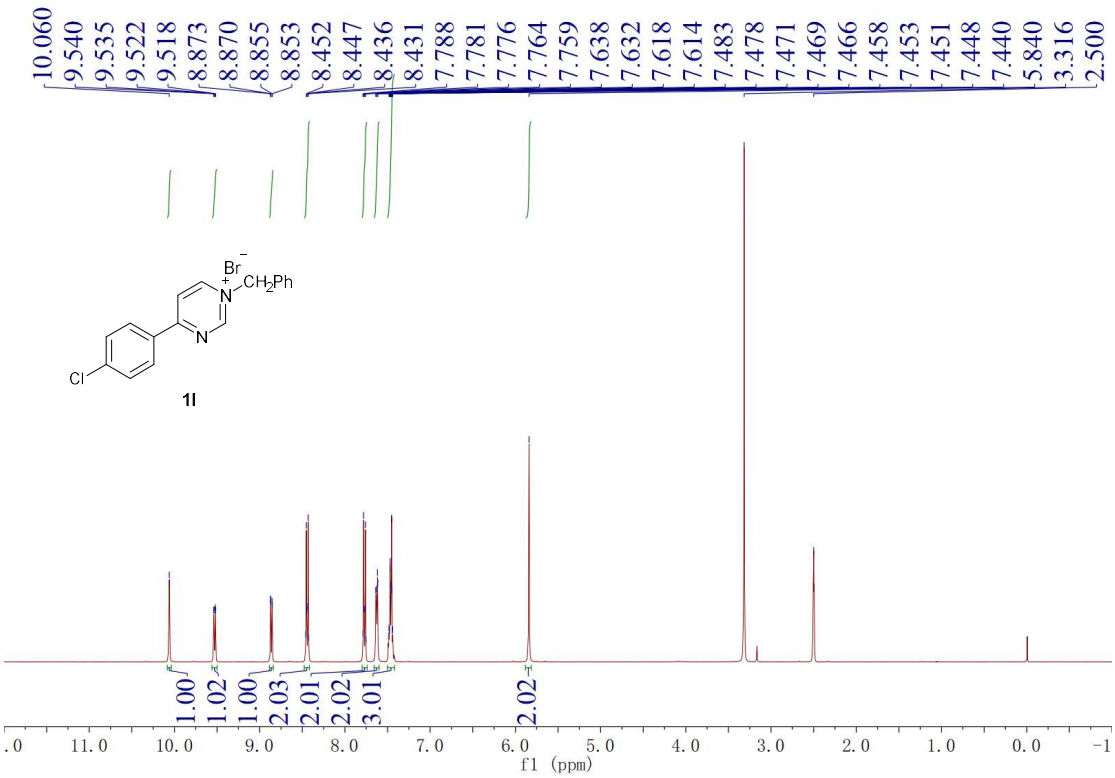
^{13}C-NMR Spectrum (100 MHz, DMSO-d_6) of Compound 1j



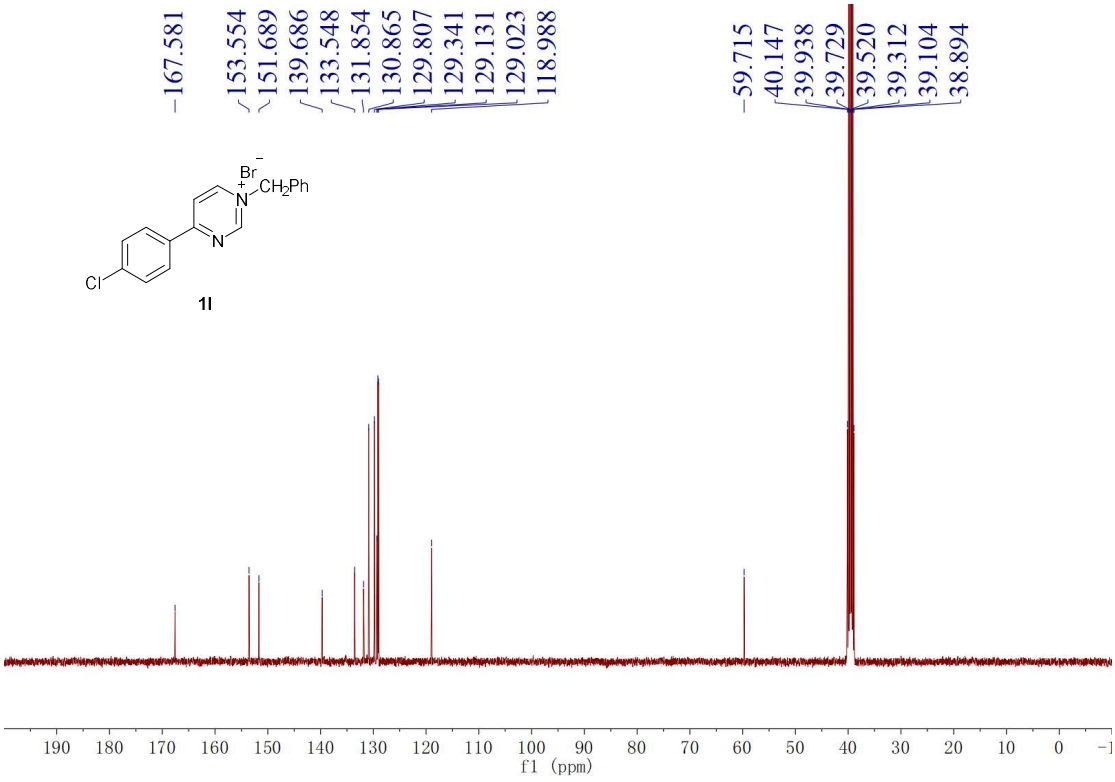
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1k



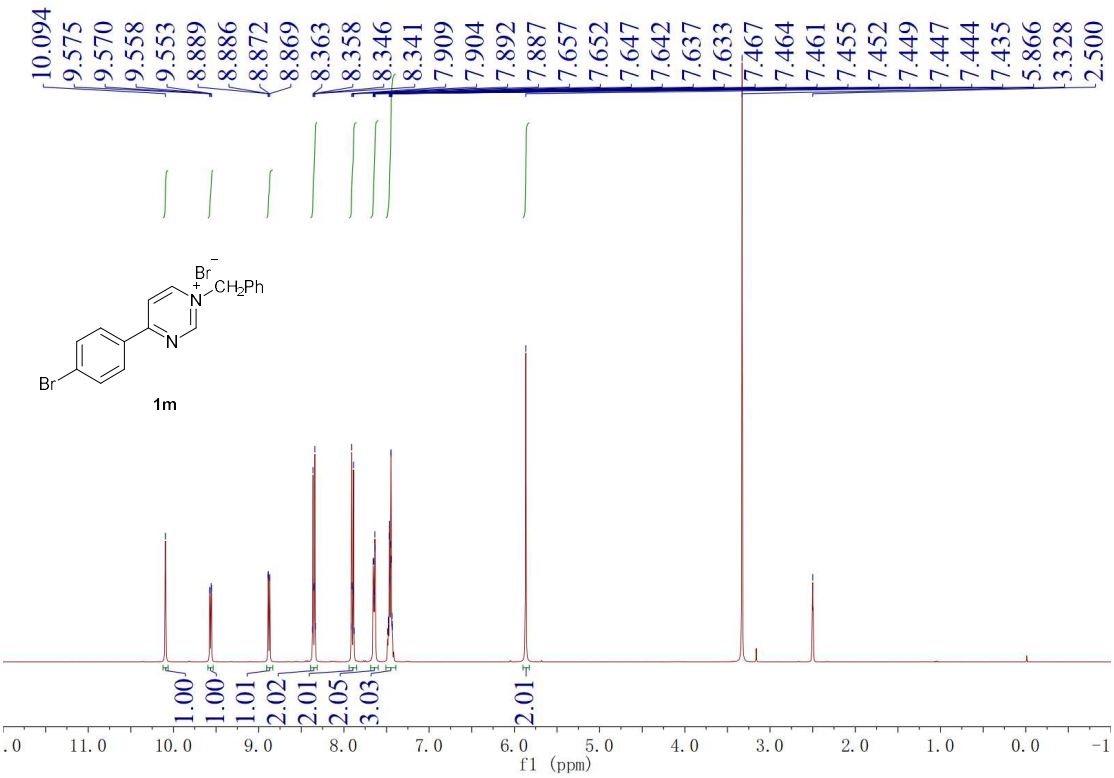
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1k



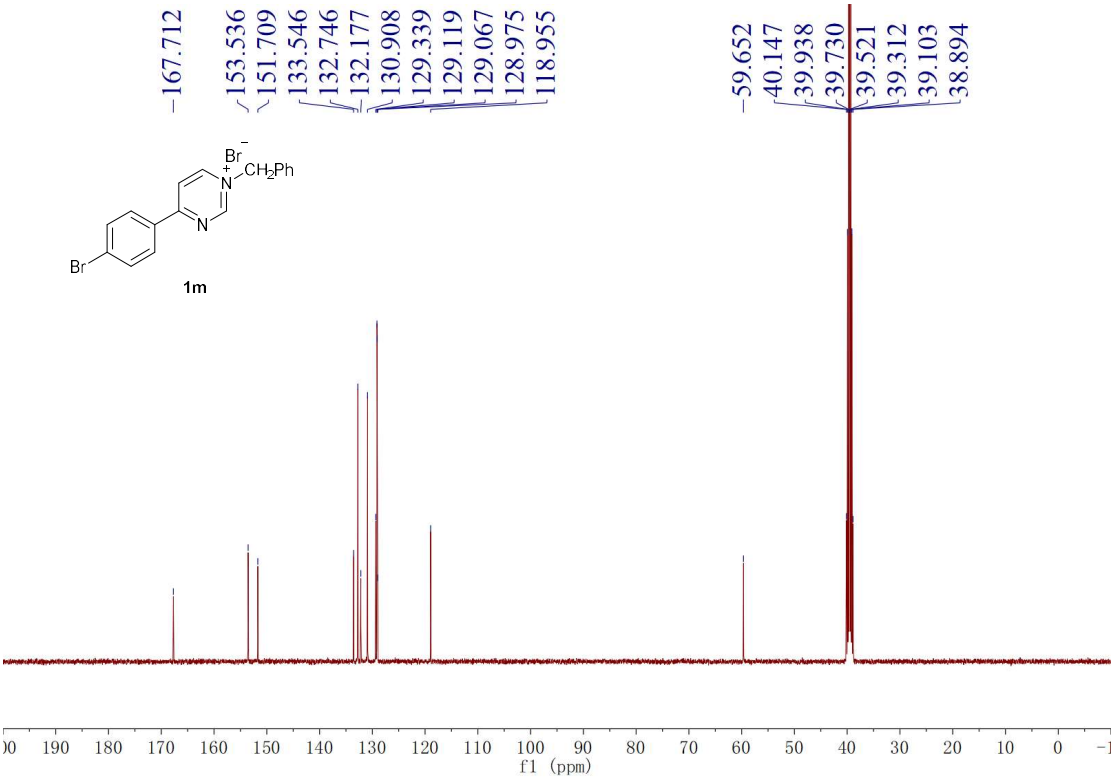
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1l



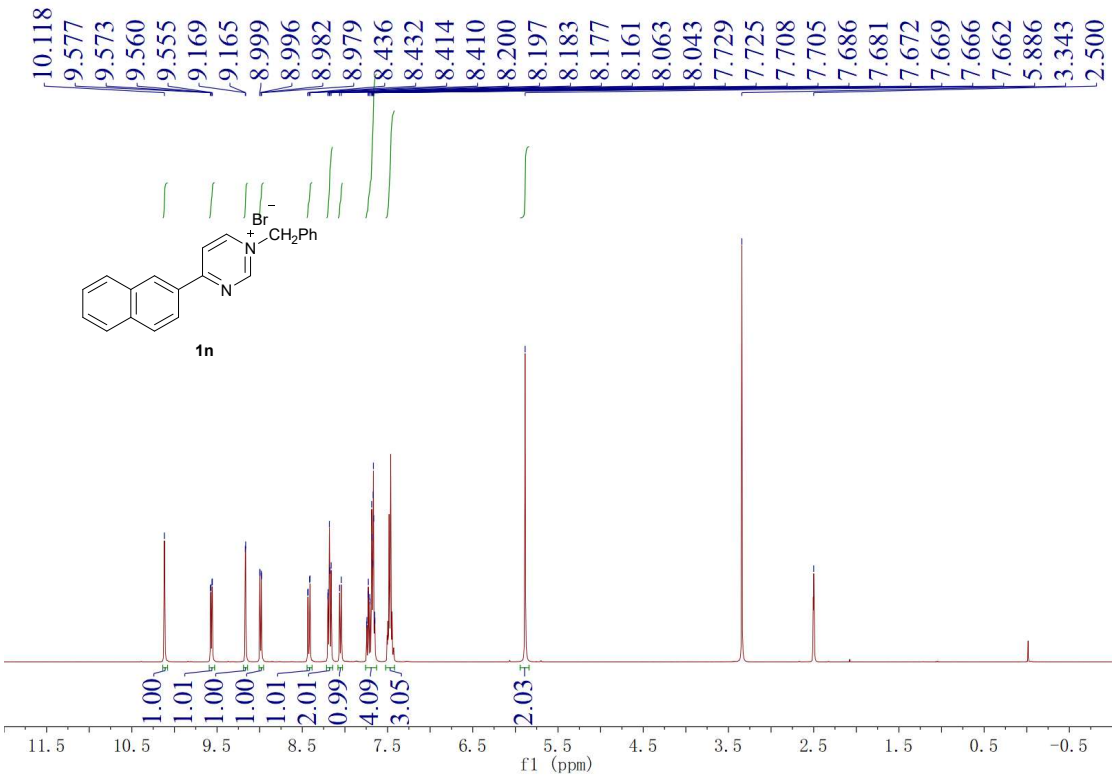
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1l



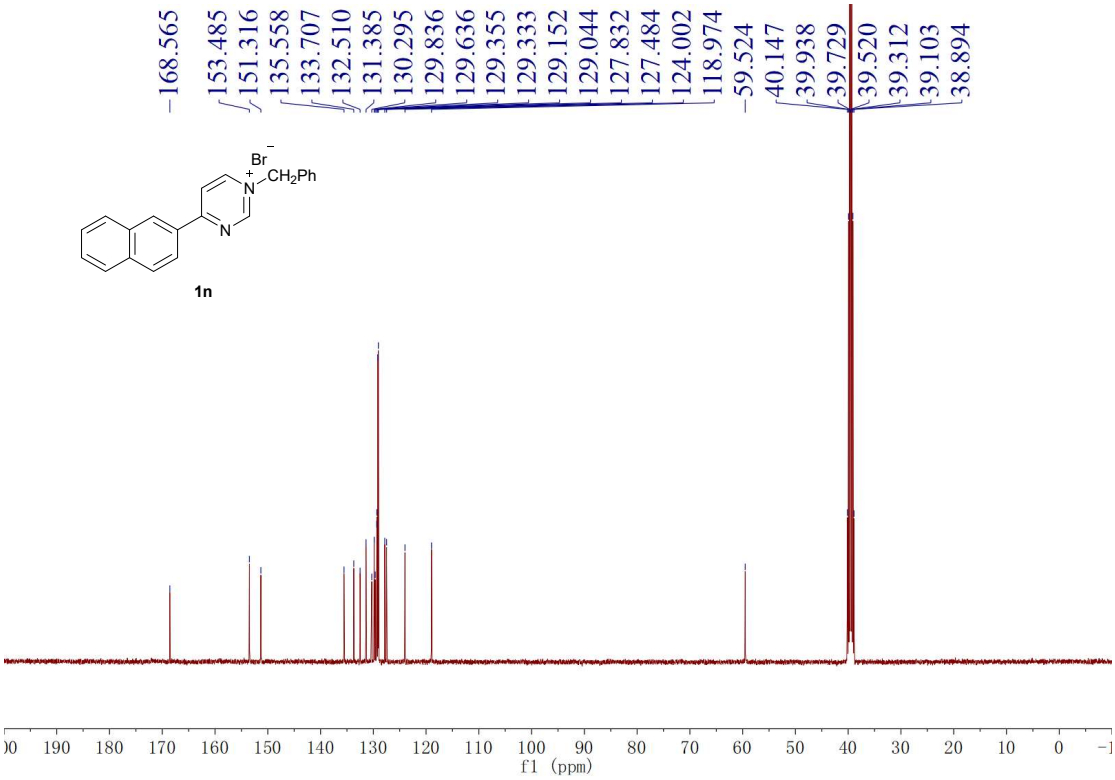
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1m



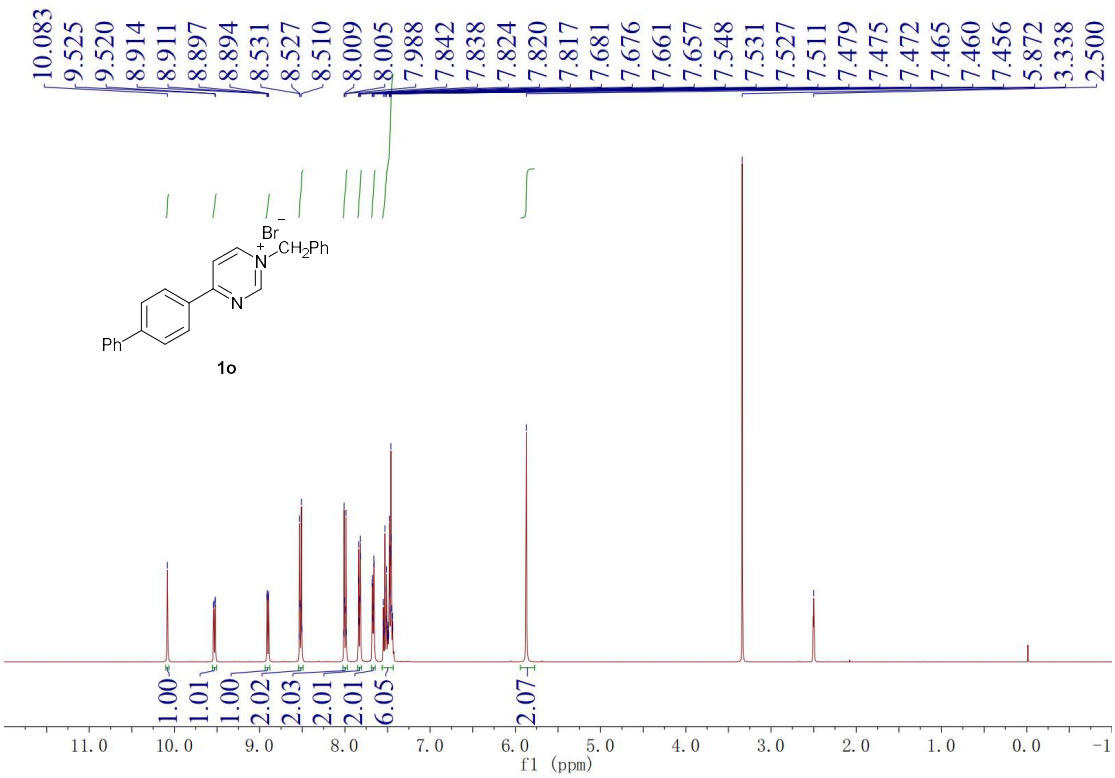
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1m



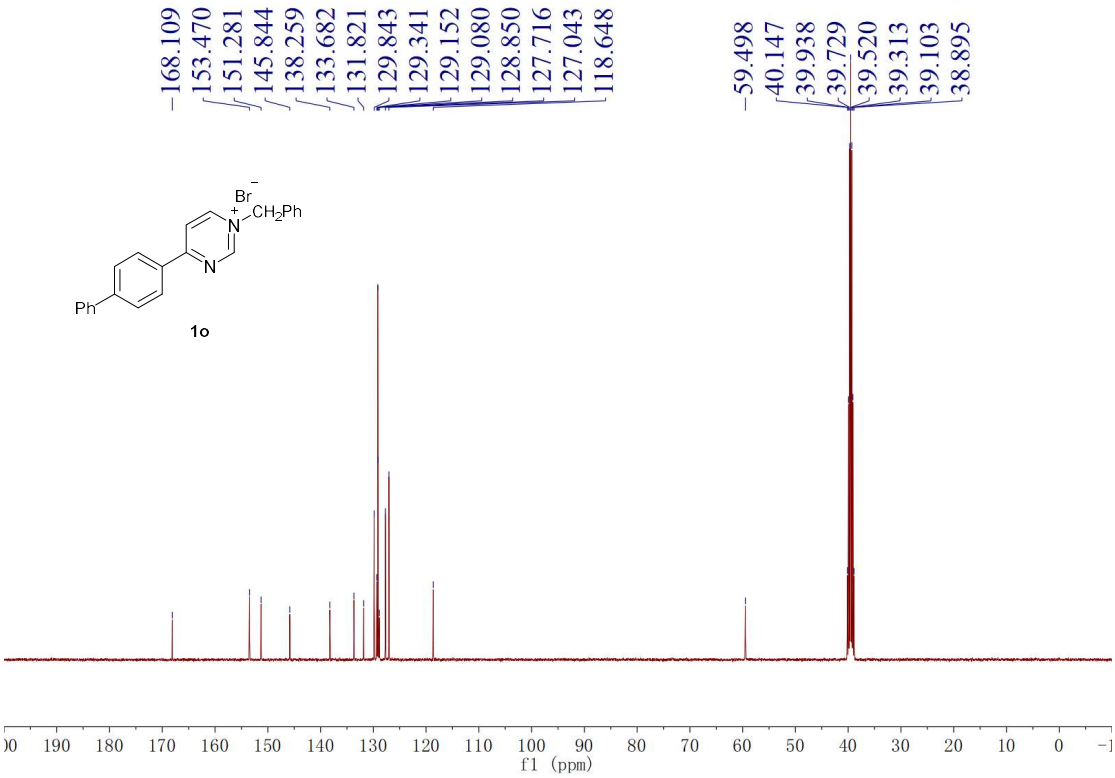
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1n



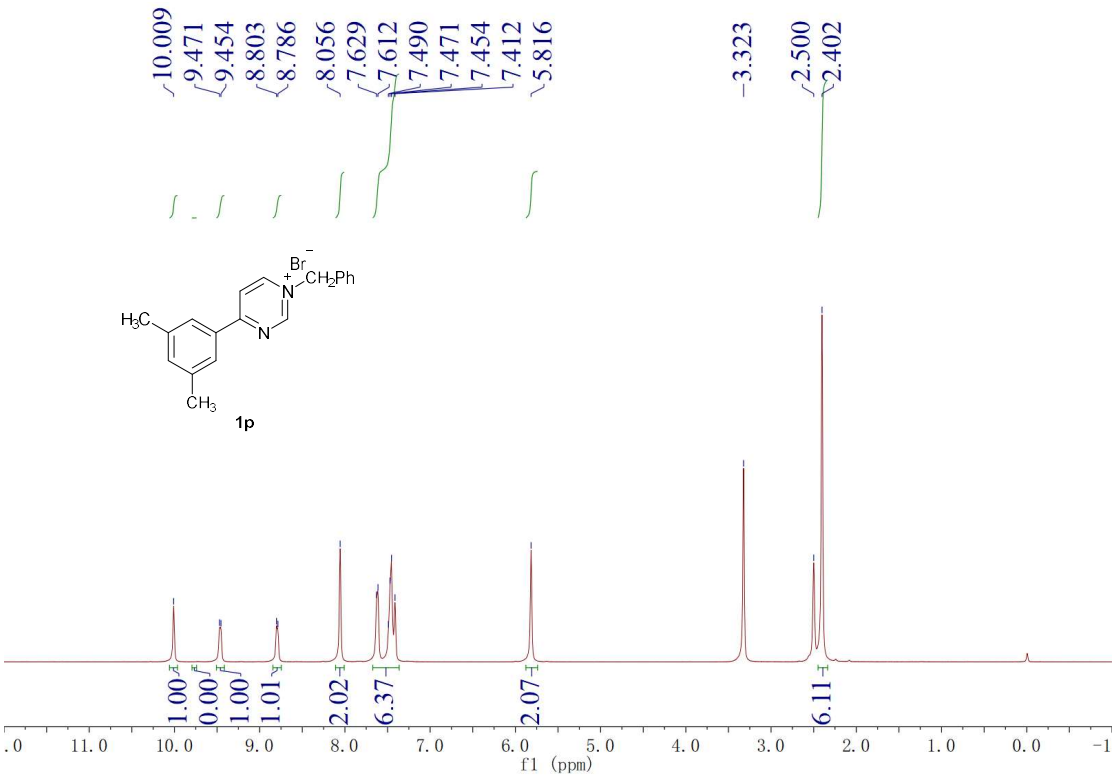
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1n



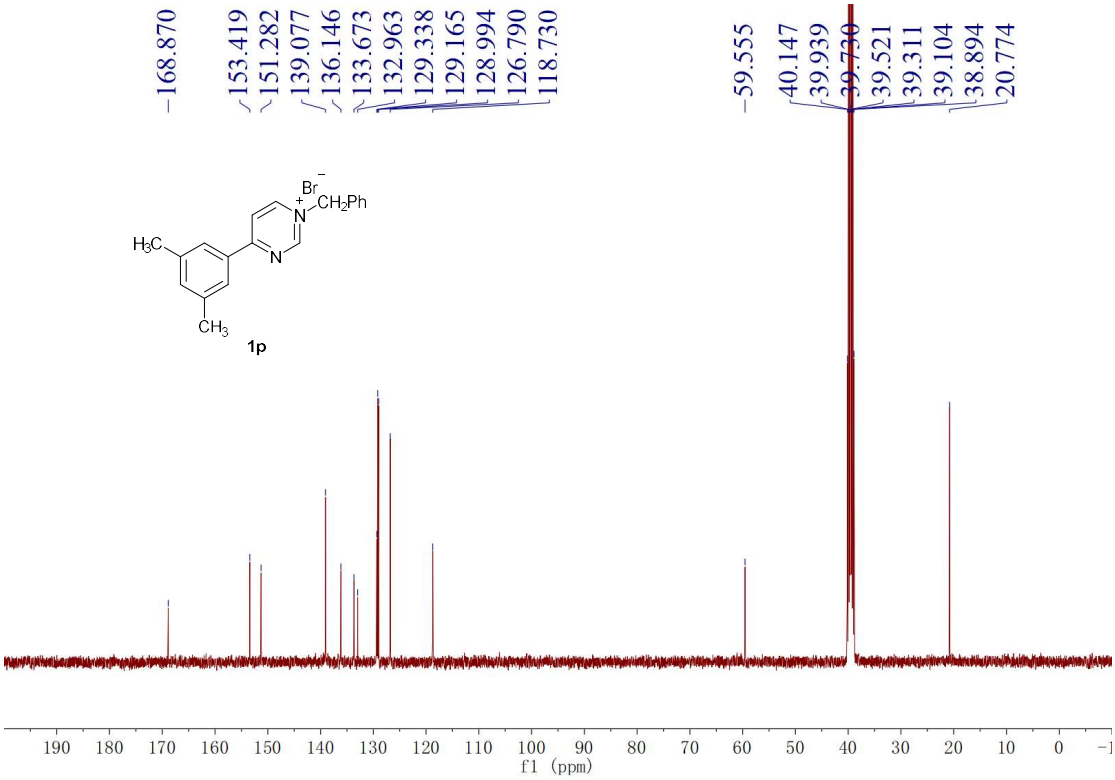
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1o



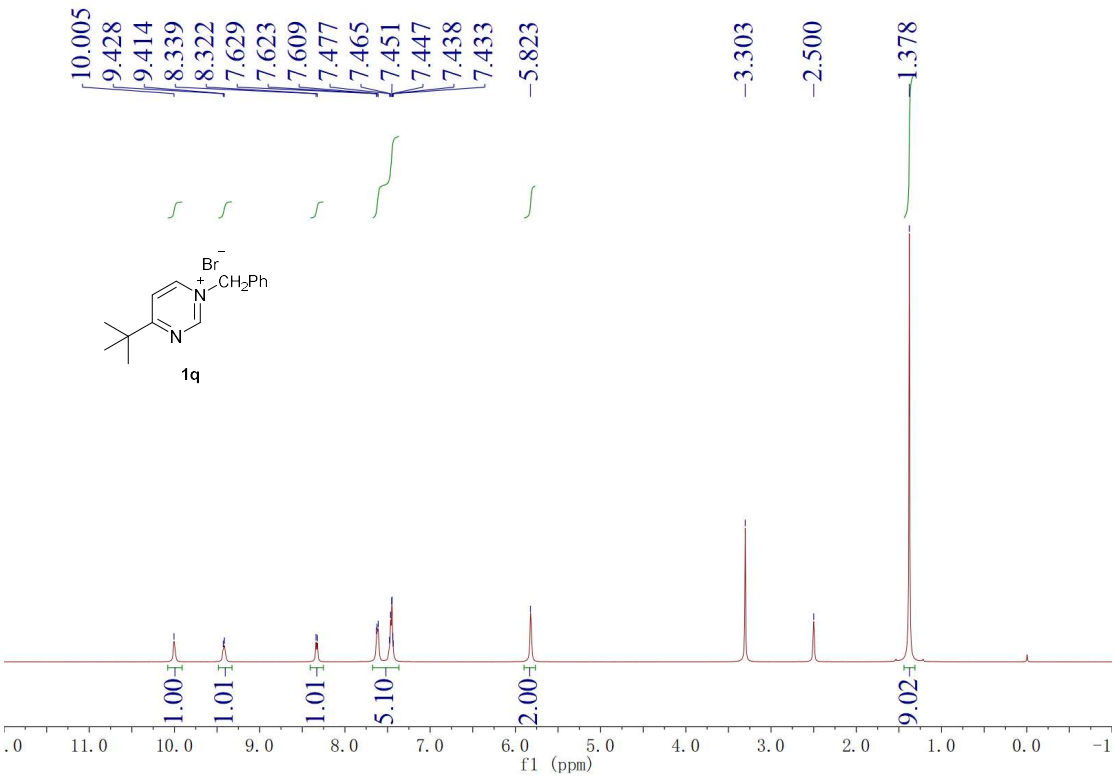
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1o



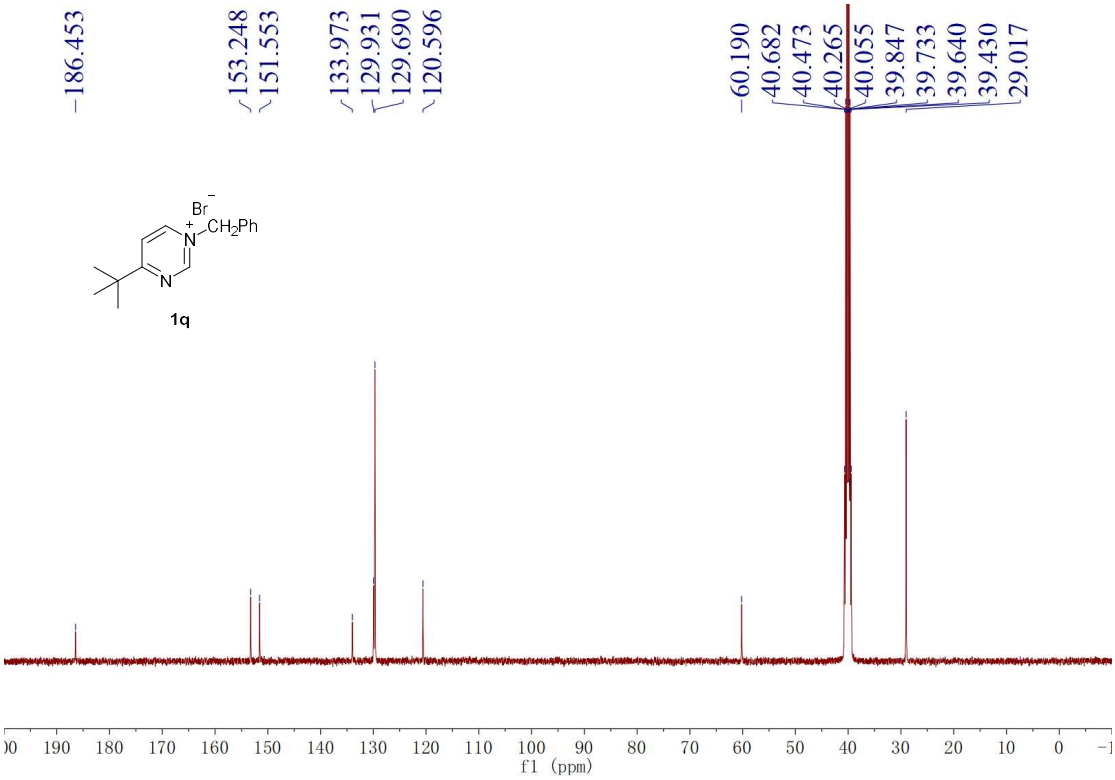
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1p



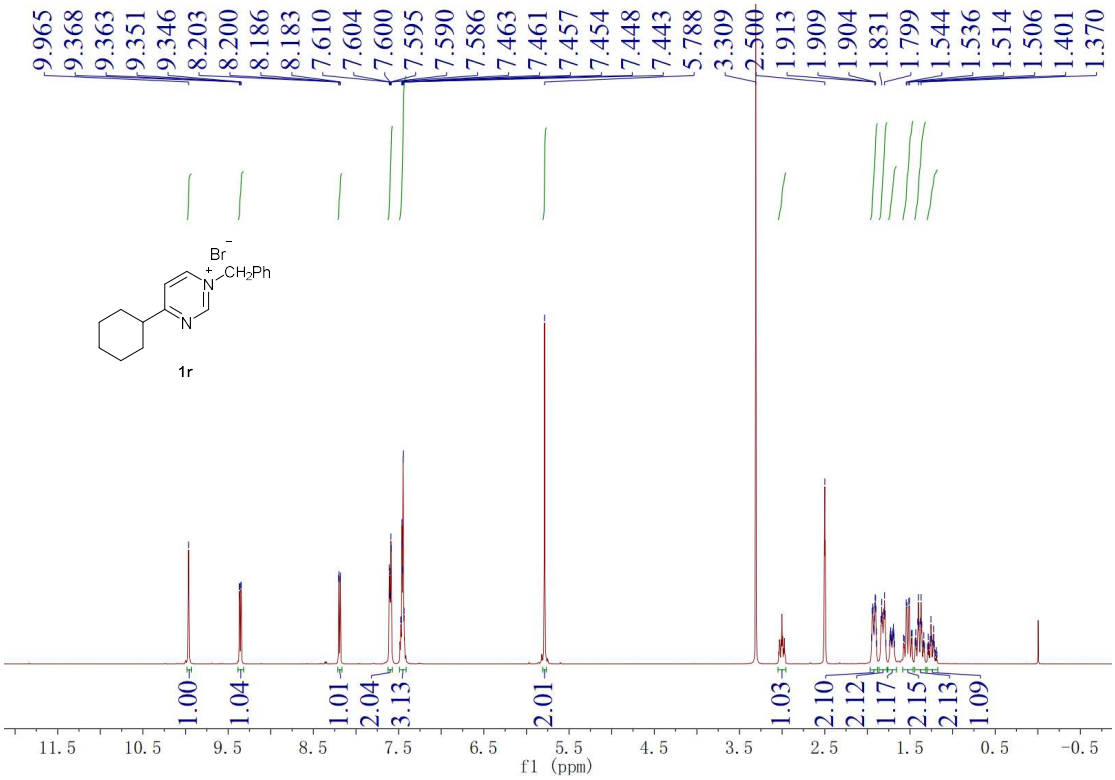
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1p



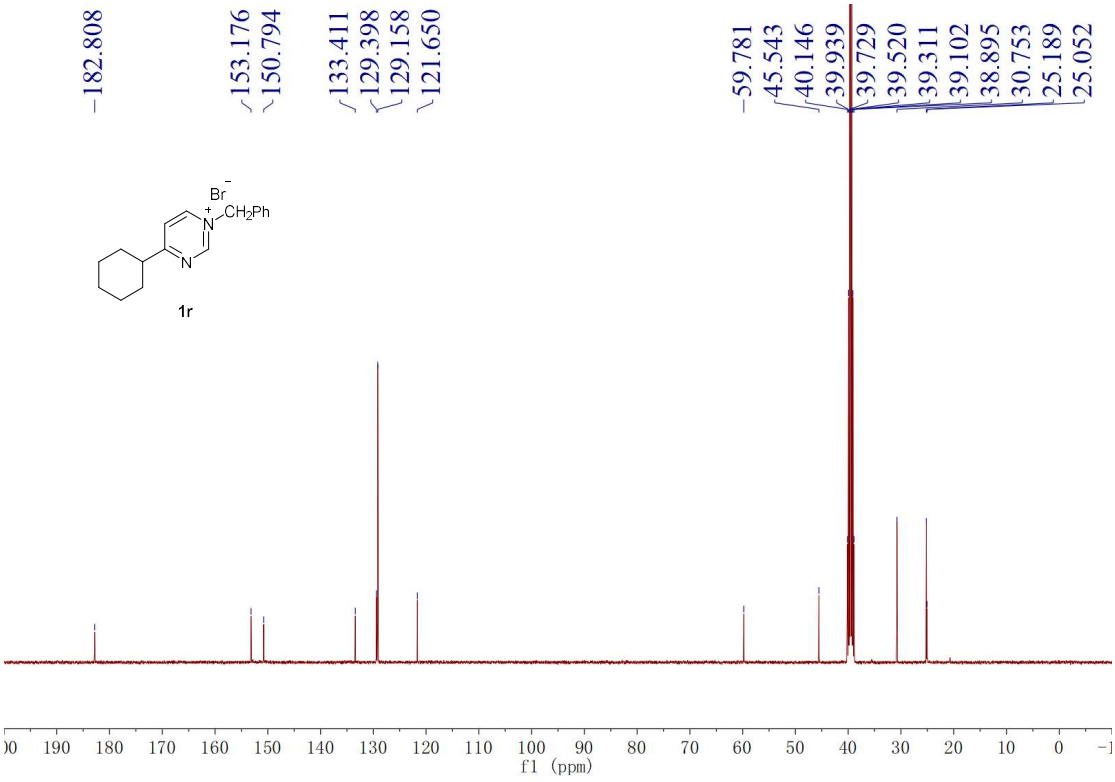
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1q



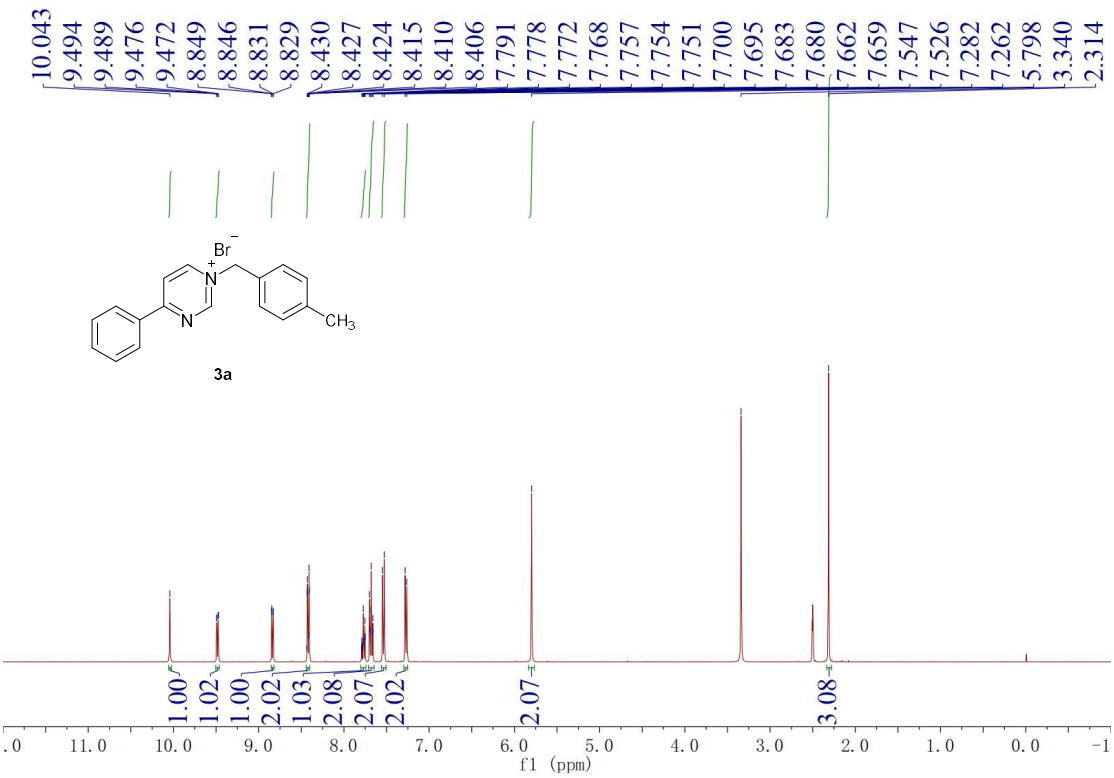
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1q



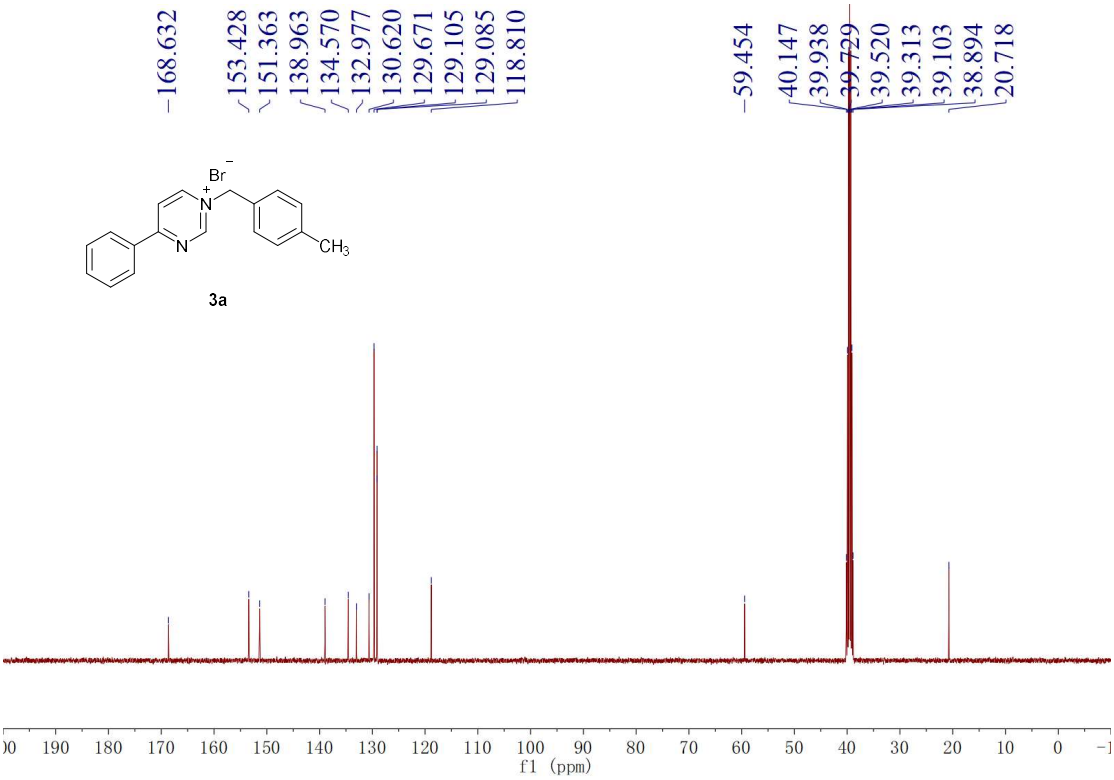
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 1r



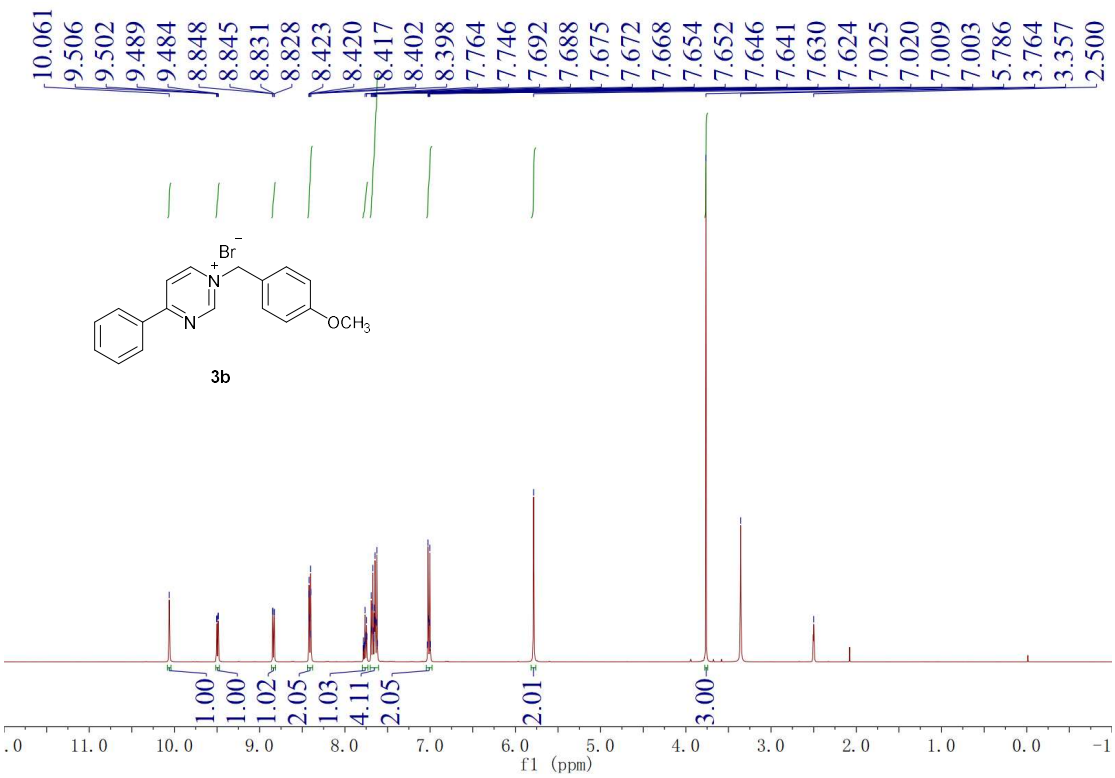
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 1r



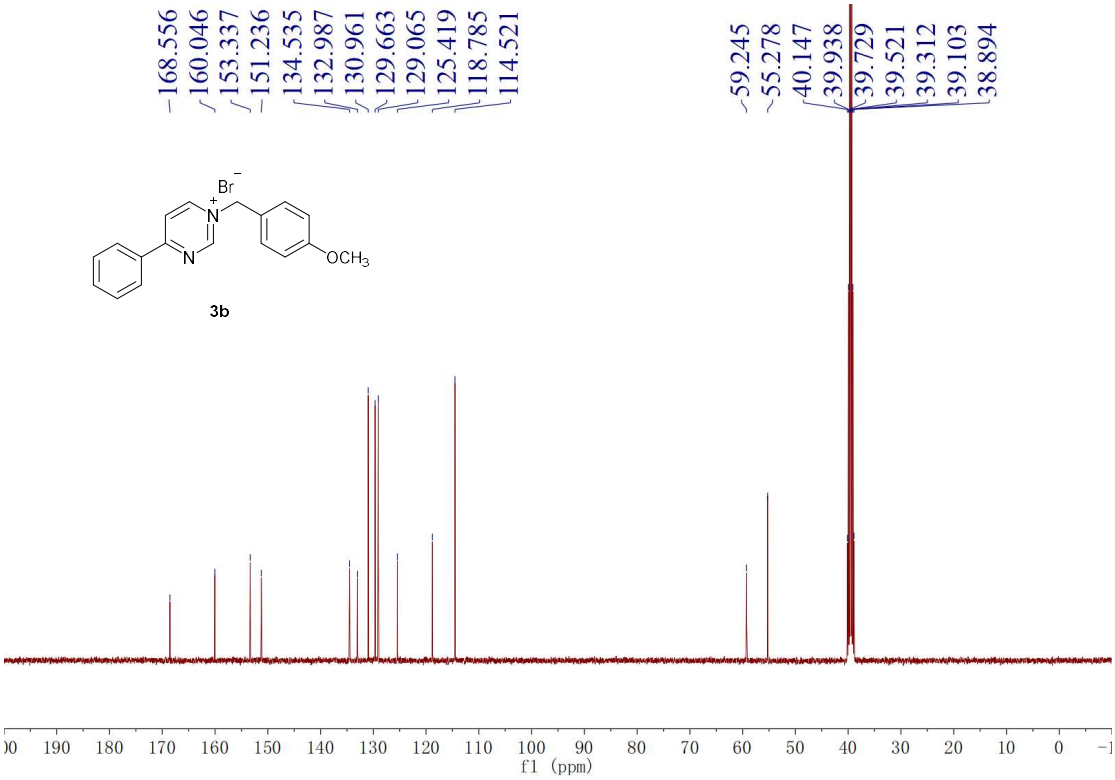
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3a



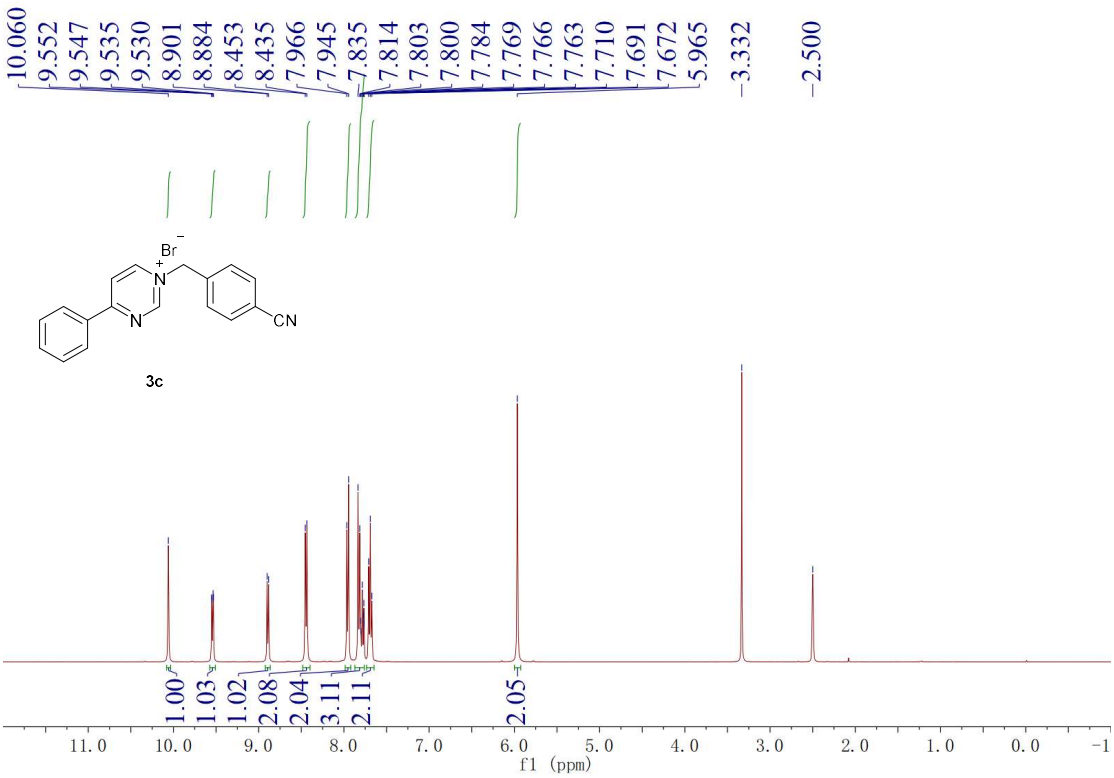
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3a



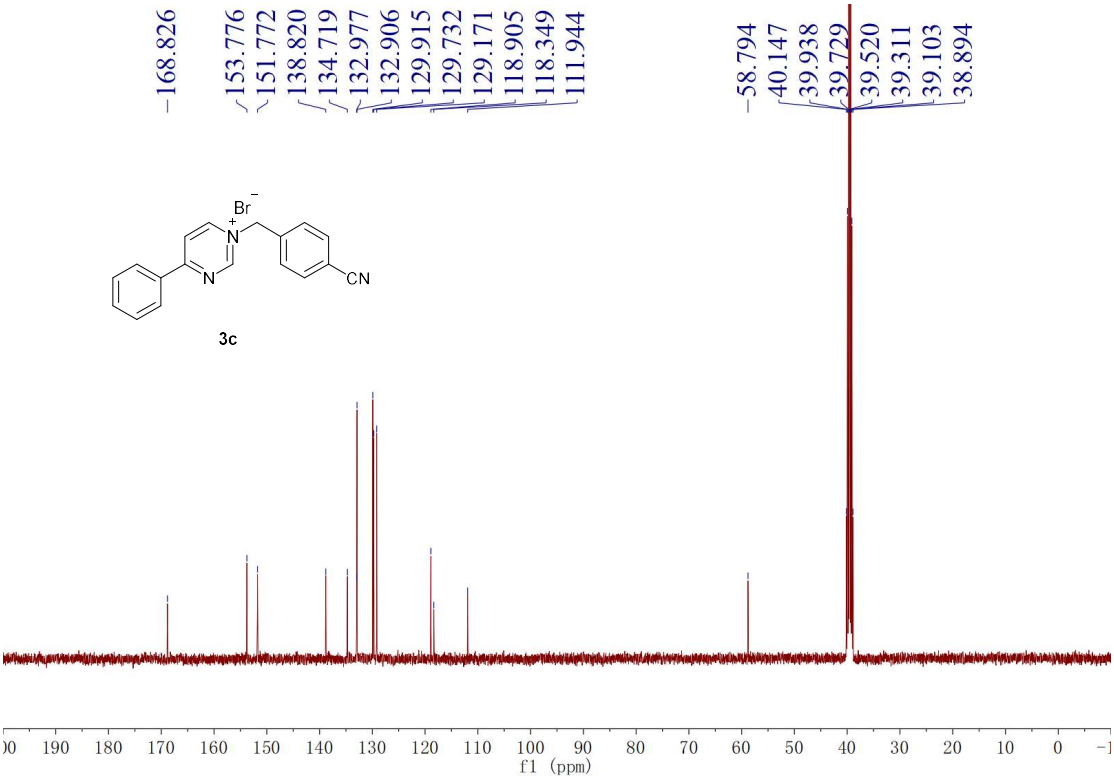
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3b



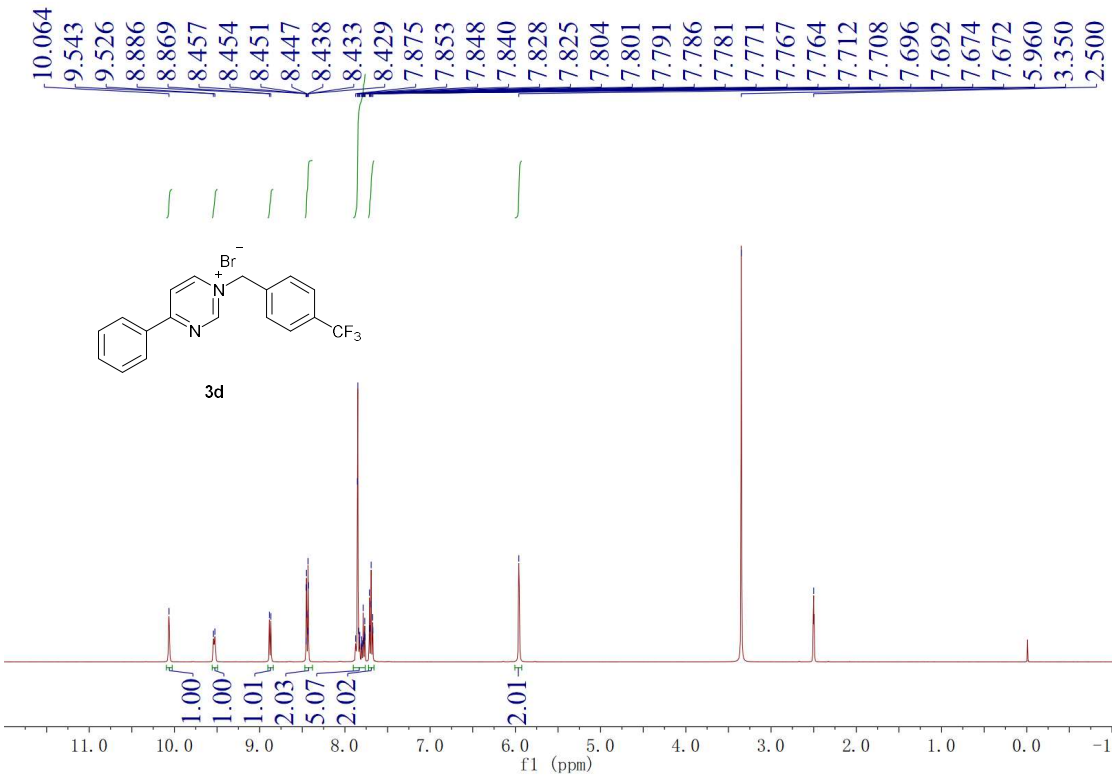
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3b



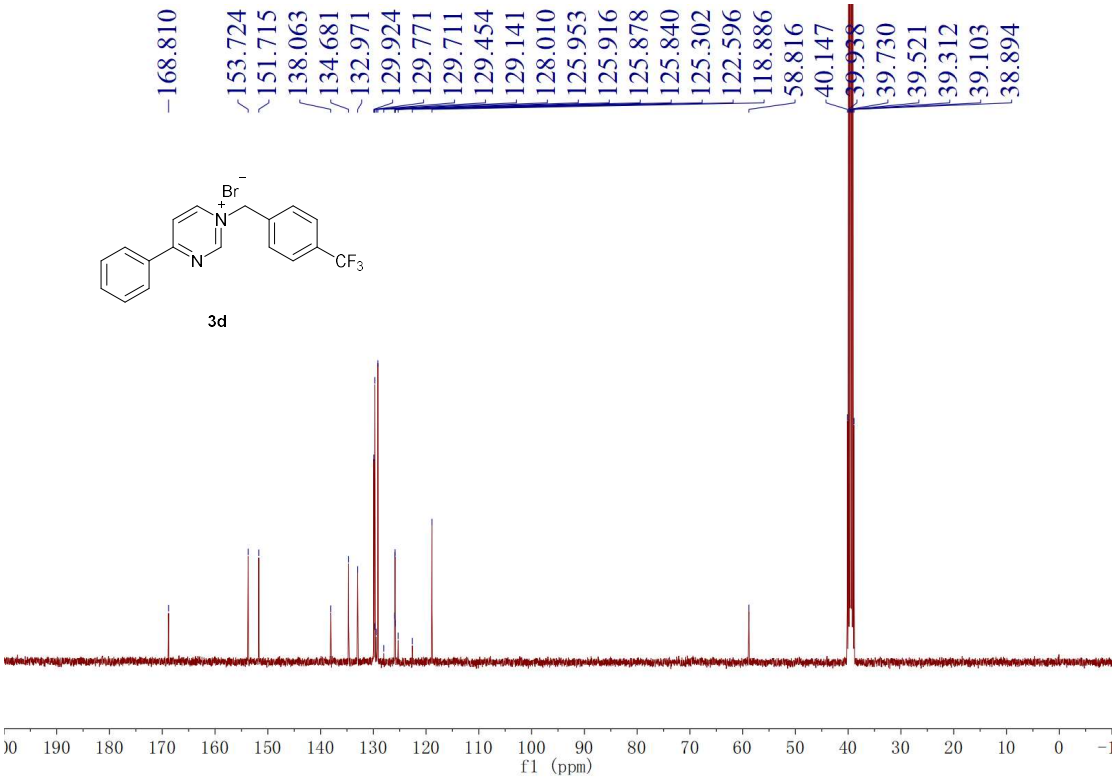
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3c



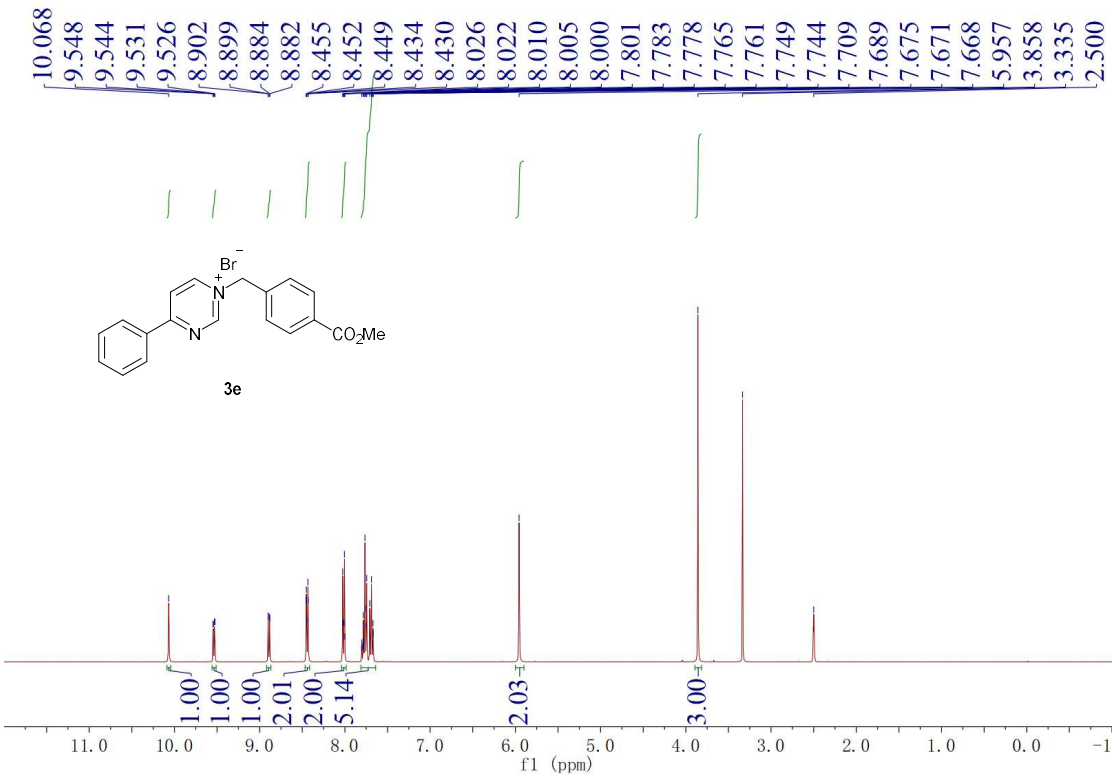
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3c



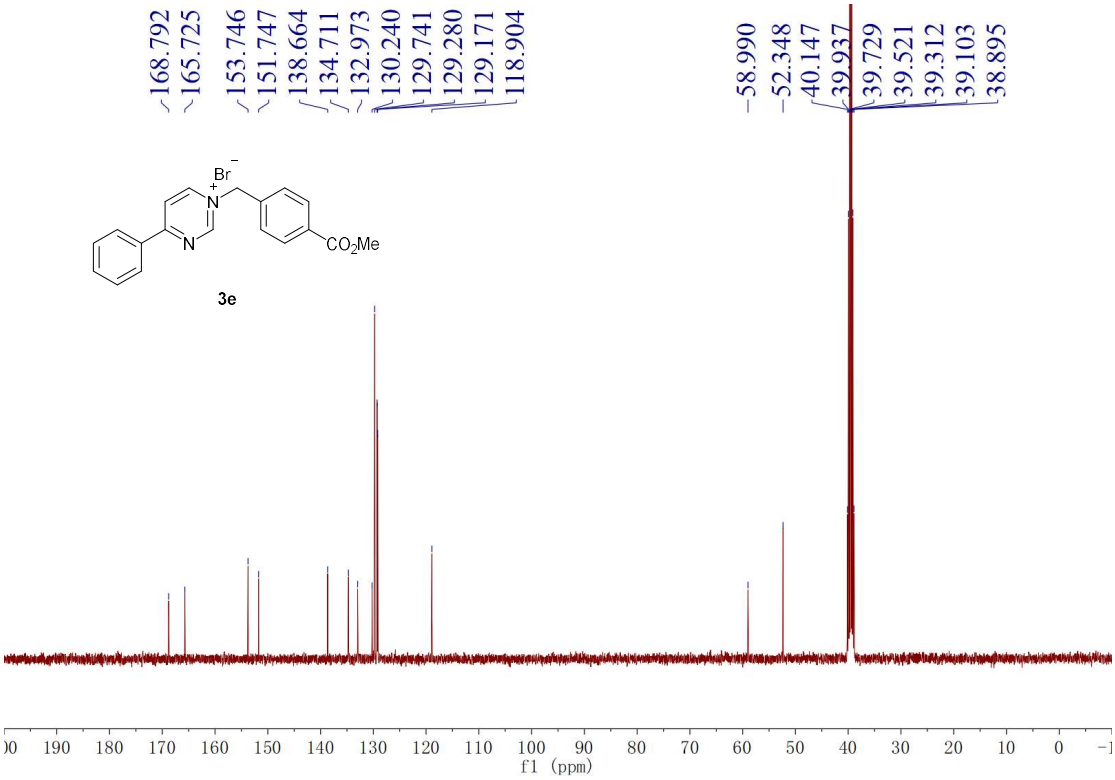
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3d



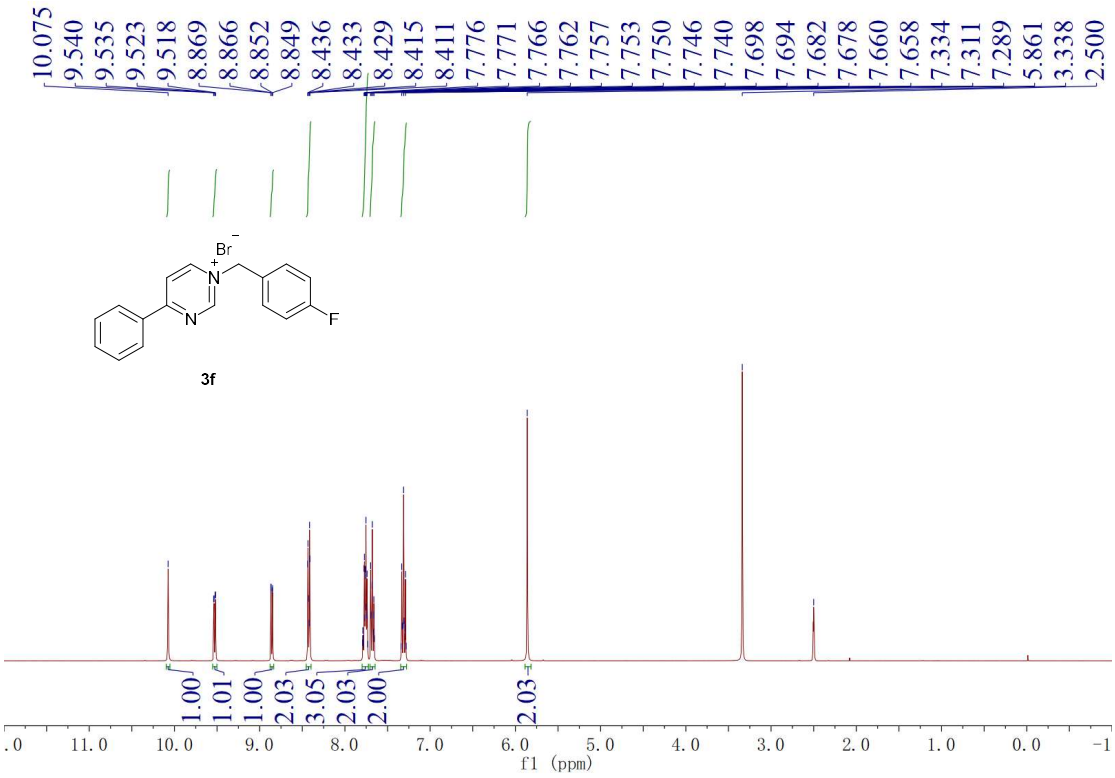
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3d



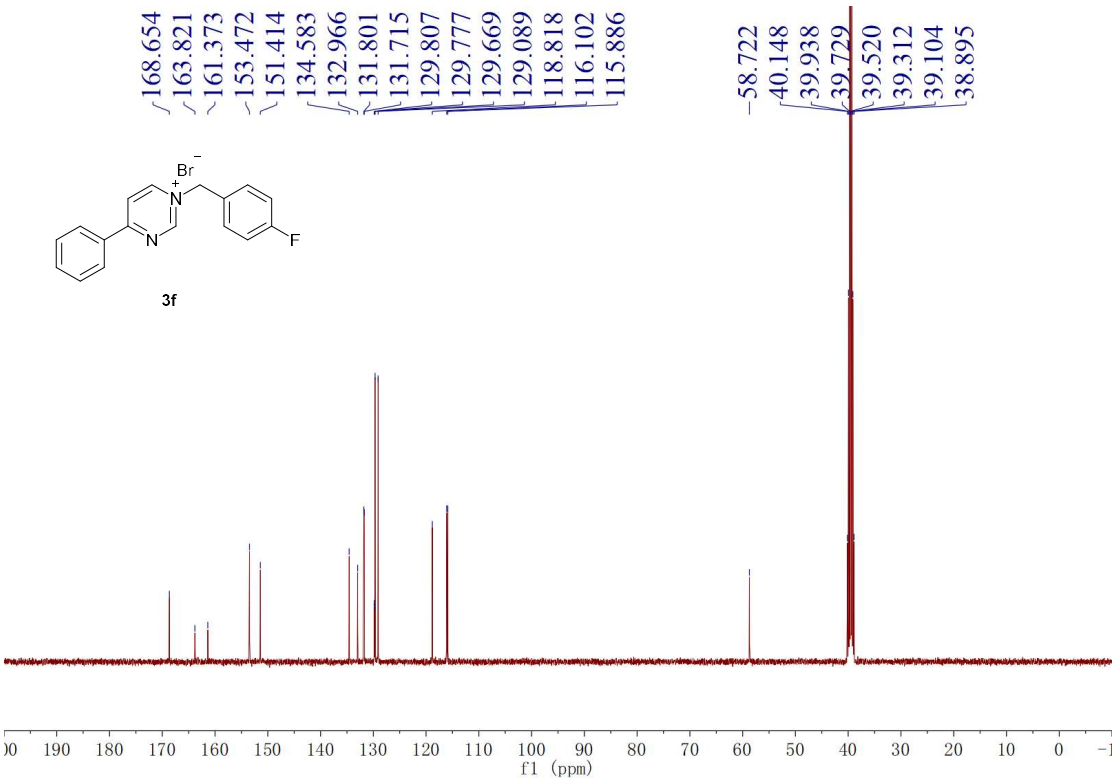
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3e



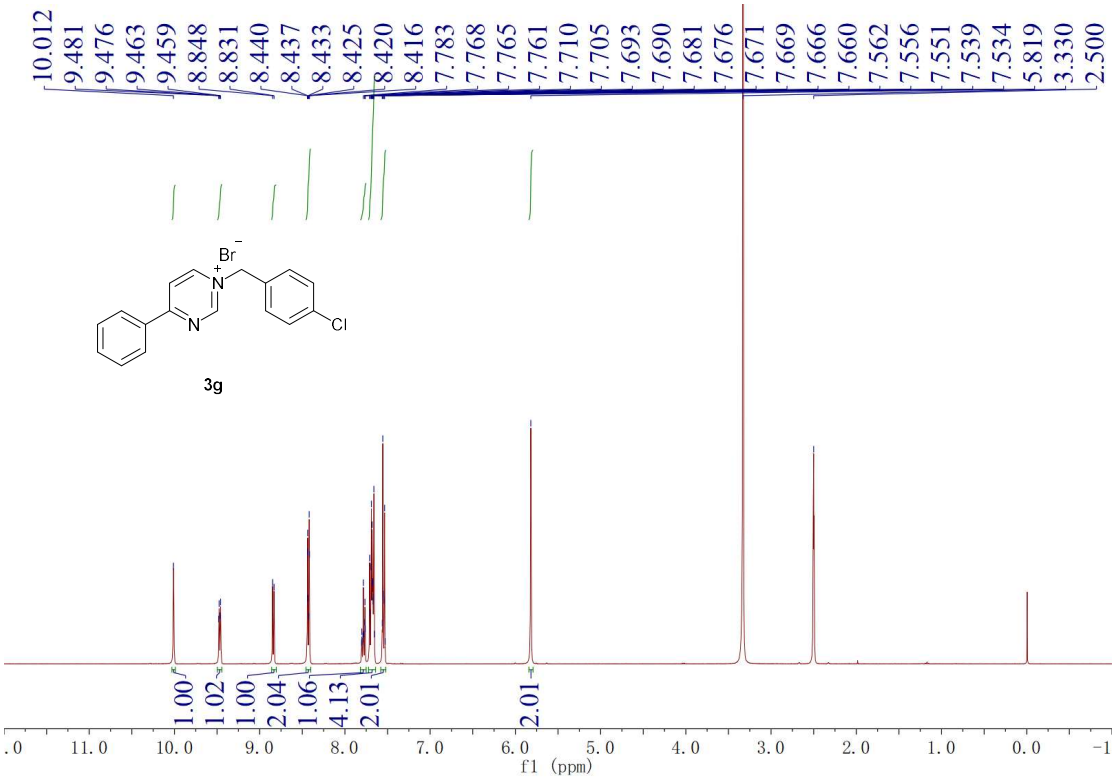
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3e



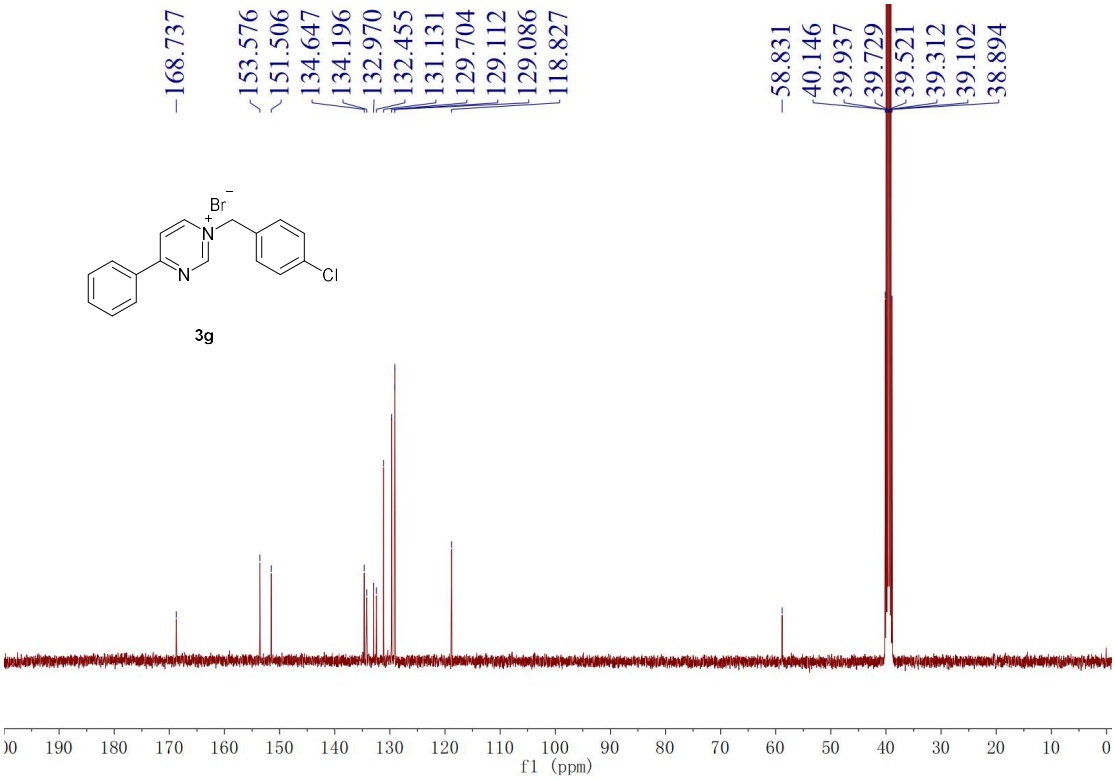
[1]H-NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3f



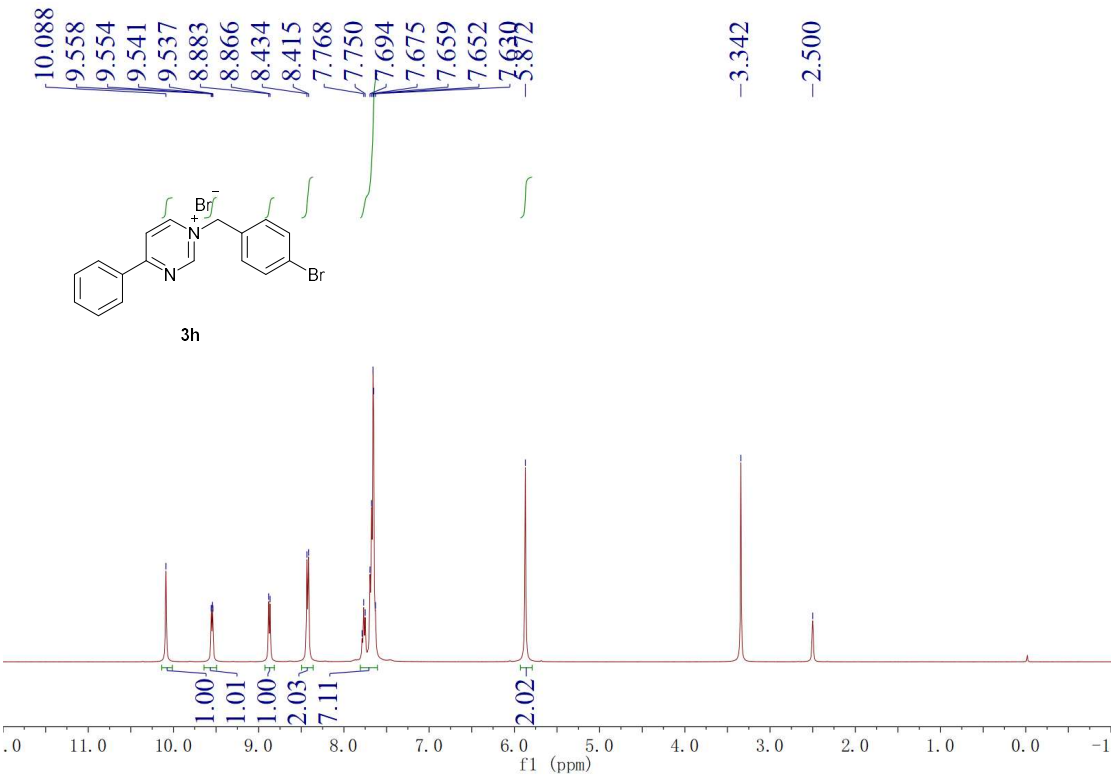
[13]C-NMR Spectrum (100 MHz, DMSO-d_6) of Compound 3f



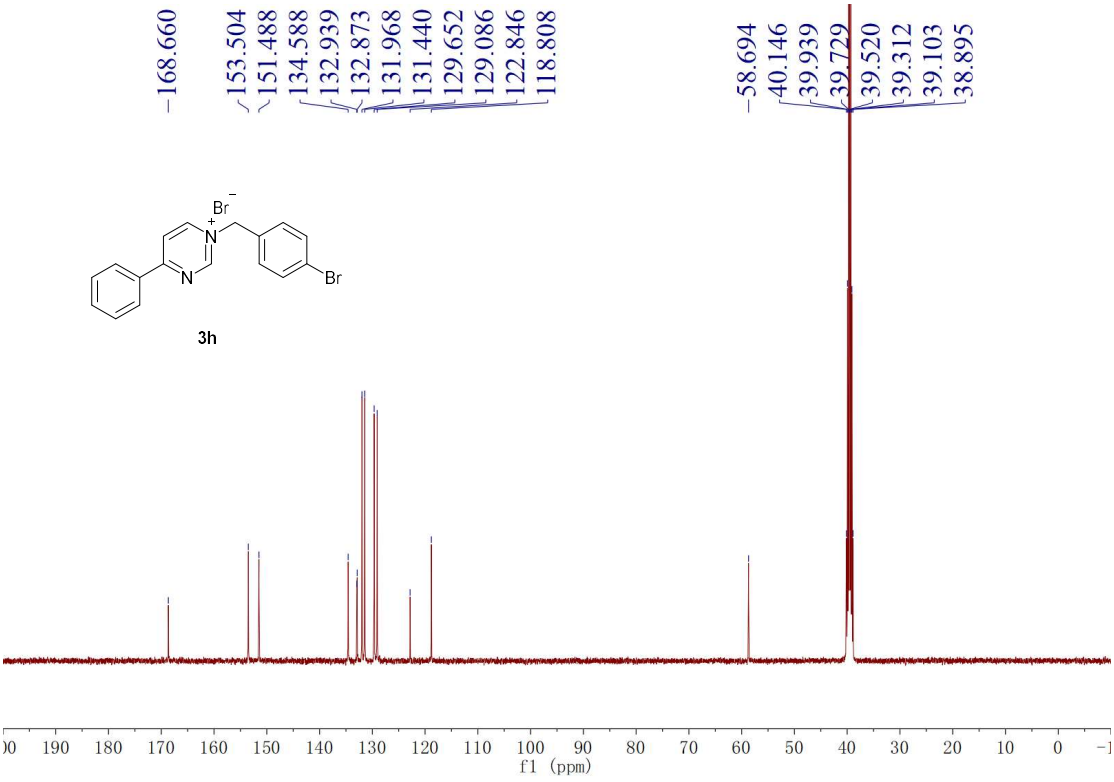
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3g



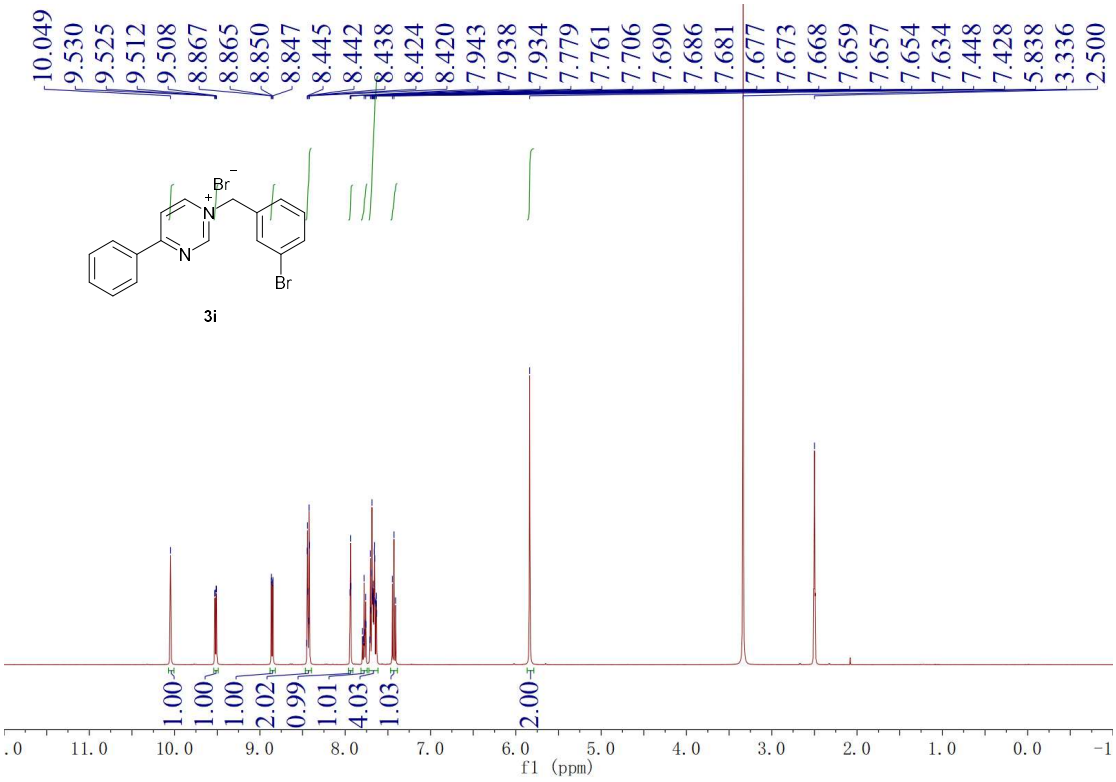
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3g



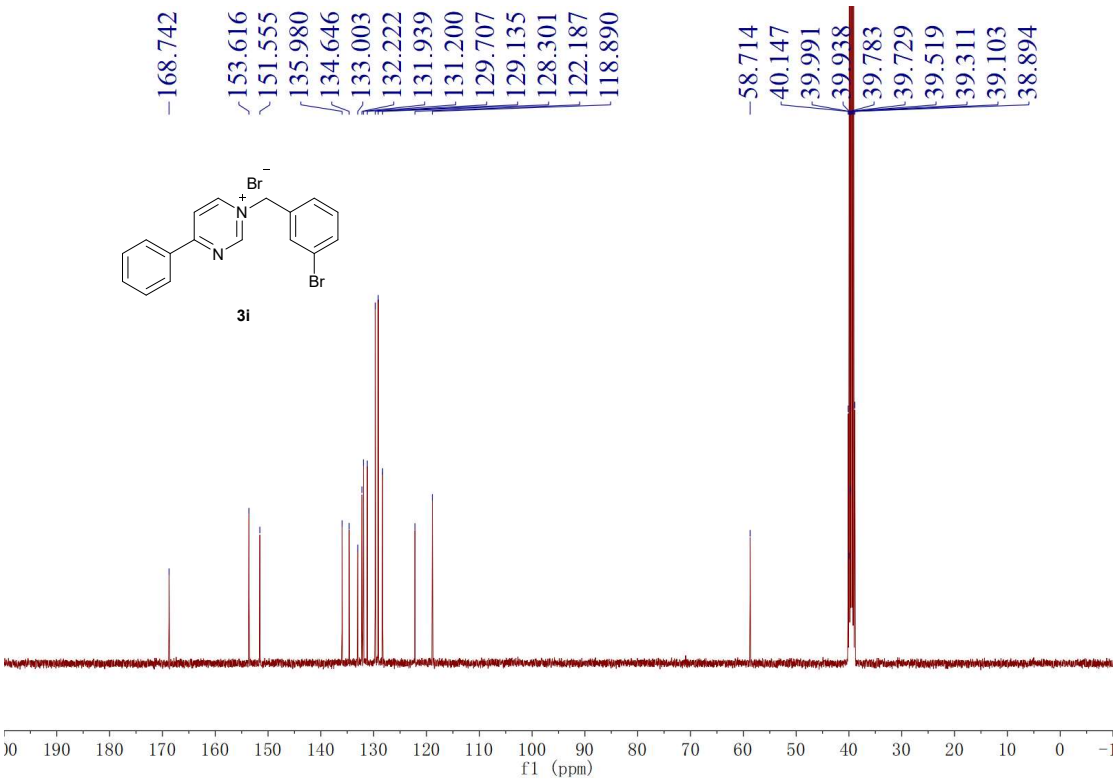
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3h



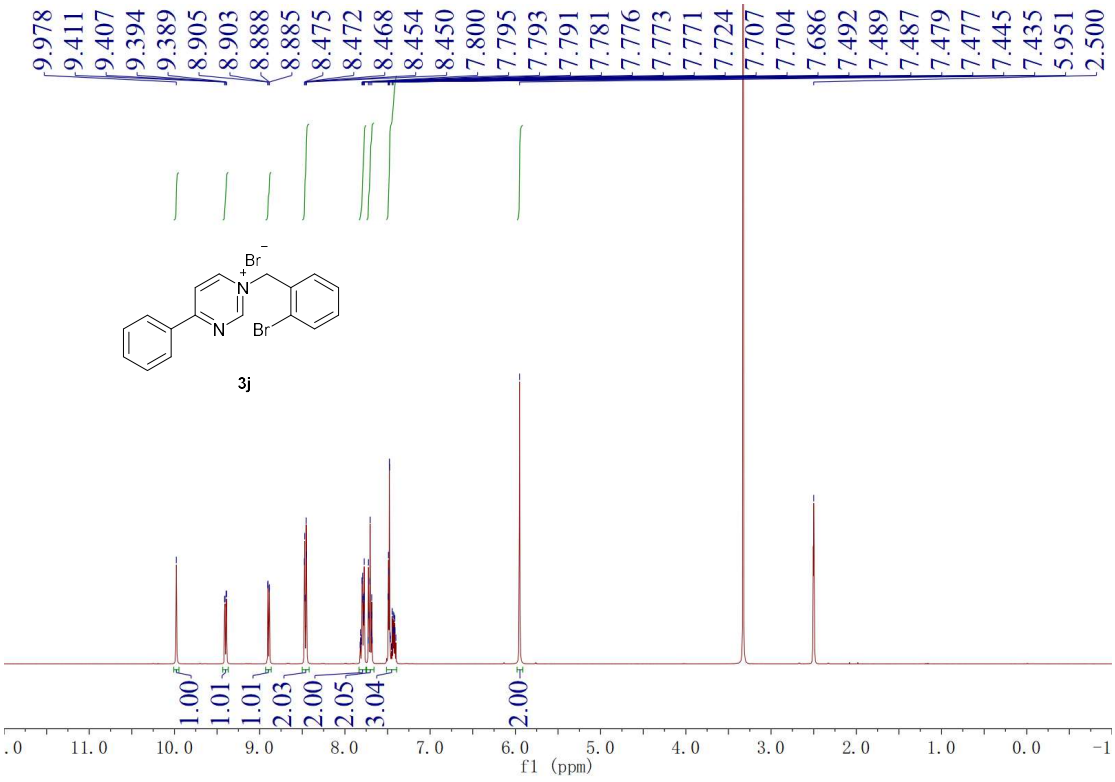
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3h



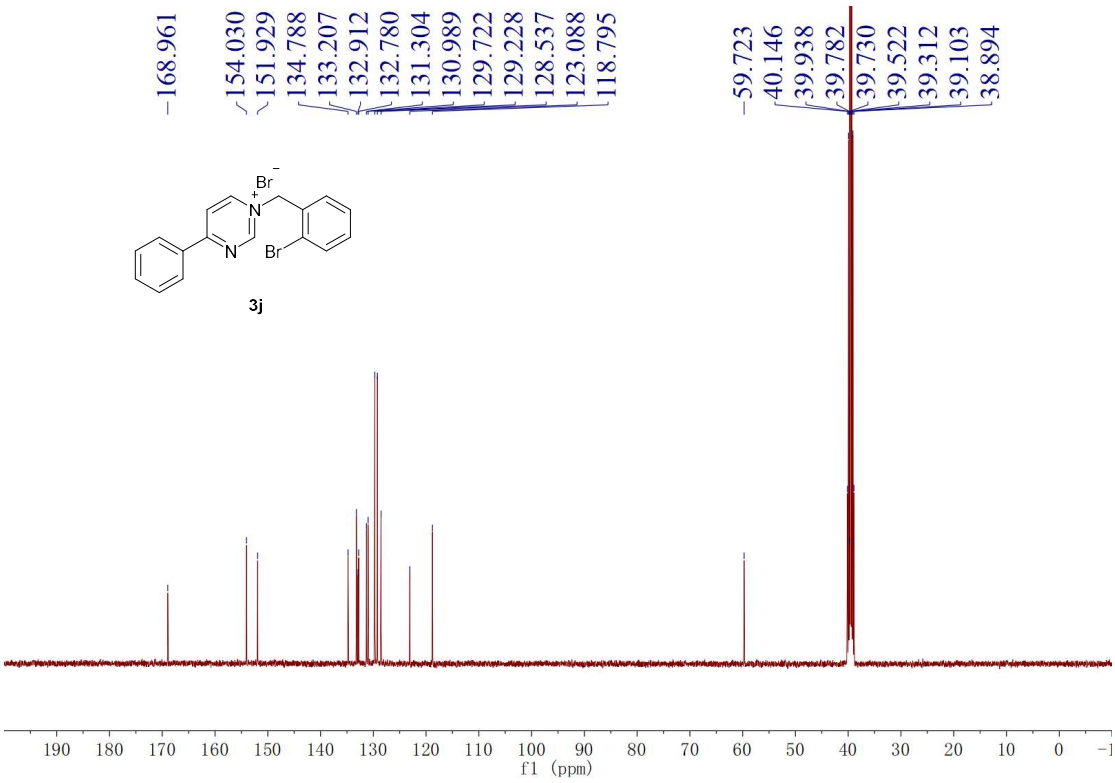
[1]H-NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3i



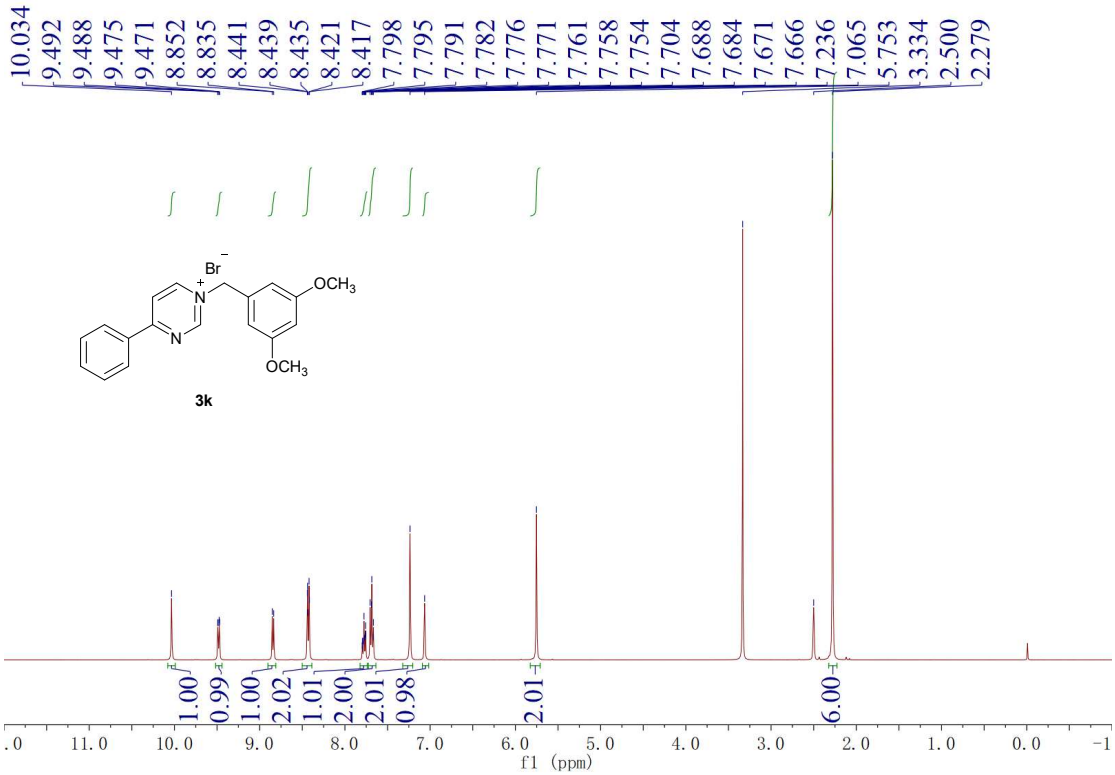
[13]C-NMR Spectrum (100 MHz, DMSO-d_6) of Compound 3i



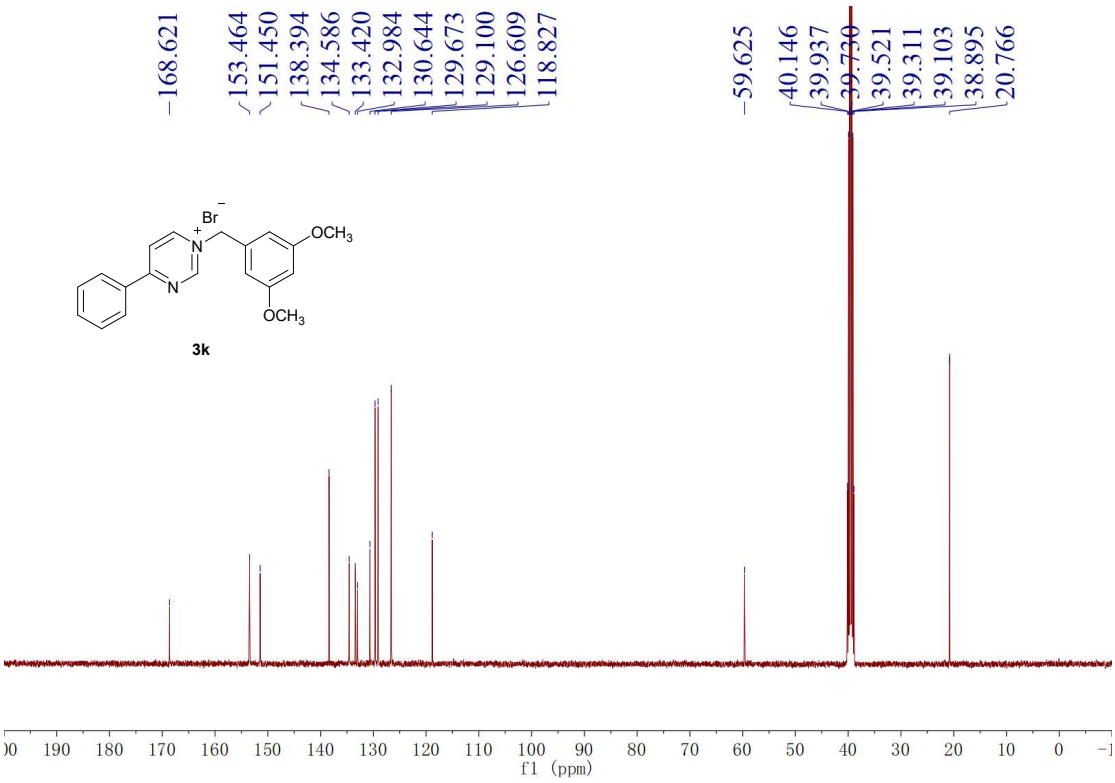
[1]H-NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3j



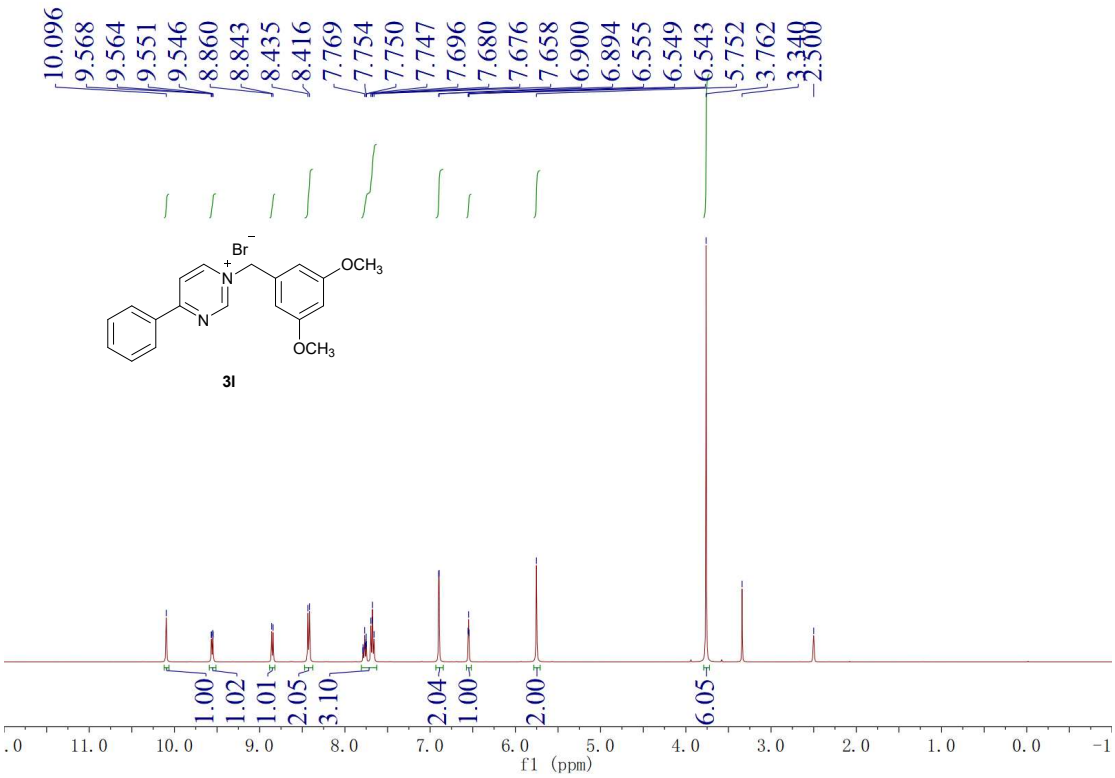
[13]C-NMR Spectrum (100 MHz, DMSO-d_6) of Compound 3j



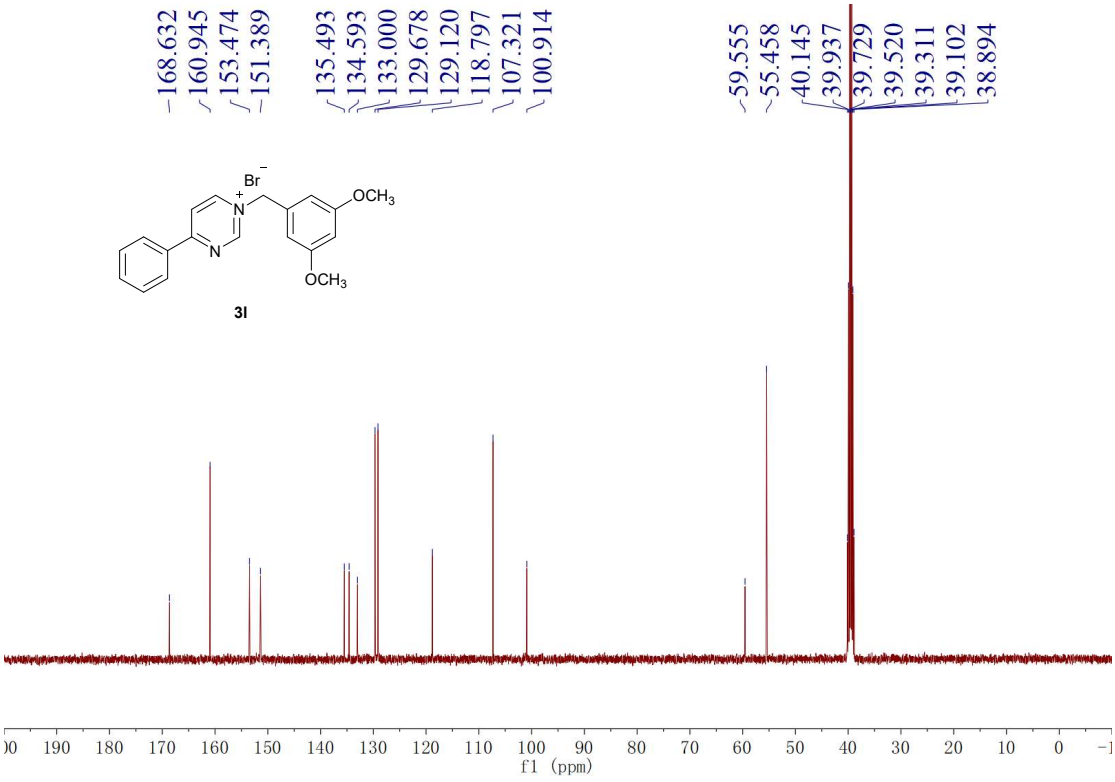
[1]H-NMR Spectrum (400 MHz, DMSO-d_6) of Compound 3k



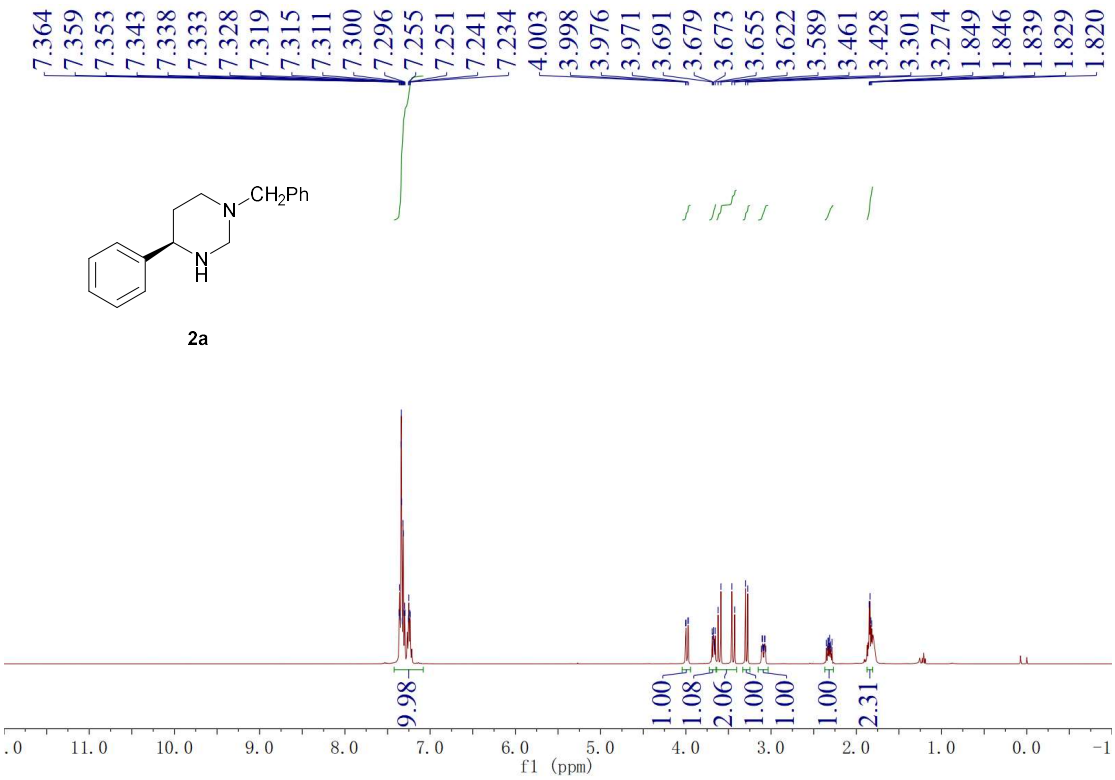
[13]C-NMR Spectrum (100 MHz, DMSO-d_6) of Compound 3k



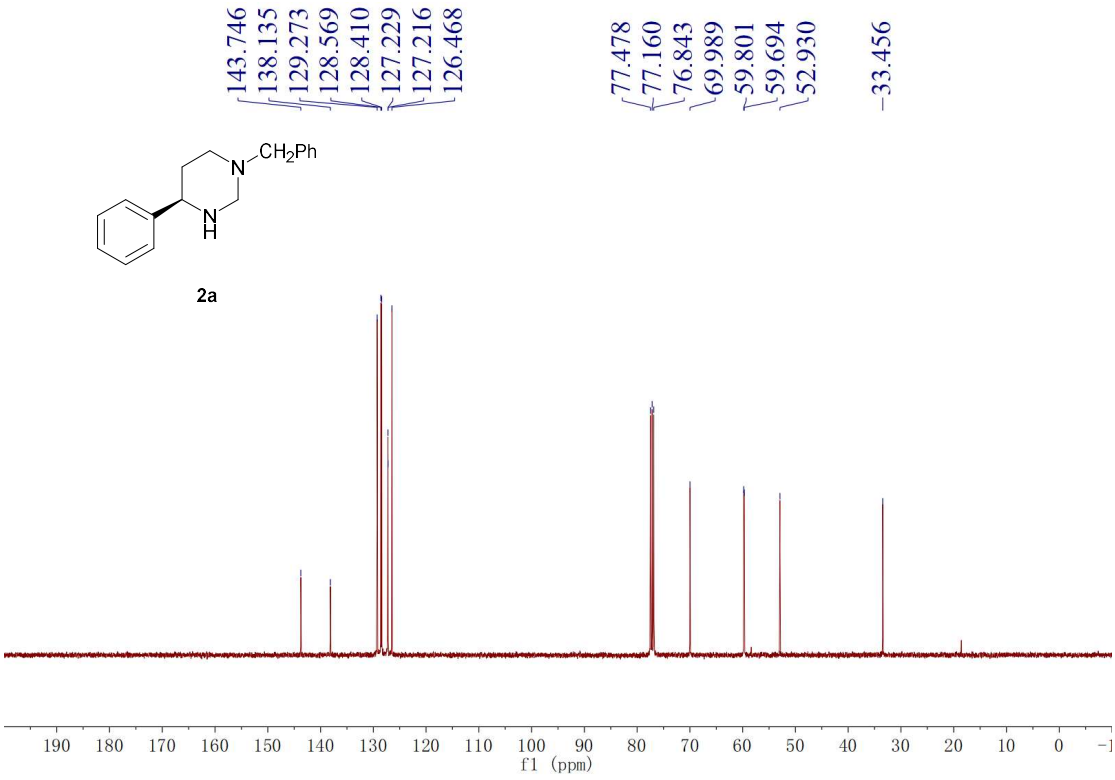
[1]H-NMR Spectrum (400 MHz, DMSO-*d*6) of Compound 3l



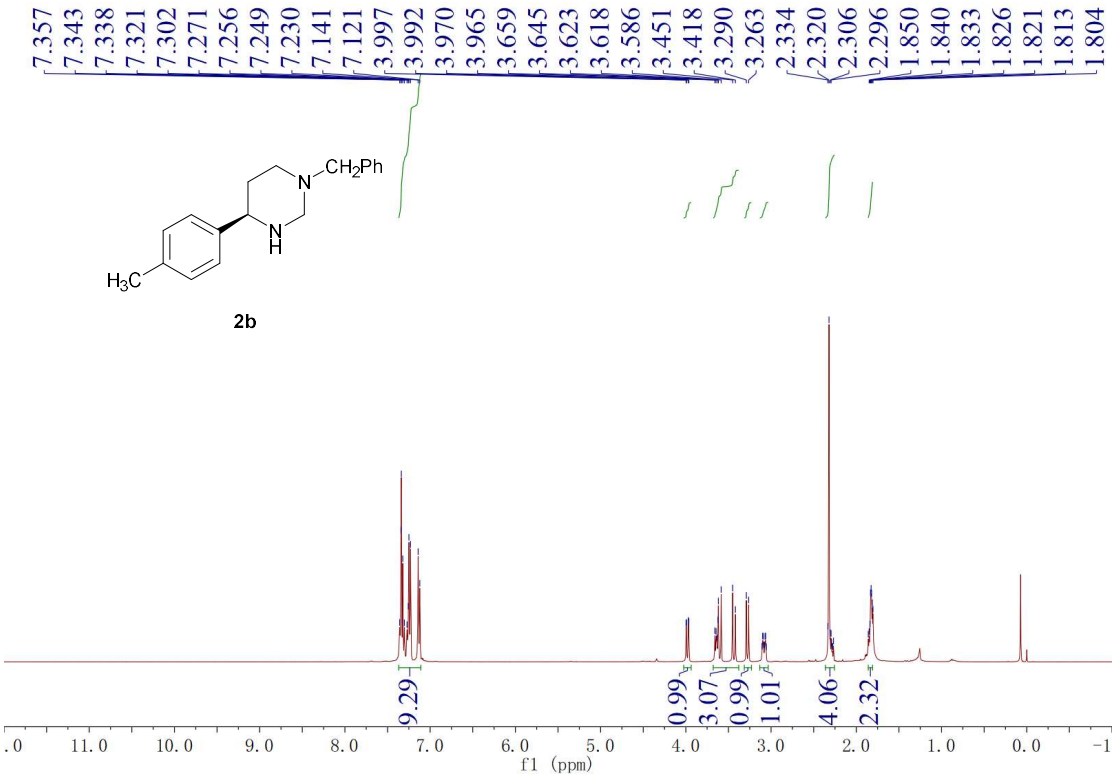
[13]C-NMR Spectrum (100 MHz, DMSO-*d*6) of Compound 3l



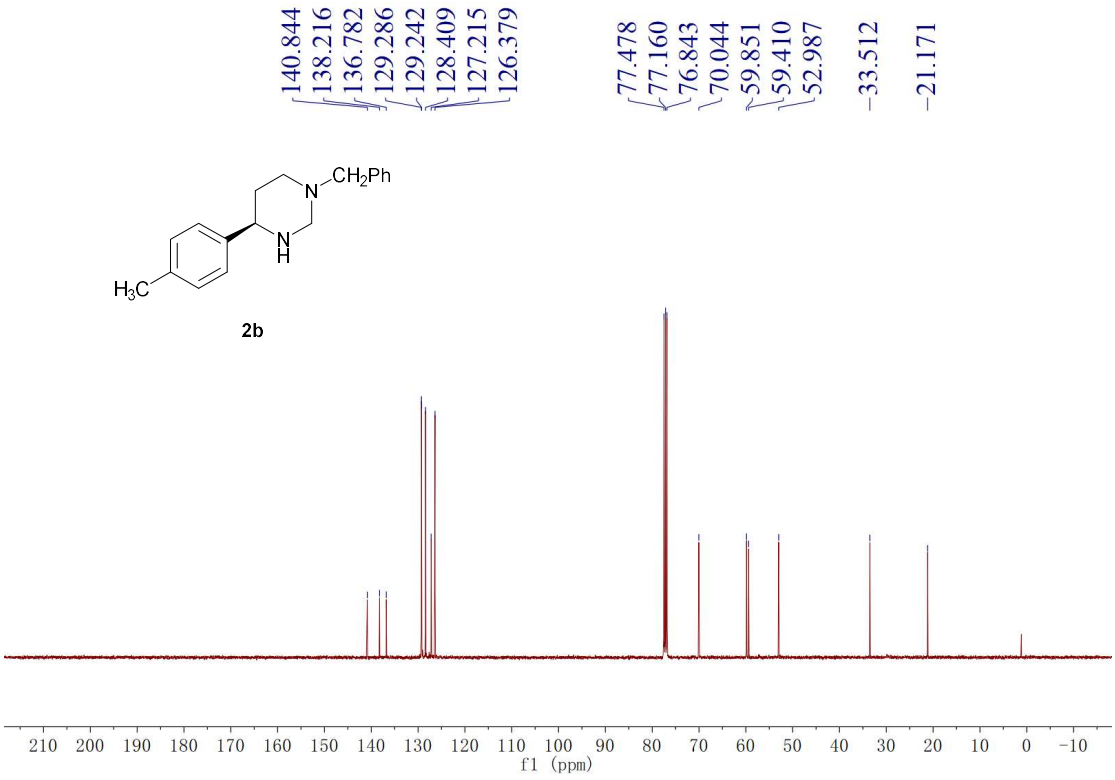
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2a



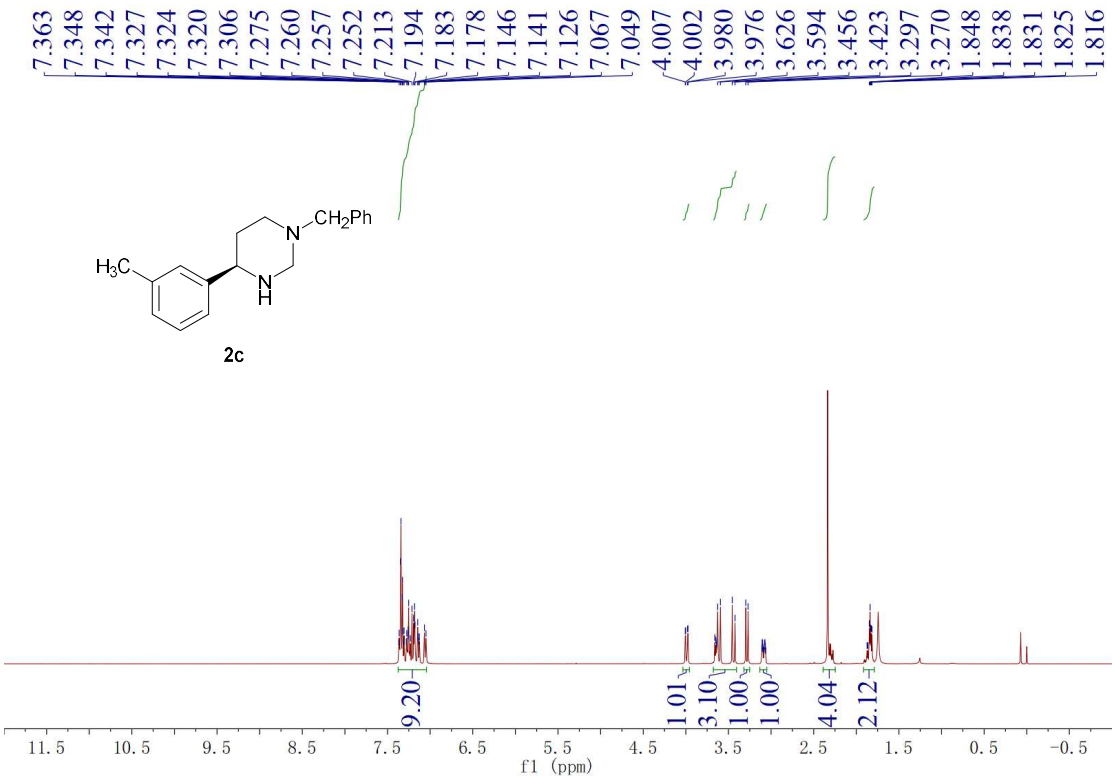
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2a



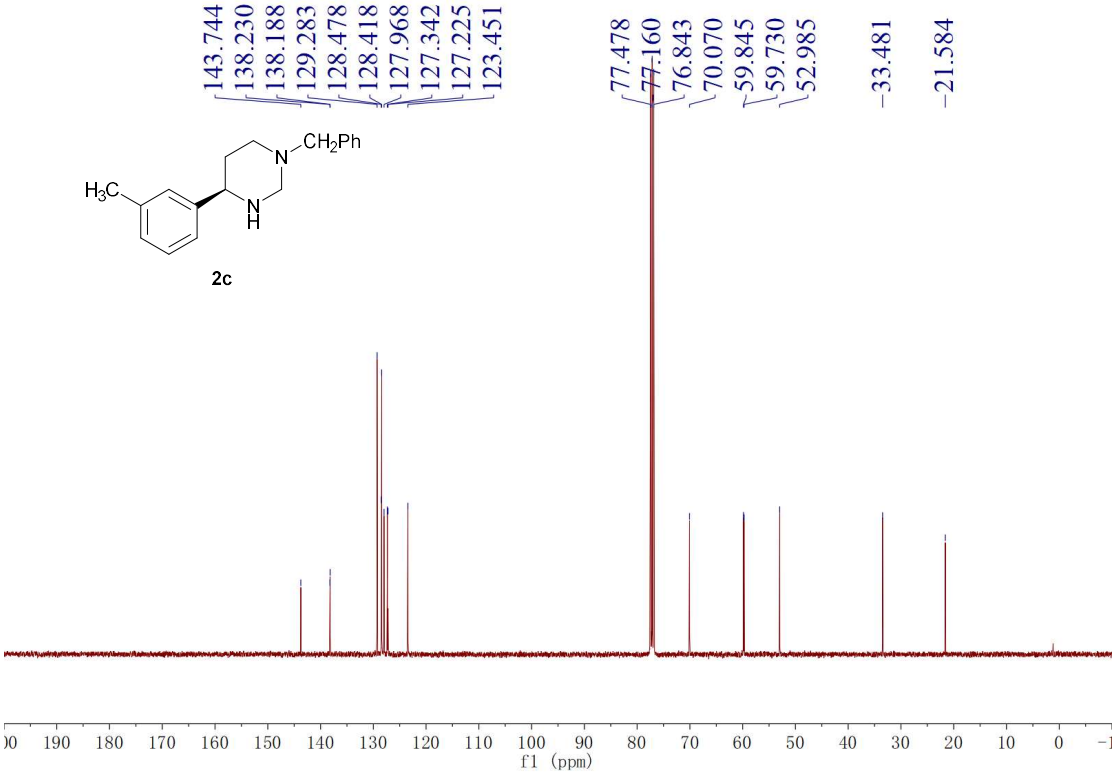
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2b



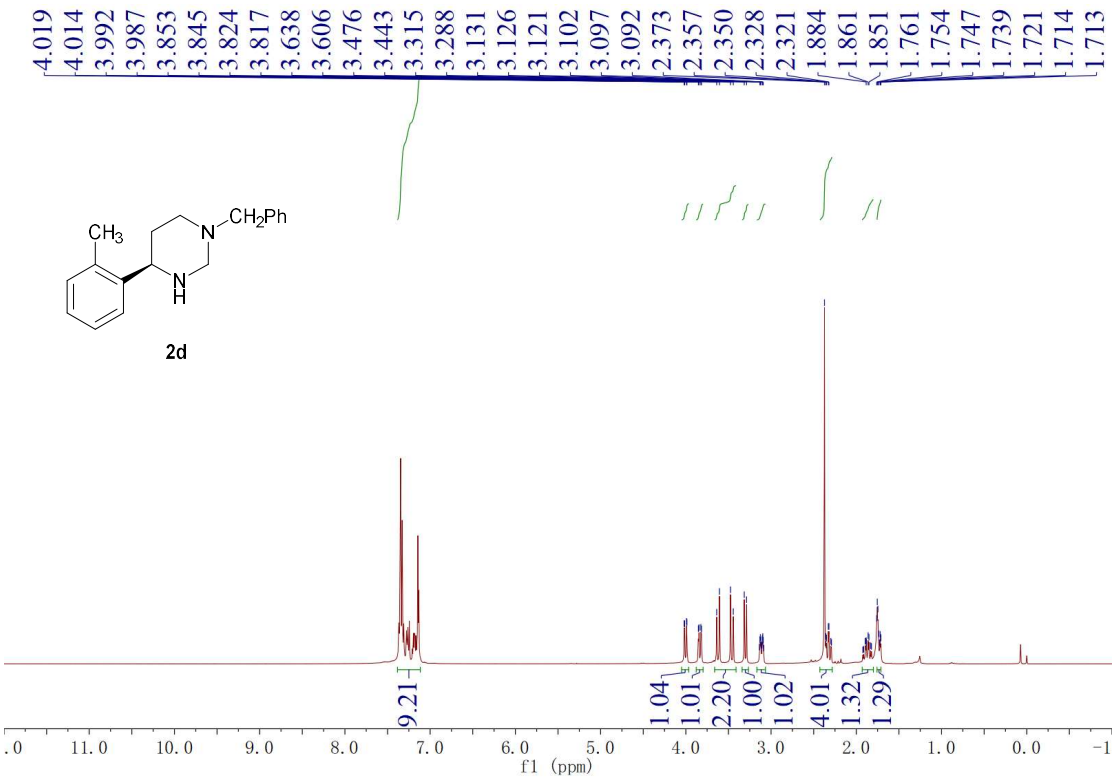
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2b



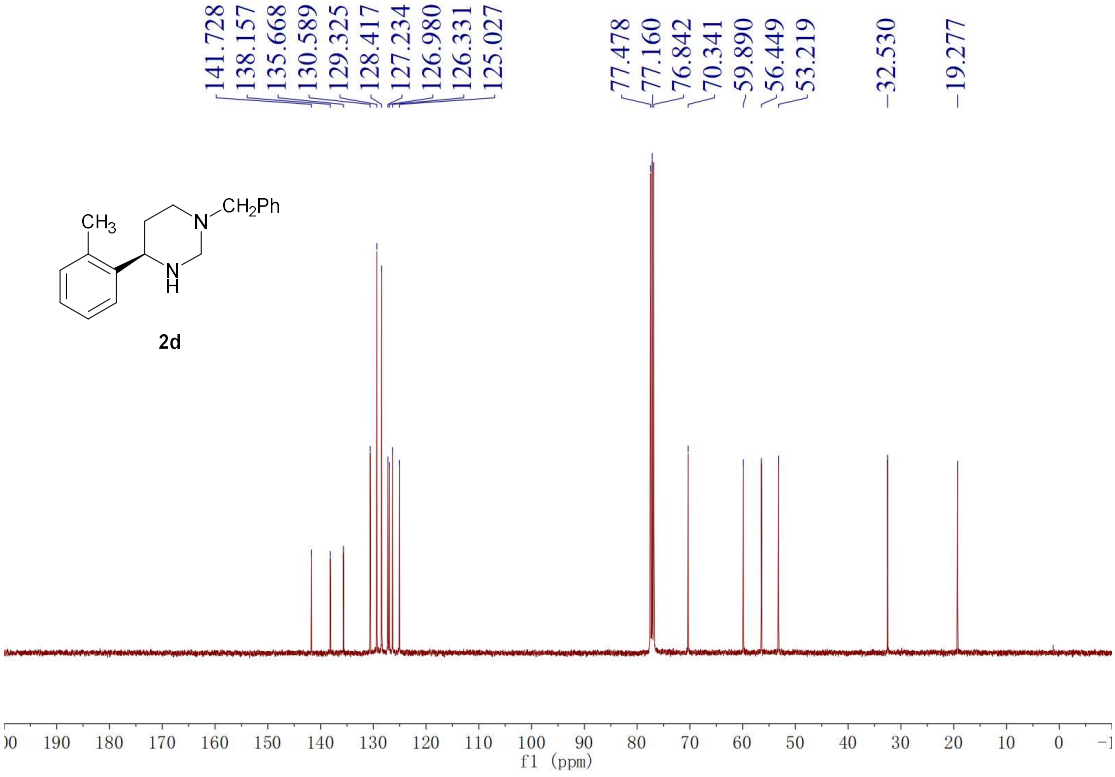
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2c



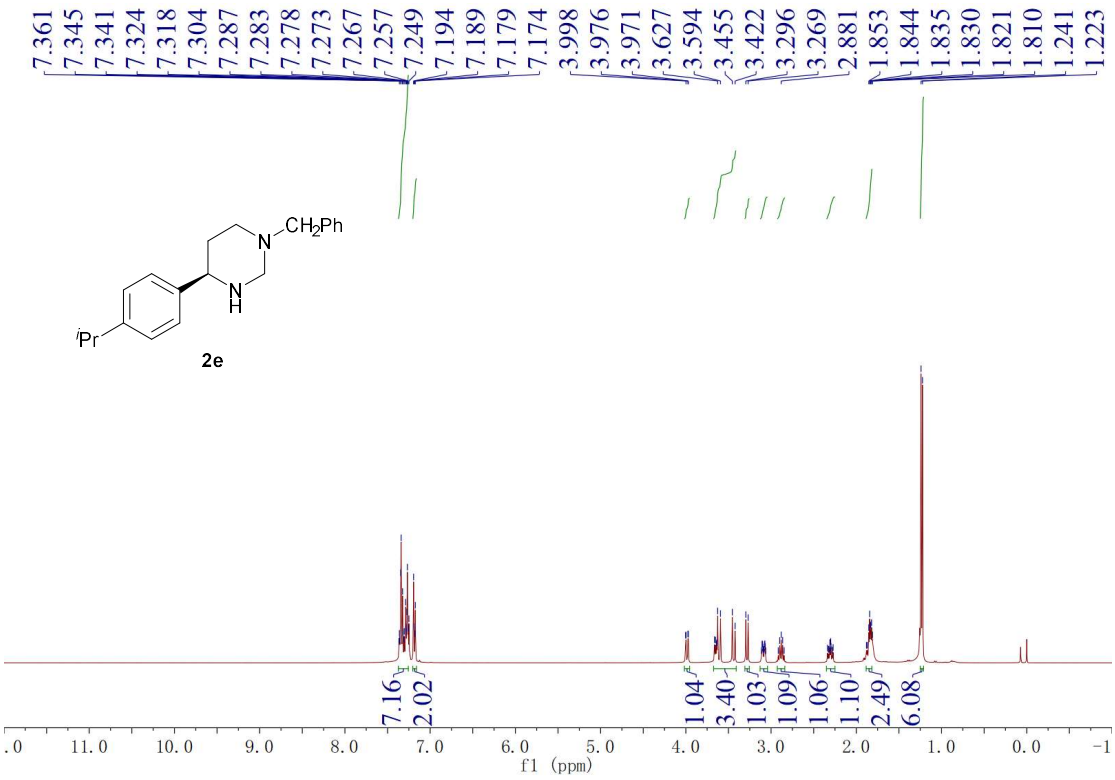
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2c



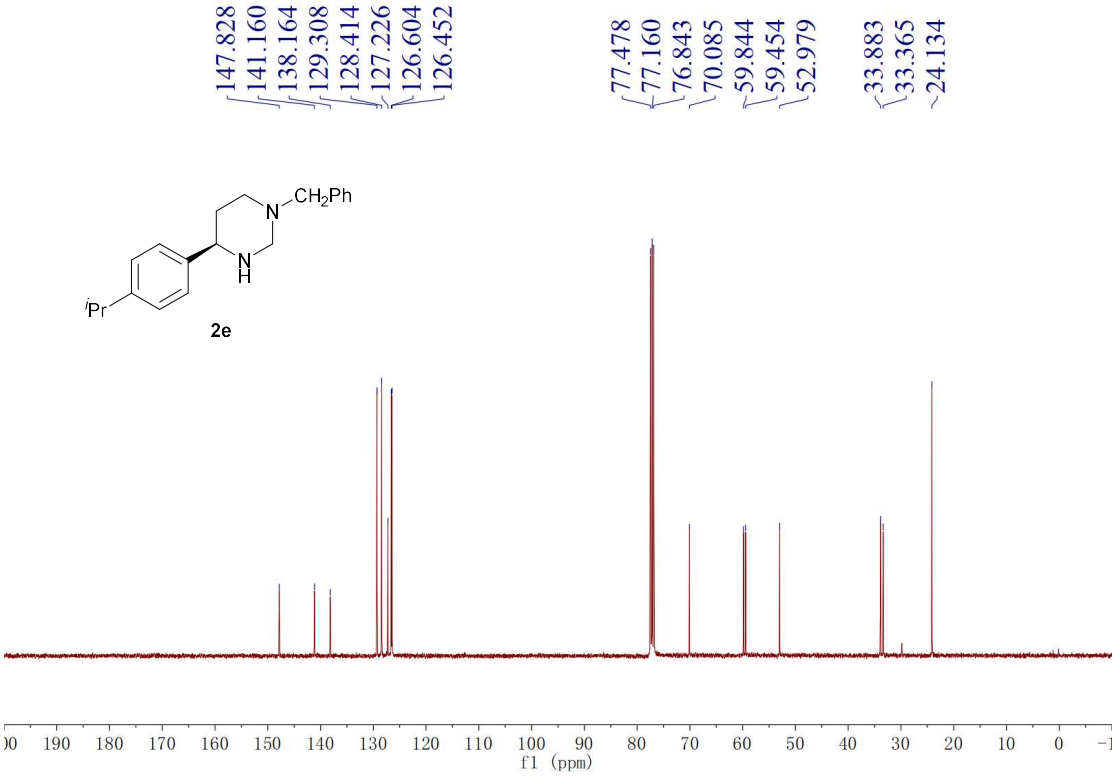
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2d



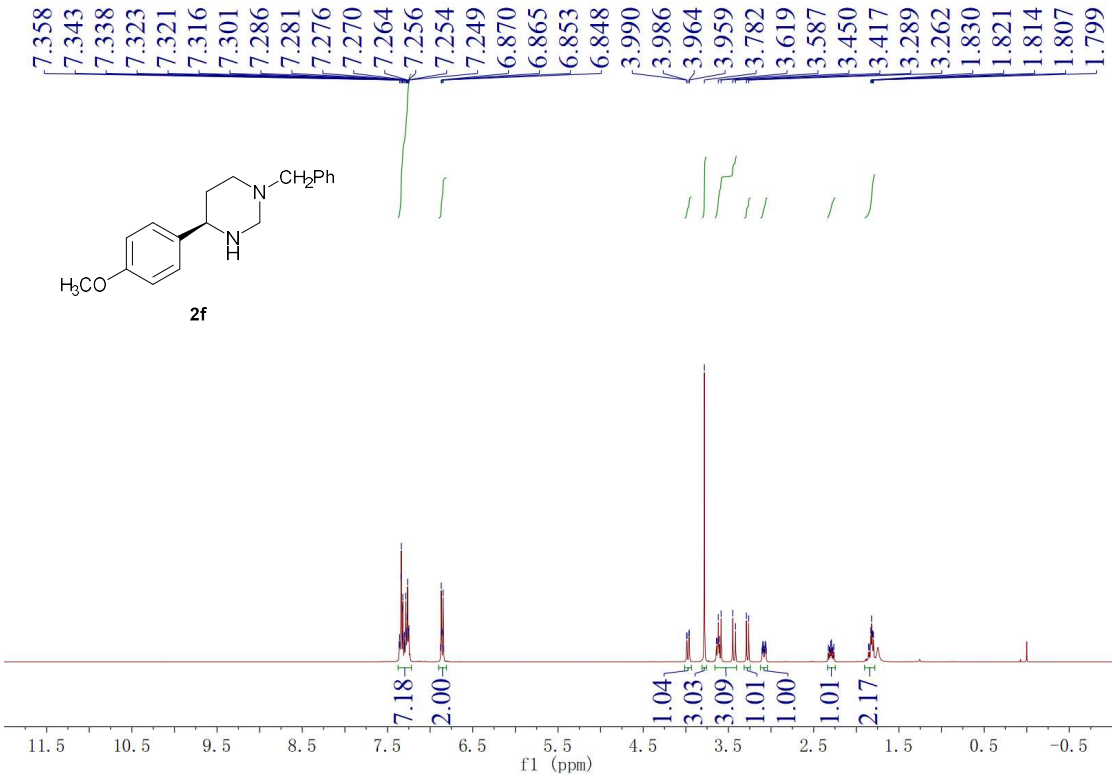
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2d



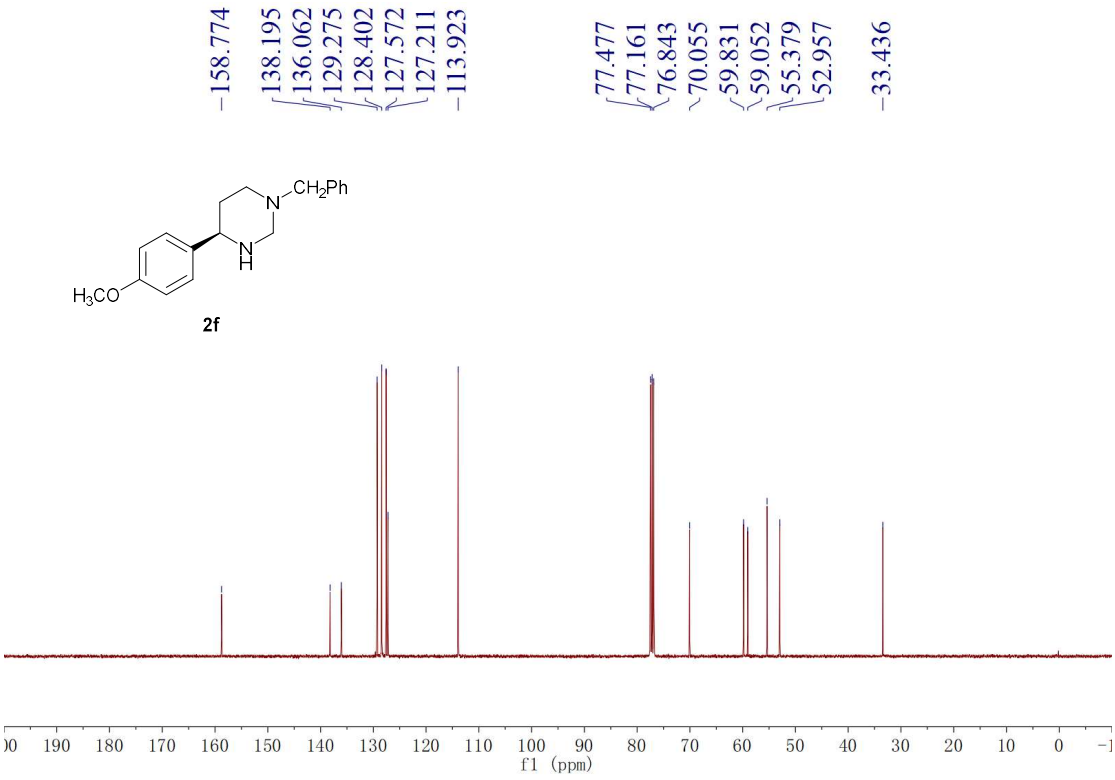
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2e



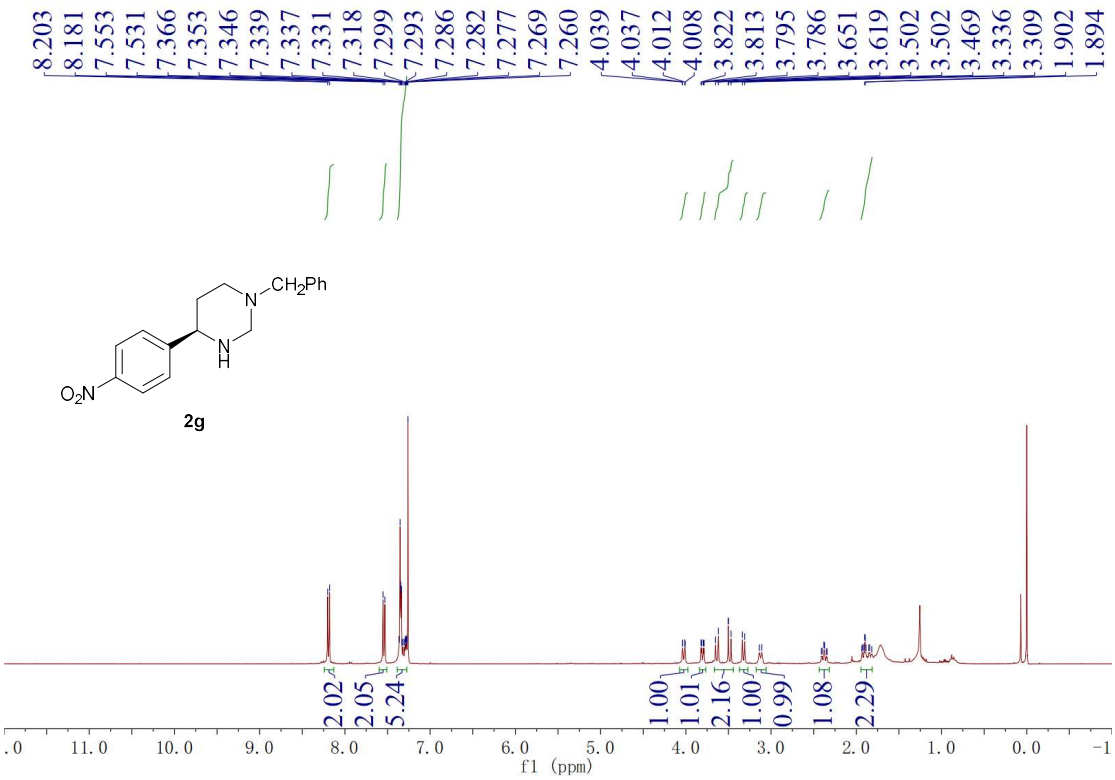
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2e



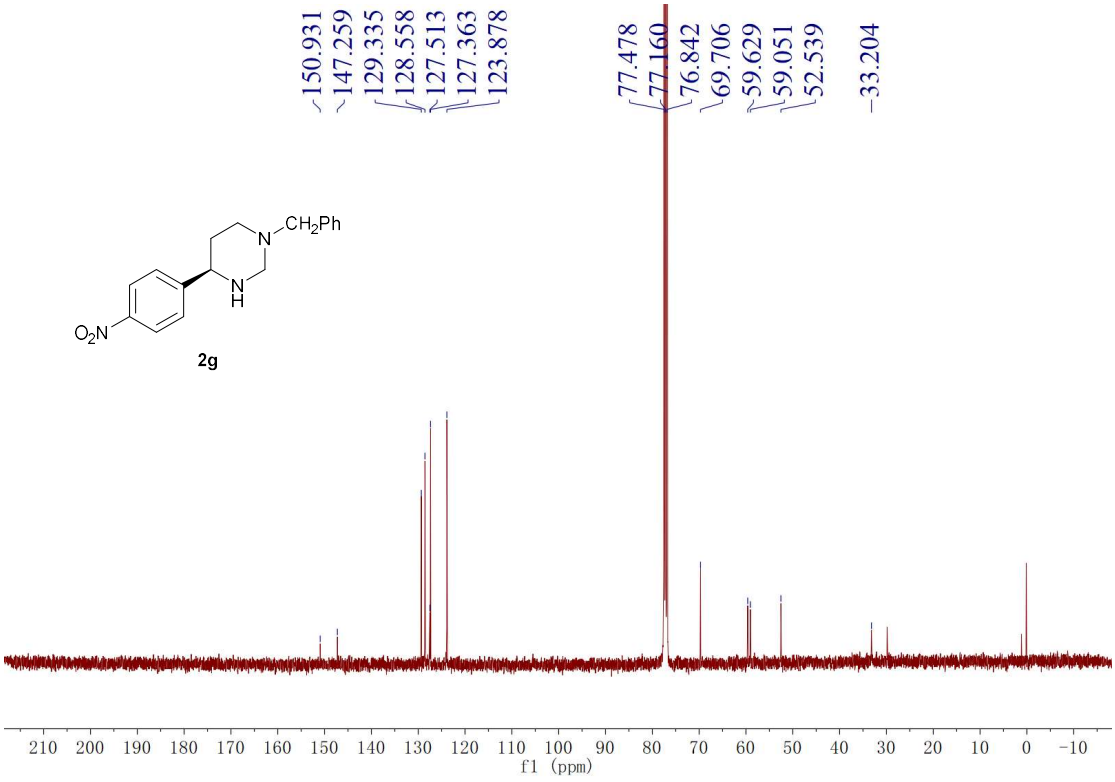
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2f



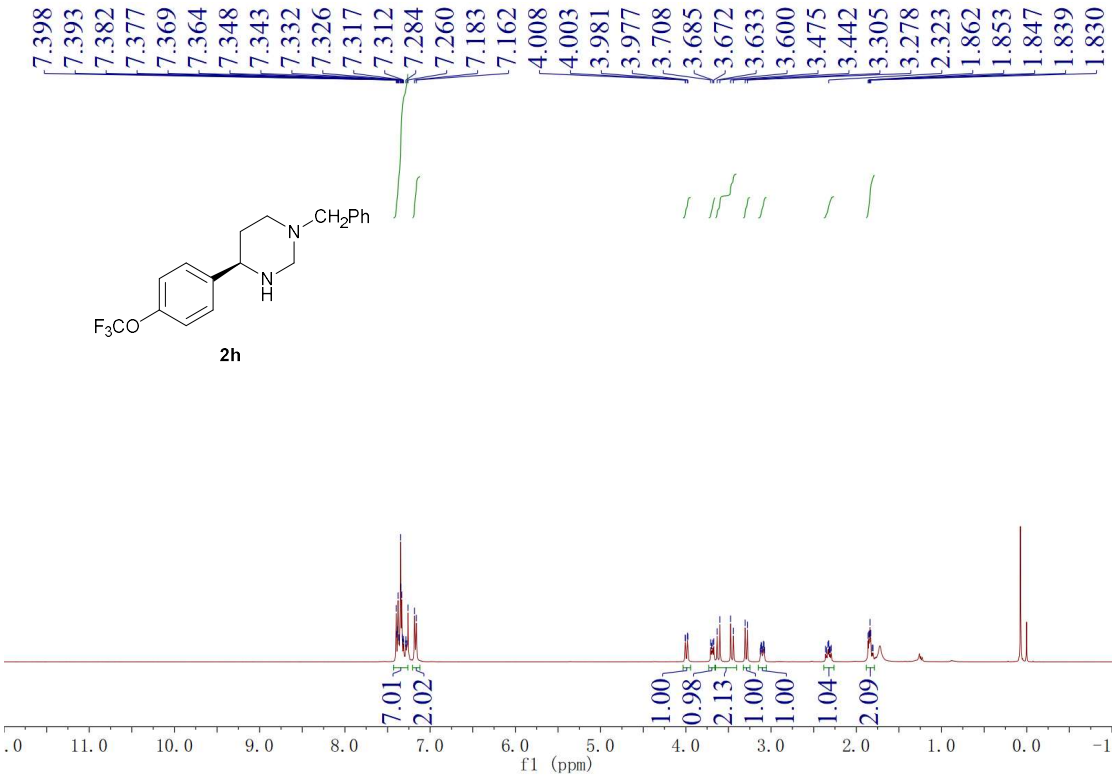
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2f



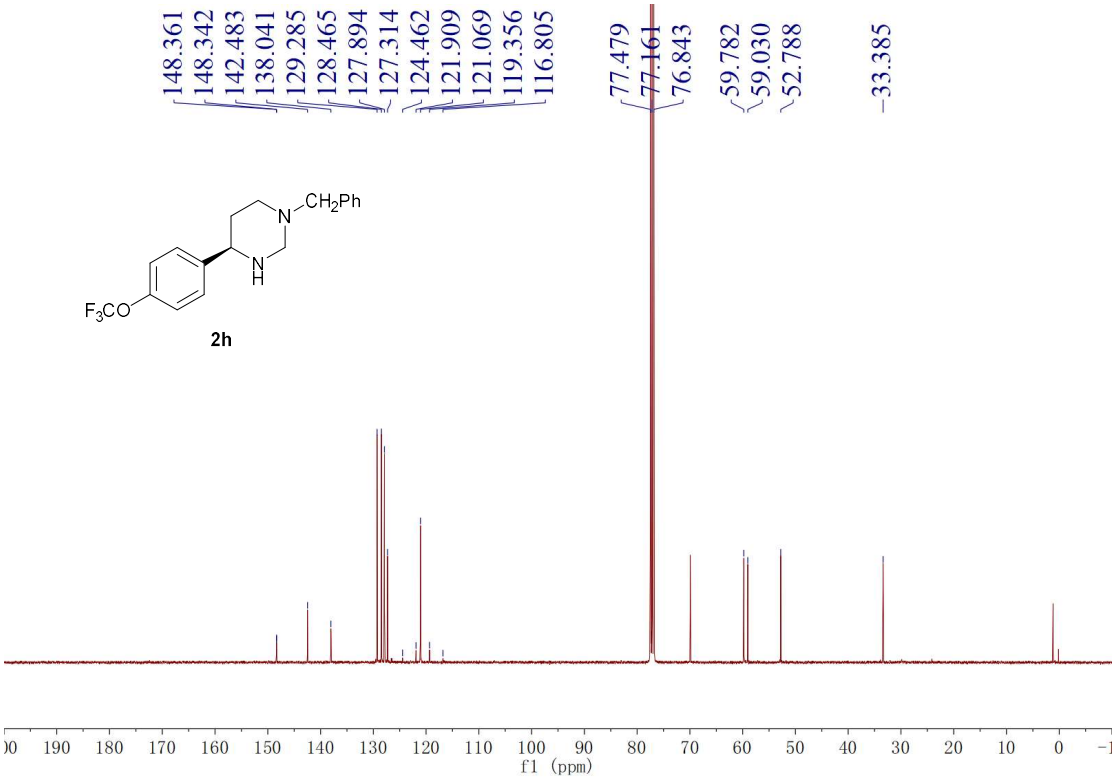
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2g



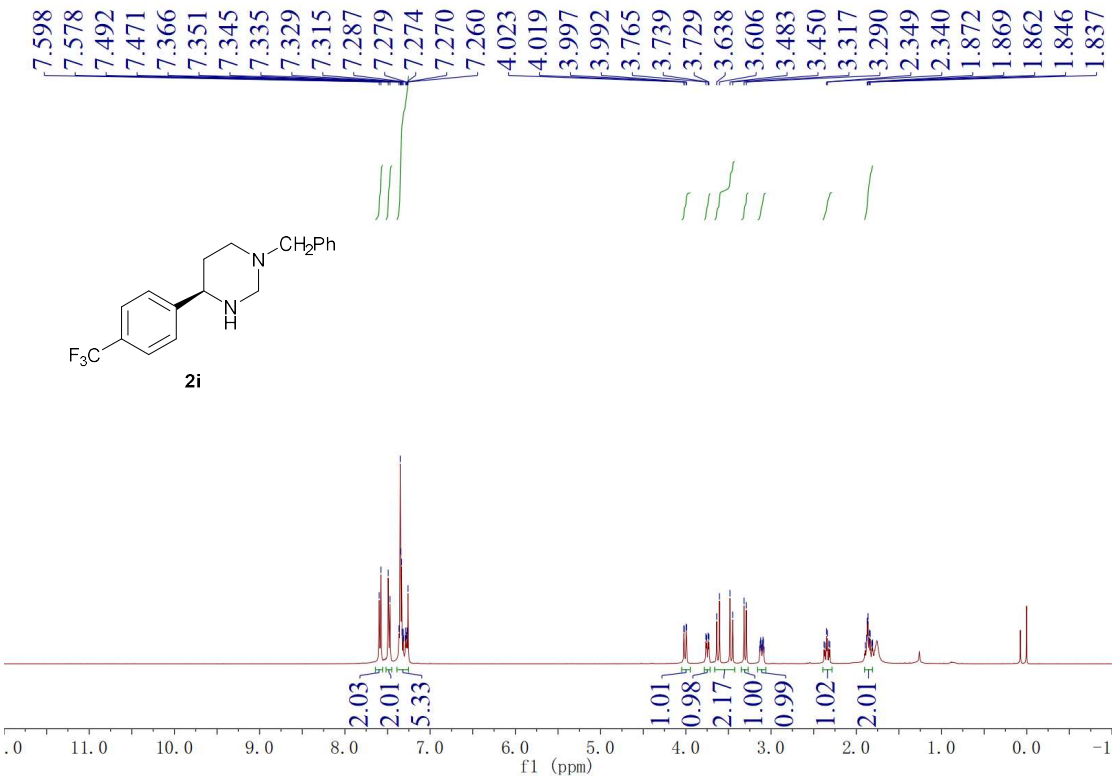
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2g



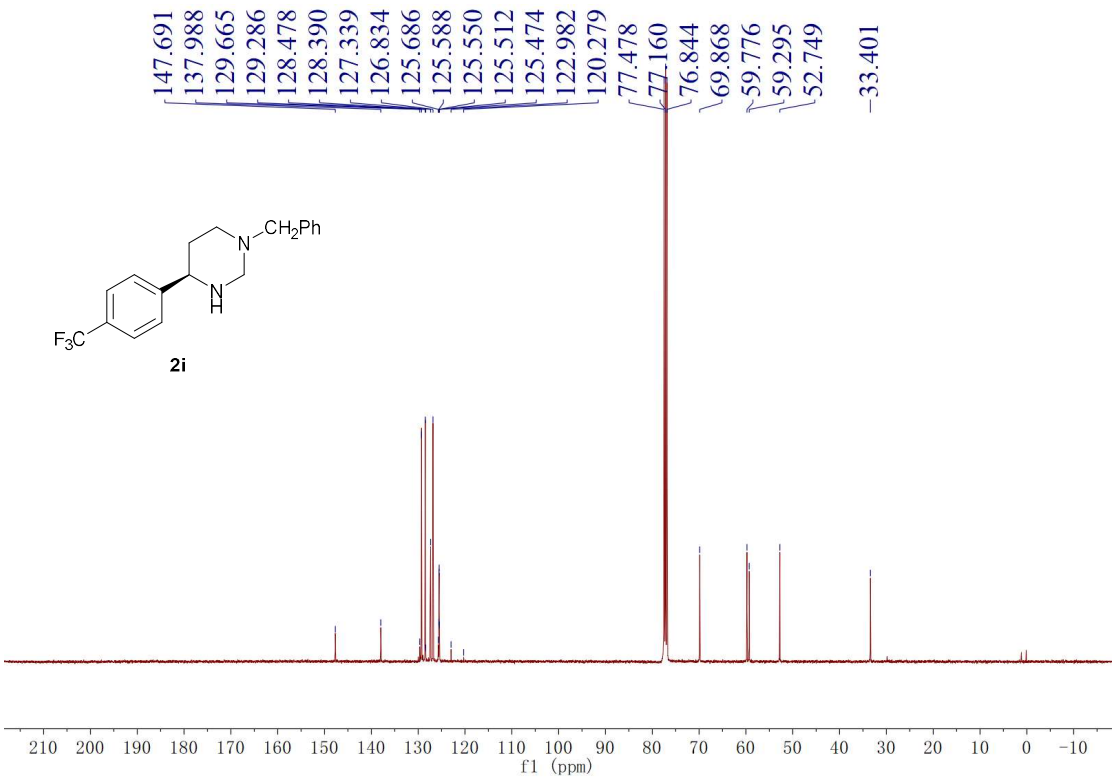
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2h



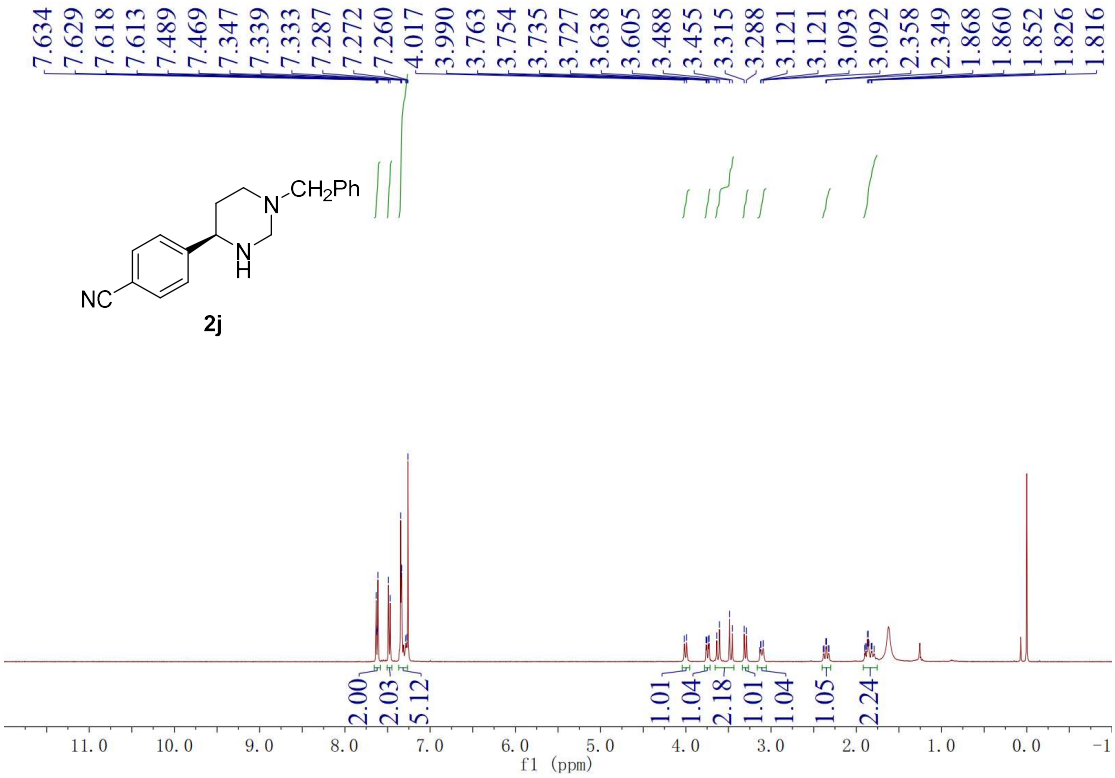
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2h



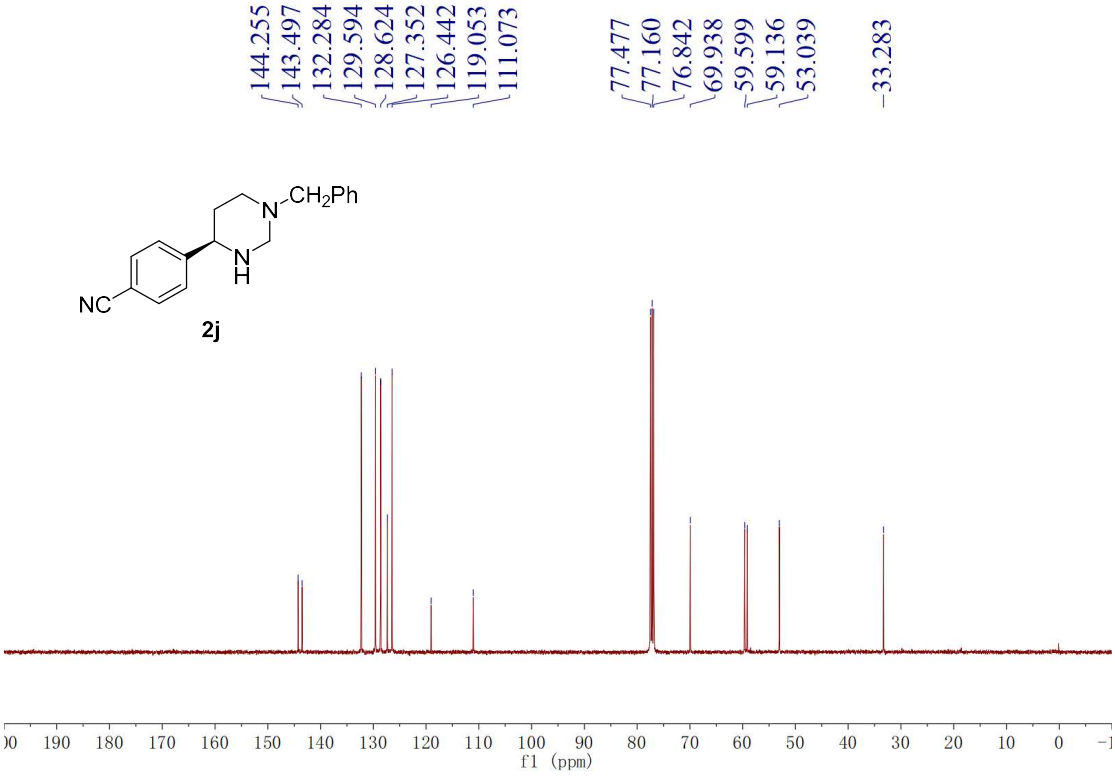
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2i



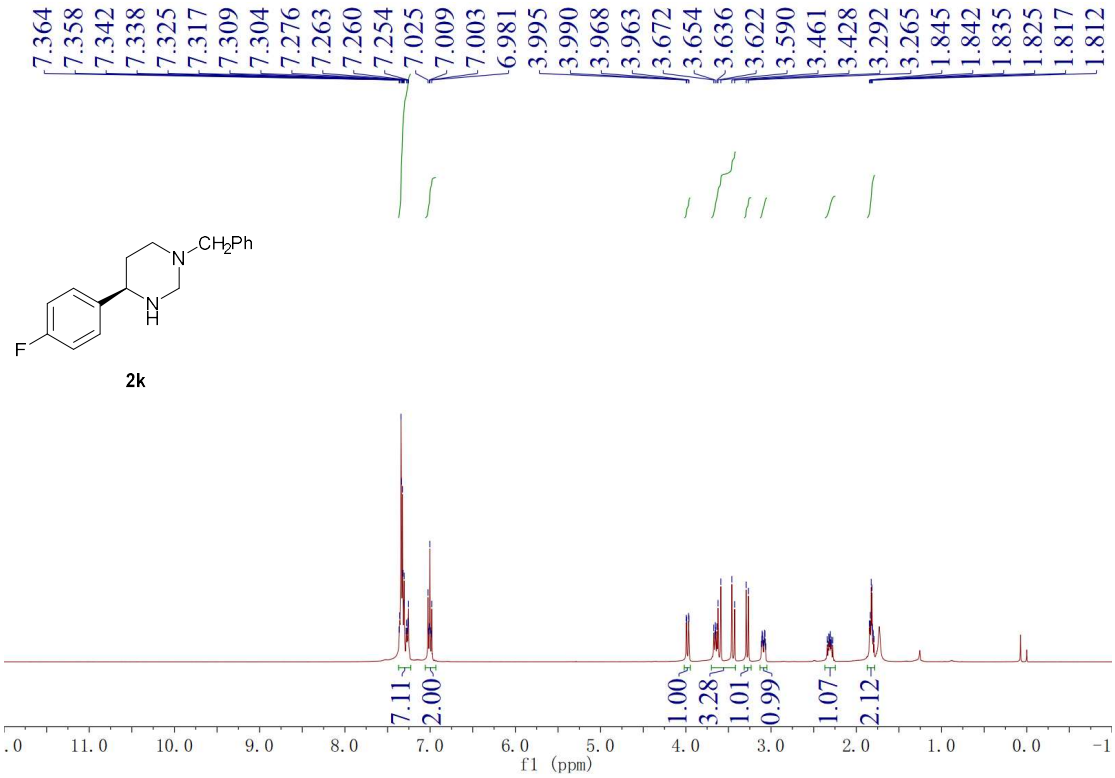
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2i



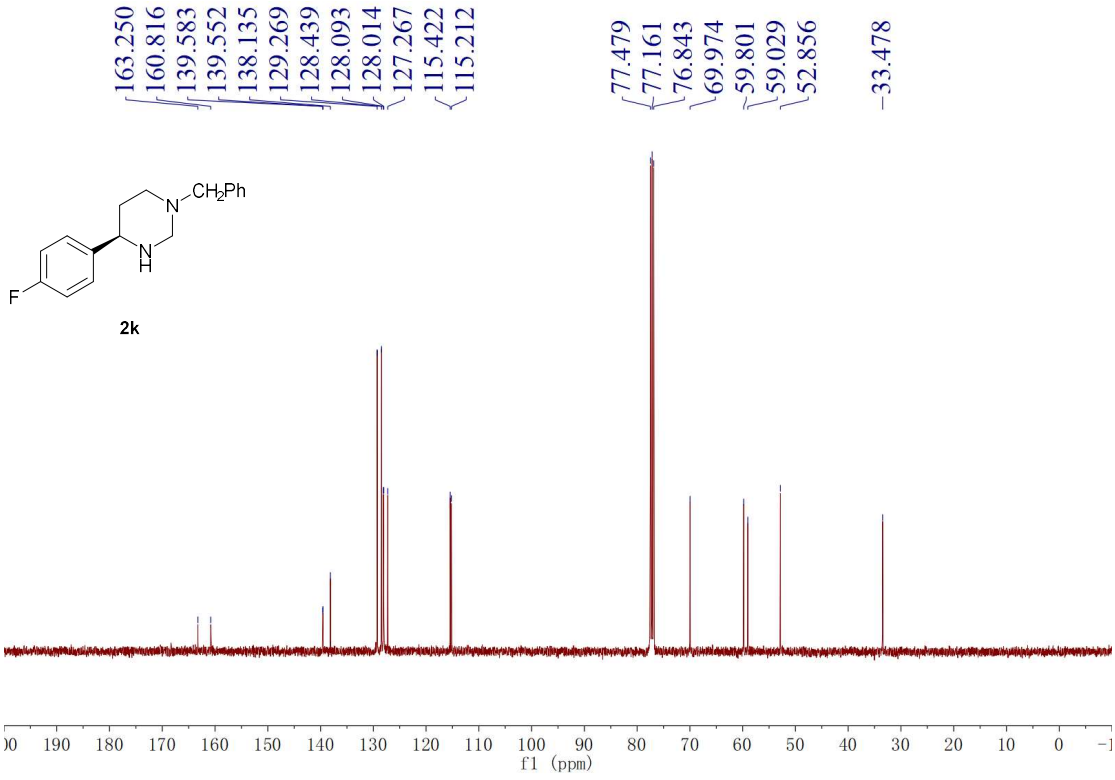
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2j



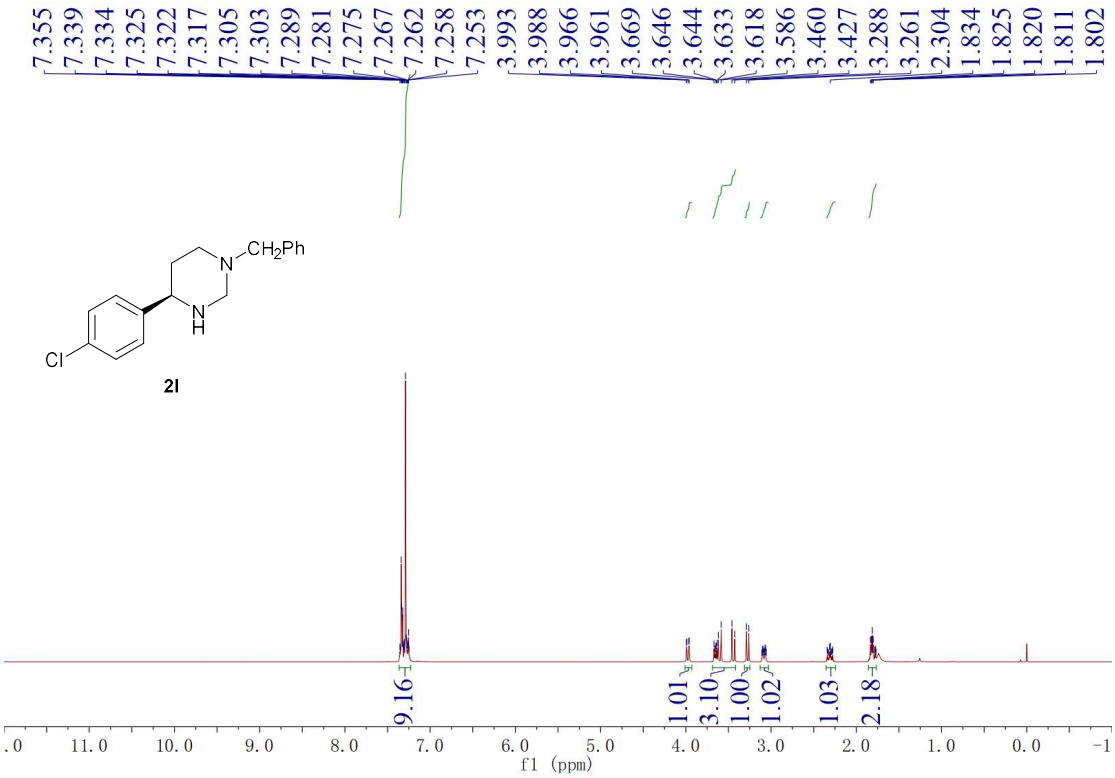
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2j



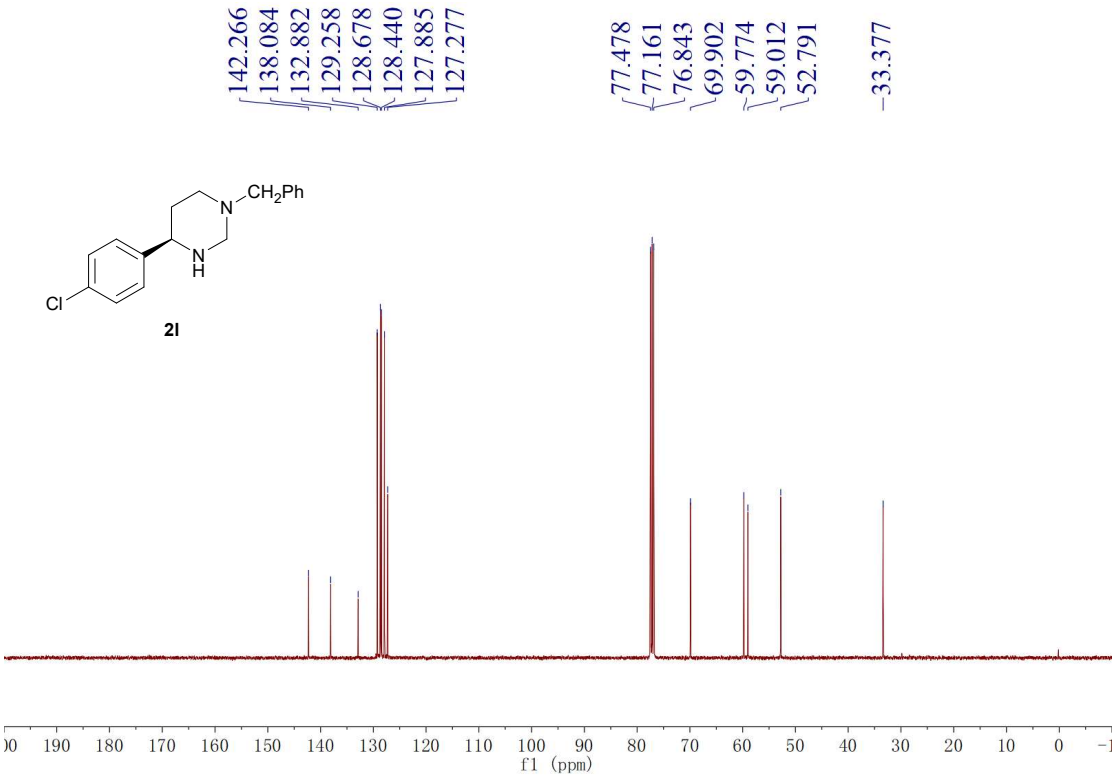
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2k



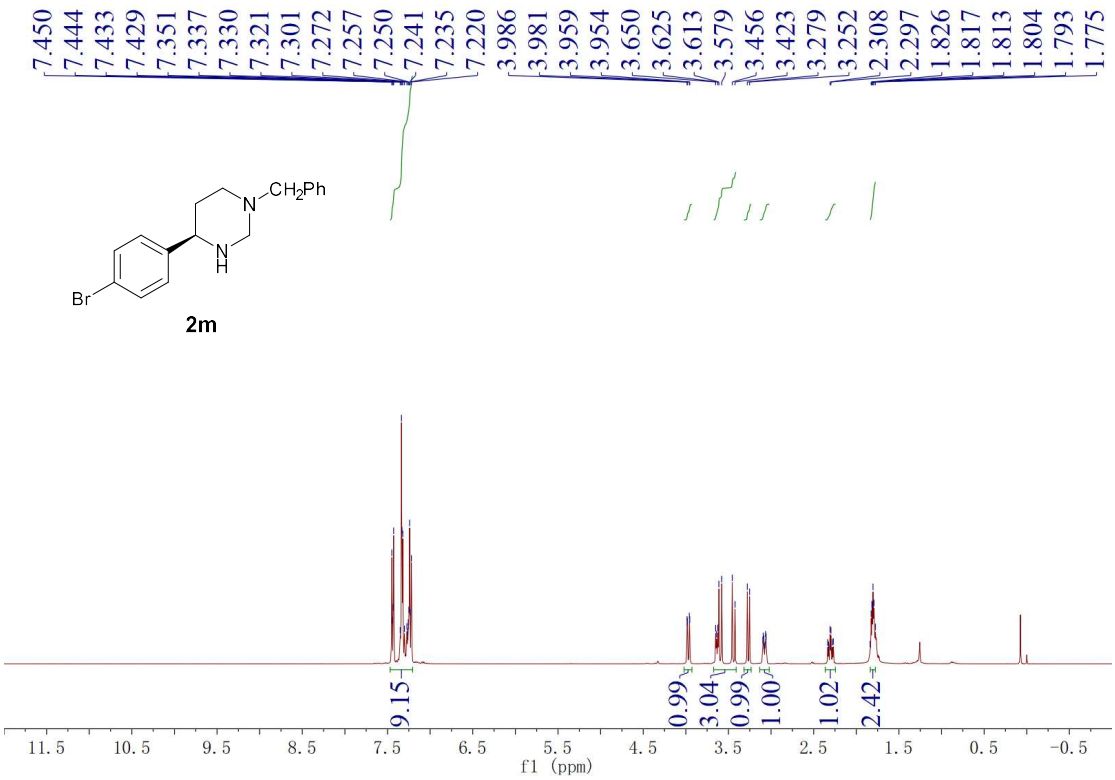
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2k



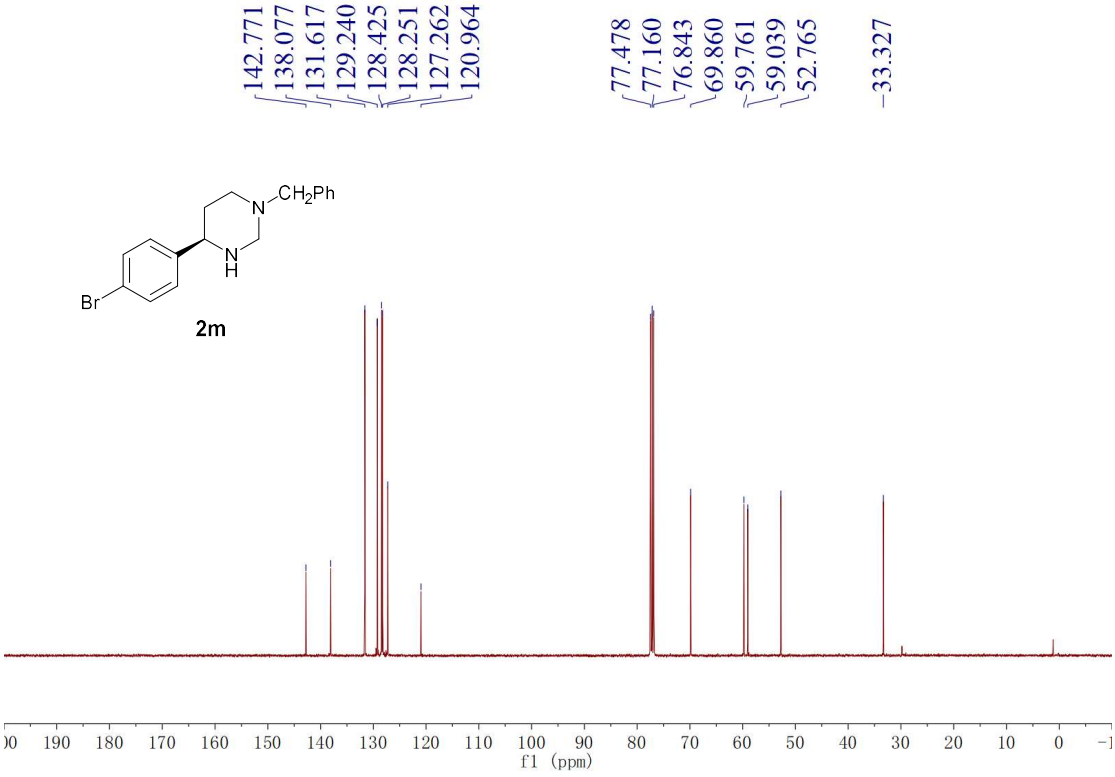
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2l



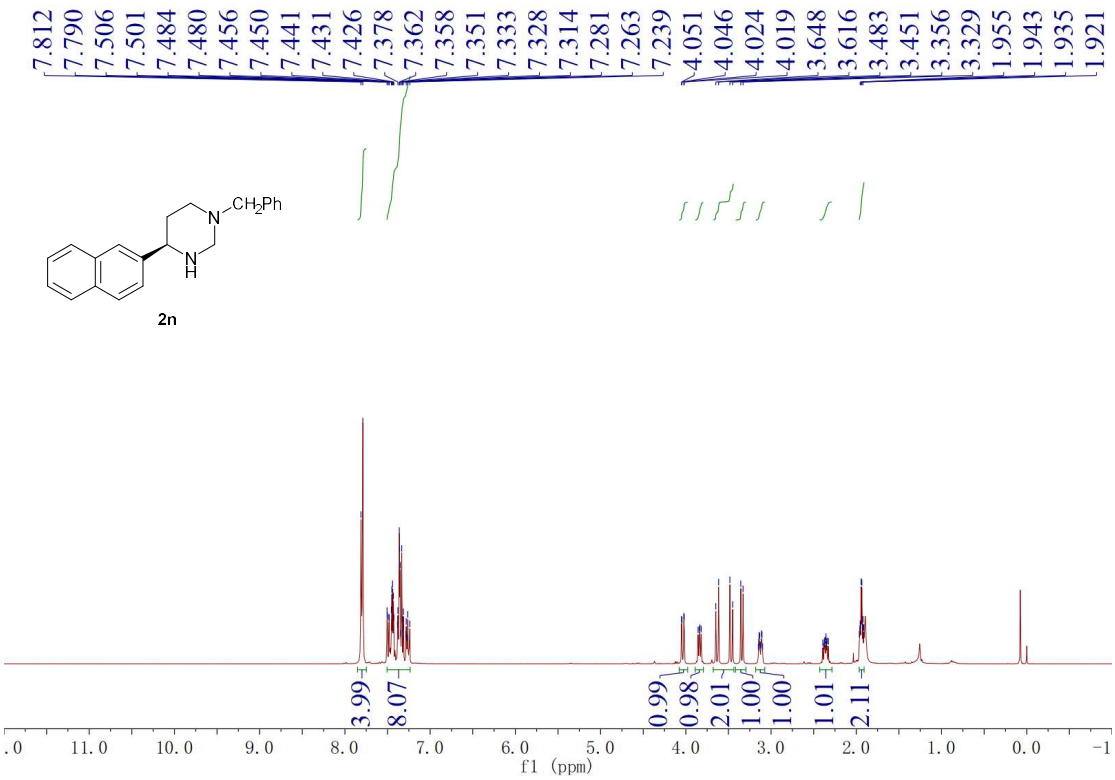
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2l



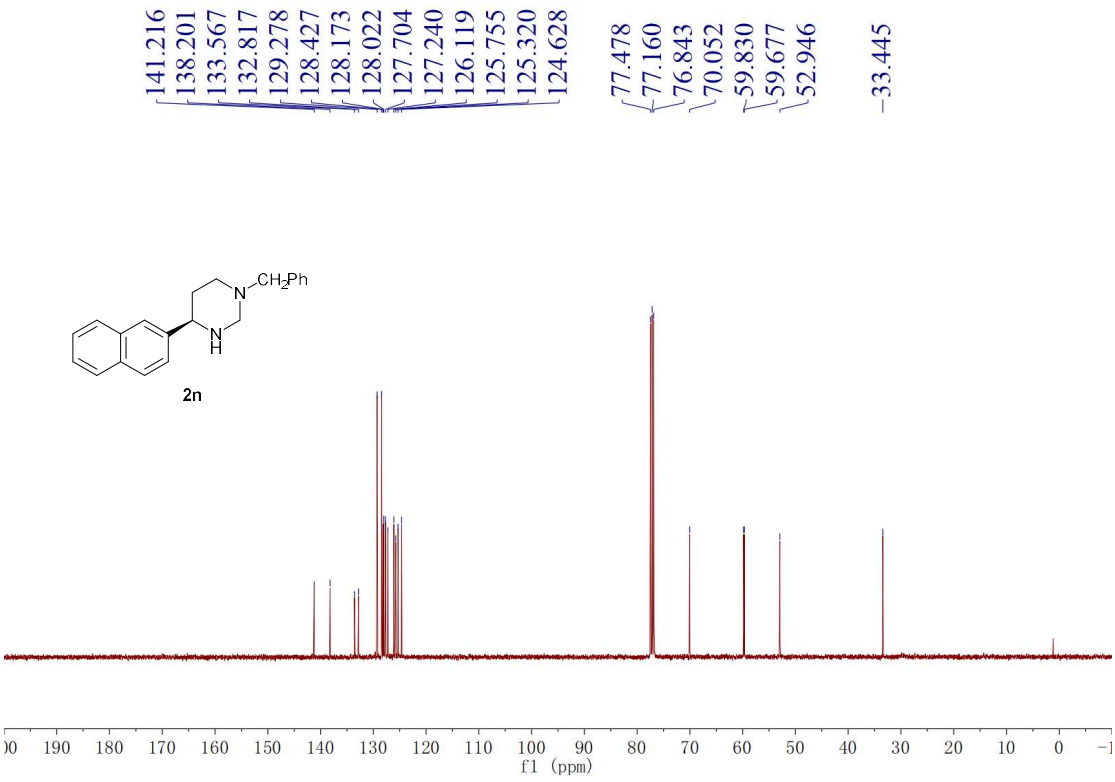
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2m



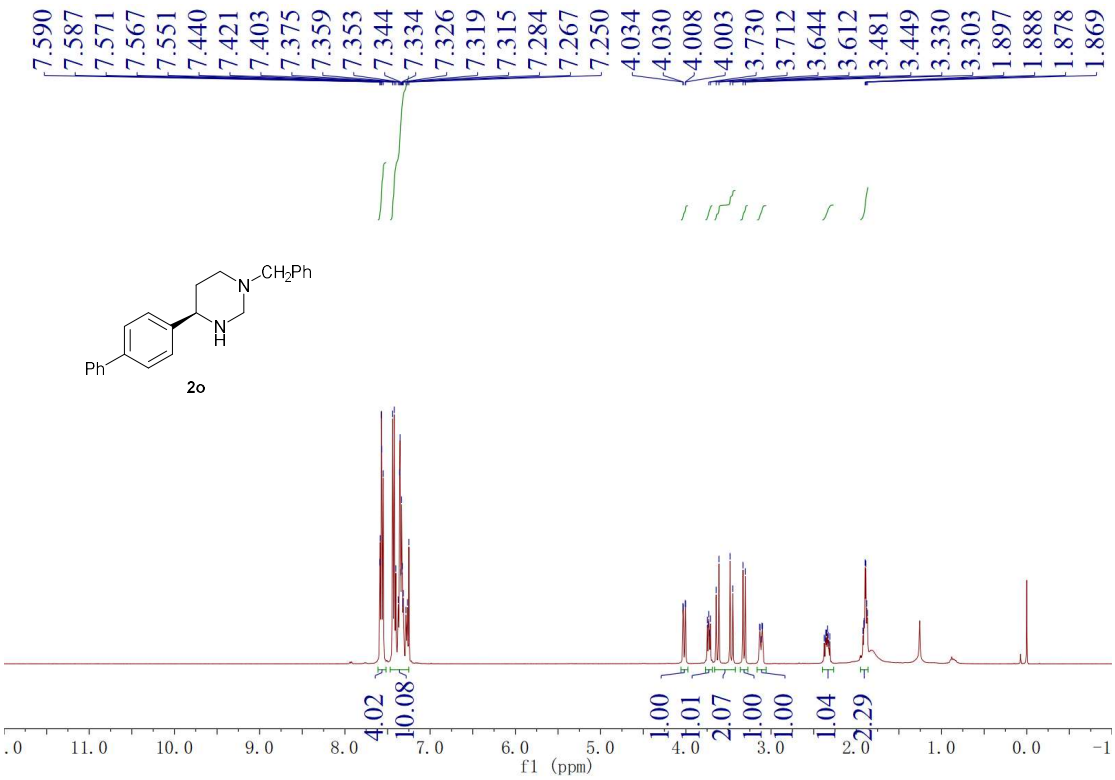
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2m



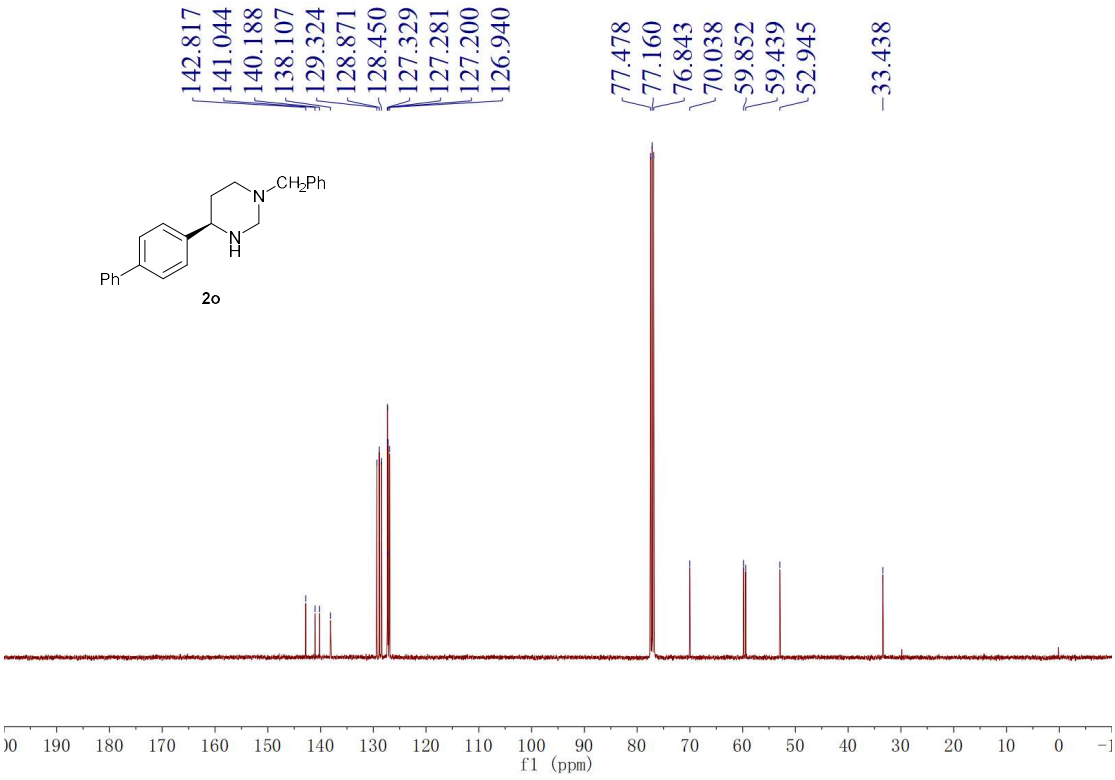
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2n



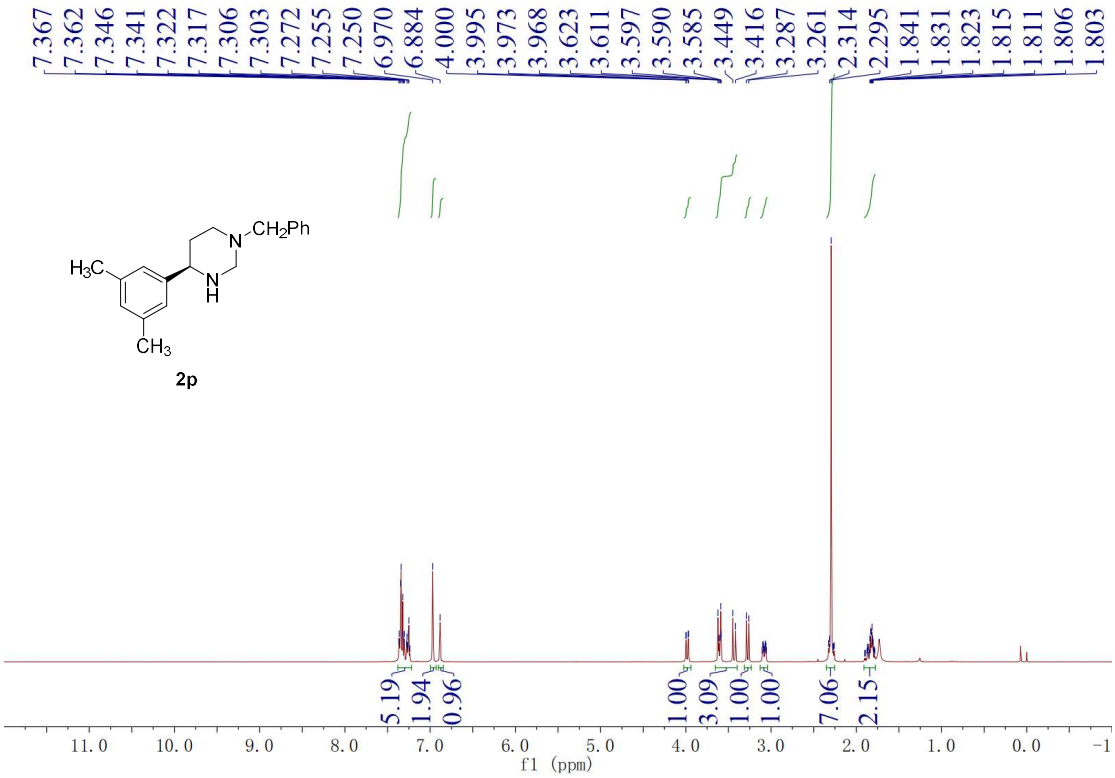
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2n



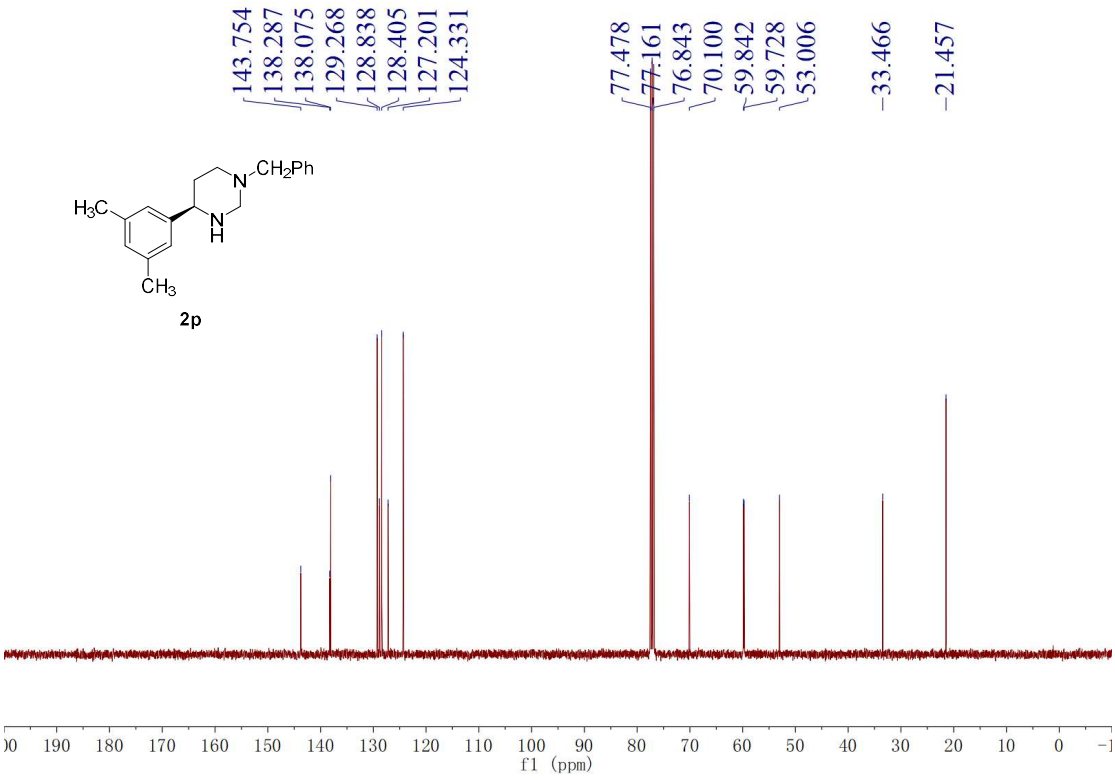
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2o



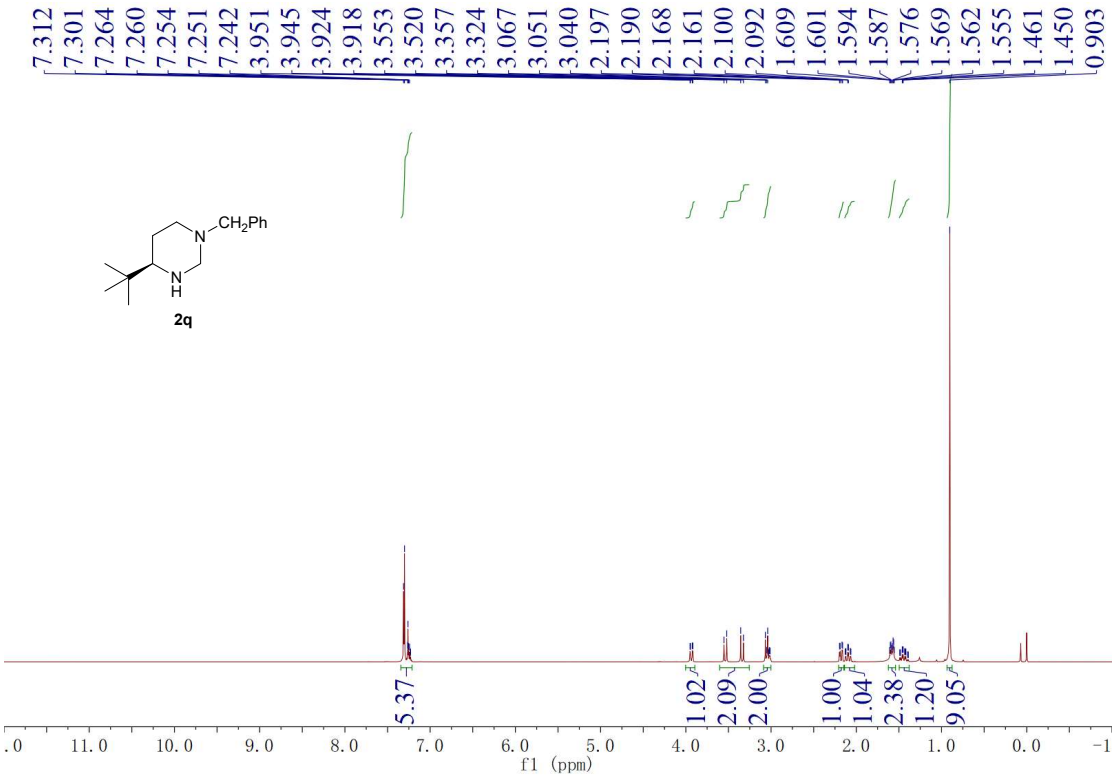
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2o



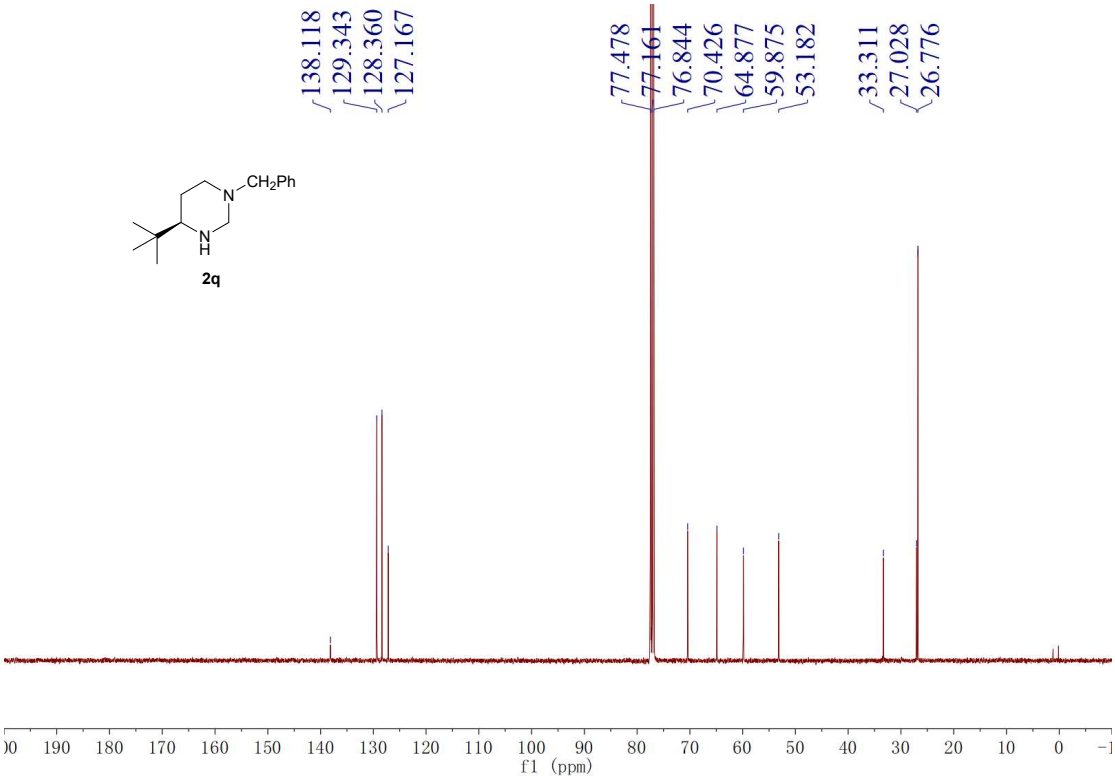
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2p



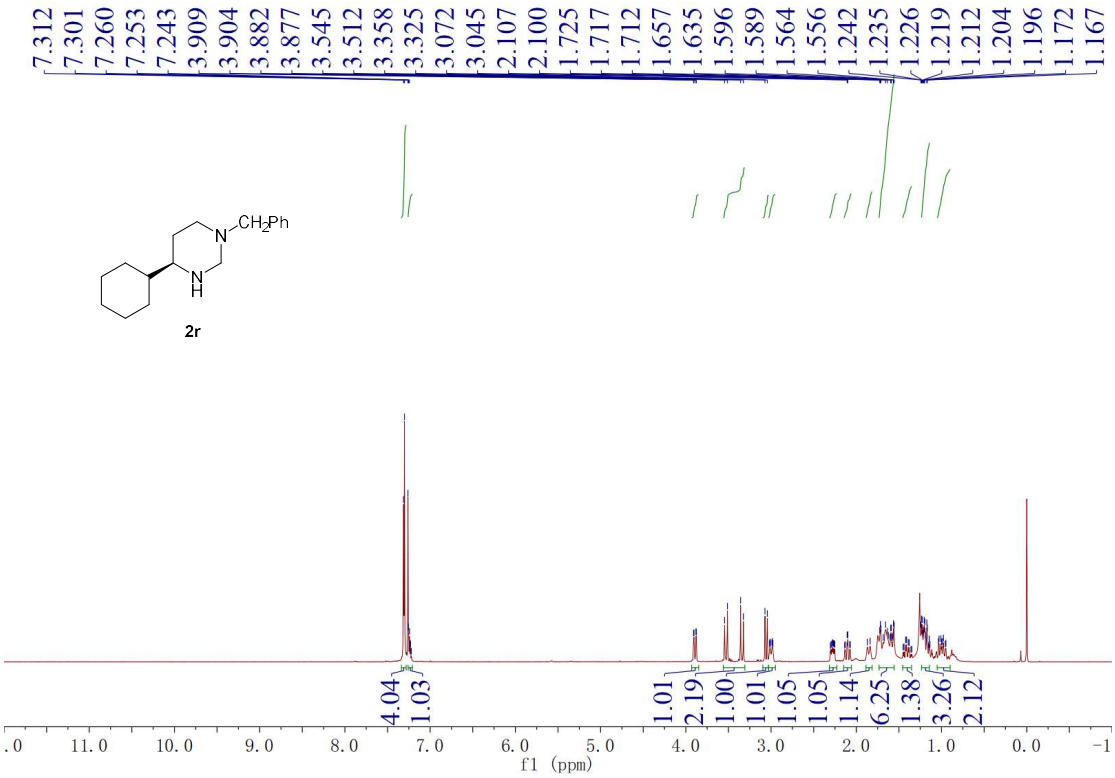
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2p



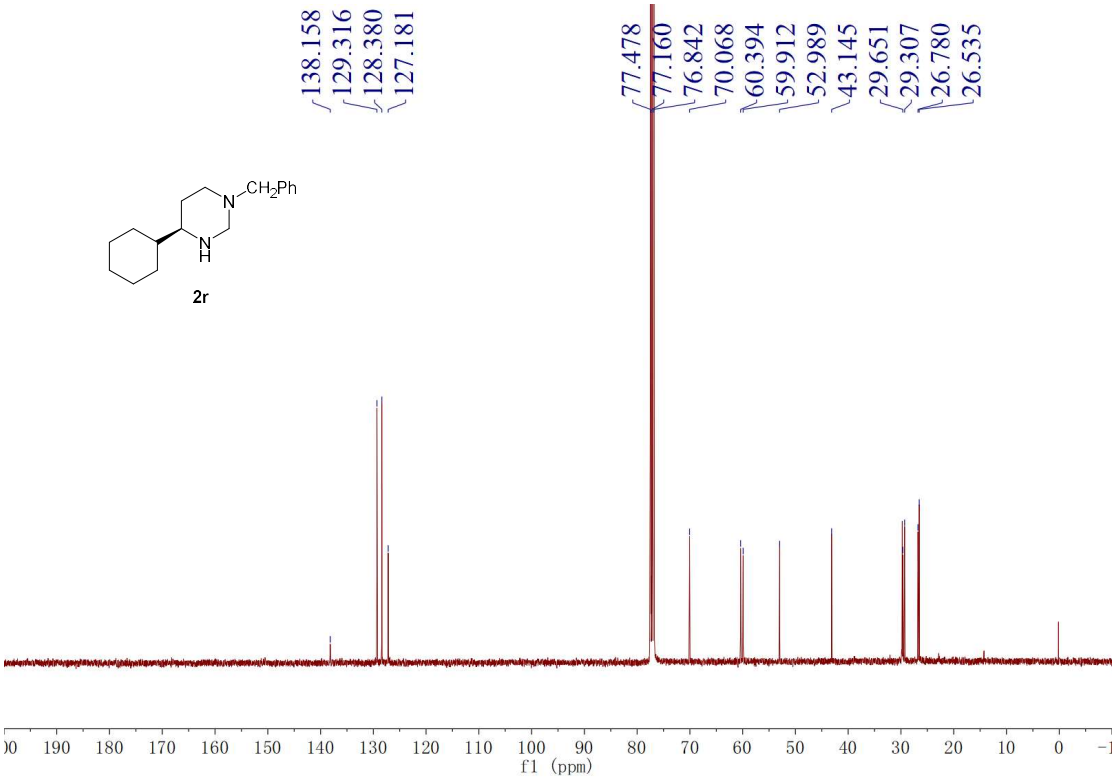
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2q



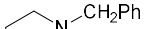
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2q

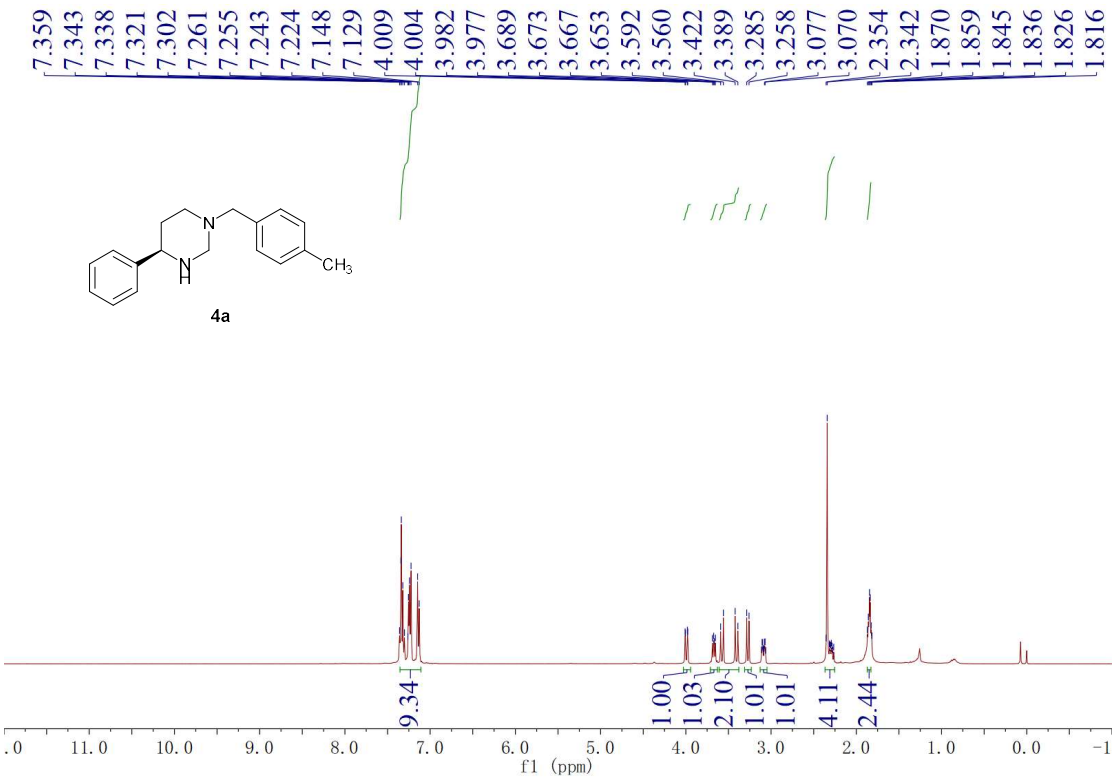


[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 2r

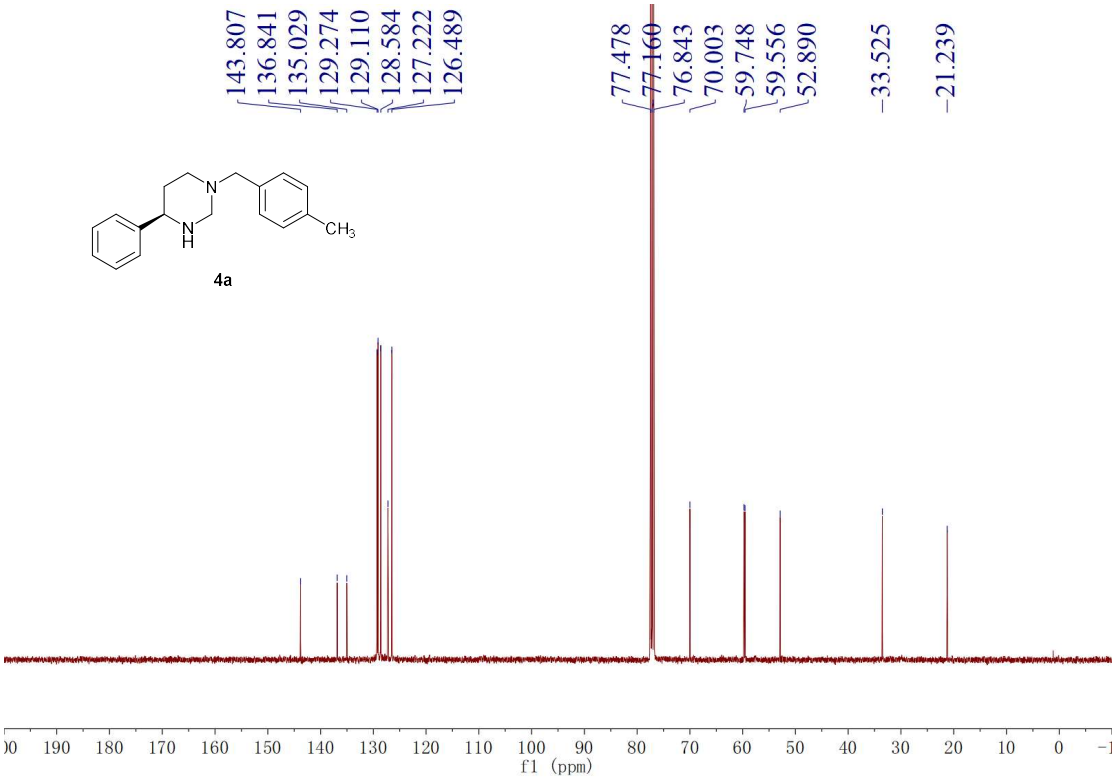


[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 2r

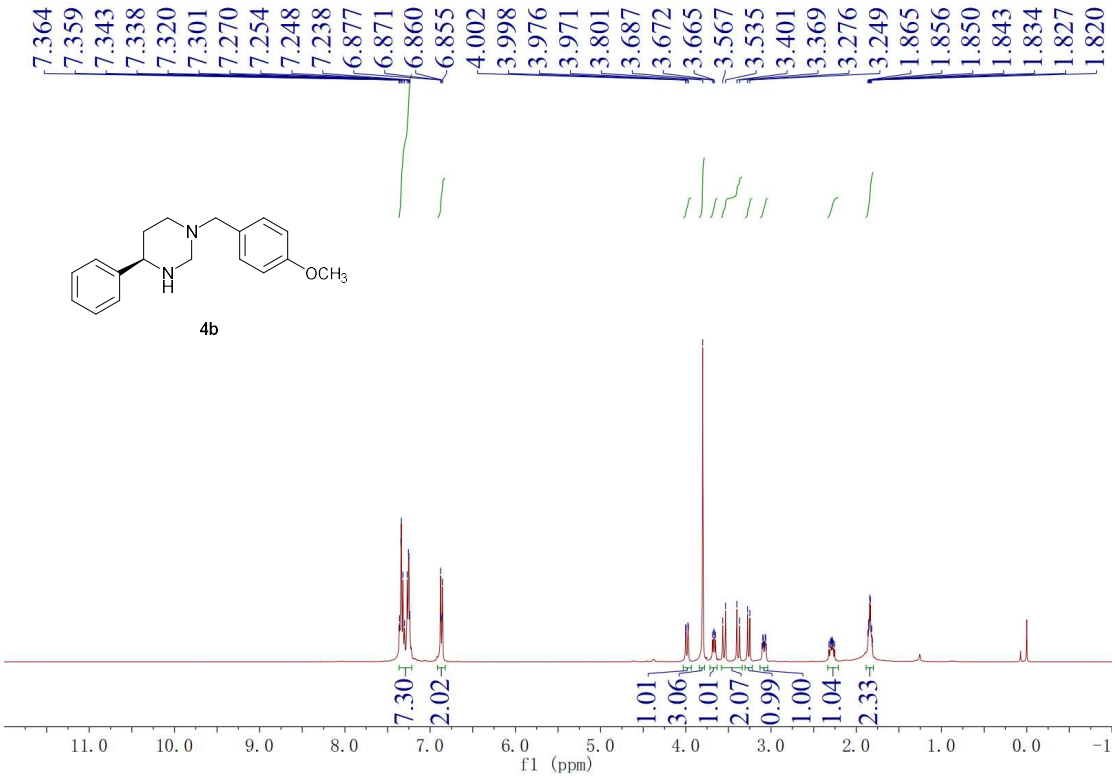




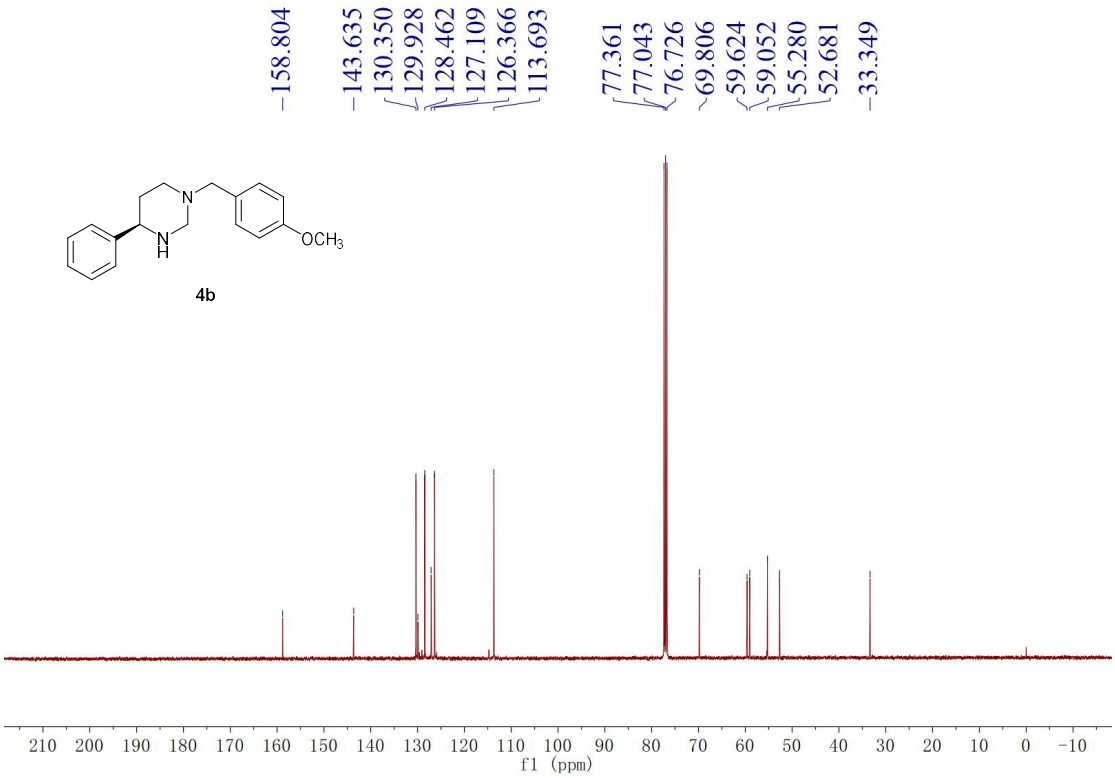
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4a



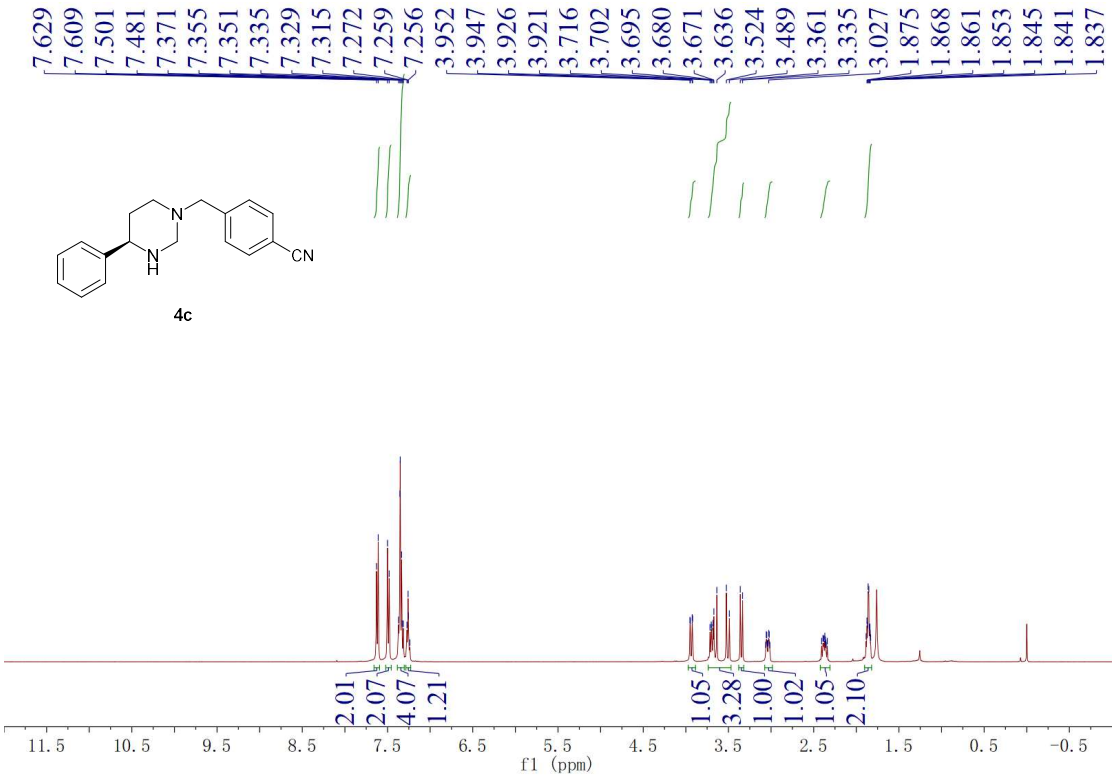
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4a



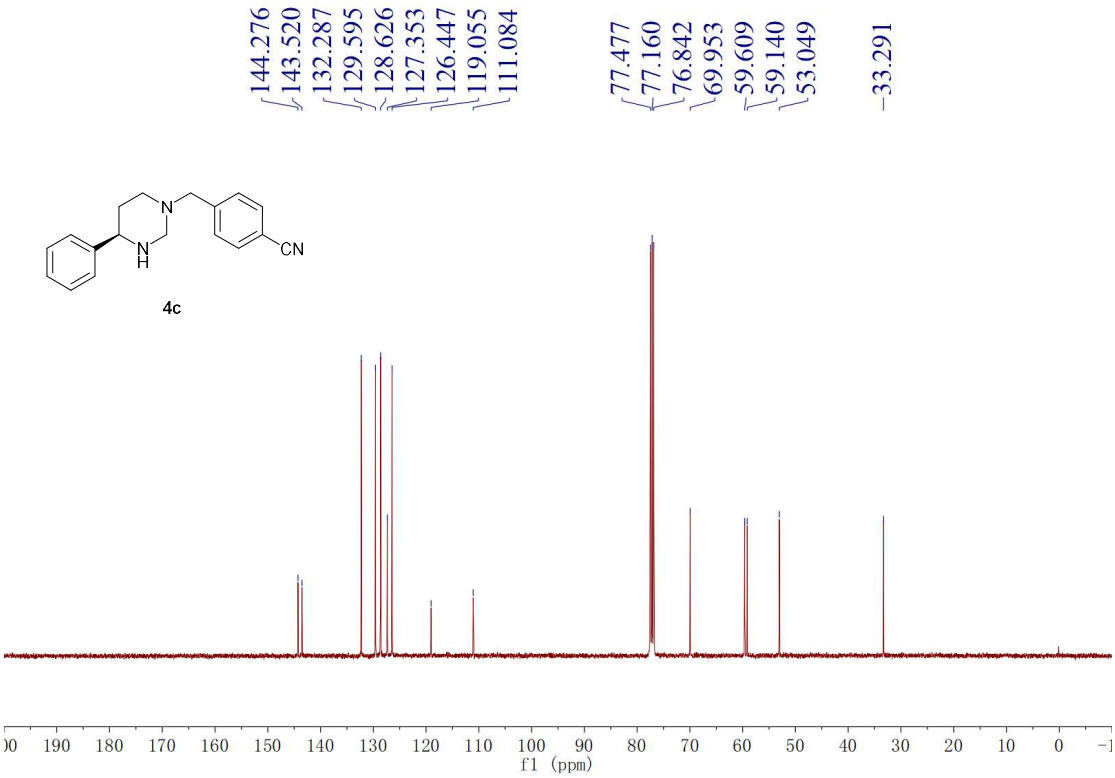
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4b



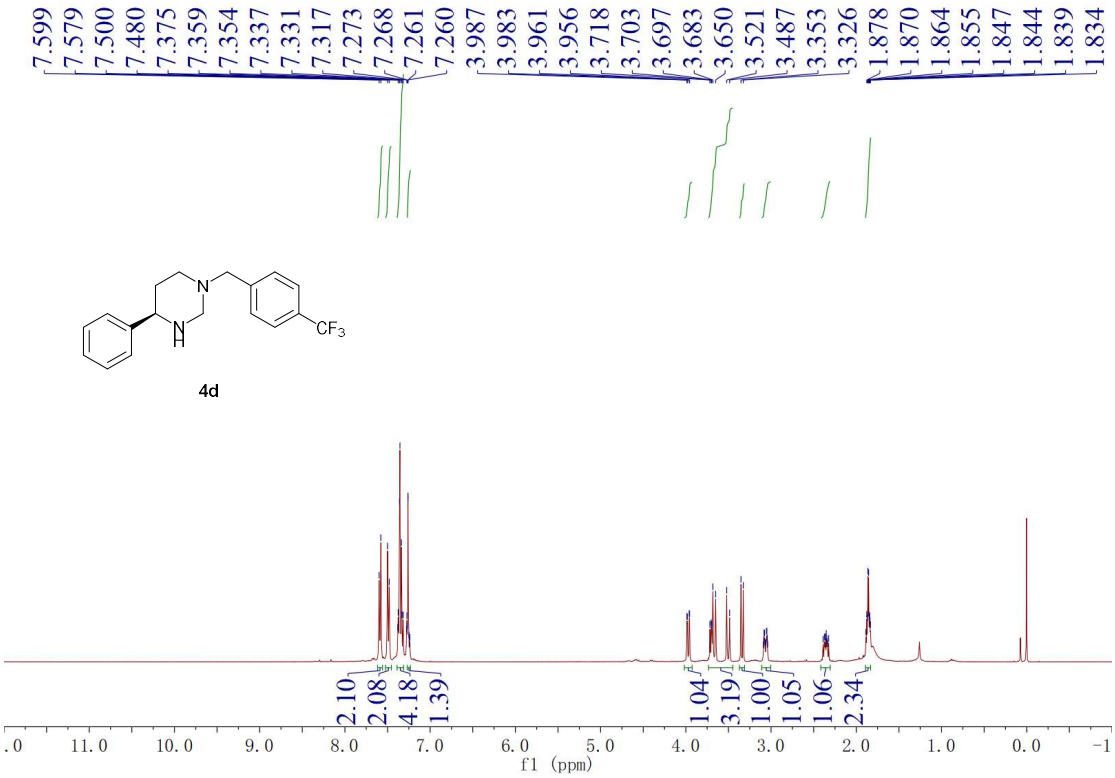
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4b



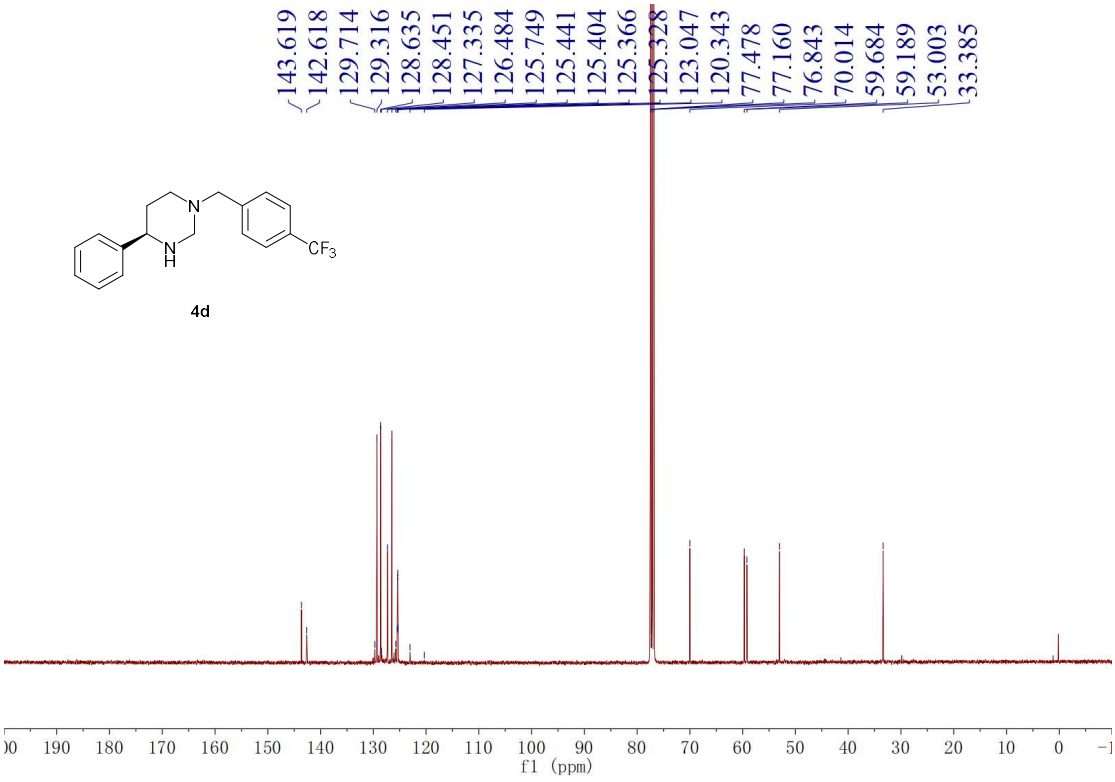
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4c



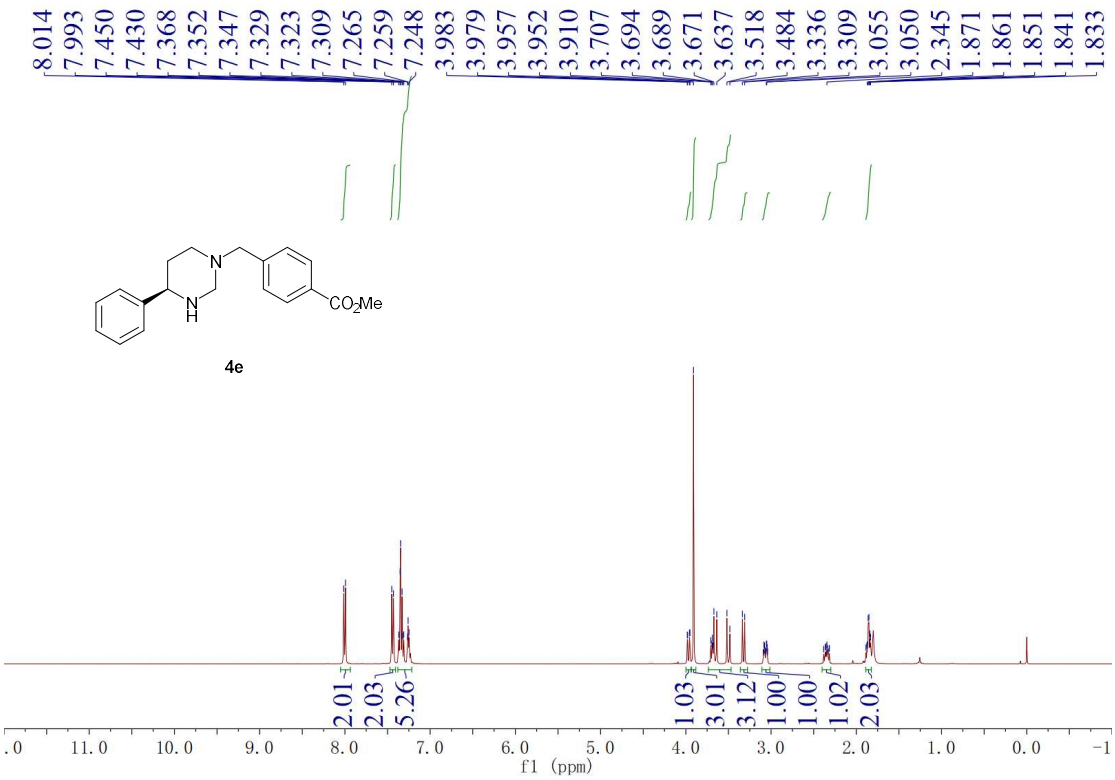
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4c



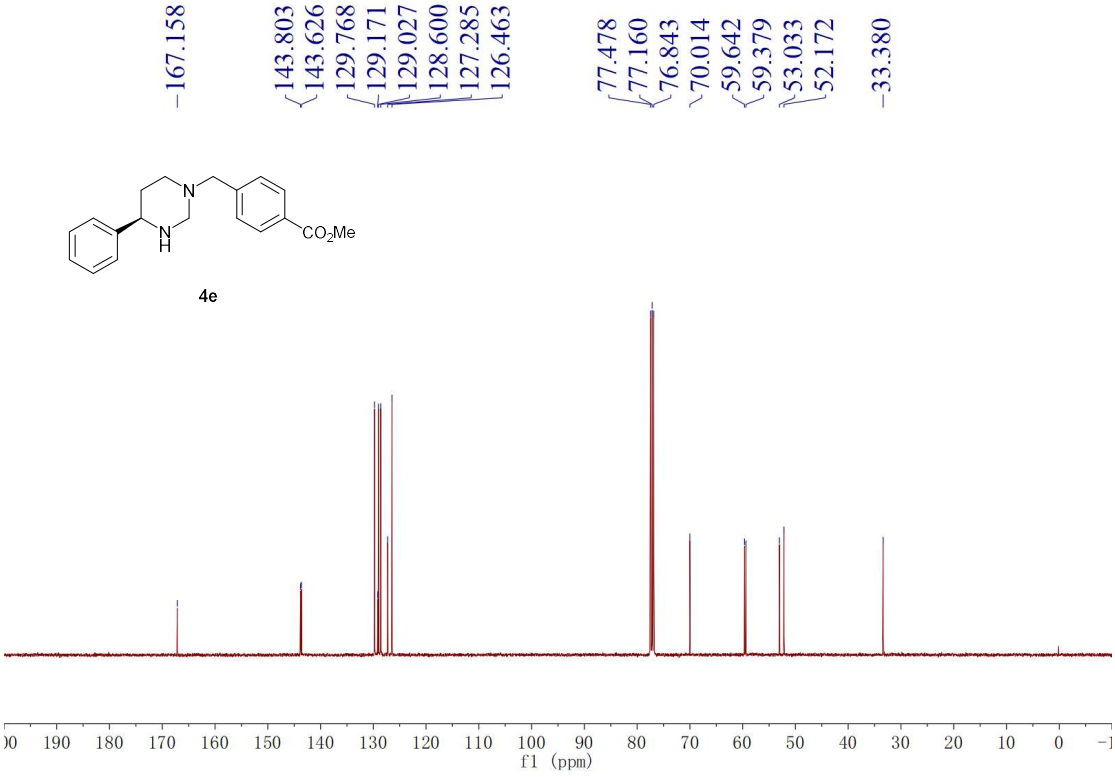
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4d



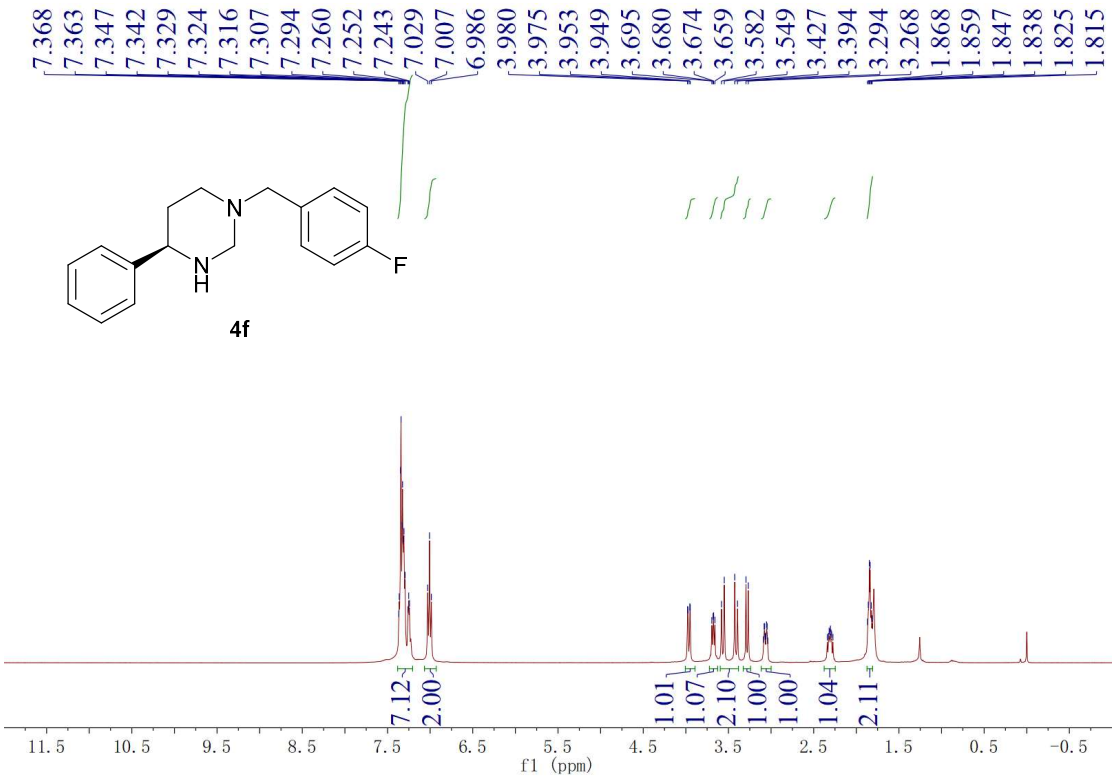
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4d



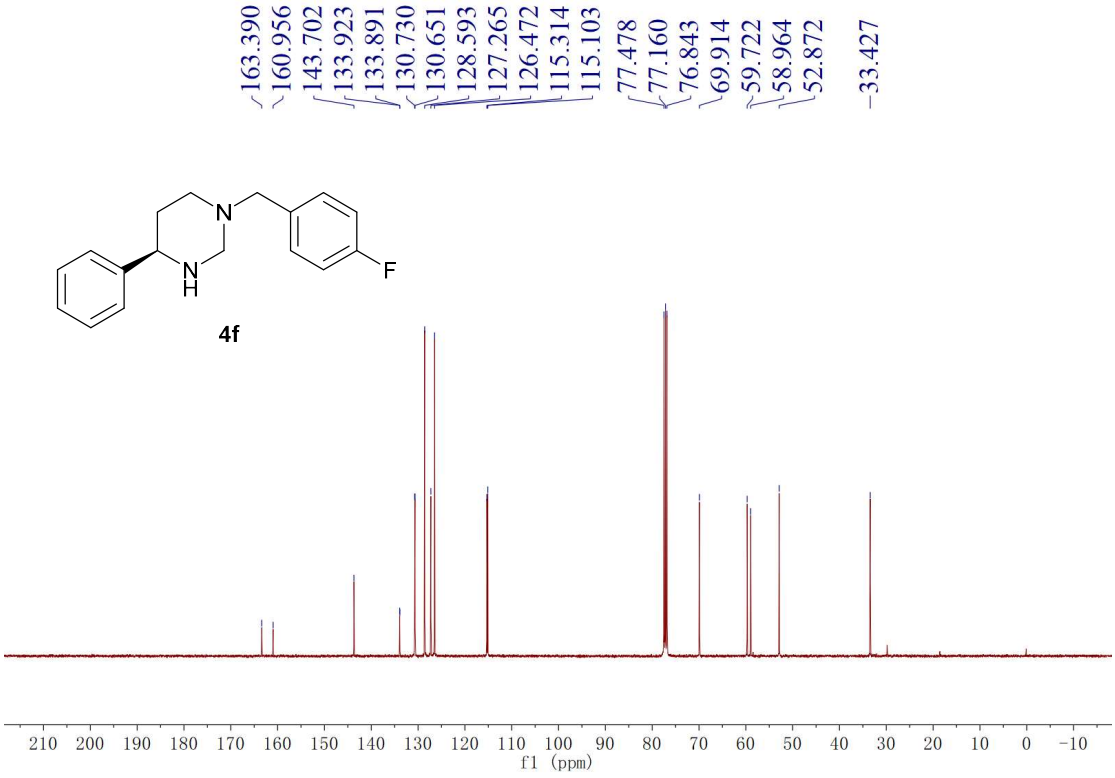
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4e



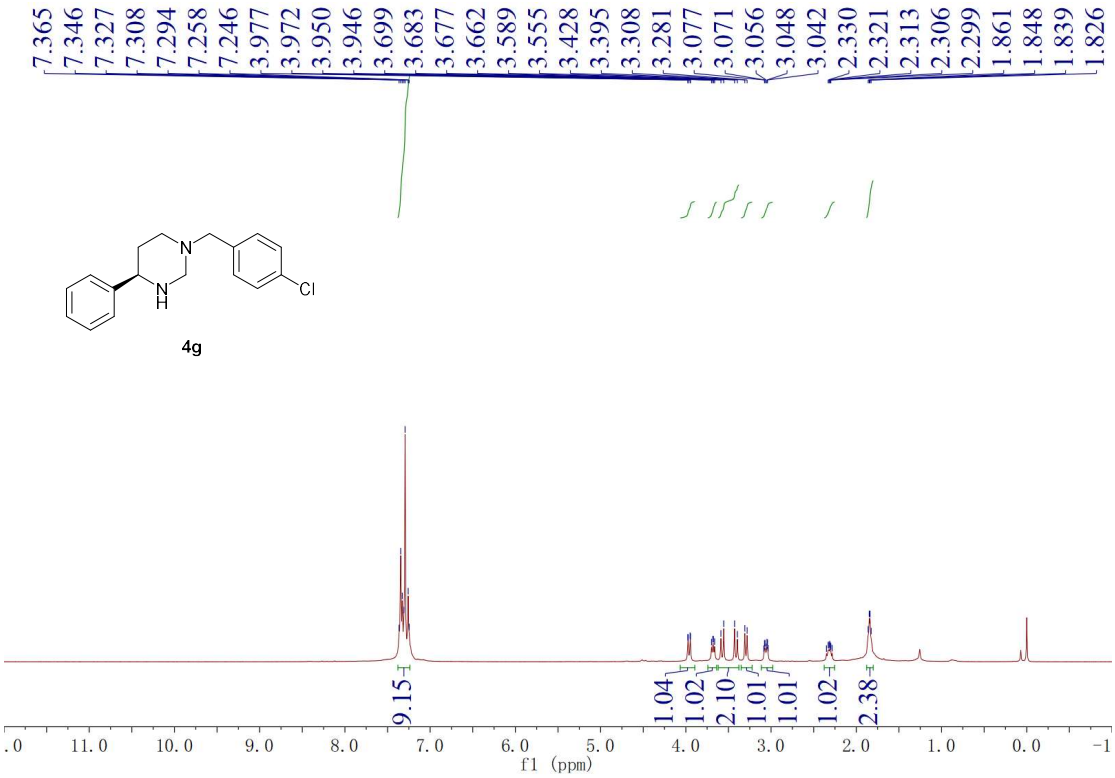
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4e



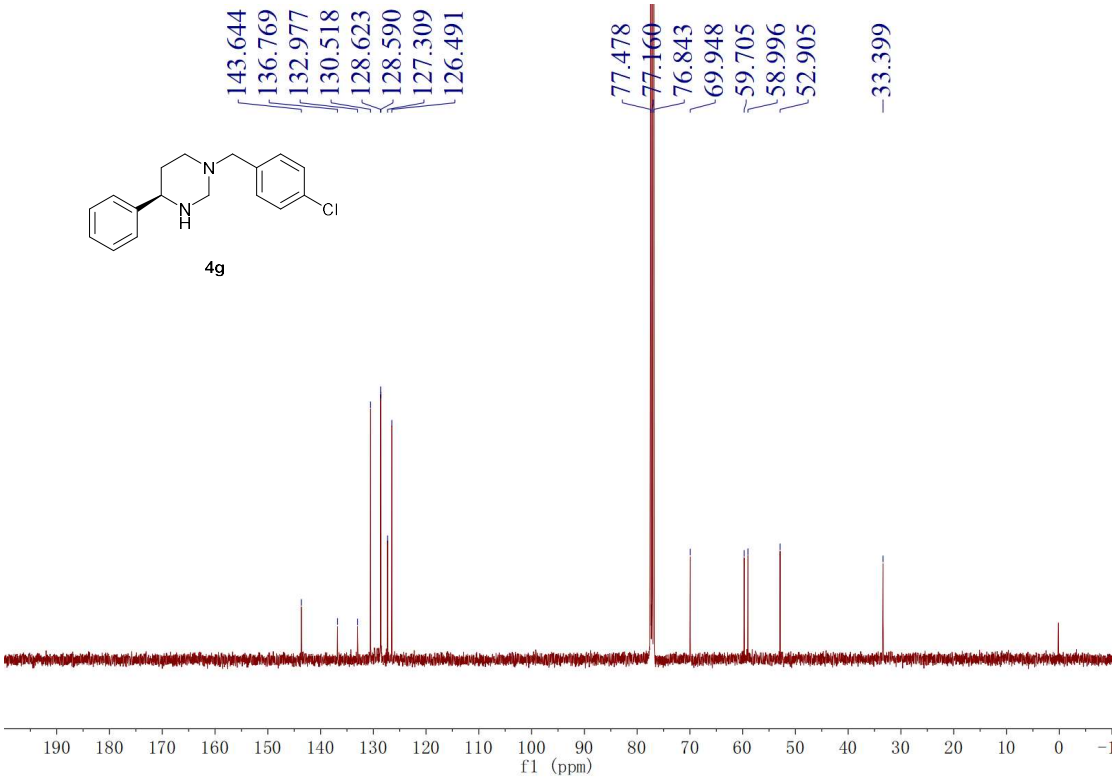
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4f



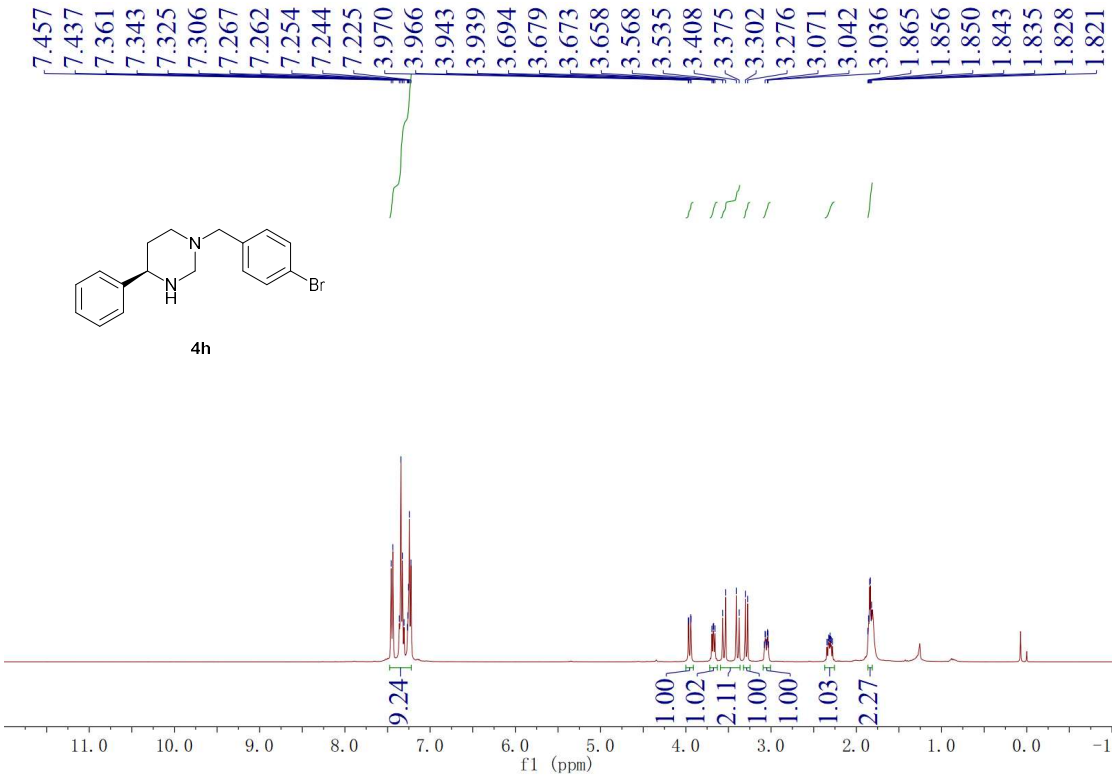
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4f



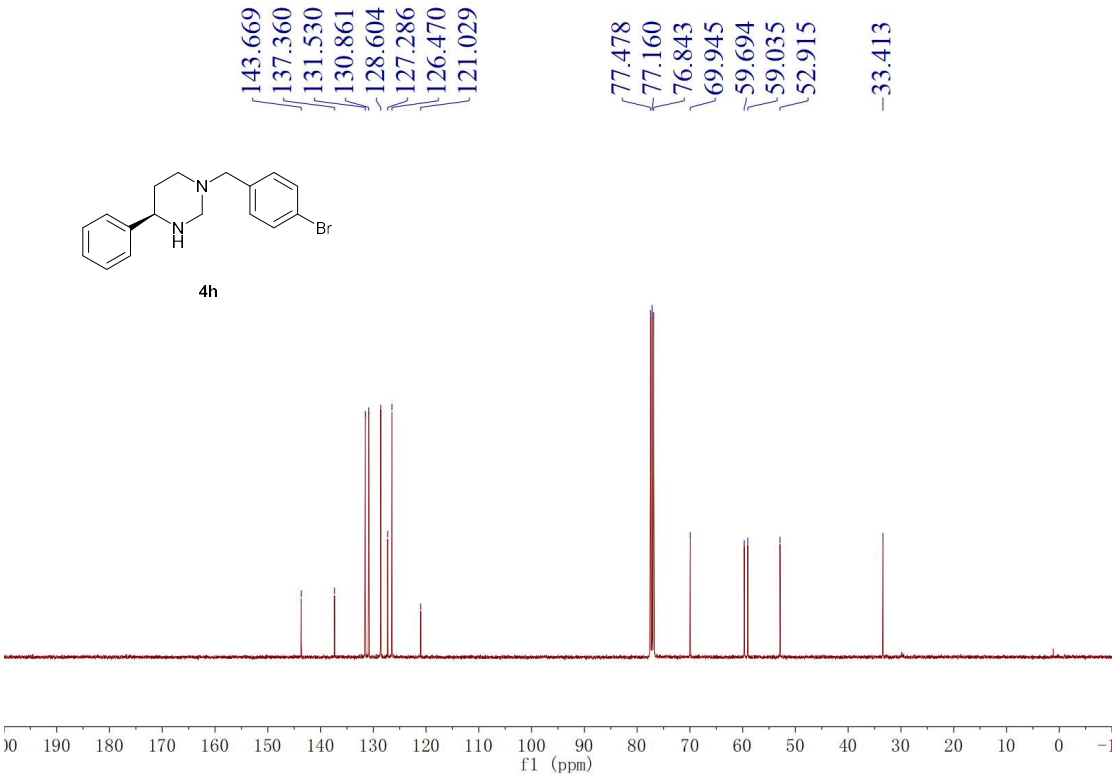
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4g



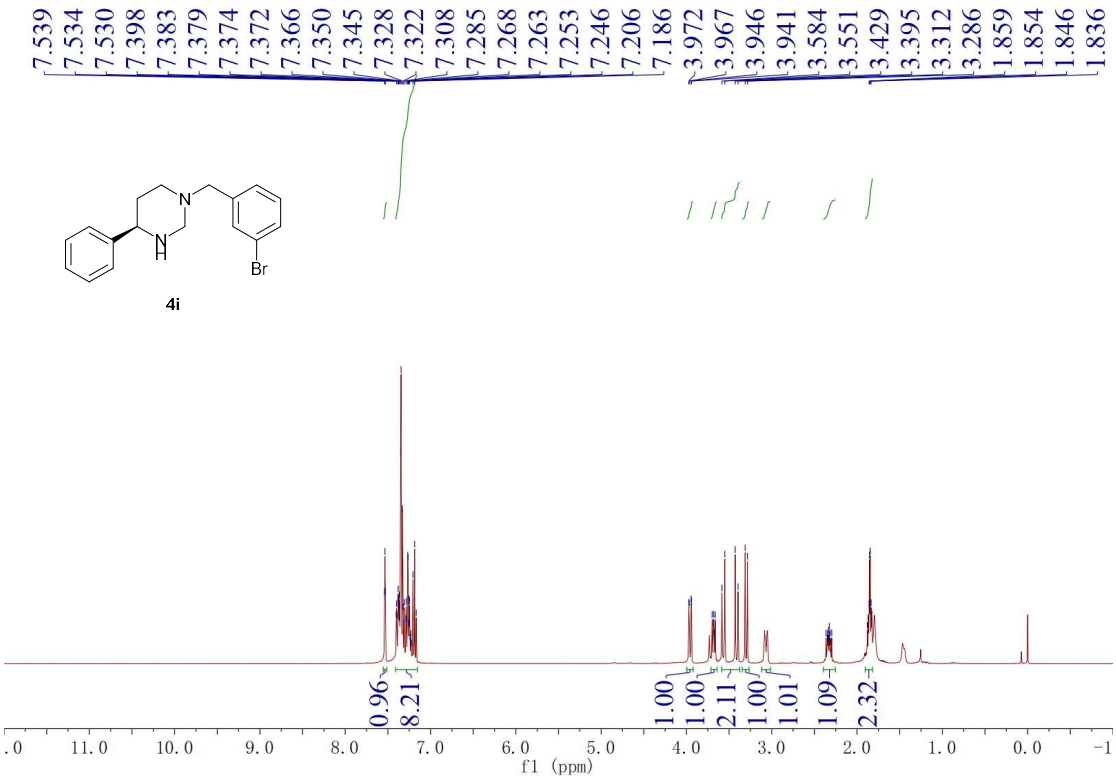
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4g



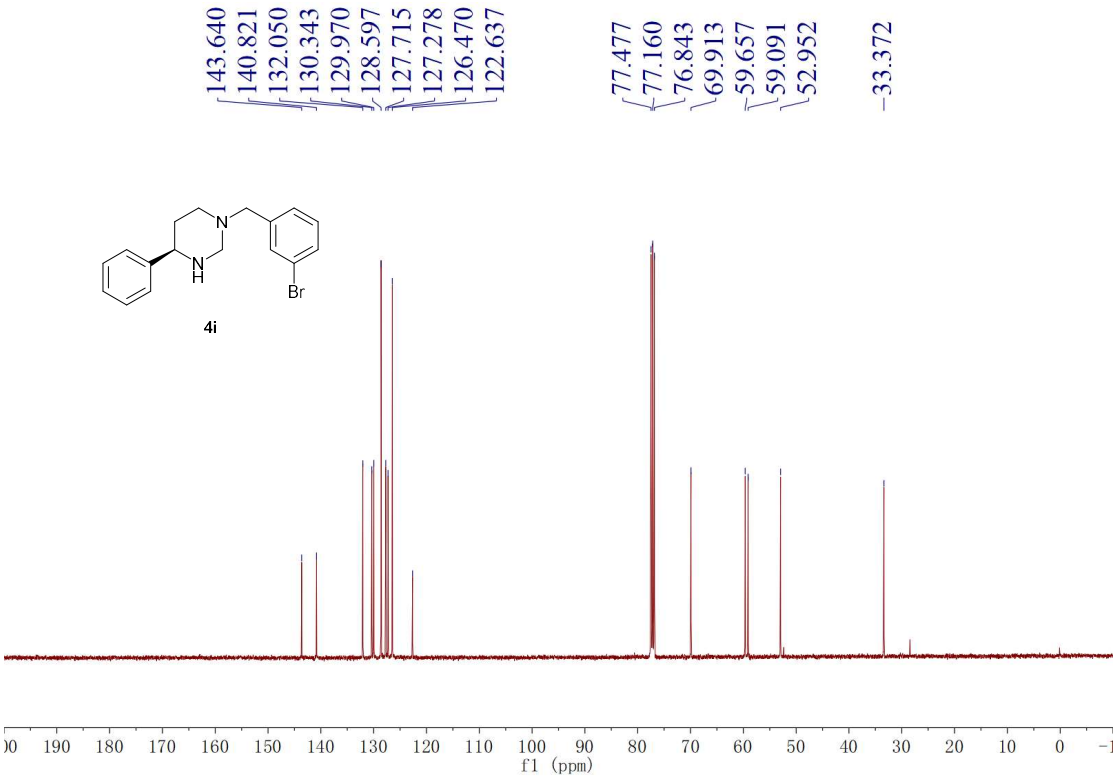
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4h



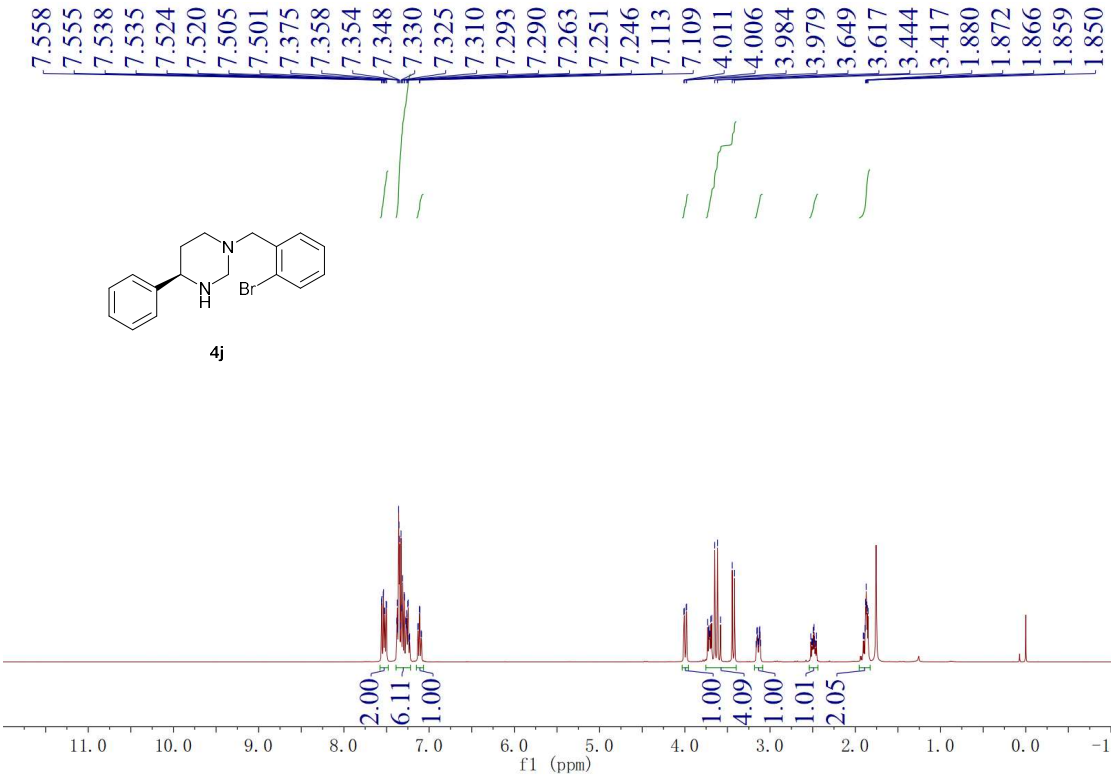
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4h



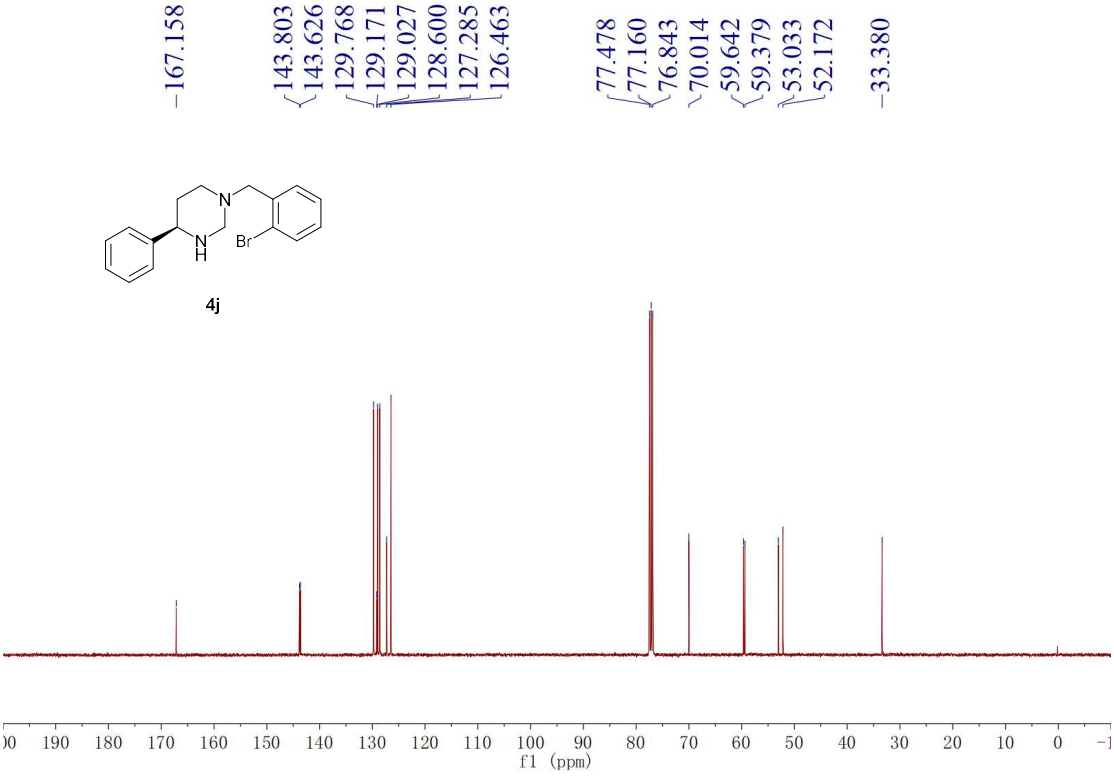
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4i



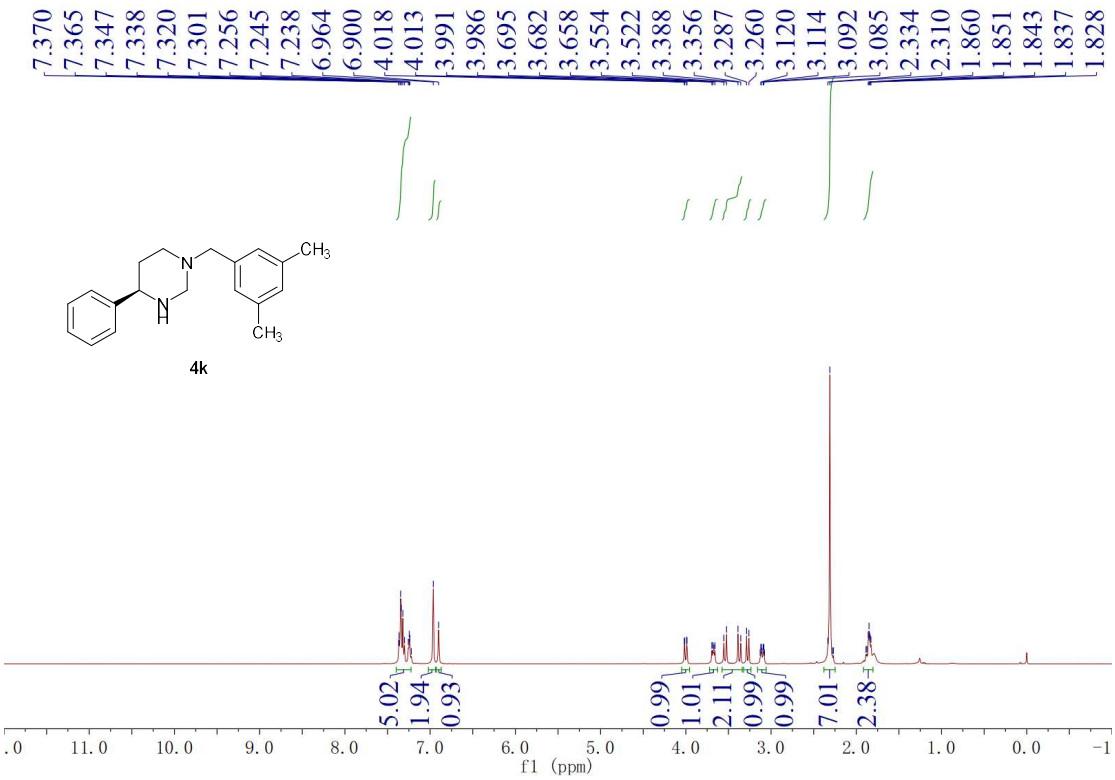
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4i



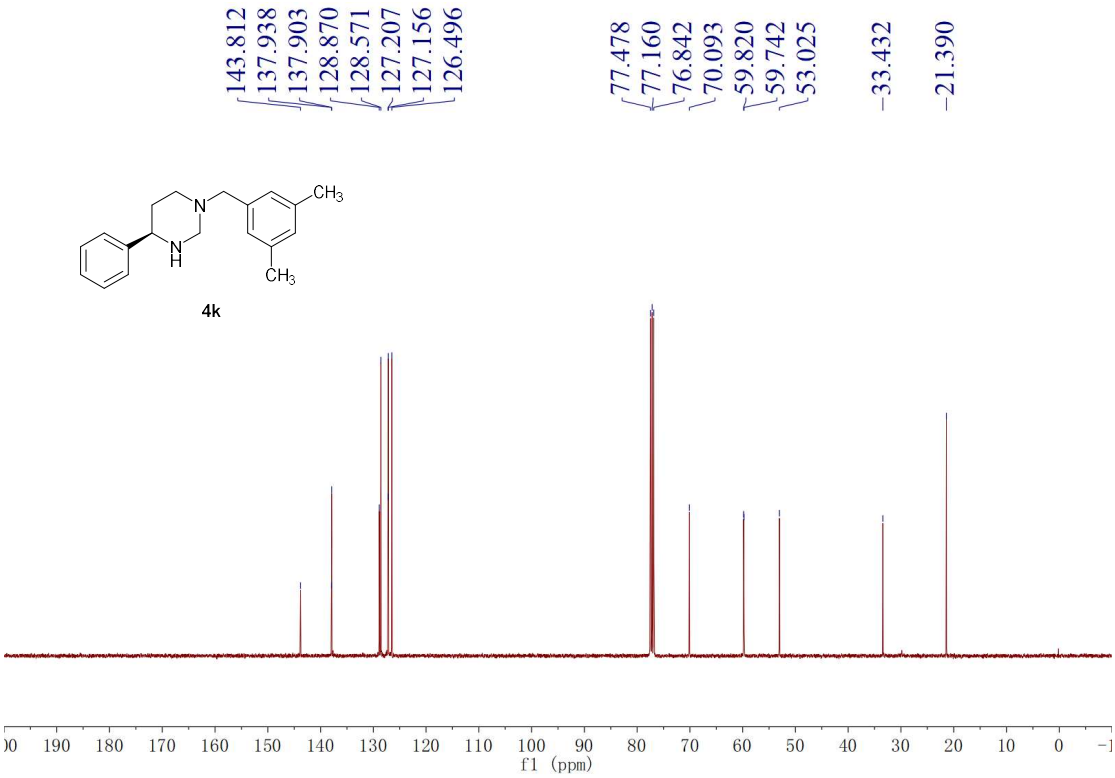
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4j



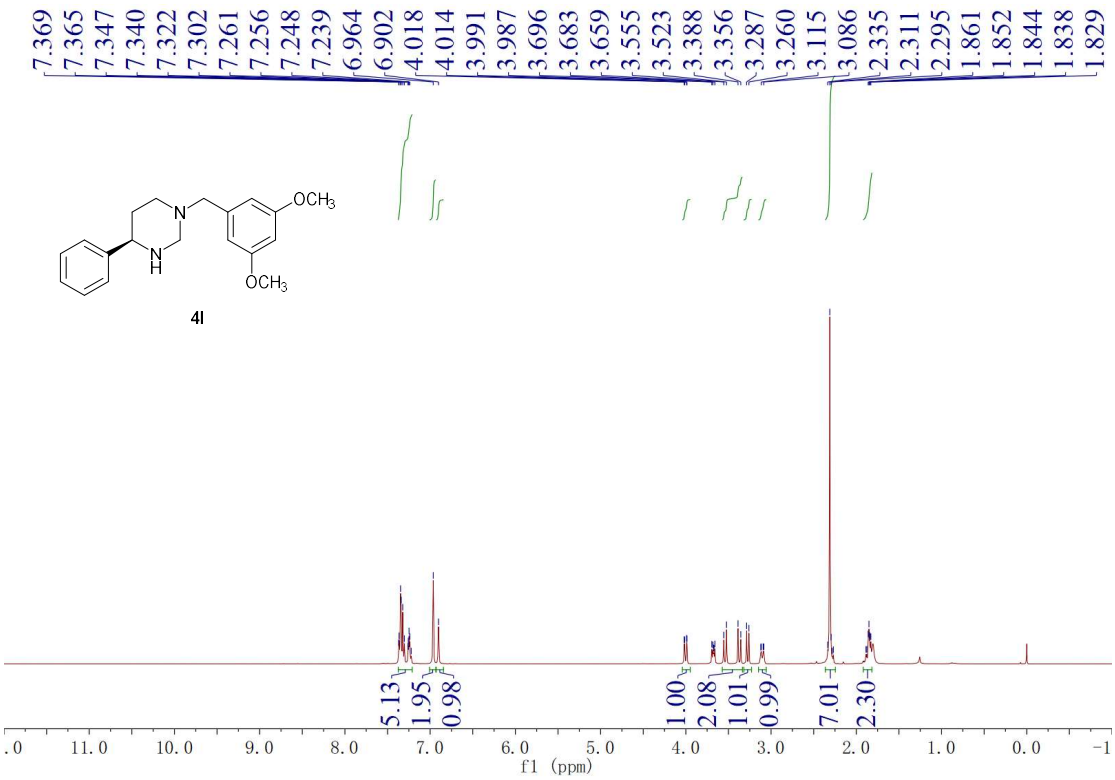
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4j



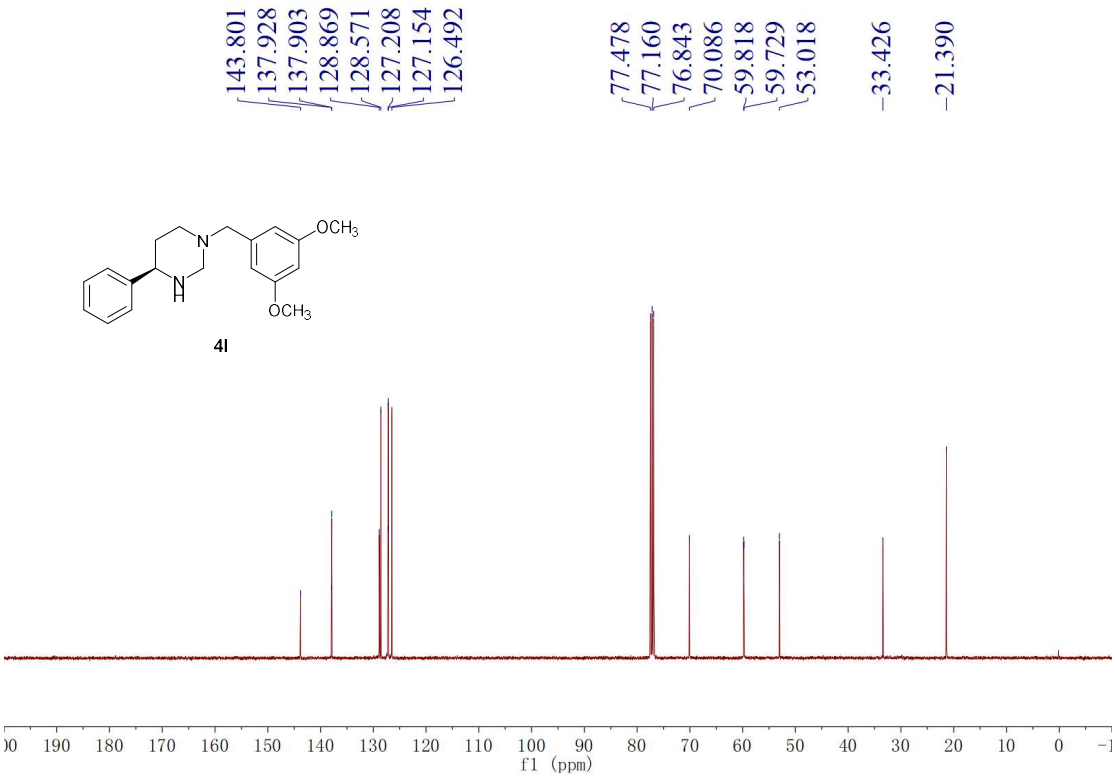
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4k



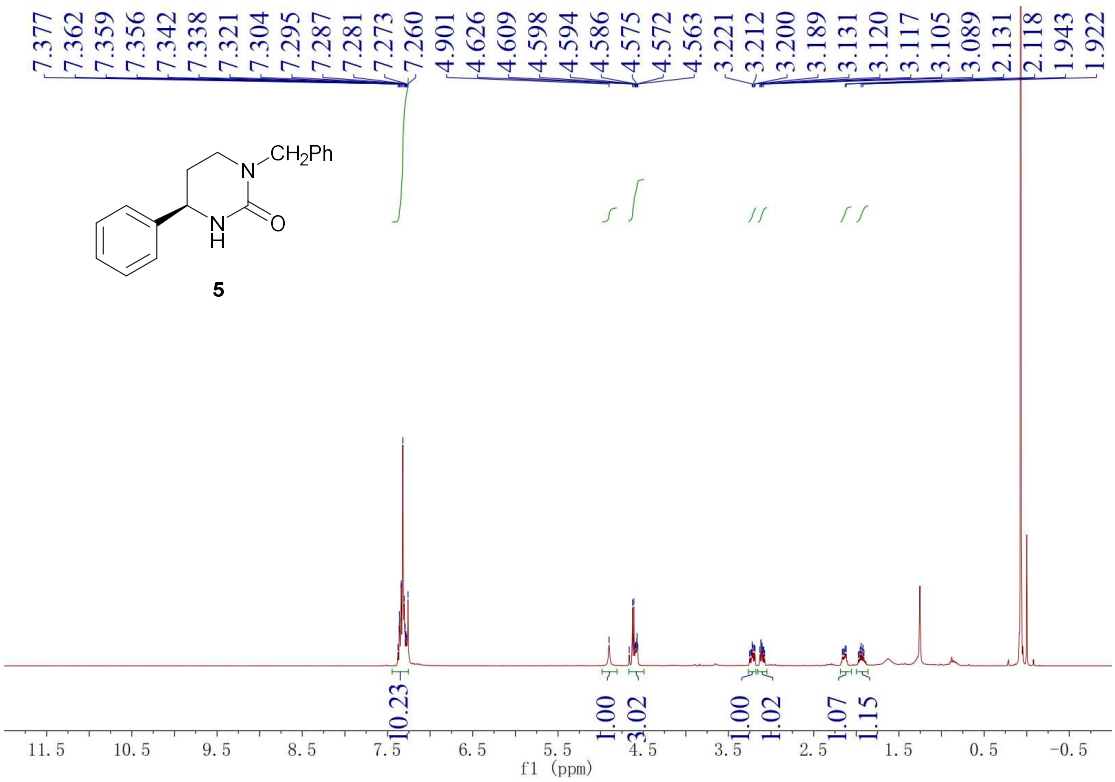
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4k



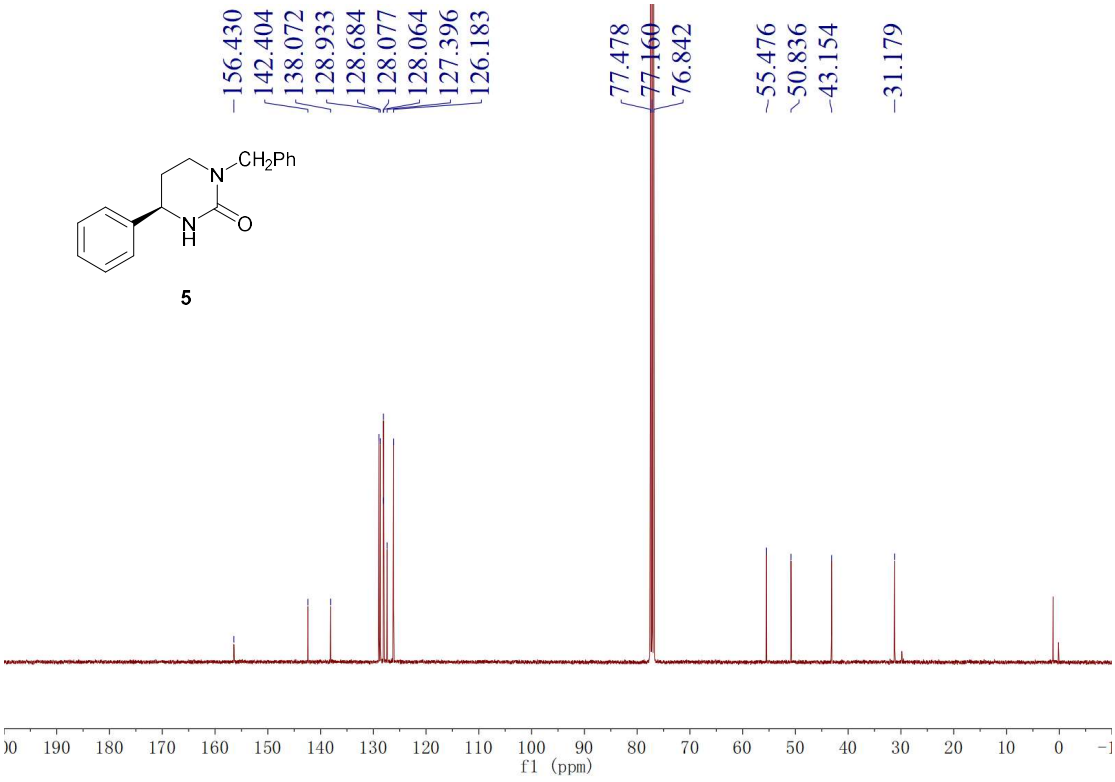
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 4l



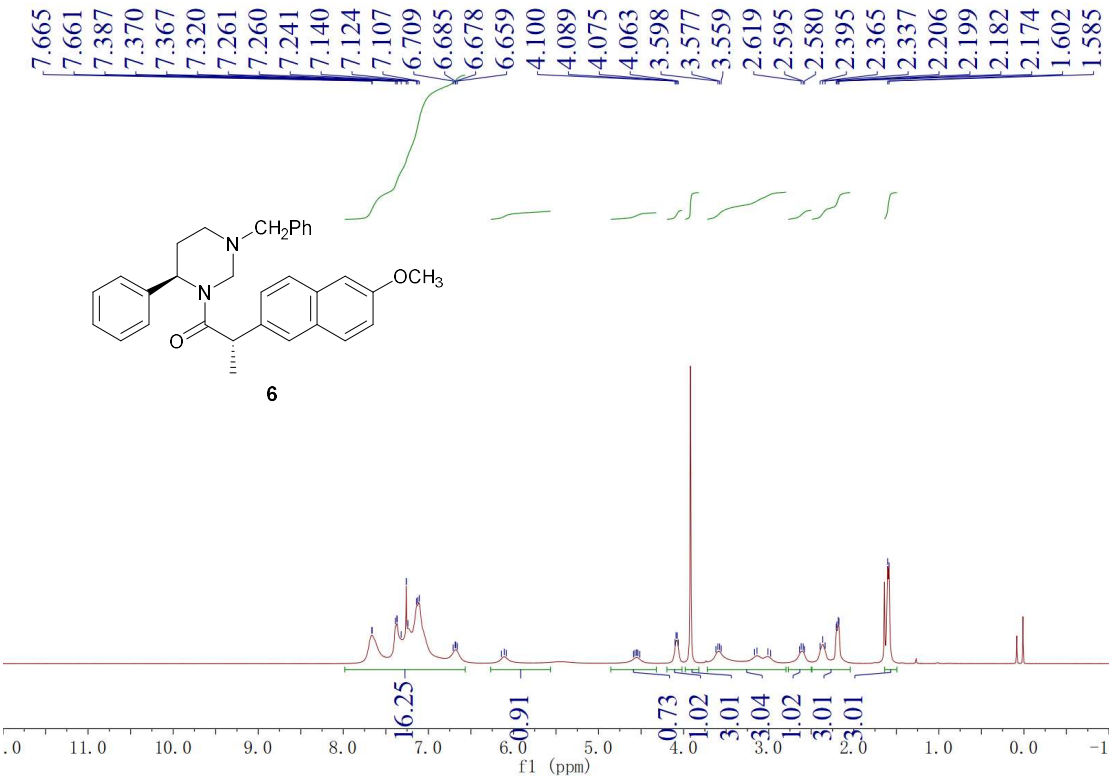
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 4l



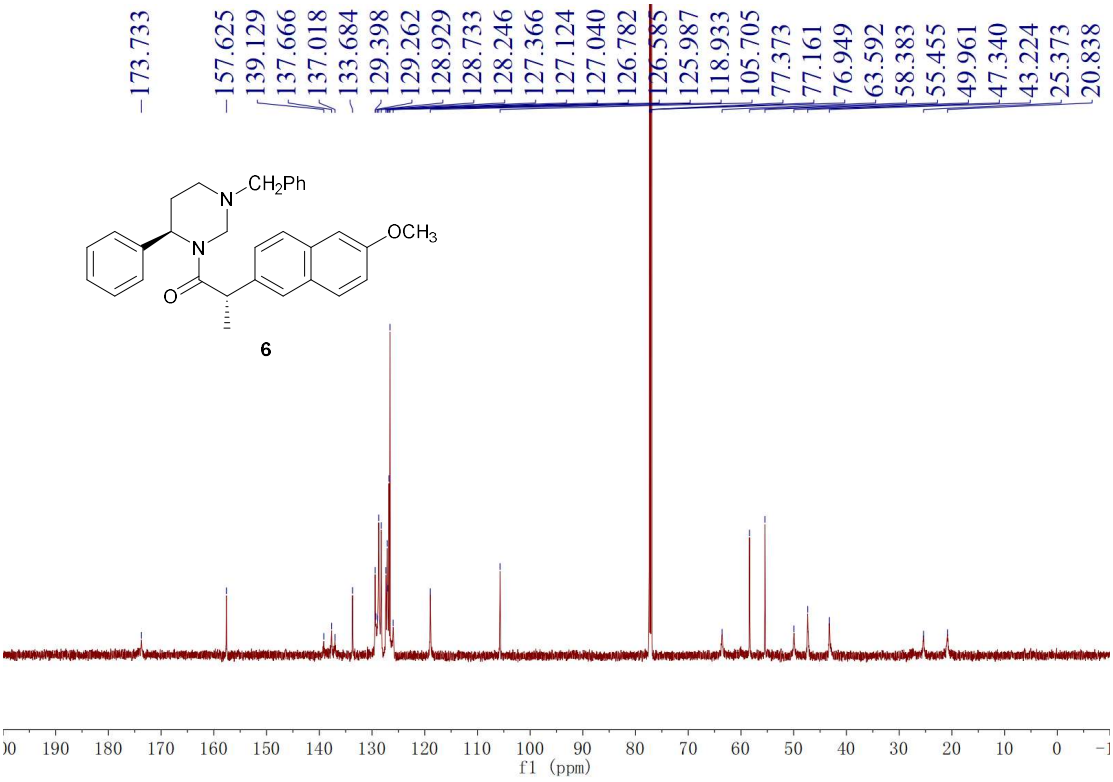
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 5



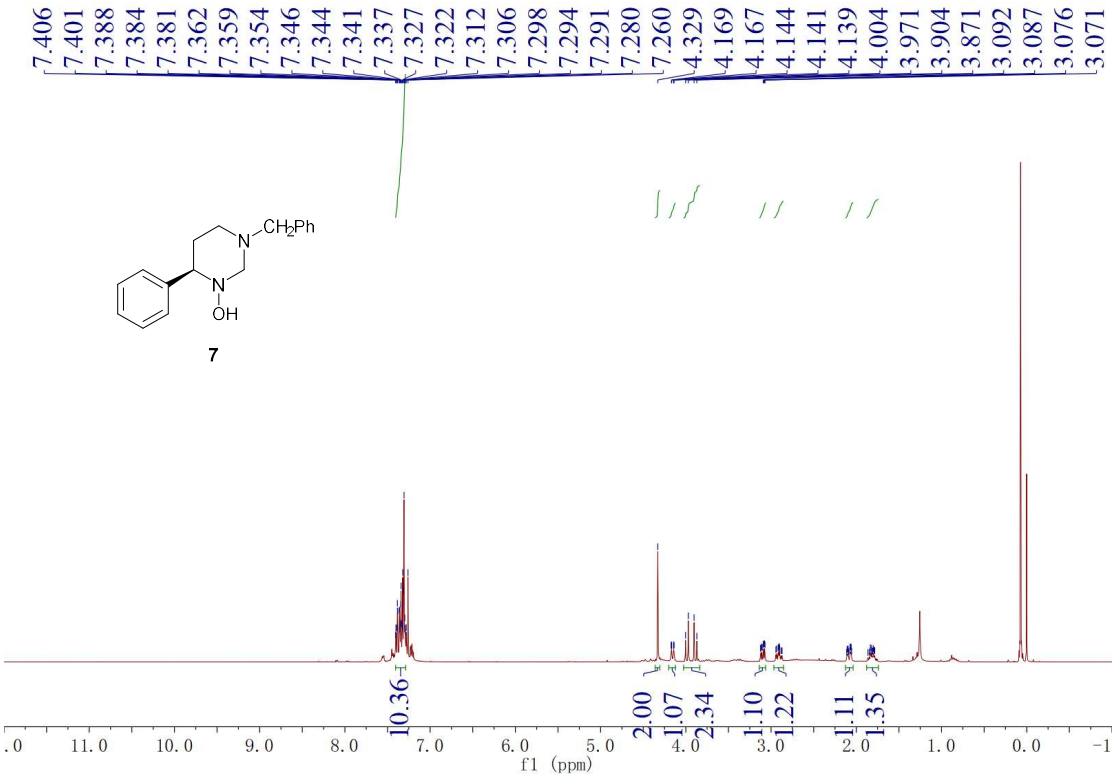
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 5



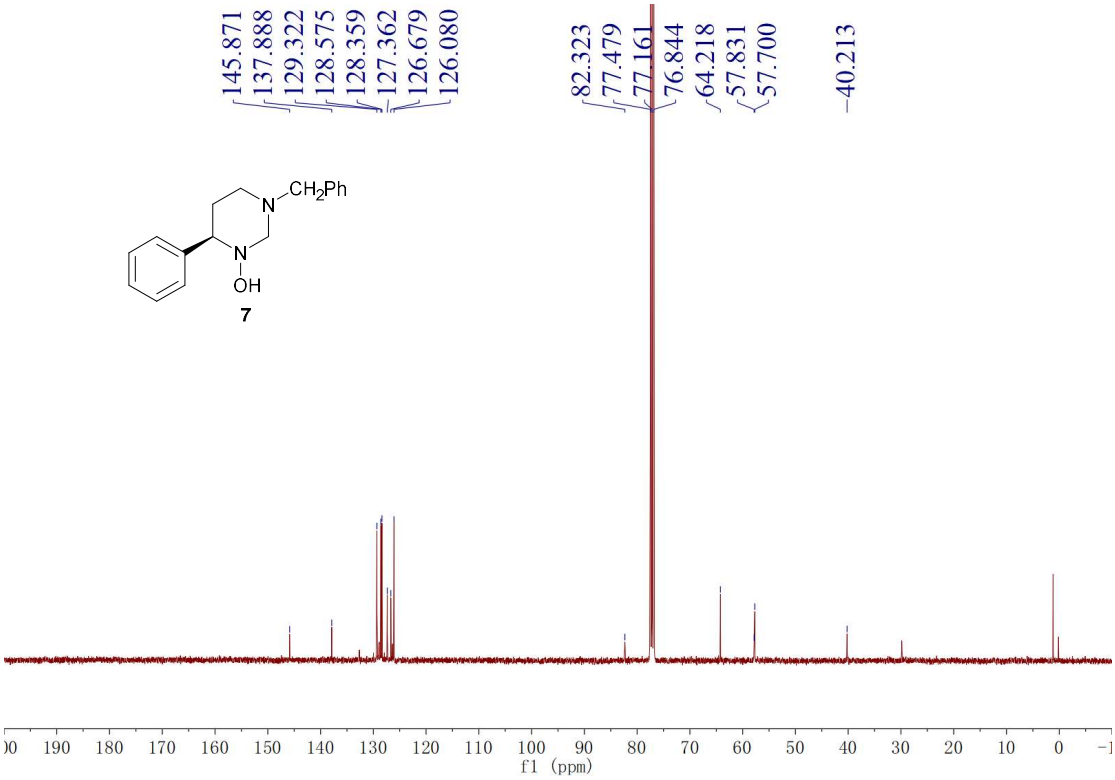
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 6



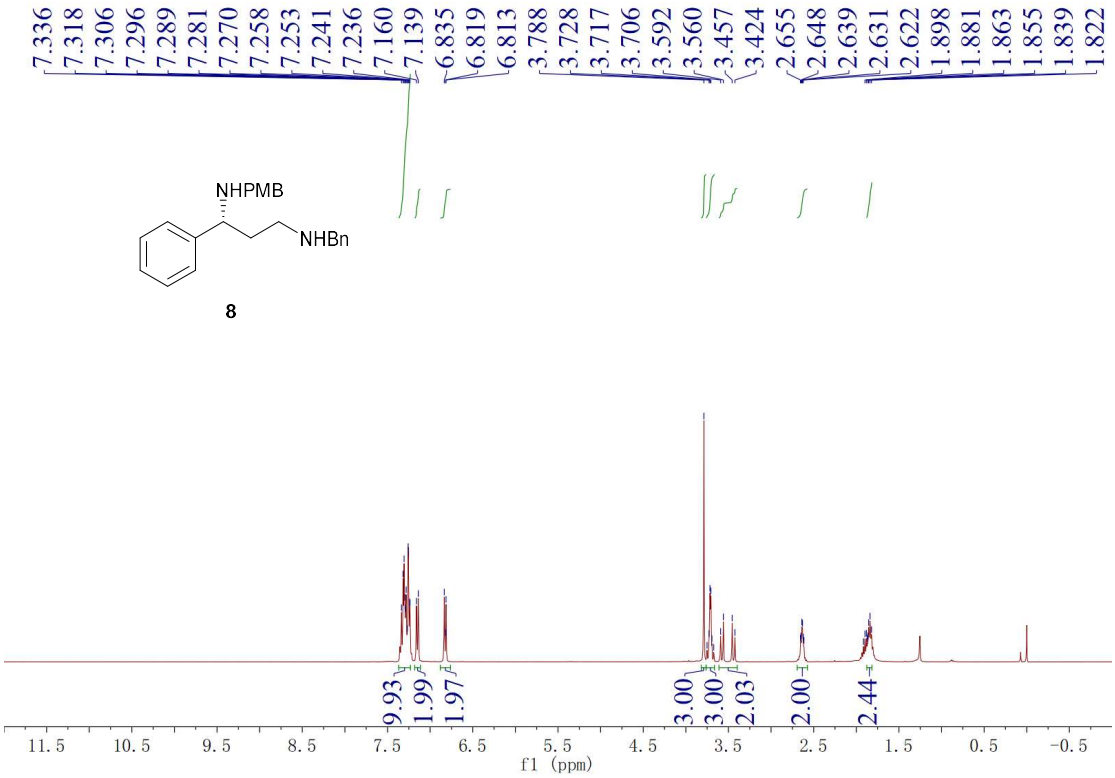
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 6



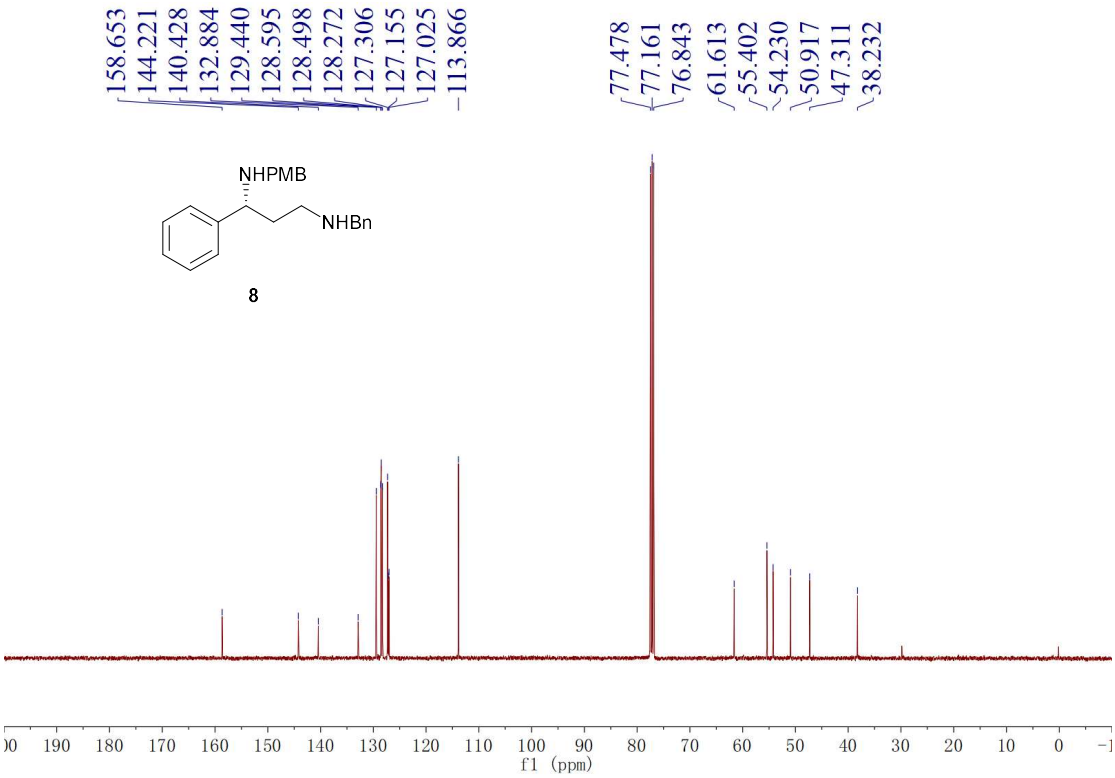
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 7



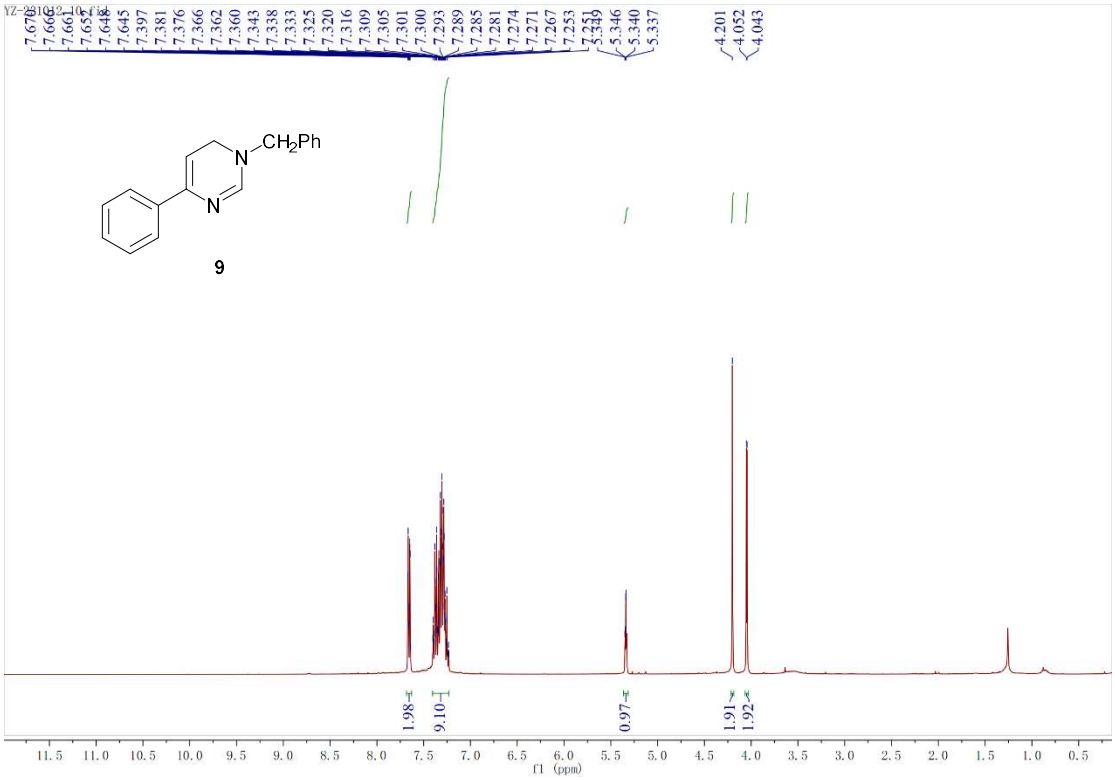
[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 7



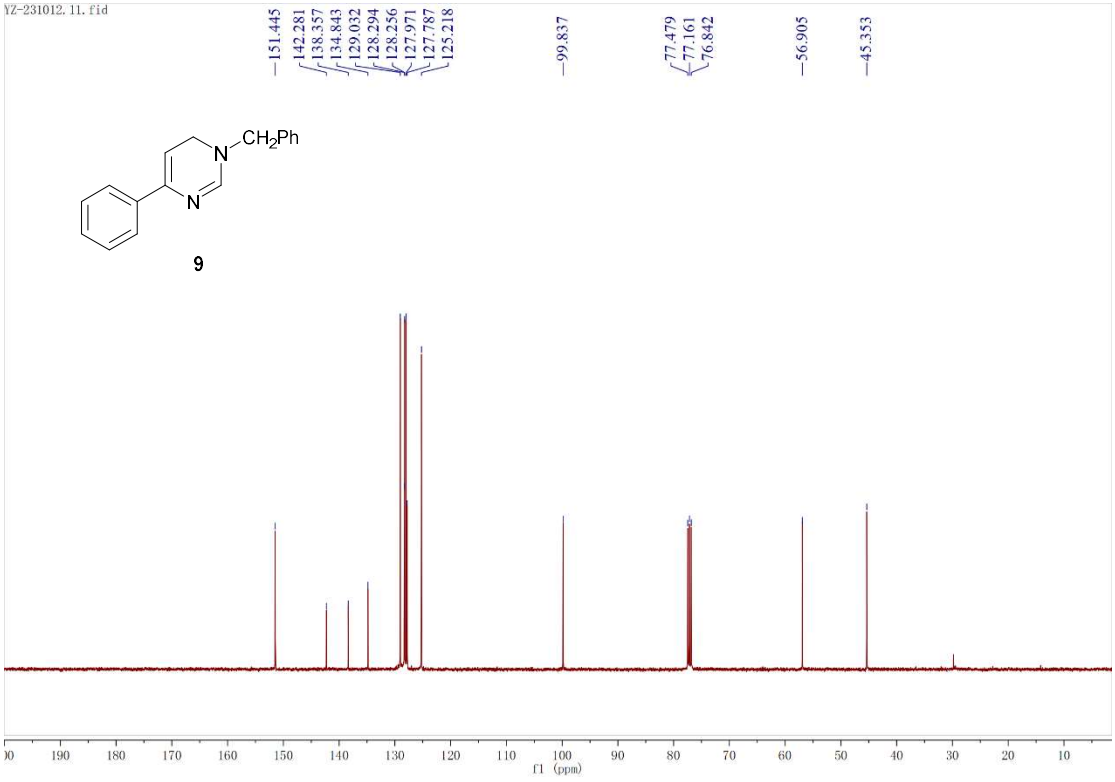
[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 8



[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 8



[1]H-NMR Spectrum (400 MHz, Chloroform-*d*) of Compound 9



[13]C-NMR Spectrum (100 MHz, Chloroform-*d*) of Compound 9

5. Crystallographic Data

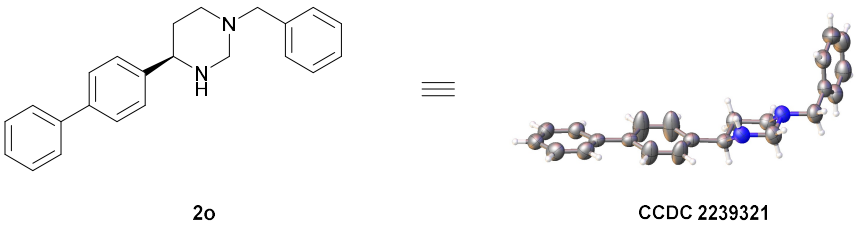


Figure S3. ORTEP of the molecular structure of **2o**

CCDC 2239321 contains the supplementary crystallographic data for compound **2o**.

Empirical formula	$C_{23}H_{24}N_2$
Formula weight	328.44
Temperature/K	297.0
Crystal system	monoclinic
Space group	$P2_1$
a/Å	15.1560(3)
b/Å	6.05280(10)
c/Å	20.8658(4)
α/°	90
β/°	104.9340(10)
γ/°	90
Volume/Å^3	1849.50(6)
Z	4
ρ_{calc}g/cm^3	1.180
μ/mm^{-1}	0.525
F(000)	704.0
Crystal size/mm^3	0.45 × 0.35 × 0.19
Radiation	CuKα (λ = 1.54178)
2Θ range for data collection/°	4.382 to 134.14
Index ranges	-17 ≤ h ≤ 18, -7 ≤ k ≤ 7, -24 ≤ l ≤ 24
Reflections collected	33674
Independent reflections	6569 [R_{int} = 0.0513, R_{sigma} = 0.0342]
Data/restraints/parameters	6569/1/454
Goodness-of-fit on F^2	1.065
Final R indexes [I>=2σ (I)]	R_1 = 0.0457, wR_2 = 0.1214
Final R indexes [all data]	R_1 = 0.0513, wR_2 = 0.1257
Largest diff. peak/hole / e Å^{-3}	0.22/-0.24

Flack parameter	0.08(18)

These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.